

Analysis of Volatile Compounds and Triglycerides of Seed Oils **Extracted from Different Poppy Varieties** (Papaver somniferum L.)

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Poppy seed oil (Oleum Papaveris Seminis) is used for culinary and pharmaceutical purposes, as well as for making soaps, paints, and varnishes. Astonishingly, hardly anything was yet known about the volatile compounds of this promising comestible. Likewise, there are no current published data about the triglyceride (TAG) composition of poppy seed oils available. In this investigation solidphase microextraction (SPME) with DVB/Carboxen/PDMS Stable-Flex fiber was applied to the study of volatile compounds of several seed oil samples from Papaver somniferum L. (Papaveraceae). 1-Pentanol (3.3-4.9%), 1-hexanal (10.9-30.9%), 1-hexanol (5.3-33.7%), 2-pentylfuran (7.2-10.0%), and caproic acid (2.9-11.5%) could be identified as the main volatile compounds in all examined poppy seed oil samples. Furthermore, the TAG composition of these oils was analyzed by MALDI-ReTOF- and ESI-IT-MS/MS. The predominant TAG components were found to be composed of linoleic, oleic, and palmitic acid, comprising \sim 70% of the oils. TAG patterns of the different poppy varieties were found to be very homogeneous, showing also no significant differences in terms of the applied pressing method of the plant seeds.

KEYWORDS: Papaver somniferum; poppy seed oil; volatile compounds; SPME headspace; sensory analysis; mass spectrometry; triglyceride analysis

INTRODUCTION

The opium poppy (Papaver somniferum L.) is a multipurpose crop that is used as a medicinal or ornamental plant as well as a source for seeds and seed oil (1, 2). The long history of domestication and breeding of *P. somniferum* resulted in the development of several different land races, chemotype varieties, and cultivars adopted to various uses and climatic conditions. Cultivation of the plant covers a wide geographic area from Bombay to Moscow in the north and to Tanzania in the southern hemisphere (1, 3). Already in 1979 Beare et al. proved that poppy seed oil exhibited properties similar to those of sunflower oil and olive oil and considered it to be a promising oil for human consumption (4, 5). Poppy seed samples of various origins have been analyzed for oil content and fatty acid composition by many research groups. Oil contents between 33 and 49.1% were reported (5-7). The differences between white- and blue-seed varieties were compared in this respect by a Swedish research group: the white variety contained 40%

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oil and the blue only 33% (5, 7). There are large differences in the fatty acid composition of oils even in seed samples taken from the same region (5). The contents of lauric acid (0-13.4%), palmitic acid (7.8-30.66%), myristic acid (0-1.1%), stearic acid (1.4-10.9%), oleic acid (13.2-36.8%), linoleic acid (18.4-80.0%), and linolenic acid (trace-9.4%) vary over wide ranges (5, 6, 8). Obviously the proportion of linoleic acid decreases in seeds from characteristically dry and hot vegetation cycles (5, 9). The importance of the composition of fatty acids in relation to seed and seed oil quality, especially the occurrence of a bitter off-flavor, has been proven in many investigations. The development of a bitter flavor is apparent due to the action of lipoxygenase on linoleic acid on the seed surface (5).

Today poppy seed oil is especially used as adjuvant for pharmaceutical and medicinal diagnostics besides its application as a high-quality and delicious edible oil (10). Poppy seed oil is used, for example, as a carrier for cancerostatics in the treatment of hepatocellular carcinoma (11) and as a carrier for cyclosporin A (12). Iodized poppy seed oil can be used for correcting iodine deficiency (13) and as a diagnostic adjuvant for sonography, hysterosalpingography, and angiography (14). The British Pharmacopoeia (15) describes the composition and application of the so-called "iodiced oil fluid injection", a sterile

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iodine addition product of the ethyl esters of fatty acids obtained from poppy seed oil as radio-opaque injection. Furthermore, poppy seed oil is part of high-class oil-paints and varnishes (16) and of soaps, ointments (17, 18), and massage oils (18). Poppy seed oil is isolated by manual pressing at room temperature (10) as well as by extraction using supercritical CO_2 (19).

Triglycerides (TAGs) comprise >90% of common plant seed oils, in which they play a major role as energy storage molecules. They are synthesized de novo from plant carbohydrates by the action of stereospecific acylglycerol-synthetases dependent on the availability and level of expression of cellular fatty acids (FA). TAGs contain three fatty acid substituents, which can vary in chain length, degree of unsaturation, and position of double bonds, esterified to a glycerol backbone.

