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Triacylglycerols profiling in plant oils important in food industry, dietetics and cosmetics using high-performance liquid chromatography–atmospheric pressure chemical ionization mass spectrometry

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ABSTRACT

Optimized non-aqueous reversed-phase high-performance liquid chromatography method using acetonitrile–2-propanol gradient elution and the column coupling in the total length of 45 cm has been applied for the high resolution separation of plant oils important in food industry, dietetics and cosmetics. Positive-ion atmospheric pressure chemical ionization mass spectrometry is used for the unambiguous identification and also the reliable quantitation with the response factors approach. Based on the precise determination of individual triacyglycerol concentrations, the calculation of average parameters important in the nutrition is performed, i.e. average carbon number, average double bond number, relative concentrations of essential, saturated, monounsaturated and polyunsaturated fatty acids. Results are reported in the form of both chromatographic fingerprints and tables containing relative concentrations for all triacylglycerols and fatty acids in individual samples. In total, 264 triacylglycerols consisting of 28 fatty acids with the alkyl chain length from 6 to 26 carbon atoms and 0 to 4 double bonds have been identified in 26 industrial important plant oils.

1. Introduction

Triacylglycerols (TGs) are natural compounds synthesized by the esterification of glycerol with FAs under the enzymatic catalysis. In human organism, they serve as a source of energy stored in fat tissues, thermal and mechanical protective layer surrounding important organs, source of essential FAs (linoleic and linolenic acids), fat-soluble vitamins and other non-polar compounds. They form an important part of human diet and their imbalances can lead to several human diseases, i.e. coronary heart disease, dyslipidaemia, obesity or inborn errors of metabolism. The deficiency of essential FAs necessary for the biosynthesis of long-chain polyunsaturated FAs important for cell membranes leads to problems in nearly every tissue in the body. The main sources of TGs in the human diet are oil plants and especially oils prepared from them [1,2]. The total world production of oil plants in 2006 according to the Food and Agriculture Organization of the United Nations (FAO) reached 743 million tonnes [3]. The biggest producer of oil plants is the USA with almost 15% of the world production followed by Indonesia (14%), China (11%), Malaysia (11%), Brazil (8%), India (7%), Argentina (6%) and 27 European Union member states (5%). Plant seeds can contain from 10–20% oil (wheat germs, soybean) up to 45–65% for highly oily seeds (peanuts, almonds, walnuts) [1]. Some oils are also prepared from plant pulps (palm, olive, avocado). Almost 80% of the total world production of edible oils (127 million tonnes) is represented by 4 plant oils only, i.e. palm (29%), soybean (28%), rapeseed (14%) and sunflower (8%) oils [3]. Other important edible plant oils are peanut, cottonseed, coconut, palmkernel maize, olive and sesame oils [4] with the total production 1–4%. The final use of plant oils depends on their composition and the comprehensive triacylglycerol profiling brings valuable information in this respect.

Individual FAs can differ in the number of carbon atoms (CNs), number of double bonds (DBs) and *cis*-/*trans*-configuration of DBs. Hundreds of natural FAs have been identified so far in the nature and their combinations in TGs, different stereochemical positions *sn*-1, 2 or 3 on the glycerol backbone (regioisomers) or *R*/*S* optical configuration of TGs esterified in *sn*-1 and *sn*-3 positions by two different FAs (optical isomers) lead to enormous complexity. Two techniques of high-performance liquid chromatography (HPLC) are widely used in the analysis of TG mixtures, silver ion normal-phase HPLC (Ag-HPLC) and non-aqueous reversed-phase HPLC

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(NARP-HPLC). Ag-HPLC is widely used for the separation of lipids containing DBs due to the formation of week reversible complexes with silver ions [5,6]. In Ag-HPLC, TGs are separated according to the number [5,7], position [8] and *cis*-/*trans*-configuration [9,10] of DBs. The retention of TGs increases with the increasing number of DBs and TG regioisomers can also be separated under carefully optimized chromatographic conditions [10–14]. In NARP-HPLC [15–30], TGs are separated according to acyl chain lengths and the number of DBs. The retention of TGs is governed by the equivalent carbon number (ECN), which is defined as ECN = CN − 2DB. The separation of most TGs within one ECN group is feasible [19,22,23,25–27] under optimized chromatographic conditions [25,26]. The separation of *cis*-/*trans*-isomers [18,21], DB positional isomers [17,27,29] or partially separated regioisomers [24] has also been reported in NARP-HPLC.

