Original article [1]

Fatty acid composition of seeds from Bolivian cultivated quinoa (Real), wild quinoa (Ajara), and scarified quinoa residues (Mojuelo)

Carolina Triguero, Maribel Lozano, Giovanna R. Almanza*

Instituto de Investigaciones Químicas IIQ-*Bioorgánica*, Universidad Mayor de San Andrés UMSA, Av. Villazón N° 1995, La Paz, Bolivia

Keys: *Bolivian quinoa real, Wild quinoa – Ajara, Scarified quinoa residues - Mojuelo, Unsaturated fatty acids, GC/MS Profiles of fatty acids;* **Claves:** *Quinua real boliviana, Quinua silvestre – Ajara, Residuos de escarificado de quinua – Mojuelo, ácidos grasos insaturados, Perfiles GC/MS de ácidos grasos.*

ABSTRACT

Quinoa (*Chenopodium quinoa* Willd.) is a highly nutritious pseudocereal, appreciated for its amino acid and fatty acid (FA) profile. Bolivia ranks as the world's second-largest producer, generating over a million tons of scarified residues (Mojuelo) annually. Wild quinoa ("Ajara", *C. quinoa* var. *melanospermum*), abundant in the Altiplano, remains largely untapped. This study analyzed lipid content and FA methyl esters in cultivated quinoa ("real blanca"), wild quinoa ("Ajara"), and Mojuelo using gas chromatography–mass spectrometry (GC–MS). All samples were rich in unsaturated FAs, mainly linoleic (~50%) and oleic (~35%) acids. Wild quinoa had the highest lipid content (3.60%) and FA yield (92.27%), followed by cultivated quinoa (2.33%; 90.69%) and Mojuelo (1.12%; 89.71%). Saturated FAs were ≤10%, with only palmitic acid detected. "Ajara" displayed the most promising nutritional profile, underscoring its potential as a valuable food resource.

RESUMEN

La quinua (*Chenopodium quinoa* Willd.) es un pseudocereal altamente nutritivo, valorado por su perfil de aminoácidos y ácidos grasos. Bolivia, segundo productor mundial, genera más de un millón de toneladas de residuos de escarificado (Mojuelo) al año. La variedad silvestre "Ajara" (*C. quinoa* var. *melanospermum*), común en el Altiplano, sigue poco aprovechada. Este estudio analizó el contenido lipídico y la composición de ácidos grasos en semillas de quinua cultivada ("real blanca"), silvestre ("Ajara") y Mojuelo, usando cromatografía de gases–espectrometría de masas. Todas las muestras mostraron predominancia de ácidos grasos insaturados, especialmente linoleico (~50%) y oleico (~35%). La quinua silvestre tuvo el mayor contenido lipídico (3,60%) y rendimiento de ácidos grasos (92,27%), seguida por la cultivada y el Mojuelo. Los ácidos grasos saturados fueron ≤10%, destacando el palmítico. La "Ajara" mostró el perfil más prometedor como fuente nutricional.

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INTRODUCTION

Quinoa (*Chenopodium quinoa* Willd.) is a traditional Andean crop, originally domesticated in Bolivia and Perú, that stands out for its high nutritional value. Several studies have demonstrated its superiority over conventional grains such as rye, rice, barley, and oats due to the higher quantity and quality of its nutrients.[1] Quinoa proteins are particularly relevant, since they contain a well-balanced profile of essential amino acids—including lysine, methionine, and threonine—that are often limited in cereals like wheat and maize.[1] [2] The carbohydrate content (32–69%) is comparable to that of wheat and rice, with starch as the predominant fraction. In addition, quinoa exhibits a distinctive lipid profile (5.5–7.4 g/100 g), composed mainly of unsaturated fatty acids (oleic, linoleic, and α-linolenic acids), which represent nearly 88% of the total.[3] This lipid composition, together with its high levels of vitamins (E, C, B2, B6, folic acid) and minerals (calcium, magnesium, iron, potassium)[2], provides quinoa with relevant functional and health-promoting properties[3].

