

Preliminary Studies on Composition, Quality and Oxidative Stability of Commercial Avocado Oil Produced in Chile

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Abstract: Avocado oil is a relatively new oil in the market and is highly appreciated by the consumers because of its fine aroma, pleasant taste and health benefits. A study on the characterization of commercial avocado oils produced in Chile was conducted in order to discuss their quality parameters. The study was applied to two marketed avocado oils. The main analytical parameters evaluated to the oils were: fatty acid composition, total chlorophylls, total carotenoids, tocopherols, acid value, peroxide value, total phenolic compounds, polar compounds, oil stability, UV absorption and 3.5-stigmastadiene content. The fatty acid compositions of the studied oils were according with oil composition of pulp pure of avocado fruit. The analysis of tocopherols by high performance liquid chromatography (HPLC) revealed significant differences between the avocado oils studied. Total phenolic compounds, oil stability, UV Absorption characteristics, peroxide value, acid value, tocopherols content, total chlorophylls, total carotenoids and polar compounds were also significantly different between the commercial studied oils. All the above results show a different quality between both commercial avocado oils, showing that the sample C has worse values for the parameters of quality as those required by legislation in many countries. Also, 3.5-stigmastadiene content shows high concentration for one of the commercial avocado oil evaluated which demonstrates the presence of refined oil or that the oil has been submitted to high temperatures. On the other hand it is remarkable that despite the fact that there are many differences in quality parameters, both oils are labeled and marketed as extra virgin quality oils, demonstrating the need to regulate the classification of appreciated oils by the consumers.

Key words: Avocado oil, 3.5-estigmastadiene, polar compounds, quality parameters.

1. Introduction

Oils and fats are highly complex mixtures containing a wide range of components, where each of the groups in turn can contain a very wide range of chemically similar analytes. The most important group of compounds presents in oil and fats are the triacylglycerols (TAG), triesters of glycerol with three fatty acids [1]. Each group of compounds present in oil has been used to determine quality of oils highly appreciated even these compounds have been analyzed by a variety of techniques and analytical methods to identify issues of contamination and/or adulteration with less expensive oils [2].

Presently, avocado oil is not highly significant within the world context. However, in the recent years, the national production of avocados in Chile has increased its cultivation area steadily, while simultaneously contributing to the production of avocado oil [3]. So it is possible to find several products in the Chilean market.

Due to the composition of its fatty acids, the avocado oil meets the nutritional requirements that focus on the reductions of the amount of saturated fats in food. It is characterized by the fact of having a low amount of saturated fatty acids (between 10% and 19%,

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depending of the variety and maturity stage), a high amount of oleic acid (close to 80%), and acceptable level of fatty acids polyunsaturated (11%-15%) and no cholesterol. This helps prevent diseases such as cancer, diabetes, Alzheimer's and heart disease course, as they are directly related to the presence of cholesterol [4]. Also avocado oil is rich of β -sitosterol, E vitamin and other components of the unsaponifiable fraction with biological activity [5, 6].

Avocado oil has the advantage which is obtained by means of a cold extraction method that allows maintaining in the oil significant amounts of the bioactive compounds present in the fruit as occurs in olive oil extraction. However, it should be mentioned that, when obtained by non-cold-press extraction procedures, physical and chemical characteristics of the final product can suffer changes [7].

Minor components as tocopherols and phenolic compounds are of great importance as natural antioxidants of vegetable oils and are also added to oils for improving their stability against oxidation [8]. Crude vegetable oils as so called extra-virgins also contain different components such as sterols, carotenoids and phospholipids, which increase their stability and also can be used to detect contamination and/or adulteration of appreciated oils with low quality vegetable oils decreasing their nutritional and commercial value according to data published by various authors [9, 10]. Others authors [11] indicated that low concentrations of refined oil can be detected by the presence of 3.5-stigmastadiene, substance produced by dehydration of β -sitosterol as a result of thermal treatment favored by bleaching earth, analogously to how it produces 3.5-cholesta diene from cholesterol in butter refined [12].

Though the production of avocado oil in the world is small compared with other oils, Chile is among the leading producers. At the present, avocado oil produced in Chile is dominated by the Hass variety. Its presence on the markets is only occurring in the present century, and limited published information still exists on this oil [13]. In this sense there are just a few regulations that regulate the quality of avocado oil, opposite to what happens with others appreciated oils. Mexican rule proposes just two categories for avocado oil and is not sufficient in terms of the quality parameters that can be determined in the different obtained methods and storage conditions of the oils, as with occurs in appreciated vegetable oils [14]. Avocado oil is highly appreciated because of its fine aroma, pleasant taste and health benefits. According to the literature reviewed, there is not too much information about different qualities of avocado's oil. Therefore, in this regard there is much work to do on quality and authenticity of avocado oil. Detection of deterioration compounds is an important criterion for the determination of quality and the protection of wealth and health of consumers.

The aim of this work was to study the composition, quality and oxidative stability of commercial avocado oil produced in Chile.