UV detection at low wavelengths (205 or 210 nm) [18,20,22,25,30,31] is used for the detection of common TGs. UV detection provides a linear response, but very low sensitivity for saturated TGs disables their quantitation [25]. Evaporative light-scattering detection (ELSD) [15,20,25,32] is an alternative detection technique used for lipids, but the non-linear response is a disadvantage for the quantitative analysis [20,25]. Moreover, large differences among individual RFs of FAs complicate a simple calculation of RFs of mixed-acid TGs [25]. Charged aerosol detection (CAD) is a new HPLC detection technique with almost universal response for non-volatile compounds with a growing importance in the lipid analysis [28,33,34]. Mass spectrometry (MS) coupled to HPLC is the most powerful tool for the identification of lipids. Atmospheric pressure chemical ionization (APCI) provides best results for TGs [16,17,19–22,25–27] because of the full compatibility with common NARP conditions, easy ionization of non-polar TGs and the presence of both protonated molecules $[M+H]^+$ and fragment ions $[M+H-R_iCOOH]^+$. The spectra interpretation can be simplified by the software algorithm combining $[M+H]^+$ and $[M+H-R_iCOOH]^+$ information [35]. Predominant FA in *sn*-2 position can be determined from APCI mass spectra based on the lower cleavage preference from this position [19,20,22,36,37]. The precise ratio of regioisomers can be obtained by the measurement of calibration curves with both positional isomers [22,37,38]. APCI-MS provides a linear calibration [16,25] and comparable sensitivity for saturated and unsaturated TGs [25]. The first APCI-MS quantitative approach [16] calculates RFs of FAs by comparison of FA composition calculated from the TG composition using HPLC/APCI-MS with FA composition from GC/MS analysis of methyl esters after the transesterification. RFs of mixed-acid TGs were calculated by multiplication of RFs of FAs present in TGs. RFs were also calculated from the comparison of TG composition of randomized sample with their statistically calculated composition. In another approach [25], RFs of 23 single-acid TG standards are calculated from calibration parameters of these TGs related to triolein as one of the most widespread TGs in nature. RFs of mixed-acid TGs are calculated as the arithmetic mean of RFs of individual FAs present in each TG. The precision of the method is verified by validated GC/FID analysis of methyl esters.

The main goal of our work is the detailed analytical characterization of TG composition in a wide range of plant oils important in food industry, dietetics and cosmetics by means of our previously developed method for their NARP-HPLC separation and quantitation based on RFs approach with APCI-MS detection [25]. Average parameters of FA contents in all TGs are calculated including average equivalent carbon number (aECN), average carbon number (aCN), average number of double bonds (aDB), relative concentrations of essential, saturated, monounsaturated and polyunsaturated FAs.

2. Experimental

2.1. Materials

Acetonitrile, 2-propanol (HPLC gradient grade), hexane (HPLC grade), trimyristin, tripalmitin, tripalmitolein, trimargarin, triolein, trilinolein, α-trilinolenin were purchased from Sigma–Aldrich (St. Louis, MO, USA). Tristearin, γ-trilinolenin, model mixtures of TG standards GLC435 (all saturated single-acid TGs from C7 to C22) and GLC406 (C16:0, C18:0, C18:1, C18:2, C18:3, C20:0, C20:1 and C22:1) were purchased from Nu-Chek-Prep (Elysian, MN, USA). Solvents were filtered through a 0.45 μm Millipore filter and degassed by continuous stripping with helium. Samples of palm oil (*Elaeis guineensis*), peanut oil (*Arachis hypogaea*), cottonseed oil (*Gossypium hirsutum*), olive oil (*Olea europaea*) and cocoa butter (*Theobroma cacao*) were purchased from Augustus Oils (Bordon, UK) and samples of kukui oil (*Aleurites moluccana*) and wheat germ oil (*Triticum vulgare*) were purchased from Fragrant Earth (Glastonbury, UK). Plant oils from rapeseed (*Brassica napus*), soybean (*Glycine max*), sunflower (*Helianthus annuus*), coconut palm (*Cocos nucifera*), maize (*Zea mays*), sesame (*Sesamum indicum*), safflower (*Carthamus tinctorius*), grape seed white (*Vitis vinifera*), grape seed red (*Vitis vinifera*), linseed (*Linum usitatissimum*), avocado pear (*Persea americana*), blackcurrant (*Ribes nigrum*), redcurrant (*Ribes rubrum*), borage (*Borago officinalis*) and evening primrose (*Oenothera biennis*) were prepared in our laboratory according to the following procedure. 10–15 g of seeds were carefully crushed in a mortar to fine particles, which were mixed with 15 mL of hexane. The mixture was stirred occasionally for 15 min. The solid particles were filtered out using a rough filter paper and then the extract was filtered again using a fine filter with 0.45 μm pores. From the filtered extract, hexane was evaporated yielding pure plant oil. Oil samples were dissolved in an acetonitrile–2-propanol–hexane mixture (1:1:1, v/v/v) to prepare the initial solution of plant oil with the concentration 10 g/L. Then this solution was diluted with the same solvent mixture to prepare the working solution with the concentration of each TGs within the calibration range. 10 μl of diluted solution was injected in triplicate for HPLC analysis.

