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^1H and ^{13}C NMR investigation of oils extracted from exotic fruits

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Abstract. Exotic fruit seeds are waste of industrial preparation of foods and human consumption. The contents in terms of nutrients of oils extracted from exotic fruit seeds are not fully understood, and they remain object of study. We propose a practical, inexpensive, qualitative and quantitative approach based on the use of ^1H and ^{13}C NMR spectroscopy for the fatty acid chain profiling of these oils. The composition of eleven seed oils was investigated. The amounts of linoleic (from 3.5% in Rambutan to 84.6% in Feijoa), oleic (from 6.9% to 68.7% in Papaya), and saturated fatty acid chains (from 7.9% in Feijoa to 49.5% in Rambutan) were determined. The total contents of unsaturated fatty acid (MUFA and PUFA) chains in oils ranged from 37.5% in Mangosteen to 91.5% in Feijoa. The oils were characterized by saturated/unsaturated (SFA/PUFA) ratios ranging from 0.08 to 1.07, with values which were superior to that commonly reported for extra virgin olive oil. These ratios are potentially favorable for human health. The ANOVA test showed the model to be remarkably significant ($p < 0.05$). Spectral data agreed those reported in the literature for conventional methods. Although linolenic acid was not detected in all oils, their fatty acid chain profiles make them desirable in terms of nutrition and as alternative energy sources.

1. Introduction

Edible fruits are used for the industrial production of juices and foodstuffs. Large amounts of agro-industrial waste, such as seeds, peels and pulps, are by-products coming from the industrial food processing. The recovery and recycling of these products, commonly discarded and produced in very high percentages with respect to the weight of the whole fruits, could be a valuable source of added economic value, especially in the case of seeds which offer the possibility for the oil extraction.

In fact, seeds and vegetable oils cover an important role as nutraceuticals, and in the food, cosmetic, pharmaceutical, industry [1]. Nowadays, the fiber waste from fruits is used as a sustainable adsorbent of water organic pollutants [2-4], as an alternative to other polymeric and carbon materials [5, 6]. Another possible use of seeds from fruits is the extraction of oil and fats which can successfully be applied in the production of biodiesel [7-10] as an answer to the growing global request for alternative and green energy sources. It is obvious that a seed oil can be destined to any different industrial



transformations depending on the molecular composition of the oil. Pointing out the attention on exotic fruit seed oils, in the literature there are not so much information about the characteristics of their nutritional contents. For the most part of the commercially available exotic fruits, the collected data refer to their proximate compositions, expressed as total amounts of proteins, fibers, vitamins, carbohydrates, mineral ashes, water contents. In some cases, the metabolic profile of phytochemicals, e.g. the antioxidants, is reported [11].

In recent years, many exotic fruits have attracted increasing attention, and they have been investigated for their bioactivities [12]. Many exotic fruits are safe to the consumers, however industrially underutilized. In particular, seed oils extracted from exotic fruits have sparingly been analyzed to give information about their principal nutritional parameters which can have health benefits and outcomes.

The knowledge of fatty acid chain profiles in exotic fruit seed oils might be of great importance in order to propose these natural resources as worldwide distributed foods, special ingredients, and matrices useful to produce environmentally sustainable biodiesel. Moreover, it is of interest that exotic fruit seed oils are object of studies devoted to the search for other economically convenient products, and widely used as raw materials and inputs for the industrial production of pharmaceutical formulations and cosmetics [13].

Seed oils are mainly composed by triacylglycerols (TAGs) which are the most important source of essential fatty acids, playing a privileged role in many functions that are necessary for human health [14-17]. Consumers are interested in the health benefits produced by monounsaturated and polyunsaturated fatty acids (MUFA and PUFA, respectively). Oleic (18:1, ω -9), linoleic (18:2, ω -6), linolenic (18:3, ω -3) acids are the most important components in diets [ref].

As suggested by nutritionists, the MUFA and PUFA should correctly balance the saturated fatty acid (SFA) fractions, in order to reduce the risk of cardiovascular disease and atherogenesis, to contrast impaired insulin sensitivity, obesity, and type 2 diabetes [18-20]. On the other hand, world economies, urbanization and living habits necessitate an increasing demand for alternative energy sources. As a consequence, it is apparent that biofuels produced from non-edible seed oils can also be promising candidates for the production of valuable new energy resources.

The present report aims at investigating the fatty acid chain profiles in oils extracted from seeds of a series of common exotic fruits. The fatty acid composition of these seeds, considered to be by-products and materials to be discarded, could define their possible added industrial economic values, as foods or animal feed, as ingredients in cosmetic formulations, and to throw more information on the utilization as biodiesel.

Thus, the main goal of this work was the characterization of exotic fruit seed oils in terms of their percentages of the different structures of fatty acid chains. The fatty acid chain profiles of seed oils were evaluated by high-resolution ^1H and ^{13}C Nuclear Magnetic Resonance (NMR) quantitative spectroscopy [21, 22]. NMR plays an ever-increasing role in the study of properties of fats and oils of animal and vegetable origin [23-25].