MALDI- and ESI-MS are fast detection methods for TAG analysis of plant oils (20-23). For our purposes a high-resolution MALDI mass spectrometer was used for comparison of TAG patterns of the different poppy seed oils. A quantitative evaluation of the individual TAG species from MALDI mass spectra based on measured signal intensities allows the determination of their percentual proportion of the oils. Tandem mass spectrometry (MS/MS) can be used to specify the FA chain length and the degree of unsaturation of individual TAG components directly from whole oil samples An ion trap mass spectrometer coupled with an electrospray ion source was used to perform ESI-MS/MS experiments based on fragment ion analysis by collision-induced dissociation (CID) of selected TAG molecules.

As poppy seed oil is a promising edible fat (10), it seemed to be worthwhile to investigate the volatile compounds and the triglyceride composition of seed oils from different poppy seed varieties within the scope of fundamental research and with regard to quality assurance.

MATERIALS AND METHODS

Sample Material. Gray poppy seed oil was extracted by pressing gray poppy seeds at room temperature (20 °C). White poppy seed oil was extracted by pressing white poppy seeds at room temperature. Blue poppy seed oil A was extracted by pressing blue poppy seeds at room temperature. Blue poppy seed oil B was extracted from blue poppy seeds that had been heated at 60 °C for 30 min by pressing afterward at room temperature. (All poppy seeds were obtained from local commercial growers from the Waldviertel region and Styria, Austria.)

Gray poppy seed oil from Hungary extracted in 1868 was made available from the Dr. Julius Wiesner collection of the Technological University of Vienna.

Volatile Compound Analysis. *Olfactoric Evaluation.* The olfactoric evaluation of the poppy seed oil samples was made by an experienced panel of professional perfumers, flavorists, and aroma chemists (10 assessors). Half a milliliter of each oil sample was applied to standard odor strips. Evaluation of volatile compounds was done by three 1 min steps. For flavor evaluation 5 mL of each sample was tasted directly. All samples were evaluated at room temperature (22 °C).

Sampling Preparation and Determination of Volatile Compounds by SPME-GC-MS. Samples were gained by solid-phase microextraction using a Supelco 57348, 2 cm, 50/30 μ m, DVB/Carboxen/PDMS Stable-Flex fiber directly of the headspace of 10 mL of each fatty poppy seed oil at room temperature for 60 min. The used fiber is especially recommended for analyses of volatile compounds, and in comparison to other fibers, this one performed best in our experiments After sampling, the SPME device was placed immediately into a splitless mode injection port of the GC-MS instrument. SPME (24, 25) in combination with GC-MS analysis is an already very well-established method for the detection and identification of volatile compounds (26– 28). The volatile compounds were separated using a 30 m × 0.25 mm (i.d.) HP-5-MS nonpolar column, film thickness = 0.25 μ m, and alternatively using a 30 m × 0.25 mm (i.d.) Nukol FFAP polar column, film thickness = 0.25 μ m, which were attached to a Hewlett-Packard model HP-6890 gas chromatograph equipped with a HP 5972A mass selective detector. The ionization voltage was 70 eV. The initial temperature of the column, 38 °C, was held for 1 min and then increased 5 °C/min to a temperature of 220 °C and held for 2 min. The injector port transfer line temperature was 250 °C. The split ratio was 1:37, and the split flow was 31.1 mL/min. The column head pressure was 7 psi, the flow rate was 1.0 mL/min, the average velocity was 36 cm/s, and the total flow was 41.8 mL/min (carrier, helium 5.0). The spectrometer was operated in electron-impact (EI) mode. The scan range was from 10 to 300 amu.

Compound identification was based on comparison of retention indices and mass spectra with those of authentic compounds. Retention indices of the sample compounds were determined on the basis of homologue *n*-alkane hydrocarbons analyzed under the same GC-MS conditions. The reference compounds were obtained from an in-house authentic sample collection of the Federal Office and Research Centre of Agriculture, Vienna, Austria, obtained from Aldrich (Milwaukee, WI) and Fluka (Darmstadt, Germany).