2.2. HPLC/APCI-MS conditions

The chromatographic apparatus consisted of a Model 616 pump with a quaternary gradient system, a Model 996 diode-array UV detector, a Model 717+ autosampler, a thermostated column compartment and a Millennium chromatography manager (all from Waters, Milford, MA, USA). The HPLC conditions: two chromatographic columns Nova-Pak C_{18} (300 mm × 3.9 mm and 150 mm × 3.9 mm, 4 μm, Waters) connected in series, a flow rate of 1 mL/min, an injection volume of 10 μL, column temperature of 25 °C and a mobile phase gradient with the slope of 0.65%/min: 0 min—100% acetonitrile, 106 min—31% acetonitrile–69% 2-propanol, 109 min—100% acetonitrile. The injector needle was washed with the mobile phase before each injection. The column hold-up volume, t_M, was 3.20 min for the system with 300 + 150 mm Nova-Pak C_{18} columns. The UV detection at 205 nm and positive-ion APCI-MS were coupled in series. The Esquire 3000 ion trap analyzer (Bruker Daltonics, Bremen, Germany) in the mass range m/z 50–1200 was used with the following setting of tuning parameters: pressure of the nebulizing gas of 70 psi, the drying gas flow rate of 3 L/min, temperatures of the drying gas and APCI heater were 350 °C and 400 °C, respectively. The reconstructed ion current chromatograms in the region m/z 300–1200 were used for the peak integration. Presented peak areas correspond to averaged values from three consecutive chromatographic runs. Individual reconstructed ion current chromatograms

were used to support the identification and apportionment of coeluting peaks.

3. Results and discussion

3.1. Chromatographic behavior of triacylglycerols

The retention of TGs in NARP-HPLC systems increases with increasing ECN reflecting the relation between CNs and DBs in all acyl chains, i.e. ECN = CN − 2DB. Most of TGs within one ECN group are also separated in this work including the partial separation of critical pairs of TGs, i.e. SLO (t_R = 85.1 min) and OOP (85.4) with ECN = 48. The retention behavior of TGs in one ECN group is strongly influenced by the FA composition in individual TGs, mainly by the unsaturation degree and acyl chain lengths. For example, the group of OOO (t_R = 84.0 min), OOP (85.4), POP (87.0) and PPP (88.7) with ECN = 48 is well resolved in our optimized chromatographic system. The retention of TGs within one ECN group increases with decreasing DB number in acyl chains, i.e. with replacing of oleic acid by palmitic acid or linoleic acid by palmitoleic acid, as demonstrated by retention times of pairs LLL (t_R = 65.3 min) and LLPo (65.7) with ECN = 42, OLL (71.8) and OLPo (72.2) with ECN = 44, OLO (77.9) and OOPo (78.3) with ECN = 46, etc.

Retention times of identified TGs collected by the analysis of 26 natural samples (Figs. 1–3) together with the knowledge of effects of individual FAs on the retention behavior are very useful for the confirmation of positive identification or the prediction of retention times of unknown TGs. Retention times of identified TGs in the wide range of analyzed samples are used for the identification of TGs containing FAs with unusual positions of DBs (double bond positional isomers). As shown previously [27], TG double bond positional isomers have shifted retention times in comparison to common TGs containing FAs with the same number of CNs and the same number of DBs. Characteristic shifts in their retention factors (Δk) can be used for the identification of TGs containing Δ5 polymethylene interrupted FAs in conifer seed oils, and unusual gamma-linolenic acid (Δ6,9,12–18:3, γLn) in blackcurrant (*R. nigrum*) and redcurrant (*R. rubrum*) (Fig. 2C) oils. In NARP-HPLC systems, TGs containing γLn have a higher retention in comparison to TGs containing only Ln (Table 1), for example pairs of DB positional isomers LnLnLn (t_R = 48.3 min) and LnLnγLn (49.0), LnLSt (49.4) and γLnLSt (50.1), LnLLn (54.0) and LnLγLn (54.7), etc. The differences in retention factors of TGs containing one γLn and TGs containing only Ln are constant with an average value Δk = 0.22. Differences in retention factors for TGs containing two and three γLn acids correspond approximately two times and slightly more than three times of Δk value of one γLn, i.e. Δk = 0.44 and Δk = 0.72, respectively. TGs containing only γLn without any Ln have been identified in borage (*B. officinalis*) (Fig. 2D) and evening primrose (*O. biennis*) (Fig. 3B) oils, which does not enable the direct comparison of both DB positional isomers containing Ln and γLn as for blackcurrant and redcurrant oils. The presence of γLn in TGs has been identified based on shifted retention times and additionally confirmed by the retention time of commercial standard of γLnγLnγLn. Retention times of all TGs in analyzed oils are in agreement with retention times from other analyzed samples and