In this work, ^1H and ^{13}C NMR techniques were complementary employed, allowing the calculations of SFA, MUFA, and PUFA fractions in each oil object of investigation. In particular, the spectroscopic analysis delivered the oleic (O, C18:1, ω -9), linoleic (L, C18:2, ω -6), and saturated (S, Cn:0) fatty acid contents. The attention was pointed out on the amounts of linoleic and linolenic (Ln, C18:3, ω -3) acids, from which the L/Ln ratio can be determined and evaluated as a possible nutritional quality parameter for all oils, according to the current literature [26].

In particular, ^{13}C NMR allowed to ascertain the presence or absence of ω -3 fatty acid chains in seed oils, especially when the triplet signal, assignable to the terminal methyl group of the linolenic acid chain, cannot unambiguously be detected or integrated in the respective ^1H NMR spectrum. All fatty acid profiles determined by the spectroscopic method were in good accordance with the already reported profiles, which have been obtained by the GC-FID and GC-MS conventional analyses.

2. Materials and methods

2.1. Sampling

The following exotic fruits were used: Annona cherimola, Carambola (*Averrhoa carambola* L., star fruit), Feijoa (*Feijoa sellowiana* Berg), Guava (*Psidium guajava* L., variety white flesh), Mango (*Mangifera indica*), Mangosteen (*Garcinia mangostana* L.), Papaya (*Carica papaya* L., variety formosa), *Passiflora edulis* (*Passiflora edulis* Sims, variety *edulis*; yellow passion fruit), *Passiflora flavicarpa* (*Passiflora edulis* Sims, variety *flavicarpa*; purple passion fruit), Pitaya (*Hylocereus undatus*, variety white flesh), and Rambutan (*Nephelium lappaceum* L.). Fruits were collected from local markets in Italy. Fruit pericarps and seeds were separated. The seeds were recovered from the fresh fruits, washed, dried under the sun action until constant weight, and blended to powder before extraction. In the case of fruits containing kernel seeds, e.g. mango, the kernels were separated, dried, cracked, and the seed were powdered by a grind. Seed oils extracted from eleven exotic fruits were subjected to ^1H and ^{13}C NMR spectroscopic analysis.

2.2. Seed extraction and oil recovery

Extraction of oils was performed in a Soxhlet apparatus charged with hot hexane, using cellulose thimbles, according to the standard method [27]. For all experiments, equal amounts (2 g) of dried and powdered seeds were used. Extraction was carried out over 6 h, to remove the total lipid content. After this time, hexane solutions were dried over Na_2SO_4 , paper filtered, and evaporated under reduced pressure at room temperature (rotary evaporator). The amounts of recovered oils were expressed as the lipid percentage in 100 g seed powder dry matter. All seeds furnished considerable weights of total lipid extracts. The recovered amounts of seed oil from each one kind of exotic fruit were as follows: Annona 27.5 ± 1.4 %, Carambola 72.3 ± 3.6 %, Feijoa 9.9 ± 0.4 %, Guava 16.9 ± 0.6 %, Mango 11.3 ± 0.3 %, Mangosteen 23.5 ± 0.4 %, Papaya 75.7 ± 4.1 %, *Passiflora edulis* 26.5 ± 0.7 %, *Passiflora flavicarpa* 18.2 ± 0.5 %, Pitaya 30.9 ± 1.0 %, Rambutan 36.2 ± 1.6 %. Extractions were carried out in triplicate, and percentages were referred to 100 g of dried seeds.

2.3. Chemicals and solvents

All chemicals and solvents for extraction, standards and deuterated chloroform for spectroscopy (99.5% isotopically pure, containing 0.1% TMS), were purchased from Sigma-Aldrich (Milano, Italy). Standards of TGA (tristearin, trimiristin, tripalmitin, tripalmitolein, triolein, trilinolein, and trilinolenin) used for signal assignment in ^{13}C qNMR spectra recorded on samples of seed oils were 99.9% pure.

2.4. NMR spectroscopy

Aliquots (100 mg) of each seed oil were dissolved in deuterated chloroform (0.6 mL) in 5 mm NMR tubes. A Bruker Avance AC 300 Ultrashield spectrometer, equipped with a 5 mm BBO probe with Z-axis gradient coils was used for all spectral analyses. All spectra were recorded at 298 K. All proton spectra were recorded at a ^1H frequency of 300.132 MHz, applying a standard zg90 pulse sequence, with the lock on the deuterium resonance of CDCl_3 . All carbon spectra were recorded at 75.03 MHz. Relaxation times (T_1) were determined for all carbons on samples of each single standard TGA (100 mg in 0.6 mL CDCl_3) and in mixture, by using a pulse sequence and method as suggested by the literature [32]. For the quantitative analysis a delay of 10 s (equal to 5 times the highest T_1 value) between each scan was applied. Acquisition and elaboration parameters for ^1H and ^{13}C spectra were as previously published [28-31]. Carbon resonances were assigned by recording spectra of TGAs as a single component and as a mixture, upon the same instrumental conditions and concentrations used for the analysis of oil samples. The comparison between experimental data and the available literature reports confirmed the signal assignment.

