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Detection of Adulteration of Poppy Seed Oil with Sunflower Oil Based on Volatiles and Triacylglycerol Composition

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Although poppy seed oil is an expensive article of trade, no literature about identification methods for adulteration with cheaper vegetable oils, like sunflower oil, has been published. This kind of adulteration is a challenge for routine analytical methods, such as the determination of fatty acid composition, because of almost similar fatty acid ratios. The detection of adulteration of poppy seed oils with sunflower oils at different levels (5−40%, w/w) by using SPME−GC−MS and MALDI-ToF-MS is the subject of our investigation. With the mentioned SPME−GC−MS method, it was possible to detect an admixture of sunflower oils in all relevant (5−40%) amounts by using α-pinene as a marker compound. Admixture of sunflower oil with high levels of triolein (high-oleic acid type) could be undoubtedly detected by MALDI-MS down to the 5−10% level. In contrast, adulteration of pure poppy seed oil by "standard" sunflower oils remained indistinguishable using this MALDI-MS.

KEYWORDS: Poppy seed oil (*Oleum papaveris*); sunflower oil (*Oleum helianthus*); adulteration; SPME−GC−MS; MALDI-MS; α-pinene; triacylglycerols

INTRODUCTION

Adulteration of fats and fat products has been a problem and challenge for analytics for decades. Deliberate adulteration has been used to increase economic benefits by increasing the yield of production of fats by undetectable or hardly detectable admixtures. On the other hand, accidental contamination has been reported in terms of producing food products (*1*).

To detect adulteration of fats and fat products, analytical tests were established to characterize fats and oils. Older measurements such as the iodine value used to obtain information about unsaturation of fats and saponifiable matter to give a measure of the average molecular weight of constituents in fatty matrices were developed long ago. Some of those methods such as the iodine value are still used today in routine measurements as they do not require highly sophisticated equipment (*2*−*4*).

Today, chromatographic methods such as GLC or RP-HPLC are the most popular ones used in routine measurements in monitoring authenticity, in monitoring adulteration, and in traceability studies of fats and fatty oils (*5*, *6*). Routine purity analysis of edible oils and fats is simply based on analyzing the fatty acid (FA) ratios compared to authentic samples in accordance with the FAO/WHO criteria (*7*). Therefore, the analysis of fatty acid methyl esters by GC−FID or GC−MS (based on measurements of retention times and indices compared to authentic samples, including the quantification of individual components) is the simplest and most commonly used technique. Detection limits of these methods are situated usually in the 5−10% range of foreign fat in the blend, but in some cases, these methods do not satisfy the analyst. As fats are natural products, the fatty acid ratio varies enormously due to natural climate differences and regional variations (*8*−*18*). Furthermore, as normally most of the common FAs are present in the majority of oils, purity can only be unequivocally evaluated if considerably elevated levels of a particular FA are present in the foreign oil spectrum (*19*).

The analytical method SPME (solid-phase microextraction), established in the 1990s as a means of extracting and preconcentrating pollutants in water (*20*), provides a solvent-free and therefore environmental protective method usually used in combination with GC−MS analytics. Compared to time- and cost-expensive dynamic headspace techniques such as purge and trap, with SPME a simple alternative has been established in the area of food analytics (*21*−*23*).

The feasibility of oil authenticity testing based on the analysis of triacylglycerol (TAG) profiles was tested in several studies (*7*). Although TAGs are directly related to the FA composition of oils, they exhibit plant-specific structures, which are genetically determined due to the action of stereospecific acylglycerol synthetases of plants. Since the FA distribution on the glycerol

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backbone remains preserved during analysis, TAG patterns of oils usually provide a larger amount of information than a simple FA profiling. Oil adulteration can usually be detected due to unique TAG species or elevated levels of common TAGs that are less prominent or absent in the genuine oil sample. On the basis of chromatographic methods, the analysis of complete TAGs provides information about not only prevalent fatty acids but also their stereospecificity. For example, the analysis of TAG has been developed for the authenticity control of chocolate, since admixture of other fats should not exceed a maximum of 5% of the end product (*24*).

