Analysis of the Volatile Fraction from Sunflower Oil Extracted Under Pressure

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ABSTRACT: This study concerns the analysis of volatile components that may contribute to the formation of the flavor of the oil extracted from sunflower seeds. The compounds were trapped on a charcoal cartridge, then desorbed and analyzed by gas chromatography/mass spectrometry. The principal compounds were terpenes (about 225 mg/L) consisting of α-pinene (80%), limonene (5%), sabinene (3.3%), β-pinene (1.8%), 1,2,6,6-tetramethyl-1,3-cyclohexadiene (1.5%), and camphene (1.2%). There were also a small amount of hexanal (1.3%) and traces (<1%) of unidentified compounds, which probably correspond to other terpenic hydrocarbons and to terpenic alcohols and/or aldehydes.

JAOCS 73, 713–716 (1996).

KEY WORDS: Gas chromatography, mass spectrometry, sunflower oil, terpenic hydrocarbons, volatile compounds.

Today, many consumers are interested in "natural" products and in products that have undergone little processing by industry, retaining (more or less intact) some of their original features. In the Mediterranean basin, extra-virgin olive oil is desired for its taste and its nourishing characteristics (1). Seed oils lack positive organoleptic properties; they are tasteless and colorless because refining removes every macroscopic distinctive trait. For this reason, they are not appreciated in those countries where it is customary to use the more savory olive oil. Thus, oilseeds can be extracted under simple pressure without refining. Oils extracted from seeds, such as maize, sunflower, soy, and walnut, by a process under pressure without heat and refining have a small market in northern Europe and in France, due probably to the scant use of extra-virgin olive oil in those countries, where there is no internal olive production. Some of those products have recently appeared also in Italy, particularly in stores specialized in selling herbs and diet products (2). The oils obtained in a process in which simple pressure is used without generation of heat may retain some aromatic components that are characteristic of the original seed; therefore, we studied the volatile components that may contribute to the formation of flavor in the oil extracted from sunflower seeds.

EXPERIMENTAL PROCEDURES

Ten different sunflower oil samples, extracted from seeds cultivated in different locations, were obtained from Alfa Olii Crudi (Girasolio, Alfa Olii Crudi Fabro, Italy) by using the pressure system "Baglioni." This system consists of an oil press, which uses crushed olive stones as draining matter, working at 600 kg/cm^2 (3). The volatile components were adsorbed on a grafitized-charcoal cartridge (1-01R J. Rektorik—analytical accessories, Geneva, Switzerland) by bubbling inert gas (He) (60 mL/min, 15 min) through 10 mL of the oil, contained in a test tube submerged in a thermostatic bath at 37°C, according to the dynamic headspace technique (4–8). The adsorbed components were desorbed for 5 s by using a Rektorik MW1 microwave desorber, coupled with a gas chromatograph/mass spectrometer (Finnigan Mat Magnum, San Jose, CA) equipped with a Supelcowax 10 column (60 m × 0.25 mm i.d.; Supelco, Inc., Supelco Park, Bellefonte, PA). Helium was used as carrier gas with a pressure of 0.5 bar. The introduction of the desorbed vapors into the column was performed with a "split system" of 1/60; the temperature of the interface desorber/gas chromatograph was 150°C, and the oven temperature was programmed from an initial isotherm of 50°C for 2 min to 230°C at a rate of 2°C/min. The mass spectra were obtained by using electronic impact and chemical ionization techniques, with methane as the reaction gas. The identification of the compounds was performed by comparing the retention times with those of pure standards and by comparison and interpretation of the mass spectra. Quantitative evaluation was performed by the internal standard method, with the addition of 0.432 mg of (+) 3-carene into 10 mL of oil.

