

UNIVERSIDADE FEDERAL DA PARAÍBA
CENTRO DE TECNOLOGIA
PROGRAMA DE PÓS-GRADUAÇÃO EM CIÊNCIA E
TECNOLOGIA DE ALIMENTOS

ISABELLE DE LIMA BRITO POLARI

**AVALIAÇÃO DO POTENCIAL NUTRICIONAL E
ANTIOXIDANTE DE VARIEDADES DE QUINOA**
(Chenopodium quinoa Willd.)

JOÃO PESSOA–PB

2017

Isabelle de Lima Brito Polari

**Avaliação do potencial nutricional e antioxidante de variedades de
quinoa (*Chenopodium quinoa* willd.)**

João Pessoa–PB

2017

Isabelle de Lima Brito Polari

**Avaliação do potencial nutricional e antioxidante de variedades de
quinoa (*Chenopodium quinoa* willd.)**

Tese apresentada ao Programa de Pós-Graduação em Ciência e Tecnologia de Alimentos, do Centro de Tecnologia, da Universidade Federal da Paraíba, em cumprimento aos requisitos para obtenção do título de Doutor em Ciência e Tecnologia de Alimentos.

Orientadora: Prof.^a Dra. Angela Maria Tribuzy de Magalhães Cordeiro

Co-Orientador: Prof.^o Dr. Antonio Gouveia de Souza

JOÃO PESSOA–PB

2017

Catálogo na publicação
Seção de Catalogação e Classificação

P762a Polari, Isabelle de Lima Brito.

Avaliação do potencial nutricional e antioxidante de variedades de quinoa (*Chenopodium quinoa willd.*) / Isabelle de Lima Brito Polari. - João Pessoa, 2017.
130 f. : il.

Orientação: Angela Maria Tribuzy de Magalhães Cordeiro.
Coorientação: Antonio Gouveia de Souza.
Tese (Doutorado) - UFPB/CT.

1. Tecnologia de alimentos. 2. Quinoa - Propriedades funcionais. 3. Características nutricionais - Quinoa. I. Cordeiro, Angela Maria Tribuzy de Magalhães. II. Souza, Antonio Gouveia de. III. Título.

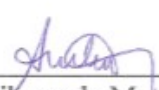
UFPB/BC

ISABELLE DE LIMA BRITO

AVALIAÇÃO DO POTENCIAL NUTRICIONAL E ANTIOXIDANTE DE VARIEDADES
DE QUINOA (*Chenopodium quinoa* Willd.)

Defesa de doutorado aprovada em 21 de Junho de 2017.

BANCA EXAMINADORA



Prof.ª Dra. Angela Maria Tribuzy de Magalhães Cordeiro - PPGCTA/CT/UFPB

Coordenador da Banca Examinadora

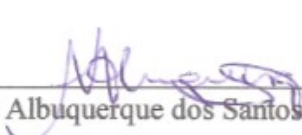
Profª Dra. Marta Maria da Conceição – PPGCTA/CT/UFPB

Membro interno



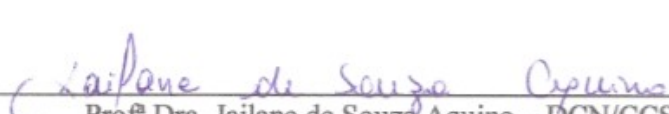
Profª Dra. Maria Elieidy Gomes de Oliveira - PPGCTA/CCS/UFPB

Membro interno



Profª Dra Nataly Albuquerque dos Santos- CTDR/CT/UFPB

Membro externo



Profª Dra. Jailane de Souza Aquino – DCN/CCS/UFPB

Membro externo

Dedico esta conquista

*Aos meus Pais, **Antonio e Sônia** (em memória), por serem meu alicerce, pelo incentivo e amor incondicional, pelos esforços diários e contínuos que sempre dedicaram para minha formação, crescimento pessoal e profissional. A quem devo tudo que tenho e sou.*

*Aos meus filhos, **Ana Beatriz, Maria Letícia e Lucas Emanuel**, por tudo que representam em minha vida e por me darem força para seguir em frente.*

Ao meu esposo Emanuel, pela compreensão e apoio

Aos meus irmãos, pelo incentivo e torcida.

AGRADECIMENTOS

Primeiramente, a **Deus** pelas inúmeras bênçãos concedidas;

Aos **meus pais**, meus ídolos e mestres, minha fortaleza, meu verdadeiro alicerce;

A **minha mãe**, por ter sonhado antes de mim este sonho, por abraçar a causa e cuidar das minhas filhas para que eu pudesse seguir nos estudos. Ela sempre foi minha maior incentivadora e quem me impulsionou em cada situação de desânimo. O mérito é antes de tudo, dela.

Aos **meus filhos**, pela compreensão nas ausências, pela torcida em cada etapa e por serem responsáveis pelas minhas tentativas diárias de seguir em frente;

Ao meu esposo pelo apoio e torcida;

A toda minha família pelo apoio, incentivo e confiança;

Ao Programa de Pós-Graduação em Ciência e Tecnologia de Alimentos, pela oportunidade;

A minha orientadora, Prof.^a Dra. Angela Maria Tribuzy de Magalhães Cordeiro, pelo apoio, confiança e amizade construída;

Ao meu co-orientador, Prof.^o Antonio Gouveia de Souza, pela oportunidade e confiança que me foram depositadas e por tornar possível a realização deste trabalho;

Aos professores, Prof.^o Dr. Flávio Honorato e Prof.^o Dr. Anoar Abdias, pelo auxílio na estatística do trabalho;

À família Lacom, a qual me orgulho em fazer parte;

Aos meus amigos de turma 2013.1, Amanda Sant'ana, Angela Lima, Daline Araújo, Estefânia Garcia, Inês Queiroga, Íris Braz, Jéssica Bezerra, Sinara Fragoso e Vânia da Silva pelos momentos e aprendizados compartilhados;

Aos técnicos de laboratório, que contribuíram para a realização deste trabalho;

Aos meus companheiros de laboratório, em especial, Bruno Meireles e Maristela Alcântara, pelos momentos de alegria e aprendizados partilhados;

A CAPES, pela bolsa de estudo concedida;

A todos que contribuíram de forma direta ou indireta para realização deste trabalho.

“Feliz aquele que transfere o que sabe e aprende o que ensina”.

(Cora Coralina)

RESUMO

A quinoa (*Chenopodium quinoa* Willd.) é considerada um alimento com propriedades funcionais por conter compostos que estão associados a diversos benefícios à saúde. Considerando o interesse crescente no uso destas sementes na prevenção de doenças e no seu potencial para indústria de alimentos, o presente estudo oferece inicialmente abordagens científicas, em forma de revisão bibliográfica destacando as características nutricionais, tecnológicas e os benefícios fisiológicos associados ao consumo da quinoa em diferentes tipos de doenças. As sementes de quinoa, na variedade branca e vermelha, cultivadas no Brasil e na Bolívia foram avaliadas quanto aos seus perfis nutricionais e atividade antioxidante, assim como dos seus respectivos óleos. As sementes desengorduradas foram analisadas através de um delineamento experimental, quanto às condições de extração dos compostos fenólicos e atividade antioxidante. Um modelo polinomial de primeira ordem foi desenhado para avaliar os efeitos das variáveis independentes: temperatura (32-68 °C), tempo (6,5-19,5 h) e concentração de etanol (19-76%) sobre a extração de fenólicos totais (TFT), atividade antioxidante (DPPH; FRAP; ABTS) e identificação e quantificação dos fenólicos por cromatografia líquida de alta eficiência. As condições ótimas de extração foram analisadas utilizando metodologia de superfície de resposta e obtidas através da maximização simultânea dos parâmetros analisados. Para a variedade branca brasileira o ponto máximo do planejamento (68 °C; 19,5 h; 76% de etanol) obteve as maiores respostas para TFT, ABTS e concentração de fenólicos. Já para a branca boliviana, nas mínimas condições (32 °C; 6,5 h; 19% de etanol) foi identificado maior TFT e DPPH; contudo, para a quantificação de fenólicos, as condições máximas de temperatura e concentração de etanol obtiveram maiores respostas (68°C; 6,5h; 76% de etanol). Para quinoa vermelha boliviana estas mesmas condições foram responsáveis pelas respostas estatisticamente significativas para todas as variáveis dependentes e concentração de fenólicos. Dentre os ácidos fenólicos, os 2,5-dihidroxibenzóico, sinápico, ferúlico, salicílico e elágico e, os flavonóides, kampferol, miricetina, quercetina, catequina e a rutina como majoritária, foram os compostos responsáveis pela elevada atividade antioxidante das sementes. O modelo estatístico demonstrou relevância na utilização da mistura de solventes “verdes” na extração de fenólicos das sementes de quinoa. Da mesma forma, os óleos *in natura* extraídos a partir das sementes apresentaram elevada estabilidade oxidativa, com período de indução de até 8,11 horas. Os óleos obtiveram também importante destaque quanto a capacidade antioxidante, de modo que foram necessários apenas 7,65; 6,81 e 6,07 µL dos óleos das variedades brancas brasileira e boliviana e vermelha boliviana, respectivamente, para eliminar 50% do radical livre DPPH. Foram identificados ainda ácidos graxos predominantemente poliinsaturados, presença de aminoácidos essenciais e minerais nutricionalmente importantes como magnésio, manganês, ferro e selênio na constituição das sementes. A quinoa branca do Brasil se destacou quanto a sua qualidade nutricional comparado às outras sementes analisadas. Dessa forma, o presente estudo confirmou a quinoa como alimento de elevada capacidade antioxidante, apresentando potencial de uso na promoção da saúde e para indústria alimentícia.

Palavras-chave: *Chenopodium quinoa*; propriedades funcionais; antioxidantes naturais.

ABSTRACT

Quinoa (*Chenopodium quinoa* Willd.) is considered a food with functional properties because it contains compounds that are associated with several health benefits. Considering the growing interest in the use of these seeds in the prevention of diseases and their potential for food industry, the present study offers initially scientific approaches, in the form of a bibliographic review highlighting the nutritional characteristics, technological and the physiological benefits associated with the consumption of quinoa in different types of diseases. The quinoa seeds, in the white and red variety, cultivated in Brazil and Bolivia were evaluated for their nutritional profiles and antioxidant activity, as well as their respective oils. The degreased seeds were analyzed through an experimental design, regarding the extraction conditions of phenolic compounds and antioxidant activity. A first order polynomial model was designed to evaluate the effects of the independent variables: temperature (32-68 ° C), time (6.5-19.5 h) and ethanol concentration (19-76%) on the extraction of total phenols (TFT), antioxidant activity (DPPH, FRAP, ABTS) and identification and quantification of phenolics by high performance liquid chromatography. The optimal extraction conditions were analyzed using response surface methodology and obtained through the simultaneous maximization of the analyzed parameters. For the Brazilian white variety the maximum point of planning (68 ° C, 19.5 h, 76 % ethanol) obtained the highest responses for TFT, ABTS and phenolic concentration. Already for the white Bolivian, in the minimum conditions (32 ° C, 6.5 h, 19% ethanol) greater TFT and DPPH were identified; however, for the quantification of phenolics, the maximum conditions of temperature and ethanol concentration obtained higher responses (68 ° C, 6,5h, 76% ethanol). For Bolivian red quinoa, these same conditions were responsible for the statistically significant responses for all dependent variables and phenolic concentration. Among phenolic acids, 2,5-dihydroxybenzoic, synapic, ferulic, salicylic and ellagic and, flavonoids, kampferol, myricetin, quercetin, catechin and rutin as the major, were the compounds responsible for the high antioxidant activity of the seeds. The statistical model demonstrated relevance in the use of the "green" solvent mixture in the extraction of phenolics from quinoa seeds. Similarly, the in natura oils extracted from the seeds presented high oxidative stability, with an induction period of up to 8.11 hours. The oils also obtained important importance as to the antioxidant capacity, so it was only necessary 7.65; 6.81 and 6.07 µL of the oils of the Brazilian, Bolivian and Bolivian red varieties respectively, to eliminate 50% of the DPPH free radical. It was also identified polyunsaturated fatty acids, presence of essential amino acids and nutritionally important minerals such as magnesium, manganese, iron and selenium in the constitution of the seeds. The white quinoa of Brazil was highlighted as to its nutritional quality compared to the other seeds analyzed. Therefore, the present study confirmed quinoa as a high antioxidant capacity food, with potential for use in health promotion and for the food industry.

Key words: *Chenopodium quinoa*; functional properties; natural antioxidants.

LISTA DE FIGURAS

Figura 1 – Fluxograma das etapas e análises realizadas no experimento.	19
Figura 2 – Sementes de quinoa A - Quinoa branca do Brasil (QBBR); B - Quinoa branca da Bolívia (QBBo); C- Quinoa vermelha da Bolívia (QVBo).	20
Figura 3 – Estabilização do radical DPPH.	29
Figura 4 – Redução do complexo TPTZ com Fe^{3+}	29
Figura 5 – Estabilização do radical ABTS ⁺ por um antioxidante e sua formação pelo persulfato de potássio.....	30

ARTIGO I

Fig. 1 – Schematic representation of a quinoa seed cross section.....	67
Fig. 2 - Potential use of quinoa in food industry. Source: USDA, 2015.	68

ARTIGO II

Fig. 1. Quinoa seeds. A: Brazilian white quinoa (BrWQ), B: Bolivian white quinoa (BoWQ), and C: Bolivian red quinoa (BoRQ).	91
Fig. 2. Yields of BrWQ, BoWQ, and BoRQ seed extracts.	91
Fig. 3. Response surfaces for the TPC and BrWQ AA.	92
Fig. 4. Response surfaces for the TPC and BoWQ AA.	93
Fig. 5. Response surfaces for the TPC and BoRQ AA.	94
Fig. 6a. Chromatogram of the phenolics of the white quinoa extract, BrWQ variety, obtained by HPLC.	95
Fig. 6b. Chromatogram of the phenolics of the white quinoa extract, BoWQ variety, obtained by HPLC.	95

Fig. 6c. Chromatogram of the phenolics of the white quinoa extract, BoRQ variety, obtained by HPLC.	96
--	----

ARTIGO III

Figura 1 – Análise de infravermelho dos óleos de quinoa.	119
--	-----

LISTA DE TABELAS

Tabela 1a – Valores decodificados do planejamento linear para os três fatores.	26
Tabela 1b – Planejamento linear 23 com os valores experimentais e previstos para as variáveis independentes.	26
Tabela 2 – Valores decodificados do planejamento corrigidos para volume de solvente.	26

ARTIGO I

Table 1 - Amino acid concentrations in quinoa seeds compared with cereals and the FAO/WHO standard.	69
Table 2 - Monosaccharide composition of insoluble dietary fiber from quinoa.	70
Table 3 - Micronutrients present in quinoa seeds, compared with other grains.	71

ARTIGO II

Table 1a Values decoded from the independent variables in the linear model.	97
Table 1b 2 ³ experimental design with the decoded experimental values of the independent variables.	97
Table 2 TPC and antioxidant capacity according to the DPPH, ABTS, and FRAP of quinoa extracts prepared with ethanol/water solutions according to the experimental design.	98
Table 3 Regression coefficients and equations of the first-order mathematical models of response variables.	99
Table 4 Identification and concentration (mg/100 g seed) of phenolics by HPLC of the three varieties of quinoa.	100

ARTIGO III

Tabela 1. Composição química das sementes de quinoa.	111
--	-----

Tabela 2. Composição protéica das sementes de quinoa.	113
Tabela 3. Perfil de aminoácidos das variedades de quinoa.	114
Tabela 4. Teor de minerais das variedades de quinoa.	115
Tabela 5. Contribuição da quinoa para a ingestão dietética diária de minerais recomendada para adultos, expressa em % (valor nutricional obtido por 100g de alimentos)/ Ingestão recomendada.	116
Tabela 6. Perfil de ácidos graxos (g/100 de ácidos graxos) de três amostras de óleo de quinoa.	117
Tabela 7- grupos de compostos orgânicos encontrados por espectroscopia de infravermelho médio de acordo com número de onda e modo de vibração.	120
Tabela 8. Análise dos óleos das sementes de quinoa.	121

LISTA DE ABREVIATURAS E SIGLAS

AA	Atividade antioxidante
AAT	Atividade antioxidante total
ABTS^{•+}	2,2'-azino-bis-(3-etilbezotiazolina-6-ácido sulfônico)
ACE	Enzima conversora de angiotensina
ADA	Associação dietética americana
ANOVA	Análise de variância
AOAC	Official Methods of Analysis
AOCS	American Oil Chemists' Society
CCF	Concentração de compostos fenólicos
CG-EM	Cromatografia à Gás acoplada ao Espectrômetro de Massa
CLAE	Cromatografia Líquida de Alta Eficiência
CMC	Carboximetilcelulose
DCV	Doença cardiovascular
DNA	Ácido desoxiribonucleico
DPPH•	2,2-difenil-1-picril-hidrazila
EROS	Espécies reativas de oxigênio
FAO	Food and Agriculture Organization of the United Nations/ Organização das Nações Unidas para Alimentação e Agricultura
FRAP	Poder antioxidante de redução do Ferro
GABA	g-aminobutírico
IG	Índice glicêmico
IL6	Interleucina 6
IMC	Índice de massa corporal
OMS	Organização Mundial de Saúde
PI	Período de Indução
PUFA	Ácidos graxos poliinsaturados
QBBr	Quinoa branca do Brasil
QBBó	Quinoa branca da Bolívia
QVBó	Quinoa vermelha da Bolívia
TBARS	Espécies reativas ao ácido tiobarbitúrico
TFT	Teor de fenólicos totais

TG	Análise Termogravimétrica
TNF-α	Fator de necrose tumoral
TPTZ	2, 4, 6 – Tri (2-piridil) – 1,3,5 – triazina
TROLOX	6-hidroxi-2,5,7,8-tetrametilcroman-2-ácido carboxílico
USDA	United States Department of Agriculture

SUMÁRIO

1 INTRODUÇÃO.....	17
2 MATERIAL E MÉTODOS.....	19
2.1. LOCAL DE EXECUÇÃO DO EXPERIMENTO.....	19
2.2 MATERIAIS E REAGENTES.....	20
2.3 AQUISIÇÃO DA MATÉRIA PRIMA.....	20
2.4 CARACTERIZAÇÃO DAS SEMENTES.....	21
2.4.1 Composição Centesimal	21
2.4.2 Identificação das frações protéicas.....	21
2.4.3 Perfil de aminoácidos.....	21
2.4.4 Análise de minerais.....	22
2.5 OBTENÇÃO DOS ÓLEOS.....	22
2.5.1 Extração com Hexano.....	22
2.6 CARACTERIZAÇÃO DOS ÓLEOS.....	23
2.6.1 Perfil de ácidos graxos.....	23
2.6.2. Dienos e Trienos conjugados.....	23
2.6.3 Estabilidade oxidativa	23
2.6.4 Análise de Infravermelho.....	24
2.6.5 Atividade Antioxidante dos óleos.....	24
2.7 PREPARO DAS SEMENTES.....	24
2.8 PLANEJAMENTO EXPERIMENTAL.....	25
2.9 OBTENÇÃO DOS EXTRATOS VEGETAIS.....	27
2.10 DETERMINAÇÃO DO CONTEÚDO DE FENÓLICOS TOTAIS.....	27
2.11 IDENTIFICAÇÃO E QUANTIFICAÇÃO DOS COMPOSTOS FENÓLICOS ...	27
2.12 DETERMINAÇÃO DA ATIVIDADE ANTIOXIDANTE DOS EXTRATOS.....	28

2.12.1 Método de sequestro de radicais livres DPPH• (2,2-difenil-1-picril-hidrazila).....	28
2.12.2 Poder antioxidante de redução do ferro (FRAP).....	29
2.12.3 Método ABTS.....	30
2.13 ANÁLISE ESTATÍSTICA.....	30
REFERÊNCIAS.....	31
3. RESULTADOS.....	35
3.1 ARTIGO I: Propriedades químicas, funcionaise tecnológicas da quinoa (<i>Chenopodium quinoa</i> Willd.) – Revisão	36
3.2 ARTIGO II: Aplicação da metodologia de superfície de resposta na otimização da extração de compostos fenólicos e capacidades antioxidantes de diferentes variedades de quinoa (<i>Chenopodium quinoa</i>Willd.)	72
3.3 ARTIGO III: Perfil Nutricional de sementes e de óleos de quinoa (<i>Chenopodium quinoa</i>Willd.) cultivadas no Brasil e na Bolívia.	102
4 CONCLUSÕES.....	127
5 ANEXOS	128
5.1 ANEXO 1 – Comprovante de Submissão do artigo 1: <i>Chemical, functional and technological properties of quinoa (Chenopodium quinoa Willd.): A review</i>	129
5.2 ANEXO 2 – Comprovante de Submissão do artigo 2: <i>Application of response surface methodology to optimize extraction of phenolic compounds and antioxidant capacity of different quinoa (Chenopodium quinoa Willd.) varieties</i>.....	130

1.INTRODUÇÃO

O consumo de alimentos ditos funcionais é crescente e está diretamente associado a preocupação do consumidor com saúde e bem-estar (FALGUERA et al., 2012). Dessa forma, cada vez mais se sustenta, em base científica, a tese de que os vegetais e seus princípios ativos têm um papel importante na prevenção de doenças crônicas e degenerativas (ANDRÉ et al., 2010, MAGANHA et al., 2010). Dentre os diversos constituintes presentes na quinoa, os polifenóis, as fibras, predominantemente insolúveis, ácidos graxos essenciais, carboidratos complexos, proteínas e seus peptídeos têm sido correlacionados a efeitos fisiológicos na prevenção de diversas doenças, tais como obesidade, diabetes mellitus, doenças cardiovasculares, câncer, hipertensão arterial e lesões gástricas (NOWAK et al., 2016). Estes estudos têm impulsionado o uso da quinoa na dieta humana, assim como tem incentivado a indústria na produção de alimentos adicionados com esta semente e/ou seus constituintes (BRITO et al., 2014; GRAF et al., 2014; SWIECA et al., 2014).

A quinoa (*Chenopodium quinoa* Willd.) é uma planta cultivada tradicionalmente na região andina há milhares de anos apresentando-se bem adaptada a diversas condições climáticas (JACOBSEN, 2011; RAZZAGHI et al., 2012). Descrita como um pseudocereal, sua constituição a caracteriza como alimento funcional por apresentar valor nutricional agregado, além da nutrição básica. É isenta de glúten, composta de proteínas de elevado valor biológico, ácidos graxos ω -3 e ω -6, vitaminas (niacina, riboflavina, vitamina B6 e ácido fólico) e minerais (fósforo, potássio, cálcio, magnésio, manganês, ferro e selênio), além de apresentar em suas constituição compostos bioativos (JAMES, 2009; KONISHI et al., 2004; ANDO et al., 2002). Porém, sua composição pode variar de acordo com o solo, adubação, irrigação, características ambientais, climáticas e a variedade estudada (HIROSE et al., 2010).

Estudos reportam que os polifenóis presentes na quinoa apresentam capacidade antioxidante e atuam na diminuição dos fatores de risco para cardiopatias, aterosclerose, diabetes, Doença de Alzheimer e câncer (GÓMEZ-CARAVACA et al., 2011; ABDERRAHIM et al., 2015; ALBERTI et al., 2014). As propriedades antioxidantes são atribuídas a capacidade do fenólico em sequestrar radicais livres ou quelar os ions metálicos envolvidos na sua produção (WANASUNDARA; SHAHIDI, 2005; WOOTTON-BEARD et al., 2011). Dentre essas substâncias, os principais flavonóides presentes na quinoa são a quercetina e o kaempferol, enquanto os ácidos caféico, ferúlico, vanílico, *p*-cumarico e benzóico são os principais ácidos fenólicos, contendo ainda importantes teores de α -tocoferol

e γ -tocoferol (NG et al., 2007; VALENCIA-REPRO-CARRASCO et al., 2010; HIROSE et al., 2010).

O uso de antioxidantes naturais, extraídos de vegetais, pelas indústrias têm crescido devido às suas propriedades antimicrobianas, antioxidantes e estabilizantes de alimentos, além de atrair os consumidores que buscam alimentos diferenciados. Contudo, a extração desses compostos varia de acordo com o método, natureza química da amostra, tipo de solventes e condições utilizadas (ALBERTI et al., 2014; PRASAD et al., 2011). A extração com solvente é o método mais comum usado para isolar antioxidantes naturais (REZAIE et al., 2015). Dessa forma, há maior interesse da comunidade científica e consumidores em utilizar solventes naturais, isento ou com menor teor de toxicidade, conhecidos como solventes “verdes”, uma vez que estes parecem seguros quando utilizados em alimentos.

Diante da importância da qualidade nutricional e inúmeros benefícios da quinoa reportados na literatura, este trabalho propõe uma compilação dos dados sobre esta semente na forma de uma revisão bibliográfica, assim como investigar as propriedades nutricionais e as condições de extração dos compostos antioxidantes de diferentes variedades de sementes de quinoa, cultivadas no Brasil e na Bolívia e seus respectivos óleos.

1.1 OBJETIVO GERAL

Avaliar o potencial nutricional e antioxidante de sementes de quinoa.

1.2 OBJETIVOS ESPECÍFICOS

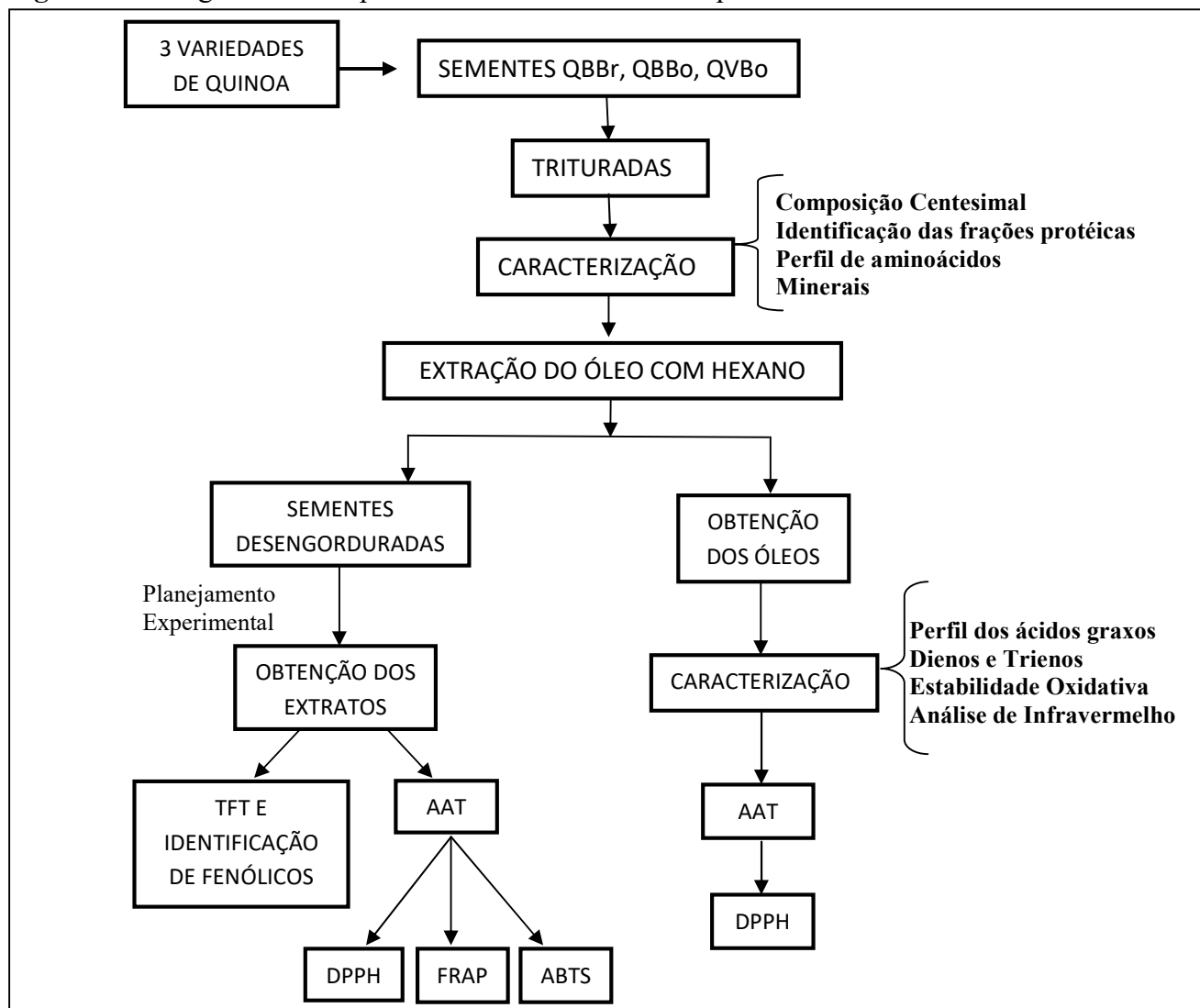
- Avaliar o perfil nutricional de diferentes variedades de sementes de quinoa produzidas no Brasil e na Bolívia;
- Extrair e caracterizar os óleos das variedades de quinoa estudadas;
- Obter extratos das sementes a partir de planejamento experimental;
- Avaliar a influência das variáveis independentes na extração de compostos fenólicos e atividade antioxidante dos extratos;
- Identificar os pontos ótimos de extração para cada variedade a partir das análises de superfície de resposta, equações polinomiais e maior identificação de teor de fenólicos totais (TFT), atividade antioxidante (AA) e identificação de fenólicos;

2. MATERIAL E MÉTODOS

2.1. LOCAL DE EXECUÇÃO DO EXPERIMENTO

Todos os procedimentos e ensaios foram realizados na Universidade Federal da Paraíba, no Laboratório de Combustíveis e Materiais (LACOM), do Departamento de Química, do Centro de Ciências Exatas e da Natureza; no Laboratório de Química de Alimentos (LAQA), do Departamento de Engenharia de Alimentos, do Centro de Tecnologia e no Laboratório de Processamento Vegetal, do Departamento de Tecnologia de Alimentos, do Centro de Tecnologia e Desenvolvimento Regional – CTDR, de acordo com o fluxograma apresentado na Figura 1.

Figura 1. Fluxograma das etapas e análises realizadas no experimento.



QBBr – Quinoa branca brasileira; QBBo – Quinoa branca boliviana; QVBo – Quinoa vermelha boliviana; AAT - atividade antioxidante total; TFT - Teor de fenólicos total;

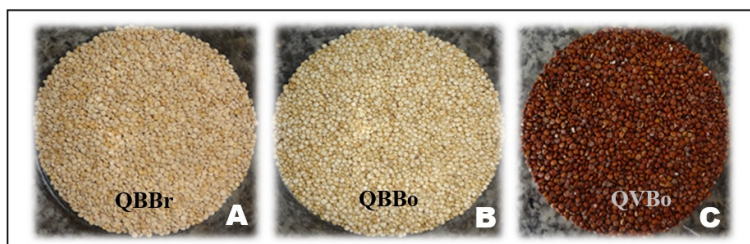
2.2 REAGENTES

Os padrões de ácido gálico e os reagentes TPTZ (2,4,6 – Tri (2-piridil) – 1,3,5 - triazina), DPPH• (2,2-difenil-1-picril-hidrazila), TROLOX (6-hidroxi-2,5,7,8-tetrametilcroman-2-ácido carboxílico); ácidos fenólicos: ácido 3,4 dihidroxibenzóico (protocatequímico), 4 hidroxibenzoico, salicílico, siríngico, ácido 2,5 dihidroxibenzóico (gentísico), vanílico, elágico, p-cumárico, sinápico, *trans*-cinâmico, caféico e ferúlico e flavonoides: rutina, miricetina, quercetina, naringina, kaempferol, catequina, hesperetina, crisina foram obtidos da Sigma-Aldrich® (St. Louis, EUA). O reagente Folin-Ciocalteu foi adquirido da Merck® (Darmstadt, Alemanha). Os reagentes cloreto de ferro (III) hexahidratado ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), acetato de sódio trihidratado, carbonato de sódio, cloreto de ferro (II) tetrahidratado ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), sulfato de ferro (III) pentahidratado ($\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$) foram adquiridos da Vetec Química Fina Ltda (Duque de Caxias, Brasil). Os solventes n-hexano, acetona, etanol, isopropanol, clorofórmio ambos de grau analítico, foram obtidos da FMAIA® (São Paulo, Brasil). O metanol, hexano e acetonitrila grau HPLC foram adquiridos da J.T. Baker (Phillipsburg, USA) e os gases nitrogênio e oxigênio da White Martins.

2.3 AQUISIÇÃO DA MATÉRIA PRIMA

As sementes de quinoa nacionais, obtidas de uma mesma colheita, foram adquiridas diretamente com o produtor localizado na região Centro-oeste do país. Enquanto que as sementes importadas (branca e vermelha) oriundas e cultivadas na cidade de La Paz, na Bolívia, foram adquiridas de um mesmo lote, com a empresa Vitalim, localizada na cidade de Jaraguá do Sul em Santa Catarina e responsável pela embalagem e distribuição no Brasil (Figura 2). Foram utilizados 2 Kg de cada variedade de quinoa para realização dos experimentos.

Figura 2. Sementes de quinoa.



A - Quinoa branca do Brasil (QBBR); B - Quinoa branca da Bolívia (QBBo); C - Quinoa vermelha da Bolívia (QVBa).

2.4 CARACTERIZAÇÃO DAS SEMENTES

2.4.1 Composição centesimal

A determinação de proteínas, umidade e cinzas foram realizadas de acordo com AOAC (2012). Os lipídios foram determinados segundo metodologia descrita por Bligh e Dyer (1959) e os carboidratos foram quantificados em açúcares solúveis total e redutor pelo método DNS (MILLER, 1959).

2.4.2 Identificação das frações protéica das sementes

As proteínas da quinoa foram fracionadas e quantificadas de acordo com Osborne (1924) com algumas modificações. As concentrações das frações de albumina, globulina, prolaminas e glutelinas foram estimadas de acordo com o método de Bradford (1976), utilizando uma curva padrão de albumina de soro bovino.

A fração de albumina foi extraída com água deionizada (1 g/10 mL). A suspensão foi misturada durante 1 h, a 4 °C e, posteriormente, centrifugada a 5000 rpm, durante 20 min a 4 °C e o sobrenadante foi recolhido. O sedimento foi resuspenso em 0,05 mol/L de Tris HCl (pH 8,0) contendo 0,5 mol/L de NaCl e a mistura foi centrifugada nas mesmas condições já descritas. O sobrenadante foi dialisado e a proteína solúvel designada como fração de globulina. Sequencialmente, as prolaminas foram extraídas do resíduo com 70 mL/100 mL de etanol e novamente centrifugados. O sedimento final foi extraído com 0,1 mol/L de $\text{Na}_2\text{B}_4\text{O}_7 \cdot \text{H}_2\text{O}$ (pH 10) para obtenção das frações de glutelinas. As frações foram armazenadas sob 4 °C até o momento de sua utilização.

2.4.3 Perfil de Aminoácidos

A determinação de aminoácidos das variedades de quinoa foi de acordo com a metodologia descrita por White (1986), que constitui uma hidrólise ácida de ácido clorídrico com fenol a 1%, seguida de derivatização com o reagente Fenilisotiocianato (PITC). Os aminoácidos foram separados, identificados e quantificados por Cromatografia Líquida de Alta Eficiência – CLAE (VARIAN, Water 2690, Califórnia, USA) acoplado com coluna de fase reversa C18 (PICO-TAG, 3,9 x 150 mm). A detecção foi realizada em comprimento de

onda de 254 nm, à temperatura de 35 °C com tempo de corrida de 21 min e fluxo de 1 mL/min.

2.4.4 Análises de minerais

A digestão das amostras foi realizada em um sistema de digestão por micro-ondas Berghof, modelo *Speedwave four* (Harretstrabe, Alemanha). As sementes trituradas foram pesadas (0,4 g) e colocadas em tubos Teflon para digestão (DAP-60+). Uma mistura de ácido nítrico a 65% (3 mL) e peróxido de hidrogênio a 35% (3 mL) foi cuidadosamente adicionada. Após repouso de, aproximadamente, 30 minutos, os tubos foram adequadamente fechados e introduzidos no micro-ondas. Os gradientes de temperatura, pressão e tempo utilizados foram determinados pelo fabricante para sementes oleaginosas. Após digestão, os tubos foram arrefecidos até à temperatura ambiente e as amostras digeridas foram filtradas.

Os elementos químicos (Ca, Fe, Mg, P, K, Na, Al, Mn, Cu, Zn, Se, Cr, Co) foram determinados usando um espectrômetro de emissão óptica com plasma acoplado indutivamente ICP-MS Thermo Scientific, segundo a norma EPA (1998) (Massachusetts, EUA).

2.5 OBTENÇÃO DOS ÓLEOS DE QUINOA

2.5.1 Extração com hexano

Para extração do óleo, as amostras de sementes (QBBR, QBBo e QVBo) foram trituradas em processador mecânico (Pratic Blender Cadence, BLD300), pesadas (30 g) e adicionadas a 200 mL de hexano. As misturas foram submetidas a agitação de 200 rpm em incubadora (modelo TE-420, TECNAL), Piracicaba, Brasil por 4 h, a temperatura de 40 °C. Posteriormente, o hexano foi retirado e reservado, enquanto as amostras foram novamente diluídas em 100 mL de hexano e submetidas às mesmas condições por mais 2 horas. O hexano foi novamente recolhido, adicionado ao primeiro volume e evaporado em estufa de circulação de ar a 35 °C.

2.6 CARACTERIZAÇÃO DOS ÓLEOS

2.6.1 Perfil de Ácidos Graxos

Para os óleos das variedades QBBr, QBBo e QVBo, foram realizadas a esterificação dos ácidos graxos presentes seguindo a metodologia descrita por Hartman e Lago (1973). A identificação e quantificação dos ésteres de ácidos graxos foram realizadas utilizando-se um cromatógrafo gasoso (VARIAN 430-GC, Califórnia, EUA), acoplado com coluna capilar de sílica fundida (CP WAX 52 CB, VARIAN, Califórnia, EUA). Foi utilizado o hélio como gás de arraste (vazão de 1mL/min). As condições do CG foram: Temperatura do injetor e detector de 250 °C; temperatura inicial do forno de 100 °C, aumentando-se 2,5 °C/min até atingir 240 °C, permanecendo-se por 30 min, totalizando em tempo total de corrida de 86 min. Aliquotas de 1,0 µL do extrato esterificado foram injetadas em injetor tipo Split/Splitless e os cromatogramas foram registrados em *software* tipo *Galaxie Chromatography Data System*. Os ácidos graxos foram identificados por comparação dos tempos de retenção dos ésteres metílicos das amostras com padrões Supelco ME19 - Kit (*Fatty Acid Methyl Esters* C4 - C24).