In Bolivia, the industrial processing of quinoa generates large amounts of scarified residues known as “Mojuelo”, which remain underutilized despite being potential sources of bioactive compounds such as saponins and fatty acids.[4]

Quinoa (*Chenopodium quinoa* Willd) possesses significant genetic diversity, including its wild relatives like “Ajara” (*Chenopodium quinoa var. melanospermum*) that is also distributed in the Bolivian highlands. This wild quinoa possesses agronomic characteristics of interest such as resistance to harsh environmental conditions, and has been traditionally used in medicine and occasionally as food. Although its consumption is limited due to its small grain size and black coloration, preliminary studies indicate that it has a nutritional composition (proteins, lipids, carbohydrates and fiber) comparable to that of cultivated quinoa.[5]

The types of fatty acids present in quinoa seeds have been identified as similar to those of soybeans and corn[2], which are considered a better nutritional alternative to oilseeds because their essential fatty acids are healthier unsaturated fatty acids, mainly linoleic and alpha-linolenic acid[3]. Quinoa oils have been reported to contain around 89.4% unsaturated fatty acids.[6] Therefore, quinoa oil has beneficial health properties, such as reducing the risk of inflammatory and cardiovascular diseases.

In this study, we analyzed the fatty acid (FA) composition of cultivated Bolivian quinoa seeds (*C. quinoa* Willd. “quinua real blanca”), wild quinoa seeds (*C. quinoa var. melanospermum*, “Ajara”), and quinoa scarified residues (Mojuelo) using gas chromatography–mass spectrometry (GC–MS).

RESULTS AND DISCUSSION

Evaluation of the fatty acid FAs profiles of the three quinoa samples was initially performed by obtaining the total lipid extract, followed by transesterification to produce fatty acid methyl esters (FAMEs). The FAMEs were evaluated by GC–EI analysis followed by a MS analysis of each peak observed in the chromatogram. Peak identification was achieved by comparison of their mass spectra with a standard library available in the GC-MS database. The relative abundance of each FA was expressed as a percentage of the total FAME content (%), calculated from:

$Ax/A_{TOT} \times 100$ (1)

(where Ax refers to the peak area of the FAME considered and A_{TOT} refers to the total peak area of the FAMEs contained in the sample). The names of the identified FAMEs along with the relative percentage are reported in Table 2.

Total lipid extraction

Fatty acids and other non-polar substances were extracted from the three quinoa samples by Soxhlet reflux, and the non-polar resulting extracts were concentrated by rota-evaporation until to remove all the solvent. The dried lipid extracts were then weighted to determine the yields (Table 1). The highest lipid yield was obtained for wild quinoa “Ajara”, which is particularly relevant since, to our knowledge, no previous data have been reported for this wild quinoa variety identified as *Chenopodium quinoa var. melanospermum.* In comparison, cultivated quinoa seeds (“real blanca”) and scarified residues (“Mojuelo”) presented lower yields.

Table 1. Yield of Lipid Extracts from quinoa samples.

Nº	Sample	Yield (%)
1	Cultivated quinoa seeds “real blanca”	2,33
2	Wild quinoa “Ajara”	3,60
3	Quinoa residue” Mojuelo”	1,12

GC-MS analysis of FAMEs

The GC chromatograms of the three quinoa samples showed similar profiles (Figure 1). In particular, the cultivated quinoa seeds (*Chenopodium quinoa* var. *real*, “real blanca”) and the scarified residues, obtained from the Irupana Andean Organic Food company, displayed almost identical chromatograms. This similarity can be explained by the fact that the company primarily processes quinoa of the “real” variety from the Southern Bolivian Altiplano, which was also the source of the cultivated seeds analyzed in this study. By contrast, the chromatogram of the wild quinoa (“Ajara”, *C. quinoa* var. *melanospermum*) exhibited slight differences, consistent with its distinct genetic variety.