2.5. Statistics

Fatty acid chain profiles were expressed as a percentage of the total acyl chains identified and grouped as follows: saturated fatty acid (SFA), monounsaturated fatty acid (ω -9, MUFA) and polyunsaturated acid (ω -3 and ω -6, PUFA). Minor and unresolved fatty acids were not reported. Analyses were carried out in triplicate. All results were expressed as mean value \pm standard deviation (SD). Each ^1H and ^{13}C spectrum was recorded in triplicate, and resonance signals selected for the quantitative analysis were integrated seven times. The integral values showed variations limited to the third decimal figures, so that the corresponding standard deviations were not considered. Percentages of each fatty acid chain group were calculated from the integral values, by the methods already reported [28,33]. A one-way analysis of variance (ANOVA) was performed to calculate significant differences in means, and multiple comparisons of means were done by the LSD (least significance difference) test. A probability value of $p < 0.05$ was considered significant, and only significant differences were considered and reported in Table 1, unless stated otherwise.

3. Results and discussions

Physical, chemical and nutritional characteristics of oils are mainly influenced by the kind and proportions of the fatty acid components. There are scanty reports on the fatty acid composition of under-utilized tropical fruit seed oils in the literature. Some of these reports appear to show wide variation, and are all related to GC-FID and GC-MS analyses. Studies carried out by NMR spectroscopy are sparingly available.

High-resolution ^1H NMR spectroscopy is one of the most versatile primary analytical methods. It provides very detailed structural information, and represents a powerful analytical tool used for the metabolic profiling of natural vegetable and animal complex matrices [34-35]. Nowadays, NMR spectroscopic techniques are successfully applied covering identification and structure elucidation of organic and bioorganic compounds [36-42], precise quantitative determination of individual analytes and multicomponent analysis [43,44], as well as so-called "non-targeted screening" aided by chemometrics [45-50] and with the powerful support of mass spectrometry [51-55]. Since NMR delivers for each molecule its own spectral fingerprint with high selectivity, not only quantification of ingredients is possible, but also comparison, discrimination or classification of foods, beverages and other consumer products can be achieved [56, 57], together with insights on the principal nutritional parameters. NMR techniques are used for quantitative analysis according to the requirements of DIN/ISO 17025. Great advantages of the NMR methods are the quantification of a single analyte without the pure reference substance, by applying another standard; external calibration, high precision and accuracy, no need for analyte derivatization or chemical manipulations during sample preparation, simultaneous quantitation of a set of analytes. However, the characteristic high specificity of NMR cannot be guaranteed or cannot be achieved when necessary signals for identification are not clearly visible in the spectrum, and/or cannot be assigned due to signal overlap. Integration of the signals, useful for quantitative purposes, could limit the obtainment of unambiguous results when peaks to be integrated are not well-resolved or display unsatisfying signal-to-noise (S/N) ratios. To overcome these limitations, ^{13}C NMR techniques can be applied. The resolution and simplicity of carbon signals in proton decoupled spectra, ensure that the analyzed signal does not overlap with other components. If appropriate instrumental conditions are selected, and a pulse sequence is correctly applied in order to zeroing reciprocal signal influences and distortions due to the nuclear Overhauser effect (NOE), proton decoupled ^{13}C spectra can represent a powerful tool for quantitative determinations of the principal components present in complex mixtures [58-60].

Seed oil samples were first subjected to the proton analysis. Spectra of all samples showed the same set of signals which were characteristics of relatively simple mixtures of triacylglycerols (TAGs). The typical plot of a high-resolution ^1H NMR spectrum of a seed oil, recorded in deuterated chloroform, is illustrated in Figure 1.