2.6.2 Dienos e Trienos Conjugados

Os dienos e trienos foram quantificados em absorbância de 232 e 270 nm empregando-se um espectrofotômetro UV-*vis* da Shimadzu, modelo UV-2550 (Kyoto, Japão), utilizando cubetas de quartzo com 1 cm de caminho óptico. As soluções de óleo foram preparadas em Isooctano na concentração de 1 mg/mL.

2.6.3 Estabilidade oxidativa

Os ensaios de estabilidade oxidativa foram realizados em duplicata no equipamento 873 Biodiesel Rancimat da marca Metrohm (Herisau, Suíça), utilizando a metodologia da AOCS Cd 12b-92 (2009). Neste método, 2 g da amostra foram expostas a uma temperatura de 110 °C, sob fluxo constante de ar (10 L/h). O resultado foi expresso como período de indução (PI), em horas, determinado automaticamente a partir do ponto de inflexão da curva, pelo programa 873 Biodiesel Rancimat Control.

2.6.4 Análise de Infravermelho

A análise de infravermelho foi realizada utilizando equipamento Espectrofotômetro Infravermelho por Transformada de Fourie – (FTIR) da marca Shimadzu, modelo Prestige-21 (Kyoto, Japão), utilizando o método de reflectância atenuada (ATR). Os espectros foram obtidos na faixa de $4000\text{-}650\text{ cm}^{-1}$, com resolução de 4 cm^{-1} e 32 varreduras.

2.6.5 Atividade Antioxidante dos óleos

A atividade antioxidante dos óleos foi obtida através do método DPPH em diferentes concentrações de óleo (3, 5 e 10 μL) usando o Trolox como padrão. O volume foi ajustado a 1 mL pela adição de etanol de uma solução metanólica 2,2-difenil-1-picrilhidrazil radical (DPPH, 250 μL a 0,5 mM) e Tween 20 (5 μL). Os tubos foram armazenados à temperatura ambiente no escuro durante 60 min (GORINSTEIN et al., 2003). O controle foi preparado nas mesmas condições, sem amostra de óleo. A leitura da absorbância foi realizada em espectrofotômetro UV-Vis (Shimadzu, modelo UV-2550 Kyoto, Japão) a 515 nm e a eliminação dos radicais foi expressa em EC50 (Concentração Efetiva para reduzir em 50% o radical DPPH) que indica o volume (μL) de óleo necessário para eliminar 50% do radical livre DPPH. O potencial antioxidante é inversamente proporcional ao valor de EC50.

2.7 PREPARO DAS SEMENTES

As sementes de quinoa foram inicialmente trituradas em processador mecânico (Pratic Blender Cadence, BLD300) e desengorduradas como descrito anteriormente (item 2.5.1). As amostras desengorduradas foram secas em estufa de ar circulante a uma temperatura de $30\text{ }^{\circ}\text{C}$ e acondicionadas, separadamente, em recipientes de vidro com tampa, protegidos da luz e sob refrigeração até realização das análises.

2.8 PLANEJAMENTO EXPERIMENTAL PARA OBTENÇÃO DOS EXTRATOS VEGETAIS

Para produção dos extratos de cada variedade de quinoa foi desenhado um planejamento experimental 2^3 com três pontos centrais e oito principais. O objetivo foi avaliar os parâmetros de extração e identificar a relação entre as variáveis do processo e suas respostas no modelo linear, bem como otimizar as condições de extração de compostos fenólicos totais e a atividade antioxidante (DPPH, FRAP e ABTS) dos extratos de quinoa (BOX; BEHNKEN, 1960).

O software Statistic 7.0 (StatSoft, 2004) foi utilizado para realizar o desenho experimental e análise estatística. Os resultados para o conteúdo de fenólicos totais, DPPH, FRAP e ABTS foram expressos como média $\pm$ desvio padrão e gerado a análise de variância (ANOVA) ($p < 0,05$) para cada resposta. Estes dados foram utilizados para determinar a significância estatística, os coeficientes de regressão (R^2) e o modelo para otimizar a região global das respostas. A partir desses instrumentos, foi aplicado um polinômio de primeira ordem para prever as variáveis de resposta (Eq. 1):

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_1 x_2 + \beta_5 x_1 x_3 + \beta_6 x_2 x_3 + \beta_7 x_1 x_2 x_3 \quad (\text{Eq.1})$$

Onde y é a resposta, β_0 é a média e os coeficientes β_1 , β_2 e β_3 são os coeficientes de regressão para os termos linear e β_4 , β_5 , β_6 , e β_7 representam os coeficientes de efeito das interações (Eq. 1) (BRUNS et al., 2006). A adequação do modelo foi prevista considerando o erro puro e a partir da análise de regressão (R^2) e ANOVA ($p < 0,05$). O significado da regressão dos coeficientes foi analisado por meio do teste Tukey e na presença de coeficientes não significativos, estes foram removidos para se obter um modelo reduzido.

As variáveis independentes utilizadas foram temperatura X_1 (32-68 °C), tempo X_2 (6,5-19,5 h) e concentração de etanol (etanol: água) X_3 (19-76%); enquanto as variáveis de resposta foram teor de fenólicos totais (Y_1) e capacidade antioxidante através dos métodos DPPH (Y_2), FRAP (Y_3) e ABTS (Y_4). A seleção dos pontos dos três fatores foi baseada em estudos prévios descritos por Abderrahim et al. (2015); Alberti et al. (2014) e Prasad et al. (2011).

Cada variável a ser otimizada foi codificada em três níveis -1, 0, 1 (Tabela 1). Após determinados os valores descodificados para +1, 0 e -1 foi desenhado o planejamento fatorial

com onze experimentos randomizados, sendo destes, três representando o ponto central e oito os pontos principais (Tabela 2).

Tabela 1 - Valores descodificados do planejamento linear para os três fatores.

Variável	- 1	0	+ 1
Temperatura	32 °C	50 °C	68 °C
Tempo	6,5 h	13 h	19,5 h
Concentração de Etanol	19%	47,5%	76%

Tabela 2 - Planejamento linear 2^3 com os valores experimentais e previstos para as variáveis independentes.

Experimento	Variáveis Independentes		
	X ₁	X ₂	X ₃
1	-1 (32)	-1 (6,5)	-1 (19)
2	-1 (32)	1 (19,5)	1 (76)
3	1 (68)	-1 (6,5)	1 (76)
4	1 (68)	1 (19,5)	-1 (19)
5	-1 (32)	-1 (6,5)	1 (76)
6	-1 (32)	1 (19,5)	-1 (19)
7	1 (68)	-1 (6,5)	-1 (19)
8	1 (68)	1 (19,5)	1 (76)
9	0 (50)	0 (13)	0 (47,5)
10	0 (50)	0 (13)	0 (47,5)
11	0 (50)	0 (13)	0 (47,5)

*x₁ Temperatura (°C); x₂ Tempo (h); x₃ Concentração etanol (%)

De acordo com a pureza do etanol (95%), fez-se necessário a correção para um volume de 100 mL de solvente. Dessa forma, as concentrações passam para 20% (- 1), 50% (0), 80% (+ 1) conforme expresso na Tabela 3.

Tabela 3 - Valores descodificados do planejamento corrigidos para volume de solvente.

Variável	- 1	0	+ 1
Temperatura	32 °C	50 °C	68 °C
Tempo	6,5 h	13 h	19,5 h
Concentração	20%	50%	80%

2.9 OBTENÇÃO DOS EXTRATOS VEGETAIS

Para obtenção dos extratos, foram pesados 10 g das amostras na proporção soluto-solvente de 1:10. As misturas foram submetidas às condições de concentração, temperatura e tempo determinadas para cada experimento do planejamento e mantidas sob agitação mecânica em Incubadora TE-420, TECNAL (Piracicaba, Brasil). Seguidos da centrifugação (5000 x g por 15 min) em centrífuga himac CF 5RX, HITACHI (Tóquio, Japão) filtração a vácuo e secagem em estufa com circulação de ar a 35 °C, por 15 horas, para eliminação do solvente remanescente. Os extratos concentrados foram armazenados ao abrigo da luz, sob refrigeração até o momento de sua utilização.

2.10 DETERMINAÇÃO DO CONTEÚDO DE FENÓLICOS TOTAIS

O teor de fenólicos totais dos extratos das sementes de quinoa foi determinado em triplicata, pelo método espectrofotométrico, utilizando o reagente Folin-Ciocalteu (ROSSI; SINGLETON, 1965), com algumas adaptações. Inicialmente, cada extrato foi diluído em água numa concentração de 5 mg/mL. Uma alíquota de 240 µL dos extratos foi transferida para tubos de ensaio, os quais foram adicionados de 60 µL do reagente Folin-Ciocalteu e submetidos a agitação por 60 segundos. Em seguida, foi acrescida ao tubo uma alíquota de água destilada e de uma solução de Na₂CO₃ a 15%, sendo o volume final da mistura de 3 mL e então novamente agitados por mais 30 segundos. A mistura foi deixada em repouso a temperatura ambiente por duas horas, na ausência de luz. Posteriormente, foi realizada leitura a 760 nm, empregando-se um espectrofotômetro UV-vis da Shimadzu, modelo UV-2550. O ácido gálico foi usado na curva padrão (0,001-0,020 mg/mL em etanol) e os resultados expressos em miligrama de equivalente de ácido gálico por g do extrato seco (mg EAG/g).

2.11 IDENTIFICAÇÃO E QUANTIFICAÇÃO DOS COMPOSTOS FENÓLICOS

Para identificação dos compostos fenólicos da quinoa foi utilizado a metodologia descrita por Nagendra Prasad et al. (2009) com adaptações. Foi utilizada a Cromatografia líquida de alta eficiência (CLAE) de fase reversa, usando o módulo de separação (LC-20 AT, Shimadzu Corporation, Japão) equipado com uma coluna C18 (SUPELCOSIL™ LC-PAH

HPLC Column, 250 x 4,6 mm, tamanho de partícula 5 μ m, Sigma-Aldrich, St. Louis, EUA) e um detector UV-VISÍVEL (Rheodyne, EUA). As amostras foram eluídas em sistema de gradiente que consistiram nas seguintes fases móveis: solvente A (2% de ácido acético, v/v) e solvente B (acetonitrila: metanol, 2:1, v/v), em fluxo constante de 1 mL/min. A temperatura da coluna foi mantida a 40 °C e o volume de injeção foi de 20 μ L.

O sistema de gradiente obedeceu a seguinte programação: iniciado a partir de 90% de A em 0 min, 88% de A em 3 min, 85% de A em 6 min, 82% de A em 10 min, 80% de A em 12 min, 70% de A em 15 min, 65% de A em 20 min, 60% de A em 25 min, 50% de A de 30-40 min, 75% de A em 42 min e 90% de A em 44 min. Os picos dos compostos fenólicos foram monitorizados a 280 nm.

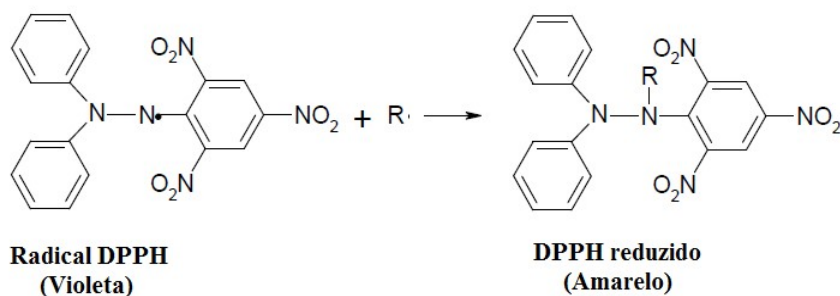
Os compostos fenólicos foram identificados por meio da comparação dos tempos de retenção com os padrões de ácidos fenólicos e flavonoides, sendo quantificados em concentrações de mg/mL e os cromatogramas foram registrados no software LabSolutions Data System.

2.12 DETERMINAÇÃO DA ATIVIDADE ANTIOXIDANTE DOS EXTRATOS

2.12.1 Método de sequestro de radicais livres DPPH• (2,2-difenil-1-picril-hidrazila)

A atividade antioxidante foi determinada utilizando a metodologia descrita por Brand-Willams, Cuvelier e Berset (1995) com modificações, através da capacidade dos antioxidantes presentes nas amostras em sequestrar o radical estável DPPH• (Figura 3). Em triplicata, alíquotas de 90 μ L da amostra (5 mg/mL) foram misturadas com etanol e 2.700 μ L da solução de DPPH•. Após 30 min em ambiente escuro em banho de agitação, foi efetuada a leitura a 517 nm, em espectrofotômetro UV-vis da Shimadzu, modelo UV-2550. Uma curva controle foi preparada utilizando Trolox (100-2000 μ mol/L em etanol) como padrão. Os resultados foram expressos em micromol Trolox por grama do extrato seco (μ mol ET/g de extrato).

Figura 3. Estabilização do radical DPPH .



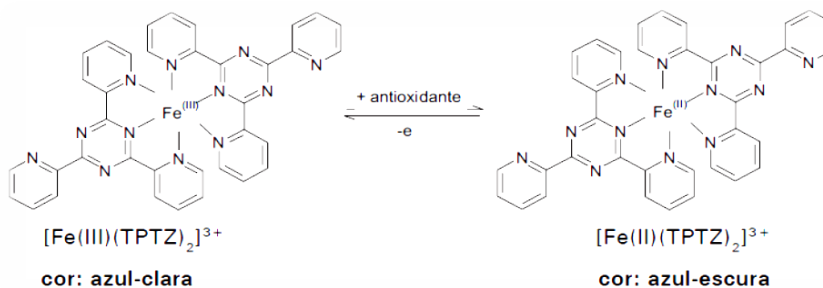
Fonte: RUFINO et al. (2007).

2.12.2 Poder antioxidante de redução do ferro (FRAP)

A capacidade antioxidante pelo método FRAP (Ferric Reducing Antioxidant Power) foi baseado na capacidade de um antioxidante em reduzir o Fe^{3+} para Fe^{2+} (Figura 4). Seguindo a metodologia de Rufino et al. (2006) com adaptações. Foi preparado o reagente de FRAP com tampão acetato 300 mmol/L (pH 3.6), 2,4,6-tris (2-pyridyl)-s-triazine (TPTZ) a 10 mmol/L em uma solução de HCl 40 mmol/L e FeCl_3 20 mmol/L.

Uma alíquota de 90 μL do extrato foi transferida para um tubo de ensaio e adicionado 0,27 mL de água ultrapura e 2,7 mL do reagente FRAP. A mistura foi homogenizada em banho termostatzado a 37 °C por 30 min. Após o resfriamento a temperatura ambiente, as amostras e padrões foram lidos a 595 nm. A curva padrão foi realizada com Trolox (100-2000 $\mu\text{mol/L}$ em etanol). Os resultados foram expressos em micromol equivalente Trolox ($\mu\text{mol ET/g}$ de extrato).

Figura 4. Redução do complexo TPTZ com Fe^{3+} .

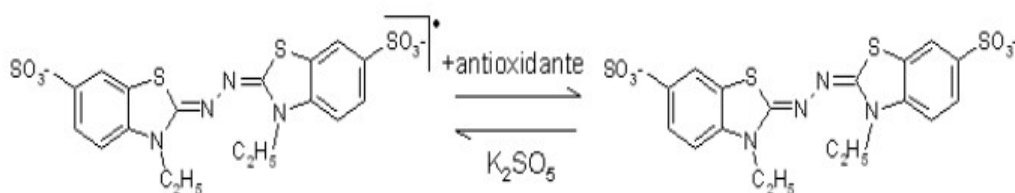


Fonte: RUFINO et al. (2006).

2.12.3 Método ABTS

A capacidade de sequestrar o radical 2,2'-azino-bis-(3-etilbezotiazolina-6-ácido sulfônico ABTS^{•+}) foi determinado segundo método descrito por Rufino et al. (2007). O radical ABTS^{•+} foi gerado a partir da reação da solução aquosa de ABTS (7 mmol/L) com persulfato de potássio (140 mmol/L). A solução foi mantida ao abrigo da luz, em temperatura ambiente por 16 horas (Figura 5). Em seguida, a solução foi diluída em etanol até obter absorvância de $0,70 \pm 0,05$ nm, em comprimento de onda a 734 nm. As alíquotas de 30, 60 ou 90 µL dos extratos a uma concentração de 5 mg/mL foram adicionados a solução de ABTS^{•+}, e a absorvância medida após 6 min, em UV-vis da Shimadzu, modelo UV-2550. A capacidade antioxidante da amostra foi calculada em relação à atividade do antioxidante Trolox, nas mesmas condições, e os resultados expressos em capacidade antioxidante equivalente ao Trolox (µmol ET/g de extrato).

Figura 5. Estabilização do radical ABTS^{•+} por um antioxidante e sua formação pelo persulfato de potássio.



Fonte: RUFINO et al. (2007).

2.13 ANÁLISE ESTATÍSTICA

A adequação dos modelos foi prevista considerando o erro puro, análise de regressão (R_2) e ANOVA ($p < 0,05$) utilizando programa Statistic 7.0 (StatSoft Inc, USA). O significado da regressão dos coeficientes foi analisado por meio de um teste-t. Na presença de coeficientes não significativos, estes foram removidos para se obter um modelo reduzido. O teste Tukey foi aplicado visando identificar as diferenças significativas entre as médias dos experimentos para cada variável dependente do planejamento estatístico considerando $p < 0,05$.

Para a análise estatística da composição das sementes e óleos de quinoa foram realizadas pela aplicação da ANOVA e o teste Tukey, visando identificar diferenças significativas entre as médias considerado para a diferença entre as médias de 5% ($p < 0,05$).

REFERÊNCIAS

- ABDERRAHIM, F.; HUANATICO, E.; SEGURA, R.; ARRIBAS, S.; GONZALEZ, M. C.; CONDEZO-HOYOS, L. Physical features, phenolic compounds, betalains and total antioxidant capacity of coloured quinoa seeds (*Chenopodium quinoa* Willd.) from Peruvian Altiplano. **Food Chemistry**, v. 183, p. 83–90, 2015.
- ALBERTI, A.; ZIELINSKI, A. A. F.; ZARDO, D. M.; DEMIATE, I. M.; NOGUEIRA, A.; MAFRA, L. I. Optimisation of the extraction of phenolic compounds from apples using response surface methodology. **Food Chemistry**, v. 149, p. 151–158, 2014.
- ALVAREZ-JUBETE, L.; ARENDT, E. K.; GALLAGHER, E. Nutritive value and chemical composition of pseudocereals as gluten-free ingredients. **International Journal of Food Sciences and Nutrition**, v. 60, p. 240–257, 2009.
- ANDRÉ, C.; CASTANHEIRA, I.; CRUZ, J. M.; PASEIRO, P.; SANCHES-SILVA, A. Analytical strategies to evaluate antioxidants in food: a review. **Trends in Food Science & Technology**, v. 21, p. 229–246, 2010.
- AOAC. ASSOCIATION OF OFFICIAL ANALYTICAL CHEMISTRY. **Official methods of analysis of the Association of Official Analytical Chemistry**. 19. ed. Gaithersburg: AOAC, 2012. 3000 p
- AOCS American Oil Chemists Society. **Official Methods and Recommended Practices of the AOCS** (6th ed.). Champaign: AOCS, 2009.
- ASAO, M.; WATANABE, K. Functional and Bioactive Properties of Quinoa and Amaranth. **Food Science and Technology Research**, v. 16, p. 163–168, 2010.
- BLIGH, E. G.; DYER, W. J. A rapid method of total lipid extration and purification. **Canadian Journal of Biochemistry and Physiology**, v. 37, p. 911–917, 1959.
- BOX, G. E. P.; BEHNKEN, D. W. American Society for Quality Some New Three Level Designs for the Study of Quantitative Variables Society for Quality Stable URL : <http://www.jstor.org/stable/1266454> Your use of the JSTOR archive indicates your acceptance of the Terms & Conditions of Use. **Technometrics**, v. 2, p. 455–475, 1960.
- BRADFORD, M. M. Rapid and sensitive method for quantitation of microgram quantities of protein utilizing principle of protein-dye binding. **Analytical Biochemistry**, v. 72, p. 248–254, 1976.
- BRAND-WILLIAMS, W.; CUVELIER, M. E.; BERSET, C. Use of free radical method to evaluate antioxidant activity. **LWT - Food Science and Technology**, v. 28, p. 25–30, 1995.
- BRUNS, R. E., SCARMINO, I. S., BARROS NETO, B. **Statistical design – chemometrics**. Amsterdam: Elsevier, 2006, p. 273.
- EPA. **Método 6020A (SW-846)**: plasma indutivamente acoplado-espectrometria de massa, 1998.

ESPINOSA-DIEZ, C.; MIGUEL, V.; MENNERICH, D.; KIETZMANN, T.; SÁNCHEZ-PÉREZ, P.; CADENAS, S.; LAMAS, S. Antioxidant responses and cellular adjustments to oxidative stress. **Redox Biology**, v. 6, p. 183–197, 2015.

FALGUERA, V.; ALIGUER, N.; FALGUERA, M. An integrated approach to current trends in food consumption: moving toward functional and organic products? **Food Control**, v. 26, p. 274–281, 2012.

GAWLIK-DZIKI, U.; ŚWIECA, M.; SUŁKOWSKI, M.; DZIKI, D.; BARANIAK, B.; CZYŻ, J. Antioxidant and anticancer activities of *Chenopodium quinoa* leaves extracts – In vitro study. **Food and Chemical Toxicology**, v. 57, p. 154–160, 2013.

GÓMEZ-CARAVACA, A. M.; SEGURA-CARRETERO, A.; FERNÁNDEZ-GUTIÉRREZ, A.; CABONI, M. F. Simultaneous determination of phenolic compounds and saponins in quinoa (*Chenopodium quinoa* Willd) by a liquid chromatography-diode array detection-electrospray ionization-time-of-flight mass spectrometry methodology. **Journal of Agricultural and Food Chemistry**, v. 59, p. 10815–10825, 2011.

GORINSTEIN, S.; MARTIN-BELLOSO, O.; KATRICH, E.; LOJEK, A.; CIZ, M.; GLIGELMO-MIGUEL, N.; HARUENKI, R.; PARK, Y.S.; JUNG, S.T.; TRAKHTENBERG, S. Comparison of the contents of the main biochemical compounds and the antioxidant activity of some Spanish olive oils as determined by four different radical scavenging tests. **Journal of Nutritional Biochemistry**, v. 14, p. 154–159, 2003.

GRAF, B. L.; POULEV, A.; KUHN, P.; GRACE, M. H.; LILA, M. A.; RASKIN, I. Quinoa seeds leach phytoecdysteroids and other compounds with anti-diabetic properties. **Food Chemistry**, v. 163, p. 178–185, 2014.

HARTMAN, L.; LAGO, R. C. A. Rapid preparation of fatty acids methyl esters. **Laboratory Practice**, v. 22, p. 475–476, 1973.

HIROSE, Y.; FUJITA, T.; ISHII, T.; UENO, N. Antioxidative properties and flavonoid composition of *Chenopodium quinoa* seeds cultivated in Japan. **Food Chemistry**, v. 119, p. 1300–1306, 2010.

KUMPUN, S.; MARIA, A.; CROUZET, S.; EVRARD-TODESCHI, N.; GIRAULT, J.; LAFONT, R. Ecdysteroids from *Chenopodium quinoa* Willd., an ancient Andean crop of high nutritional value. **Food Chemistry**, v. 125, p. 1226–1234, 2011.

LAMOTHE, L. M.; SRICHUWONG, S.; REUHS, B. L.; HAMAKER, B. R. Quinoa (*Chenopodium quinoa* W.) and amaranth (*Amaranthus caudatus* L.) provide dietary fibres high in pectic substances and xyloglucans. **Food Chemistry**, v. 167, p. 490–496, 2015.

MAGANHA, E. G.; HALMENSCHLAGER, R. C.; ROSA, R. M.; HENRIQUES, J. A. P.; RAMOS, A. L. L. P.; SAFI, J. Pharmacological evidences for the extracts and secondary metabolites from plants of the genus *Hibiscus*. **Food Chemistry**, v. 118, p. 1–10, 2010.

MASISI, K.; BETA, T.; MOGHADASIAN, M. H. Antioxidant properties of diverse cereal grains: A review on *in vitro* and *in vivo* studies. **Food Chemistry**, v. 196, p. 90–97, 2016.

MILLER, G.L. Use of dinitrosalicylic acid reagent for determination of reducing sugar. **Analytical Chemistry**, v. 31, p. 426-428, 1959.

MIRANDA, M.; VEGA-GÁLVEZ, A.; URIBE, E.; LÓPEZ, J. Procedia Food Science Physico-chemical analysis , antioxidant capacity and vitamins of six ecotypes of chilean quinoa (*Chenopodium quinoa*). **Procedia Food Science**, v. 11, p. 1439–1446, 2011.

MOTHÉ, C. G.; AZEVEDO, A. D. **Análise Térmica de Materiais**. São Paulo, Editora Artliber, 2009.

MYERS, R. H.; MONTGOMERY, D. C. **Response surface methodology: process and product optimization using designed experiments**. New York: John Wiley and Sons, 2002.

NAGENDRA PRASAD, K.; YANG, B.; YANG, S.; CHEN, Y.; ZHAO, M.; ASHRAF, M.; JIANG, Y. Identification of phenolic compounds and appraisal of antioxidant and antityrosinase activities from litchi (*Litchi sinensis* Sonn.) seeds. **Food Chemistry**, v. 116, p. 1–7, 2009.

NASCIMENTO, A. C.; MOTA, C.; COELHO, I.; GUEIFÃO, S.; SANTOS, M.; MATOS, A. S.; CASTANHEIRA, I. Characterisation of nutrient profile of quinoa (*Chenopodium quinoa*), amaranth (*Amaranthus caudatus*), and purple corn (*Zea mays* L.) consumed in the North of Argentina: proximates, minerals and trace elements. **Food Chemistry**, v. 148, p. 420–426, 2014.

NOWAK, V.; DU, J.; CHARRONDIÈRE, U. R. Assessment of the nutritional composition of quinoa (*Chenopodium quinoa* Willd.). **Food Chemistry**, v. 193, p. 47–54, 2016.

OSBORNE, T. The vegetable proteins. **Green**, NY: Longmans. p. 1642-1649, 1924.

PRASAD, K. N.; HASSAN, F. A.; YANG, B.; KONG, K. W.; RAMANAN, R. N.; AZLAN, A.; ISMAIL, A. Response surface optimisation for the extraction of phenolic compounds and antioxidant capacities of underutilised *Mangifera pajang* Kosterm. peels. **Food Chemistry**, v. 128, p. 1121–1127, 2011.

PREGO, I.; MALDONADO, S.; OTEGUI, M. Seed Structure and Localization of Reserves in *Chenopodium quinoa*. **Annals of Botany**, v. 82, p. 481–488, 1998.

RAZZAGHI, F.; PLAUBORG, F.; JACOBSEN, S.; RICHARDT, C.; NEUMANN, M. Effect of nitrogen and water availability of three soil types on yield , radiation use efficiency and evapotranspiration in field-grown quinoa. **Agricultural Water Management**, v. 109, p. 20–29, 2012.

REZAIE, M.; FARHOOSH, R.; IRANSHAHI, M.; SHARIF, A.; GOLMOHAMADZADEH, S. Ultrasonic-assisted extraction of antioxidative compounds from Bene (*Pistacia atlantica* subsp. *mutica*) hull using various solvents of different physicochemical properties. **Food Chemistry**, v. 173, p. 577–583, 2015.

ROSSI, J. A. J.; SINGLETON, V. L. Colorimetry of total phenolics with phosphomolybdic phosphotungstic acid reagents. **American Journal of Enology and Viticulture**, v. 16, p. 144-158, 1965.

RUFINO, M. D. S. M., ALVES, R. E., BRITO, E. S. DE, MORAIS, S. M. DE, SAMPAIO, C. D. G., PÉREZ-JIMÉNEZ, J., & SAURA-COLIXTO, F. D. Metodologia Científica: Determinação da Atividade Antioxidante Total em Frutas pelo Método de Redução do Ferro (FRAP). **Comunicado Técnico Embrapa**, v. 125, p. 1–4, 2006.

RUFINO, M. D. S. M., ALVES, R. E., BRITO, E. S. DE, MORAIS, S. M. DE, SAMPAIO, C. D. G., PÉREZ-JIMÉNEZ, J., & SAURA-COLIXTO, F. D. Metodologia Científica: Determinação da Atividade Antioxidante Total em Frutas pela Captura do Radical Livre DPPH. **Comunicado Técnico Embrapa**, v. 127, p. 1–4, 2007.

SINGLETON VL, ROSSI JA. Colorimetry of total phenolics with phosphomolybdic-phosphotungstic acid reagents. **American Journal of Enology and Viticulture**, v. 16, p. 144-158, 1965.

STATSOFT. Inc. **Statistica**: data analysis software system. Disponível em: <www.statsoft.com> Version 7.0, 2004.

TANG, Y.; LI, X.; ZHANG, B.; CHEN, P. X.; LIU, R.; TSAO, R. Characterisation of phenolics, betanins and antioxidant activities in seeds of three *Chenopodium quinoa* Willd. genotypes. **Food Chemistry**, v. 166, p. 380–388, 2015.

WANASUNDARA, P. K. J. P. D.; SHAHIDI, F. Antioxidants: Science, Technology, and Applications. In **Bailey's Industrial Oil and Fat Products**. v. 1. Edible oil and fat products: chemistry, properties, and health effects. 6 ed, Ed. Fereidoon Shahidi, 2005.

WHITE, K.L. An overview of immunotoxicology and carcinogenic polycyclic aromatic-hydrocarbons in the environmental. **Journal of Environmental Science and Health**, v. 4, p. 163-202, 1986.

WOOTTON-BEARD, P. C.; MORAN, A.; RYAN, L. 2011. Stability of the total antioxidant capacity and total polyphenol content of 23 commercially available vegetable juices before and after in vitro digestion measured by FRAP, DPPH, ABTS and Folin–Ciocalteu methods. **Food Research International**, v. 44, p. 217–224, 2011.

RESULTADOS

Os resultados obtidos com o desenvolvimento desta tese proporcionaram a elaboração dos artigos descritos a seguir:

ARTIGO 1. “Propriedades químicas, funcionais e tecnológicas da quinoa (*Chenopodium quinoa* Willd.) – Revisão”, que foi submetido ao periódico Journal of Functional Foods, Qualis A1, para Ciência de Alimentos.

ARTIGO 2. “Aplicação da metodologia de superfície de resposta na otimização da extração de compostos fenólicos e capacidades antioxidantes de diferentes variedades de quinoa (*Chenopodium quinoa* Willd.)”, que foi submetido ao periódico Food Chemistry, Qualis A2, para Ciência de Alimentos.

ARTIGO 3 – Perfil Nutricional de sementes e óleos de quinoa (*Chenopodium quinoa* Willd.) cultivadas no Brasil e na Bolívia. que será submetido ao periódico Revista de Alimentação Humana, Qualis B1, para Ciência de Alimentos.

Chemical, functional and technological properties of quinoa (*Chenopodium quinoa* Willd.): A review

Isabelle de Lima Brito^{1,2}, Antonio Gouveia de Souza¹, Angela Maria Tribuzy de Magalhães Cordeiro^{1,3,*}

¹ *Programa de Pós Graduação em Ciência e Tecnologia de Alimentos, Centro de Tecnologia - CT, Universidade Federal da Paraíba, João Pessoa, Paraíba, Brazil.*

² *Departamento de Gestão e tecnologia Agroindustrial, Centro de Ciências Humanas, Sociais e Agrárias (CCHSA), Universidade Federal da Paraíba (UFPB), João Pessoa, Paraíba, Brazil.*

³ *Departamento de Tecnologia de Alimentos, Centro de Tecnologia e Desenvolvimento Regional - CTDR, Universidade Federal de Paraíba, João Pessoa, Paraíba, Brazil.*

*Corresponding Author: Angela M^a Tribuzy de M. de Cordeiro
Departamento de Tecnologia de Alimentos, Centro de Tecnologia e Desenvolvimento Regional - CTDR/UFPB
Avenida dos Escoteiros, s/nº, Mangabeira VII, Distrito Industrial de Mangabeira, João Pessoa, Paraíba, Brazil, CEP 58055-000 Phone: +55 83 3216-7947; e-mail: atribuzycordeiro@gmail.com

ABSTRACT

Quinoa (*Chenopodium quinoa* Willd) is a seed with important nutritional and technological potential and a promising food for the food industry because of its wide range of possible uses and functional properties. The purpose of the present review is to evaluate the nutritional quality of quinoa seeds and relate their consumption to possible health benefits. Studies have reported substantial variations in quinoa nutrient concentrations depending on production characteristics, plant variety and extraction methods. Studies have also reported the technological potential of quinoa as an ingredient in food formulations and for the prevention and treatment of various diseases.

Key-words: *Chenopodium quinoa*; nutritional foods; functional properties; technological potential.

Content

1. Introduction
 2. Origin, production and consumption
 3. Nutritional characteristics
 4. Functional properties of quinoa
 - 4.1 Quinoa and prebiotic effects
 - 4.2 Quinoa in the prevention and treatment of obesity and diabetes mellitus
 - 4.3 Quinoa in the prevention and treatment of cardiovascular diseases
 - 4.4 Quinoa in the prevention and treatment of high blood pressure
 - 4.5 Quinoa in the treatment of gastric lesions
 - 4.6 Quinoa in the protection against oxidative processes
 - 4.7 Quinoa in cancer prevention
 5. Benefits of quinoa in the preparation of food products
 - 5.1 Bakery products
 - 5.2 Formulation of protein concentrates and hydrolysates
 - 5.3 Production of edible films
 6. Conclusion
 - References
-

1. Introduction

Quinoa seeds (*Chenopodium quinoa* Willd.) have been used as food by Andean peoples for thousands of years. The quinoa crop is well adapted to different climate conditions (Jacobsen, 2011). In its composition, quinoa presents protein with good amino acid balance, complex carbohydrates, and remarkable polyphenol content and is considered a source of calcium, iron, zinc and vitamins (Abugoch James, 2009; Repo-Carrasco, Espinoza, & Jacobsen, 2003; Schoenlechner, Drausinger, Ottenschlaeger, & Jurackova, 2010).

Because of its nutritional composition, quinoa presents technological and functional properties and has potential for use in the food industry. In addition to its use in the formulation of various food products, quinoa also decreases the risk of several diseases, such as obesity, diabetes, cardiovascular diseases and cancer (Asao & Watanabe, 2010; Berti, Riso, Monti, & Porrini, 2004; Gawlik-Dziki et al., 2013). However, its mineral, vitamin and polyphenol concentrations may vary with the variety studied, environmental factors and production characteristics (Hirose, Fujita, Ishii, & Ueno, 2010).

Recent studies have reported an increasing search in modern society for foods that provide health benefits in addition to basic nutrition. Consumers therefore tend to prefer foods that clearly provide some functional benefits (Bitzios, Fraser, & Haddock- Fraser, 2011; Falguera, Aliguer, & Falguera, 2012). Studies of quinoa use in the formulation of several food products and of its health benefits have been increasing recently (Brito et al., 2014; Graf et al., 2014; Swieca, Sęczyk, Gawlik-Dziki, & Dziki, 2014). However, further studies of its properties and benefits are necessary to promote its cultivation and technological use.

2. Origin, production and consumption

Quinoa is a seed and is considered a pseudocereal. Quinoa originated in the Andes, where it has been cultivated for 5000 years (Oelke, Putnam, Teynor, & Oplinger, 2012). Its production and consumption are currently spreading worldwide because of its important nutritional qualities and resulting functional characteristics (Abugoch James, 2009; Hirose et al., 2010; Nascimento et al., 2014; Nowak, Du, & Charrondière, 2016). Because of its high genetic diversity, quinoa adapts to the most adverse climatic and geographical conditions (Razzaghi, Plauborg, Jacobsen, Richardt, & Neumann, 2012). However, its composition may vary with the soil, fertilization, irrigation, environmental and climate conditions, and the studied variety (Hirose et al., 2010).

According to *The Statistics Division of the Food and Agriculture Organization of the United Nations* (FAOSTAT), the cultivated quinoa area and total production in the primary producing countries (Bolivia, Peru and Ecuador) increased by up to 300% between 1992 and 2010. Its production in the Andean region was approximately 70,000 tons in 2009, and quinoa is cultivated in more than 70 countries (FAO, 2016).

The name *quinoa* designates both the plant and the seed. It is an annual species with a growing cycle between 80 and 150 days depending on the variety. Quinoa presents wide leaves and is between 1 and 2 m in height. Its production has crossed continental borders, and it can be grown from sea level up to 3800 m (Bhargava, Shukla, & Ohri, 2006). Quinoa belongs to the class Dicotyledoneae, family Chenopodiaceae (Marticorena & Quezada, 1985). Quinoa is primarily consumed as seeds or seed-derived products (flour, flakes, extruded products) (Bhargava et al., 2006; Collar, 2016; Cueto et al., 2015).

Its seeds originate from simple dry fruits (achenes) containing a single starchy seed of flat cylindrical shape with a diameter between 2 and 2.5 mm and a width between 1.2 and 1.6 mm (Figure 1) (Spehar, 1998). The seeds may be bitter or sweet, depending on their composition (Dini, Tenore, & Dini, 2010). Their structure comprises a pericarp, an episperm (testa), a perisperm and an embryo. The perisperm is the site of starch storage and therefore the seed storage tissue. Its color results from the combined pericarp and episperm colors and may vary from white to gray and black or be yellow and red (Borges, Bonomo, Paula, Oliveira, & Cesário, 2010). Betalains are quinoa pigments presenting functional properties similar to the properties of phenolic compounds, including antioxidant and anti-inflammatory effects (Tang et al., 2015a).

The outer layers of quinoa seeds present antinutritional compounds such as saponins, phytates, tannins and protease inhibitors in addition to calcium oxalate (Comai et al., 2007). These compounds are partially or completely removed by abrasion, washing and thermal processing (Gómez-Caravaca, Segura-Carretero, Fernández-Gutiérrez, & Caboni, 2011).

Quinoa may be directly consumed as seeds, flours and flakes and as a component of various food preparations (Figure 2).