RESULTS AND DISCUSSION

Figure 1 shows a gas chromatogram of the volatile components of sunflower oil. The principal compounds were terpenic hydrocarbons, most of which have one ring and two double bonds or two rings and one double bond. They have the same number of carbon atoms and are isomers with a molecular weight of 136.24. The most abundant compound, in all samples analyzed, was α-pinene. Limonene (mass spectra are given in Figure 2), β-pinene, camphene, and a small quantity

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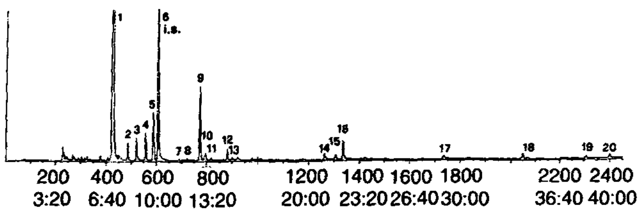

FIG. 1. Gas chromatogram of the volatile components of sunflower oil. The peaks' references are given in Table 1.

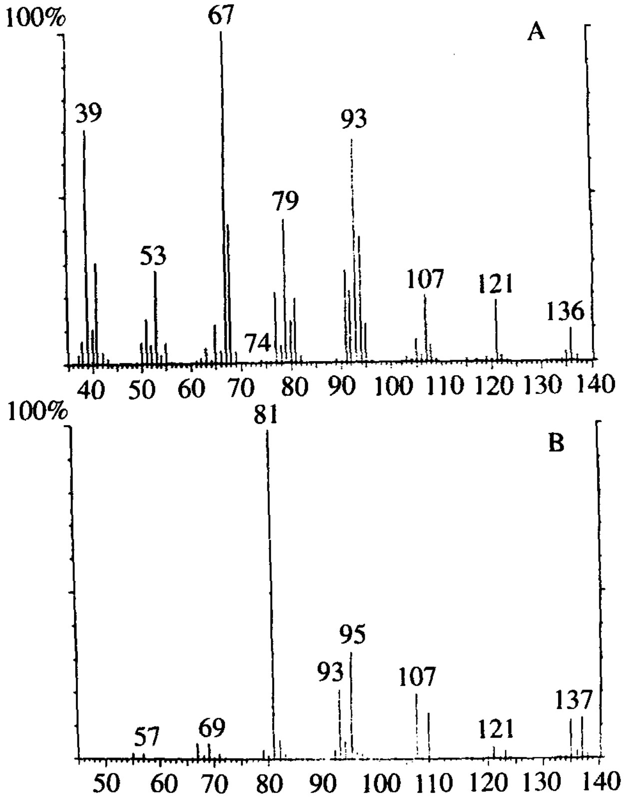

FIG. 2. Mass spectra obtained by (A) electronic impact and (B) chemical ionization of peak 9 in Figure 1 (limonene).

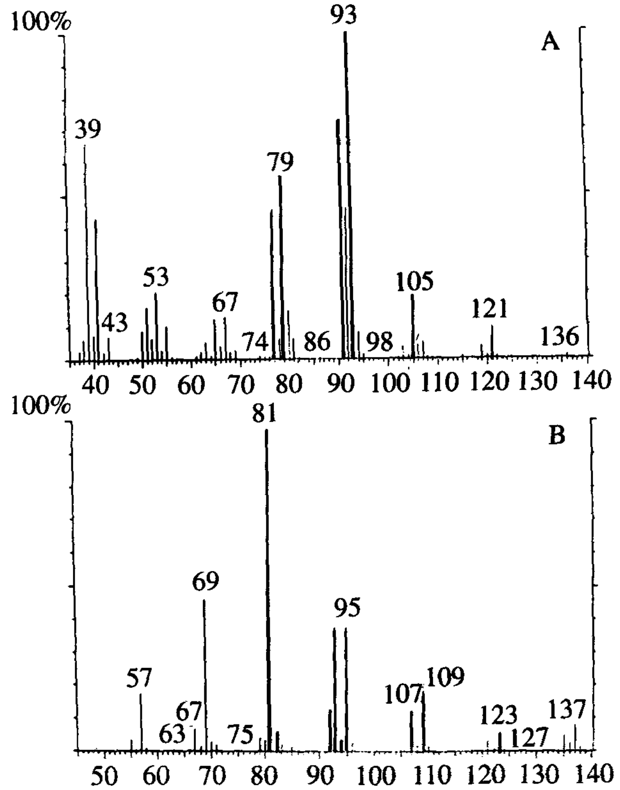

FIG. 3. Mass spectra obtained by (A) electronic impact and (B) chemical ionization of peak 12 .