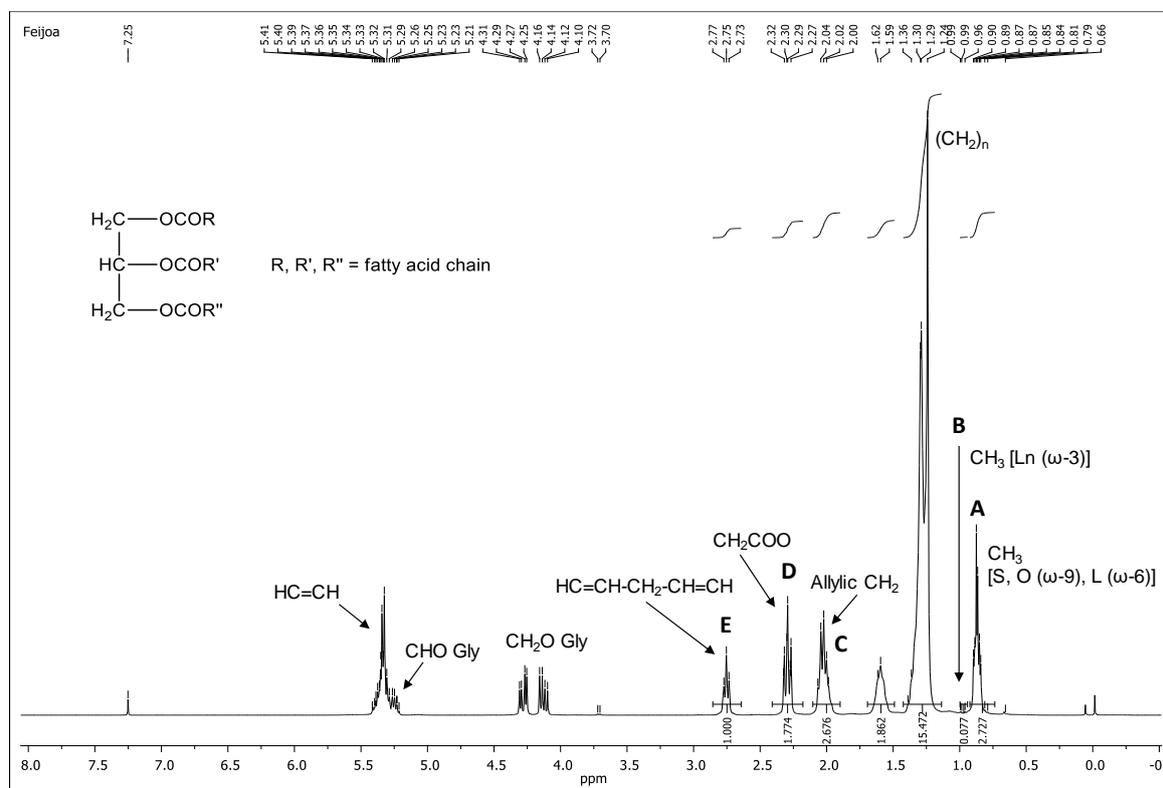


Figure 1. Full high-resolution ^1H NMR spectrum as obtained for a sample of Feijoa seed oil. Letters A-E show the integrated proton signals useful to determine the fatty acid chain profile.

Figure 1 displays the complete proton spectrum obtained for the oil extracted from feijoa seeds. This spectrum was chosen as an explicative example. Relevant and intense signals in the ^1H NMR spectra of all seed oils were observed. Peaks at 0.85–0.87 ppm were generated by the terminal methyl protons in S, O, and L acyl chains, and a strong signal centered at ca 1.30 ppm was attributed to the methylene protons of all hydrocarbon chains; the signal at 1.52–1.54 ppm was assigned to β -carbonyl methylene protons in all fatty acid chains, allylic protons gave a multiplet centered at 2.20 ppm, and a triplet at 2.25–2.28 ppm was assigned to the α - CH_2 protons in all fatty acid chains. Signals in the region between 4.00 and 4.50 ppm were generated by the methylene protons in the sn-1 and sn-2 positions of the glycerol moiety, and the complex multiplet at 5.21–5.48 ppm was due to the overlap of the resonances generated by olefinic protons and the sn-2 methyne in the glycerol backbone. Another well-distinguishable signal, appearing as a triplet centered at 0.97, is assigned to the protons of the terminal methyl group in the polyunsaturated fatty chain, and it generally characterizes oils containing linolenic acid in variable amounts. However, this signal did not appear in proton spectra recorded for all seed oils which were the object of this study. As reported elsewhere, [24] five signals appearing in the spectral window between 0.70 and 2.90 ppm should be selected in order to determine the oil profile. They comprise the four signals signed by the letters A, C-E in Figure 1, while the letter B conventionally indicates the integral of the signal generated by the linolenic methyl group. The spectrum reported in Figure 1 lacks this triplet, as well as all the spectra recorded for all oils (Figure 2), making not possible the ω -3 determination. As a consequence, the method based on the values of signal intensities cannot fully be applied, suggesting the need for a supplement of information obtainable by ^{13}C NMR.