Recently, modern MS techniques, such as APCI-, ESI-, and MALDI-MS, gained more attention since they offer the possibility of TAG profiling directly from whole oil samples also in combination with separation by RP-HPLC and identification of the components by MS/MS experiments (*25*−*27*).

It was shown in several studies that MALDI-MS is suited for qualitative as well as quantitative TAG analysis in comparative oil studies (*28*−*30*). Sample preparation is easy to perform and less time-consuming than that in most of the chromatographic methods. Hence, MALDI-MS provides great potential as a routine analytical technique in all fields of oil quality control.

On the basis of these achievements, we were interested in analyzing adulteration of poppy seed oils (*Oleum papaveris*) with different amounts of sunflower oils (*Oleum helianthus annuus*) as this admixture is difficult to investigate due to similar fatty acid profiles (*8*−*18*). Poppy seed oils belong to a group of oils with high pharmacological and dietary value (*11*). The high linoleic acid content favors the cholesterol-lowering properties of the oil and serves as a precursor for prostaglandins and the long chain polyunsaturated n-6 fatty acids (*31*, *32*).

Oils for pharmaceutical and medicinal purposes traditionally have to fulfill restrictive quality criteria that can be considerably weakened by adulteration. Consequently, it is the analytical challenge to distinguish between cheaper sunflower oil as an admixture of rare and expensive poppy seed oil in the scope of economic reasons, as admixtures of sunflower oil and poppy seed oil seem to be a popular practice used by some local oil producers (*33*). A new combination of well-established analytical methods is presented here.

MATERIALS AND METHODS

Sample Material. White poppy seed oil (A), gray poppy seed oil (B), and blue poppy seed oil (C) were purchased from local commercial growers from the Waldviertel region, Lower Austria. To obtain oils A−C, pure white, gray, and blue poppy seeds, respectively, were commercially cold pressed and simply filtered. Sunflower oil (D) from Germany for blending with pure poppy seed oils A−C, obtained by commercial cold pressing, was purchased from a local shop. A second German sunflower oil (E), a French sunflower oil (F), and one Austrian sunflower oil (G), also purchased from local shops, were used in comparison measurements. To obtain oils D−F, cold pressing conditions were applied to untreated sunflower seeds. In contrast, to obtain sunflower oil G, sunflower seeds were heated to 60 °C for 30 min prior to being subjected to cold pressing conditions. With these prepressing conditions, a higher yield of oil and a more intense flavor could be established.

SPME−GC−MS and TAG measurements were carried out with pure poppy seed oils A−C and pure sunflower oils D−G, respectively. Sunflower oil D was used to adulterate poppy seed oils A−C at levels of 5, 10, 20, 30, and 40% (w/w). All produced blends were also included at the sample setting for SPME−GC−MS and TAG measurements.

SPME−GC−MS Analysis. Headspace solid-phase microextraction (SPME) was used to analyze the headspace volatiles from pure poppy seed oils, sunflower seed oils, and blends of poppy seed oils with admixture of 5−40% sunflower oils. Oil samples (5 g) were added to 10 mL SPME vials, sealed with aluminum foil, and extracted isothermally for 2 h to produce sufficient amounts of analytes at room temperature by using a preconditioned Supelco 57348 2 cm, 50/30 μm DVB/Carboxen/PDMS Stable-Flex fiber, which is especially suited for analysis of volatile compounds as shown by Doleschall et al. (*34*).