2. Materials and Methods

2.1 Oil Samples

Commercial avocado oils Hass variety (samples C and R) were purchased in Chilean market and were labeled as virgin avocado oils. Avocado fruits Hass variety were purchased in a Spanish market. Oils from avocado fruit were obtained by 6 h Sohxlet extraction with petroleum ether, previously the fruit samples were dried. Once acquired, all the samples of oils were kept at -30 °C until analysis.

2.2 Reagents and Standards

All reagents were of analytical grade. Standard of 3.5-cholestadiene and chlorophyll-a was purchased from Sigma-Aldrich (Sigma-Aldrich Química, Madrid, Spain).

2.3 Analytical Determinations

Fatty acid composition of the oil samples was determined by gas chromatography fitted with a flame

ionization detector (FID) previous preparation of the fatty acid methyl esters derivatives. A Hewlett Packard Model: 5890 Series II gas chromatograph equipped with a split-splitless injector and automatic autosampler, and coupled to a computerized Chromcard system for data aquisition was used. It was fitted with a SP2380 capillary column (30 m length, 0.25 mm i.d., 0.20 µm film thickness). The carrier gas was hydrogen at a flow rate of 1 mL/min. the temperatures of the injector and detector were held at 220 °C and 250 °C, respectively. The initial oven temperature was 180 °C and a temperature gradient from 180 °C to 220 °C at 3 °C/min was applied. The injection volume was 1 µL. The details of the method were described by Ourrach et al. in 2012 [15].

The analyses of total chlorophylls and carotenoids were based on the evaluation described previously by Minguez-Mosquera et al. [16], where maximum absorption at 670 nm was related to chlorophyll fraction, while the maximum absorption at 470 nm was related to the carotenoid fraction. Tocopherols were determined following the method proposed by International Union of Pure and Applied Chemistry (IUPAC) [17]. Total phenols content was quantified colorimetrically as proposed by Ranalli et al. in 1999 [18].

Determination of oil quality parameters (free acidity, peroxide value and UV absorption characteristics (K 232 y K270)) was done according to the analytical methods described in the EC Regulations. Oxidative stability was carried out using Rancimat (Metrohm, Herisau Switzerland) apparatus and was evaluated as proposed by Gutierrez in 1989 [19], with some slight modifications. The content of total polar compounds was determined gravimetrically according to the method proposed by Dobarganes et al. in 2000 [20].

Total polyphenols content was quantified colorimetrically. The phenolic content was extracted according to the method described by Rehab and Anany in 2012 [21]. Briefly the analytes were isolated by a triple extraction of solution of oil (15 g) in hexane (10 mL) with methanol/water (10 mL, 60:40 v/v). The

absorbance was measured at 725 nm against the blank using a spectrophotometer UV-Visible Spectrometers PG Instruments T80+. Gallic acid was used as the standard and the results were given as gallic acid equivalents according to the proposed method by Gutierrez et al. [22] and Folin-Ciocalteau reagent (Merck) was added to a suitable aliquot of the combined extracts. All samples were analyzed at least in triplicate unless otherwise stated.

Steroidal hydrocarbons determinations; the quantification of 3.5-stigmastadiene in avocado oils follows the methodology standardized by the IUPAC [23]. Mass spectrum was obtained from a gas chromatographer Trace GC Ultra equipped with a mass detector Finnigan Polaris, column DB-5MS (length 30 m, film thickness 0.25 µm and column I.D. 0.25 mm), electron impact mass spectra were obtained at 70 eV of electron energy, and monitored from mass to charge ratio (m/z) 60-700. The ion source was fixed at 200 °C. Chromatographic conditions were as follows: The oven temperature was programmed from 80 °C to 270 °C at 8 °C/min, and then held isothermally for 10 min. Relative composition of the individual constituents was determined from the peaks and are relative to the total peak area.

3. Results and Discussion

Fatty acid composition for all avocado oils showed a composition having a high content of oleic acid (> 60%) (Table 1) for both commercial origin oils and the oil

Table 1FAMEs percentage in commercial (C and R) andpure avocado oils.

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Sample	С		R		Pure			
	Mean	SD	Mean	SD	Mean	SD		
C16:0	12.79	0.0634	13.41	0.0011	17.37	0.0015		
C16:1	3.34	0.0006	3.81	0.0005	7.52	0.0002		
C18:0	0.98	0.0003	0.63	0.0003	0.63	0.0002		
C18:1	67.69	0.0019	65.43	0.0018	62.89	0.0019		
C18:2	13.54	0.0004	15.15	0.0006	10.64	0.0004		
C20:0	0.18	0.0003	0.09	0.0001	0.07	0.0003		
C18:3	1.21	0.0001	1.26	0.0001	0.72	0.0001		
C20:1	0.28	0.0001	0.23	0.0001	0.16	0.0002		

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obtained from the pulp of the fruit. This acid varied between 62.9% and 67.7%. The palmitic content varied between 12.8% and 17.4%. Linoleic acid (C18:2) varied between 10.6% and 15.2%. The avocado oil samples also contained low amounts of linolenic acid (C18:3), arachidic acid (C20:0) and palmitoleic (C16:1). These results are according with fatty acid profile for avocado oil data published elsewhere [24]. Commercial avocado oil samples were found to have a higher percentage of polyunsaturated fatty acids (15%) due to their high content in linoleic acid.