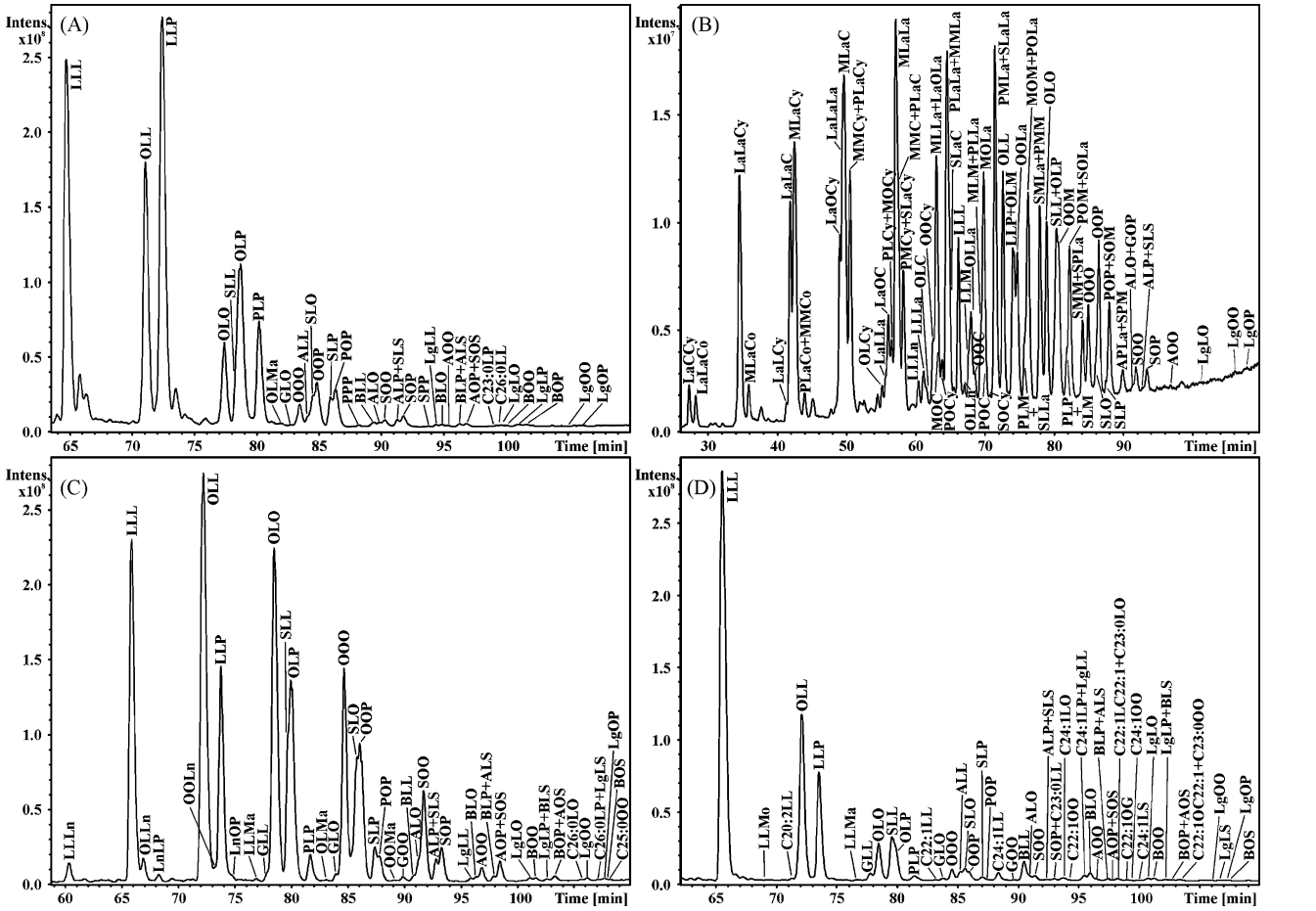

Fig. 1. NARP-HPLC/APCI-MS analysis of plant oils: (A) cottonseed (*Gossypium hirsutum*), (B) coconut (*Cocos nucifera*), (C) sesame (*Sesamum indicum*) and (D) safflower (*Carthamus tinctorius*).

