Analysis of Volatile Compounds in Almond and Plum Kernel Oils

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Almond and plum kernel oils were analyzed for volatile flavor components by headspace sampling, gas chromatography and mass spectrometry. The most important volatiles at 37°C, from both fruit oils, are derivatives of benzene, *n*-alkanes, cycloalkanes, aromatics and furan compounds. The structures were established mainly by interpretation of mass spectral data in comparison with literature data.

KEY WORDS: Almond oil, aqueous enzymatic extraction, plum kernel oil, volatiles.

Plum is a widely grown fruit in Europe. Yugoslavia plum production exceeds 250,000 tons a year and, after consumption of the fruit, the kernel remains as waste. Studies of the oil extracted from the plum kernel have been conducted recently (1,2). The composition and characteristics of plum kernel oil are similar to those of almond oil, so plum kernel oil could be used in the cosmetic industry as a substitute for almond oil. The main fatty acids of both oils are oleic (64–78%) and linoleic (17–21%) acid (3–5).

The purpose of introducing an aqueous enzymatic process may vary. A new product that could not otherwise be made may be produced by an enzymatic method, or an existing and well-known product may be enzymatically produced with less use of conventional unit operations. Cell-wall-degrading enzymes are used in extraction processes to improve yields and facilitate separation of extracted vegetable components. Processing under mild conditions is thereby possible, and extracted components are left unharmed. Gentle treatment of the raw material is achieved, and only a few by-products are produced that may affect taste and smell of the final product.

The aim of the present study was to identify and compare volatile compounds from the similar oils from almond and plum kernel. Volatile constituents responsible for the characteristic flavor properties of these oils have not been reported before. Normal body temperature of 37°C was chosen for the collection of volatiles, because the major application of almond and plum kernel oils is in the cosmetic industry.

MATERIALS AND METHODS

Plum kernels (*Prunus domestica* L.) and almonds (*Amygdalus communis*) were obtained from industrial sources (Percipan, Osecina, Yugoslavia). Both oils were isolated by aqueous enzymatic extraction and analyzed for volatiles. Headspace collection of volatile flavor compounds and their analyses by gas chromatography–mass spectrometry (GC–MS) were performed as described by Taylor and Mottram (6).

Aqueous enzymatic extraction. To extract plum kernel and almond oils by an aqueous enzymatic method, it was necessary to degrade the cell walls to increase the permeability for oil. The extraction was divided into the following steps: Pre-treatment, release of oil and separation of products. Pre-treatment included milling and heat treatment to inactivate existing enzymes and inhibitors. The plum kernels and almonds were dry-milled on a pin mill with no screen inserted. The milled seed was dispersed in water and heated under stirring for 1 min at 70°C. Liquid/solid ratio of 2:1 was used. Prior to the enzymatic reaction, the slurry was wet-milled and subsequently cooled to 50°C. The aqueous phase was increased to the ratio of 4:1. The oil release was performed by enzymatic degradation of the cell-wall polysaccharides. Multiactivity enzyme complex Viscozyme 120 L (Novo Industry A/S, Copenhagen, Denmark) was used. The enzyme reaction was performed according to the procedure recommended by the manufacturer under the following conditions: enzyme dosage, 0.5% (w/w); temperature, 45°C, pH, 4.5; reaction time, 2 h. At the end of the enzyme treatment, the whole medium was centrifuged for 5 min at 5,000 × *g*. To recover as much free oil as possible, the supernatant from the decanter was centrifuged again for 15 min at 5,000 × *g*. Most of the oil leaves the centrifuge as clear oil but may contain some water. The peroxide values were less than 1 for both oils.

Headspace sampling. For collection of the volatile compounds, the oil samples were transferred to 250-mL conical flasks. Each flask was fitted with a Dreschel head (courtesy of A.J. Taylor, University of Nottingham, Great Britain) and a glass-lined, stainless-steel trap (1.5 mm o.d. × 0.7 mm i.d.) packed with Tenax (SGE Ltd., Milton Keynes, United Kingdom) was attached by a stainless-steel reducing union to the head outlet. During collection of the volatile components, the oil samples were stirred slowly while the flask was heated for 60 min at 37°C. The volatiles were swept onto the absorbent in the trap by a flow of dry nitrogen (30–40 mL min^{-1}). At the end of this period, the flask was removed, and the trap was flushed with dry nitrogen (30–40 mL min^{-1}) for 2 min to remove moisture.

