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Volatile Aroma Components of Cold Pressed Virgin Oils from Several Venezuelan Seeds.

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Research Article

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ABSTRACT

The contents of volatile compounds of oils from safflower, sunflower, colza, sesame and grape seeds were determined. The virgin oils were extracted by cold pressing, cleaned by centrifugation and stored in dark glass bottles at 10°C. SPME-GC-MS was applied for extraction, separation and identification of the organic compounds present in the volatile fraction. The identification was also confirmed by comparison of the linear retention indices and the mass spectra with those of standard compounds.. The sesame oil contained small concentrations of hydrocarbons (0.66 mg Kg^{-1}) and carboxylic acids (1.35 mg Kg^{-1}), while the alcohols (3.71 mg Kg^{-1}) and aldehydes (2.16 mg Kg^{-1}) were the most important in safflower virgin oil. The α Pinene was the most abundant among the terpenes of the sunflower oil. All classes of volatile compounds (hydrocarbons, terpenes, alcohols, carboxylic acids, aldehydes and ketones) were detected in the evaluated virgin oils hemp oil. The results showed the variety of compounds that contribute to the flavour of the seed oils, for that reason, future sensory studies are needed to evaluate the acceptance of these virgin oils.

INTRODUCTION

Actually there is a growing interest in newer sources of edible oils with components such as biophenols, sterols and other biologically active compounds with potential benefits to health for that reason, many seeds, fruits, mesocarps and nuts have been evaluated for their oil content, fatty acid composition, etc. Because the refining process of these oils reduced drastically the concentration of the most important minor constituents, the use of virgin oils became as a promising alternative to preserve the original chemical composition.

Volatiles compounds in virgin oils are mainly produced by the oxidation induced by endogenous plant enzymes through the lipoxygenase pathway, while chemical oxidation or exogenous enzymes derived from microbial activity are associated with sensory defects. For instance, fungi have the ability to oxidize free fatty acids to produce compounds such as 2-heptanone and 2-nonanone [4], the presence of other compounds sucha as 1-penten-3-one has been proposed as a marker of metallic-off flavour or the nonanal as a marker for oxidation [9, 10]] while 2-pentenal and 2-heptenal are the main rancidity indicators.

However, the quality of the vegetable virgin oils may depend on market preferences, which are based on consumer perception of aroma, taste and colour; objectionable aroma and taste may lead to product rejection. For that reason, it was necessary to evaluate the type and quantity of the volatile compounds present in virgin oils obtained by mechanical pressing from the oily seeds commercialized in Venezuela.

MATERIALS AND METHODS

Seed samples

Clean and healthy seeds of safflower, colza, sesame and sunflower were obtained from local markets. The grape seeds were supplied by a Venezuelan wine industry as a by product, in this case, the seeds were taken to the

laboratory and cleaned by hand to remove little rocks, shoots, bushes, leafs, etc., and then the seeds were wrapped in polyethylene bags.

Oil extraction

All seeds were milled (< 1 mm) and the virgin oils were expelled by using a hydraulic press designed and manufactured for this study. The crude oils were centrifuged at 5000 g by 10 minutes to remove the solid material that accompanies the oil after the extraction. The quality of the clean virgin seed oils was assessed by the peroxide value and the free acidity measurements.

Analytical methods

The peroxide values of the virgin seed oils were determined by the iodometric assay (CEE 2568/91). The analysis of the fatty acid composition of the triacylglicerols was made by GC after the derivatization to methyl esters by vigorous shaking of a solution of the oil in hexane with 0.4 mL of 2 N methanolic potash solutions. The methyl esters were injected in an Agilent GC 4890 provided with a FID detector. The separation was done in a HP 5 (30 m length) column. Nitrogen was employed as the carrier gas with a flow of 1 mL min^{-1}. The temperatures of injector and detector were 250°C and the oven temperature was set at 210°C. The volume of sample injected was 1 µL.