Analysis of Triglycerides. Sample Preparation and Solvents for MALDI and ESI-MS. The matrix substance 2,4,6-trihydroxyacetophenone (THAP) and chloroform were purchased from Fluka (Buchs, Switzerland). All other solvents and sodium acetate were obtained from Merck in the highest available purity grade. Oil samples were dissolved in pure chloroform (1 mg/mL). THAP was dissolved in methanol with a concentration of 10 mg/mL. For MALDI sample preparation a droplet of sample (0.3 μ L) was first deposited on the target directly followed by an equal volume of matrix. Sample and matrix immediately crystallized at room temperature. For ESI-MS the oil samples were dissolved in chloroform/methanol 50:50 (v/v) containing 1 mM sodium acetate at a concentration of 1 mg/mL.

Determination of TAG. MALDI mass spectra were measured on an AXIMA-CFR (Kratos-Shimadzu, Manchester, U.K.) reflectron timeof-flight (ReTOF) mass spectrometer equipped with a nitrogen laser (337 nm, 3 ns pulse width) with delayed extraction in positive ion mode. The delay time was set according to m/z 900. The ion acceleration voltage in the reflectron mode was set at 20 kV. Stainless steel targets with 384 sample spots (~5 mm diameter) were used for the sample preparation. Single laser shots (100–500) were accumulated to give a final mass spectrum. Monoisotopic peak resolution could be obtained for all TAG species on the applied matrix system. All data are displayed without using a smoothing algorithm.

ESI-MS/MS experiments were performed by an Esquire 3000plus 3D quadrupole ion trap (IT) instrument (Bruker Daltonik, Leipzig, Germany) in the positive ion mode. Samples were introduced into the mass spectrometer via direct infusion (flow rate = $250 \ \mu$ L/h) by applying a Cole Palmer 74900 syringe pump (Cole-Palmer Instruments, London, U.K.). Capillary voltage was set to 4.5 kV. Nebulizer and drying gas (nitrogen) was maintained at 12 psi with a flow rate of 9 L/min. Dry gas temperature was set to 250 °C. Trap scanning was performed at a rate of 13000 units/s within the range of m/z 50–1000. The isolation width for precursor ion selection was set to 2 Da. Collision energy was adjusted to \geq 95% precursor suppression. The data acquisition time was ~2–3 min.

RESULTS AND DISCUSSION

Olfactoric Evaluation. Samples from five different poppy seed oils were evaluated by a panel of professional perfumers, flavorists, and aroma chemists. The samples of gray, white, and blue (A) poppy seed oils, all extracted from untreated poppy seeds at room temperature (20 °C), were generally described as having a mild, fatty, nutty smell and flavor. The blue poppy seed oil B samples, which were isolated from heated poppy seeds (60 °C for 30 min), were evaluated as having a much stronger fatty, green, and even roasted smell and flavor. The gray poppy seed oil from the Dr. Julius Wiesner collection of the Technological University of Vienna, produced in 1868, has a weak, but still typical, poppy-like odor (see **Table 1**)

Table 1. Olfactoric Evaluation

sample	smell	flavor
gray poppy seed oil white poppy seed oil blue poppy seed oil A	weak, fatty, nutty, sweet walnut, hazelnut, peanut, green weak, nutty, peas peel	nutty, sweet, peanut aftertaste mild, walnut, green fatty, peanut, full-bodied
blue poppy seed oil B gray poppy seed oil 1868	strong, fatty, green, roasted weak, fatty	strong, fatty, roasted, nutty, green, powerful