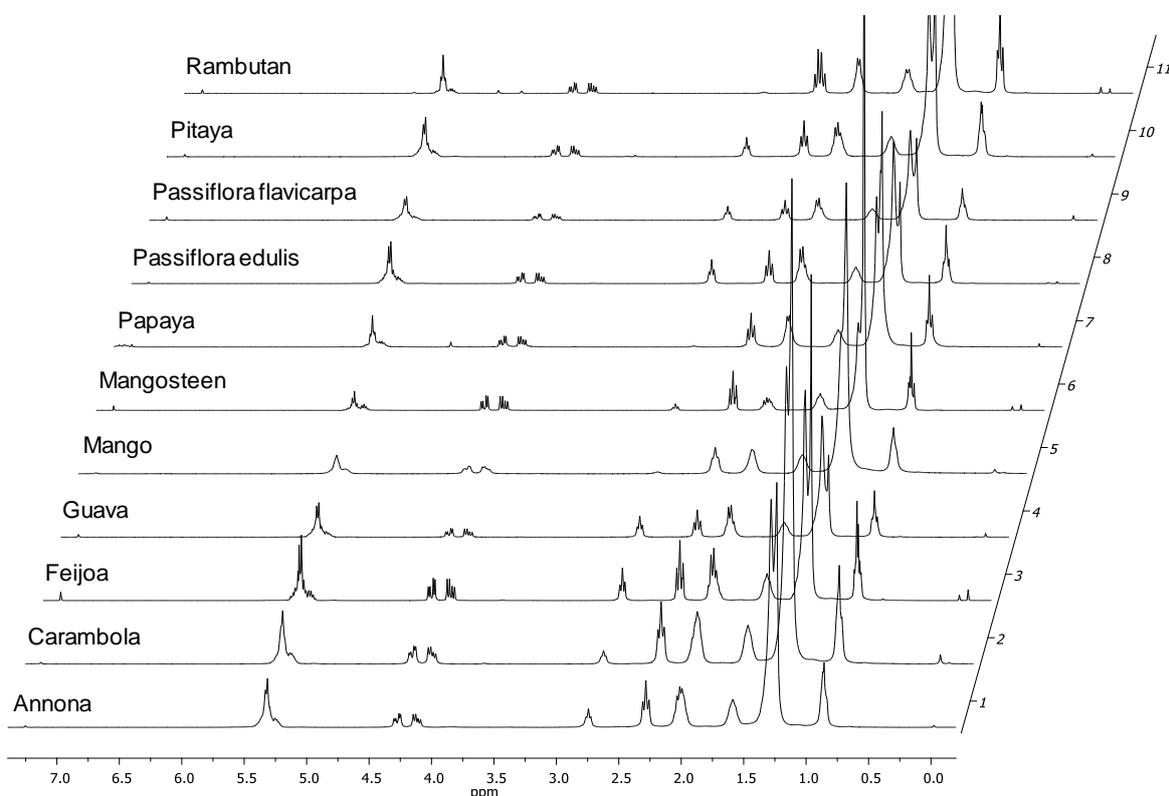


Figure 2. Stacked plots of high-resolution ^1H NMR spectra obtained for all eleven exotic fruit seed oils.

The strong similarities between the spectra obtained from oils and those recorded for a mixture of standard triacylglycerols, suggested using a simple mathematical method already applied to determine the fatty acid acyl chain compositions in a series of edible oils [24]. The intensities of the four resolved signals A, C-E (Figure 1) were used. The repeatability of NMR measurements was verified by recording spectra in triplicate for each seed oil as obtained by the Soxhlet extraction. The integration limits of each signal were carefully defined, and sample spinning was avoided in order to exclude any contribution of side peaks and artifacts. The method showed an excellent repeatability. Integration of each spectrum was repeated seven times, so that the deviation of all measures was limited at level of the third decimal figure. The intensity of the signal E was calibrated at 1.00, and used as reference value for the integration of the other four signals A, C, and D. Unexpectedly, all recorded proton spectra did not feature the ω -3 methyl signal in a detectable intensity. Nevertheless, this was not indicative for the total absence of linolenic acid chains (Ln) in seed oils, thus the presence of this fatty acid was not excluded directly on the basis of the proton spectra. As the ω -3 contents cannot be estimated, seed oil profiles were expressed as mainly composed by oleic, linoleic, and saturated fatty acid chains (O, L, and S, respectively, in Table 1). Due to the lacking values of linolenic acid chains, the commonly accepted nutritional ratio between the contents of ω -6 and ω -3 was not calculated. Finally, as highlighted by ^1H NMR spectra, no signals attributable to diglycerides (DAG) were observed in the region between 3.50 and 4.00 ppm, for all samples subjected to the analysis, suggesting the oils to be predominantly composed by TAGs [61, 62].

We therefore carried out the high-resolution ^{13}C NMR analysis of seed oils, to confirm the presence of the fatty acid chain detected and quantified by ^1H NMR, and to identify and semi-quantitate the principal fatty acids present in samples, without determine their regioisomeric distributions on the three carbons of the glycerol backbone, as commonly reported for vegetable oils and fats [63-68].

^{13}C NMR has the advantages of shorter analysis times, precision and accuracy over laborious conventional chemical hydrolysis methods based on GC-FID and GC-MS techniques. However, high-resolution ^{13}C NMR techniques were only sparingly employed in determining the fatty acid chain profile in oils and fats, maybe due to the operational protocols which must be optimized in order to achieve the best instrumental settings for quantitative purposes. The last aspect might increase the times required for the analysis, although ^{13}C qNMR could be challenging in defining profiles of vegetable complex matrices. Another advantage of ^{13}C qNMR consists in its striking versatility and powerful when the target of the analysis is the determination of analytes present in very low concentrations, whose molecular structure furnished proton resonance signals that can strongly overlap signals generated by the other components of the natural complex matrix. For all considered oils, the absence of detectable amounts of free fatty acids in all samples, this means also amounts lower than the sensitivity limit of the spectroscopic method, was assessed by high-resolution proton decoupled ^{13}C NMR experiments.