Determination of volatile compounds

This procedure was adapted from Vichi et al [9]. Solid phase microextraction (SPME) followed by GC were used to analyze the volatile compounds in the oil samples. 1.5 g of oil spiked with 4-methyl-2-pentanol (as internal standard) to a concentration of 1.5 µg/g was placed in a 10 mL vial fitted with a silicone septum. SPME sampling was performed by exposing the DVB/Carboxen/PDMS fiber (50/30 µm, 2 cm long from Supelco Inc., Bellefonte, PA) for 30 min in the headspace of the sample maintained at 40ºC; it was then retracted into the needle and immediately transferred and desorbed for 1 min in the injection port of an Agilent 5890 Series gas chromatograph equipped with a flame ionization detector (FID). Compounds were separated on a Supelcowax-10 column (30 m x 0.25 mm x 0.25 µm, Supelco Inc., Bellefonte, PA) under the following conditions: injection port temperature 260ºC; helium flow 0.8 mL/min; oven temperature ramp: 35ºC for 10 min, 3ºC/min up to 160ºC and then 15ºC/min up to 200ºC (maintained for 5 min). Volatile compounds were identified by comparison of retention times and mass spectra of standard substances (Sigma Aldrich) added to refined olive oil. The equipment used was an Agilent 5975C Series mass spectrometer (Agilent Technologies, USA) equipped with an electron ionization (EI+) detector and coupled to an Agilent 6850 Series gas chromatograph; the capillary column was a DB-Wax (30 m x 0.25 mm x 0.25 µm, J&W Scientific, USA). Helium was employed as carrier gas at a flow rate of 0.8 mL/min. The transfer line temperature was 280ºC and the temperature of the ionization source and the quadrupole were 230ºC and 150ºC respectively, with an electromultiplier voltage of +941 eV.

Identification of volatile compounds

The identification was carried out by mass spectrometry and later checked with available standards. The identity of the volatiles was determined by comparison of their mass spectra data with the information of Wiley Data Base and NBS75k libraries. The volatile compounds were also identified using the relative retention times of the standards with respect to the internal standard 4-methyl-2-pentanol.

RESULTS AND DISCUSSION

Chemical characterization of the virgin oils

The lowest peroxide values (table 1) were obtained for sesame un sunflower oils with free acidities of 0.21 and 0.2 % respectively. The virgin oil grape seeds the highest PV value (10 $meqO_2$ Kg^{-1}), which may be consequence of the natural oxidation processes during the storage of the seeds, considering that this material is a by product of the wine industry and less cares are taken for it disposal. On the other hand, the oxidation in safflower and colza virgin oils has occurred in a lesser extent with PV values less than 10 $meqO_2$ $Kg^{-1.}$

In general, the virgin oils showed low concentrations of saturated fatty acids and variable amounts of mono and polyunsaturated fatty acids such as oleic, linoleic and linolenic acids. The presence of this kind of fatty acids as well as the degree of oxidation detected will be of great importance in the evaluation of the volatile compounds profile.

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Table 1: Peroxyde value, free acidity and fatty acid profile of the pressed virgin oils.

	Safflower	Colza	Sesame	Sunflower	Grape
Peroxide Value ($meqO_2\ Kg^{-1}$)	6.44	7.82	1.25	1.29	9.93
Acidity (% Oleic acid)	0.42	0.38	0.21	0.20	2.16
Fatty Acids	Concentration (%)				
16:0	6.33	0.00	10.4	3.64	8.10
16:1	0.00	0.00	0.00	0.00	0.00
18:0	2.45	2.12	5.40	4.01	4.50
18:1ω9	13.4	72.6	40.9	86.8	20.5
18:2ω6	77.0	23.8	42.7	4.76	66.5
18:3	0.00	0.00	0.61	1.21	0.40
20:0	0.00	1.50	0.00	0.00	0.00
22:0	0.84	0.00	0.00	0.00	0.00

Volatile profiles of pressed virgin oils

The flavour compounds in vegetable oils are low molecular weight compounds which vaporise at room temperature, some of them can dissolve in the mucus of the olfactory epithelium, reaching the olfactory receptors to give the odour sensation. In consequence, the global sensation of odour of a virgin vegetable oil depends on two factors, the type and concentration of the different volatile molecules present. In this work, the volatile compounds were classified in seven groups (table 2), compounds belonging to each of these groups were detected in all oil samples. The higher concentration of total volatiles was found in the sunflower virgin oil (17.9 $\mu g\ g^{-1}$), followed by the virgin oil from grape seeds with a concentration of 15.1 $\mu g\ g^{-1}$. The total volatile concentrations of safflower and colza virgin oils were 7.49 and 6.31 $\mu g\ g^{-1}$ respectively, while the sesame oil showed the lowest volatile concentration with only 2.28 $\mu g\ g^{-1}$.