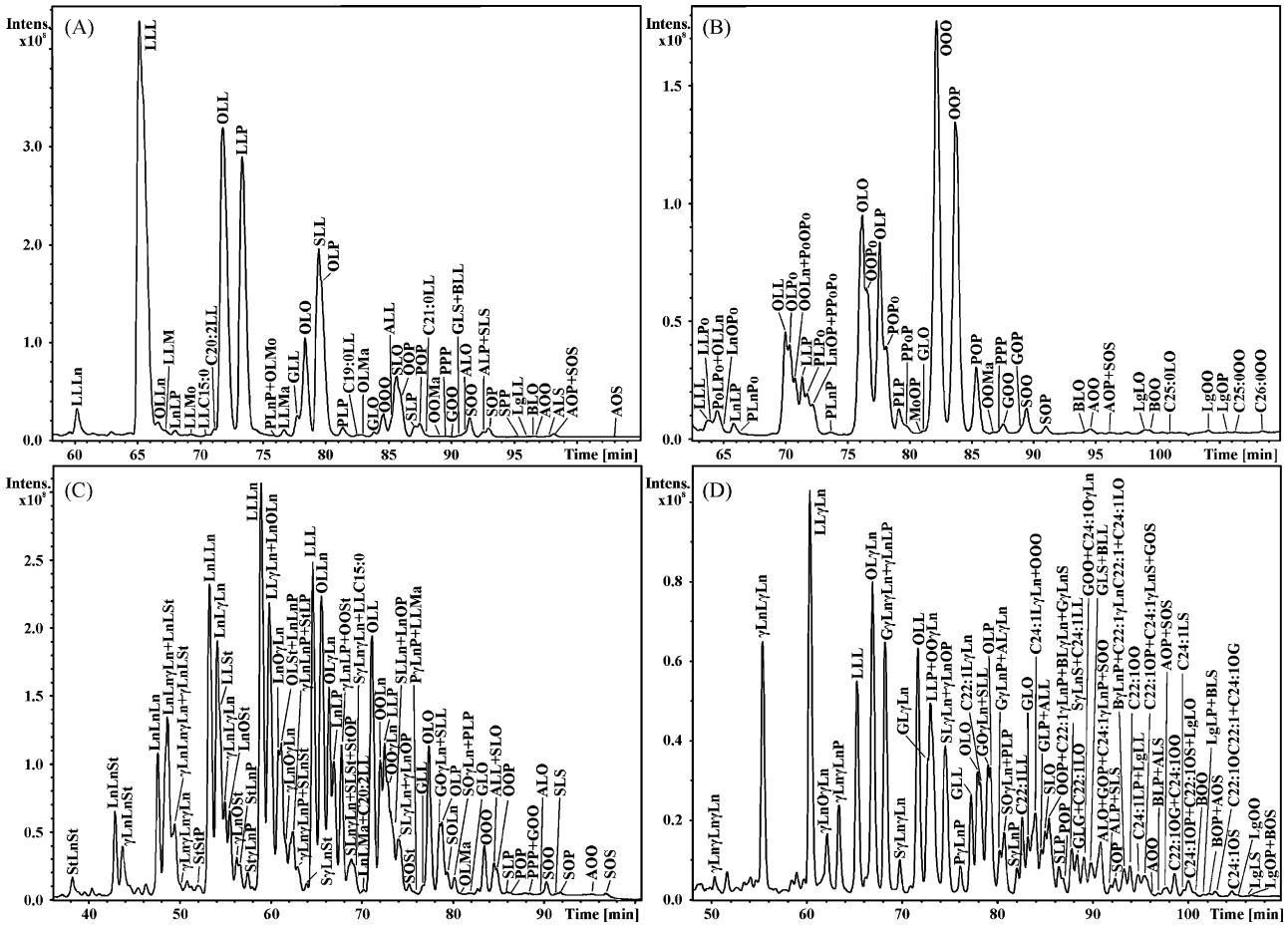

Fig. 2. NARP-HPLC/APCI-MS analysis of plant oils: (A) grape seed-red (*Vitis vinifera*), (B) avocado (*Persea americana*), (C) redcurrant (*Ribes rubrum*) and (D) borage (*Borago officinalis*).

showed very good reproducibility at least during several months of work. Each TG has been positively identified based on the agreement of retention times and the presence and relative abundances of characteristic ions in their APCI mass spectra, i.e. $[M+H]^+$ and $[M+H-R_iCOOH]^+$ ions. The DB positions are determined by the use of identical standards for common FAs, but in case of unusual FAs (e.g. C20:2, C22:1 and C24:1) the DB positions are deduced only from literature data without supporting experimental data.