GC-MS. Chromatography was performed on a Hewlett-Packard 5890 gas chromatograph equipped with a Unijector (SGE Ltd.) set in the concentrator headspace mode and fitted with a BP20 Column (SGE Ltd.) (25 m long × 0.22 mm i.d.), which terminated in the ion source of a Hewlett-Packard (Palo Alto, CA) 5790 mass spectrometer. Helium was the carrier gas at 1 mL min^{-1}. Volatile components were desorbed from the Tenax traps directly onto the capillary column by heating the trap at 230°C in the Unijector for 5 min while cooling the front of the column in solid CO_2/acetone. After desorption, the temperature was raised to 40°C and then programmed at 4°C min^{-1} to 230°C and held there for 10 min. The mass spectrometer was operated in the electron impact mode with electron energy of 40 eV and ion source temperature of 230°C. A continuous scan mode with a scan time of 1 s over a mass range of 30–400 was employed. All GC–MS data were monitored, stored and processed with an NBS REVE L data system (Hewlett Packard). Chromatograms were integrated to locate the mass spectra peaks and ten best library fits were obtained by means of a macro program and printed out. Volatile components were identified by comparison of their mass spectra with library spectra (7).

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Where authentic references were not available, a tentative identification was made on the basis of interpretation of the mass spectral data (8).

RESULTS AND DISCUSSION

The aim of the present study was to identify volatiles from plum kernel and almond oils by headspace sampling and GC–MS. The volatile compounds isolated from almond oil are presented in Table 1, and those from plum kernel oil are listed in Table 2. Qualitative examination by GC–MS of the headspace volatiles obtained from the almond oil indicated the presence of at least 20 compounds. Among volatile components detected were: alkylfuranones, *n*-alkanes, cyclopentadiene and aromatic compounds, such as benzaldehyde, methyl phenol, benzyl alcohol and some alkylbenzenes. The main volatile peaks were methyl benzene, benzaldehyde and benzyl alcohol. Two alkylfuranones were identified. These compounds have been reported as off-flavors in certain fats and oils, *e.g.*, they impart a bean grassy odor characteristic of soybean oil (9). The identified *n*-alkanes included octane, *n*-tridecane, *n*-tetradecane and hexadecane, which apparently do not contribute to flavor (10). Six alkyl derivatives of benzene were found in almond oil, and although they are often found as artifacts (from Tenax degradation), control experiments with no almond oil showed only traces of a few alkylbenzenes. A methyl phenol was detected in the sample. Phenolic derivatives are common constituents of many herbs and spices and are significant contributors to their overall sensory impact (11). One of the major volatile compounds formed from almond oil is benzaldehyde, which has been reported as a predominant volatile of kernel oils from the botanical family Rosaceae (12). Benzyl alcohol was identified as another of the dominant volatile components. This aromatic compound is a common volatile of essential oils extracted from plants (11).

Analysis of plum kernel oil by GC–MS indicated a complex composition, consisting of fifty or more components, including *n*-alkanes, aliphatic acids and esters, cycloalkanes, cycloalkenes and aromatics such as furans, phenols, alkylbenzenes, benzoic acid and esters, benzaldehyde and its derivatives and benzyl alcohol. Benzaldehyde and benzyl alcohol are the major volatiles identified. Several aliphatic compounds identified in the plum kernel oil, such as decane, a substituted heptane, a linear alkane, hexanoic acid, 3-methyl-pentanoic acid and methyl nonanoate are known to be minor volatiles in oils with large quantities of oleic acid (13). Methyl decene and ethyl-9-octadecenoate could be products of oleic acid oxidation (14). The presence of the methyl ester of linoleic acid, identified in the sample, can be explained by the fatty acid composition of plum kernel oil (3–5). Cycloalkanes and cycloalkenes were identified. We concluded that analytical procedural artifacts did not contribute to these peaks, because backgrounds were thoroughly examined under comparable experimental conditions before sample analysis. As with almond volatiles, phenol and methyl phenols were found in plum kernel volatiles. The mono-, di- and trialkyl-substituted benzenes were positively identified by comparison with mass spectra of authentic compounds. Benzoic acid and its two alkyl esters, methyl benzoate and ethyl benzoate, were detected. Benzaldehyde and benzyl alcohol were identified as the major volatiles from plum kernel oil. A possible explanation for the formation of benzaldehyde could be amygdaline hydrolyses under the conditions employed in aqueous enzymatic extraction. This cyanogenic glycoside has been found in the kernel of most fruits belonging to the family Rosaceae (15).