Table 2: Concentrations of volatile compounds in cold pressed virgin oils.

	Safflower	Colza	Sesame	Sunflower	Grape
Hydrocarbons	0.45 ± 0.05	1.82 ± 0.09	0.66 ± 0.04	1.54 ± 0.06	1.20 ± 0.09
Alcohols	3.71 ± 0.12	1.97 ± 0.10	0.18 ± 0.06	0.27 ± 0.03	4.50 ± 0.14
Aldehydes	2.16 ± 0.09	1.66 ± 0.08	0.03 ± 0.02	1.55 ± 0.05	8.30 ± 0.25
Ketones	Bdl	0.04 ± 0.02	Bdl	Bdl	Bdl
Esters	Bdl	0.09 ± 0.03	Bdl	Bdl	Bdl
Carboxylic Acids	0.94 ± 0.07	0.27± 0.06	1.35 ± 0.09	Bdl	Bdl
Terpenes	0.23 ± 0.06	0.46 ± 0.05	0.06 ± 0.03	14.5 ± 0.09	1.10 ± 0.08
TOTAL	7.49	6.31	2.28	17.9	15.1

Bdl: Below the detection limit

Hydrocarbons

In all virgin oils the hydrocarbons were present in variable amounts. For instance, in the safflower oil were identified the nhexane (0.29 $\mu g\ g^{-1}$) and ndecane (0.07 $\mu g\ g^{-1}$) as the most important hydrocarbons. The linear chain hexane, heptane and octane were identified in the virgin colza oil (0.79, 0.21 and 0.63 $\mu g\ g^{-1}$), but the sesame and sunflower oil only contained nhexane in concentratios of 0.39 and 1.29 $\mu g\ g^{-1}$. In the virgin grape oil were identified only two hydrocarbons: n octane (0.40 $\mu g\ g^{-1}$) and styrene (0.80 $\mu g\ g^{-1}$).

Oxygenated compounds

The oxygenated compounds such as alcohols, aldehydes and ketones play an important role in the flavour and taste of vegetable oils [1]. Salch et al [8] reported that lipoxygenase catalize, besides the hydroperoxyde formation, also the hydroperoxide cleavage via an alcoxy radical to yield final products such as C-5 alcohols. Homolytic hydriperoxide lyase activity, catalyzing the specific cleavage of 13-hydroperoxide of linoleic acid to form

2-penten-1-ol, which was found by Kondo et al. [5] in soybean. Also, the detection of pentenols in several virgin oils suggests that the alcoxy radical is an intermediate during the aroma biogeneration [3].

The volatile alcohols were detected in all oils samples in variable concentrations. For instance, the alcohol concentrations ranged between 0.18 μg g^{-1} for sesame oil to 3.71 μg g^{-1} in the virgin safflower oil. Among the most important alcohols in the head space of the virgin oils were the pentanol and the hexanol with fruity flavours, their were present in safflower (2.61 and 0.71 μg g^{-1}), colza 0.05 and 0.38 μg g^{-1}) and grape seed (3.40 and 0.80 μg g^{-1}) virgin oils. Other alcoholic substances also present in the safflower and colza oils were the 2 and 3 – methylbutanol which are associated with winey and woody odours respectively. Salch et al [8] reported that lipoxygenase catalize, besides the hydroperoxyde formation, also the hydroperoxide cleavage via an alcoxy radical to yield final products such as C-5 alcohols. Homolytic hydriperoxide lyase activity, catalyzing the specific cleavage of 13-hydroperoxide of linoleic acid to form 2-penten-1-ol, which was found by Kondo et al. [5] in soybean. Also, the detection of pentenols in several virgin oils suggests that the alcoxy radical is an intermediate during the aroma biogeneration [3].