3. Nutritional Characteristics

Quinoa was recently designated a functional food because of its good amino acid balance, polyphenol content and high vitamin E concentration, and it is considered a source of

fiber, another's vitamins and minerals (Abugoch James, 2009). Because of its nutritional quality, the *Food and Agriculture Organization of the United Nations* (FAO) declared 2013 the "International Year of Quinoa" and considered quinoa one of the crops destined to offer food safety in the 21st century (Nowak et al., 2016; Jacobsen, 2011; Schoenlechner, Wendner, Siebenhandl-ehn, & Berghofer, 2010).

The quality of a food's protein is determined by the proportion of essential amino acids, which cannot be synthesized by humans and must therefore be obtained from the diet. All essential amino acids are present in quinoa seeds (Table 1), which present a total protein content between 14.5% and 17.41% (Alvarez-Jubete, Arendt, & Gallagher, 2009; Koziół, 1992; Meneguetti, Brenzan, Batista, Bazotte, & Silva, 2011; Stikic, Glamoclija, Demin, Vucelic-radovic, & Jovanovic, 2012). In addition, its digestibility is 83%, compared to 91% for milk casein (Schoenlechner, Wendner, et al., 2010). Compared to cereal grains, quinoa presents higher total protein concentrations on a dry basis (16.3%) than barley (11%), rice (7.5%) and corn (13.4%), comparable to wheat (15.4%), and lower only than legume seeds (Ruales & Nair, 1993; Abugoch James, 2009). Albumins and globulins are the major protein fraction in quinoa seeds (44%-47%) (Jancurová, Minarovičová, & Dandár, 2009).

Recent studies reported the potential of quinoa antioxidant protein hydrolysates (Nongonierma & Fitzgerald, 2015) and protein isolate for use in food and the pharmaceutical industry (Föste, Elgeti, Brunner, Jekle, & Becker, 2015).

According to the FAO/USDA (1985) protein standard, considering the recommendations of the WHO/FAO (1985) for essential amino acids, quinoa consumption meets 44.21% of the dietary requirements for leucine, 46.78% for threonine, 38.77% for isoleucine, 33% for valine, 31.21% for phenylalanine, and the dietary requirements for all non-essential amino acids.

Carbohydrates comprise 67% to 74% of quinoa seed dry matter, of which 52%-60% is starch and 11% amylose (Jancurová et al., 2009). The fiber concentration varies between 7% and 15.99% seed dry weight, of which most is insoluble fiber (78%) (Lamothe, Srichuwong, Reuhs, & Hamaker, 2015). Quinoa is therefore a good fiber source because the WHO/FAO recommends a daily ingestion of 25 to 30 g fiber, with a 3:1 insoluble:soluble fiber ratio (Abugoch James, 2009; R. A.-M. Repo-Carrasco-Valencia & Serna, 2011).

The dietary fiber present in quinoa helps protect against the development of chronic diseases, most likely because of the interaction of bioactive compounds with the human intestinal microbiota (Repo-Carrasco, Espinoza, & Jacobsen, 2003). Studies have demonstrated that this interaction contributes to increasing the number of bifidobacteria and

lactobacillus, which play an important role in health and have beneficial effects on intestinal functioning and nutrient absorption (Tuohy, Conterno, Gasperotti, & Viola, 2012; Wu et al., 2011).

Carbohydrates play essential roles in nutrition, are energy sources, act on satiety or gastric emptying, control blood glucose and insulin production by the pancreas, enhance protein glycosylation, and affect cholesterol and triglyceride metabolism (FAO, 2015).

The quinoa carbohydrate fractions have been investigated because they are associated with a variety of biological activities (Berti et al., 2004; Cordeiro et al., 2012). The carbohydrate fractions were determined by various authors (Table 2).

Cordeiro et al. (2012) investigated the monosaccharide composition of quinoa and identified a high proportion of arabinans, alone or in arabinan-rich pectic polysaccharides (66%-98.5%), followed by galacturonic acid (0-27%) and small proportions of rhamnose (2%-7%) and galactose (2%-8.5%). However, Wefers, et al. (2015) and Lamothe et al. (2015) also investigated the monosaccharide composition of insoluble quinoa fiber and observed lower percentages of arabinose (43.3% and 15.3%, respectively) and galacturonic acid percentages of 17.2% and 28.5%, respectively. These differences may have been the result of differences in cultivars or because of plant development. Some polysaccharides have been related to the protection of the gastric mucosa, such as arabinogalactan (Tanaka et al., 2010) and galactomannoglucan (Silva & Parente, 2010). Wefers, Gmeiner, Tyl, & Bunzel (2015) also demonstrated that intra- and/or intermolecular arrangements of arabinan chains in quinoa insoluble fiber were directly involved with diferulic acids, which may have a major effect on plant cell wall architecture in addition to being phenolic acids with likely antioxidant activity.

Quinoa lipids also present interesting characteristics. Their contents vary between 2% and 10%, primarily comprise polyunsaturated fatty acids (57.5%) (Alvarez-Jubete et al., 2009; Elsohaimy, Refaay, & Zaytoun, 2015), and present essential fatty acids in their composition, such as palmitic, oleic and linolenic acid, among the saturated, monounsaturated and polyunsaturated acids, respectively (Peiretti, Gai, & Tassone, 2013; Tang et al., 2015). The majority of quinoa lipids are neutral lipids, of which 50% are triglycerides (Abugoch James, 2009; Cordeiro et al., 2012; Jancurová et al., 2009). However, the seed lipid fraction has been reported to present high concentrations of vitamin E, carotenoids and tocopherols, which confer oxidative stability (Alvarez-jubete et al., 2010; Przygoda & Wejnerowska, 2015). In addition, quinoa lipids present high concentrations of vitamins and minerals, particularly iron, magnesium, selenium, folate, beta-carotene, and vitamins A and E (Table 3) (Stikic et al., 2012; Tang et al., 2015).

Quinoa is considered an interesting option for celiacs because it contains no gluten, a protein present in wheat, oats, rye and barley (Asao & Watanabe, 2010). Celiac disease is caused by a permanent intolerance to gluten, which manifests through inflammation and partial or total atrophy of the intestinal mucosa and is therefore related to poor absorption of important nutrients (Ribeiro et al., 2016; Lebwohl, Ludvigsson, & Green, 2015).

Quinoa seeds also have a high concentration of phenolic compounds, which are secondary metabolites with a role in protecting plants against adverse climatic conditions. Phenolic compounds may be present in a free form or linked to sugars by glycosidic bonds and confer antioxidant activity to seeds (Asao & Watanabe, 2010; Brakez, Daoud, Harrouni, Tachbib, & Brakez, 2016; Tang et al., 2015). Their antioxidant properties are attributed to their free radical scavenging capacity or their ability to chelate metal ions involved in free radical formation (Wanasundara & Shahidi, 2005; Wootton-Beard; Moran & Ryan, 2011).

The antioxidant action of quinoa seeds is also a result of the presence of tocotrienols and tocopherols, which play essential physiological roles, such as an anticoagulant and a regulator of metabolic processes (Joana Gil-Chávez et al., 2013). Tocotrienols and tocopherols are important in the prevention of several chronic degenerative diseases, such as cardiopathies, atherosclerosis, diabetes, Alzheimer's disease and cancers (Abderrahim et al., 2015; Gómez-Caravaca, Segura-Carretero, Fernández-Gutiérrez, & Caboni, 2011).

The prominent phenolic compounds in quinoa are flavonoids, quercetin, kaempferol, and the following phenolic acids: caffeic, ferulic, p-coumaric, vanillic and p-OH-benzoic acids (Repo-Carrasco-Valencia, Hellström, Pihlava, & Mattila, 2010; Stikic et al., 2012; Tang, Li, Zhang, et al., 2015).

4. Functional Properties of Quinoa

Functional foods have been increasing in importance in the food industry, and their consumption is increasing, most likely because of their associations with a decreased risk of disease and health promotion. The Academy of Nutrition and Dietetics (formerly the American Dietetic Association - ADA) recommends that foods be evaluated not only in terms of their macro- and micronutrients. The contents of other physiologically active compounds and their role in health promotion should also be evaluated based on scientific evidence (Hasler & Brown, 2009).

The possible beneficial effects of quinoa consumption on health have been investigated (Gómez-Caravaca et al., 2011; Simnadis, Tapsell, & Beck, 2015). Hydrophilic bioactive compounds from quinoa, such as phenolic acids and flavonoids with antioxidant activity, have high functional potential. The polyphenols present in quinoa affect numerous risk factors of cardiovascular diseases, such as endothelial function, platelet aggregation, and level of lipid oxidation in blood plasma, decreasing the probability of developing dyslipidemias (Quideau et al., 2011). Polyphenols can also protect against cancer by decreasing DNA damage (Abugoch James, 2009; Gawlik-Dziki et al., 2013).

Hemalatha, Bomzan, Rao, et al. (2016) investigated whole grain quinoa and its milled fractions for their phenolic composition and respective antioxidant properties. Ferulic acid, rutin and quercetin were the predominant polyphenols detected, being present in higher proportions in bran. However, all analyzed quinoa forms were observed to be polyphenol sources and to have possible health benefits.

4.1 Quinoa and prebiotic effects

Food fibers are related to intestinal homeostasis and have beneficial physiological effects, including laxative effects and/or attenuation of hypercholesterolemia and/or attenuation of hyperglycemia (Howlett et al., 2010). The dietary fiber present in quinoa helps protect against the development of chronic diseases, most likely because of its high percentage of insoluble fiber, having beneficial effects on intestinal functioning and nutrient absorption (Repo-Carrasco et al., 2003; Tuohy et al., 2012).

In a recent study, Villegas, Brown, Giori, & Hebert (2016) investigated the production of g-aminobutyric acid (GABA) by various bacterial strains isolated from quinoa and amaranth sourdoughs under various incubation temperatures, times and monosodium glutamate concentrations, the primary factors affecting GABA synthesis. Glutamate is first decarboxylated (Li & Cao, 2010) and must then be incorporated into the medium or food at high concentrations to be converted into GABA. Quinoa fermentation with *Lactobacillus brevis* CRL 1942 resulted in the highest levels of GABA production under optimal culture conditions (270 mM monosodium glutamate, 30 °C, for 48 h) with a conversion rate of ~ 90%. Quinoa sourdough therefore produced high levels of GABA, indicating a new prebiotic trait.

GABA is an amino acid that acts as an inhibitory neurotransmitter in the central nervous system, with hypotensive, diuretic and tranquilizing actions (Pouliot-Mathieu et al., 2013; Somkuti, Renye, & Steinberg, 2012).

4.2 Quinoa in the prevention and treatment of obesity and diabetes mellitus

Obesity is a public health problem that has concerned health organizations worldwide (Mackey, Olson, DiFazio, & Cassidy, 2016). Obesity is a risk factor for several pathologies, particularly diabetes, cancers and cardiovascular diseases (Arnold et al., 2016; Lavie et al., 2016; Platt, Beckett, Kohler, Niedowicz, & Murphy, 2015). However, the highest incidences of obesity are associated with the high consumption of industrially processed foods (Abdullah, Mokhtar, Bakar, & Al-Kubaisy, 2015; Louzada et al., 2015). Natural strategies to delay the progression of obesity are therefore interesting to the scientific community (Ells et al., 2005).

Measures that encourage healthy habits and behaviors are essential to the prevention of obesity and its co-morbidities (Mackey et al., 2016). The consumption of natural foods, whole cereals and bioactive compounds is an interesting alternative for the treatment of obesity by assisting the body's homeostasis mechanisms (Mohamed, 2014).

Recent studies highlight the importance of associating dietary protein with foods with a low glycemic index to achieve satiety and maintain weight (Nilsson, Holst, & Bjorck, 2007; Larsen et al., 2010). Fiber, particularly insoluble fiber, plays a fundamental role in intestinal homeostasis and the delay of glucose and nutrient absorption, whereas protein helps with satiety and, consequently, weight loss. The dietary protein and fiber content of quinoa are therefore important for the treatment and prevention of obesity and diabetes (Clifton, 2012).

Low-glycemic index diets and/or diets rich in high quality protein are associated with regulation of weight, blood glucose, and metabolic syndrome risk factors (Augustin et al., 2015). This association is similar to that of fiber, particularly insoluble fiber, which is present in a higher proportion in quinoa (Abugoch James, 2009; Lamothe et al., 2015). In addition to its protein and fiber contents, the hypoglycemic effect of quinoa can also be attributed to antioxidant activity. This was observed by Nongonierma, Le Maux, Dubrulle, Barre, & FitzGerald (2015), who evaluated, *in vitro*, a quinoa protein isolate with a purity of $40.73 \pm 0.90\%$, hydrolyzed with exogenous enzymes to release bioactive peptides.

Berti et al. (2004) observed greater satiety with quinoa consumption compared with other gluten-free cereals and attributed this increased satiety to the lower glycemic index (GI)

of pasta containing quinoa flour because foods with a high GI induce higher insulin secretion and decreased concentrations of metabolic fuels during the postprandial period, which may trigger prolonged hyperphagia in an attempt to restore energy homeostasis (David & Ludwig, 2002). According to this study, the lower GI was associated with lower seed starch digestibility, whereas the satietogenic effect was associated with the presence of various components, particularly fibers.

Hemalatha, Bomzan, Rao, & Sreerama (2016) studied whole grain quinoa and its milled fractions for their phenolic composition, antioxidant activity and inhibitory effects on α -amylase and α -glucosidase activities. They determined quinoa to be a functional ingredient, with ferulic acid, rutin and quercetin as its predominant phenolic compounds. In addition, these bioactive compounds, both from whole grain and milled fractions, were observed to be potent enzyme inhibitors. This result is interesting with regard to the control of postprandial hyperglycemia because the enzyme inhibition delays the absorption of dietary carbohydrates (Adisakwattana, Fortes, Chantarasinlapin, Thammarat, & Yibchok-Anun, 2009).

Foucault et al. (2014) studied mice fed a high-fat diet and observed that diet supplementation with quinoa extracts increased fecal lipid excretion without changes in stool amount. The anti-obesity effect of quinoa extracts can be explained by changes in glucose metabolism and decreased dietary lipid absorption, resulting in decreased storage in adipose tissue.

Graf et al. (2014) reported a significant decrease in fasting blood glucose in obese hyperglycemic mice fed quinoa seeds. The authors attributed this effect to phytoecdysteroids and the bioactive compounds present in seeds. In addition to decreasing blood glucose and the resulting therapeutic effect, phytoecdysteroids have also been reported to have anabolic effects, improving sport performance (Gorelick-Feldman et al., 2008) and preventing osteoporosis (Kapur, Wuttke, Jarry, & Seidlova-Wuttke, 2010; Seidlova-Wuttke et al., 2010).

This finding is consistent with that of Paško, Zagrodzki, Bartoń, Chłopicka, & Gorinstein (2010), who reported that tocopherols and polyphenols present in quinoa seeds were responsible for the hypoglycemic effect of a diet supplemented with quinoa seeds on rats when compared with a control group and a group subjected to oxidative stress by administration of a fructose rich diet (31% of diet during 5 weeks).

Kumpun et al. (2011) identified ecdysteroids in quinoa seeds, which are natural phytochemicals with a plant protection function. Ecdysteroids are stable during food processing and have medicinal properties when ingested, such as decreased blood glucose in

diabetic patients, decreased serum cholesterol levels, and possibly prevention of osteoporosis (Gao et al., 2008; Seidlova-Wuttke et al., 2010).

Similarly, Augustin et al. (2015) reported that whole grain quinoa contributes to decreased postprandial blood glucose because of its low glycemic load and index. Whole grain quinoa can act in the prevention and treatment of insulin resistance, diabetes, coronary heart disease, and obesity. The authors also reported the presence of phenolic compounds in quinoa, such as rutin, which has known antioxidant power, decreasing oxidative stress and increasing the beneficial effects on diabetic neuropathy (Tian et al., 2016).

4.3 Quinoa in the prevention and treatment of cardiovascular diseases

Cardiovascular diseases (CVD) are the primary cause of mortality in the world, contributing to 48% of deaths from non-transmissible diseases, even higher than cancers (WHO, 2012).

The consumption of foods with a low glycemic index that are rich in fiber and phytochemicals, such as whole grains, is related to a reduced risk of developing CVD, among other pathologies (Lavie et al., 2016; Seal, 2006). Diets with a low glycemic index have been reported to help lower LDL cholesterol (Goff, Cowland, Hooper, & Frost, 2013), triglycerides (Wolever et al., 2013), and plasminogen activator inhibitor-1, which are involved in blood coagulation, and thus decrease cardiovascular effects (Jensen et al., 2008) and the inflammatory marker (reactive C protein), particularly in individuals with a body mass index (BMI) higher than 25 (Wolever et al., 2008).

Phenolic compounds are also related to the prevention of CVD. Ferulic acid, rutin and quercetin, present in quinoa (Hemalatha, Bomzan, Sathyendra Rao, & Sreerama, 2016), were reported to have antithrombotic and anticoagulant activities (Choi et al., 2015). Polyphenols, saponins and alkaloids found in plant extracts have anti-inflammatory properties and a protective effect against cytotoxic cerebral edema in cerebral ischemia, decreasing its neural damage (Panickar, 2015).

The positive effects of quinoa against cardiovascular diseases may also be related to its protein quality and levels of unsaturated fatty acids, vitamins and tocopherols (Gómez-Caravaca et al., 2011; Quideau et al., 2011). Paško, Zagrodzki, Bartoń, Chłopicka, & Gorinstein (2010a) performed *in vivo* tests and reported that diet supplementation with quinoa seeds decreased the negative biochemical effects of diets with added fructose in rats, resulting in decreases of 26% in total cholesterol, 57% in LDL, 11% in triglycerides, and 10% in

glucose, in addition to inhibiting the decrease in HDL levels observed in animals fed only fructose.

The International Atherosclerosis Society developed a new set of recommendations for the prevention of dyslipidemia, with primary prevention being based on lifestyle changes and consumption of functional foods such as quinoa to decrease atherogenic lipoproteins (Grundy et al., 2014).

Quinoa lipids are predominantly composed of polyunsaturated fatty acids (PUFAs), with interesting amounts of essential fatty acids such as omega 3 and omega 6 (Przybylski, Chauhan, & Eskin, 1994). Their functions in the human body are related to disease prevention. They can be incorporated into the phospholipid bilayer of cell membranes, affect membrane fluidity and permeability, and modulate the function of membrane ion channels, preventing lethal arrhythmias (Endo & Arita, 2015). Recent studies reported that consumption of polyunsaturated fatty acids is associated with benefits in the treatment of heart surgery patients (Gajos, 2016) and the prevention of thrombosis, atherosclerosis, arrhythmia and cardiac insufficiency (Endo & Arita, 2015). In addition, omega 3 supplementation has been associated with symptom improvement in patients with acute depression (Chhetry et al., 2016).

In addition to essential fatty acids, quinoa lipids include carotenoids, tocopherols and tocotrienols, which are bioactive substances with high antioxidant potential that are important, for example, for the prevention of cardiopathies and atherosclerosis (Abderrahim et al., 2015; Gómez-Caravaca et al., 2011; Przygoda & Wejnerowska, 2015).

4.4 Quinoa in the prevention and treatment of arterial hypertension

Hypertension is an important risk factor in the development of cardiovascular diseases (World Health Organization, 2012). Bioactive peptides from dietary protein have been investigated for their role in various mechanisms of blood pressure regulation and because of their antioxidant properties related to antihypertensive activity, which act via inhibition of the angiotensin I-converting enzyme, which converts angiotensin I to angiotensin II and is a powerful vasoconstrictor (Martínez-Maqueda, Miralles, Recio, & Hernández-Ledesma, 2012; Udenigwe & Mohan, 2014).

The antioxidant, antihypertensive and antiallergenic activities of quinoa and amaranth were compared to those of wheat, buckwheat, barley, rice and three varieties of millet in an *in vitro* study. No antibody reaction to gluten was observed for quinoa and amaranth. Regarding

antioxidant activity, quinoa presented high angiotensin I-converting enzyme inhibition activity, which was equal to that of buckwheat but higher than that of the remaining cereals. Consumption of quinoa and amaranth was therefore concluded to be important in the prevention of arterial hypertension (Asao & Watanabe, 2010). This was also demonstrated by Aluko & Monu (2003), who observed antioxidant capacity and angiotensin I-converting enzyme inhibition activity in hydrolyzed quinoa protein concentrate. This result is consistent with the *in vivo* study by Ogawa et al. (2001) in which quinoa ingestion led to suppression of the increase in systolic blood pressure in spontaneously hypertensive rats.

4.5 Quinoa in the treatment of gastric lesions

Some polysaccharides protect gastric mucosal cells, possibly through their ability to increase mucus synthesis and/or their ability to bind to the surface mucosa, forming a protective coating against acute attack and preventing the penetration of necrotizing agents (Silva & Parente, 2010).

Cordeiro et al. (2012) identified the cell wall polysaccharides of quinoa seeds after the removal of starch. Arabinan and pectic polysaccharide fractions were extracted and determined to have gastroprotective activity on ethanol-induced gastric lesions in rats. Gastroprotective activity had previously been reported and attributed to other plant polysaccharides, such as arabinogalactan (Tanaka et al., 2010) and galactomannoglucan (Silva & Parente, 2010).

4.6 Quinoa in the protection against oxidative processes

Reactive oxygen species (ROS) are involved in physiological signaling responses, namely, in defense mechanisms against infectious agents, contributing to cellular homeostasis. However, at high concentrations, ROS can behave as toxic products involved in cell and tissue dysfunction and promote oxidative stress, resulting in pathophysiological effects (Espinosa-Diez et al., 2015).

Antioxidants are organic substances able to neutralize the harmful effects of oxidation. They can be components of food products, present in their composition, such as in plants, or added as preservatives to various foods (fats, oils). Plants contain natural phytochemicals that are involved in plant protection and may play an antioxidant role in the human body when ingested (Huang, Boxin, & Prior, 2005). However, the antioxidant potential of cereals and

seeds depends on their bioavailability, absorption and utilization (Masisi, Beta, & Moghadasian, 2016).

Quinoa is considered an important source of phytochemicals with antioxidant action, such as flavonoids, phenolic acids, tocopherols, carotenoids, peptides, fat-soluble vitamins, fatty acids and other compounds (Abugoch James, 2009; Tang et al., 2015), which can modulate physiological responses and prevent increases in oxidative stress (Chlopicka, Pasko, Gorinstein, Jedryas, & Zagrodzki, 2012; Letelier, Rodríguez-Rojas, Sánchez-Jofré, & Aracena-Parks, 2011).

Abderrahim et al. (2015) analyzed white, red and black quinoa seeds produced in Peru and determined that they are a natural source of phenolic compounds (1.23-3.41 mg GAE/g) and betalains (0.15-6.10 mg /100 g) and present antioxidant activity (119.8-335.9 μ mol Trolox equivalent/kg). Asao & Watanabe (2010) observed higher phenolic content in quinoa (42.3 mg GAE/g) than in amaranth (22.6 mg GAE/g) and seven other cereals, all grown in Japan. Dini et al. (2010) investigated the antioxidant activity of sweet quinoa (grown in Ecuador) and bitter quinoa seeds (grown in Peru) before and after cooking and observed higher antioxidant activity in bitter uncooked seeds because cooking caused a significant loss of antioxidant capacity and phenolic compounds in the water. In addition to the previously known bioactive compounds, Lutz, Martínez, & Martínez (2013) identified the isoflavones daidzein (1.15 to 0.70 mg/100 g) and genistein (0.25 to 0.05 mg/100 g) in quinoa seeds, confirming the nutritional potential of quinoa.

In a recent study, De Carvalho et al. (2014) investigated the nutritional benefits of daily ingestion of quinoa or corn flakes in postmenopausal women, using health and oxidative stress biochemical markers (glutathione, thiobarbituric acid reactive species - TBARS, and vitamin E). Women not receiving hormone therapy, vitamin supplementation or lipid-lowering agents, without infectious diseases and non-smoking, consumed 25 g of quinoa flakes (QF) or corn flakes (CF) daily for four consecutive weeks.

A significant increase in fiber and protein ingestion (59.05% and 13.88%, respectively), decreases in total cholesterol and LDL cholesterol, and an increase in glutathione levels were only observed in group QF, whereas significant decreases in triglycerides and TBARS and increases in urinary excretion of enterolignans were significant in both groups. TBARS result from lipid peroxidation and are produced under oxidative stress conditions. Conversely, glutathione is related to antioxidant defense, and its deficiency promotes oxidative stress, which is a risk factor for several chronic diseases (Wu et al., 2004).

These results demonstrate a correlation between QF ingestion and protection against the effects of oxidative stress, indicating a possible beneficial effect of QF ingestion.

Similarly, Pasko et al. (2010) investigated the effect of diet supplementation with quinoa seeds on oxidative stress in rats, induced by a fructose-rich diet (31%), and observed that quinoa supplementation resulted in decreased levels of malondialdehyde and increased antioxidant enzyme activity (superoxide dismutase, catalase and glutathione peroxidase) in the plasma, heart, kidney, testis, lungs and pancreas, indicating decreased production of free radicals during some pathological states and a possible protective effect of quinoa seeds against oxidative stress.

4.7 Quinoa in cancer prevention

Cancer is an important, multi-causal public health problem with growing incidence worldwide, responsible for millions of deaths each year (Amin, Kucuk, Khuri, & Shin, 2009; Ferlay et al., 2010). Cancer may be related to external factors (tobacco, UV radiation, food additives or excesses) and/or internal factors (genetics, low immunity) related to oxidative stress (Ashrani et al., 2016).

Food components may have therapeutic effects on cancer cells. Some PUFAs (Pettersen et al., 2016) and phytochemicals present high potential for cancer prevention because of their antioxidant properties and/or role as adjuvants in cell metabolism; additional advantages of their use include safety, low cost and bioavailability (Abugoch James, 2009; Alvarez-jubete et al., 2010; Arnold et al., 2016; Gullett et al., 2010; Nascimento et al., 2014).

Quinoa leaves were observed to present antioxidant and anti-cancer activity *in vitro*, and these effects were attributed to the presence of phenolic compounds and their high bioavailability (Gawlik-Dziki et al., 2013). Phenolic compounds have been associated with free radical scavenging through reducing power, metal chelation, protection against lipid peroxidation, and lipoxygenase inhibition. These findings suggest the potential of quinoa leaves for protection not only against cancer development but also against proinflammatory processes. Such effects have previously been observed in studies that related the presence of polyphenols to protective factors against DNA damage (Abugoch James, 2009; Alvarez-jubete et al., 2010).

5 Utilization of quinoa in the elaboration of food products

Quinoa seeds are considered a pseudograin because of their chemical characteristic and the possibility of using their starch in a similar manner to cereal crops (Bhargava et al., 2006). Quinoa starch is gluten free and presents important technological properties, such as solubility, foam formation, water retention, gelation and emulsifying capacities. Its insoluble fiber is not altered by heat treatment, resulting in changes and improvement in texture and stabilization of food during production and storage. This allows the use of quinoa in several industrial applications (Abugoch, Omero, Tapia, Silva, & Rivera, 2008; Capitani, Spotorno, Nolasco, & Tomás, 2012; Ruales & Nair, 1993).

Betaines and betalains are natural pigments present in quinoa. Betaine concentrations are higher in quinoa (3930-6000 µg/g) than in wheat (174-706 µg/g), corn (50-150 µg/g), buckwheat (> 20 µg/g) or amaranth (646 µg/g) (Ross, Zangger, & Guiraud, 2014). These pigments have demonstrated higher antioxidant activity than polyphenols (Neagu & Barbu, 2014) and can be used as a natural coloring agent in dairy products, soups, sauces, cosmetics and pharmaceuticals (Esatbeyoglu, Wagner, Schini-Kerth, & Rimbach, 2015).

Recent studies have reported a growing search for foods providing additional benefits to the human body. The use of quinoa in food formulations has therefore been the focus of recent studies aimed at improving the nutritional quality of food and supplying differentiated products to the market (Bitzios et al., 2011; Falguera et al., 2012).

Quinoa has been used in the formulation of various food products, such as bread (Calderelli, de Benassi, Visentainer, & Matioli, 2010; Gawlik-Dziki et al., 2015; Stikic et al., 2012), cookies (Brito et al., 2014), pasta (Giménez, Drago, Bassett, Lobo, & Sammán, 2016; Mariotti, Iametti, Cappa, Rasmussen, & Lucisano, 2011), extruded products (Cueto et al., 2015), biofilms (Araujo-farro, Podadera, Sobral, & Menegalli, 2010; Caro et al., 2016), plant milk (Casarotti, Carneiro, & Penna, 2014; Giménez et al., 2016; Pineli et al., 2015), chocolates (Schumacher et al., 2010), breakfast cereals (Joye, Lamberts, Brijs, & Delcour, 2011), and protein extracts and hydrolysates (Föste et al., 2015; Nongonierma & Fitzgerald, 2015).

5.1 Bakery products

The use of various grains in the formulation of breads, cookies, cakes, pasta and other products with partial or total replacement of wheat flour has been widely studied. An increasing number of people are looking for foods with added nutritional value, either because

of health concerns or because they have food restrictions, such as celiac disease (Annunziata & Vecchio, 2011).

The rheological behavior of dough varies with the nature of the protein matrix, quantities of starch, fat and fiber, presence of additives, and processing conditions (Chillo et al., 2009). Starch is the primary component of quinoa seeds, primarily comprising amylose, which interferes directly with quinoa's physical-chemical properties such as texture and gelling capacity (Li, Wang, & Zhu, 2016). The starch fraction also comprises bioactive glycosides and presents high freeze-thaw stability, making it an ideal thickener in frozen foods and other applications in which resistance to retrogradation is desired (Thoufeek Ahamed, Singhai, Kulkarni, & Pal, 1998). Machado Alencar, Steel, Alvim, de Moraes, & Andre Bolini (2015) demonstrated that it is possible to develop gluten-free breads with the addition of quinoa and amaranth. Such breads have sensory properties similar to wheat-based bread but with higher protein, lipid and ash contents.

Alvarez-jubete & Arendt (2010) investigated the physical properties of ingredients with functional potential, such as amaranth, quinoa and buckwheat, in the formulation of gluten-free breads. Microscopy analysis of the breads confirmed the presence of natural emulsifiers in pseudocereals, resulting in products with good acceptance. The authors also observed that quinoa, buckwheat seeds and sprouts were good potential sources of polyphenols to improve the nutritional quality of breads because these compounds and their antioxidant activity are reduced but not lost after cooking.

Calderelli et al. (2010) evaluated the physical-chemical properties and acceptance of breads enriched with quinoa or linseed and observed that breads enriched with quinoa presented balanced essential fatty acid contents, lower saturated fatty acid contents, and higher consumer acceptance.

Some studies partially replaced wheat flour with quinoa flour to add nutritional value to breads. Iglesias-Puig, Monedero, & Haros (2015) tested a 25% or 50% replacement of wheat flour with quinoa flour and observed that bread made with quinoa presented lower specific loaf volume and crumb firmness but good acceptance with increased quinoa flour content. In addition, quinoa increased the bread's nutritional value in terms of dietary fiber, minerals (calcium, iron and zinc), proteins with high biological value, and lipids. Stikic et al. (2012) observed that the inclusion of up to 20% quinoa flour in wheat bread had a positive effect on the rheological properties of bread dough and resulted in bread with a higher protein content and good sensory acceptance. Chlopicka, Pasko, Gorinstein, Jedryas, & Zagrodzki (2012) tested 15% or 30% replacement of wheat flour with quinoa, buckwheat and amaranth

in bread formulations and confirmed that their antioxidant properties were retained even after baking.

In addition to presenting high acceptance and improved protein and mineral contents, breads enriched with quinoa may also present functional biological properties. Swieca, Sęczyk, Gawlik-Dziki, & Dziki (2014) observed antioxidant characteristics and the presence of phenolic compounds in bread enriched with quinoa leaves, resulting from interactions between phenolics, proteins and starch in the fortified bread. This result was also reported by Alvarez-jubete et al. (2010), who observed the presence of quercetin and kaempferol in breads enriched with 50 and 100% quinoa. The addition of pseudocereals therefore increased the polyphenol contents in these products.

The addition of quinoa as a base ingredient in the formulation of cookies resulted in interesting rheologic and functional characteristics, resulting in a gluten-free product with high fiber and mineral contents and good consumer acceptance (Brito et al., 2014).

Extruded products and pasta with quinoa additions have also been studied. Cueto et al. (2015) developed extruded corn products enriched with quinoa flour (20%), chia (5%), or powder extract of purple corn (2%) and evaluated their physical and mechanical properties. The mixture with chia exhibited a lower expansion rate, whereas the mixture with quinoa had a favorable expansion rate and resulted in the lowest density values, allowing the production of extruded products with good sensory characteristics. Chillo et al. (2009) developed a spaghetti with quinoa and oats, using two structuring agents, carboxymethyl cellulose (CMC) and pregelatinized starch, in three different percentages: 0.1%, 0.2%, and 0.3% and 10%, 20%, and 30%, respectively. Oat pasta with CMC and pregelatinized starch presented higher stress at break, most likely because of the presence of oat gluten, whereas quinoa pasta presented greater firmness (Rosell & Foegeding, 2007).

Recent studies reported that the addition of quinoa improves the nutritional value without negatively affecting rheological properties because of the carbon dioxide holding capacity of gluten-free pasta (Brito et al., 2014; Elgeti et al., 2014). Similar results were observed by Mastromatteo et al. (2011), who evaluated the effects of quinoa, corn and soybean flour on spaghetti quality characteristics and observed higher elongation and shear viscosity for formulations with higher corn content. Pasta viscosity is known to be directly affected by the chemical composition of starch and its degree of gelatinization (Chillo et al., 2009).

These results were confirmed by Giménez et al. (2016), who evaluated the nutritional quality of corn spaghetti enriched with 30% bean flour (*Vicia faba*) and 20% quinoa flour

(*Chenopodium quinoa*) by clinical analyses and *in vitro* digestion. The authors produced gluten-free spaghetti with increased protein biological value, with amino acids corrected for digestibility by more than 30%. The enriched pastas also supplied 10%–20% of recommended fiber daily intake. The addition of quinoa flour resulted in higher unsaturated fatty acid and iron contents, and the addition of bean flour increased the zinc content.

Rizzello, Lorusso, Montemurro, & Gobbetti (2016) studied *in vitro* quinoa flour fermentation and developed quinoa sourdough using selected lactic bacteria (*Lactobacillus plantarum* T6B10 and *Lactobacillus rossiae* T0A16). A wheat bread made using 20% (w/w) of quinoa sourdough improved the bread's chemical, textural, and sensory characteristics. The digestibility, phenolic content and antioxidant activity were also significantly increased, which is consistent with Masisi, Beta, & Moghadasian (2016).

5.2 Formulation of protein concentrates and hydrolysates

Diverse research is currently focused on peptides derived from food protein, which, in addition to presenting antioxidant properties, can be used in the formulation of new functional and differentiated products (Sarmadi & Ismail, 2010).

Because quinoa is a source of high quality protein and presents higher protein content than cereals such as corn, oats, rye or barley (USDA, 2015), it has been studied as a pseudocereal with great potential for the development of protein hydrolysates with functional characteristics (Nongonierma & Fitzgerald, 2015).

However, Föste et al. (2015) observed that under optimal extraction conditions (pH 10, 20°C, and 1 h), quinoa bran exhibits a higher protein yield (68%) than the whole grain (52%), most likely because of the larger contact surface of bran protein with water, favoring protein extraction.

Pineli et al. (2015) developed a quinoa milk with hypoallergenic characteristics and a protein content 5.66 times higher than that of rice milk, half that of cow's milk (USDA, 2011), and 36% higher than that in commercial quinoa milk. In addition, Pineli's milk had lower sodium and lipid contents, a low glycemic index (52), and an acceptance similar to rice milk by consumers with the indication of plant milk consumption.

Elsahaimy et al. (2015) studied a quinoa protein isolate with hypoallergenic characteristics and observed that it presented higher digestibility (78.37%) than grains such as wheat and rice, high solubility at alkaline pH (10), and interesting technological characteristics such as foaming capacity and high stability although with low emulsifying

capacity. This result is consistent with that of Abugoch, Omero, Tapia, Silva, & Rivera (2008), who used alkaline pH (9 and 11) in the formulation of quinoa protein concentrates. The authors also observed higher solubility at pH 9 and an amino acid composition meeting the daily requirements for infants and children, rendering the quinoa protein isolate useful as a possible alternative for infant and children nutrition and as an ingredient in nutritional beverages, sauces and soups.

Meneguetti, Brenzan, Batista, Bazotte, & Silva (2011) evaluated the *in vivo* effects, primarily the functional and toxicological potential, of a quinoa protein hydrolysate characterized as rich in essential amino acids, particularly branched-chain amino acids (leucine, isoleucine and valine). The hydrolyzed extracts did not result in hepatic or renal toxicity in rats after 30 days of supplementation, and the supplemented groups of rats (sedentary and exercised) presented decreased food intake, fat deposition, and blood triglyceride and cholesterol levels.

5.3 Production of edible films

Edible films were developed as a response to the challenges of preserving processed food properties by developing a protective system (Fadini et al., 2013). Proteins and polysaccharides are biopolymers that have been extensively studied for edible film production because they are completely biodegradable, often edible, and protect against environmental conditions (Falguera, Quintero, Jiménez, Muñoz, & Ibarz, 2011; Valenzuela, Abugoch, & Tapia, 2013). However, because of their hydrophilic nature and high water vapor permeability, plasticizers must be used to obtain elastic films (Kowalczyk & Baraniak, 2011).

Among polysaccharides, starch is generally used in biofilm production. Starch is a renewable biopolymer comprising amylose and amylopectin, is the primary component of quinoa, and can form transparent biodegradable films that are edible without any prior chemical treatment (Abugoch James, 2009; Araujo-farro et al., 2010).

Film solutions comprising quinoa starch, prepared using glycerol as a plasticizer (16.6-33.4 g glycerol/100 g quinoa starch on a dry basis), were prepared, analyzed and optimized (21.2 g glycerol/100 g quinoa starch, pH 10.7, 36 °C for 14 h), resulting in films resistant to mechanical pressure, with optimal barrier properties and good oxygen permeability (Araujo-farro et al., 2010).