After sampling had been carried out, the SPME device was placed immediately into the GC−MS instrument. To separate the volatile compounds, a 60 m × 0.25 mm (inside diameter) RTx-5 (Restec) nonpolar column, with a film thickness of 0.25 μm, was attached to a Hewlett-Packard HP-6890 model gas chromatograph equipped with an HP-5972 mass selective detector. The following column temperature program sequence was used. An initial temperature of 38 °C was held for 1 min and then increased at a rate of 2.5 °C/min to 175 °C. From this point, the temperature was increased at a rate of 50 °C/min to 220 °C which was held for 2 min. The injector port temperature was 250 °C. After using the splitless mode for 4 min, the split ratio was set to 1:40 to expurgate the GC−MS system. A constant flow of 1 mL/min was applied (carrier helium 5.0). The transfer line temperature was 250 °C which resulted in an ion source temperature of approximately 160 °C. Mass spectra were recorded in the electron impact mode (EI). An ionization voltage of 70 eV was used, and a scan range of 10−300 amu was applied. The ion source temperature was set to 230 °C. This method had already been successfully applied in volatile compound analysis of chestnuts (*22*) and of fatty seed oils gained from flax and false flax (*23*). Characteristic volatile compounds were identified by comparing their retention indices and mass spectra with those of standard compounds and with those of Wiley 275, NBS 75K, and in-house mass spectra libraries. Retention indices of the sample compounds were determined on the basis of homologue *n*-alkane hydrocarbons analyzed under the same GC−MS conditions. The used reference compounds were obtained by the in-house authentic sample collection of the Federal Office and Research Center of Agriculture (Vienna, Austria) obtained from Aldrich (Milwaukee, WI) and Fluka (Darmstadt, Germany). After analysis on a nonpolar column, peak area percentages were calculated by using integration data (percentage related to the total level of volatiles). The average quantitative composition was determined by internal normalization. For each analyzed oil, four samples and four replications of each sample were used (standard deviation for detected marker compound α-pinene of <1%).

Triacylglycerol Analysis. *Sample Preparation for MALDI- and ESI-MS*. A sodium ferrocyanide {$Na_4[Fe(CN)_6]$} suspension in methanol containing 5% (v/v) glycerol was used as a matrix for the TAG analysis (*35*). Oil samples were dissolved in pure chloroform at a concentration of ∼1 mg/μL. Sample preparation was carried out by applying a droplet of matrix suspension (0.4 μL) at first on the target plate immediately followed by an equal volume of sample forming a thin film on the stainless steel target surface. For ESI-MS, the oil samples were dissolved at a concentration of ∼1 mg/mL in a 50:50 (v/v) chloroform/methanol mixture containing 1 mM sodium acetate.

Mass Spectrometry. Instrumentation and data acquisition parameters for MALDI and ESI experiments were consistent with those recently described (*36*). A MALDI-RTOF (AXIMA-CFR, Kratos-Shimadzu, Manchester, U.K.) instrument equipped with a nitrogen laser (λ = 337 nm) was used for all measurements. Mass spectra were recorded in the positive reflectron mode by applying delayed ion extraction for optimized mass resolution. Five hundred single laser shots were collected to give a final mass spectrum. Monoisotopic peak resolution could be obtained for all TAG species on the applied matrix system. All data were displayed using the Savitzky−Golay smoothing algorithm. Additionally, MS/MS experiments were performed by using an ion-trap mass spectrometer (ESQUIRE 3000+, Bruker Daltonik, Leipzig, Germany) in the positive ionization mode via direct sample infusion (flow rate of 250 μL/h). The capillary voltage and dry gas temperature were set to 4.5 kV and 250 °C, respectively. Nebulizer and drying gases (nitrogen) were maintained at 12 psi with a flow rate of 9 L/min. For CID experiments, helium was used as the collision gas (He pressure of 1.0×10^{-5} mbar) and the isolation width was set to 1.0 Da for monoisotopic precursor ion selection. The collision energy was adjusted to obtain ≥95% precursor suppression (fragmentation amplitude of 1.0−1.5 V). The data acquisition time was approximately 2−5 min.