The aldehydes along with the alcohols were the most abundant compounds in the head spaces of the virgin oils evaluated. The grape seed oil exhibited the highest concentration of this carbonyl compounds with a concentration of 8.30 μg g^{-1}, with the pentanal, octanal and the unsaturated 2-hexenal at concentrations of 4.20, 1.90, 1.40 μg g^{-1} respectively.

The right chain aldehyde octanal, which was also identified in the sunflower virgin oil (1.36 μg g^{-1}) is a derivative of the oxidation of linoleic acid. It is well known that the pentanal with an odour threshold of 0.24 μg g^{-1} is associated with a sensory description of woody; biter oil was detected in grape seed oil, while the hexanal which was present only in the safflower and colza virgin oils (1.84 and 1.12 μg g^{-1}) have been associated with oxidation processes..

The presence of these compounds in vegetable oils was associated with the oxidation of the free fatty acids such as linoleic and linolenic acids [6]; for example, García-Martinez et al [2] found that hexanal was the most important volatile compounds detected in the safflower oil after 10 days of heating at 60°C, which was derived from the 13 hydroperoxydes formed by the autooxidation of linoleic acids. Other compounds such as pentanal, trans-2-heptanal and trans-2-octenal also were identified as products of the decomposition of the hydroperoxides produced on the linoleic acid molecules.

The 2-methylbutanal and 3-methylbutanal are present in cold pressed safflower and colza oils but they were absent in sunflower and grape seed oils. On the other hand, the nonanal, which is used as a marker for oxidation [9], was only detected in the cold pressed colza oil (0.05 μg g^{-1}).

The carboxylic acids and esters which are other oxygenated compounds important for the flavour of fatty foods, were detected in only three virgin oils: safflower (0.94 μg g^{-1}), colza (0.27 and 0.09 μg g^{-1}) and sesame (1.35 μg g^{-1}) cold pressed oils, with the hexanoic and pentanoic acids as the most important.

Volatile terpenes

The terpenes are secondary metabolites produced by most plants, they were present in all oils samples with concentrations from 0.06 μg g^{-1} for the sesame oil to 14.5 μg g^{-1} for sunflower virgin oil. The Terpenes (pinene, limonene and others) are widespread in nature, mainly in plants as constituents of essential oils and most of them, identified as GRAS (Generally Recognized As Safe), have been found to inhibit the growth of cancerous cells, decrease tumor size, decrease cholesterol levels and decrease microorganism concentration in vitro. For example, d-limonene suppresses hepatic HMG-COA reductase activity, a rate limiting step in cholesterol synthesis, and modestly lower cholesterol levels in animals. D-limonene and geraniol reduced mammary tumors or suppressed the growth of transplanted tumors [7]. Results (table 3) showed that limonene, α and β pinene were present in almost all virgin oils, while camphene, thujene and terpinene were only present in the cold pressed sunflower oil, which also had the greatest amount of this kind of volatile compounds.

CONCLUSION

In general, these results showed the wealthy of volatile compounds detected, mainly in the unconventional virgin oils, which impact in their flavour and eventual acceptation by the consumers. For that reason a detailed evaluation of each class of compounds along with sensory evaluations are necessary in the future.

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Table 3: Concentrations of volatile terpenes in cold pressed virgin oils.

Volatile terpene	Safflower	Colza	Sesame	Sunflower	Grape
Camphene	Bdl	Bdl	Bdl	0.24 ± 0.03	Bdl
Limonene	0.09 ± 0.02	0.42 ± 0.05	Bdl	0.23 ± 0.03	0.50
Thujene	Bdl	Bdl	Bdl	1.16 ± 0.06	Bdl
α - Pinene	0.12 ± 0.02	0.04 ± 0.01	0.03 ± 0.01	11.2 ± 0.11	Bdl
β - Pinene	Bdl	Bdl	0.03 ± 0.01	0.45 ± 0.05	0.60
γ - Terpinene	Bdl	Bdl	Bdl	0.19 ± 0.03	Bdl
Bdl: Below the detection limit					

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