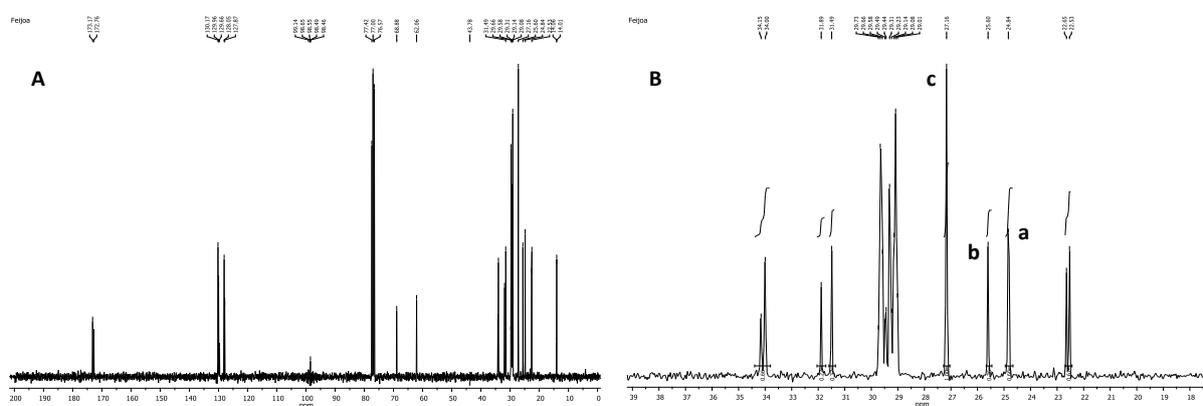


Figure 3. (A) Full high-resolution ^{13}C NMR spectrum as obtained for a sample of Feijoa seed oil; (B) spectral window showing the integrated carbon signals useful to determine the fatty acid chain profile.

A spectrum recorded for a sample of pitaya seed oil is reported in Figure 3A. The plot showed different series of signals distributed in distinguishable and narrow regions. The spectral window displayed in Figure 3B shows the resonances used for the quantitative determinations. Referring to Figure 3B, the spectral region between 21.0 and 28.0 ppm contains signals which can be assigned to the carbons picked for quantitation. In particular, in the spectrum of Feijoa seed oil, the signal at ca 24.8 ppm was assigned to allylic C-3 of all the saturated, oleic and linoleic acid chains present in each oil. The signal appearing at ca 25.6 ppm indicated the resonance generated by C-11, the allylic position to both double bonds, thus it was indicative for the total number of linoleic acid chains. Carbons C-8, C-11 of O and C-8, C-14 of L, allylic to cis double bond, gave signals at ca 27.2 ppm, representing twice the total number of O and L chains. Similar ppm values can be assigned to the same classes of carbons in all the other oils. The integrals of these signals allowed us to quantitate the contents of S, O and L chains, as they were determined from the intensities of the respective peaks (a, b, and c; Figure 3B). A set of simple mathematical equations, according to a previously reported method [69] was applied to compute the S, O, and L percentages (Table 1). Since no signals were found in the spectral region centered at ca 32.0 ppm, the presence of trans double bonds [70] in the seed oils can be excluded, at least upon the sensitivity limits of the spectroscopic method. Correlations between signals and the different acyl chain structures were assigned by recording spectra for each standard TGA and for a mixture of these compounds, under the same instrumental, concentration, and temperature conditions. The assignment was further supported and confirmed by the literature data [71-74]. Figure 4 displays the stacked plots of all seed oils analyzed.