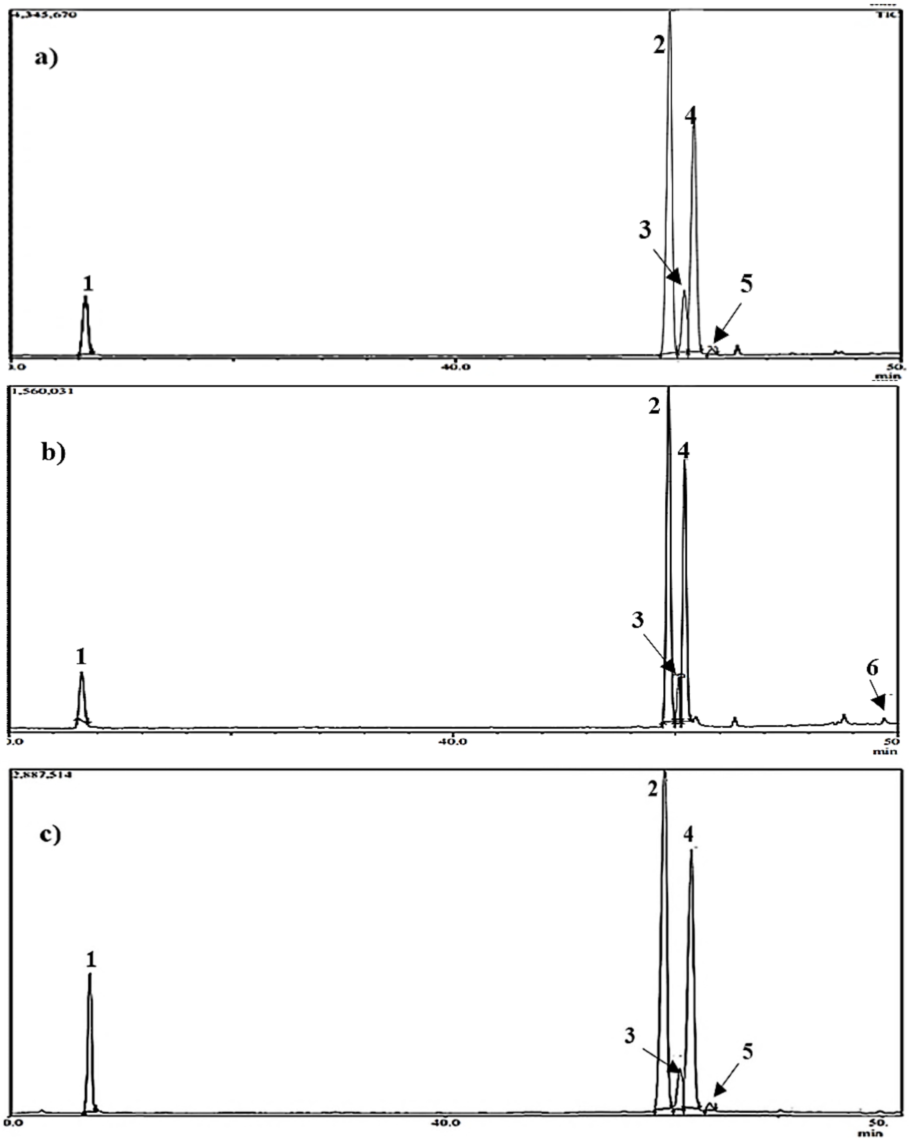


Figure 1. GC-MS fatty methyl esters profile of a) Cultivated quinoa seeds “real blanca”, b) Wild quinoa “Ajara” c) Quinoa residue “Mojuelo”.