Table 2. Volatile Compounds in Gray, White, Blue (A) and (B), and Historical Gray (186	8) Poppy	Seed Oils
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		concentration ^d				
compound ^{a,b}	RI¢	gray poppy seed oil	white poppy seed oil	blue poppy seed oil A	blue poppy seed oil B	gray poppy seed oil (1868)
ethanol	503	2.7				
acetic acid	660		1.7	1.4	4.2	3.5
2-methylbutanal	662				3.2	
pentan-2-one	687				7.0	
pentanal	699	1.8	2.3	1.7	2.2	2.6
3-methvl-1-butanol	737				2.2	
pentanol	766	4.9	3.4	3.3	3.4	1.8
butane-2,3-diol	782				3.6	
hexanal	798	23.0	30.9	10.9	4.78	13.9
2-methylpyrazine	799				1.4	
hexanol	865	33.7	11.4	5.3	8.2	1.0
pentanoic acid	893	2.4	4.3	10.6	1.0	0.7
heptan-2-one	888	1.8			4.8	5.2
heptanal	900				1.4	
2,5-dimethylpyrazine	889				1.4	
γ -butyrolactone					1.3	
α-pinene	934			11.2	0.6	0.7
camphene	946				0.8	
trans-2-heptenal	956	7.2	2.0	0.9	0.8	19.1
1-octen-3-ol	980					5.8
2-pentylfuran		7.8	8.9	8.8	10.0	2.6
caproic acid	970	6.4	8.0	11.5	3.2	2.9
3-carene	1013			13.8		
<i>p</i> -cymene	1029			0.9		2.8
limonene	1031			3.2	0.8	2.7
3-octen-2-one	1037	1.2	2.0	0.6	0.4	3.3
γ -hexalactone		1.5	1.1	0.5	0.5	
, trans-2-octenal	1051					3.2
2-ethyl-3,5-dimethylpyrazine					0.4	
nonanal	1104				0.6	

^a Listed in order of increasing retention index on a nonpolar HP-5-MS column. ^b Compound identified by retention index and mass spectra correlation with those of reference volatiles (authentic samples). ^c Retention indices using a nonpolar HP-5-MS column. ^d Concentration calculated by percent peak area of GC-MS analysis using a nonpolar HP-5-MS column. Average quantitative composition was taken by internal normalization. For each poppy seed oil, five samples and four replications for each sample were used.

Volatile Compounds Detected by SPME-GC-MS. The volatiles of the poppy seed oil samples were trapped by SPME and analyzed by GC-MS using columns of different polarities to identify the volatile compounds of these natural products. Results are listed in Table 2. In all measured samples 1-pentanal, 1-hexanal, and caproic acid seem to be responsible for the fatty, nutty olfactory impression. The sweet and fruity impressions can be attributed to 1-pentanol, 3-octen-2-one, and γ -hexalactone. Green notes are caused by trans-2-heptenal, 2-pentylfuran, and also 1-hexanal. The significantly high amount of 1-hexanal (30.9%) in white poppy seed oil headspace is in good correlation with the green note of the smell, described in the olfactoric evaluation. In addition to the volatile compounds mentioned above, in blue poppy seed oil A samples 3-carene, limonene, and p-cymene, well-known for their sweet and citrusy odor, and α -pinene, responsible for a sharp, pine flavor, could be identified. Astonishingly, almost all volatiles that could be detected in the headspace of gray, white, and blue A poppy seed oil sample were also part of the headspace of the 137year-old gray poppy oil sample. In this volatile fraction trans-2-heptenal (19.1%) and 1-hexanal (13.9%) represent the dominating green and fatty components. Moreover, 1-octen-3-ol and 2-octenal amplify the herbaceous and champignon-like impression. As expected, quite a number of typical roasted and sweet volatile substances were detected in the headspace of the blue poppy seed oil B samples, extracted from heated poppy seeds. The dominant fatty—nutty impression is compounded by 1-heptanal, 2-methylpyrazine, 2,5-dimethylpyrazine, and 2-ethyl-3,5-dimethylpyrazine, representing typical products from the Maillard reaction, which have already been detected in the aroma of cheese and roasted beef (29). 2-Methylbutanal is responsible for the strong roasted and nutty flavor, described by the perfumeurs and flavorists (see **Table 1**). The fruity and sweet side notes of these samples can be attributed to 2-pentanone, 2-heptanone, and γ -butyrolactone.

In a Chinese paper, published in 1990, Li et al. (30) reported on the composition of the volatile oil of *P. somniferum* seeds. Hexanal, 2-heptanone, heptanal, 3-octen-2-one, and 2-pentylfuran, being part of the volatile fraction of fatty poppy seed oils (see **Table 2**), were detected in the volatile oil of poppy seeds. All of the other published volatile substances of poppy seeds such as eicosene, azulene, β -bisabolene, and 2,6,6-



Figure 1. Comparison of TAG compositions of (a) gray poppy seed, (b) blue poppy seed A, and (c) white poppy seed oils by MALDI-MS; signals represent [M + Na]⁺ ions. FA composition of TAGs is indicated: L, linoleic acid; O, oleic acid; P, palmitic acid; S, stearic acid.