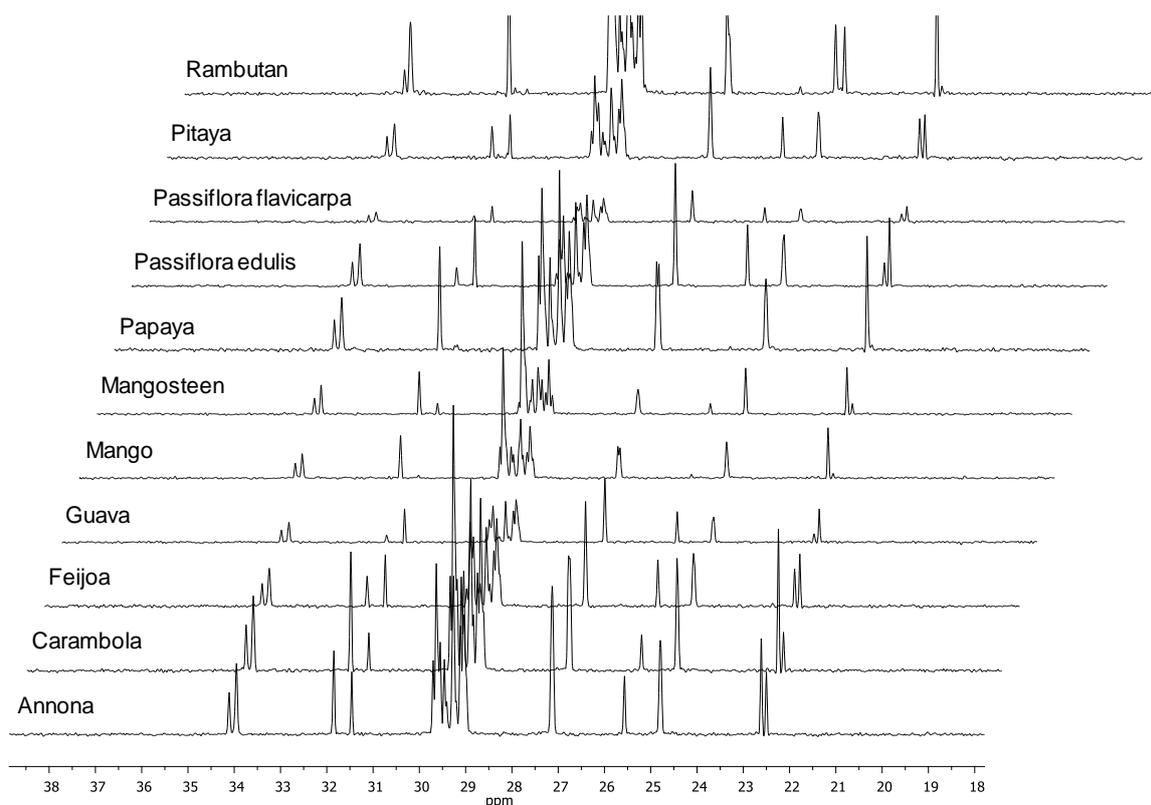


Figure 4. Stacked plots of high-resolution ^{13}C NMR spectra obtained for all eleven exotic fruit seed oils.

The proton decoupled carbon spectra excluded also the presence of free fatty acids in oils. In fact, in all recorded carbon spectra, no signals generated by the COOH resonance in free fatty acid chains were detected in the narrow spectral region between 175 and 180 ppm.

Thus, considering the sensitivity limits of the instrument and spectroscopic method, the obtained data were mainly referred to the triacylglycerol fatty acid chain profiles.

This evidence highlighted the triacylglycerols (TGAs) to be the predominant components (95-97%) of all the recovered oils. Data obtained by ^1H and ^{13}C spectra for all oils are collected in Table 1. Fatty chain acyl chain profiles are expressed as mean values together with the respective standard deviations.

A rapid overview of data reported in Table 1, allows to make some considerations about the oil compositions. In all the investigated oils, the saturated fatty acid chains were found in amounts ranging from 7.9% to 49.5%.

The most important components of the starfruit seed kernels of Carambola were oleic and linoleic acids, together forming about 69.2% of the total fatty acid chain profile. A high prevalence of MUFA and PUFA, with the predominance of ω -6 chains, was observed for the seed oil extracted from Feijoa fruits.

Guava fruits also gave an oil rich in unsaturated fatty acid chains, with linoleic and oleic acid being present in 74.4% and 9.9%, respectively. Mango seed kernel oil was characterized by high amounts of oleic acid (46.4%), while Mangosteen produced an oil containing the essential linoleic acid in very small proportions (3.7%).

In Mangosteen, saturated (47.3%) and oleic acid (33.8%) chains were the most prevalent components of the seed oil. Analysis of the Papaya seed oil composition revealed that oleic fatty acid chains were present in 68.7%, while the amount of linoleic acid was relatively low (4.5%).

Table 1. Fatty acid chain profiles of exotic fruit seed oils, as calculated from ^1H and ^{13}C NMR data.