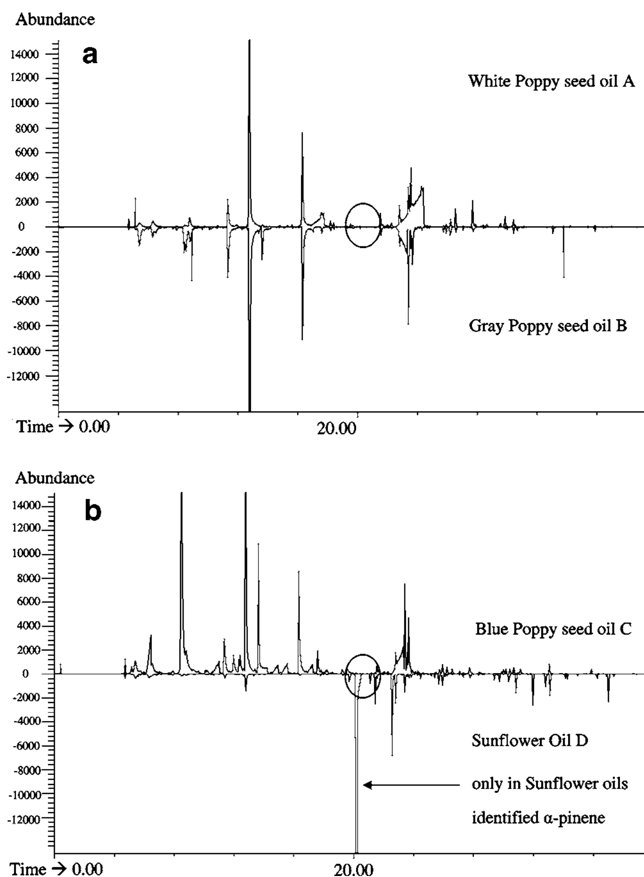

Figure 1. (**a**) SPME–GC–MS chromatogram from pure white poppy seed oil A and pure gray. (**b**) SPME–GC–MS chromatogram from pure blue poppy seed oil C and pure sunflower seed oil D. Only in sunflower oil D was α-pinene identified (circle).

RESULTS AND DISCUSSION

Results from SPME. We were interested in finding marker compounds for the detection of adulteration of expensive poppy seed oils with cheap sunflower oils in the volatile spectrum of the oils. During the SPME–GC–MS analysis, α-pinene (RI of 934 on the nonpolar column) could be found as the predominant peak in the headspace of all examined sunflower oils. In contrast, this component could be identified only as a minor or even lacking compound in poppy seed oil varieties (*36*). Poppy seed oils (A–C) examined in this study did not contain any α-pinene. According to the chromatograms shown in panels **a** and **b** of **Figure 1**, it can be proven, at first, that α-pinene can be used as a marker compound for adulteration of poppy seed oil with sunflower oil. This monoterpene has already been used as a molecular tracer for nonrefined oils by Grob et al. (*37*).

The results from our SPME measurements of pure sunflower oils were in good accordance with those previously done by Cioni et al. In this study, high contents of the monoterpene hydrocarbon α-pinene were found in the oils. Using hydrodistillation, 53.6% α-pinene was found in cultivar 'Carlos' and 43.1% α-pinene in cultivar 'Florom' 350 (*38*).

As a result of the SPME measurements with a 2 h extraction time, it could be shown that α-pinene was always the most significant peak in the headspace of all the sunflower oils that were examined. The peak area percentage of α-pinene in sunflower oils was determined to be 57% of the total peak area in sunflower oil D. In sunflower oil E, the α-pinene content was 62%. In sunflower oil F, the α-pinene content was 65%, and in sunflower oil G, probably as a result of previous heating, α-pinene comprised only 14% of the total peak area. At an admixture of 5% sunflower oil with poppy seed oil, an unequivocally detectable amount of α-pinene (17–28% vs a peak area of 100%) was found.