Lilian Abugoch, Tapia, Villamán, Yazdani-pedram, & Díaz-dosque (2011) used blends of quinoa protein extract and chitosan, resulting in a material with enhanced

mechanical properties compared to pure chitosan films, being more hydrophilic and presenting higher elasticity, thickness and permeability. Valenzuela, Abugoch, & Tapia (2013) also attributed the ability to form films to the properties of quinoa protein and lipids combined with chitosan. The authors produced films using quinoa protein extract at alkaline pH (8 and 12) and chitosan, with the addition of three different concentrations of sunflower oil (2.9, 3.8 and 4.7 g/100 ml). The optimal conditions (pH 8; 1:1 quinoa:chitosan; sunflower oil: 2.9 g/100 ml) were determined based on the resulting mechanical and barrier properties of the films. The optimized film was tested by Valenzuela et al. (2015) for fresh strawberries. Coated fruits exhibited a longer shelf life, particularly because of the antifungal activity of chitosan combined with the plasticizing properties of quinoa protein and sunflower oil.

Caro et al. (2016) also observed the effectiveness of films produced from quinoa in increasing the useful life of fresh fruits. The authors prepared and evaluated films combining quinoa protein with chitosan and glycerol, using inkjet printing with nanoparticles of chitosan-tripolyphosphate or thymol. Thymol resulted in higher antimicrobial activity against *Listeria innocua*, *Staphylococcus aureus*, *Salmonella typhimurium*, *Enterobacter aerogenes*, *Pseudomonas aeruginosa* and *Escherichia coli* than chitosan-tripolyphosphate films.

6. Conclusion

The present review reports the nutritional effects of quinoa, revealing it to be promising for the food industry and for health promotion because of its functional characteristics. This study also indicates that quinoa seed cultivation should be promoted because of its potential for human nutrition and food safety by encouraging greater public investment and awareness of the benefits of quinoa as a component of a balanced diet.

However, some human health mechanisms and functions must be further investigated to better direct the use of quinoa in industry and by consumers.

Acknowledgments

The authors thank the Coordination for the Improvement of Higher Level Personnel (Coordenação de Aperfeiçoamento de pessoal do Nível Superior – CAPES) for the scholarship awarded to I.L.B.

References

- Abderrahim, F., Huanatico, E., Segura, R., Arribas, S., Gonzalez, M. C., & Condezo-Hoyos, L. (2015). Physical features, phenolic compounds, betalains and total antioxidant capacity of coloured quinoa seeds (*Chenopodium quinoa* Willd.) from Peruvian Altiplano. *Food Chemistry*, 183, 83–90.
- Abdullah, N. N., Mokhtar, M. M., Bakar, M. H. A., & Al-Kubaisy, W. (2015). Trend on Fast Food Consumption in Relation to Obesity among Selangor Urban Community. *Procedia - Social and Behavioral Sciences*, 202, 505–513.
- Abugoch James, L. E. (2009). Quinoa (*Chenopodium quinoa* Willd.): composition, chemistry, nutritional, and functional properties. *Advances in Food and Nutrition Research*, 58, 1–31.
- Abugoch, L. E., Omero, N. R., Tapia, C. A., Silva, J., & Rivera, M. (2008). Study of Some Physicochemical and Functional Properties of Quinoa (*Chenopodium Quinoa* Willd) Protein Isolates. *Journal of Agricultural and Food Chemistry*, 56, 4745–4750.
- Abugoch, L. E., Tapia, C., Villamán, M. C., Yazdani-pedram, M., & Díaz-dosque, M. (2011). Food Hydrocolloids Characterization of quinoa protein and chitosan blend edible films. *Food Hydrocolloids*, 25(5), 879–886.
- Alberti, A., Zielinski, A. A. F., Zardo, D. M., Demiate, I. M., Nogueira, A., & Mafra, L. I. (2014). Optimisation of the extraction of phenolic compounds from apples using response surface methodology. *Food Chemistry*, 149, 151–158.
- Alvarez-jubete L, A. M., & Arendt, and K, Gallagher, E. (2010). Baking properties and microstructure of pseudocereal Xours in gluten-free bread formulations. *European Food Research and Technology*, 230, 437–445.
- Alvarez-Jubete, L., Arendt, E. K., & Gallagher, E. (2009). Nutritive value and chemical composition of pseudocereals as gluten-free ingredients. *International Journal of Food Sciences and Nutrition*, 60(4), 240–257.
- Alvarez-jubete, L., Wijngaard, H., Arendt, E. K., & Gallagher, E. (2010). Polyphenol composition and *in vitro* antioxidant activity of amaranth , quinoa buckwheat and wheat as affected by sprouting and baking. *Food Chemistry*, 119(2), 770–778.
- Amin, A. R. M. R., Kucuk, O., Khuri, F. R., & Shin, D. M. (2009). Perspectives for cancer prevention with natural compounds. *Journal of Clinical Oncology*, 27(16), 2712–2725.
- Annunziata, A., & Vecchio, R. (2011). Functional foods development in the European market: A consumer perspective. *Journal of Functional Foods*, 3(3), 223–228.
- Araujo-farro, P. C., Podadera, G., Sobral, P. J. A., & Menegalli, F. C. (2010). Development of films based on quinoa (*Chenopodium quinoa* , Willdenow) starch. *Carbohydrate Polymers*, 81(4), 839–848.
- Arnold, M., Leitzmann, M., Freisling, H., Bray, F., Romieu, I., Renehan, A., & Soerjomataram, I. (2016). Obesity and cancer: An update of the global impact. *Cancer Epidemiology*, 41, 8–15.
- Asao, M., & Watanabe, K. (2010). Functional and Bioactive Properties of Quinoa and Amaranth. *Food Science and Technology Research*, 16(2), 163–168.

- Ashrani, A. A., Gullerud, R. E., Petterson, T. M., Marks, R. S., Bailey, K. R., & Heit, J. A. (2016). Risk factors for incident venous thromboembolism in active cancer patients: A population based case-control study. *Thrombosis Research*, 139, 29–37.
- Augustin, L. S. A., Kendall, C. W. C., Jenkins, D. J. A., Willett, W. C., Astrup, A., Barclay, A. W., & Poli, A. (2015). Glycemic index, glycemic load and glycemic response: An International Scientific Consensus Summit from the International Carbohydrate Quality Consortium (ICQC). *Nutrition, Metabolism, and Cardiovascular Diseases : NMCD*, 25(9), 795–815.
- Berti, C., Riso, P., Monti, L. D., & Porrini, M. (2004). In vitro starch digestibility and *in vivo* glucose response of gluten-free foods and their gluten counterparts. *European Journal of Nutrition*, 43(4), 198–204.
- Bhargava, A., Shukla, S., & Ohri, D. (2006). *Chenopodium quinoa* — An Indian perspective, 23(April 2005), 73–87.
- Bitzios, M., Fraser, I., & Haddock-Fraser, J. (2011). Functional ingredients and food choice: Results from a dual-mode study employing means-end-chain analysis and a choice experiment. *Food Policy*, 36(5), 715–725.
- Borges, J. T., Bonomo, R. C., Paula, C. D., Oliveira, L. C., & Cesário, M. C. (2010). Physicochemical and nutritional characteristics and uses of quinoa (*Chenopodium quinoa* Willd.). *Temas Agrarios*, 15(1), 9 – 23.
- Brakez, M., Daoud, S., Harrouni, M. C., Tachbib, N., & Brakez, Z. (2016). *Halophytes for Food Security in Dry Lands. Halophytes for Food Security in Dry Lands*. Elsevier.
- Brito, I. L., de Souza, E. L., Felex, S. S. S., Madruga, M. S., Yamashita, F., & Magnani, M. (2014). Nutritional and sensory characteristics of gluten-free quinoa (*Chenopodium quinoa* Willd)-based cookies development using an experimental mixture design. *Journal of Food Science and Technology*, 52(9), 5866–5873.
- Calderelli, V. A. S., de Benassi, M. T., Visentainer, J. V., & Matioli, G. (2010). Quinoa and flaxseed: Potential ingredients in the production of bread with functional quality. *Brazilian Archives of Biology and Technology*, 53(4), 981–986.
- Caro, N., Medina, E., Díaz-Dosque, M., López, L., Abugoch, L., & Tapia, C. (2016). Novel active packaging based on films of chitosan and chitosan/quinoa protein printed with chitosan-tripolyphosphate-thymol nanoparticles via thermal ink-jet printing. *Food Hydrocolloids*, 52, 520–532.
- Casarotti, S. N., Carneiro, B. M., & Penna, A. L. B. (2014). Evaluation of the effect of supplementing fermented milk with quinoa flour on probiotic activity. *Journal of Dairy Science*, 97(10), 6027–35.
- Chhetry, B. T., Hezghia, A., Miller, J. M., Lee, S., Rubin-Falcone, H., Cooper, T. B., & Sublette, M. E. (2016). Omega-3 polyunsaturated fatty acid supplementation and white matter changes in major depression. *Journal of Psychiatric Research*, 75, 65–74.
- Chillo, S., Civica, V., Iannetti, M., Suriano, N., Mastromatteo, M., & Nobile, M. A. Del. (2009). Properties of quinoa and oat spaghetti loaded with carboxymethylcellulose sodium salt and pregelatinized starch as structuring agents. *Carbohydrate Polymers*, 78(4), 932–937.

- Chlopicka, J., Pasko, P., Gorinstein, S., Jedryas, A., & Zagrodzki, P. (2012). LWT - Food Science and Technology Total phenolic and total flavonoid content , antioxidant activity and sensory evaluation of pseudocereal breads. *LWT - Food Science and Technology*, 46(2), 548–555.
- Choi, J., Kim, D., Park, S., Lee, H., Kim, K., Kim, K., & Kim, S. (2015). Anti-thrombotic effect of rutin isolated from *Dendropanax morbifera* Leveille. *Journal of Bioscience and Bioengineering*, 120(2), 181–186.
- Clifton, P. (2012). Effects of a high protein diet on body weight and comorbidities associated with obesity. *The British Journal of Nutrition*, 108 Suppl , S122–9.
- Collar, C. (2016). *Encyclopedia of Food and Health*. *Encyclopedia of Food and Health*. Elsevier.
- Comai, S., Bertazzo, A., Bailoni, L., Zancato, M., Costa, C. V. L., & Allegri, G. (2007). Food Chemistry The content of proteic and nonproteic (free and protein-bound) tryptophan in quinoa and cereal flours. *Food Chemistry*, 100, 1350–1355.
- Cordeiro, L. M. C., Fátima, V. De, Baggio, C. H., Fernanda, M., Werner, D. P., Moura, L., & Iacomini, M. (2012). Arabinan and arabinan-rich pectic polysaccharides from quinoa (*Chenopodium quinoa*) seeds : Structure and gastroprotective activity. *Food Chemistry*, 130(4), 937–944.
- Cueto, M., Porras-saavedra, J., Farroni, A., Alamilla-beltrán, L., Schöenlechner, R., Schleining, G., & Buera, P. (2015). Physical and mechanical properties of maize extrudates as affected by the addition of chia and quinoa seeds and antioxidants. *Journal of Food Engineering*, 167, 139–146.
- David, S., & Ludwig, M. (2002). The Glycemic Index: Physiological Mechanisms Relating to Obesity, Diabetes, and Cardiovascular Disease. *American Medical Association*, 287(18), 2414–2423.
- De Carvalho, F. G., Ovídio, P. P., Padovan, G. J., Jordão Junior, A. A., Marchini, J. S., & Navarro, A. M. (2014). Metabolic parameters of postmenopausal women after quinoa or corn flakes intake - a prospective and double-blind study. *International Journal of Food Sciences and Nutrition*, 65(3), 380–5.
- Dini, I., Tenore, G. C., & Dini, A. (2010). LWT - Food Science and Technology Antioxidant compound contents and antioxidant activity before and after cooking in sweet and bitter *Chenopodium quinoa* seeds. *LWT - Food Science and Technology*, 43(3), 447–451.
- Elgeti, D., Nordlohne, S. D., Föste, M., Besl, M., Linden, M. H., Heinz, V., & Becker, T. (2014). Volume and texture improvement of gluten-free bread using quinoa white flour. *Journal of Cereal Science*, 59(1), 41–47.
- Ells, L. J., Campbell, K., Lidstone, J., Kelly, S., Lang, R., & Summerbell, C. (2005). Prevention of childhood obesity. *Best Practice & Research. Clinical Endocrinology & Metabolism*, 19(3), 441–54.
- Elsohaimy, S. A., Refaay, T. M., & Zaytoun, M. A. M. (2015). Physicochemical and functional properties of quinoa protein isolate. *Annals of agricultural sciences*, 1–9.
- Endo, J., & Arita, M. (2015). Cardioprotective mechanism of omega-3 polyunsaturated fatty acids. *Journal of Cardiology*, 67(1), 22–27.
- Esatbeyoglu, T., Wagner, A. E., Schini-Kerth, V. B., & Rimbach, G. (2015). Betanin-A food colorant

- with biological activity. *Molecular Nutrition and Food Research*, 59(1), 36–47.
- Espinosa-Diez, C., Miguel, V., Mennerich, D., Kietzmann, T., Sánchez-Pérez, P., Cadenas, S., & Lamas, S. (2015). Antioxidant responses and cellular adjustments to oxidative stress. *Redox Biology*, 6, 183–197.
- Fadini, A. L., Rocha, F. S., Alvim, I. D., Sadahira, M. S., Queiroz, M. B., Alves, R. M. V., & Silva, L. B. (2013). Mechanical properties and water vapour permeability of hydrolysed collagen-cocoa butter edible films plasticised with sucrose. *Food Hydrocolloids*, 30(2), 625–631.
- Falguera, V., Aliguer, N., & Falguera, M. (2012). An integrated approach to current trends in food consumption: Moving toward functional and organic products? *Food Control*, 26(2), 274–281.
- Falguera, V., Quintero, J. P., Jiménez, A., Muñoz, J. A., & Ibarz, A. (2011). Edible films and coatings: Structures, active functions and trends in their use. *Trends in Food Science & Technology*, 22(6), 292–303.
- Ferlay, J., Shin, H. R., Bray, F., Forman, D., Mathers, C., & Parkin, D. M. (2010). Estimates of worldwide burden of cancer in 2008: GLOBOCAN 2008. *International Journal of Cancer*, 127(12), 2893–2917.
- Föste, M., Elgeti, D., Brunner, A.-K., Jekle, M., & Becker, T. (2015). Isolation of quinoa protein by milling fractionation and solvent extraction. *Food and Bioproducts Processing*, 96, 20–26.
- Foucault, A. S., Even, P., Lafont, R., Dioh, W., Veillet, S., Tomé, D., & Quignard-Boulangé, A. (2014). Quinoa extract enriched in 20-hydroxyecdysone affects energy homeostasis and intestinal fat absorption in mice fed a high-fat diet. *Physiology and Behavior*, 128, 226–231.
- Gajos, G. (2016). *Handbook of Lipids in Human Function*. *Handbook of Lipids in Human Function*. Elsevier.
- Gawlik-Dziki, U., Dziki, D., Świeca, M., Sęczyk, Ł., Różyło, R., & Szymanowska, U. (2015). Bread enriched with *Chenopodium* quinoa leaves powder – The procedures for assessing the fortification efficiency. *LWT - Food Science and Technology*, 62(2), 1226–1234.
- Gawlik-Dziki, U., Świeca, M., Sułkowski, M., Dziki, D., Baraniak, B., & Czyż, J. (2013). Antioxidant and anticancer activities of *Chenopodium* quinoa leaves extracts – In vitro study. *Food and Chemical Toxicology*, 57, 154–160.
- Giménez, M. A., Drago, S. R., Bassett, M. N., Lobo, M. O., & Sammán, N. C. (2016). Nutritional improvement of corn pasta-like product with broad bean (*Vicia faba*) and quinoa (*Chenopodium quinoa*). *Food Chemistry*, 199, 150–156.
- Gómez-Caravaca, A. M., Segura-Carretero, A., Fernández-Gutiérrez, A., & Caboni, M. F. (2011). Simultaneous determination of phenolic compounds and saponins in quinoa (*Chenopodium quinoa* Willd.) by a liquid chromatography-diode array detection-electrospray ionization-time-of-flight mass spectrometry methodology. *Journal of Agricultural and Food Chemistry*, 59, 10815–10825.
- Graf, B. L., Poulev, A., Kuhn, P., Grace, M. H., Lila, M. A., & Raskin, I. (2014). Quinoa seeds leach phytoecdysteroids and other compounds with anti-diabetic properties. *Food Chemistry*, 163, 178–185.

- Grundy, S. M., Arai, H., Barter, P., Bersot, T. P., Betteridge, D. J., Carmena, R., & Zhao, D. (2014). An International Atherosclerosis Society Position Paper: global recommendations for the management of dyslipidemia--full report. *Journal of Clinical Lipidology*, 8(1), 29–60.
- Gullett, N. P., Ruhul Amin, A. R. M., Bayraktar, S., Pezzuto, J. M., Shin, D. M., Khuri, F. R., & Kucuk, O. (2010). Cancer prevention with natural compounds. *Seminars in Oncology*, 37(3), 258–81.
- Hemalatha, P., Bomzan, D. P., Rao, B. V. S., & Sreerama, Y. N. (2016). Distribution of phenolic antioxidants in whole and milled fractions of quinoa and their inhibitory effects on α -amylase and α -glucosidase activities. *Food chemistry*, 199, 330–338.
- Hemalatha, P., Bomzan, D. P., Sathyendra Rao, B. V., & Sreerama, Y. N. (2016). Distribution of phenolic antioxidants in whole and milled fractions of quinoa and their inhibitory effects on α -amylase and α -glucosidase activities. *Food Chemistry*, 199, 330–338.
- Hirose, Y., Fujita, T., Ishii, T., & Ueno, N. (2010). Antioxidative properties and flavonoid composition of Chenopodium quinoa seeds cultivated in Japan. *Food Chemistry*, 119(4), 1300–1306.
- Howlett, J. F., Betteridge, V. A., Champ, M., Craig, S. A. S., Meheust, A., & Jones, J. M. (2010). The definition of dietary fiber – discussions at the Ninth Vahouny Fiber Symposium: building scientific agreement. *Food & Nutrition Research*, 54(3), 112–129.
- Huang, D., Boxin, O. U., & Prior, R. L. (2005). The chemistry behind antioxidant capacity assays. *Journal of Agricultural and Food Chemistry*, 53(6), 1841–1856.
- Iglesias-Puig, E., Monedero, V., & Haros, M. (2015). Bread with whole quinoa flour and bifidobacterial phytases increases dietary mineral intake and bioavailability. *LWT - Food Science and Technology*, 60(1), 71–77.
- Jacobsen, S.-E. (2011). The Situation for Quinoa and Its Production in Southern Bolivia: From Economic Success to Environmental Disaster. *Journal of Agronomy and Crop Science*, 197(5), 390–399.
- Jancurová, M., Minarovičová, L., & Dandár, A. (2009). Quinoa - A review. *Czech Journal of Food Sciences*, 27(2), 71–79.
- Jensen, L., Sloth, B., Krog-Mikkelsen, I., Flint, A., Raben, A., Tholstrup, T., & Astrup, A. (2008). A low-glycemic-index diet reduces plasma plasminogen activator inhibitor-1 activity, but not tissue inhibitor of proteinases-1 or plasminogen activator inhibitor-1 protein, in overweight women. *Am J Clin Nutr*, 87(1), 97–105.
- Joana Gil-Chávez, G., Villa, J. A., Fernando Ayala-Zavala, J., Basilio Heredia, J., Sepulveda, D., Yahia, E. M., & González-Aguilar, G. A. (2013). Technologies for Extraction and Production of Bioactive Compounds to be Used as Nutraceuticals and Food Ingredients: An Overview. *Comprehensive Reviews in Food Science and Food Safety*, 12(1), 5–23.
- Joye, I. J., Lamberts, L., Brijs, K., & Delcour, J. a. (2011). In situ production of γ -aminobutyric acid in breakfast cereals. *Food Chemistry*, 129(2), 395–401.
- Kowalczyk, D., & Baraniak, B. (2011). Effects of plasticizers, pH and heating of film-forming solution on the properties of pea protein isolate films. *Journal of Food Engineering*, 105(2), 295–

305.

- Kozioł, M. J. (1992). Chemical composition and nutritional evaluation of quinoa (*Chenopodium quinoa* Willd.). *Journal of Food Composition and Analysis*, 5(1), 35–68.
- Kumpun, S., Maria, A., Crouzet, S., Evrard-todeschi, N., Girault, J., & Lafont, R. (2011). Ecdysteroids from *Chenopodium quinoa* Willd., an ancient Andean crop of high nutritional value. *Food Chemistry*, 125(4), 1226–1234.
- Lamothe, L. M., Srichuwong, S., Reuhs, B. L., & Hamaker, B. R. (2015). Quinoa (*Chenopodium quinoa* W.) and amaranth (*Amaranthus caudatus* L.) provide dietary fibres high in pectic substances and xyloglucans. *Food Chemistry*, 167, 490–496.
- Larsen, T. T. M., Dalskov, S.-M. S., van Baak, M., Jebb, S. a, Papadaki, A., Pfeiffer, A. F. H., & Astrup, A. (2010). Diets with high or low protein content and glycemic index for weight-loss maintenance. *The New England Journal of Medicine*, 363(22), 2102–13.
- Lavie, C. J., De Schutter, A., Parto, P., Jahangir, E., Kokkinos, P., Ortega, F. B., & Milani, R. V. (2016). Obesity and Prevalence of Cardiovascular Diseases and Prognosis—The Obesity Paradox Updated. *Progress in Cardiovascular Diseases*.
- Lebwohl, B., Ludvigsson, J. F., & Green, P. H. (2015). Celiac disease and non-celiac gluten sensitivity. *BMJ*, 351, h 4347.
- Letelier, M. E., Rodríguez-Rojas, C., Sánchez-Jofré, S., & Aracena-Parks, P. (2011). Surfactant and antioxidant properties of an extract from *Chenopodium quinoa* Willd seed coats. *Journal of Cereal Science*, 53(2), 239–243.
- Li, G., Wang, S., & Zhu, F. (2016). Physicochemical properties of quinoa starch. *Carbohydrate Polymers*, 137, 328–338.
- Louzada, M. L. da C., Baraldi, L. G., Steele, E. M., Martins, A. P. B., Canella, D. S., Moubarac, J.-C., & Monteiro, C. A. (2015). Consumption of ultra-processed foods and obesity in Brazilian adolescents and adults. *Preventive Medicine*, 81, 9–15.
- Lutz, M., Martínez, A., & Martínez, E. A. (2013). Daidzein and Genistein contents in seeds of quinoa (*Chenopodium quinoa* Willd.) from local ecotypes grown in arid Chile. *Industrial Crops and Products*, 49, 117–121.
- Machado Alencar, N. M., Steel, C. J., Alvim, I. D., de Moraes, E. C., & Andre Bolini, H. M. (2015). Addition of quinoa and amaranth flour in gluten-free breads: Temporal profile and instrumental analysis. *LWT - Food Science and Technology*, 62(2), 1011–1018.
- Mackey, E. R., Olson, A., DiFazio, M., & Cassidy, O. (2016). Obesity Prevention and Screening. *Primary Care: Clinics in Office Practice*, 43(1), 39–51.
- Mariotti, M., Iametti, S., Cappa, C., Rasmussen, P., & Lucisano, M. (2011). Characterisation of gluten-free pasta through conventional and innovative methods: Evaluation of the uncooked products. *Journal of Cereal Science*, 53(3), 319–327.
- Martínez-Maqueda, D., Miralles, B., Recio, I., & Hernández-Ledesma, B. (2012). Antihypertensive peptides from food proteins: a review. *Food & Function*, 3(4), 350–361.
- Masisi, K., Beta, T., & Moghadasian, M. H. (2016). Antioxidant properties of diverse cereal grains: A

- review on *in vitro* and *in vivo* studies. *Food Chemistry*, 196, 90–97.
- Mastromatteo, M., Chillo, S., Iannetti, M., Civica, V., Alessandro, M., & Nobile, D. (2011). Original article Formulation optimisation of gluten-free functional spaghetti based on quinoa , maize and soy flours, 1201–1208.
- Meneguetti, Q. A., Brenzan, M. A., Batista, M. R., Bazotte, R. B., & Silva, D. R. (2011). Biological Effects of Hydrolyzed Quinoa Extract from Seeds of *Chenopodium quinoa* Willd. 1 1. *Journal of Medicinal Food*, 14(6), 653–657.
- Mohamed, S. (2014). Functional foods against metabolic syndrome (obesity, diabetes, hypertension and dyslipidemia) and cardiovascular disease. *Trends in Food Science & Technology*, 35(2), 114–
- Nascimento, A. C., Mota, C., Coelho, I., Gueifão, S., Santos, M., Matos, A. S., & Castanheira, I. (2014). Characterisation of nutrient profile of quinoa (*Chenopodium quinoa*), amaranth (*Amaranthus caudatus*), and purple corn (*Zea mays* L.) consumed in the North of Argentina: proximates, minerals and trace elements. *Food Chemistry*, 148, 420–6.
- Neagu, C., & Barbu, V. (2014). Principal component analysis of the factors involved in the extraction of beetroot betalains. *Journal of Agroalimentary Processes and Technologies*, 20(4), 311–318.
- Nongonierma, A. B., & Fitzgerald, R. J. (2015). Quinoa (*Chenopodium quinoa* Willd .) protein hydrolysates with *in vitro* dipeptidyl peptidase IV (DPP-IV) inhibitory and antioxidant properties. *Journal of Cereal Science*, 65, 112–118.
- Nongonierma, A. B., Le Maux, S., Dubrulle, C., Barre, C., & FitzGerald, R. J. (2015). Quinoa (*Chenopodium quinoa* Willd.) protein hydrolysates with in vitro dipeptidyl peptidase IV (DPP-IV) inhibitory and antioxidant properties. *Journal of Cereal Science*, 65, 112–118.
- Nowak, V., Du, J., & Charrondière, U. R. (2016). Assessment of the nutritional composition of quinoa (*Chenopodium quinoa* Willd.). *Food Chemistry*, 193, 47–54.
- Panickar, K. S. (2015). *Bioactive Nutraceuticals and Dietary Supplements in Neurological and Brain Disease*. *Bioactive Nutraceuticals and Dietary Supplements in Neurological and Brain Disease*. Elsevier.
- Pasko, P., Barton, H., Zagrodzki, P., Izewska, A., Krosniak, M., Gawlik, M., & Gorinstein, S. (2010). Effect of Diet Supplemented with Quinoa Seeds on Oxidative Status in Plasma and Selected Tissues of High Fructose-Fed Rats. *Plant Foods for Human Nutrition*, 65(2), 146–151.
- Pásko, P., Barton, H., Zagrodzki, P., Izewska, A., Krosniak, M., Gawlik, M., & Gorinstein, S. (2010a). Effect of Diet Supplemented with Quinoa Seeds on Oxidative Status in Plasma and Selected Tissues of High Fructose-Fed Rats. *Plant Foods for Human Nutrition*, 65(2), 333–338.
- Paško, P., Bartoń, H., Zagrodzki, P., Gorinstein, S., Fołta, M., & Zachwieja, Z.(2009).Anthocyanins, total polyphenols and antioxidant activity in amaranth and quinoa seeds and sprouts during their growth. *Food Chemistry*, 115(3), 994-998.
- Peiretti, P. G., Gai, F., & Tassone, S. (2013). Fatty acid profile and nutritive value of quinoa (*Chenopodium quinoa* Willd.) seeds and plants at different growth stages. *Animal Feed Science and Technology*, 183(1-2), 56–61.
- Pettersen, K., Monsen, V. T., Hakvåg Pettersen, C. H., Overland, H. B., Pettersen, G., Samdal, H., &

- Schönberg, S. A. (2016). DHA-induced stress response in human colon cancer cells - Focus on oxidative stress and autophagy. *Free Radical Biology & Medicine*, 90, 158–72.
- Pineli, L. de L. de O., Botelho, R. B. A., Zandonadi, R. P., Solorzano, J. L., de Oliveira, G. T., Reis, C. E. G., & Teixeira, D. da S. (2015). Low glycemic index and increased protein content in a novel quinoa milk. *LWT - Food Science and Technology*, 63(2), 1261–1267.
- Platt, T. L., Beckett, T. L., Kohler, K., Niedowicz, D. M., & Murphy, M. P. (2015). Obesity, diabetes, and leptin resistance promote tau pathology in a mouse model of disease. *Neuroscience*, 315, 162–174.
- Pouliot-Mathieu, K., Gardner-Fortier, C., Lemieux, S., St-Gelais, D., Champagne, C. P., & Vuilleumard, J.-C. (2013). Effect of cheese containing gamma-aminobutyric acid-producing lactic acid bacteria on blood pressure in men. *PharmaNutrition*, 1(4), 141–148.
- Prego, I., Maldonado, S., & Otegui, M. (1998). Seed Structure and Localization of Reserves in *Chenopodium quinoa*. *Annals of Botany*, 82(4), 481–488.
- Przybylski, R., Chauhan, G. S., & Eskin, N. A. M. (1994). Characterization of quinoa (*Chenopodium quinoa*) lipids, 51, 187–192.
- Przygoda, K., & Wejnerowska, G. (2015). Extraction of tocopherol-enriched oils from Quinoa seeds by supercritical fluid extraction. *Industrial Crops and Products*, 63, 41–47.
- Razzaghi, F., Plauborg, F., Jacobsen, S., Richardt, C., & Neumann, M. (2012). Effect of nitrogen and water availability of three soil types on yield , radiation use efficiency and evapotranspiration in field-grown quinoa. *Agricultural Water Management*, 109, 20–29.
- Repo-Carrasco, R., Espinoza, C., & Jacobsen, S.-E. (2003). Nutritional Value and Use of the Andean Crops Quinoa (*Chenopodium quinoa*) and Kañiwa (*Chenopodium pallidicaule*).pdf. *Food Reviews International*, 19(1-2), 179 – 189.
- Repo-Carrasco-Valencia, R. A.-M., & Serna, L. A. (2011). Quinoa (*Chenopodium quinoa*, Willd.) as a source of dietary fiber and other functional components. *Ciência and Tecnologia de Alimentos*, 31(1), 225–230.
- Repo-Carrasco-Valencia, R., Hellström, J. K., Pihlava, J.-M., & Mattila, P. H. (2010). Flavonoids and other phenolic compounds in Andean indigenous grains: Quinoa (*Chenopodium quinoa*), kañiwa (*Chenopodium pallidicaule*) and kiwicha (*Amaranthus caudatus*). *Food Chemistry*, 120(1), 128–133.
- Ribeiro, M., Rodriguez-Quijano, M., Nunes, F. M., Carrillo, J. M., Branlard, G., & Igrejas, G. (2016). New insights into wheat toxicity: Breeding did not seem to contribute to a prevalence of potential celiac disease's immunostimulatory epitopes. *Food Chemistry*, 213, 8–18.
- Rizzello, C. G., Lorusso, A., Montemurro, M., & Gobbetti, M. (2016). Use of sourdough made with quinoa (*Chenopodium quinoa*) flour and autochthonous selected lactic acid bacteria for enhancing the nutritional, textural and sensory features of white bread. *Food Microbiology*, 56, 1–13.
- Rosell, C. M., & Foegeding, A. (2007). Interaction of hydroxypropylmethylcellulose with gluten proteins: Small deformation properties during thermal treatment. *Food Hydrocolloids*, 21(7), 1092–1100.

- Ross, A. B., Zangger, A., & Guiraud, S. P. (2014). Cereal foods are the major source of betaine in the Western diet--analysis of betaine and free choline in cereal foods and updated assessments of betaine intake. *Food Chemistry*, 145, 859–65.
- Ruales, J., & Nair, B. M. (1993). Content of fat, vitamins and minerals in quinoa (*Chenopodium quinoa*, Willd) seeds. *Food Chemistry*, 48(2), 131–136.
- Sarmadi, B. H., & Ismail, A. (2010). Antioxidative peptides from food proteins: A review. *Peptides*, 31(10), 1949–1956.
- Schoenlechner, R., Drausinger, J., Ottenschlaeger, V., & Jurackova, K. (2010). Functional Properties of Gluten-Free Pasta Produced from Amaranth , Quinoa and Buckwheat. *Plant Foods for Human Nutrition*, 65, 339–349.
- Schoenlechner, R., Wendner, M., Siebenhandl-ehn, S., & Berghofer, E. (2010). Pseudocereals as alternative sources for high folate content in staple foods. *Journal of Cereal Science*, 52(3), 475–479.
- Schumacher, A. B., Brandelli, A., Macedo, F. C., Pieta, L., Klug, T. V., & Jong, E. V. (2010). Chemical and sensory evaluation of dark chocolate with addition of quinoa (*Chenopodium quinoa* Willd.). *Journal of Food Science and Technology*, 47(2), 202–206.
- Seal, C. J. (2006). Whole grains and CVD risk. *The Proceedings of the Nutrition Society*, 65(1), 24–34.
- Simnadis, T. G., Tapsell, L. C., & Beck, E. J. (2015). Physiological Effects Associated with Quinoa Consumption and Implications for Research Involving Humans: a Review. *Plant Foods for Human Nutrition*, 70(3), 238–249.
- Somkuti, G. A., Renye, J. A., & Steinberg, D. H. (2012). Molecular analysis of the glutamate decarboxylase locus in *Streptococcus thermophilus* ST110. *Journal of Industrial Microbiology and Biotechnology*, 39(7), 957–963.
- Spehar, C. R. (1998). NOVAS CULTIVARES Quinoa BRS Piabiru : alternativa para diversificar. *Pesq. Agropec. Bras*, (1), 889–893.
- Stikic, R., Glamoclija, D., Demin, M., Vucelic-radovic, B., & Jovanovic, Z. (2012). Agronomical and nutritional evaluation of quinoa seeds (*Chenopodium quinoa* Willd.) as an ingredient in bread formulations. *Journal of Cereal Science*, 55(2), 132–138.
- Swieca, M., Sęczyk, L., Gawlik-Dziki, U., & Dziki, D. (2014). Bread enriched with quinoa leaves - the influence of protein-phenolics interactions on the nutritional and antioxidant quality. *Food Chemistry*, 162, 54–62.
- Tang, Y., Li, X., Zhang, B., Chen, P. X., Liu, R., & Tsao, R. (2015). Characterisation of phenolics, betanins and antioxidant activities in seeds of three *Chenopodium quinoa* Willd. genotypes. *Food Chemistry*, 166, 380–8.
- Thoufeek Ahamed, N., Singhai, R. S., Kulkarni, P. R., & Pal, M. (1998). A lesser-known grain, *Chenopodium quinoa*: Review of the chemical composition of its edible parts. *Food and Nutrition Bulletin*, 19(1), 61–70.
- Tian, R., Yang, W., Xue, Q., Gao, L., Huo, J., Ren, D., & Chen, X. (2016). Rutin ameliorates diabetic

- neuropathy by lowering plasma glucose and decreasing oxidative stress via Nrf2 signaling pathway in rats. *European Journal of Pharmacology*, 771, 84–92. 1
- Tuohy, K. M., Conterno, L., Gasperotti, M., & Viola, R. (2012). Up-regulating the Human Intestinal Microbiome Using Whole Plant Foods, Polyphenols, and/or Fiber. *Journal of Agricultural and Food Chemistry*, 60(36), 8776–8782.
- Udenigwe, C. C., & Mohan, A. (2014). Mechanisms of food protein-derived antihypertensive peptides other than ACE inhibition. *Journal of Functional Foods*, 8, 45–52.
- USDA (United States Department of Agriculture). (2015). National Nutrient Database for Standard Reference Release 28.
- Valenzuela, C., Abugoch, L., & Tapia, C. (2013). Quinoa protein–chitosan–sunflower oil edible film: Mechanical, barrier and structural properties. *LWT - Food Science and Technology*, 50(2), 531–
- Valenzuela, C., Tapia, C., López, L., Bunger, A., Escalona, V., & Abugoch, L. (2015). Effect of edible quinoa protein-chitosan based films on refrigerated strawberry (*Fragaria×ananassa*) quality. *Electronic Journal of Biotechnology*, 18(6), 406–411.
- Villegas, J. M., Brown, L., Savoy de Giori, G., & Hebert, E. M. (2016). Optimization of batch culture conditions for GABA production by *Lactobacillus brevis* CRL 1942, isolated from quinoa sourdough. *LWT - Food Science and Technology*, 67, 22–26.
- Wefers, D., Gmeiner, B. M., Tyl, C. E., & Bunzel, M. (2015). Phytochemistry Characterization of diferuloylated pectic polysaccharides from quinoa (*Chenopodium quinoa* Willd.). *Phytochemistry*, 116, 320–328.
- Wolever, T. M. S., Gibbs, A. L., Chiasson, J.-L., Connelly, P. W., Josse, R. G., Leiter, L. A., & Ryan, E. A. (2013). Altering source or amount of dietary carbohydrate has acute and chronic effects on postprandial glucose and triglycerides in type 2 diabetes: Canadian trial of Carbohydrates in Diabetes (CCD). *Nutrition, Metabolism, and Cardiovascular Diseases : NMCD*, 23(3), 227–34.
- Wu, G. D. et al. (2011). Linking Long-Term Dietary Patterns with Gut Microbial Enterotypes. *Science*, 334, 105-108.

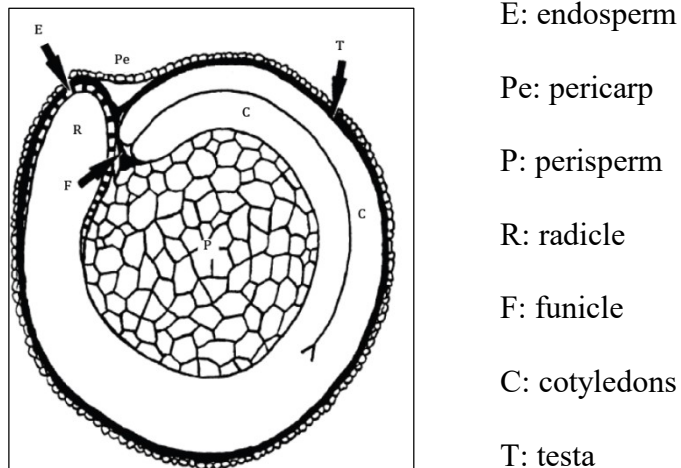


Fig. 1 - Schematic representation of a quinoa seed cross section (Prego, Maldonado, & Otegui, 1998).