3.2. APCI-MS profiling of triacylglycerol composition in natural mixtures

In analyzed samples, TGs have been identified using positive-ion APCI-MS based on both protonated molecules $[M+H]^+$ used for the molecular weight assignment and fragment ions $[M+H-R_iCOOH]^+$ used for the identification of individual FAs. The standard notation of TGs using initials of FA trivial names (Table 2) arranged according to their *sn*-1, *sn*-2 and *sn*-3 positions has been used. FAs in *sn*-1 and *sn*-3 positions cannot be resolved using NARP-HPLC/APCI-MS and they are considered as equivalent. FAs in these positions are arranged according to their decreasing molecular weights, for example TG containing oleic, palmitic and linoleic acids with linoleic acid in *sn*-2 position is designated as OLP but not PLO. Unlike to *sn*-1 and *sn*-3 positions, the FA in *sn*-2 position can be identified according to the ratio of fragment ions $[M+H-R_iCOOH]^+$, because the neutral loss of FA from the middle *sn*-2 position is less favored in comparison to *sn*-1 and *sn*-3 positions and therefore it provides the fragment ion with lower relative abundance than statistically expected. In nature, regioisomers are present in mixtures and relative abundances of fragment ions are composed from fragment ions of all isomers. Relative abundances of $[M+H-R_iCOOH]^+$ fragment ions also depend on the number of DBs and CNs, thus the precise determination of FA in *sn*-2 position can be achieved only by using regioisomeric standards, but not all of them are commercially available. Therefore, only predominant FAs in the *sn*-2 position are designated. In agreement with previously published data, the *sn*-2 position in plant oils is preferentially occupied by unsaturated FAs, mainly linoleic acid.

Properly optimized chromatographic conditions together with APCI-MS detection enable successful identification of the largest number of TG species in natural complex mixtures, for example 88 TGs identified in borage oil (comparing to 79 TGs reported in ref. [8]), 77 in blackcurrant oil (56 in ref. [8]), 66 in soybean oil (52 in ref. [22]; 39 in ref. [19]; 26 in ref. [16]; 12 in ref. [36]), 61 in evening primrose oil (39 in ref. [8]; 21 in ref. [19]), etc. Totally, 264 TG species have been unambiguously identified in 26 analyzed plant oils, which is the largest number of identified TGs reported so far.

3.3. APCI-MS quantitation of triacylglycerols

Our previously developed HPLC/APCI-MS method of quantitative analysis of TGs using RFs [25] has been applied for the quantitation of TGs in natural samples. Briefly, RFs of individual FAs (Table 2) are calculated from calibration parameters of 23 commercially available single-acid TG standards of $R_1R_1R_1$ type (i.e. single-acid saturated TGs from C7:0 to C22:0 and