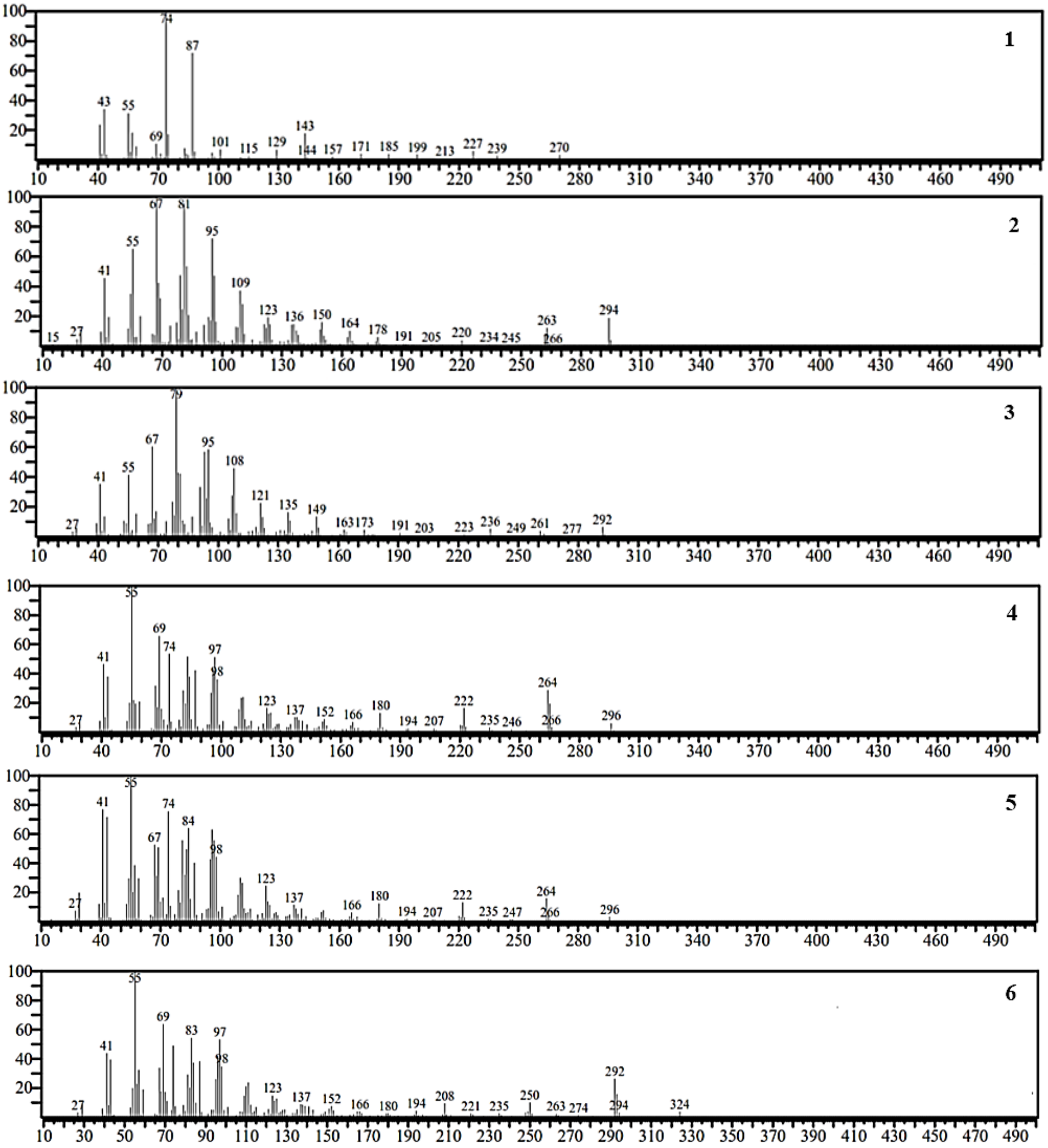
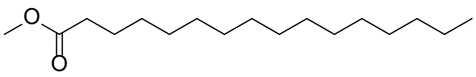


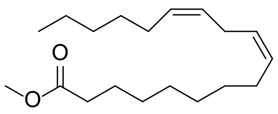
Figure 2. Mass spectra of identified FAMEs in the three quinoa samples; 1) Methyl palmitate, 2) Methyl linoleate, 3) Methyl linolenate, 4) Methyl oleate, 5) (Z)-6-Octadecenoic acid, methyl ester, 6) cis-11-Eicosenoic acid, methyl ester.