Figure 2. Identification of FA composition of individual TAG components by ESI-CID-MS: (a) MS/MS of *m*/*z* 877.5; (b) *m*/*z* 901.6. Fragment ions exhibit neutral losses of linoleic acid (18:2) and palmitic acid (16:0) of the sodiated precursor ions; positions of the acyl groups at the glycerol backbone are solely indicative.

trimethyl-2-cyclohexen-1-ol could not be found in the volatile fraction of our examined poppy seed oil samples.

TAG. The poppy seed oils were subjected to MALDI-MS analysis to obtain TAG patterns of the different samples. Recently, THAP was evaluated as a very suitable matrix for lipid analysis. This matrix system mainly provides sodiated TAG molecular ions with high sensitivity, which is a considerable advantage for the analysis of complex oil samples (*31*). In **Figure 1** the TAG compositions of gray, blue, and white poppy seed oil can be seen for comparison. The mass spectra represents

the $[M + Na]^+$ ions of the main TAG components of the oils. At least five different TAGs consisting of linoleic, oleic, and palmitic acid, respectively, representing >70% of the oils, could be observed.

The FA constitution of the individual TAG components was elucidated by MS/MS experiments based on the neutral loss of the acyl substituents (RCOOH) from the sodiated precursor ions (23, 31). In **Figure 2** the corresponding mass spectra of the main TAG components of the oils at m/z 877 and 901 are shown. The fragment ion analysis clearly revealed that m/z 877 consists

Table 3. TAG Compositions of the Different Poppyseed Oil Varieties Analyzed by MALDI- and ESI-MS/MS

			composition calcd by peak intensity c (% \pm SD)			
TAG <i>m/z</i> [M + Na] ⁺	[M + Na - RCOOH] ^{+ a}	fatty acid composition ^b	gray poppy seed oil	white poppy seed oil	blue poppy seed oil A	blue poppy seed oil B
851.4	na	16:0/16:0/18:2	_	0.3 ± 0.2	0.1 ± 0.2	0.2 ± 0.2
853.4	597.4/665.9	16:0/16:0/18:1	-	1.2 ± 0.0	1.2 ± 0.3	0.8 ± 0.1
855.4	na	16:0/16:0/18:0	-	0.4 ± 0.0	0.5 ± 0.1	0.2 ± 0.1
861.4	na	na	-	0.7 ± 0.2	0.3 ± 0.2	0.3 ± 0.3
863.4	na	na	-	0.2 ± 0.2	0.2 ± 0.3	0.1 ± 0.2
865.4	na	na	-	0.1 ± 0.2	-	-
869.6	na	na	-	-	-	0.1 ± 0.1
875.4	na	18:2/18:3/16:0	0.8 ± 0.1	0.8 ± 0.0	0.8 ± 0.1	0.6 ± 0.1
877.4	597.2/621.2	18:2/18:2/16:0	17.8 ± 0.9	18.0 ± 0.5	16.3 ± 0.5	16.6 ± 0.4
879.4	597.4/599.4/623.4	18:1/18:2/16:0	7.8 ± 0.6	7.2 ± 0.3	9.2 ± 0.3	6.1 ± 0.2
881.4	599.4/625.4	18:1/18:1/16:0	1.3 ± 0.1	1.0 ± 0.4	2.1 ± 0.4	1.2 ± 0.1
883.4	na	18:0/18:1/16:0	0.2 ± 0.0	-	0.2 ± 0.1	-
885.4	na	18:0/18:0/16:0	-	0.3 ± 0.2	0.2 ± 0.2	0.5 ± 0.3
887.4	na	na	-	0.4 ± 0.1	0.2 ± 0.2	0.2 ± 0.3
889.6	na	na	-	-	-	0.1 ± 0.2
891.4	na	na	0.3 ± 0.2	0.3 ± 0.2	0.1 ± 0.1	0.4 ± 0.0
893.4	na	na	1.2 ± 0.7	0.7 ± 0.1	1.0 ± 0.2	1.5 ± 0.3
895.4	na	18:3/18:3/18:3	0.9 ± 0.1	0.3 ± 0.0	0.7 ± 0.1	0.7 ± 0.3
897.4	na	18:2/18:3/18:3	0.2 ± 0.1	0.1 ± 0.2	0.3 ± 0.1	0.3 ± 0.1
899.4	na	18:2/18:2/18:3	0.8 ± 0.4	0.8 ± 0.2	0.6 ± 0.1	0.7 ± 0.1
901.4	621.2	18:2/18:2/18:2	21.0 ± 1.1	24.6 ± 1.0	19.1 ± 1.5	24.3 ± 0.9
903.4	621.4/623.4	18:1/18:2/18:2	13.2 ± 0.4	13.2 ± 0.2	13.3 ± 0.6	12.9 ± 0.8
905.5	623.4/625.4	18:1/18:1/18:2	7.9 ± 0.4	7.3 ± 0.4	9.0 ± 0.3	7.5 ± 0.3
907.5	623.4/625.4/627.4	18:0/18:1/18:2	1.9 ± 0.1	1.8 ± 0.3	2.6 ± 0.4	1.9 ± 0.3
909.5	na	18:0/18:1/18:2	0.3 ± 0.0	0.3 ± 0.0	0.4 ± 0.1	0.3 ± 0.1
911.4	na	18:0/18:1/18:1	0.5 ± 0.0	0.5 ± 0.0	0.4 ± 0.1	0.3 ± 0.0
915.4	na	na	0.2 ± 0.0	-	-	0.1 ± 0.1
917.4	na	na	2.5 ± 0.4	1.1 ± 0.3	1.3 ± 0.3	2.6 ± 0.6
919.4	na	na	1.9 ± 0.3	0.7 ± 0.1	1.3 ± 0.2	1.4 ± 0.3
921.5	na	na	0.7 ± 0.1	0.5 ± 0.1	0.9 ± 0.1	0.9 ± 0.2
923.5	na	na	0.6 ± 0.1	0.1 ± 0.2	0.4 ± 0.1	0.3 ± 0.1
931.5	na	na	0.1 ± 0.1	0.1 ± 0.2	-	-
933.5	na	na	0.4 ± 0.0	0.4 ± 0.1	0.1 ± 0.2	0.4 ± 0.0
935.5	na	na	0.3 ± 0.0	0.1 ± 0.2	0.3 ± 0.2	-
937.4	na	na	0.1 ± 0.1	0.1 ± 0.2	0.3 ± 0.2	0.1 ± 0.2