TAG Analysis by MALDI-MS. Genuine poppy seed oils exhibit quite similar FA compositions usually containing ∼9–22% palmitic acid (16:0), 1–11% stearic acid (18:0), 11–37% oleic acid (18:1), and linoleic acid (18:2) in the range of 41–77%, the latter varying more widely depending mainly on the climatic conditions (*14*, *39*). Even previous studies have shown that poppy seed oil exhibited properties similar to those of sunflower and olive oils and considered it a promising oil for human consumption (*40*). Like poppy oil, "native" sunflower oil also belongs to the group of "linoleic acid-rich" oils with contents of 46–76% (18:2), but in contrast, due to plant breeding and cultivation, various cultivars for producing seed oils enriched in other fatty acids, especially 16:0 (25–27%) and 18:1 (70–92%), have been grown (*9*, *16*–*18*).

In our study, two groups of sunflower oils were evaluated for adulteration purposes, one of them belonging to the "high-oleic acid" type (sunflower oil D) and the three other representing the characteristic "standard" type (sunflower oils E–G). All these oils, except of sunflower oil G, were obtained from the corresponding untreated plant seeds via cold pressing methods. As expected from our previous study (*36*), the poppy seed oils exhibited homogeneous TAG profiles, which appeared to be very similar to those of sunflower oils E–G but turned out to be totally different from that of sunflower oil D. Hence, one oil of each group was chosen for our subsequent adulteration study. For this purpose, poppy oil C was spiked with increasing amounts of sunflower oil D or G in the range of 5–40% (w/w). From each oil, the FA compositions of TAG were determined by MS/MS experiments and the relative percentage of the corresponding TAG species was calculated from MALDI mass spectra (see **Table 1**). TAGs at *m/z* 901 (LLL), 903 (LLO), and 877 (LLP) were the most abundant components of all analyzed poppy seed oils as well as of sunflower oils E–G, followed by *m/z* 905 (LOO) and 879 (LOP), comprising altogether up to 90% of the oils. TAG compositions of the poppy varieties (grown in Austria) used in this study were comparable with those previously described (*36*) but exhibit slightly increased amounts of the most prominent components at *m/z* 877 (LLP) and 901 (LLL) in the range of 8–20% most probably due to different methods of cultivation. Some trace components in the range of 0.1–1% were found especially in the upper mass range (*m/z* >931) comprising TAG-containing arachidonic (20:0), gadoleic (20:1), and behenic acid (22:0). Quantification of these components is rather difficult because of the considerably increased contribution of background noise to the signals and consequently higher standard variations. Nevertheless, these components could be found especially in sunflower oils E–G but were more or less absent in the poppy seed oils. In contrast, the predominant TAG in sunflower oil D corresponds to triolein (*m/z* 907) with an abundance of ≥74%. MS/MS experiments revealed that the same ion species of pure sunflower oils E–G were instead mainly composed of LOS with an abundance between 4 and 7%. This component was only present in trace amounts (<0.5%) in all the poppy seed oils. Consequently, if poppy seed oil C was mixed with sunflower oil D, the corresponding TAG profile was alterated in favor of triolein (*m/z* 907), increasing significantly from the 10% level of adulteration. In contrast, although some differences in the relative amounts of TAG between poppy seed oil C and sunflower oil G could be realized (**Table 1**), adulteration could

Table 1. Compositions of Relevant TAGs of Poppy Seed and Sunflower Oils Analyzed by MALDI-MS