The names of the identified FAMEs and their relative percentage are reported in Table 2. It shows that the major components in all three quinoa samples were methyl linoleate **2)** which is present in approximately 50%, and methyl oleate **4**) present in approximately 35%. Overall, unsaturated fatty acids (UFAs) represented the predominant fraction, with 90.69% in cultivated quinoa seeds ("real blanca"), 92.27% in wild quinoa ("Ajara"), and 89.71% in scarified residues ("Mojuelo"). These results are consistent with previously reported data.[7]

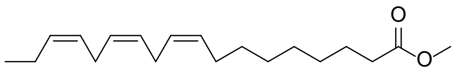
As shown in Table 2 and Figure 3, methyl palmitate **1**) was the only saturated FAME detected, reaching 7.70% in wild quinoa and close to 10% in both cultivated seeds and scarified residues. Notably, wild quinoa exhibited not only the highest lipid yield and the greatest proportion of UFAs, but also one additional FAME **6)** that was not detected in the other two samples. Taken together, these findings indicate that the FAs profile of wild quinoa (Ajara) is more favorable than that of cultivated quinoa ("real blanca") and its processing residue.



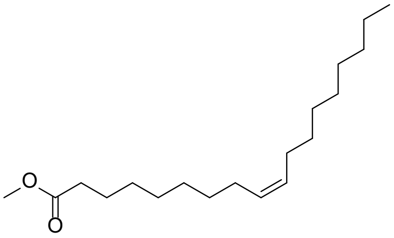
1) Methyl palmitate



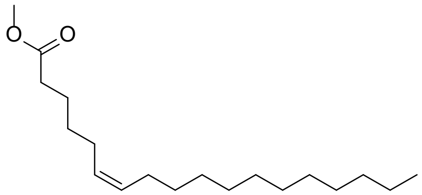
2) Methyl linoleate



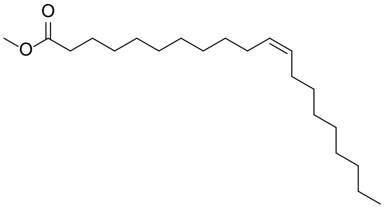
3) Methyl linolenate



4) Methyl oleate



5) (Z)-6-Octadecenoic acid, methyl ester



6) cis-11-Eicosenoic acid, methyl ester

Figure 3. Structures of identified FAMEs by GC-MS.

Table 2. Semi quantitative percentage of FAMEs in quinoa samples

FAMEs	Molecular Weight	Retention time $(T_{R/min})$	Cultivated quinoa seed	Wild quinoa “Ajara seed”	Quinoa residue “Mojuelo”
				(%)	
Methyl palmitate **1)** $C_{17}H_{34}O_2$	270	31.645	9.31	7.70	10.24
Methyl linoleate **2)** $C_{18}H_{34}O$	266	44.850	48.7	50.5	47.9
Methyl linolenate **3)** $C_{19}H_{32}O_2$	292	45.205	7.91	5.65	5.06
Methyl Oleate **4)** $C_{19}H_{36}O_2$	296	45.253	33.4	34.5	35.9
(Z)-6-Octadecenoic acid, methyl ester **5)** $C_{19}H_{36}O_2$	296	45.478	0.68	Nd	0.85
cis-11-Eicosenoic acid, methyl ester **6)** $C_{21}H_{40}O_2$	324	50.218	Nd	1.62	Nd

Nd= no determined

Peak detection was performed by comparing it with a Mass Material database (NIST), which has assessed mass spectrometry libraries and offers associated software tools for identifying compounds using the MS data from the apparatus, selecting those that displayed over a 95% match in the mass spectra.