^a Sodiated diacylglycerol fragment ions. ^b Fatty acid composition calculated on neutral loss of RCOOH. ^c Compositions are expressed by the percentage of peak intensities (mean ± SD of four individual measurements comprising 500 individual laser shots each) of total detected TAG in the range of *m*/*z* 840–950 of MALDI mass spectra. na, no MS/MS data and FA composition available; –, below the limit of detection.



Figure 3. Influence of pressing method and storage on TAG composition of blue poppy seed oils: (a) 60 °C treatment, fresh; (b) cold pressing, fresh; (c) cold pressing, after short storage at room temperature. All peaks represent $[M + Na]^+$ ions.

of two linoleic and one palmitic acid substituent, whereas m/z 901 contains three linoleic acid residues exclusively. The components at m/z 879 and 903 contain one double bond less

(2 Da mass increments), corresponding to a substitution of linoleic acid by one oleic acid residue in both cases. Further substitution by oleic and stearic acid could be realized in the

cases of m/z 881, 905, and 907, respectively. Unless MS/MS data could not be obtained from all TAG species, the FA composition of some minor components could be assigned by calculation from the mass differences.

On the basis of on these results the percentual TAG compositions of the different poppy seed oils were calculated from the peak intensities of MALDI mass spectra (Table 3). More than 25 individual TAG constituents could be identified from whole oil samples. Besides the main components, minor TAG species in the mass range below m/z 870 and above m/z910 could be identified, representing only 5-10% of the oils. A very homogeneous overall TAG composition could be observed from the analyzed oil samples with some variability of minor components, especially in the case of gray poppy seed oil. Different pressing methods and short storage time had no significant influence on TAG composition, exhibiting only marginal signal intensity differences also in the case of components in the range of m/z 851–869 or 915–937 of the oils (Figure 3; Table 3). No useful mass spectra could be recorded from gray poppy seed oil from the year 1868 at all. In this case the oil constitution was considerably changed to higher viscosity, probably due to polymerization and alteration of the TAG components during the long storage time ("aging effects").