of hexanal are also shown in the chromatogram. All of these compounds were identified by the mass spectra and by the addition of the pure standard to the oil. Hexanal is an oxidation by-product (9), and it is present in various amounts in the analyzed samples. Peaks 10, 11, and 12 probably correspond to other unidentified terpenic hydrocarbons. The mass spectra, both from electronic impact and chemical ionization, of peak 12 in Figure 3 are similar to the mass spectrum of limonene. The latter part of the chromatogram also shows small quantities of some other unidentified compounds (identified by the numbers 15, 17, 19, and 20 in Fig. 1), which may be positional or geometric isomers of terpenic alcohols and/or terpenic aldehydes. The mass spectra of peaks 19 and 20 (electronic impact and chemical ionization) are shown in Figures 4 and 5, respectively.

Mean percentages, minimum and maximum values of concentration (mg/L), retention times, and molecular weights of the components present in quantities greater than 0.1% of ten different oil samples are reported in Table 1. α-Pinene represents more than 80% of the whole fraction, which is about 200 mg/L, and all other components comprise <5% of the whole, with concentrations between 0.1 and 10.6 mg/L. The unidentified peaks that may correspond to terpenic hydrocarbons are indicated with x-ene, and those that may correspond to terpenic alcohols and/or aldehydes are indicated as x-o. The literature contains many studies on the volatile constituents of alimentary oils; except for olive oil (10–13), they concern processed materials, and the volatile compounds are contaminants (14), derived from the oxidative degradation of hydroperoxides (15,16) or from the reaction between lipids and amino acids (17) at high temperature. Oils obtained by simple pressure, on the contrary, may retain some aromatic component present in the original seed. The principal volatile components present in sunflower oil extracted under pressure are similar in composition to the aromatic constituents of sunflower stems as reported by Buchbauer *et al.* (18); however, limonene is present in the oil in larger amounts (2.7 vs. 0.3%).

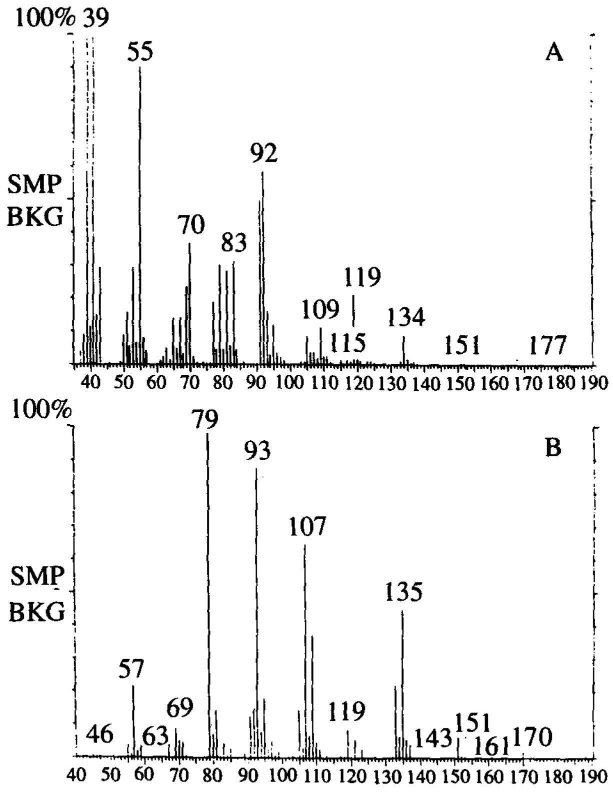

FIG. 4. Mass spectra obtained by (A) electronic impact and (B) chemical ionization of peak 19; SMP, sample; BKG, background.