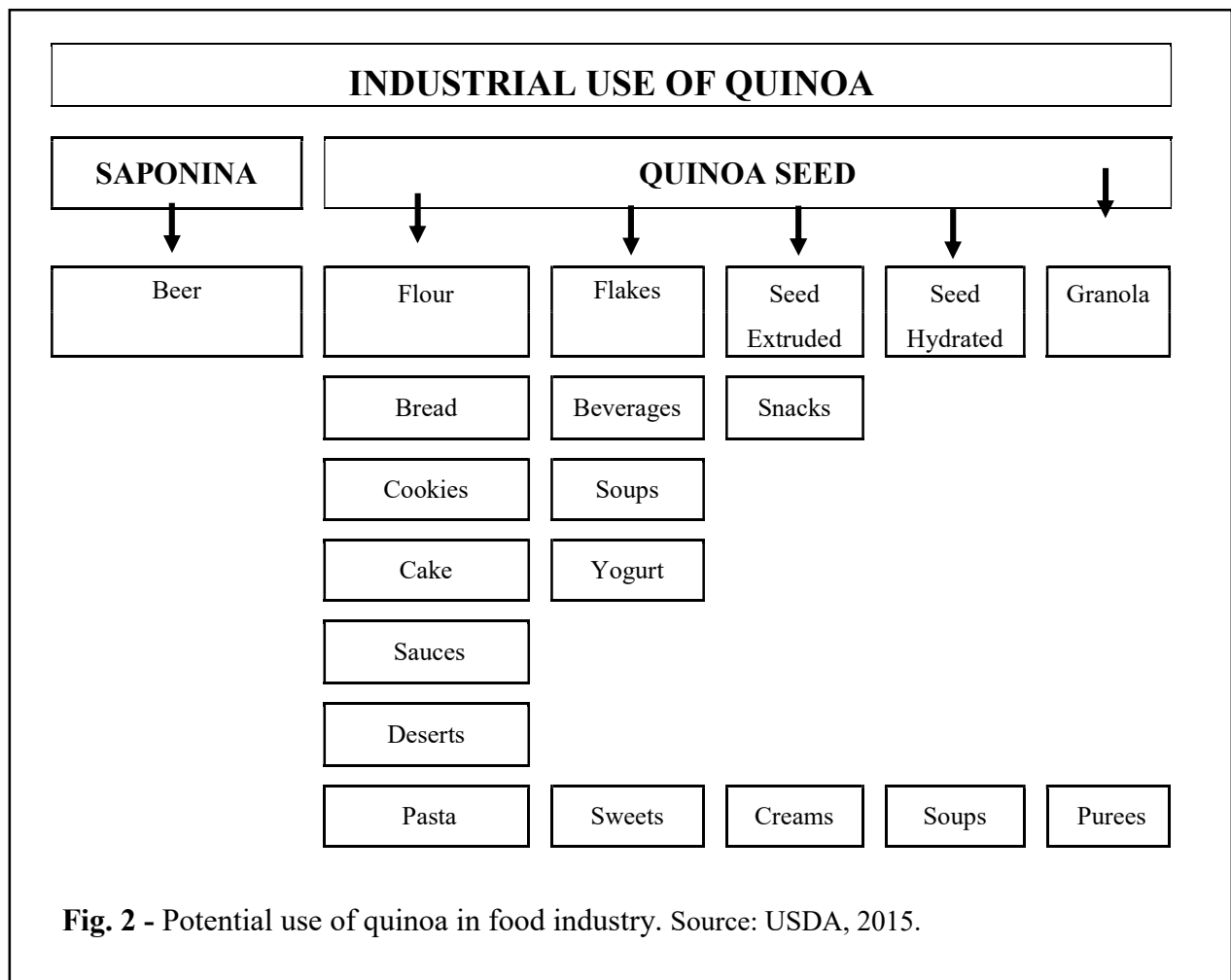


Table 1 - Amino acid concentrations in quinoa seeds compared with cereals and the FAO/WHO standard.

Amino acids g/100 g seed	USDA, 2015 Quinoa	Rice	Oats	Corn	FAO/WHO 1985
Tryptophan*	0.17	0.17	0.23	0.07	0.50
Threonine*	0.42	0.34	0.58	0.35	0.90
Isoleucine*	0.50	0.36	0.70	0.34	1.30
Leucine*	0.84	0.67	1.28	1155.00	1.90
Lysine*	0.77	0.37	0.70	0.27	1.60
Methionine*	0.31	0.19	0.31	0.20	1.70
Cystine	0.20	0.22	0.41	0.17	-
Phenylalanine*	0.59	0.56	0.90	0.46	1.90
Tyrosine	0.27	0.23	0.57	0.38	0.46
Valine*	0.59	0.49	0.94	0.48	1.80
Arginine	1091.00	0.50	1.19	0.47	0.46
Histidine*	0.41	0.22	0.41	0.29	1.60
Alanine	0.59	0.39	0.88	0.71	0.26
Aspartic Acid	1134.00	0.62	1.45	0.66	0.88
Glutamic Acid	1865.00	2.59	3.71	1768.00	1.75
Glycine	0.70	0.36	0.84	0.39	0.20
Proline	0.77	1.18	0.93	0.82	0.61
Serine	0.57	0.42	0.75	0.45	0.53

*Essential amino acids; Source: (USDA, 2015).

Table 2 - Monosaccharide composition of insoluble dietary fiber from quinoa.

	Lamothe et al., 2015	Wefers et al., 2015	Cordeiro et al., 2012
Galacturonic acid	28.5	17.2	0 - 27
Arabinose	15.3	43.3	66 - 98.5
Glucose	21.7	17.3	*nq
Galactose	6.7	5.7	0 - 8.2
Rhamnose	6.5	4.9	0 - 7
Xylose	9.9	7.5	*nq
Mannose	3.2	2.6	*nq

*nq = not quantified.

Table 3 - Micronutrients present in quinoa seeds, compared with other grains.

Nutrients	Quinoa	Amaranth	Corn	Wheat	Oats	Barley
Calcium, mg/100 g	47.0	159.0	7.0	32.0	54.0	67.0
Iron, mg/100 g	4.6	7.61	2.7	4.6	4.7	2.5
Magnesium, mg/100 g	197.0	248.0	127.0	131.0	177.0	79.0
Phosphorus, mg/100 g	457.0	557.0	210.0	355.0	523.0	221.0
Potassium, mg/100 g	563.0	508.0	287.0	432.0	429.0	280.0
Zinc, mg/100 g	3.1	2.9	3.5	3.3	4.0	213.0
Sodium, mg/100 g	5.0	4.0	2.0	2.0	2.0	9.0
Copper, mg/100 g	0.6	0	-	-	-	0.4
Selenium µg/100 g	8.5	0	-	-	-	7.7
Vitamin A (Retinol), IU	14.0	2.0	-	9.0	-	1.0
Vitamin and (α-tocopherol), g/100 g	2.4	1.2	-	1.0	-	-
Vitamin B3 (Niacin), mg/100 g	1.5	0.9	3.6	4.4	0.14	0.11
Folate, µg/100 g	184.0	82.0	-	38.0	56.0	23.0
Beta-carotene, µg/100 g	8.0	-	-	5.0	-	-
Choline, mg/100 g	70.2	-	-	-	-	37.8
Betaine, mg/100 g	630.4	-	-	-	-	-

Source: USDA, 2015

ARTICLE

Application of response surface methodology to optimize extraction of phenolic compounds and antioxidant capacity of different quinoa (*Chenopodium quinoa* Willd.) varieties

Isabelle de Lima Brito^{1,2}, Maristela Alves Alcântara¹, Bruno Raniere Lins de Albuquerque Meireles^{1,3}, Anoar Abbas El-Aouar⁴, Antonio Gouveia de Souza¹, Angela Maria Tribuzy de Magalhães de Cordeiro^{1,5,*}

¹ Graduate Program in Food Science and Technology, Center for Technology - CT, Federal University of Paraíba (UFPB), João Pessoa, Paraíba, Brazil.

² Department of Management and Agroindustrial Technology. Center of Human, Social and Agrarian Sciences. (CCHSA), Federal University of Paraíba (UFPB), João Pessoa, Paraíba, Brazil.

³ Academic Unit of Food Technology, Center for Agriculture and Food Science and Technology, Federal University of Campina Grande (UFCG), Pombal, Paraíba, Brazil.

⁴ Department of Food Engineering, Center for Technology (CT), Federal University of Paraíba (UFPB), João Pessoa, Paraíba, Brazil.

⁵ Department of Food Technology, Center for Technology and Regional Development (CTDR), Federal University of Paraíba (UFPB), João Pessoa, Paraíba, Brazil.

*Corresponding author: Angela M^a Tribuzy de M. de Cordeiro
Departamento de Tecnologia de Alimentos, Centro de Tecnologia e Desenvolvimento Regional – CTDR/UFPB
Avenida dos Escoteiros, s/nº, Mangabeira VII, Distrito Industrial de Mangabeira, João Pessoa, Paraíba, Brazil, CEP 58055-000 Phone: +55 83 3216-7947; e-mail: atribuzycordeiro@gmail.com

Abstract

In this study the efficiency of phenolic compounds extraction and antioxidant activity of three different quinoa varieties using response surface methodology was investigated. The effects of temperature (32-68 °C), time (6.5-19.5 h) and ethanol concentration (19-76%) were evaluated for total phenolic content (TFC), antioxidant activity (DPPH, FRAP and ABTS) and phenolic profile. For the BrWQ variety, the highest TFC responses and antioxidant activity were expressed in the minimization and maximization of planning, respectively. In BoWQ, the TFC and DPPH values were obtained from the minimum points of the independent variables. As for BoRQ, all significant responses were obtained by extraction at 68 °C for 6.5 h using 76% ethanol. The statistical model demonstrated the efficiency of the green solvent mixture and the influence of the parameters on the extraction of antioxidant compounds from quinoa seeds, identified as a source of phenolic compounds, as main 2,5-dihydroxybenzoic and ferulic acids and rutin.

Keywords: *Chenopodium quinoa*; phenolics compounds; experimental design; antioxidant.

1. Introduction

Quinoa (*Chenopodium quinoa* Willd.) is a pseudocereal of Andean origin whose human consumption has been associated with health for thousands of years (Miranda, Vega-gálvez, Uribe, & López, 2011). Quinoa belongs to the family Chenopodiaceae and has been extensively studied to demonstrate its nutritional quality and benefits (Asao & Watanabe, 2010; Gawlik-Dziki et al., 2013; Graf et al., 2014).

The composition of quinoa stands out for its fiber content, absence of gluten, adequate levels of key micronutrients, including minerals and vitamins, and the presence of essential amino acids and fatty acids (Alvarez-Jubete et al., 2009; Hirose et al., 2010; Lamothe et al., 2015). Quinoa also contains bioactive constituents, such as carotenoids, tocopherols, and polyphenols, that are responsible for protecting the plant against adverse climatic conditions and are highly correlated with its antioxidant activity (AA) (Alvarez-Jubete et al., 2009; Abderrahim et al., 2015; Tang et al., 2015b).

Antioxidants are substances that protect cells against oxidative damage caused by excess reactive oxygen species (ROS). ROS are naturally produced by the body, but their excess may result in changes in the DNA, lipids, and proteins of cells (Espinosa-Diez et al., 2015). Therefore, ROS are important in the prevention of chronic-degenerative diseases, such as heart disease, atherosclerosis, diabetes, Alzheimer's disease, and cancer (Abderrahim et al., 2015).

Studies by Gawlik-Dziki et al. (2013) and Tang et al. (2015b) identified ferulic, sinapic, and gallic acids as the main phenolic acids of quinoa and kaempferol and quercetin and rutin as their main flavonoids. However, variety, soil, irrigation, and adverse climatic conditions affect the presence of these compounds (Razzaghi et al., 2012).

In addition to crop growth conditions, extraction conditions affect the quantification and identification of plant phytochemicals, including the chemical nature of the sample, solvent and temperature used, extraction time, stirring, and solute/solvent ratio (Alberti et al., 2014; Prasad et al., 2011). According to Andreo & Jorge (2006), the efficacy of extraction of plant phenolic compounds depends on the solvent mixture because the chemical nature of phenolic compounds ranges from simple to highly polarized. Nevertheless, the use of solvents in food has been a constant concern, with a trend toward using substances with lower toxicity that are known as "green solvents".

Several studies have shown increasing interest in the extraction and quantification of these bioactive compounds from quinoa seeds (Alberti et al., 2014; Gawlik-Dziki et al., 2013; Tang, Li, Zhang, et al., 2015). However, methanol has been predominantly used in phenolic characterization and AA studies (Hirose et al., 2010; Lamothe et al., 2015; R. Repo-Carrasco-Valencia et al., 2010; Tang, Li, Chen, et al., 2015).

Accordingly, this study proposes to assess the effects of the following parameters on the extraction of compounds with antioxidant potential from the seeds of quinoa produced in Brazil and Bolivia: temperature, time, and concentration of green solvents (ethanol/water). RSM is considered a key tool to assess the effects of independent variables and their interactions as well as improve and optimize processes by reducing time and costs (Alberti et al., 2014; Prasad et al., 2011). The objective of the study is to apply an experimental design using response surface methodology (RSM) to identify the best extraction conditions.

2. Materials and methods

2.1. Reagents

The following phenolic acid standards were purchased from Sigma-Aldrich (Sigma Co., USA): 3,4-dihydroxybenzoic (protocatechuic) acid, 4-hydroxybenzoic acid, salicylic acid, syringic acid, 2,5-dihydroxybenzoic (gentisic) acid, vanillic acid, ellagic acid, p-coumaric acid, sinapic acid, *trans*-cinnamic acid, caffeic acid, and ferulic acid. The following flavonoids were purchased from Sigma-Aldrich: rutin, myricetin, quercetin, naringin, kaempferol, catechin, hesperetin, and chrysin. The gallic acid standard and 2,2-diphenyl-1-picrylhydrazyl (DPPH), 2,4,6-tris(2-pyridyl)-s-triazine (TPTZ), and 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox) were also purchased from Sigma-Aldrich. The Folin-Ciocalteu reagent was supplied by Merck. The reagents iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), sodium acetate trihydrate ($\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$), and sodium carbonate (Na_2CO_3) were supplied by Vetec Química Fina Ltda. The gases (synthetic air and nitrogen) were purchased from White Martins, Brazil. Purelab (Elza) ultrapure water was used. High-purity solvents and the other analytical quality reagents and solvents were purchased from J.T. Baker.

2.2. Quinoa seeds

Two kilograms of each seed variety were used to perform the experiments. Quinoa seeds produced in Brazil were grown in the city of Goiás and were purchased directly from the producer (Figure 1A). The imported seeds (white and red) grown in La Paz, Bolivia, (Figure 1B, 1C) were purchased from the company Vitalim, which is located in the city of Jaraguá do Sul in Santa Catarina and is responsible for packaging and distribution in Brazil. Quinoa grown in Brazil is identified as the BRS Piaburu variety, which was introduced in Brazil and adapted to the soil and climate of the country by the Brazilian Agricultural Research Corporation (Empresa Brasileira de Pesquisa Agropecuária – EMBRAPA) beginning in 1992 (Spehar & Souza, 1993).

The seeds were vacuum-packed and stored under refrigeration until analysis.

2.3. Experimental design

A 2^3 experimental design with three central points and eight axial points was used to prepare the plant extracts of each quinoa variety. The temperature X_1 (32-68°C), time X_2 (6.5-19.5 h), and ethanol concentration X_3 (19-76%) were the independent variables used, whereas the response variables included the total phenolic content (TPC) (Y_1) and antioxidant capacity using the following methods: the DPPH method (Y_2), the ferric reducing antioxidant power (FRAP) method (Y_3), and the Trolox equivalent antioxidant capacity (ABTS) method (Y_4). Each variable was encoded using three levels, -1, 0, and +1, for optimization (Table 1a). The levels of the three independent variables were selected based on previous studies conducted by Abderrahim et al. (2015) and Alberti et al. (2014).

After determining the values coded as -1, 0, and +1, factorial planning was designed using the software Statistic 7.0 (StatSoft Inc., USA) with eleven randomized experiments, including three representing the central point (Table 1b). The results of TPC, DPPH, FRAP, and ABTS were expressed as the mean±standard deviation, and analysis of variance (ANOVA; $p<0.05$) was performed for each response. These data were used to determine significance, regression coefficients, and the model to optimize the global area of responses. Using these instruments, a first-order polynomial (Equation 1) was applied to predict the response variables:

$$y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_1 X_2 + \beta_5 X_1 X_3 + \beta_6 X_2 X_3 + \beta_{10} X_1 X_2 X_3 \quad (1)$$

where y is the response; β_0 is the mean; β_1 , β_2 , and β_3 are the regression coefficients for the linear terms; and β_4 , β_5 , β_6 , and β_{10} are the coefficients of interaction effects (Bruns, Scarmino, & Barros Neto, 2006). Model fit was predicted considering the pure error and based on analysis of regression (R^2) and ANOVA ($p < 0.05$). The significance of the regression coefficients was analyzed using the t-test, and non-significant coefficients were removed to obtain a reduced model.

2.4. Preparation of extracts

Seeds were ground in a food processor to prepare the plant extracts (Pratic Blender Cadence, BLD300) because ground quinoa has a higher antioxidant potential than whole-grain quinoa (Hemalatha, Bomzan, Rao, et al., 2016).

Seeds were ground with solvent in a 1:10 solute-solvent ratio. Then, 10 g of crushed ground samples were weighed and subjected to the concentration, temperature, and time conditions determined for each experiment (Table 1b). Subsequently, the samples were centrifuged for 15 min at 5000 rpm, and the filtered supernatant was dried in a convection oven at 35°C for 24 h to remove the remaining solvent. The concentrated extracts were collected and stored in the dark and under refrigeration until use.

All quinoa extracts were prepared at a concentration of 5 mg/mL to perform the tests.

2.5. Extract yield

The yields of the 11 experiments using different solvent concentrations, times, and temperatures were assessed by gravimetry of the dry extract produced from 10 g of seed and expressed in grams.

2.6. Determination of the TPC

The TPC (Total Phenolic Content) was determined by the colorimetric method, using the Folin-Ciocalteu reagent (Singleton and Rossi, 1965), with modifications. First, 240 μ L aliquots of the prepared extracts were mixed with 60 μ L of the Folin-Ciocalteu reagent, 180 μ L of 15% sodium carbonate solution, and distilled water to a volume of 3 mL. The reaction mixture was left standing for 2 h, in the dark, at room temperature. Readings were then performed using a UV-vis spectrophotometer (Shimadzu, model UV-2550) at 760 nm. A

standard curve of gallic acid (0.001-0.020 mg/mL in ethanol) was designed using the same conditions. The results were expressed as milligrams of gallic acid equivalents per gram of quinoa extract (mg GAE/g; $r^2=99.39$).

2.7. DPPH• free radical sequestration method

The AA was determined using the method described by Brand-Williams, Cuvelier, & Berset (1995) based on the capacity of antioxidants present in the samples to sequester the stable radical DPPH•, with modifications. Triplicate sample aliquots (5 mg/mL) were mixed with ethanol and 2,700 μ L of DPPH• solution. After 30 min under stirring, in the dark and at room temperature, readings were taken using a UV-vis spectrophotometer (Shimadzu, model UV-2550) at 517 nm. A control curve was designed using Trolox (0.5 to 4 μ g/mL) as the standard. The results were expressed as micromoles of Trolox per gram of dry extract (μ mol ET/g extract; $r^2=99.80$).

2.8. Antioxidant capacity according to the FRAP method

The AA according to the FRAP method is based on the capacity of an antioxidant to reduce Fe^{3+} to Fe^{2+} , following the method by Rufino et al. (2006), with modifications. The FRAP reagent was prepared immediately before use with 300 mmol/L acetate buffer (pH 3.6) and 10 mmol/L 2,4,6-tris (2-pyridyl)-s-triazine (TPTZ) in a 40 mmol/L HCl and 20 mmol/L FeCl_3 solution. For this test, 60 μ L and 90 μ L aliquots of the extracts prepared were transferred to test tubes, mixed with 270 μ L of ultrapure water and supplemented with 2.7 mL of the FRAP reagent. The mixture was homogenized in a 37°C bath for 30 min. Subsequently, the samples were cooled to room temperature, and the absorbances of the mixtures were read at 595 nm. The standard curve was constructed with Trolox (100-2000 μ mol/L in ethanol), and the results were expressed as μ mol TE/g extract ($r^2=99.70$).

2.9. ABTS method

The capacity to sequester the 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid; $\text{ABTS}^{\bullet+}$) radical was determined according to the method described by Rufino et al. (2007). The $\text{ABTS}^{\bullet+}$ radical was generated through the reaction of the aqueous solution of ABTS (7 mM) with potassium persulfate (140 mM). The solution was kept in the dark, at room

temperature, for 16 h. Then, the solution was diluted in ethanol to an absorbance of 0.70 ± 0.05 nm at a wavelength of 734 nm. Next, 30, 60, and 90 μL aliquots of the extracts at a concentration of 5 mg/mL were added to the ABTS^{•+} solution, and the absorbance was measured after 6 min in a UV-vis spectrophotometer (Shimadzu UV-2550). The antioxidant capacity of the sample was calculated in relation to the AA of Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) under the same conditions, and the results were expressed as $\mu\text{mol TE/g extract}$ ($r^2=99.62$).

2.10. Identification and quantification of phenolic compounds of quinoa extracts by HPLC

The method described by Nagendra Prasad et al. (2009), with adaptations, was used to identify phenolic compounds. Reverse-phase high-performance liquid chromatography (HPLC) was performed using a separation module (LC-20 AT, Shimadzu Corporation, Japan) equipped with a C18 column (SUPELCOSIL™ LC-PAH HPLC Column, 250 x 4.6 mm, 5- μm particle size, Sigma-Aldrich, St. Louis, MO, USA) and a UV-VISIBLE detector (Rheodyne, USA). The samples were eluted under a constant flow of 1 mL/min in a gradient system consisting of the following mobile phases: solvent A (2% acetic acid, v/v) and solvent B (acetonitrile: methanol, 2:1, v/v). The column temperature was maintained at 40°C, and the injection volume was 20 μL .

The gradient system was programmed as follows: 90% A at 0 min, 88% A at 3 min, 85% A at 6 min, 82% A at 10 min, 80% A at 12 min, 70% A at 15 min., 65% A at 20 min, 60% A at 25 min, 50% A at 30-40 min, 75% A at 42 min, and 90% A at 44 min. The peaks of phenolic compounds were monitored at 280 nm. Phenolic compounds were identified by comparing the retention times with standards of phenolic acids and flavonoids and quantified using the calibration curve. The software LabSolutions (Shimadzu) was used to control the LC-UV and data processing system.

2.11. Statistical analysis

Model fit was predicted considering the pure error, regression analysis (R_2) and ANOVA ($p < 0.05$). The significance of the regression coefficients was analyzed using the t-test. Non-significant coefficients were removed to obtain a reduced model. The Tukey test was applied to identify significant differences between the experimental means of each

dependent variable of the statistical design, using the open-access software Action 2.9 (ACTION, 2016), with a 5% significance level ($p < 0.05$) between means.

3. Results and discussion

3.1. Extract yields

The extract yields varied as a function of solvent concentrations. Extracts with ethanol concentrations less than or equal to 47.5% had higher yields (Figure 2). This result was clearer for BoRQ at a concentration of 19% ethanol (experiments 1, 4, 6, and 7).

Studies show that solvent solubility and polarity are relevant factors for the extraction process and extract yield (Asao & Watanabe, 2010; Bey, Louaileche & Zemouri, 2013). Furthermore, quinoa consists of water-soluble compounds, including carbohydrates with bioactive polysaccharides, biopeptides, and fibers (R. Repo-Carrasco-Valencia et al., 2010). However, high water concentration during extraction tends to dissolve these constituents, particularly at high temperatures (Bey et al., 2013), which may explain the higher yields of extracts 4 and 7.

3.2 Model analysis

The experimental values of the TPC (Y_1), AA, DPPH (Y_2), FRAP (Y_3), and ABTS (Y_4) for the significant models are outlined in Table 2. ANOVA and response surface analysis were used to obtain first-order polynomial equations.

The model significance was studied based on the coefficients of determination (R^2) and pure error ($p > 0.05$), which indicate the model fit in terms of accurately predicting the variation of all study parameters and their responses (TPC, DPPH, FRAP, and ABTS). The coefficients of determination (R^2), their adjusted values, the models considered significant, the solvent concentration (water/ethanol 19-76%, v/v), time (6.5-19.5 h), and temperature (32-68°C) effects on TPC, and the AA of the extracts are reported in Table 3.

However, some models were non-significant in their linear form, such as DPPH for the varieties BrWQ and BoRQ and ABTS and FRAP for BoWQ, and the curvature of these models was assessed to test the possible quadratic trend of these dependent variables.

3.3. Effects of extraction parameters on the TPC and AA

The effects of the three independent variables on the TPC and AA were reported using the coefficients of significance of first-order polynomial equations ($p < 0.05$). Thus, higher values of the coefficients express a stronger effect on a specific parameter, and the positive sign indicates a direct relationship, whereas the negative sign corresponds to an inverse relationship between the dependent and independent variables analyzed. The central point responses (experiments 9, 10, and 11) showed reproducibility in the three quinoa varieties studied.

The phenolic content of the BrWQ variety ranged from 20.36 to 35.12 mg GAE/g extract (Table 2). Time had no effect on the total phenolic extraction, whereas ethanol concentration had a stronger effect than the other parameters ($\beta_3 = +3.08$), and a specific temperature range had a negative effect ($\beta_1 = -2.58$), according to the polynomial equation. The strongest responses of the TPC were observed in experiments 1 and 8, showing increased phenolic compound extraction efficiency in different situations, when lower temperatures were combined with lower ethanol concentrations or when higher temperatures were combined with higher ethanol concentrations (Table 3, Figure 3A). Experiment 1 may be explained by the solubility of non-phenolic compounds in the extract, such as sugars, proteins, ascorbic acid, and phytic acid, which are more soluble in water than in ethanol (Asao & Watanabe, 2010; Bey et al., 2013). Conversely, the significance of experiment 8 may be associated with increased ethanol penetration into the plant matrix and improved extraction of phenolic compounds (Jayaprakasha, Girennavar, & Patil, 2008).

The increase of temperature on the extraction of phenolics observed in experiment 8 was also verified by Prasad et al. (2011), who observed higher results of total phenolics in mango fruits extracted with 68% ethanol at 55 °C. Given the effects of various factors, such as solvent polarity, on the extraction of phytoconstituents, the boiling point (78 °C) and low viscosity of ethanol may have improved ethanol diffusion into the plant matrix, thereby positively affecting the extraction of bioactive substances (Wijekoon, Bhat, & Karim, 2011).

In the AA assays of BrWQ, only the models for FRAP and ABTS were significant. Ethanol concentration had a stronger effect on ABTS ($\beta_3 = +13.47$), whereas temperature adversely affected both methods (Figure 3B and 3C), and time had a weaker effect on the results ($\beta_3 = +4.87$ for FRAP and $\beta_3 = +3.36$ for ABTS).

Experiments 8 and 2 had the highest significant response of AA, assessed by the capacity to sequester the ABTS^{•+} radical. However, using the FRAP method, which is based

on the capacity of a sample compound to reduce Fe^{3+} to Fe^{2+} by electron donation (Terpinc, Polak, Makuc, Ulrih, & Abramović, 2012), the minimum levels of the independent variables in experiment 1 were responsible for the higher response (Table 2).

Experiments 1 and 8 had higher TPCs, which were confirmed by the more significant values of AA according to the ABTS (experiments 2 and 8) and FRAP (experiment 1) assays.

Based on the statistical model of the TPC of BoWQ seeds, temperature had the strongest effect ($\beta_1=-3.42$), and the most significant response was expressed in experiment 1 with the lowest temperature (32°C), whereas the ethanol: water ratio had no effect on the quantification of phenolics (Table 3; Figure 4). However, experiments 3 and 5 also showed significant TPCs, regardless of temperature range (Table 2).

Only DPPH was significant for AA. Lower temperature and shorter extraction time, combined with higher ethanol concentration, produced higher results from experiment 1 ($89.26 \mu\text{mol TE/g dry extract}$), in agreement with the results from the TPC. However, experiments 2, 3, and 5 exhibited heightened AA (82.03 , 79.59 , and $82.26 \mu\text{mol TE/g dry extract}$, respectively).

The response surfaces represented by the contour lines (Figure 4), the experimental values (Table 2), and the models (Table 3) showed that as the temperature and extraction time increase, the TPC and DPPH decrease (experiments 4 and 1) at a fixed ethanol concentration value. Most likely, the extended time of plant exposure to a high temperature (68°C) promoted the degradation of compounds responsible for AA because the loss of phenolic compounds during processing at high temperatures has already been reported by other authors (Kreft, Fabjan, & Yasumoto, 2006).

Therefore, the minimal conditions of experiment 1 of the BoWQ variety were most significant for TPC and AA, followed by experiment 2 for DPPH, experiment 3 for TPC, and experiment 5 for both.

For BoRQ, ethanol concentration had a stronger effect on the TPC and AA, according to the polynomial equations and response surfaces (Table 3; Figure 5). The strongest responses were assessed in experiment 3, at 76% ethanol, with coefficients of $\beta_3=+6.28$, $+23.68$, and $+62.25$ for the TPC, ABTS, and FRAP, respectively, whereas the model was non-significant for the DPPH assay.

The coefficients of the time variable (β_2) in the polynomial equations were found to be -2.15 for phenolics, -12.66 for ABTS, and -16.83 for FRAP, adversely affecting the dependent variables analyzed. Temperature was the independent variable with the weakest effect on the responses, with no significant difference in the TPC (Table 3). Experiments 3

and 8 show that the shortest extraction time (6.6 h) led to the strongest responses for total phenolics (42.84 mg GAE/mg dry extract), FRAP (171.77 μ M TR/g dry extract), and ABTS (238.50 μ M Trolox/g dry extract) when varying only time, corroborating the aforementioned results.

The responses of experiments 2 and 6 or 4 and 8 show the importance of ethanol concentration: as the extraction concentration of ethanol increases, the responses increase. This result is most likely due to the increased solubility of phenolics in the ethanol and water mixture, and ethanol is the solvent with the lower viscosity and higher plant penetration power, according to Jayaprakasha, Girennavar, & Patil (2008). Conversely, in experiments 1 and 6, at lower ethanol concentrations (19%) and temperatures (32°C) and shorter times, the highest values of the total phenolics and AA were those of experiment 1, which had the shortest extraction time (6.5 h).

Thus, “green” solvents combined with different time and temperature conditions were found to be efficient in extracting antioxidant compounds from quinoa seeds, presenting high application potential in the food and pharmaceutical industries to develop products with added health benefits.

3.4. Identification of phenolic compounds by HPLC

The retention time and the concentrations of the phenolic compounds (CPC) identified in the quinoa extracts of the BrWQ, BoWQ, and BoRQ varieties are outlined in Table 4. Nineteen phenolic compounds were identified for each quinoa variety, based on the retention time corresponding to the existing standards. Peaks were positively identified and confirmed when all data coincided with the reference standards. Each phenolic compound was quantified using a calibration curve.

The most prominent phenolic compounds in the hydroalcoholic extracts of the three quinoa varieties were the 2,5-dihydroxybenzoic, ferulic, ellagic, and salicylic acids, with rutin as the exceptional flavonoid and predominant polyphenol in BoWQ and BoRQ. However, catechin and sinapic acid also stood out in BoRQ and BrWQ, respectively.

Previous studies using methanolic extraction of quinoa differ from our results regarding the predominance of rutin. Among the 23 types of free or conjugated phenolics, Tang et al. (2015) identified kaempferol and quercetin as the predominant flavonoids, with vanillic and ferulic acids standing out among the phenolic acids of white, red, and black quinoa varieties grown in South America. Similarly, Repo-Carrasco-Valencia et al. (2010)

identified phenolics in quinoa varieties grown in Peru and reported the predominance of 8 compounds, with the concentrations of quercetin and kaempferol standing out among flavonoids and ferulic, p-coumaric, benzoic, and vanillic acids among phenolic acids. Conversely, Hirose et al. (2010) found higher quantities of quercetin in Japanese seeds and considerable concentrations of kaempferol in both types of seeds when comparing the AA of seeds grown in Japan (150 ± 3 - 225 ± 7 $\mu\text{mol}/100$ g seed) with seeds grown in South America (74.6 ± 2 - 142 ± 4 $\mu\text{mol}/100$ g seed).

The use of different solvents may explain the lower quercetin and kaempferol concentrations and the markedly higher rutin concentration in this study. The rutin increase most likely occurred because rutin is a more polar compound than the other phenolics and has a stronger affinity for the “green” solvents used. Furthermore, mixtures of solvents and surfactants can facilitate the antioxidant mechanism of rutin and other flavonoids (Chat, Najar, & Dar, 2013).

Of the quinoa varieties analyzed, BrWQ had a higher concentration of phenolics (1,326.8 mg/100 g seed) than BoWQ (1267.6 mg/100 g seed) and BoRQ (782.6 mg/100 g seed; Table 4). However, red quinoa had higher TPC and AA, which may be explained by the presence of pigments and other antioxidant compounds, also reported by Tang et al. (2015b).

In the BrWQ variety, experiment 8, with maximum levels of the independent variables (76% ethanol/68 °C/19.5 h), was responsible for maximizing the TPC and AA responses by ABTS (Table 2), matching the highest level of phenolics identified by HPLC and only the lower level in the FRAP assay. The compounds 2,5-dihydroxybenzoic acid>rutin>salicylic acid>ferulic acid>3,4-dihydroxybenzoic acid>ellagic acid>catechin stood out in experiment 8, with values of 314.6, 303.2, 151.6, 142.5, 128.8, 79.8, and 49.0 mg/100 g seed, respectively (Figure 6a).

This result may be explained by seed stress from adapting to the Brazilian soil and climate. The climate has typically high temperatures for long periods, which contributes to increased phenolic content in the seeds because these bioactive compounds are plant defense components and promote increased resistance to adverse climatic conditions in Brazil. These conditions include the temperature of arid and semi-arid regions, wherein drought and soil salinity are prominent (Spehar, 2006).

Plant heating may help to extract specific phenolic compounds by softening the plant tissues and weakening the interactions between the proteins and polysaccharides of phenols, enabling increased polyphenol migration to the solvent, according to Shi et al. (2003). Conversely, increased temperature also increases the solubility of compounds and reduces the

viscosity and surface tension of the solvent, thereby increasing their diffusion and extraction rates, according to Ju & Howard (2003).

The total value of CPC identified and quantified by HPLC in the BoWQ variety was highest in experiment 3 (1267.6 mg/100 g seed), in agreement with the high TPC and AA assessed in the experimental design. These responses are more significant when using shorter times (experiments 1, 3, and 5). Experiment 1, with minimum values for all independent variables, gave the most significant response, followed by experiments 3 and 5. These results follow a trend reported by Gan & Latiff (2011), who identified increased phenol content in bean pods at a 35°C temperature and 100 min extraction time, similar to the conditions of experiment 1 in this study.

The predominant phenolics in BoWQ were rutin>2,5-dihydroxybenzoic acid>sinapic acid>ferulic acid at 726.2, 156.2, 150.5, and 58.1 mg/100 g seed, respectively, and their peaks are shown in Figure 6b.

In BoRQ, the maximum levels of the independent variables (76%/6.5 h/68°C), corresponding to experiment 3, were responsible for the simultaneous extraction optimization of the TPC, AA, and CCF by HPLC. This result was most likely due to the characteristics of the growing region, with lower plant stress than other Amazon and coastal regions. Thus, quinoa growth in Bolivia is characterized by high altitudes and lower temperatures or shorter plant exposure time to high temperatures during the warm seasons (Jancurová et al., 2009). The predominant phenolics identified in BoRQ were rutin>ferulic acid>ellagic acid>2,5-dihydroxybenzoic acid>salicylic acid (338.0, 140.2, 87.10, 45.5, and 42.9 mg/100 g seed). The peaks of extract phenolics with the most identifications for each quinoa variety are shown in Figure 6c.

Phenolic compounds have been extensively studied in the food and pharmaceutical industries due to their beneficial health effects. These phytochemicals are reported because they have antioxidant and anti-inflammatory properties (Hirose et al., 2010). The polyphenols present in quinoa have already been related to the prevention of various chronic diseases, including obesity, diabetes, high blood pressure, cardiovascular diseases, and even cancer (Gawlik-Dziki et al., 2013; Lamothe et al., 2015; Tang, Li, Zhang, et al., 2015).

Rutin is the major phenolic compound in extracts of quinoa for QBBo and QVBo and in an expressive concentration in QBBr, according to planning and mixing of green solvents, represented 22.85; 57.28 and 43.19% of the phenolics identified for the various QBBr, QBBo and QVBo, respectively. Rutin is classified as a flavonoid and has functions associated with the treatment of diabetic neuropathy (Tian et al., 2016). It is also considered a power ful anti-

thrombotic agent for cardiovascular diseases (Choi et al., 2015). Ellagic acid, with higher expression in the BrWQ extracts (≤ 103.0 mg/100 g seed) and BoRQ (≤ 87.1 mg/100 g seed) varieties, is considered a powerful antioxidant (Zhang, Xiong, Peng, Gao, & Zhou, 2011), is involved in the apoptosis of cancer cells in patients with lymphocytic leukemia (Salimi et al., 2015), and is reported as an anti-hyperglycemic agent (Kyriakis et al., 2015). 2,5-Dihydroxybenzoic or gentisic acid, found in a higher proportion in BrWQ (≤ 314.6 mg/100 g seed), is associated with neuroprotective activity (Kabra, Bhandari, Sharma, & Gupta, 2014), the inhibition of low-density lipoprotein (LDL) oxidation and anti-atherogenic effects (Ashidate et al., 2005). Conversely, ferulic acid, found in the three study varieties (≤ 142.5 , ≤ 93.6 , and ≤ 140.4 mg/100 g seed for BrWQ, BoWQ, and BoRQ, respectively), may act as a potent anti-inflammatory by inhibiting the transcription of certain inflammatory mediators, such as interleukin-6 (IL-6) and tumor necrosis factor alpha (TNF- α) (Lampiasi & Montana, 2016).

3.3. Model optimization

Model optimization was based on extraction maximization and the identification of total phenolics and AA. The data were crossed, and the parameters were analyzed by RSM using contour lines (Bey et al., 2013).

The optimal extraction parameters were determined by the statistical analysis of the TPC, AA, and CPC (Concentration of phenolic compounds) optimization. The best performance of BrWQ occurred at 68°C, 19.5 h, and 76% ethanol, corresponding to experiment 8. The best conditions for the BoWQ and BoRQ varieties included the shortest extraction time of 6.5 h at 68°C and 76% ethanol, corresponding to experiment 3 for BoRQ and the conditions of experiment 1 for BoWQ (32°C, 6.5 h, and 19% ethanol).