			composition calculated from peak intensity (% ± standard deviation)[c]						
TAG *m*/*z* [M + Na]+	fatty acid composition[a]	letter code[b]	poppy seed oil A	poppy seed oil B	poppy seed oil C	sunflower oil D	sunflower oil E	sunflower oil F	sunflower oil G
851.4	*18:3/16:0/16:0*	*LnPP*		0.1 ± 0.2	0.2 ± 0.2	0.2 ± 0.4	0.2 ± 0.2	0.6 ± 0.6	0.1 ± 0.2
853.4	18:2/16:0/16:0	LPP	1.0 ± 0.1	0.8 ± 0.1	1.3 ± 0.2	0.2 ± 0.3	1.4 ± 0.1	1.5 ± 0.3	1.9 ± 0.1
855.4	*18:1/16:0/16:0*	*OPP*	0.1 ± 0.0		0.2 ± 0.0		0.1 ± 0.1	0.2 ± 0.2	
875.4	18:3/18:2/16:0	LnLP	1.1 ± 0.1	0.6 ± 0.6	1.0 ± 0.1		0.1 ± 0.2	0.2 ± 0.1	0.3 ± 0.0
877.4	18:2/18:2/16:0	LLP	24.2 ± 1.5	23.5 ± 0.7	27.1 ± 0.8		13.1 ± 0.6	14.2 ± 1.2	13.9 ± 0.2
879.4	18:2/18:1/16:0	LOP	3.8 ± 0.4	3.5 ± 0.6	5.1 ± 0.3	1.3 ± 0.2	6.2 ± 0.2	5.4 ± 0.4	5.7 ± 0.2
881.4	*18:1/18:0/16:0*	*LSP*	0.3 ± 0.3	0.4 ± 0.3			3.0 ± 0.3[d]	2.1 ± 0.6[d]	2.6 ± 0.5[d]
	18:1/18:1/16:0	OOP				9.2 ± 1.5	*e*	*e*	*e*
885.4	*18:0/18:0/16:0*	*SSP*	1.1 ± 0.4	2.0 ± 1.2			0.4 ± 0.2	0.2 ± 0.1	1.2 ± 0.7
895.4	18:3/18:3/18:3	LnLnLn	0.4 ± 0.3	0.3 ± 0.3	0.3 ± 0.0		0.5 ± 0.0	0.3 ± 0.1	0.5 ± 0.2
897.4	18:3/18:3/18:2	LnLnL			0.1 ± 0.1	0.7 ± 0.2	0.3 ± 0.3		0.2 ± 0.0
899.4	18:3/18:2/18:2	LnLL	1.3 ± 0.1	1.2 ± 0.1	1.2 ± 0.2	0.1 ± 0.2	0.1 ± 0.1		0.3 ± 0.3
901.4	18:2/18:2/18:2	LLL	43.5 ± 1.0	41.1 ± 1.0	39.5 ± 0.5	1.4 ± 0.4	24.9 ± 0.6	29.8 ± 1.0	27.5 ± 1.9
903.4	18:2/18:2/18:1	LLO	12.5 ± 0.6	15.1 ± 0.3	14.0 ± 0.1	1.4 ± 0.3	23.4 ± 0.6	24.3 ± 2.7	23.6 ± 1.2
905.5	18:2/18:1/18:1	LOO	7.3 ± 0.1	7.4 ± 0.2	7.0 ± 0.3	6.8 ± 0.5	14.4 ± 0.9	13.0 ± 0.9	14.0 ± 1.4
907.5	18:2/18:1/18:0	LOS	0.1 ± 0.2	0.5 ± 0.3	0.4 ± 0.1		7.2 ± 0.8	4.1 ± 1.0	3.7 ± 0.7
	18:1/18:1/18:1	OOO				74.4 ± 3.9			
909.5	18:2/18:0/18:0	LSS	0.5 ± 0.2	0.4 ± 0.2			0.6 ± 0.3[d]	0.3 ± 0.4[d]	0.6 ± 0.4[d]
	18:1/18:1/ 18:0	OOS					*e*	*e*	*e*
931.5	18:2/18:2/20:1	LLG	0.2 ± 0.2	0.1 ± 0.2			0.2 ± 0.2	0.2 ± 0.2	0.2 ± 0.2
933.5	18:2/18:2/20:0	LLA	0.6 ± 0.1	0.2 ± 0.2	0.4 ± 0.1	0.4 ± 0.3	0.8 ± 0.2	0.7 ± 0.1	0.7 ± 0.2
935.5	*18:2/18:1/20:0*	*LOA*	0.1 ± 0.1	0.1 ± 0.2	*e*	*e*	0.3 ± 0.1	0.2 ± 0.2	0.2 ± 0.1
	18:1/18:1/20:1	*OOG*				0.9 ± 0.3[d]	*e*	*e*	*e*
937.4	*18:1/18:1/20:0*	*OOA*	0.1 ± 0.3	0.1 ± 0.2		0.4 ± 0.2	0.3 ± 0.0	0.2 ± 0.1	0.3 ± 0.0
939.5	*18:1/18:0/20:0*	*OSA*					0.1 ± 0.1	0.4 ± 0.7	0.1 ± 0.1
961.5	*18:2/18:2/22:0*	*LLB*					0.5 ± 0.0	0.4 ± 0.3	0.6 ± 0.0
963.5	*18:2/18:1/22:0*	*LOB*					0.4 ± 0.1	0.2 ± 0.2	0.4 ± 0.1
965.5	*18:1/18:1/22:0*	*OOB*				1.1 ± 0.3	0.2 ± 0.0	0.1 ± 0.0	0.1 ± 0.1
967.5	*18:1/18:0/22:0*	*OSB*			0.6 ± 0.2	0.4 ± 0.0			
969.5	*18:0/18:0/22:0*	*SSB*		0.1 ± 0.2		0.1 ± 0.2			