TABLE 1

Identity of Volatiles from Almond Oil at 37°C

Retention time (min)	Compound	Accuracy of identification[a]	Identity[b]
0.82	Dihydrofuran-3-one-5-ethyl	x	MS
1.12	Dihydroguran-3-one-5-propyl	x	MS
1.472	Octane	xx	MS
1.80	Mixed spectrum		
1.986	Methyl benzene	xxx	MS
2.981	Ethyl benzene	xx	MS
3.098	1,2-Dimethyl-benzene	xx	MS
3.198	1,3-Dimethyl-benzene	xx	MS
3.990	1,4-Dimethyl-benzene	xx	MS
4,502	Propyl benzene	xx	MS
5.315	1-Methyl-indene	xx	MS
6.959	Unknown, MW = 168		
7.069	*n*-Tridecane		ms
9.630	*n*-Tetradecane		ms
12.245	2 or 3-Methyl-cyclopent-2-en-1-one	x	MS
12.458	Benzaldehyde	xxx	MS
14.607	Hexadecane	x	MS
20.902	Benzyl alcohol	xxx	MS
21.500	Cyclopentadienes		ms
23.704	Unknown, MW = 205		
25.328	Methyl phenol	xx	MS

[a]Match quality: x > 85.3%; xx > 95%; xxx > 98.9%. MW, molecular weight.

[b]Methods of identification: MS, mass spectrum agrees with literature spectrum; ms, interpretation of mass spectrum alone.

TABLE 2

Identity of Volatiles from Plum Kernel Oil at 37°C

Retention time (min)	Compound	Accuracy of identification[a]	Identity[b]
0.723	A substituted cyclohexane	x	MS
1.058	1-Methyl-1-ethyl-cyclopentane	xx	MS
1.62	Decane	xx	MS
2.199	Cyclobutene	xx	MS
3.318	Ethyl benzene	xxx	MS
3,434	1,2-Dimethyl-benzene	xxx	MS
3.549	1,3-Diethyl-benzene	xx	MS
4.363	1,4-Dimethyl-benzene	xx	MS
4.862	2-Ethyl-toluene		ms
5.168	3-Ethyl-toluene		ms
5.245	4-Ethyl-toluene		ms
5.513	Unknown MW = 138		
5.774	Propyl toluene	xxx	MS
6.042	Propyl benzene		ms
6.500	1,3,5-Trimethyl-benzene	x	MS
6.925	Unknown, MW = 168		
7.099	A substituted heptane	x	MS
7.235	*n*-Tridecane	x	MS
7.628	A linear alkane	x	MS
7.761	2-Ethyl-furan	x	MS
7.879	Unknown, MW = 148		
8.666	2-Methyl-2-cyclopentan-1-one	xx	MS
9.711	An ethyl-heptane	x	MS
10.214	Dimethyl-propyl-benzene		ms
12.851	Benzaldehyde	xxx	MS
13.439	2-Methyl-furan	x	MS
13.693	Cyclodecane	x	MS
14.362	Ethyl-cyclopentene		ms
14.923	2-Cyclohexen-1-one	x	MS
15.464	Unknown, MW = 136		
15.626	3-Methyl-furan	x	MS
16.137	Propyl-cyclopentene	xx	MS
16.273	Butyl-cyclopentene	xx	MS
16.411	A methoxy-furan	x	MS
17.601	Unknown, MW = 150		
17.992	A methyl-decene	x	MS
18.382	Methyl-benzoate	xx	MS
19.319	Ethyl-benzoate	xx	MS
20.074	3-Methoxy-benzaldehyde	xx	MS
21.117	Benzyl alcohol	xxx	MS
21.609	Benzene-ethanol	xxx	MS
22.691	3-Methyl-pentanoate	x	MS
22.888	Phenol	x	MS
24.840	Hexanoic acid	x	MS
25.190	A methyl phenol	xxx	MS
25.349	A methyl phenol	xx	MS
25.881	4-Butyl-benzoic acid		ms
28.279	Methyl-nonanoate	xx	MS
28.649	Unknown, MW = 371		
31.596	Benzoic acid	xxx	MS
32.204	Ethyl-9-octadecenoate	xxx	MS
32.994	Methyl-9,12-octadecadienoate	xx	MS

[a] See Table 1, footnote a.

[b] See Table 1, footnote b.

A number of miscellaneous volatile compounds were not identified, although some structural features were apparent in others.

Both Tables 1 and 2 list a compound with the ion molecular weight = 168. The mass spectra of the two compounds are practically identical, suggesting that two isomers are present. Comparison with mass spectral data of known dienals did not agree with the apparent molecular ion *m/z* 168. The compounds may be alkyl-furans, although no standards were available for comparison. The comparison of volatiles of plum kernel and almond oil showed that the main volatile components are benzaldehyde and benzyl alcohol. The majority of volatile compounds were identical for both oils, but some volatiles, such as cycloalkenes, alkenes, aliphatic acids and their esters, found in the plum kernel oil, were not present in the almond oil. We are unaware of any literature data concerning volatiles of these oils. Further research is needed to quantitate and determine the sensory characteristics of the volatile compounds in almond and plum kernel oils.

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