4. Conclusions

The white and red quinoa seeds studied herein are sources of bioactive compounds and have high antioxidant potential. The results showed the efficacy of “green solvents” for extracting phenolic compounds from seeds and their specificities regarding the variety and exposure to different temperatures, times, and ethanol concentrations. Higher CPC values of BoWQ and BoRQ were identified in experiment 3 (1267.7 and 782.6 mg/100 g seed, respectively), matching the higher TPC and AA of BoRQ. However, the highest extraction of

phenolic compounds and AA of BoWQ occurred in experiment 1, corresponding to the minimal values of the independent variables ($X_1=32\text{ }^{\circ}\text{C}$, $X_2=6.5\text{ h}$, and $X_3=19\%$ ethanol). Notwithstanding, experiment 3 also showed significant and expressive responses of the TPC and AA, when the independent variables showed the maximum values for the parameters analyzed ($X_1=68\text{ }^{\circ}\text{C}$, $X_2=6.5\text{ h}$, and $X_3=76\%$ ethanol).

The TPC, ABTS, and CCF of the BrWQ variety were significant and evident in the extraction corresponding to experiment 8 ($X_1=68\text{ }^{\circ}\text{C}$, $X_2=19.5\text{ h}$, and $X_3=76\%$ ethanol), particularly the compounds 2,5-dihydroxybenzoic acid, rutin, salicylic acid, ferulic acid, 3,4-dihydroxybenzoic acid, ellagic acid, catechin, 4-hydrobenzoic acid, caffeic acid, and myricetin.

Thus, “green” solvents may be used to extract antioxidant compounds from quinoa seeds with high application potential in the food and pharmaceutical industries, either in the composition of formulations and food protection or in the development of nutraceuticals.

Acknowledgments

The authors thank the Coordination for the Improvement of Higher Level Personnel (Coordenação de Aperfeiçoamento de pessoal do Nível Superior – CAPES) for the scholarship awarded to I.L.B.

References

- Abderrahim, F., Huanatico, E., Segura, R., Arribas, S., Gonzalez, M. C., & Condezo-Hoyos, L. (2015). Physical features, phenolic compounds, betalains and total antioxidant capacity of coloured quinoa seeds (*Chenopodium quinoa* Willd.) from Peruvian Altiplano. *Food Chemistry*, 183, 83–90.
- Abugoch James, L. E. (2009). Quinoa (*Chenopodium quinoa* Willd.): composition, chemistry, nutritional, and functional properties. *Advances in Food and Nutrition Research*, 58, 1–31.
- Alberti, A., Zielinski, A. A. F., Zardo, D. M., Demiate, I. M., Nogueira, A., & Mafra, L. I. (2014). Optimisation of the extraction of phenolic compounds from apples using response surface methodology. *Food Chemistry*, 149, 151–158.
- Alvarez-Jubete, L., Arendt, E. K., & Gallagher, E. (2009). Nutritive value and chemical composition of pseudocereals as gluten-free ingredients. *International Journal of Food Sciences and Nutrition*, 60(4), 240–257.
- Alvarez-jubete, L., Wijngaard, H., Arendt, E. K., & Gallagher, E. (2010). Polyphenol composition and in vitro antioxidant activity of amaranth , quinoa buckwheat and wheat as affected by sprouting and baking. *Food Chemistry*, 119(2), 770–778.

- Asao, M., & Watanabe, K. (2010). Functional and Bioactive Properties of Quinoa and Amaranth. *Food Science and Technology Research*, 16(2), 163–168.
- Ashidate, K., Kawamura, M., Mimura, D., Tohda, H., Miyazaki, S., Teramoto, T., & Hirata, Y. (2005). Gentisic acid, an aspirin metabolite, inhibits oxidation of low-density lipoprotein and the formation of cholesterol ester hydroperoxides in human plasma. *European Journal of Pharmacology*, 513(3), 173–9.
- Bey, M. B. ., Louaileche, H. ., & Zemouri, S. (2013). Optimization of phenolic compound recovery and antioxidant activity of light and dark dried fig (*Ficus carica* L.) varieties. *Food Science and Biotechnology*, 22(6), 1613–1619.
- Chat, O. A., Najar, M. H., & Dar, A. A. (2013). Evaluation of reduction kinetics of 2,2-diphenyl-1-picrylhydrazyl radical by flavonoid glycoside Rutin in mixed solvent based micellar media. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 436, 343–353.
- Choi, J., Kim, D., Park, S., Lee, H., Kim, K., Kim, K., & Kim, S. (2015). Anti-thrombotic effect of rutin isolated from *Dendropanax morbifera* Leveille. *Journal of Bioscience and Bioengineering*, 120(2), 181–186.
- Espinosa-Diez, C., Miguel, V., Mennerich, D., Kietzmann, T., Sánchez-Pérez, P., Cadenas, S., & Lamas, S. (2015). Antioxidant responses and cellular adjustments to oxidative stress. *Redox Biology*, 6, 183–197.
- Gan, C.-Y., & Latiff, A. A. (2011). Optimisation of the solvent extraction of bioactive compounds from *Parkia speciosa* pod using response surface methodology. *Food Chemistry*, 124(3), 1277–1283.
- Gawlik-Dziki, U., Świeca, M., Sułkowski, M., Dziki, D., Baraniak, B., & Czyż, J. (2013). Antioxidant and anticancer activities of *Chenopodium quinoa* leaves extracts – *In vitro* study. *Food and Chemical Toxicology*, 57, 154–160.
- Graf, B. L., Poulev, A., Kuhn, P., Grace, M. H., Lila, M. A., & Raskin, I. (2014). Quinoa seeds leach phytoecdysteroids and other compounds with anti-diabetic properties. *Food Chemistry*, 163, 178–185.
- Hemalatha, P., Bomzan, D. P., Rao, B. V. S., & Sreerama, Y. N. (2016). Distribution of phenolic antioxidants in whole and milled fractions of quinoa and their inhibitory effects on α -amylase and α -glucosidase activities. *Food Chemistry*, 199, 330–338.
- Hirose, Y., Fujita, T., Ishii, T., & Ueno, N. (2010). Antioxidative properties and flavonoid composition of *Chenopodium quinoa* seeds cultivated in Japan. *Food Chemistry*, 119(4), 1300–1306.
- Jancurová, M., Minarovičová, L., & Dandár, A. (2009). Quinoa - A review. *Czech Journal of Food Sciences*, 27(2), 71–79.
- Kabra, M., Bhandari, S., Sharma, A., & Gupta, R. (2014). Evaluation of anti-parkinson's activity of gentisic acid in different animal models. *Journal of Acute Disease*, 3(2), 141–144.
- Kreft, I., Fabjan, N., & Yasumoto, K. (2006). Rutin content in buckwheat (*Fagopyrum esculentum* Moench) food materials and products. *Food Chemistry*, 98(3), 508–512.
- Kyriakis, E., Stravodimos, G. A., Kantsadi, A. L., Chatzileontiadou, D. S. M., Skamnaki, V.

- T., & Leonidas, D. D. (2015). Natural flavonoids as antidiabetic agents. The binding of gallic and ellagic acids to glycogen phosphorylase b. *FEBS Letters*, 589(15), 1787–94.
- Lamothe, L. M., Srichuwong, S., Reuhs, B. L., & Hamaker, B. R. (2015). Quinoa (*Chenopodium quinoa* W.) and amaranth (*Amaranthus caudatus* L.) provide dietary fibres high in pectic substances and xyloglucans. *Food Chemistry*, 167, 490–496.
- Lampiasi, N., & Montana, G. (2016). The molecular events behind ferulic acid mediated modulation of IL-6 expression in LPS-activated Raw 264.7 cells. *Immunobiology*, 221(3), 486–93.
- Miranda, M., Vega-gálvez, A., Uribe, E., & López, J. (2011). Procedia Food Science Physico-chemical analysis , antioxidant capacity and vitamins of six ecotypes of chilean quinoa (*Chenopodium quinoa*). *Procedia Food Science*, 11, 1439–1446.
- Nagendra Prasad, K., Yang, B., Yang, S., Chen, Y., Zhao, M., Ashraf, M., & Jiang, Y. (2009). Identification of phenolic compounds and appraisal of antioxidant and antityrosinase activities from litchi (*Litchi sinensis* Sonn.) seeds. *Food Chemistry*, 116(1), 1–7.
- Nowak, V., Du, J., & Charrondière, U. R. (2016). Assessment of the nutritional composition of quinoa (*Chenopodium quinoa* Willd.). *Food Chemistry*, 193, 47–54.
- Prasad, K. N., Hassan, F. A., Yang, B., Kong, K. W., Ramanan, R. N., Azlan, A., & Ismail, A. (2011). Response surface optimisation for the extraction of phenolic compounds and antioxidant capacities of underutilised *Mangifera pajang* Kosterm. peels. *Food Chemistry*, 128(4), 1121–112
- Razzaghi, F., Plauborg, F., Jacobsen, S., Richardt, C., & Neumann, M. (2012). Effect of nitrogen and water availability of three soil types on yield , radiation use efficiency and evapotranspiration in field-grown quinoa. *Agricultural Water Management*, 109, 20–29.
- Repo-Carrasco-Valencia, R., Hellström, J. K., Pihlava, J.-M., & Mattila, P. H. (2010). Flavonoids and other phenolic compounds in Andean indigenous grains: Quinoa (*Chenopodium quinoa*), kañiwa (*Chenopodium pallidicaule*) and kiwicha (*Amaranthus caudatus*). *Food Chemistry*, 120(1), 128–133.
- Rufino, M. D. S. M., Alves, R. E., Brito, E. S. De, Morais, S. M. De, Sampaio, C. D. G., Pérez-jiménez, J., & Saura-Colixto, F. D. (2006). Metodologia Científica: Determinação da Atividade Antioxidante Total em Frutas pelo Método de Redução do Ferro (FRAP). *Comunicado Técnico Embrapa*, 125, 1–4.
- Salimi, A., Roudkenar, M. H., Sadeghi, L., Mohseni, A., Seydi, E., Pirahmadi, N., & Pourahmad, J. (2015). Ellagic acid, a polyphenolic compound, selectively induces ROS-mediated apoptosis in cancerous B-lymphocytes of CLL patients by directly targeting mitochondria. *Redox Biology*, 6, 461–71.
- Shi, J., Yu, J., Pohorly, J., Young, C., Bryan, M., & Wu, Y. (2003). Optimization of the extraction of polyphenols from grape seed meal by aqueous ethanol solution. *Food Agriculture and Environment*, 1, 42–47.
- Spehar, C. R. (2006). Adaptation of quinoa (*Chenopodium quinoa* Willd .) to increase the agricultural and alimentary diversity in Brazil. *Cadernos de Ciência & Tecnologia*, 23(1), 41–62.

- Statsoft. Inc. **Statistica**: data analysis software system. <www.statsoft.com> Version 7.0, 2004.
- Tang, Y., Li, X., Zhang, B., Chen, P. X., Liu, R., & Tsao, R. (2015a). Characterisation of phenolics, betanins and antioxidant activities in seeds of three *Chenopodium quinoa* Willd. genotypes. *Food Chemistry*, 166, 380–388.
- Tang, Y.; Li, X.; Chen, P. X.; Zhang, B.; Hernandez, M.; Zhang, H.; Marcone, M.F.; Liu, R. & Tsao, R. (2015). Characterisation of fatty acid, carotenoid, tocopherol/tocotrienol compositions and antioxidant activities in seeds of three *Chenopodium quinoa* Willd. genotypes. *Food Chemistry*, 174, 502–508 .
- Tian, R., Yang, W., Xue, Q., Gao, L., Huo, J., Ren, D., & Chen, X. (2016). Rutin ameliorates diabetic neuropathy by lowering plasma glucose and decreasing oxidative stress via Nrf2 signaling pathway in rats. *European Journal of Pharmacology*, 771, 84–92.
- Zhang, J., Xiong, Y., Peng, B., Gao, H., & Zhou, Z. (2011). Density functional study on the bioactivity of ellagic acid, its derivatives and metabolite. *Computational and Theoretical Chemistry*, 963(1), 148–153.
- Wijekoon, M. M. J. O., Bhat, R., & Karim, A. A. (2011). Effect of extraction solvents on the phenolic compounds and antioxidant activities of bungakantan (*Etligeria latior* Jack) inflorescence.

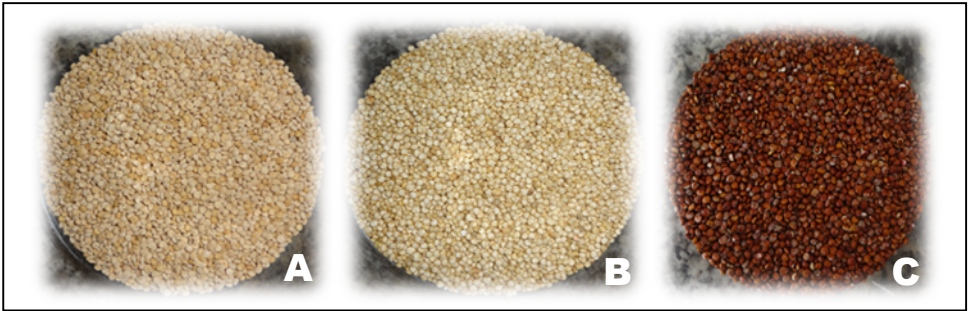


Fig. 1. Quinoa seeds. A: Brazilian white quinoa (BrWQ), B: Bolivian white quinoa (BoWQ), and C: Bolivian red quinoa (BoRQ).

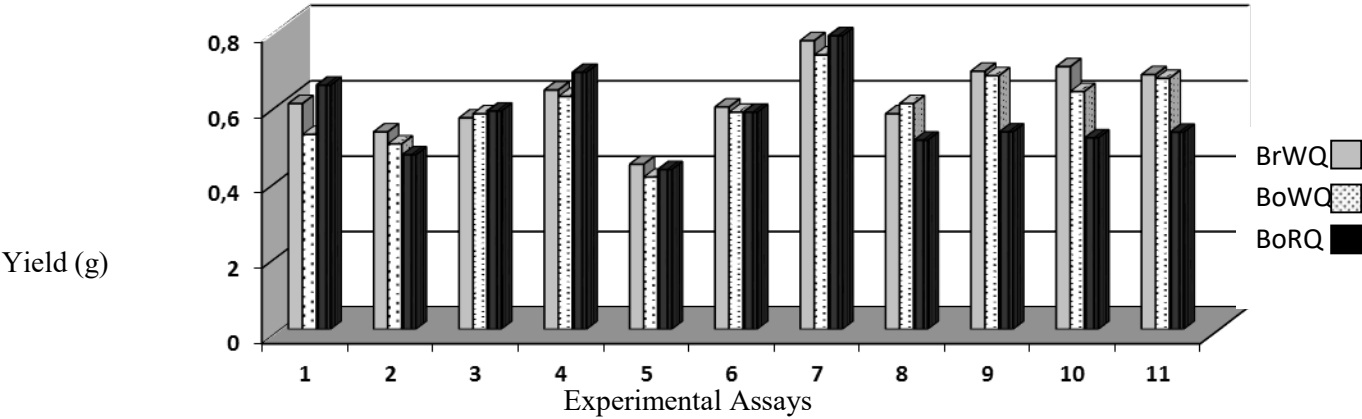


Fig. 2. Yields of BrWQ, BoWQ, and BoRQ seed extracts.

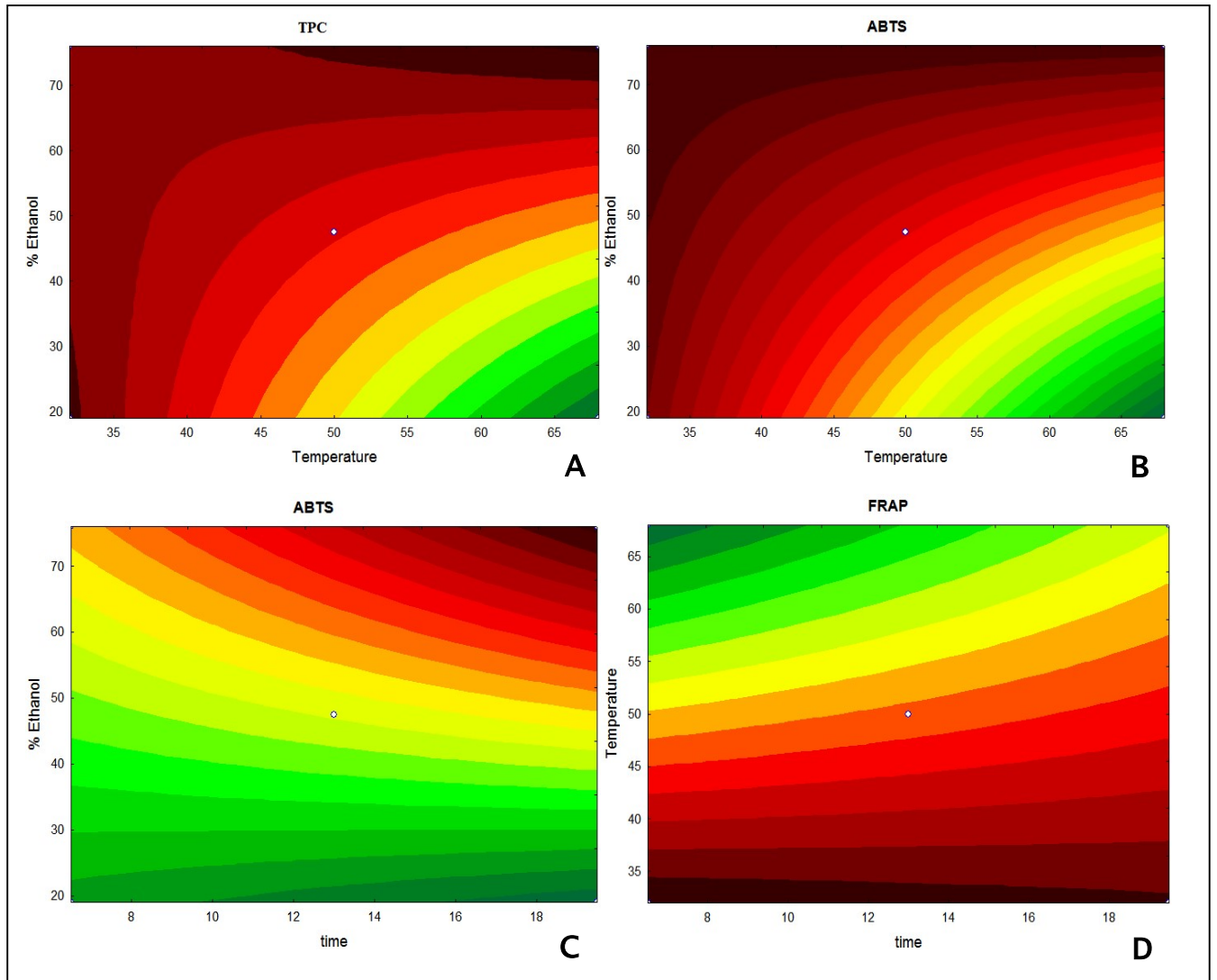


Fig. 3. Response surfaces for the TPC and BrWQ AA.

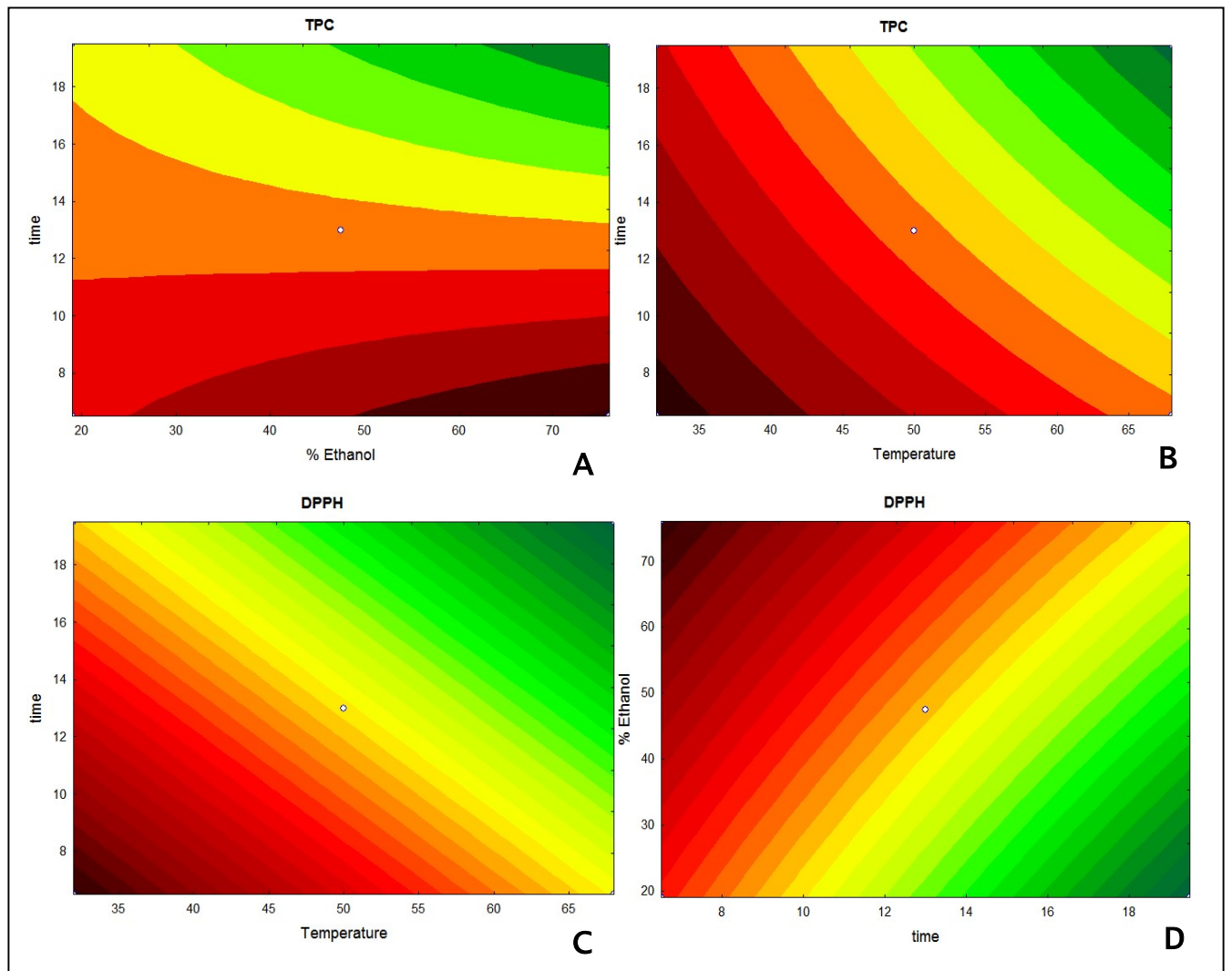


Fig. 4. Response surfaces for the TPC and BoWQ AA.

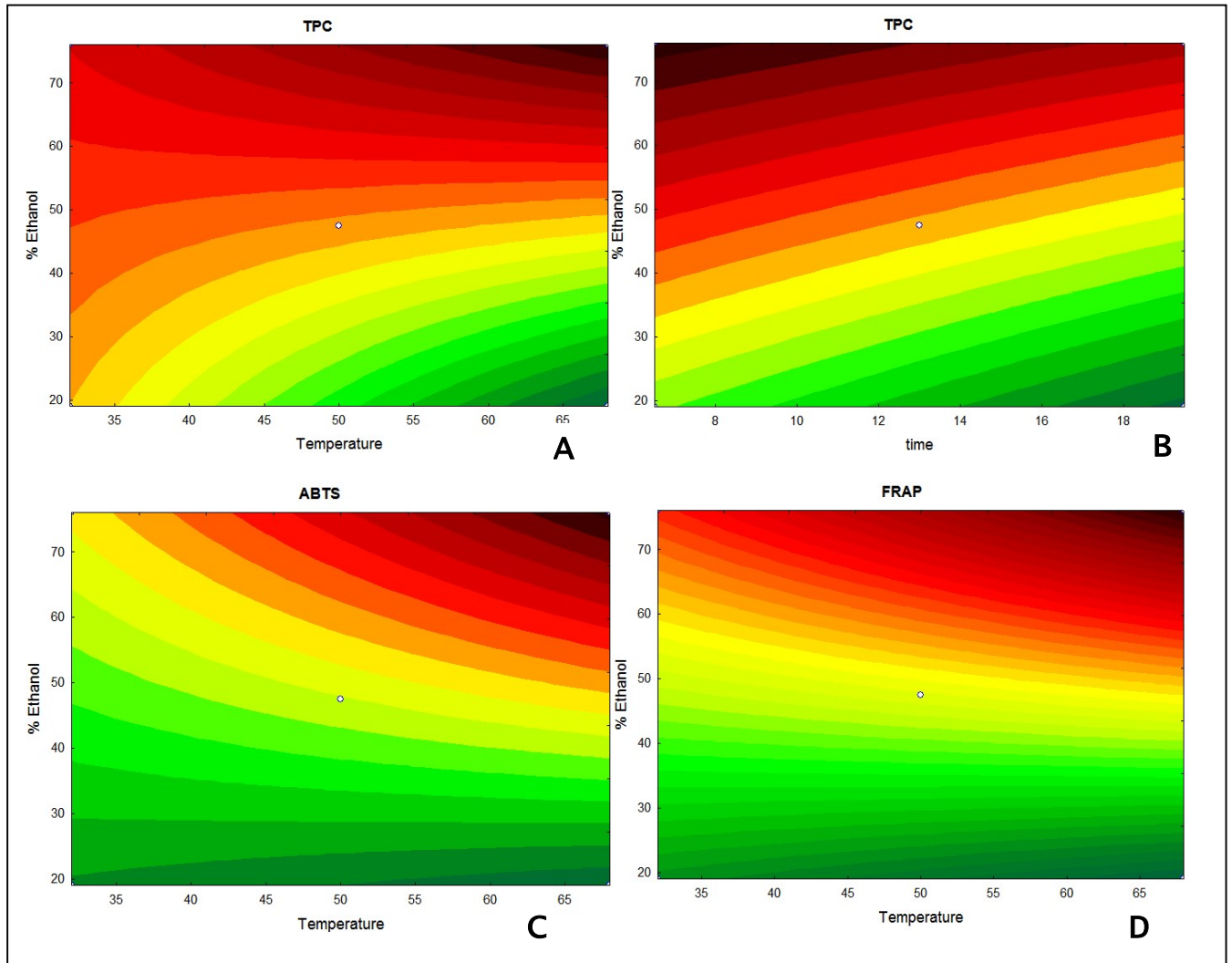


Fig. 5. Response surfaces for the TPC and BoRQ AA.

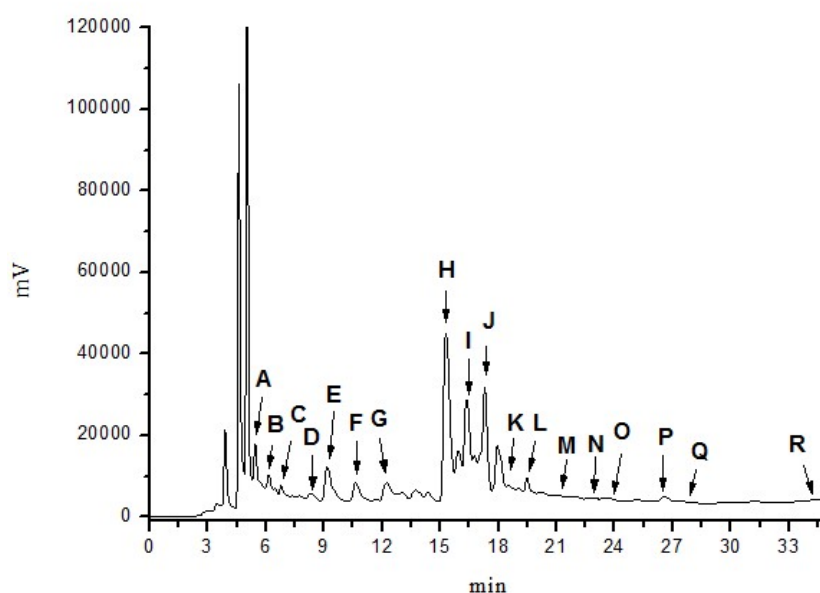


Fig. 6a. Chromatogram of the phenolics of the white quinoa extract, BrWQ variety, obtained by HPLC. Peaks: A: 3,4-Dihydroxybenzoic acid, B: Catechin, C: 2,5-Dihydroxybenzoic acid, D: 4-Hydroxybenzoic acid, E: Vanillic acid, F: Syringic acid, G: p-Coumaric acid, H: Ferulic acid, I: Ellagic acid, J: Rutin, K: Myricetin, L: Salicylic acid, M: Caffeic acid, N: Quercetin, O: trans-Cinnamic acid, P: Kaempferol, Q: Hesperetin, and R: Chrysin.

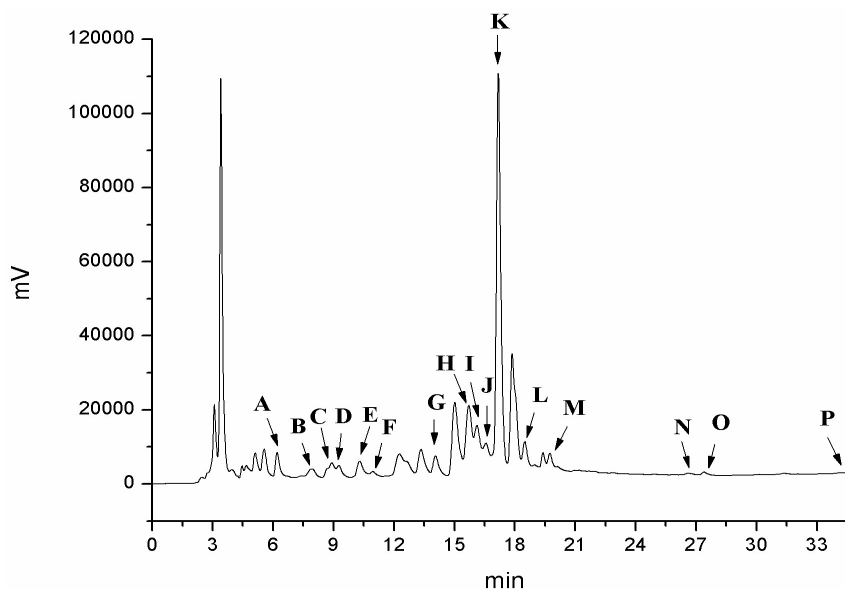


Fig. 6b. Chromatogram of the phenolics of the white quinoa extract, BoWQ variety, obtained by HPLC. Peaks: A: 3,4-Dihydroxybenzoic acid, B: Catechin, C: 2,5-Dihydroxybenzoic acid, D: 4-Hydroxybenzoic acid, E: Vanillic acid, F: Syringic acid, G: p-Coumaric acid, H: Sinapic acid, I: Ferulic acid, J: Ellagic acid, K: Rutin, L: Salicylic acid, M: Myricetin, N: Naringenin, O: Kaempferol, and P: Chrysin.

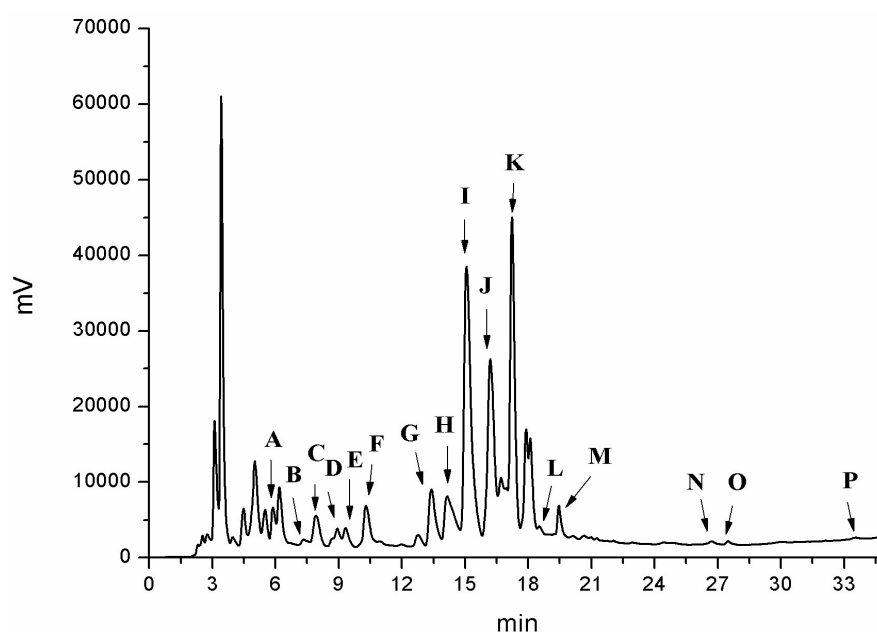


Fig. 6c. Chromatogram of the phenolics of the white quinoa extract, BoRQ variety, obtained by HPLC. Peaks: A: 3,4-Dihydroxybenzoic acid, B: Catechin, C: 2,5-Dihydroxybenzoic acid, D: 4-Hydroxybenzoic acid, E: Vanillic acid, F: Syringic acid, G: p-Coumaric acid, H: Ferulic acid, I: Ellagic acid, J: Rutin, K: Myricetin, L: Salicylic acid, M: Caffeic acid, N: Quercetin, O: trans-Cinnamic acid, P: Kaempferol.

Table 1a

Values decoded from the independent variables in the linear model.

Variable	-1	0	+1
Temperature	32°C	50°C	68°C
Time	6.5 h	13 h	19.5 h
Ethanol Concentration	19%	47.5%	76%

Table 1b 2^3 experimental design with the decoded experimental values of the independent variables.

Experiment	Independent Variables					
	X_1		X_2		X_3	
1	-1	(32)	-1	(6.5)	-1	(19)
2	-1	(32)	1	(19.5)	1	(76)
3	1	(68)	-1	(6.5)	1	(76)
4	1	(68)	1	(19.5)	-1	(19)
5	-1	(32)	-1	(6.5)	1	(76)
6	-1	(32)	1	(19.5)	-1	(19)
7	1	(68)	-1	(6.5)	-1	(19)
8	1	(68)	1	(19.5)	1	(76)
09	0	(50)	0	(13)	0	(47.5)
10	0	(50)	0	(13)	0	(47.5)
11	0	(50)	0	(13)	0	(47.5)

* X_1 : Temperature (°C), X_2 : Time (h), and X_3 : Ethanol concentration (%).

Table 2

TPC and antioxidant capacity according to the DPPH, ABTS, and FRAP of quinoa extracts prepared with ethanol/water solutions according to the experimental design.

Independent Variables				Dependent Variables							
Exp				BrWQ			BoWQ		BoRQ		
	X ₁	X ₂	X ₃	TPC ^A	ABTS ^C	FRAP ^D	TPC ^A	DPPH ^B	TPC ^A	ABTS ^C	FRAP ^D
1	-1	-1	-1	35.12 ^a	124.88 ^b	154.88 ^a	32.17 ^a	89.26 ^a	34.25 ^{bc}	110.51 ^f	93.39 ^g
2	-1	1	1	33.74 ^{bc}	131.84 ^a	150.63 ^b	26.70 ^{de}	82.03 ^b	34.02 ^{bc}	112.07 ^e	157.08 ^c
3	1	-1	1	33.32 ^{bcd}	113.33 ^{cd}	68.17 ^g	29.39 ^b	79.59 ^c	42.84 ^a	171.77 ^a	238.50 ^a
4	1	1	-1	21.18 ^h	74.14 ^e	92.28 ^e	21.71 ^h	47.92 ^h	17.56 ^f	76.73 ^h	34.50 ⁱ
5	-1	-1	1	30.43 ^{ef}	112.66 ^{cd}	87.50 ^f	28.82 ^{bc}	82.26 ^b	31.58 ^{cd}	107.18 ^g	145.83 ^d
6	-1	1	-1	31.14 ^{cde}	111.40 ^d	85.94 ^f	27.57 ^d	53.03 ^g	23.15 ^e	56.88 ⁱ	33.50 ⁱ
7	1	-1	-1	20.36 ^h	69.47 ^e	65.00 ^h	21.24 ^h	52.58 ^g	17.63 ^f	77.18 ^h	55.50 ^h
8	1	1	1	34.91 ^{ab}	129.84 ^a	85.67 ^f	15.49 ⁱ	47.48 ^h	34.40 ^{bc}	119.70 ^b	173.50 ^b
9	0	0	0	30.92 ^{def}	114.73 ^{cd}	106.58 ^{cd}	25.90 ^{ef}	63.37 ^d	29.84 ^d	116.84 ^d	126.67 ^{ef}
10	0	0	0	30.67 ^{def}	115.55 ^c	108.89 ^c	25.61 ^f	62.14 ^{de}	29.77 ^d	116.21 ^d	125.42 ^{ef}
11	0	0	0	30.09 ^{efg}	115.70 ^c	108.39 ^c	25.17 ^{fg}	60.37 ^{ef}	31.70 ^{cd}	119.10 ^c	127.25 ^e

Exp: Experiments, X₁: temperature, X₂: time, X₃: ethanol concentration, BrWQ: Brazilian white quinoa, BoWQ: Bolivian white quinoa, and BoRQ: Bolivian red quinoa.

Values are expressed as the mean (n=3) on a dry basis.

Different letters in the same column represent significant results according to the Tukey test (p<0.05).

^AResults are expressed as mg GAE/g extract for TPC; ^B, ^C and ^D expressed μ mol TE/g of dry extract for antioxidant activities (DPPH, ABTS, and FRAP).

Table 3

Regression coefficients and equations of the first-order mathematical models of response variables.

Variety	Response	Mathematical Model	R ²	R ² adjusted	Pure error
BrWQ	Y1	TCP=30.17-2.58*A+3.08*C+3.60*A*C+1.00*B*C-0.82*A*B*C	0.996	0.987	0.36
	Y ₃	FRAP=101.27-20.98*A+4.87*B+6.32*A*B+15.29*B*C-17.73*A*B*C	0.978	0.927	2.95
	Y4	ABTS=110.32-11.75*A+3.36*B+13.47*C+1.94*A*B+5.56*B*C-2.60*A*B*C	0.975	0.916	0.55
BoWQ	Y1	TCP=25.43-3.42*A-2.52*B-0.84*A*B+0.77*A*C-1.49*B*C-2.11*A*B*C	0.998	0.994	0.27
	Y ₂	DPPH=65.46-9.88*A-9.15*B+6.07*C-7.93*A*B*C	0.971	0.92	4.05
BoRQ	Y1	TCP=29.70-2.15*B+6.28*C+4.23*A*C-2.74*A*B*C	0.992	0.973	2.39
	Y ₃	FRAP=119.19+9.03*A-16.83*B+62.25*C-4.67*A*B+18.25*A*C+3.39*B*C-14.39*A*B*C	0.994	0.981	1.75
	Y ₄	ABTS=107.65+7.34*A-12.66*B+23.68*C+10.71*A*C-13.77A*B*C	0.956	0.854	4.62

A: Temperature, B: Time, and C: Ethanol concentration, wherein Y₁: total phenolics, Y₂: DPPH, Y₃: FRAP, and Y₄: ABTS.