EXPERIMENTAL

Equipment and reagents

The equipment used was a Gas Chromatograph coupled to Mass Spectrometer GC/MS, SHIMADZU, model GC 2010 Plus, MS QP2020, made in Japan. The solvents used were: methanol and n-hexane HPLC grade purchased from Merk, petroleum ether was obtained by fractionated distillation of gasoline (60-80ºC fraction). For fatty acid esterification, potassium hydroxide and hydrochloric acid were purchased from Merk.

Plant material

Cultivated quinoa seeds "quinua real blanca" were purchased from the Challapata town market (Oruro Department, Bolivia) in November 2024. Samples of wild quinoa "Ajara" were provided by the PROINPA Foundation (La Paz, Bolivia) in May 2025, and scarified quinoa residue "Mojuelo" was supplied by Irupana Andean Organic Food (La Paz, Bolivia) in June 2024.

Total lipid extraction

Quinoa scarified residues (Mojuelo, 240 g; Irupana Andean Organic Food, La Paz, Bolivia) were subjected to solid–liquid Soxhlet extraction with 1 L of petroleum ether (60–80 °C) for 3 h. The solvent extract was concentrated by rotary evaporation until complete solvent removal, yielding a dried lipid fraction, which was weighed to calculate extraction yield.

Similarly, quinoa seeds of the "real blanca" variety (392 g) were ground and extracted with 1 L of petroleum ether (60–80 °C) for 3 h using a Soxhlet apparatus. The solvent was removed under reduced pressure to obtain the lipid fraction.

Wild quinoa (Ajara, 246 g) was ground and subjected to Soxhlet extraction with 1 L of petroleum ether (60–80 °C) for 3 h. After complete solvent removal, the lipid fraction was collected as a dried residue.

Preparation of fatty acid methyl esters FAMEs

Fatty acid methyl esters (FAMEs) were prepared from 500 mg of lipid fraction dissolved in 5 mL of n-hexane. The solution was saponified with 3 mL of potassium hydroxide in methanol (0.083% w/v) and refluxed at 80 °C for 30 min. Subsequently, 8 mL of hydrochloric acid in methanol (0.091% v/v) were added to complete the reaction. FAMEs were extracted with 2 mL of n-hexane, and the organic phase was filtered through a PTFE membrane filter (0.2 µm pore size) and analyzed by gas chromatography-mass spectrometry (GC-MS).[8]

GC-MS analysis

Fatty acid methyl esters were analyzed in a GC-2010 gas chromatograph GC 2010 PLUS coupled to a QP 2020 mass spectrometry detector, both from SHIMADZU. The separation of the compounds was performed using a Restek 5-Sil MS column with 5% diphenyl and 95% dimethylpolysiloxane (30 m x 0.25 mm and 0.25 µm film thickness). The injection volume was 1 µL at a total flow of 21.6 mL/min, and the column flow was 0.60 mL/min. The injector temperature was 260°C, the initial column temperature was 40°C, which was then increased to 280°C at a rate of 10°C/min held for 6 minutes, the ionization temperature used was 250°C, and the interface temperature was 280°C.For the GC analysis, the oven program was set as follows: initial temperature 80 °C (5 min), ramped to 180 °C at 10 °C/min (25 min hold), then increased to 260 °C at 4 °C/min (5 min hold). Helium was used as carrier gas at 1.01 mL/min (99.7 kPa). Ionization was carried out by electron impact at 70 eV.

In the MS, the sample was analyzed in the full scan mode with a scan speed of 20 000 mAU/sec, a mass range of 35-500m/z and a sampling frequency of 25 spectra/s; interface and ion source temperatures were 280 and 200ºC, respectively. MS ionization mode: electron ionization. Data were acquired by using the GCMS solution software ver. 4.0 (Shimadzu).