The profile of analytical parameters such as peroxide value (PV), free fatty acid content and extinction coefficients 232 and 270 (Table 2) showed significant differences between the samples (*P*-value 0.0001) when comparing means with the Student's *t*-test two-tailed with six degrees of freedom. The sample C shows the worst values. Sample R was found to have higher content in total phenols (56.9 ppm), with major stability time obtained in sample R (20 h of induction time). Sample C also shows lower content of total chlorophylls, total carotenoids and α -tocopherol (Table 3) in an amount less than half the sample R which is confirmatory of a different quality for similar products.

It is know that virgin vegetable oils as virgin olive oil are obtained by cold pressing and do not contain measurable amounts of 3.5-stigmastadiene. Due to the high temperatures in the bleaching and deodorizing part of the refining process, 3.5-stigmastadienes are formed by the dehydration of β -sitosterol (Fig. 1).

The analyte eluted in the second fraction of hydrocarbons compounds is attributed to 3.5-stigmastadiene (Fig. 2). This analyte is also considered to detect the presence of refined oil in virgin olive oil. In this sense, it is an important quality parameter for contamination and/or adulteration. The chromatographic separation runs the risk of interference to other hydrocarbons, in this sense the peak B in Fig. 2 was submitted to mass spectrometer. Full mass spectrum to peak B is showed in Fig. 3 and is according with the library of the instrument and mass spectrum published elsewhere [11]. It is also attributed to 3.5-estigmastadiene based on the mean peaks of the spectrum.

Table 2Quality parameters of commercial avocado oilsamples.

	С	R
Acidity (% C18:1)	0.4465 ± 0.018	0.5583 ± 0.015
PV (Meq O ₂ /kg)	12.95 ± 0.015	8.013 ± 0.296
K ₂₇₀	0.72 ± 0.01	0.17 ± 0.003
K ₂₃₂	4.19 ± 0.09	3.16 ± 0.06
Oxidative stability (h) ^a	14	20
Polar compounds	6.95 ± 0.3	5.93 ± 0.5
Phenols (mg/kg)	42.6 ± 1.1	56.9 ± 0.9
3.5-stigmastadiene (mg/kg)	45.6	n.d

^a Average value (n = 2);

n.d = not detected.

Table 3 Total chlorophylls, carotenoids and α -tocopherol in commercial avocado oils (data are expressed in mg/kg).

Sample	Chlorophyll	Carotenoids	a-tocopherol
С	22.3 ± 1.0	11.1 ± 0.3	40.5 ± 0.45
R	69.8 ± 4.0	46.9 ± 1.8	103.5 ± 1.03

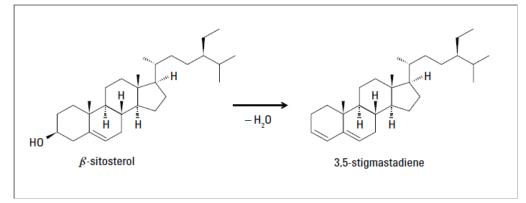


Fig. 1 Formation of 3.5-stigmastadienes by dehydration of β-sitosterol.

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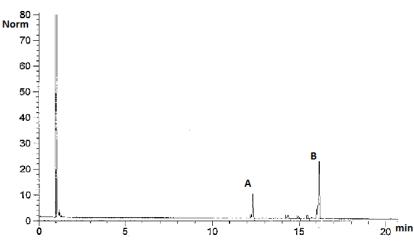


Fig. 2 Chromatogram of second fraction of hydrocarbons eluted on silica gel column of avocado commercial oil (C). Peak A: 3.5-cholestadiene (I.S.), peak B: 3.5-stigmastadiene.

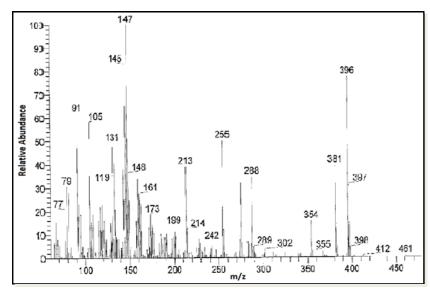


Fig. 3 Mass spectrum peak B in Fig. 2.

4. Conclusions

Fatty acids composition of both commercial avocado oils are similar between them and also with fatty acids composition of the avocado oil pure extracted from the pulp of fruit suggesting no contamination and/or other oils adulteration.

There are significant differences (Student's *t*-test) between the following quality parameters evaluated in both commercial avocado oils: UV absorption characteristics, peroxide value, acid value, tocopherols content, total chlorophylls, total carotenoids and polar compounds, indicating a lower quality for the sample C.

In the world there are few regulations concerning the quality of the avocado oil, even today, they do not cover the different qualities of avocado oils, such as what happens with the regulations which rule olive oils.

The presence of 3.5-stigmastadiene in sample C indicates subjection to high temperatures and therefore degradation of thermosensitive components.

Content of phenolic compounds, carotenoids and α -tocopherol are lower in the sample C which results in less protection for the oxidative stability of the oil.

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