As a conclusion, it could be stated that the analyzed poppy varieties showed a very homogeneous oil composition in terms of TAG components containing predominantly linoleic, oleic, and palmitic acid. More than 25 individual TAGs could be identified by the MS analysis, from which 5-7 components comprise >70% of the oils. In accordance with literature data the different poppy seed oils showed a high linoleic acid type, which is characteristic for poppy seeds grown under mid-European climatic conditions (8). Manufacturing conditions (cold pressing of untreated or of previously heated poppy seeds) had no significant influence on TAG composition, whereas long-term storage exhibited a tremendous alteration of the oil constitution.

In contrast, flavors showed a wide range of components with characteristic differences among the analyzed poppy varieties. Thirty different volatile constituents could be detected in the oils, most of them representing oxidative products of lipids. Volatiles were considerably influenced by pressing methods but remained widely unaffected by storage time, as a long-timestored gray poppy see oil sample from 1868 still showed all of the characteristic gray poppy seed oil volatile components, such as 1-pentanol, 1-hexanal, 1-hexanol, 2-pentylfuran, and caproic acid.

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LITERATURE CITED

- Levy, A.; Milo, J. Genetics and breeding of *Papaver somniferum*. In *Poppy. The Genus Papaver*; Bernáth, J., Ed.; Harwood Academic Publishers: Amsterdam, The Netherlands, 1998; p 93.
- (2) Koerber-Grohne, U. Nutzpflanzen in Deutschland. Kulturgeschichte und Biologie, 2nd ed.; Konrad Theiss Verlag: Stuttgart, Germany, 1988; p 405.

- (3) Krikorian, A. D.; Ledbetter, M. C. Some observations on the cultivation of opium poppy (*Papaver somniferum* L.) for its latex. *Bot. Rev.* **1975**, *41* (1), 30–102.
- (4) Beare, R. J. L.; Gray, L.; Nera, E. A.; Levin, O. L. Nutritional properties of poppy seed oil relative to some other oils. *Nutr. Metab.* **1979**, *23* (4), 335–346.
- (5) Bernáth, J. Utilization of poppy seed. In *Poppy. The Genus Papaver*; Bernáth, J., Ed.; Harwood Academic Publishers: Amsterdam, The Netherlands, 1998; pp 337–342.
- (6) Singh, S. P.; Khanna, K. R.; Dixit, B. S.; Srivastava, S. N. Fatty acid composition of opium poppy (*Papaver somniferum*) seed oil. *Indian J. Agric. Sci.* **1990**, *60* (5), 358–359.
- (7) Eklund, A.; Agren, G. Nutritive value of poppy seed protein. J. Am. Oil Chem. Soc. 1975, 52 (6), 188–190.
- (8) Sengupta, A.; Mazumder, U. K. Triglycerid composition of *Papaver somniferum* seed oil. J. Sci. Food Agric. 1976, 27 (3), 214–218.
- (9) Yarosh, N. P.; Megorskaya, O. M. The composition of fatty acids in free and bound lipids of poppy seeds. *Maslozhirovaya Promyshlenmost* 1975, 41 (7), 10–12.
- (10) Krist, S. Untersuchungen zum Aroma von Mohnölen und Samen diverser Mohnsorten. Doctoral dissertation, University of Vienna, Austria, 2002; p 7.
- (11) Risse, J. H.; Menzel, C.; Grunwald, F.; Strunk, H.; Biersack, H. J.; Palmedo, F. Therapy of hepatocellular cancer with iodine-131-Lipiodol. *Rom. J. Gastroenterol.* **2004**, *13* (2), 119–124.
- (12) Tibell, A.; Lindholm, A.; Sawe, J.; Chen, G.; Norrlind, B. Cyclosporin A in fat emulsion carriers: experimental studies on pharmacokinetics and tissue distribution. *Pharmacol. Toxicol.* **1995**, *76*, 115–121.
- (13) Benmiloud, M.; Chaouki, M. L.; Gutekunst, R.; Teichert, H. M.; Wood, W. G.; Dunn, J. T. Oral iodized oil for correcting iodine deficiency: optimal dosing and outcome indicator selection. *J. Clin. Endocrinol. Metab.* **1994**, 79 (1), 20–24.
- (14) Choi, B. I.; Park, J. H.; Kim, B. H.; Kim, S. H.; Han, M. C.; Kim, C. W. Small hepatocellular carcinoma: detection with sonography, computed tomography, angiography and Lipiodol-CT. *Br. J. Radiol.* **1989**, *62* (742), 897–903.
- (15) British Pharmacopoeia; The Stationary Office: London, U.K., 2001; Vol. II, p 2175.
- (16) Roth, L.; Kormann, K. Oelpflanzen Pflanzenoele; Ecomed Verlagsgesellschaft: Landsberg/Lech, Germany, 2000; p 137.
- (17) Janystin, H. Handbuch der Kosmetika und Riechstoffe, 3rd ed.; Dr. A. Huethig Verlag: Heidelberg, Germany, 1978; Vol. I, p 622.
- (18) Martindale. *The Extra Pharmacopoeia*, 33rd ed.; Reynolds, J. E. F., Ed.; The Pharmaceutical Press: London, U.K., 2002; p 1653.
- (19) Bozan, B.; Temelli, F. Extraction of poppy seed oil using supercritical CO₂. J. Food Sci. 2003, 68 (2), 422–426.
- (20) Ayorinde, F. O. Determination of the molecular distribution of triacylglycerol oils using matrix-assisted laser desorption/ionization time-of-flight mass spectrometry. *Lipid Technol.* 2000, *12* (2), 41–44.
- (21) Asbury, G. R.; Al-Saad, K.; Siems, W. F.; Hannan, R. M.; Hill, H. H. Analysis of triacylglycerols and whole oils by matrixassisted laser desorption/ionization time-of-flight mass spectrometry. J. Am. Soc. Mass Spectrom. **1999**, 10, 983–991.
- (22) Duffin, K. L.; Henion, J. D.; Shieh J. J. Electrospray and tandem mass spectrometric characterization of acylglycerol mixtures that are dissolved in nonpolar solvents. *Anal. Chem.* **1991**, *63*, 1781– 1788.
- (23) Hvattum, E. Analysis of triacylglycerols with non-aqueous reversed-phase liquid chromatography and positive ion electrospray tandem mass spectrometry. *Rapid Commun. Mass Spectrom.* 2001, *15*, 187–190.
- (24) Mazida, M. M.; Salleh, M. M.; Osman, H. Analysis of volatile aroma compounds of fresh chilli (*Capsicum annuum*) during stages of maturity using solid-phase microextraction (SPME). *J. Food Compos. Anal.* 2005, *18* (5), 427–437.