Peak detection was performed by comparing it with a Mass Material database (NIST), which has assessed mass spectrometry libraries and offers associated software tools for identifying compounds using the MS data from the apparatus, selecting those that displayed over a 95% match in the mass spectra.

Compounds

Methyl palmitate **1**); Mass spectrum of peak at retention time 31.65 min was identified as methyl palmitate showed a molecular ion peak *m/z* 270, and the base peak (100 %) ion m/z 74 as a result of McLafferty rearrangement $[CH2COHOCH3]^{+\cdot}$.[9]

Methyl linoleate **2)**; Mass spectrum of peak at retention time 44.850 min was identified as methyl linoleate showed a molecular ion peak $[M]^+$ m/z 294 and the base peak m/z 67 due to allylic un saturated fragments (ion $C_5H_7^+$), and common fragments from Alpha beta carbonyl bound breaks (typical ions C_4-C_7) and the secondary fragments *m/z* 123, 149, 179 could be due to retro-Diels rearrangements.[10]

Methyl linolenate **3)**; Mass spectrum of peak at retention time 45.210 min was identified as methyl linolenate showed a molecular ion peak $[M]^+$ m/z 292 and the base peak m/z 79, likely the $[C_6H_7]^+$and common fragments m/z 55, 67, 95 and 137 from Alpha beta bound breaks respect to the carbonyl group.[10]

Methyl oleate **4)**; Mass spectrum of peak at retention time 45.25 min was identified as methyl oleate showed a molecular ion peak $[M]^+$ m/z 296 and the base peak m/z 55, due to the alkyl fragment formation $[C_4H_7]^+$ and other common fragments m/z 264 $[M-32]^+$ due to the loss of methoxy group (OCH_3), the ion m/z 222 $[M-74]^+$ from McLafferty rearrangement, the ion m/z 97, 74, 69,55 intensive fragments due to aliphatic break bounds[11] [12]

(Z)-6-Octadecenoic acid, methyl ester **5)**; Mass spectrum of peak at retention time 45.48 min was identified as (Z)-6-Octadecenoic acid, methyl ester showed a molecular ion peak $[M]^+$ m/z 296 and the base peak m/z 55, due to the alkyl fragment formation $[C_4H_7]^+$ and other intensive fragment m/z 74 due to McLafferty rearrangement, and other ions at m/z 41, 55, 69, 97 common fragments due to aliphatic rupture near to the double bound (ions C3-C7), the ion m/z 264 $[M-32]^+$ due to the loss of methoxy group (OCH_3), the ion m/z 222 $[M-74]^+$ associate to McLafferty rearrangement.[12]

Cis-11-Eicosenoic acid, methyl ester **6)**; Mass spectrum of peak at retention time 50.22 min was identified as Cis-11-Eicosenoic acid, methyl ester showed a molecular ion peak $[M]^+$ m/z 324 and the base peak m/z 74 as a result of McLafferty rearrangement $[\mathrm{CH2COHOCH3}]^{+\cdot}$, and other ions at m/z 143 fragment due to beta bound break near to the ester group, ion m/z 222, 239, fragments due to ruptures stabilized by unsaturation.[13] [14]

CONCLUSIONS

This study demonstrates that three quinoa samples—cultivated seeds (*Chenopodium quinoa var. real*, "real blanca"), wild seeds (*C. quinoa var. melanospermum,* "Ajara"), and scarified residues ("Mojuelo")—are good sources of unsaturated fatty acids. The predominant FAs were linoleic acid (47.9–50.5%) and oleic acid (33.4–35.9%). Wild quinoa seeds ("Ajara") exhibited the most favorable FAMEs profile and the highest lipid extraction yield. This finding is particularly noteworthy, as no previous data on the fatty acid composition of *C. quinoa var. melanospermum* (Ajara) have been reported, highlighting the potential of this underutilized wild quinoa variety as a valuable nutritional resource.

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