Seed oil		SFA (S, %) ^a	MUFA (O, %) ^a	PUFA (L, %) ^a	SFA/PUFA (%) ^b
Annona	^1H	24.1 ± 1.0	37.3 ± 1.2	36.2 ± 1.6	0.33
	^{13}C	23.4 ± 0.9	37.9 ± 1.3	35.8 ± 1.6	0.32
	[75,76]	<i>24.15</i>	<i>38.58</i>	<i>35.97</i>	<i>0.32</i>
Carambola	^1H	29.3 ± 0.9	48.4 ± 1.4	20.7 ± 0.7	0.42
	^{13}C	28.8 ± 0.8	47.2 ± 1.3	22.0 ± 0.5	0.42
	[77]	<i>30.26</i>	<i>45.83</i>	<i>22.33</i>	<i>0.44</i>
Feijoa	^1H	7.2 ± 0.3	6.1 ± 0.2	82.3 ± 5.0	0.08
	^{13}C	7.9 ± 0.4	6.9 ± 0.1	84.6 ± 5.2	0.09
	[78]	<i>8.36</i>	<i>7.21</i>	<i>88.44</i>	<i>0.09</i>
Guava	^1H	10.9 ± 0.6	11.0 ± 0.4	75.8 ± 0.8	0.13
	^{13}C	11.6 ± 0.6	9.9 ± 0.3	74.4 ± 0.8	0.14
	[79,80]	<i>11.8</i>	<i>10.09</i>	<i>76.4</i>	<i>0.14</i>
Mango	^1H	44.2 ± 2.7	45.8 ± 2.6	8.1 ± 0.2	0.82
	^{13}C	42.3 ± 2.6	46.4 ± 2.6	7.0 ± 0.3	0.79
	[81]	<i>44.42</i>	<i>45.76</i>	<i>7.45</i>	<i>0.83</i>
Mangosteen	^1H	46.9 ± 1.5	33.1 ± 2.6	3.2 ± 0.2	1.29
	^{13}C	48.3 ± 1.0	33.8 ± 2.1	3.7 ± 0.1	1.29
	[82].	<i>49.5</i>	<i>34.0</i>	<i>1.30</i>	<i>1.40</i>
Papaya	^1H	23.3 ± 0.9	70.2 ± 1.3	4.1 ± 0.1	0.31
	^{13}C	21.8 ± 0.7	68.7 ± 1.5	4.5 ± 0.2	0.30
	[83,84]	<i>19.30-22.15</i>	<i>70.5-74.7</i>	<i>3.63-4.60</i>	<i>0.26-0.28</i>
Passiflora e.	^1H	9.8 ± 0.4	14.0 ± 0.9	69.9 ± 2.8	0.12
	^{13}C	10.9 ± 0.4	14.2 ± 0.6	68.4 ± 2.7	0.13
	[85]	<i>11.0</i>	<i>13.6</i>	<i>67.8</i>	<i>0.14</i>
Passiflora f.	^1H	14.1 ± 0.3	12.6 ± 0.6	70.8 ± 1.0	0.17
	^{13}C	12.3 ± 0.3	13.1 ± 0.5	71.7 ± 1.1	0.15
	[86]	<i>14.1</i>	<i>16.9</i>	<i>74.3</i>	<i>0.15</i>
Pitaya	^1H	19.8 ± 0.6	21.2 ± 0.2	51.2 ± 2.7	0.27
	^{13}C	21.0 ± 0.3	20.9 ± 0.3	49.0 ± 2.6	0.30
	[87,88]	<i>22.78</i>	<i>22.81</i>	<i>49.6</i>	<i>0.31</i>
Rambutan	^1H	51.0 ± 2.2	44.7 ± 1.0	2.8 ± 0.1	1.07
	^{13}C	49.5 ± 2.5	45.2 ± 1.1	3.5 ± 0.1	1.02
	[89,90]	<i>50.7</i>	<i>40.3</i>	<i>ND</i>	<i>1.25</i>

^a Percentages reported as the mean values ± SD for experiments carried out in triplicate. ^b Ratios calculated on the basis of the respective mean values. Squared brackets indicate the bibliographic references where the corresponding fatty acid profiles (italicized) have been published; (S, O, L

indicate the saturated, oleyl, and linoleyl fatty acid chain, respectively). The spectroscopic method highlighted similar fatty acid chain profiles for the seed oils obtained from *Passiflora edulis* (the yellow passion fruit) and *Passiflora flavicarpa* (the purple passion fruit). In these cases, the fatty acid chain profiles showed linoleic acid to be the most abundant component. The numerous grainy seeds of Pitaya produced an oil which was mainly characterized by the high amounts of unsaturated fatty acid chains. Finally, saturated (49.5%) and oleic (45.2%) fatty acid chains were predominant in Rambutan seed oil, which was recognized to contain very low amounts (3.5%) of linoleic acid. Unexpectedly, the most part of seed oils used in this study did not contain linolenic acid in detectable amounts, although the literature reports this acid to be present in very low concentrations in seed oils obtained by *Annona cherimola* [75,76], Mango [81], and Pitaya [87, 88] oily extracts. The ratio of saturated to unsaturated fatty acids (U/S, with U as the sum of oleic, and linoleic acids) ranged between 0.8 for Mangosteen, and 11.6 for Feijoa, indicating that all oils could be considered promising candidates for a healthy nutrition, and potential feedstock for the production of biodiesel. All experimental data closely agreed the data reported in the literature, obtained by GC-FID and GC-MS techniques, for the same seed oils.

4. Conclusions

The present investigation discloses information on the composition of eleven potentially edible oils extracted from seeds of commonly sold exotic fruits. The complementary use of high-resolution ^1H and ^{13}C NMR spectroscopy proved these techniques to be rapid and reliable analytical tools for the evaluation of the fatty acid acyl chain profiles of seed oils. For all oils, the percentages of saturated, oleic, and linoleic chains were determined as the most abundant components. Signals generated by protons and carbons of the linolenic acid chain were not detected by either ^1H or ^{13}C NMR analysis, demonstrating that all the investigated oils are characterized by poor contents of total ω -3. Notwithstanding, the fatty acid chain profiles might give to these unexploited seed oils a nutritional, cosmetic, and medicinal importance. The seeds were generally found to be rich in oil. Oils showed high contents linoleic and oleic acid chains, active in cholesterol metabolism and exerts a protective role against cardiovascular diseases [91-93], together with reduced amounts of the saturated components. Thus, all the investigated seed oils might favorably replace more expensive conventional oils, and they could be useful as edible oils and for industrial and energy applications. However, the safety of all oils must be assessed before use for human nutrition and/or in animal feeding.

5. References

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