- (25) Mondello, L.; Casilli, A.; Tranchida, P. Q.; Dugo, P.; Costa, R.; Festa, S.; Dugo, G. Comprehensive multidimensional GC for the characterization of roasted coffee beans. *J. Sep. Sci.* 2004, 27 (5–69), 442–450.
- (26) Doleschall, F.; Rocseg, K.; Kémeny, K. Comparison of different coated SPME fibers applied for monitoring volatile substances in vegetable oils. *Eur. J. Lipid Sci. Technol.* 2003, 105, 333– 338.
- (27) Jirovetz, L.; Buchbauer, G.; Stoyanova, A.; Balinova, A.; Guangjiun, Z.; Xihan, M. Solid phase microextraction/gas chromatographic and olfactory analysis of the scent and fixative properties of the essential oil of *Rosa damascena* L. from China. *Flavour Fragrance J.* **2005**, 20 (1), 7–12.
- (28) Krist, S.; Unterweger, H.; Bandion, F.; Buchbauer, G. Volatile compound analysis of SPME headspace and extract samples from roasted Italian chestnuts (*Castanea sativa* Mill.) using GC-MS. *Eur. Food Res. Technol.* **2004**, *219* (5), 470–473.

- (29) VCF. Database of Volatile Compounds BASIC Boelens Aroma Chemical Information Service; data provided by TNO Nutrition and Food Research: Zeist, The Netherlands, 2000.
- (30) Li, C.; Zhao, X.; Chen, N.; Chen, Y. Chemical composition of the volatile oil of *Papaver somniferum. Lanzhou Daxue Xuebao*, *Ziran Kexueban* **1990**, 26 (3), 145–146.
- (31) Stuebiger, G. Analysis of plant seed- and human plasma-derived lipids using high-resolution MALDI time-of-flight and API magnetic sector mass spectrometry in combination with HPLC and TLC. Doctoral Dissertation, University of Vienna, Austria, 2002; pp 56–63.

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