Table 4

Identification and concentration (mg/100 g seed) of phenolics by HPLC of the three varieties of quinoa

100

Phenolic Compound			BrWQ										
Peak	Time (min)	Name	1	2	3	4	5	6	7	8	9	10	11
1	5.453	3,4-Dihydroxybenzoic Acid	16.0	15.6	16.8	8.3	10.6	11.8	11.5	128.8	11.4	9.8	12.2
2	6.672	Catechin	11.0	4.2	12.3	1.7	4.0	3.5	3.8	49.0	1.4	1.4	2.7
3	7.722	2,5-Dihydroxybenzoic Acid	306.0	171.6	219.5	64.7	14.5	29.5	44.2	314.6	95.1	85.4	95.2
4	8.396	4-Hydroxybenzoic acid	2.0	9.4	9.0	5.0	2.6	3.5	3.8	28.5	1.4	2.0	1.4
5	9.779	Vanillic Acid	10.0	14.6	11.2	16.6	13.2	11.8	19.2	11.4	34.1	nd	nd
6	10.275	Syringic Acid	16.0	6.2	19.0	3.3	6.6	1.2	3.8	22.8	11.4	9.8	9.5
7	13.313	p-Coumaric Acid	6.0	6.2	6.7	3.3	5.3	4.7	5.8	10.3	5.7	5.6	5.4
8	14.521	Sinapic Acid	3.0	4.2	4.5	3.3	2.6	2.4	nd	nd	2.8	2.8	2.7
9	14.844	Ferulic Acid	137.0	137.3	137.8	61.4	38.3	17.7	67.2	142.5	113.6	105.0	106.1
10	15.956	Ellagic Acid	102.0	100.9	103.0	66.4	33.0	7.1	40.3	79.8	65.3	53.2	63.9
11	17.08	Rutin	199.0	209.0	201.6	129.5	165.0	153.4	172.8	303.2	248.5	212.8	242.1
12	19.388	Myricetin	22.0	26.0	28.0	23.2	34.3	33.0	40.3	27.4	39.8	36.4	50.3
13	19.392	Salicylic Acid	31.0	37.4	41.4	29.9	48.8	47.2	57.6	151.6	58.2	30.8	65.3
14	22.917	Caffeic Acid	14.0	18.7	20.2	24.9	19.8	17.7	32.6	28.5	22.7	23.8	25.8
15	23.225	Quercetin	3.0	4.2	4.5	3.3	4.0	3.5	9.6	9.1	7.1	4.2	6.8
16	24.978	Trans-cinnamic Acid	1.0	1.0	1.1	1.7	1.3	1.2	1.9	1.1	1.4	1.4	1.4
17	27.329	Hesperetin	5.0	6.2	6.7	6.6	6.6	5.9	7.7	9.1	7.1	7.0	13.6
18	27.368	Kaempferol	nd	nd	2.2	1.7	2.6	2.4	3.8	1.1	1.4	1.4	2.7
19	35.575	Chrysin	5.0	5.2	5.6	8.3	nd	9.4	15.4	8.0	8.5	7.0	10.9
Total			889.0	777.9	851.1	463.1	413.1	366.9	541.3	1326.8	736.9	599.8	718.0

BoWQ													
Peak	Time (min)	Name	1	2	3	4	5	6	7	8	9	10	11
1	5.485	3,4-Dihydroxybenzoic Acid	19.8	19.6	19.4	18.6	6.4	24	9.7	11.8	20.1	18.9	17.2
2	6.622	Catechin	8.3	2	1.1	9.9	2.4	17.3	2.8	2.4	33.5	30.2	30.4
3	7.871	2,5-Dihydroxybenzoic Acid	44.7	199.9	156.2	124	8.8	105.6	99.4	110.9	155.4	149.9	158.4
4	7.965	4-Hydroxybenzoic Acid	5.2	2.9	2.3	2.5	1.6	3.8	1.4	2.4	2.7	1.3	2.6
5	9.6	Vanillic Acid	12.5	9.8	14.8	12.4	8	14.4	13.8	13	14.7	12.6	13.2
6	10.263	Syringic Acid	4.2	8.8	8	2.5	4	6.7	2.8	3.5	4	3.8	4

7	13.329	p-Coumaric Acid	7.3	7.8	9.1	5	3.2	7.7	5.5	4.7	6.7	7.6	6.6
8	15.019	Sinapic Acid	36.4	114.7	150.5	54.6	1.6	102.7	22.1	36.6	34.8	34	37
9	15.704	Ferulic Acid	93.6	50	58.1	18.6	23.2	24	84.2	29.5	34.8	88.2	93.7
10	16.541	Ellagic Acid	31.2	24.5	28.5	21.1	20	23	27.6	17.7	14.7	25.2	31.7
11	17.191	Rutin	549.1	590	726.2	372	100	449.3	477.5	390.6	662	592.2	632.3
12	19.093	Myricetin	32.2	14.7	23.9	14.9	20.8	33.6	20.7	17.7	40.2	29	38.3
13	19.401	Salicylic Acid	38.5	30.4	34.2	19.8	29.6	39.4	29	23.6	53.6	42.8	46.2
14	22.817	Caffeic Acid	19.8	16.7	17.1	nd	12	16.3	19.3	18.9	20.1	18.9	23.8
15	23.171	Quercetin	4.2	2	3.4	nd	2.4	4.8	2.8	4.7	5.4	3.8	4
16	24.342	Trans-cinnamic Acid	1	1	1.1	nd	0.8	1	nd	1.2	1.3	1.3	1.3
17	27.1	Hesperetin	1	2	nd	2.5	4	1.9	2.8	2.4	1.3	2.5	1.3
18	27.409	Kaempferol	8.3	5.9	8	6.2	1.6	6.7	6.9	5.9	5.4	7.6	5.3
19	34.446	Chrysin	6.2	5.9	5.7	6.2	nd	4.8	8.3	7.1	nd	nd	nd
Total			923.5	1108.6	1267.6	690.8	250.4	887	836.6	704.6	1111	1069.8	1147.3

BoRQ													
Peak	Time (min)	Name	1	2	3	4	5	6	7	8	9	10	11
1	5.497	3,4-Dihydroxybenzoic Acid	1.3	12.9	16.9	23.4	11.8	17.7	18.7	13	12.5	12.2	12.5
2	6.699	Catechin	61.1	7.4	10.4	3.1	6.7	12.2	3.1	2	2.1	2	2.1
3	7.533	2,5-Dihydroxybenzoic Acid	15.6	11	45.5	162.2	25.2	129.2	177.8	34	18.7	13.3	10.4
4	7.915	4-Hydroxybenzoic Acid	7.8	12.9	23.4	6.2	14.3	4.1	4.7	20	20.8	18.4	19.8
5	9.322	Vanillic Acid	19.5	12	16.9	18.7	8.4	15	15.6	10	10.4	10.2	10.4
6	10.290	Syringic Acid	10.4	8.3	14.3	4.7	10.1	5.4	9.4	11	7.3	11.2	7.3
7	13.940	p-Coumaric Acid	7.8	6.4	11.7	6.2	7.6	6.8	7.8	8	7.3	8.2	8.3
8	14.704	Sinapic Acid	2.6	3.7	5.2	4.7	3.4	4.1	4.7	3	4.2	4.1	4.2
9	15.069	Ferulic Acid	61.1	94.8	140.4	26.5	96.6	12.2	39	103	84.2	87.7	91.5
10	16.199	Ellagic Acid	52	58.9	87.1	10.9	58.8	21.8	40.6	61	59.3	61.2	65.5
11	17.232	Rutin	217.1	254.8	338	126.4	230.2	142.8	218.4	239	226.7	233.6	246.5
12	19.207	Myricetin	19.5	12	7.8	40.6	5	25.8	26.5	22	6.2	7.1	6.2

13	19.453	Salicylic Acid	40.3	16.6	42.9	59.3	29.4	35.4	37.4	32	32.2	36.7	39.5
14	21.984	Caffeic Acid	nd	nd	nd	21.8	14.3	20.4	21.8	17	14.6	17.3	18.7
15	22.931	Quercetin	3.9	1.8	3.9	nd	2.5	nd	nd	2	3.1	3.1	3.1
16	24.465	Trans-cinnamic Acid	2.6	0.9	1.3	1.6	0.8	1.4	1.6	1	1	1	1
17	27.475	Hesperetin	7.8	4.6	6.5	6.2	4.2	5.4	7.8	5	6.2	6.1	7.3
18	27.475	Kaempferol	2.6	1.8	2.6	1.6	1.7	1.4	3.1	2	2.1	2	2.1
19	34.705	Chrysin	6.5	4.6	7.8	7.8	5	6.8	7.8	5	5.2	5.1	5.2
Total			539.5	525.4	782.6	531.9	536	467.9	645.8	590	524.1	540.5	561.6

BrWQ: Brazilian white quinoa, BoWQ: Bolivian white quinoa, and BoRQ: Bolivian red quinoa, identified by the retention time; nd: not detected.

Perfil Nutricional de sementes e de óleos de quinoa (*Chenopodium quinoa* Willd.) cultivadas no Brasil e na Bolívia.

Isabelle de Lima Brito^{1,2}, Maristela Alves Alcântara¹, Bruno Raniere Lins de Albuquerque Meireles^{1,3}, Maria Helena Araújo Vasconcelos⁴, Marta Suely Madruga¹, Nataly Albuquerque dos Santos⁵, Antonio Gouveia de Souza¹, Angela Maria Tribuzy de Magalhães Cordeiro^{1,5*}

¹*Programa de Pós-Graduação em Ciência e Tecnologia de Alimentos, Departamento de Ciência e Tecnologia de Alimentos, Centro de Tecnologia, Universidade Federal da Paraíba, Campus I, João Pessoa, Paraíba, Brasil;*

²*Departamento de Gestão e Tecnologia Agroindustrial, Centro de Ciência Humanas, Sociais e Agrárias, Universidade Federal da Paraíba, Campus III, Bananeiras, Paraíba, Brasil*

³*Unidade Acadêmica de Tecnologia de Alimentos, Centro de Ciências e Tecnologia Agroalimentar, Universidade Federal de Campina Grande, Pombal, Paraíba, Brasil.*

⁴*Programa de Pós Graduação em Ciência da Nutrição, Departamento de Ciências da Nutrição, Centro de Ciências da Saúde, Campus I, João Pessoa, Paraíba, Brasil*

⁵*Departamento de Tecnologia de Alimentos, Centro de Tecnologia e Desenvolvimento Regional, Campus I, Universidade Federal da Paraíba, Campus I, João Pessoa, Paraíba, Brasil*

*Corresponding author: Departamento de Tecnologia de Alimentos, *Centro de Tecnologia e Desenvolvimento Regional, Campus I, Universidade Federal da Paraíba, CEP: 58051-900, Cidade Universitária, João Pessoa, Paraíba, Brasil* E-mail: atribuzycordeiro@gmail.com

Abstract

A quinoa é uma semente classificada como pseudocereal, de origem andina. Apresenta condições variáveis de cultivo que podem interferir diretamente na sua qualidade nutricional, como a localização de produção, qualidade e nutrição do solo, clima e altitude. O objetivo deste estudo foi determinar as características nutricionais das sementes e dos óleos de diferentes variedades de quinoa (branca e vermelha), produzidas no Brasil e na Bolívia. As análises da composição centesimal demonstraram teores de lipídios entre 7 e 9,35%, proteínas entre 12,77 e 17,41 5% e carboidratos entre 58,13 e 62,65 %, além de quantidades elevadas de aminoácidos essenciais e minerais nutricionalmente importantes, como magnésio, manganês, ferro e selênio. O perfil de ácidos graxos dos óleos demonstrou elevado teor de insaturações e predominância dos ácidos linoleico, oléico e α -linolênico, palmítico e presença ainda do ácido graxo essencial, α -linolênico. O óleo apresentou volumes de 6,07 a 7,65 μ L necessários para eliminar 50% do radical livre DPPH, caracterizando elevada atividade antioxidante e elevada estabilidade oxidativa com período de indução entre 7,41 a 8,07 horas. Este estudo confirma a qualidade nutricional e o potencial antioxidante das sementes de quinoa brasileira e boliviana indicando que as condições variáveis de cultivo como a localização, qualidade e nutrição do solo, clima e altitude interferem na composição deste alimento.

Palavras Chaves: Quinoa; perfil nutricional, antioxidante.

1. Introdução

A quinoa é uma semente milenar, de origem andina e suas características nutricionais lhe permitem a atribuição de alimento funcional. É composta por proteína com importante equilíbrio aminoacídico, presença de carboidratos complexos, notável teor de polifenóis e considerada fonte de fibras, vitaminas e minerais (Abugoch James, 2009; Repo-Carrasco, Espinoza, & Jacobsen, 2003; Schoenlechner, Drausinger, Ottenschlaeger, & Jurackova, 2010). Apresenta cultura com grande variabilidade genética, adaptadas a diversas condições climáticas e geográficas (Nascimento et al., 2014; Nowak, Du, & Charrondière, 2016). Contudo, seu rendimento e qualidade nutricional variam de acordo com o local e condições de cultivo (Razzaghi, Plauborg, Jacobsen, Richardt, & Neumann, 2012).

O interesse de diversos estudos desenvolvidos com quinoa tem sido reportado além das suas propriedades funcionais, pelas suas características reológicas que favorecem à formulação de diversos produtos alimentícios, isentos de glúten, além de conferir aspectos sensoriais interessantes aos alimentos. A National Aeronautics and Space Administration (NASA), na década de noventa, classificou a quinoa como alimento emergente e a inseriu na dieta de tripulantes para missões espaciais em longo prazo, principalmente devido a sua qualidade protéica (Schlick & Bubenheim, 1993). Por sua vez, devido a sua qualidade nutricional a *Food and Agriculture Organization of the United Nations* (FAO) declarou 2013 como o "Ano Internacional da Quinoa" e reportou-a como uma das culturas destinadas a oferecer segurança alimentar no século XXI (Nowak et al., 2016; Jacobsen, 2011; Schoenlechner, Wendner, Siebenhandl-ehn, & Berghofer, 2010).

A fração lipídica da quinoa é composta predominantemente por ácidos graxos poli-insaturados, com destaque para o ácido palmítico, oléico e linolênico dentre os saturados, monoinsaturados e polinsaturados, respectivamente (Peiretti, Gai, & Tassone, 2013; Tang, Li, Zhang, et al., 2015). As sementes contém ainda compostos fitoquímicos com ação antioxidante, tais como os flavonóides, ácidos fenólicos, tocoferóis e carotenóides (Abugoch James, 2009; Tang, Li, Zhang, et al., 2015) que podem modular a resposta fisiológica e impedir aumento do estresse oxidativo (Chlopicka, Pasko, Gorinstein, Jedryas, & Zagrodzki, 2012; Letelier, Rodríguez-Rojas, Sánchez-Jofré, & Aracena-Parks, 2011). Os compostos fenólicos que se destacam na quinoa são os ácidos fenólicos caféico, ferúlico, p-cumárico, vanílico e p-OH-benzóico, juntamente com os flavonóides, quercetina e kampferol (Repo-Carrasco-Valencia, Hellström, Pihlava, & Mattila, 2010; Stikic et al., 2012; Tang, Li, Zhang et al., 2015).

Estes compostos antioxidantes são importantes na prevenção de diversas doenças crônico-degenerativas, como cardiopatias, aterosclerose, diabetes, Doença de Alzheimer e câncer (Abderrahim et al., 2015; Gómez-Caravaca, Segura-Carretero, Fernández-Gutiérrez, & Caboni, 2011).

Desta forma, o objetivo deste estudo foi caracterizar quimicamente e nutricionalmente as sementes e óleos de diferentes variedades de quinoa, bem como avaliar a estabilidade oxidativa e atividade antioxidante dos seus respectivos óleos.

2. Material e métodos

2.1. Reagentes

Os solventes e reagentes de qualidade analítica foram obtidos a partir de FMAIA[®]. Os gases (ar sintético e nitrogênio) utilizados foram adquiridos da White Martins, Brasil. O ácido nítrico (65%) e as soluções de peróxido de hidrogênio usados foram de grau ultrapura, e ácido nítrico (65%) foi destilado em primeiro lugar, no sistema de destilação do ácido (Milestone SubPUR). Uma solução de 2% de concentração de ácido nítrico foi utilizado no preparo das soluções padrão, para diluir amostras e preparar espaços em branco. Uma solução de ácido nítrico com uma concentração de 2-4% foi usada para lavar o sistema de introdução de amostras ICP-OES e ICP-MS. Soluções padrão de elementos múltiplos foram preparados a partir de padrões ICP banco de alta pureza mono-elemento contendo 1000 mg / L de cada elemento (cobre, manganês, ferro, zinco, magnésio, cálcio, fósforo, potássio e sódio). Trabalhando soluções padrão de níquel, molibdênio, estrôncio, vanádio, lítio, cobalto, selênio foram preparadas a partir de multi-elemento de solução XVI (21 elementos diluídos em ácido nítrico), de alta pureza ICP estoque padrão de 100 mg / L.

2.2. Aquisição e preparo das amostras

As sementes de quinoa branca, produzidas no Brasil, de uma mesma colheita, foram adquiridas diretamente com o produtor localizado na região Centro-oeste do país. Enquanto que as sementes importadas (branca e vermelha) cultivadas na cidade de La Paz, na Bolívia, foram adquiridas de um mesmo lote, com a empresa Vitalim, localizada na cidade de Jaraguá do Sul em Santa Catarina, sendo a mesma empresa responsável pela embalagem e distribuição no Brasil. Foi utilizado um quilograma de cada variedade de quinoa para realização do

experimento. As amostras foram armazenada em sacos de polietileno de auto-selagem a 7 °C até à sua utilização.

2.4. Caracterização das sementes

2.4.1 Composição centesimal

A umidade, proteínas e cinzas foram determinadas pelo método oficial de análises, normatizado pela AOAC (2012). Os lipídios foram determinados pelo método descrito por Bligh & Dyer (1959). Os carboidratos foram quantificados em açúcares solúveis total e redutor pelo método DNS (MILLER, 1959).

2.4.2 Identificação das frações protéica e perfil de aminoácidos das sementes

As sementes foram submetidas ao fracionamento protéico baseado em diferenças de solubilidade, de acordo com Osborne (1924), com ligeiras modificações, por Barba De La Rosa, Herrera-Estrella, Utsumi, & Paredes-López (1996) e Sandoval-Oliveros & Paredes-López (2013). Com este procedimento, foram obtidos albuminas (solúveis em água), globulinas (solúveis em soluções salinas), prolaminas (solúveis em soluções alcoólicas) e glutelinas (solúvel em álcali diluído). Todas as frações foram dialisadas, liofilizadas e armazenadas a 4 °C até à sua utilização. As concentrações de proteínas foram estimadas de acordo com o método de Bradford (1976) utilizando uma curva padrão de albumina de soro bovino (BSA).

A determinação de aminoácidos das variedades de quinoa foi realizada de acordo com a metodologia descrita por White (1986). A partir da uma hidrólise ácida de ácido clorídico com fenol a 1%, seguida de derivatação com o reagente Fenilisotiocianato (PITC). Os aminoácidos foram separados, identificados e quantificados por Cromatografia Líquida de Alta Eficiência – CLAE (VARIAN, Water 2690, Califórnia, USA) acoplado com coluna de fase reversa C18 (PICO-TAG, 3,9 x 150 mm). As fases móveis empregadas consistiram de um tampão acetato de concentração 0,0011 g/mL e pH 6,4 e, uma solução de acetonitrila a 60%. A injeção da amostra (20 µL) foi efetuada manualmente e a detecção ocorreu a 254 nm. A detecção foi realizada à temperatura de 35 °C com tempo de corrida de 21 minutos e fluxo de 1 mL/min. A curva de calibração foi construída com nove pontos, traçando-se um gráfico das alturas dos picos obtidos pela injeção de 20 µL da solução de aminoácido, preparada numa faixa de 4,17 µg/mL a 90,60 µg/mL. Em cada curva de calibração, o primeiro ponto

correspondeu ao limite de quantificação nas condições empregadas, ou seja, a menor quantidade detectável pelo método.

2.4.3 Determinação de minerais

A digestão das amostras foi realizada em um sistema de digestão por micro-ondas Berghof, modelo *Speedwave four* (Harretstrabe, Alemanha). As sementes trituradas foram pesadas (0,4 g) e colocadas em tubos Teflon para digestão (DAP-60+). Uma mistura de ácido nítrico a 65% (3 mL) e peróxido de hidrogênio a 35% (3 mL) foi cuidadosamente adicionados. Após repouso, os tubos foram adequadamente fechados e introduzidos no micro-ondas. Os gradientes de temperatura, pressão e tempo utilizados foram determinados pelo fabricante para sementes oleaginosas. Após digestão, os tubos foram arrefecidos até à temperatura ambiente e as amostras digeridas foram filtradas.

Os elementos químicos (Ca, Fe, Mg, K, Na, Al, Mn, Cu, Zn, Se, Cr) foram determinados usando um espectrômetro de emissão óptica com plasma acoplado indutivamente ICP-MS Thermo Scientific (Massachusetts, EUA), segundo a norma EPA (1998).

2.5 Extração do óleo das sementes

Para extração do óleo, as sementes foram trituradas em processador mecânico (Pratic Blender Cadence, BLD300), pesado 30 g de cada amostra e adicionadas de 300 mL de hexano. As mistura foram submetidas a agitação mecânica em Incubadora TE-420, TECNAL (Piracicaba, Brasil) por seis horas a temperatura de 40 °C. O hexano foi filtrado e evaporado em estufa de circulação de ar a 35 °C. O óleo bruto, resultante da evaporação do solvente, foi coletado e acondicionado em recipientes de vidro âmbar, sem *headspeace*, a 4 °C para análises posteriores.

2.6. Caracterização dos óleos

2.6.1 Perfil de Ácidos Graxos

Para os óleos das três variedades de quinoa estudadas, foram realizadas a esterificação dos ácidos graxos presentes seguindo a metodologia de Hartman e Lago (1973). A

identificação e quantificação dos ésteres de ácidos graxos foram realizadas utilizando-se um cromatografo gasoso (VARIAN 430-GC, California, EUA), acoplado com coluna capilar de sílica fundida (CP WAX 52 CB, VARIAN, Califórnia, EUA). Foi utilizado o hélio como gás de arraste (vazão de 1mL/min). As condições do CG foram: Temperatura do injetor 250 °C; a temperatura inicial do forno foi de 100 °C, aumentando-se 2,5 °C min⁻¹ até atingir 240 °C, permanecendo-se por 30 min, totalizando em tempo total de corrida de 86 min; a temperatura do detector foi de 250 °C. Aliquotas de 1,0 µL do extrato esterificado foram injetadas em injetor tipo Split/Splitless e os cromatogramas foram registrados em *software* tipo *Galaxie Chromatography Data System*. Os ácidos graxos foram identificados por comparação dos tempos de retenção dos ésteres metílicos das amostras com padrões Supelco ME19 - Kit (*Fatty Acid Methyl Esters* C4 - C24). Através dos dados do perfil lipídico, foi determinada a qualidade nutricional da fração lipídica das sementes de quinoas estudadas através do índice de aterogenicidade (IA) (Ulbricht & Southgate, 1991). Para tal avaliação, utilizou-se o seguinte cálculo: $(IA) = C12:0 + (4 * C14:0) + c16:0 / MUFA + PUFA$.

2.6.2 Dienos e Trienos Conjugados

O índice de dienos e trienos foram determinados segundo AOCS (2009) em absorbância de 232 e 270 nm, empregando-se um espectrofotômetro UV-*vis* da Shimadzu, modelo UV-2550, utilizando cubetas de quartzo com 1 cm de caminho óptico. As soluções de óleo foram preparadas em Isooctano na concentração de 1 mg.mL⁻¹.

2.6.3 Estabilidade termo-oxidativa dos óleos de quinoa

Os ensaios de estabilidade termo oxidativa foram realizados em duplicata no equipamento 873 Biodiesel Rancimat da marca Metrohm 873 (Herisau, Suíça) utilizando a metodologia da AOCS (Cd 12b-92) (2009). Neste método, 2 g da amostra foram submetidas a 110 °C, sob fluxo constante de ar (10 L.h⁻¹). O resultado foi expresso como período de indução (PI), em horas, determinado automaticamente a partir do ponto de inflexão da curva, pelo programa 873 Biodiesel Rancimat Control.

2.6.4 Análise de Infravermelho dos óleos de quinoa

A análise de infravermelho foi realizada utilizando equipamento Espectrofotômetro Infravermelho por Transformada de Fourier – (FTIR) da marca Shimadzu, modelo Prestige-21 (Kyoto, Japan), utilizando o método de reflectância atenuada (ATR). Os espectros foram obtidos na faixa de $4000\text{-}650\text{ cm}^{-1}$, com resolução de 4 cm^{-1} e 32 varreduras.

2.6.5 Atividade Antioxidante dos óleos

A atividade antioxidante dos óleos foi obtida através do método DPPH em diferentes volumes de óleo (3, 5 e 10 μL) usando o Trolox como padrão de referência. O volume foi ajustado a 1 ml pela adição de etanol a 0,5 mM de uma solução metanólica 2,2-difenil-1-picrilhidrazil radical (DPPH, 250 μL) e Tween 20 (5 μL). Os tubos foram armazenados à temperatura ambiente no escuro durante 60 min (Gorinstein et al., 2003). O controle foi preparadas como acima, sem amostra de óleo. A leitura da absorbância foi realizada a 515 nm e a eliminação dos radicais foi expressa em EC50 que indica o volume (μL) de óleo necessário para eliminar 50% do radical livre DPPH. O potencial antioxidante é inversamente proporcional ao valor de EC50.

2.7 Análise Estatística

A análise dos dados foram realizadas pela aplicação da ANOVA e o teste Tukey, visando identificar diferenças significativas entre as médias, utilizou-se o software Action 2.9 (ACTION, 2016), gratuito. O nível de significância considerado para a diferença entre as médias foi de 5% ($p < 0,05$). Todas as análises foram realizadas em triplicatas.

3. Resultados e discussão

3.1. *Propriedades nutricionais das sementes de quinoa*

A composição centesimal das sementes de quinoa está apresentadas na Tabela 1. A umidade das sementes variaram entre 8,70 g/100 g (QBBr) a 9,30 g/100 g (QVBo), valores inferiores aos reportados em outros estudos envolvendo quinoa (Nascimento et al., 2014; Alvarez-Jubete et al., 2010). Os teores de proteínas variaram entre 12,77 e 17,41 g /100 g,

lipídios entre 7,00 e 9,30 g / 100 g, cinzas entre 8,20 e 9,52 g/100 g e carboidratos entre 58,13 e 62,65 g / 100 g.

Tabela 1. Composição centesimal das sementes de quinoa brasileira e boliviana.

Composição (%)	QBBr*	QBBo*	QVBo*	<i>p</i> – valor
Proteína	16,57 ±0,36	17,14 ±0,06	12,77 ±0,3	< 0.0001
Carboidratos	58,13 ±0,23	58,34 ±0,19	62,65 ±0,12	-
Lipídeos	9,30 ±0,3	7,00 ±0,1	8,08 ±0,6	0.0012
Umidade	8,70 ±0,05	9,00 ±0,08	9,30 ±1,0	0.0084
Cinzas	9,30 ±0,06	9,52 ±0,1	8,20 ±0,05	0.0030

QBBr: Quinoa branca brasileira; QBBo: Quinoa branca boliviana; QVBo: Quinoa vermelha boliviana.

*Média ± desvio padrão (n=3)

Os teores de proteínas encontrados corroboram com estudos anteriores em sementes de quinoa apresentando em média 15% (Alvarez-Jubete, Arendt, & Gallagher, 2009; Koziol, 1992; Meneguetti, Brenzan, Batista, Bazotte, & Silva, 2011). No entanto, foram superiores aos reportados por Nascimento et al. (2014) para quinoa cultivada na Argentina (12,10 g /100 g), amaranto (13,4 g/100 g) e cereais como arroz (7,10 g/100 g) e milho (9,10 g/100 g). Essas diferenças nos teores de proteínas entre as sementes estudadas são provavelmente devido as diferentes condições ambientais, tipo de solo e nutrientes disponíveis e variedade estudada (Abugoch James, 2009; Nascimento et al., 2014).

O teor de lipídio diferiu entre as variedades estudadas e se mostrou superior a sementes de quinoa cultivadas no Peru (5,66%) (Repo-Carrasco-Valencia et al., 2010), enquanto foi semelhante (9,7%) ao encontrado por Ruales & Nair (1993), e superiores aos 7% e 6,31% descritos por Abugoch James (2009) e Nascimento et al. (2014), respectivamente. No entanto, para esse nutriente, os valores foram inferiores apenas ao de outras sementes consideradas oleaginosas, como linhaça (29.82 g/100 g) e chia (36.50 g/100 g). As sementes de quinoa que é de base amilácea, são frequentemente designadas pseudocereais e utilizadas como importante ingrediente em produtos de panificação (Ragaei, Abdel-Aal, & Noaman, 2006; Sandhu, Godara, Kaur, & Punia, 2015). A quinoa está exposta a uma oxidação lipídica elevada por meio da ativação de enzimas lipolíticas e aumento da área de superfície, comprometendo assim sua qualidade de manutenção. Contém quantidades relativamente elevadas de gordura em comparação com outros cereais, e é rico em vitamina E, que por ter

ação antioxidante, protege os lipídeos dos efeitos da oxidação (Ng, Anderson, Coker & Ondrus, 2006). Ainda no estudo discutido, foi observado diferenças significativas para tempo de armazenamento e temperatura na produção de ácidos gordurosos livres, hidroperóxidos de dieno conjugado e hexanal. No estudo observou-se que a farinha de quinoa armazenada à temperatura ambiente ou ligeiramente em mais alta temperatura durante um curto período de tempo resultou em alguma deterioração oxidativa, conforme medido por três testes de oxidação lipídica. Embora a quinoa seja maior em gordura do que a maioria dos cereais, as gorduras poliinsaturadas na quinoa não demonstrou-se oxidar rapidamente no tempo do estudo, mesmo no estado propício onde a área de superfície para as reações oxidativas e enzimáticas é aumentada, e em temperaturas mais altas que aceleram a atividade enzimática. Essa estabilidade pode estar ligada ao alto teor de vitamina E como foi elucidado, esse antioxidante natural faz-se presente em grandes quantidades e o fato da quinoa ser uma nova oleaginosa, como citou Koziol (1992), é reforçada e deve atrair os desenvolvedores de produtos alimentares interessados em aplicações alimentares com foco em qualidades antioxidantes naturalmente presente no alimento bruto.

Os teores de carboidratos encontrados nas variedades de quinoa branca cultivadas no Brasil e Bolívia foram semelhantes aos encontrados na Kañiwa (58,39 g/100 g) e inferiores quando comparados aos resultados em diferentes variedades de quinoa cultivadas no Peru (60,06 e 67,30 g/100 g) (Repo-Carrasco-Valencia et al., 2010). Os carboidratos e o elevado teor de fibras da quinoa têm sido reportadas com características reológicas interessantes na formulação de pães (Stikic et al. 2012), biscoitos (Brito et al., 2014), produtos extrusados (Cueto et al., 2015), cereais matinais (Joye, Lamberts, Brijs, & Delcour, 2011) e formulações de filmes biodegradáveis (Araujo-farro, Podadera, Sobral, & Menegalli, 2010), dentre outros, além de estarem associados a uma variedade de atividades biológicas (Berti, Riso, Monti, & Porrini, 2004; Cordeiro et al., 2012), tais como proteção contra o desenvolvimento de doenças crônicas e efeitos protetores da mucosa gástrica (Repo-Carrasco, Espinoza, & Jacobsen 2003).

Os teores de cinzas relatados nos resultados demonstraram valores superiores quando comparados aos teores de cinzas em variedades de quinoa Kañiwa (2,42 g/100 g) e Kiwicha (3,31 g/100 g) (Repo-Carrasco-Valencia et al., 2010).

Dentre as frações protéicas contidas nas sementes de quinoa descritas na Tabela 2, verifica-se que a maior proporção é de globulina (28,64 - 42,71 g/100 g), seguida de albumina (22,84 -25,96 g/100 g), glutelinas (12,5 -16,4 g/100 g) e prolaminas (4,1 - 6,74 g/100 g). Nos pseudocereais, como a quinoa, albuminas e globulinas reportaram a maior fração protéica em todas as variedades de quinoa estudadas. Desta forma, a quinoa pode fornecer uma opção

nutricional relevante para pessoas com intolerância ao glúten (Valencia-Chamorro 2003). Um estudo realizado por Orona-Tamayo, Valverde, Nieto-Rendón, & Paredes-López (2015) mostrou que a fração de globulina representa a mais alta concentração de peptídeos após a digestão gastrointestinal e que estes constituintes apresentam um elevado potencial para atuar como antioxidantes, quelante de íons e inibidores da enzima conversora de angiotensina na saúde humana.

Tabela 2. Fração proteica das sementes de quinoa brasileira e boliviana.

	QBBR*	QBBo*	QVBo*
Prolamina	6,74 $\pm$ 0,81	5,96 $\pm$ 0,3	4,1 $\pm$ 0,08
Albumina	22,84 $\pm$ 0,52	23,81 $\pm$ 0,04	25,96 $\pm$ 0,23
Globulina	28,64 $\pm$ 0,01	32,26 $\pm$ 0,34	42,71 $\pm$ 0,08
Glutelinas	12,5 $\pm$ 0,77	16,4 $\pm$ 0,74	14,5 $\pm$ 0,62

* g / 100g semente

Média $\pm$ desvio padrão (n=3)

A quinoa é reportada como uma semente de interessante perfil proteico devido ao seu importante equilíbrio aminoacídico e pela sua alta digestibilidade (83%), comparada a 91% da caseína (Ruales e Nair, 1993). A amostra de QBBR exibiu a presença de elevados teores dos aminoácidos ácido glutâmico, seguidos de ácido aspártico, treonina, fenilalanina, lisina e leucina (Tabela 3). Estes resultados foram semelhantes aos encontrados por Abugoch et al (2008), que demonstraram teores de ácido aspártico e ácido glutâmico superiores quando comparado aos outros aminoácidos em sementes de quinoa que se revela nos panículos imponentes de cores variadas, como verde, amarelo, vermelho, ocre e marrom. Ressalta-se que a presença de elevados níveis de ácido glutâmico e aspártico estão associados a um estímulo do sistema nervoso central e imunológico em humanos (Monda, Viggiano, Sullo, & De V, 1998; Williams et al., 2005) e a arginina como um potencial aminoácido de prevenção à doenças cardíacas (Hov, Aasarød, Sagen, & Åsberg, 2015).

A quinoa apresenta conteúdo de aminoácidos essenciais maior do que em cereais comuns. Uma quantidade inadequada de ingestão desses aminoácidos no metabolismo humano pode ocasionar alterações nos processos bioquímicos e fisiológicos (Wright et al., 2002).

Tabela 3. Perfil de aminoácidos das variedades de quinoa

Aminoácidos mg / 100g	QBBr	QBBo	QVBo	(DRI, FAO 2002) discutir texto
Histidina	1,58 ±0,1	0,90 ±0,02	0,80 ±0,07	15
Isoleucina	1,40 ±0,22	0,81 ±0,11	0,68 ±0,1	30
Leucina	2,29 ±0,02	1,34 ±0,2	1,16 ±0,21	59
Lisina	2,53 ±0,04	1,88 ±0,03	1,24 ±0,06	45
Metionina	0,88 ±0,12	0,71 ±0,01	0,49 ±0,02	16
Tirosina	2,00 ±0,09	1,06 ±0,15	1,09 ±0,1	38
Treonina	3,32 ± 0,3	2,07 ±0,09	1,79 ±0,15	23
Fenilalanina	2,60 ±0,05	1,39 ±0,31	1,29 ±0,04	6
Valina	0,33 ±0,08	0,19 ±0,03	0,20 ±0,01	39
Arginina	0,92 ±0,11	0,42 ±0,06	0,37 ±0,01	-
Alanina	0,93 ±0,14	0,54 ±0,13	0,51 ±0,04	-
Ácido aspártico	7,42 ±0,26	3,40 ±0,21	2,92 ±0,09	-
Ácido glutâmico	12,39 ±0,31	5,99 ±0,34	6,12 ±0,25	-
Glicina	1,65 ±0,06	0,96 ±0,01	0,79 ±0,02	-
Prolina	ni	ni	ni	
Serina	1,74 ±0,13	1,03 ±0,09	1,02 ±0,01	

Média ± desvio padrão (n=3)

ni- Não identificado

As diferentes variedades de quinoa apresentaram teores importantes de minerais (Tabela 4). Resultados que estão de acordo com diversos estudos prévios (Alvarez-Jubete et al., 2010; James, 2009, Konishi, Hirano, Tsuboi e Wada, 2004; Ruales & Nair, 1993 ; Valencia et al., 2010a; Vega-Galvez et al., 2010).