[a] Fatty acid composition based on MS/MS analysis (*36*); the position of acyl groups is only indicative. [b] Three-letter code of TAG fatty acid compositions (*27*); structures in italics could not be verified by MS/MS due to insufficient signal intensity. [c] Compositions are expressed as the percentage of peak intensities (% mV ± standard deviation of four measurements comprising 500 laser shots each) of total detected TAG in the range of *m*/*z* 840–980 of MALDI mass spectra after isotopical correction of the peaks (*30*). [d] Sum of TAG species. [e] Questionable component.

not be unequivocally detected in this case at any level of blending between 5 and 40%.

As a conclusion, it can be stated that selective and sensitive methods are necessary for an unambiguous detection of trace amounts of adulterants in edible oils, since they in many cases cannot be recognized by (untrained) human senses.

An adulteration of poppy seed oils with sunflower oils used in our study could be undoubtedly detected by SPME−GC−MS on the basis of detection of α-pinene as the most characteristic volatile component in sunflower seed oils. α-Pinene was predominantly present in the headspace of all analyzed sunflower oil varieties in a manner independent of their TAG profiles. Admixture of high-oleic acid sunflower oil with predominant yields of triolein could be indubitably detected in poppy seed oils by MALDI-MS, while standard sunflower oils expressed nearly undistinguishable TAG profiles, which made them undetectable in mixtures with poppy seed oils at all relevant levels.

Because of the increasingly complex nature of industrial food processing, questions about food safety and authenticity are of growing interest for consumers and control authorities. Reliable methods for food quality control are thus demanded more than ever before. During our investigation, screening of volatile compounds by SPME−GC−MS and TAG profiling by MALDI-MS turned out to be very promising and complementary tools for oil adulteration and authenticity assessments.

ABBREVIATIONS USED

CID, collision-induced dissociation; ESI, electrospray ionization; FA, fatty acid; GMO, genetically modified organism; GLC, gas−liquid chromatography; HP, high-palmitic; HO, high-oleic; HS, high-stearic; HL, high-linoleic; MALDI, matrix-assisted laser desorption ionization; MS/MS, tandem mass spectrometry; RP-HPLC, reversed-phase high-performance liquid chromatography; SPME, solid-phase microextraction; ToF- and IT-MS, time-of-flight and iontrap mass spectrometry, respectively; TAG, triacylglycerols (triglycerides); Tr, traces.

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