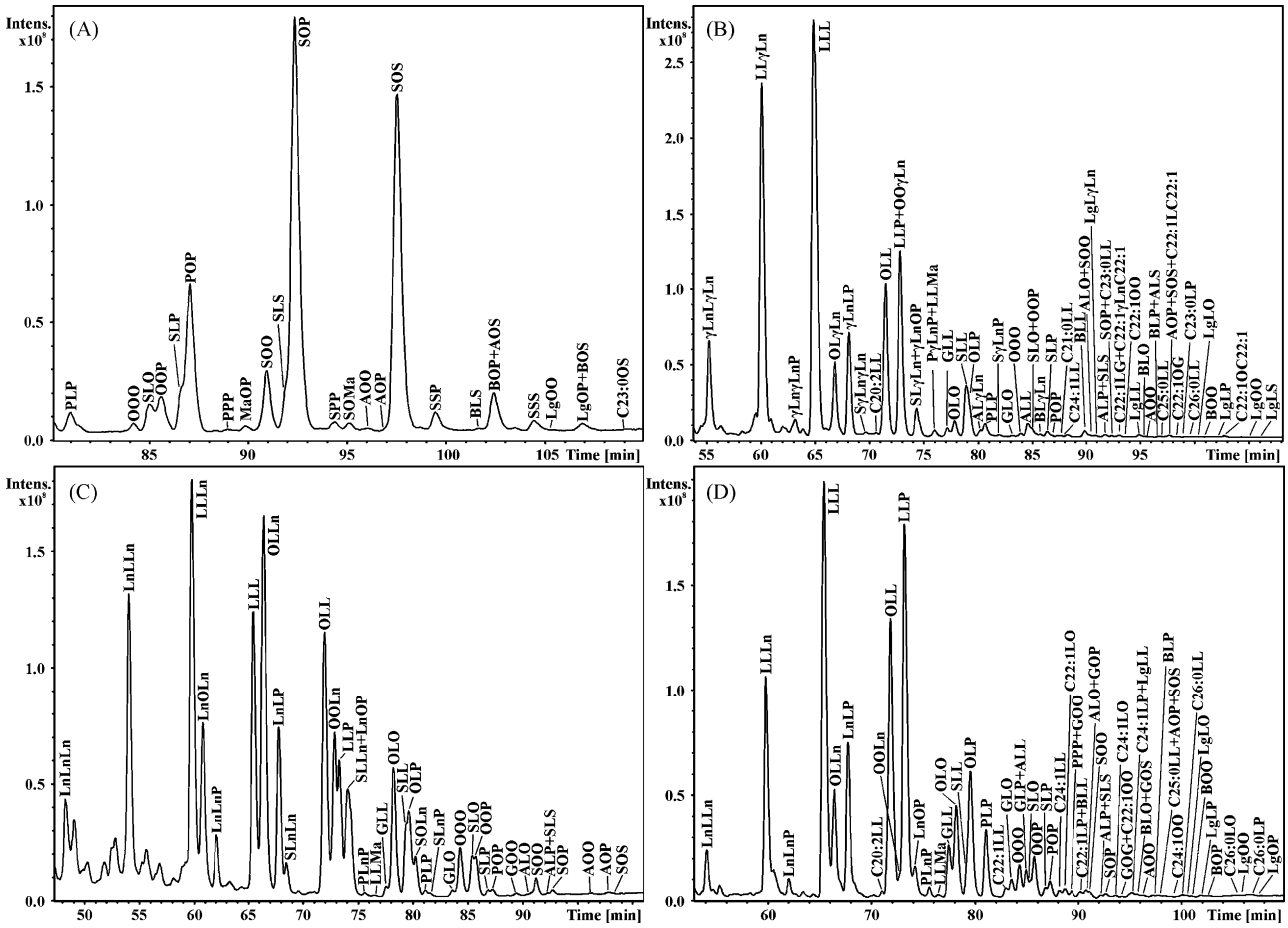

Fig. 3. NARP-HPLC/APCI-MS analysis of plant oils: (A) cocoa butter (*Theobroma cacao*), (B) evening primrose (*Oenothera biennis*), (C) kukui (*Aleurites moluccana*) and (D) wheat germ (*Triticum vulgare*).

unsaturated single-acid TGs C16:1, C18:1, C18:2, C18:3, γC18:3, C20:1 and C22:1) using the ratios of individual TGs calibration slopes to the calibration slope of triolein, for example $RF(LLL) = a_{LLL}/a_{OOO}$. RFs of mixed-acid TGs are calculated as the arithmetic mean of RFs of FAs present in TGs, for example RF(OLP) = (RF(OOO) + RF(LLL) + RF(PPP))/3. Single-acid TG standards from 9 identified trace FAs are not available, therefore their RFs have been approximated by the following way. RFs of saturated FAs, i.e. hexanoic (C6:0), tricosanoic (C23:0), tetracosanoic (C24:0), pentacosanoic (C25:0) and hexacosanoic (C26:0) acids, have been calculated from the equation $y = 2959\exp(-0.5134x) + 0.3824$ ($R^2 = 0.999$) corresponding to the dependence of RFs of 16 saturated TGs on their CNs, where y is RF and x is number of CNs. RF of stearidonic acid (C18:4) has been calculated from the equation corresponding to the dependence of RFs of unsaturated TGs with 18 CNs and 1 (OOO), 2 (LLL) and 3 (LnLnLn) DBs on the number of DBs, i.e. $y = 1.615\exp(-0.4904x)$ ($R^2 = 0.988$), where y is RF and x is number of DBs. RF values of monounsaturated palmitoleic (C16:1, RF = 1.33) and saturated palmitic (C16:0, 1.32) acids with the same CNs, gadoleic (C20:1, 0.36) and arachidic (C20:0, 0.40) acids, or erucic (C22:1, 0.42) and behenic (C22:0, 0.46) acids are very similar, therefore RFs of margaroleic (C17:1) and nervonic (C24:1) acids have been considered the same as their saturated analogues, i.e. RF(C17:1) = RF(C17:0) and RF(C24:1) = RF(C24:0). Similarly, RF of diunsaturated C20:2 acid has been considered the same as its monounsaturated analogue, i.e. RF(C20:2) = RF(C20:1). It should be emphasized that TGs containing these FAs are present in analyzed samples only at trace levels at maximum few tenth % with the exception of 1.49% nervonic acid in borage oil (Table 2). In all cases, FAs with approximated RFs form only one-third of mixed-acid TGs.