A quinoa branca brasileira apresentou teores mais elevados de cálcio, ferro, magnésio, potássio, manganês, cobre, zinco e selênio, enquanto o sódio foi superior nas variedades cultivadas na Bolívia. Estes resultados podem ser explicados em virtude das ~~per~~ diferenças de genótipos, tipo de solo, composição mineral do solo e tipo fertilizante (Miranda et al., 2010). O uso de processos abrasivos pode explicar eventuais perdas de minerais (Konishi et al., 2004; Miranda et al., 2010; Vega-Galvez et al., 2010; James, 2009), pois o fósforo, o magnésio e o potássio geralmente estão localizados em tecidos embrionários, enquanto o cálcio e o potássio são encontrados no pericarpo e na camada de semente. De acordo com

Blanca (1999) o trabalho de colheita de cereais evoluiu, passando do modo manual para as segadoras e outras máquinas que além de cortar, debulhavam o material colhido. Por fim, surgiram as colhedoras, máquinas complexas que realizam todas as etapas do processo da colheita e quando observado o processado nesse último, Couto & Alvarenga (1998), observaram e com isso, puderam afirmar que a mecanização agrícola é a principal responsável pelos danos mais graves causados as sementes. Além disso, essa variação também pode estar relacionada às condições de cultivo, como variação climática, solo, adubação, altitude e até mesmo a adaptação do vegetal ao local de produção, uma vez que a quinoa é naturalmente adaptada às condições de elevadas altitudes, enquanto no Brasil, a maior salinidade e menor altitude contribuem para aumentar as adversidades enfrentadas pela semente no processo de germinação (Moreira et al., 2012). Pode-se observar também destaque quanto ao teor de alumínio das sementes brancas cultivadas no Brasil. Isso pode ser explicado pelas características do solo de cultivo, uma vez que, trata-se de uma região com solos de características de devastação, baixa fertilidade e elevados teores de alumínio extraível (Al_3^+) pela precipitação de gibbsita ($Al(OH)_3$) parcialmente solubilizada (Klauber et al, 2011).

Tabela 4. Teor de minerais das variedades de quinoa

Minerais	QBBr	QBBo	QVBo
<i>Macroelementos (mg/100 g semente)</i>			
Cálcio	28,1 ± 0,1	20,3 ± 0,02	15,4 ± 0,02
Ferro	3,8 ± 0,05	2,9 ± 0,02	2,7 ± 0,06
Magnésio	206,4 ± 0,02	141,4 ± 0,06	155,0 ± 0,05
Potássio	1012,1 ± 0,01	601,0 ± 0,04	605,0 ± 0,06
Sódio	16,9 ± 0,01	19,4 ± 0,05	19,0 ± 0,02
<i>Microelementos (µg/ 100g semente)</i>			
Alumínio	7,0 ± 0,04	2,1 ± 0,09	1,9 ± 0,01
Manganês	2,7 ± 0,02	1,7 ± 0,02	1,5 ± 0,01
Cobre	0,6 ± 0,01	0,7 ± 0,01	tr
Zinco	3,0 ± 0,06	1,2 ± 0,01	1,9 ± 0,02
Selênio	6,7 ± 0,02	5,5 ± 0,02	5,9 ± 0,05
Cromo	tr	tr	tr

Média ± desvio padrão (n=3)

tr -Traços

3.2. Contribuições de cereais andinos para a ingestão de nutrientes de elementos essenciais

As contribuições de extração mineral expressas em % de DRI, com base em 100 gramas de sementes são apresentados na Tabela 5, considerando a idade da população de 19 anos até a população idosa. A contribuição para DRI varia entre 0,1% (para cobre em QBBR e QBBo) e 150% (para manganês em QBBR). Dessa forma, a Quinoa brasileira tem maior contribuição para a ingestão de minerais que as bolivianas, suprimindo a necessidade de até 48,5% de ferro, 49,1% de magnésio, 150% de manganês 37,5% de zinco e 11,2% de selênio com base no consumo de 100g o de sementes.

Tabela 5. Contribuição da quinoa para a ingestão dietética diária de minerais recomendada para adultos, expressa em% (valor nutricional obtido por 100g de alimentos)/ Ingestão recomendada.

Grupo	Semente	Ca	Fe	Mg	K	Mn	Cu	Zn	Se
RDI	19-50	1000 (mg/d)	8 (mg/d)	420 (mg/d)	4,7 (g/d)	2,3 (mg/d)	900 (µg/d)	11 (mg/d)	70/60 ^a (µg/d)
	QBBR	2,8	47,8	49,1	21,5	117,3	0,1	27,3	9,6/11,2 ^a
19-50anos	QBBo	2,0	35,6	33,7	12,8	73,9	0,1	10,9	7,9/9,2 ^a
	QVBo	1,5	33,1	36,9	12,9	65,2	tr	17,3	8,4/9,8 ^a
		1200 (mg/d)	8 (mg/d)	420/320 ^a (mg/d)	4,7 (g/d)	2,3/1,8 ^a (mg/d)	900 µg/d	11/8 ^a (mg/d)	70/60 ^a (µg/d)
	QBBR	2,3	47,8	49,1/64,5 ^a	21,5	117/150 ^a	0,1	27,3/37,5 ^a	9,6/11,2 ^a
> 50 anos	QBBo	1,7	35,6	33,7/44,2 ^a	12,8	73,9/ 94,4 ^a	0,1	10,9/15 ^a	7,9/9,2 ^a
	QVBo	1,3	33,1	36,9/48,4 ^a	12,9	65,2/83,3 ^a		17,3/23,8 ^a	8,4/9,8 ^a

Fonte: DRIs, Ingestão diária recomendada (2002)

^a – mulheres

tr - traços.

3. 2. Análise do perfil de ácidos graxos dos óleos de quinoa

O perfil de ácidos graxos do óleo extraído nas três variedades da quinoa analisadas apresentou elevados teores de ácido linoleico e ácido oleico, seguidos de ácido palmítico e linolênico (Tabela 6). Nesta lógica, o teor lipídico da quinoa demonstrou ser rico em ácidos graxos essenciais como o linoleico e α -linolênico corroborando com os resultados

encontrados em estudos anteriores (Ng, Anderson, Coker, & Ondrus, 2007; Repo-Carrasco et al., 2003; Marineli et al., 2014).

A relação de ácidos graxos n-6/n-3 (17,05) encontrada na variedade de quinoa branca cultivada no Brasil foi superior as outras variedades estudadas (Tuberoso et al., 2007). A razão entre a ingestão diária de alimentos fontes de ácidos graxos w-6 e w-3 assume grande importância na nutrição humana, resultando em várias recomendações que têm sido estabelecidas por autores e órgãos de saúde, em diferentes países. Segundo a WHO e FAO (1995) a razão de w-6 e w-3 se dá em 5:1 a 10:1. As sementes de quinoa apresentaram importantes concentrações desse ácido, sendo o linoleico e o α -linolênico em maior concentração na quinoa branca do Brasil e na quinoa vermelha da Bolívia, respectivamente. Segundo Turan, Sönmez & Kaya (2007) os IA indica o potencial de estímulo à agregação plaquetária, ou seja, quanto menores os valores de IA, maior é quantidade de ácidos graxos anti-aterogênicos presentes em determinado óleo/gordura e, conseqüentemente, maior é o potencial de prevenção ao aparecimento de doenças coronarianas. No presente estudo, os IA encontrados nas sementes foram reduzidos e esses valores indicam que o consumo das sementes pode prevenir o aparecimento de doenças coronarianas.

Tabela 6. Perfil de ácidos graxos (g/100 de ácidos graxos) de três amostras de óleo de quinoa.

Ácidos graxos		QBBR	QBBo	QVBo
C10:0	Ácido cáprico	0,01	0,00	0,01
C12:0	Ácido láurico	0,01	0,01	0,02
C14:0	Ácido mirístico	0,17	0,17	0,15
C15:0	Pentadecanóico	0,06	0,06	0,04
C16:0	Ácido palmítico	9,39	9,12	8,80
C17:0	Ácido Heptadecanóico (Margárico)	0,05	0,05	0,06
C18:0	Ácido esteárico	0,44	0,57	0,96
C19:0	Ácido Nonadecanóico	0,07	0,07	0,04
C20:0	Ácido eicosanóico	0,56	0,47	0,64
C21:0	Ácido Heneicosanóico	0,10	0,08	0,07
C22:0	Acido docosanóico	0,88	0,85	0,79
C23:0	Ácido Tricosanóico	0,07	0,08	0,06
C24:0	Acido lignocérico	2,15	2,00	1,70
C14:1n5c	Acido 5-tetradecenoico	0,01	0,00	0,01
C15:1n5c	cis-10-Pentadecenoic	0,01	0,01	0,01

C16:1n7	Acido palmitoleico	0,21	0,25	0,16
C17:1n7c	Ácido Heptadecenóico	0,04	0,05	0,07
C18:1n9c	Acido oléico	21,49	22,49	29,79
C18:1n11	Acido vacênico	1,08	1,08	0,95
C20:1n9	Ácido Cis-Eicosenóico	1,51	1,68	1,61
C22:1n9	Ácido Erúico	1,61	1,88	1,49
C24:1n9	Ácido nervônico	0,27	0,27	0,19
C18:2n6c	Ácido Linoléico	55,44	51,18	44,55
C20:2n6c	Acido eicosadienóico	0,16	0,15	0,11
C22:2n6c	Acido docosadienóico	0,23	0,22	0,14
C18:3n6	Acido γ -linolenico	0,16	0,18	0,14
C18:3n3	Acido α -linolênico	3,25	6,55	6,93
C20:3n3c	Acido eicosatrienóico	0,02	0,05	0,10
C20:4n6c	Acido araquidônico	0,03	0,04	0,03
C20:5n3c	Ácido eicosapentaenóico (EPA)	0,02	0,05	0,02
C22:6n3	Acido docosa-hexaenico (DHA)	0,51	0,39	0,41
	SFA	13,95	13,50	13,33
	MUFA	26,22	27,70	34,25
	AGP	59,80	58,79	52,41
	AGD*	86,46	87,06	87,62
	ω -6/ ω -3	17,05	7,81	6,43
	AI**	0,11	0,11	0,008

* Ácidos graxos desejáveis, representado pela soma das proporções de C 18:0 + MUFA+ PUFA

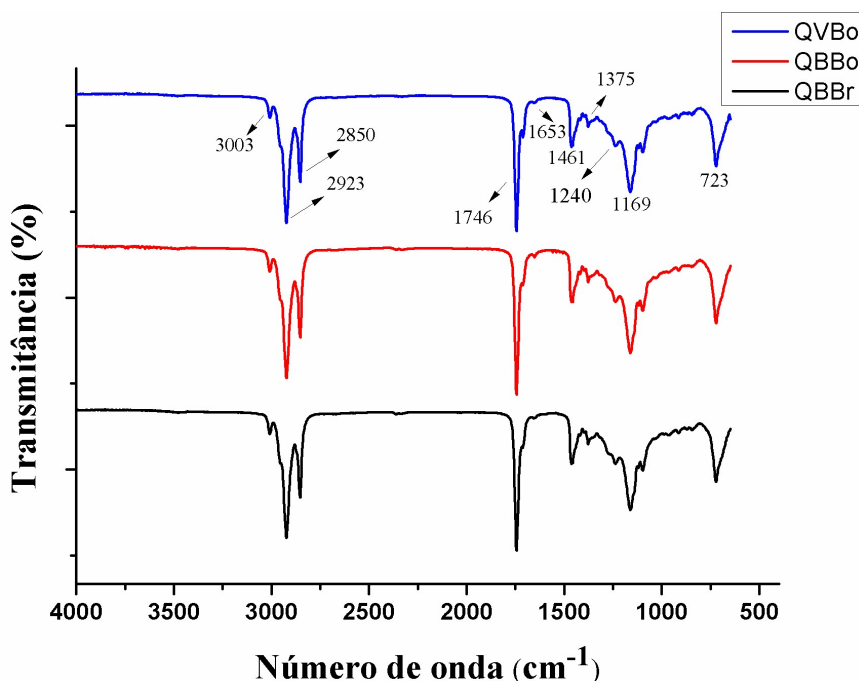
** Índice de Aterogenicidade

3.2.1 Espectroscopia de infravermelho dos óleos de quinoa

Os espectros da região do infravermelho para todas as amostras dos óleos de quinoa (QBBR, QBBo e QVBo) são apresentados na Figura 1. Os espectros apresentaram posições da banda, intensidade e número de onda bem semelhante.

Dentro das regiões funcionais ($4000\text{-}1650\text{ cm}^{-1}$), três principais bandas bem definidas foram obtidas entre $\sim 3003\text{-}2850\text{ cm}^{-1}$, caracterizando uma região que segundo Vlachos et al. (2006), pode ser atribuída às vibrações de estiramento C-H dos grupamentos metila e metileno. Em 1746 e 1653 cm^{-1} , dois picos de absorção caracterizam uma região de duplas ligações, que podem ser atribuídas ao estiramento C=O de ésteres e C=C de alcenos, respectivamente. Outras bandas de deformações e dobramentos são obtidas até $\sim 1375\text{ cm}^{-1}$. Já em 1240 e 1169 , relacionadas a vibrações de estiramento C-O de grupos éster, e em 723 cm^{-1} , vibração de balanço de CH_2 .

Figura 1. Espectro na região do infravermelho dos óleos de quinoa.



Os picos de absorção obtidos das amostras de diferentes óleos vegetais e possíveis grupos orgânicos referentes ao número de onda e modo de vibração dos mesmos são expressos na Tabela 7.

Segundo Guillén e Cabo (1997), as regiões compreendidas entre 3006 a 3008 e 1650 a 1656 cm^{-1} correspondem ao estiramento das bandas cis $=\text{C-H}$ e cis C=C , respectivamente. Estas bandas estão diretamente relacionadas com o índice de iodo, que reflete o número de insaturações do óleo. O valor alto deste índice demonstra que há maior quantidade de ácidos graxos insaturados nas amostras de óleos.

Tabela 7 - Grupos de compostos orgânicos encontrados por espectroscopia de infravermelho médio de acordo com número de onda e modo de vibração.

Número de onda (cm-1) (experimental)	Número de onda (cm-1)	Grupo orgânico	Modo de vibração
3006-3008	3009 ^{a,b,c}	=C-H (cis)	Estiramento (stretching)
2921-2923	2926 ^{a,b}	-C-H (CH ₂)	Estiramento (simétrico e assimétrico)
2852-2854	2854 ^{a,b,c}		
1741-1743	1746 ^a	-C=O (éter, aldeído, cetona, anidrido)	Estiramento
1650-1656	1654 ^a	C=C (cis)	Estiramento
1461	1465 ^a	-C-H (CH ₂)	Tesoura (scissoring)
1417	1418 ^{a,b}	=C-H (cis)	Dobramento (bending)
1396-1398	1397 ^a	=C-H (cis)	Dobramento
1377	1377 ^a	-C-H (CH ₃)	Dobramento (simétrico)
1236, 1161	1238 ^a , 1163 ^a	-C-O (éster)	Estiramento
721-723	723 ^{a,b}	-(CH ₂)-	Balanço (rocking)

^aVLACHOS et al. (2006); ^bGUILLÉN e CABO (1997); ^cZAHIR et al. (2014)

3.5. Análise da qualidade dos óleos de quinoa

As análises de qualidade dos óleos de quinoas brancas e vermelhas, cultivadas no Brasil e na Bolívia, estão expressas na tabela 8. O PI variou de 7.41 – 8.07 h durante a oxidação acelerada do óleo a 110 °C. Estes valores são semelhantes ao PI de óleo de soja.

A presença de dienos e trienos conjugados, assim como o índice de peróxido estão relacionados a qualidade e estabilidade oxidativa de óleos vegetais, sendo quanto maiores os valores de dienos e trienos, menos estáveis serão esta matriz oleaginosa (Cordeiro et al., 2012). A Agência Nacional de Vigilância Sanitária (ANVISA) determina como limite máximo de índice máximo permitido de índice de peróxido em óleo é de 10 meq kg⁻¹, enquanto os óleos de quinoa apresentaram quantidades insignificantes (ANVISA, 2016).

Neste estudo a atividade antioxidante para os óleos de quinoa foi determinada pelo ensaio de DPPH (Tabela 8). Os valores de EC₅₀ para os óleos de quinoa variaram de 6,07 a 7,65 µL. Sendo estes valores, os volumes necessários para eliminar 50% do radical livre DPPH, com uma percentagem de inibição de oxidação em sistema lipídico de 50%. Esses valores são inferiores aos determinados por Condelli et al. (2015) que reportaram EC₅₀ de 40 e 20% de inibição para óleo de oliva extra virgem, mostrando elevado poder antioxidante dos óleos de quinoa. Esta ação mais forte do óleo de quinoa em comparação ao azeite pode ser

devido composição de lipídios e presença de tocoferóis e carotenóides da quinoa (Tang, Li, Chen, et al., 2015).

Tabela 8. Análise dos óleos das sementes de quinoa

Método	Sementes		
	QBBR	QBBo	QVBo
Estabilidade oxidativa- Rancimat PI (h)	7,71	7,41	8,07
Dienos	8,41	7,81	5,81
Trienos	1,9	2,9	1,91
Índice de Peróxido	0,01	0,02	0,01
Atividade antioxidante (DPPH- EC ₅₀) µL	7,65	6,81	6,07

4. Conclusão

As sementes de quinoa branca e vermelha, brasileira e boliviana foram identificadas como fonte de carboidratos, proteína, ácidos graxos poliinsaturados, além de quantidades elevadas de aminoácidos essenciais e minerais nutricionalmente importantes como magnésio, manganês, ferro e selênio. Os óleos apresentaram elevada atividade antioxidante e estabilidade oxidativa confirmando a qualidade nutricional e o potencial antioxidante das sementes de quinoa, apresentando elevado potencial de uso na promoção da saúde e para indústria alimentícia. A semente de quinoa branca do brasil apresentou maiores qualidades nutricionais comparado as outras sementes analisadas, dessas qualidades destacou-se os níveis de lipídeos, aminoácidos essenciais, microelementos, composição de ácidos graxos e atividade antioxidante.

Referências

- Abderrahim, F., Huanatico, E., Segura, R., Arribas, S., Gonzalez, M. C., & Condezo-Hoyos, L. (2015). Physical features, phenolic compounds, betalains and total antioxidant capacity of coloured quinoa seeds (*Chenopodium quinoa* Willd.) from Peruvian Altiplano. *Food Chemistry*, 183, 83–90. ht
- Abugoch James, L. E. (2009). Quinoa (*Chenopodium quinoa* Willd.): composition, chemistry, nutritional, and functional properties. *Advances in Food and Nutrition Research*, 58, 1–31.

- Agência Nacional de Vigilância Sanitária (ANVISA). RDC no. 270, de 22 de setembro de 2005. Regulamento técnico para óleos vegetais, gorduras vegetais e creme vegetal. In: <http://portal.anvisa.gov.br/wps/content/Anvisa+Portal/Anvisa/Inicio/Alimentos/Assuntos+de+Interesse/Legislacao>. Accessed 14 mai 2012.
- Alberti, A., Zielinski, A. A. F., Zardo, D. M., Demiate, I. M., Nogueira, A., & Mafra, L. I. (2014). Optimisation of the extraction of phenolic compounds from apples using response surface methodology. *Food Chemistry*, 149, 151–158.
- Alvarez-Jubete, L., Arendt, E. K., & Gallagher, E. (2009). Nutritive value and chemical composition of pseudocereals as gluten-free ingredients. *International Journal of Food Sciences and Nutrition*, 60(4), 240–257.
- Amin, A. R. M. R., Kucuk, O., Khuri, F. R., & Shin, D. M. (2009). Perspectives for cancer prevention with natural compounds. *Journal of Clinical Oncology*, 27(16), 2712–2725.
- AOAC Association of Official Analytical Chemists. (2000). *Official methods of analysis of AOAC International* (19th ed.). Washington, D.C.: AOAC International.
- Araujo-farro, P. C., Podadera, G., Sobral, P. J. A., & Menegalli, F. C. (2010). Development of films based on quinoa (*Chenopodium quinoa* , Willdenow) starch. *Carbohydrate Polymers*, 81(4), 839–848.
- Ayerza, R., & Coates, W. (2004). Composition of chia (*Salvia hispanica*) grown in six tropical and sub-tropical ecosystems of South America. *Tropical Science*, 44(3), 131–135.
- Barba De La Rosa, A. P., Herrera-Estrella, A., Utsumi, S., & Paredes-López, O. (1996). Molecular characterization, cloning and structural analysis of a cDNA encoding an amaranth globulin. *Journal of Plant Physiology*, 149(5), 527–532.
- Berti, C., Riso, P., Monti, L. D., & Porrini, M. (2004). In vitro starch digestibility and in vivo glucose response of gluten-free foods and their gluten counterparts. *European Journal of Nutrition*, 43(4), 198–204.
- Blanca, A.L. (1999). *Maquinaria Agrícola: constitución, funcionamiento, regulaciones y cuidados*. Madrid: Ministério de Agricultura, Pesca y Alimentacion, 361p. p.327-330, cap. 31: Cosechadora de cereales. Mecanismo de trilla
- Bligh, E. G., & Dyer, W. J. (1959). A rapid method of total lipid extration and purification. *Canadian Journal of Biochemistry and Physiology*, 37, 911–917.
- Bradford, M. M. (1976). A rapid and sensitive method for the quantitation of microgram quantities of protein utilizing the principle of protein-dye binding. *Analytical Biochemistry*, 72(1-2), 248–254.
- Brito, I. L., de Souza, E. L., Felex, S. S. S., Madruga, M. S., Yamashita, F., & Magnani, M. (2014). Nutritional and sensory characteristics of gluten-free quinoa (*Chenopodium quinoa* Willd)-based cookies development using an experimental mixture design.

Journal of Food Science and Technology, 52(September), 5866–5873.

- Chlopicka, J., Pasko, P., Gorinstein, S., Jedryas, A., & Zagrodzki, P. (2012). LWT - Food Science and Technology Total phenolic and total flavonoid content , antioxidant activity and sensory evaluation of pseudocereal breads. *LWT - Food Science and Technology*, 46(2), 548–555.
- Condelli, N., Caruso, M. C., Galgano, F., Russo, D., Milella, L., & Favati, F. (2015). Prediction of the antioxidant activity of extra virgin olive oils produced in the Mediterranean area. *Food Chemistry*, 177, 233–9.
- Cordeiro, A. M. T. M., Medeiros, M. L., Santos, N. A., Soledade, L.F.B.L., Pontes A. L. Souza, Queiroz, N., Souza, A.G. (2012). Rosemary (*Rosmarinus officinalis* L.) extract - Thermal study and evaluation of the antioxidant effect on vegetable oils. *J Therm Anal Calorim*, 130(4), 937–944.
- Cordeiro, L. M. C., Fátima, V. De, Baggio, C. H., Fernanda, M., Werner, D. P., Moura, L., & Iacomini, M. (2012). Arabinan and arabinan-rich pectic polysaccharides from quinoa (*Chenopodium quinoa*) seeds : Structure and gastroprotective activity. *Food Chemistry*, 130(4), 937–944.
- Couto, S. M., ALVARENGA, L. C. (1998). Resistência de grãos de soja a impactos mecânicos. *Revista Brasileira de Armazenagem*, 23 (2), 3-9.
- Cueto, M., Porras-saavedra, J., Farroni, A., Alamilla-beltrán, L., Schöenlechner, R., Schleining, G., & Buera, P. (2015). Physical and mechanical properties of maize extrudates as affected by the addition of chia and quinoa seeds and antioxidants. *Journal of Food Engineering*, 167, 139–146.
- EPA. (1998). *Método 6020A (SW-846): plasma indutivamente acoplado-espectrometria de massa*.
- Gómez-Caravaca, A. M., Segura-Carretero, A., Fernández-Gutiérrez, A., & Caboni, M. F. (2011). Simultaneous determination of phenolic compounds and saponins in quinoa (*Chenopodium quinoa* Willd) by a liquid chromatography-diode array detection-electrospray ionization-time-of-flight mass spectrometry methodology. *Journal of Agricultural and Food Chemistry*, 59, 10815–10825.
- Guillén, M. D.; Cabo, N.(1997) Characterization of edible oils and lard by Fourier transform infrared spectroscopy. *JAOCS*, v.74, p.1281-1286.
- Hirose, Y., Fujita, T., Ishii, T., & Ueno, N. (2010). Antioxidative properties and flavonoid composition of *Chenopodium quinoa* seeds cultivated in Japan. *Food Chemistry*, 119(4), 1300–1306.
- Hov, G. G., Aasarød, K. I., Sagen, E., & Åsberg, A. (2015). Arginine, dimethylated arginine and homoarginine in relation to cardiovascular risk in patients with moderate chronic kidney disease. *Clinical Biochemistry*, 48(10-11), 646–51.

- Joye, I. J., Lamberts, L., Brijs, K., & Delcour, J. a. (2011). In situ production of γ -aminobutyric acid in breakfast cereals. *Food Chemistry*, 129(2), 395–401.
- Kozioł, M. J. (1992). Chemical composition and nutritional evaluation of quinoa (*Chenopodium quinoa* Willd.). *Journal of Food Composition and Analysis*, 5(1), 35–68.
- Letelier, M. E., Rodríguez-Rojas, C., Sánchez-Jofré, S., & Aracena-Parks, P. (2011). Surfactant and antioxidant properties of an extract from *Chenopodium quinoa* Willd seed coats. *Journal of Cereal Science*, 53(2), 239–243.
- Marineli, R. S., Moraes, É. A., Lenquiste, S. A., Godoy, A. T., Eberlin, M. N., & Maróstica Jr, M. R. (2014). Chemical characterization and antioxidant potential of Chilean chia seeds and oil (*Salvia hispanica* L.). *LWT - Food Science and Technology*, 59(2), 1304–1310.
- Meneguetti, Q. A., Brenzan, M. A., Batista, M. R., Bazotte, R. B., & Silva, D. R. (2011). Biological Effects of Hydrolyzed Quinoa Extract from Seeds of *Chenopodium quinoa* Willd. 1 1. *Journal of Medicinal Food*, 14(6), 653–657.
- Miller, G.L. (1959) Use of dinitrosalicylic acid reagent for determination of reducing sugar. *Analytical Chemistry*. 31, 426-428.
- Miranda, M., Vega-gálvez, A., López, J., Parada, G., Sanders, M., Aranda, M., & Di, K. (2010). Impact of air-drying temperature on nutritional properties , total phenolic content and antioxidant capacity of quinoa seeds (*Chenopodium quinoa* Willd.). *Industrial Crops & Products*, 32(3), 258–263.
- Monda, M., Viggiano, a, Sullo, a, & De V, L. (1998). Aspartic and glutamic acids increase in the frontal cortex during prostaglandin E1 hyperthermia. *Neuroscience*, 83(4), 1239–1243.
- Nandi, I., & Ghosh, M. (2015). Studies on functional and antioxidant property of dietary fibre extracted from defatted sesame husk, rice bran and flaxseed. *Bioactive Carbohydrates and Dietary Fibre*, 5(2), 129–136.
- Nascimento, A. C., Mota, C., Coelho, I., Gueifão, S., Santos, M., Matos, A. S., & Castanheira, I. (2014a). Characterisation of nutrient profile of quinoa (*Chenopodium quinoa*), amaranth (*Amaranthus caudatus*), and purple corn (*Zea mays* L.) consumed in the North of Argentina: Proximates, minerals and trace elements. *Food Chemistry*, 148, 420–426.
- Ng, S.-C., Anderson, A., Coker, J., & Ondrus, M. (2007). Characterization of lipid oxidation products in quinoa (*Chenopodium quinoa*). *Food Chemistry*, 101(1), 185–192.
- Nowak, V., Du, J., & Charrondière, U. R. (2016). Assessment of the nutritional composition of quinoa (*Chenopodium quinoa* Willd.). *Food Chemistry*, 193, 47–54.
- Osborne, T. B. (1924). *The vegetable proteins. Monographs on Biochemistry*. (2nd ed.). London: Longmans green and Co.

- Peiretti, P. G., Gai, F., & Tassone, S. (2013). Fatty acid profile and nutritive value of quinoa (*Chenopodium quinoa* Willd.) seeds and plants at different growth stages. *Animal Feed Science and Technology*, 183(1-2), 56–61.
- Pisoschi, A. M., & Pop, A. (2015). The role of antioxidants in the chemistry of oxidative stress: A review. *European Journal of Medicinal Chemistry*, 97, 55–74.
- Ragaei, S., Abdel-Aal, E. S. M., & Noaman, M. (2006). Antioxidant activity and nutrient composition of selected cereals for food use. *Food Chemistry*, 98(1), 32–38.
- Razzaghi, F., Plauborg, F., Jacobsen, S., Richardt, C., & Neumann, M. (2012). Effect of nitrogen and water availability of three soil types on yield, radiation use efficiency and evapotranspiration in field-grown quinoa. *Agricultural Water Management*, 109, 20–29.
- Repo-Carrasco, R., Espinoza, C., & Jacobsen, S.-E. (2003). Nutritional Value and Use of the Andean Crops Quinoa (*Chenopodium quinoa*) and Kañiwa (*Chenopodium pallidicaule*).pdf. *Food Reviews International*, 19(1-2), 179 – 189.
- Repo-Carrasco-Valencia, R., Hellström, J. K., Pihlava, J.-M., & Mattila, P. H. (2010). Flavonoids and other phenolic compounds in Andean indigenous grains: Quinoa (*Chenopodium quinoa*), kañiwa (*Chenopodium pallidicaule*) and kiwicha (*Amaranthus caudatus*). *Food Chemistry*, 120(1), 128–133.
- Ruales, J., & Nair, B. M. (1993). Content of fat, vitamins and minerals in quinoa (*Chenopodium quinoa*, Willd) seeds. *Food Chemistry*, 48(2), 131–136.
- Sandhu, K. S., Godara, P., Kaur, M., & Punia, S. (2015). Effect of toasting on physical, functional and antioxidant properties of flour from oat (*Avena sativa* L.) cultivars. *Journal of the Saudi Society of Agricultural Sciences*, 0–6.
- Sandoval-Oliveros, M. R., & Paredes-López, O. (2013). Isolation and characterization of proteins from chia seeds (*Salvia hispanica* L.). *Journal of Agricultural and Food Chemistry*, 61(1), 193–201.
- Schoenlechner, R., Drausinger, J., Ottenschlaeger, V., & Jurackova, K. (2010). Functional Properties of Gluten-Free Pasta Produced from Amaranth, Quinoa and Buckwheat. *Plant Foods for Human Nutrition*, 65, 339–349.
- Schoenlechner, R., Wendner, M., Siebenhandl-ehn, S., & Berghofer, E. (2010). Pseudocereals as alternative sources for high folate content in staple foods. *Journal of Cereal Science*, 52(3), 475–479.
- Simopoulos, A. P. (2004). Omega-6/Omega-3 Essential Fatty Acid Ratio and Chronic Diseases. *Food Reviews International*, 20(1), 77–90.
- Stikic, R., Glamoclija, D., Demin, M., Vucelic-radovic, B., & Jovanovic, Z. (2012). Agronomical and nutritional evaluation of quinoa seeds (*Chenopodium quinoa* Willd.) as an ingredient in bread formulations. *Journal of Cereal Science*, 55(2), 132–138.

- Stikic, R., Glamoclija, D., Demin, M., Vucelic-radovic, B., Jovanovic, Z., Milojkovic-opsenica, D., & Milovanovic, M. (2011). SC. *Journal of Cereal Science*.
- Tang, Y., Li, X., Chen, P. X., Zhang, B., Hernandez, M., Zhang, H., & Tsao, R. (2015). Characterisation of fatty acid, carotenoid, tocopherol/tocotrienol compositions and antioxidant activities in seeds of three *Chenopodium quinoa* Willd. genotypes. *Food Chemistry*, 166, 380–388.
- Tang, Y., Li, X., Zhang, B., Chen, P. X., Liu, R., & Tsao, R. (2015). Characterisation of phenolics, betanins and antioxidant activities in seeds of three *Chenopodium quinoa* Willd. genotypes. *Food Chemistry*, 166, 380–8.
- Tuberoso, C. I. G., Kowalczyk, A., Sarritzu, E., & Cabras, P. (2007). Determination of antioxidant compounds and antioxidant activity in commercial oilseeds for food use. *Food Chemistry*, 103(4), 1494–1501.
- Turan, H., Sönmez, G., Kaya, Y. (2007) Fatty acid profile and proximate composition of the thornback ray (*Raja clavata*, L. 1758) from the Sinop coast in the Black Sea. *Journal Fisheries Science*, 1(2), 97-103.
- Ulbricht, T. L. V. & Southgate, D. A. T. (1991). Coronary heart disease: seven dietary factors. *Lancet*, 338 (8773), 985-992.
- Vlachos, N.; Skopelitis, Y.; Psaroudaki, M.; Konstantinidou, V.; Chatzilazarou, A.; Tegou, E. (2006). Applications of Fourier transform-infrared spectroscopy to edible oils. *Analytica Chimica Acta*, v.573, p.459-465.
- Zahir, E.; Saeed, R.; Hameed, M. A.; YousuF, A.(2014), Study of physicochemical properties of edible oil and evaluation of frying oil quality by Fourier TransformInfrared (FT-IR) Spectroscopy. *Arabian Journal of Chemistry*, In Press.
- Williams, S. M., Sullivan, R. K. P., Scott, H. L., Finkelstein, D. I., Colditz, P. B., Lingwood, B. E., & Pow, D. V. (2005). Glial glutamate transporter expression patterns in brains from multiple mammalian species. *Glia*, 49(4), 520–541.
- World Health Organization (1995). Joint Consultation: fats and oils in human nutrition. *Revista de Nutrição*, 53(7), 202-5.
- WHO/FAO/UNU Expert Consultation. (2007). *Protein and amino acid requirements in human nutrition. World Health Organization technical report series*. Geneva, Switzerland.
- Williams, S. M., Sullivan, R. K. P., Scott, H. L., Finkelstein, D. I., Colditz, P. B., Lingwood, B. E., & Pow, D. V. (2005). Glial glutamate transporter expression patterns in brains from multiple mammalian species. *Glia*, 49(4), 520–541.

4. CONCLUSÕES

As sementes de quinoa foram identificadas como importantes fontes de proteína, ácidos graxos poli-insaturados, minerais e compostos bioativos com elevada atividade antioxidante. Foi confirmada a presença de compostos antioxidantes nas variedades de quinoa estudadas, dentre estes, destacaram-se os ácidos fenólicos 2,5-dihidroxibenzóico, sinápico, felúrico e salicílico, enquanto os flavonóides, a rutina foi majoritária, com presença também de kampferol, quercetina e catequina.

A metodologia de superfície de resposta obtida através do delineamento experimental, utilizando variação de temperatura, tempo e misturas de solventes “verdes”, polares (etanol-água) foi eficaz em estimar os efeitos das três variáveis independentes para extração de compostos fenólicos totais nas sementes de quinoa, bem como a capacidade antioxidante pelos ensaios DPPH, FRAP e ABTS. Contudo, o monitoramento das condições de extração se faz necessário para melhorar a preservação e utilização de seus constituintes.

Os óleos das diferentes variedades de quinoa apresentaram elevado potencial antioxidante e estabilidade oxidativa, quando comparado a outros óleos e mostraram ser fonte de ácidos graxos predominantemente poliinsaturados.

Este estudo confirma a qualidade nutricional e poder antioxidante das sementes de quinoa de diferentes variedades indicando que as condições variáveis de cultivo interferem na composição deste vegetal.

Estudos futuros são necessários para avaliar o potencial uso dos extratos de quinoa na indústria alimentícia, seja na composição de formulações ou utilização como antioxidante dos alimentos, uma vez que os extratos otimizados mostram elevada estabilidade térmica. Da mesma forma que métodos distintos de extração da fração lipídica das sementes de quinoa podem apresentar diferentes rendimentos e potenciais antioxidantes, assim como diferentes concentrações de compostos fenólicos.

5. ANEXOS

5.1 ANEXO 1 – Comprovante de Submissão do artigo 1: **Chemical, functional and technological properties of quinoa (*Chenopodium quinoa* Willd.): A review**

5.2 ANEXO 2 – Comprovante de Submissão do artigo 2: **Application of response surface methodology to optimize extraction of phenolic compounds and antioxidant capacity of different quinoa (*Chenopodium quinoa* Willd.) varieties**

ANEXO 1

From: **Journal of Functional Foods** <eesserver@eesmail.elsevier.com>

Date: 2017-06-15 18:53 GMT-03:00

Subject: A manuscript number has been assigned: JFF-D-17-01294

To: atribuzycordeiro@gmail.com, atribuzycordeiro@hotmail.com

Ms. Ref. No.: JFF-D-17-01294

Title: Chemical, functional and technological properties of quinoa (*Chenopodium quinoa* Willd.): A review

Journal of Functional Foods

Dear ANGELA TRIBUZY,

Your submission "Chemical, functional and technological properties of quinoa (*Chenopodium quinoa* Willd.): A review" has been assigned manuscript number JFF-D-17-01294.

To track the status of your paper, please do the following:

1. Go to this URL: <https://ees.elsevier.com/iff/>
2. Enter your login details
3. Click [Author Login]
This takes you to the Author Main Menu.
4. Click [Submissions Being Processed]

Thank you for submitting your work to Journal of Functional Foods.

Kind regards,

Journal of Functional Foods

Please note that the editorial process varies considerably from journal to journal. To view a sample editorial process, please click here:

http://help.elsevier.com/app/answers/detail/p/7923/a_id/160

For further assistance, please visit our customer support site at

<http://help.elsevier.com/app/answers/list/p/7923>. Here you can search for solutions on a range of topics, find answers to frequently asked questions and learn more about EES via interactive tutorials. You will also find our 24/7 support contact details should you need any further assistance from one of our customer support representatives.

ANEXO 2

Dear Dr. Isabelle de Lima Brito,

You have been listed as a Co-Author of the following submission:

Journal: Food Chemistry

Corresponding Author: ANGELA CORDEIRO

Co-Authors: Isabelle de Lima Brito; Maristela Alves Alcântara; Bruno Raniere Lins de Albuquerque Meireles; Anwar Abbas El-Aouar; Antonio Gouveia Souza;

Title: Application of response surface methodology to optimize extraction of phenolic compounds and antioxidant capacity of different quinoa (*Chenopodium quinoa* Willd.) varieties

If you did not co-author this submission, please contact the Corresponding Author of this submission at atribuzycordeiro@gmail.com; atribuzycordeiro@hotmail.com; do not follow the link below.

An Open Researcher and Contributor ID (ORCID) is a unique digital identifier to which you can link your published articles and other professional activities, providing a single record of all your research.

We would like to invite you to link your ORCID ID to this submission. If the submission is accepted, your ORCID ID will be linked to the final published article and transferred to CrossRef. Your ORCID account will also be updated.

To do this, visit our dedicated page in EES. There you can link to an existing ORCID ID or register for one and link the submission to it:

<https://ees.elsevier.com/foodchem/l.asp?i=545158&l=M7DQM0YV>

More information on ORCID can be found on the ORCID website, <http://www.ORCID.org>, or on our help page: http://help.elsevier.com/app/answers/detail/a_id/2210/p/7923

Like other Publishers, Elsevier supports ORCID - an open, non-profit, community based effort - and has adapted its submission system to enable authors and co-authors to connect their submissions to their unique ORCID IDs.

Thank you,

Food Chemistry