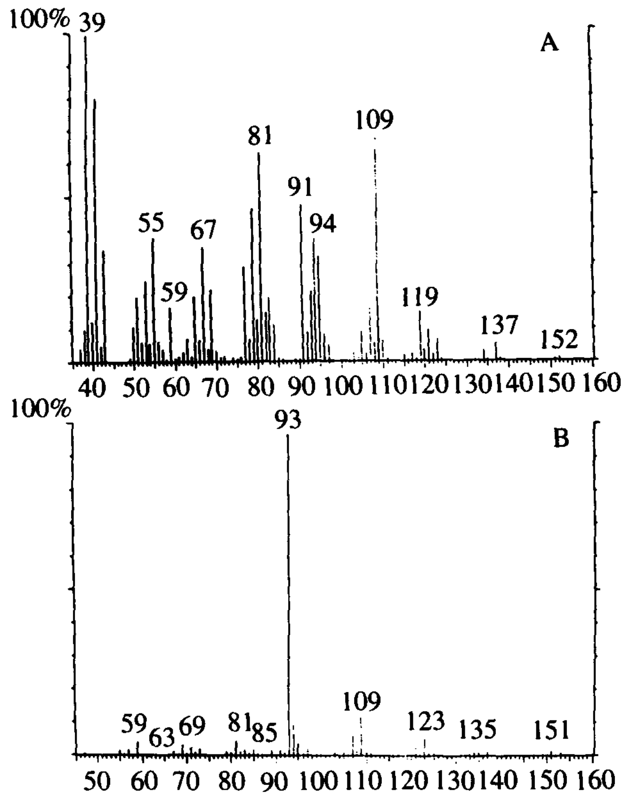

FIG. 5. Mass spectra obtained by (A) electronic impact and (B) chemical ionization of peak 20.

TABLE 1
Analysis of the Volatile Compounds Found in Sunflower Oil

Peak no.	Compound	Area (%)[a]	Concentration (mg/L) Min	Max	Time (min)[b]	MW[c]
1	α-Pinene	84.8	160	205	7.1	136
2	Camphene	1.6	2.3	4.0	8.1	136
3	Hexanal	0.6	0.3	2.6	8.7	100
4	β-Pinene	2.3	3.5	6.3	9.3	136
5	Sabinene	3.6	6.1	10.6	9.8	136
6	3-Carene (I.S.)	—	—	—	10.1	136
7	Phellandrene	0.2	0.1	0.5	11.5	136
8	α-Terpinene	0.3	0.3	1.3	12.0	136
9	Limonene	2.7	2.1	9.9	12.9	136
10	x-ene[d]	0.4	0.3	1.3	13.2	136
11	x-ene	0.1	0.2	0.4	13.6	136
12	x-ene	0.5	0.2	1.4	14.7	136
13	γ-Terpinene	0.4	0.3	1.4	15.0	136
14	x4	0.4	0.3	1.2	21.0	138?
15	x-o[e]	0.1	0.0	0.4	21.8	?
16	1,2,6,6-Tetramethyl-1,3-ciclohexadyene[f]	1.3	1.9	3.2	22.3	136
17	x-o	0.2	0.1	0.6	34.1	152
18	Calarene[f]	0.2	0.3	0.5	34.5	204
19	x7-o	0.1	0.2	0.4	38.5	?
20	x8-o	0.2	0.2	0.5	40.0	152?

[a] Mean values of ten different oil samples; I.S., internal standard.
[b] Retention time.
[c] MW, molecular weight.
[d] x-ene, Terpenic hydrocarbons.
[e] x-o, Terpenic alcohols/aldehydes.
[f] Tentatively identified only by mass spectra.

The presence of terpenic hydrocarbons in sunflower oil, extracted under pressure, may constitute a distinctive feature for the evaluation of this product, but it also gives rise to some questions about the safety and the nourishing properties of the oil, because these compounds are usually present in cosmetic and pharmaceutic products rather than in alimentary oils.

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[Received September 22, 1995; accepted March 20, 1996]