3.4. Triacylglycerol and fatty acid composition in analyzed samples

Table 1 lists HPLC/APCI-MS quantitative results of 264 TGs from the analysis of 26 plant oils important in different branches of nutrition and cosmetic industries. Identified TGs are composed of 28 FAs with 6–26 CNs and 0–4 DBs (Table 2). ECNs of all identified TGs range from 32 to 58. Only 6 TGs (PLP, OOO, OOP, POP, SOO and SOP) are detected in all samples. The number of TGs (Table 3) ranges from simple almond oil and cacao butter containing only 25 TGs to very complex blackcurrant oil with 77 TGs, redcurrant oil with 78 TGs or borage oil with 88 TGs. Identified TGs in analyzed samples can be divided into three main groups according to their concentrations. Usually about 5–6 TGs form the main constituents in each sample at the relative concentration level >5% (Table 3). From 6 (in almond and hazelnut oils) to 39 (in redcurrant and borage oils) TGs represent minor constituents with relative concentrations from 0.5 to 5.0%. Trace TG species (<0.5%) are present in a wide range from 9 TGs in cocoa butter up to 51 TGs in coconut oil.

As shown previously [25], FA composition calculated from TG composition using NARP-HPLC/APCI-MS is in a good agreement with FA composition from validated GC/FID analysis of fatty acid methyl esters after the transesterification of TGs by sodium methanoate. Therefore, FA composition of analyzed plant oils has been calculated directly from TG composition using HPLC/APCI-

Table 1
Relative concentrations [%] of all triacylglycerols identified in individual plant oils, their retention times t_R and equivalent carbon numbers

Triacylglycerol	t_R [min]	ECN	Palm	Rapeseed	Soybean	Sunflower	Peanut	Cotton	Coconut	Maize	Olive	Sesame	Almond[a]	Safflower	Grape seed—white
LaCCy	26.5	30							1.8						
LaLaCo	27.4								2.2						
LaLaCy	33.7	32							13.3						
MLaCo	35.0								3.1						
StLnSt	38.8														
LaLCy	40.5								0.5						
LaLaC	41.0	34							2.8						
MLaCy	41.6								15.2						
PLaCo	43.1								<0.1						
MMCo	43.1								0.8						
LnLnSt	43.5														
γLnLnSt	44.2														
LaOCy	48.2	36							6.2						
LnLnLn	48.3			0.1											
LaLaLa	48.6								3.5						
MLaC	49.0								1.8						
LnLnγLn	49.0														
LnLSt	49.4														
MMCy	49.6								4.0						
PLaCy	49.6								7.9						
γLnLnγLn	49.7														
γLnLSt	50.1														
γLnγLnγLn	50.6														
StStP	52.6														
LnLLn	54.0	38		0.7	2.3										
OLCy	54.3								1.0						
LnLγLn	54.7														
LaLLa	54.8								0.1						
LLSt	55.1														
LaOC	55.2								1.3						
γLnLγLn	55.4														
PLCy	55.5								0.5						
MOCy	55.7								1.9						
LnOSt	56.1														
MLaLa	56.2								1.9						
MMC	56.7								2.4						
PLaC	56.7								0.9						
γLnOSt	56.8														
StLnP	57.2														
PMCy	57.4								2.0						
SLaCy	57.4								4.7						
StγLnP	58.0														
LnLnC15:0	58.7	39													
LLLn	59.6	40		1.4	8.6				<0.1	1.6		0.4			0.9
LLLa	60.3								0.1						
LLγLn	60.4														
OLC	60.7								0.2						
LnOLn	60.8			3.0	1.3										
OOCy	61.5								1.9						
LnOγLn	61.6														
MLLa	61.8								0.1						
OLSt	61.9														
LaOLa	62.1								1.8						
LnLnP	62.1			0.6	0.9										
γLnOγLn	62.3														
MOC	62.4								0.2						
γLnLnP	62.8														
POCy	63.0								1.5						
StLP	63.1														
γLnγLnP	63.5														
PLaLa	63.7								0.8						
MMLa	63.7								1.7						
SLnSt	63.8														
SLaC	64.0								0.9						
SγLnSt	64.5														
LnLMo	63.3	41													
LnLnMa	65.6														

Table 1 (*Continued*)

Triacylglycerol	t_R [min]	ECN	Palm	Rapeseed	Soybean	Sunflower	Peanut	Cotton	Coconut	Maize	Olive	Sesame	Almond[a]	Safflower	Grape seed—white
LLL	65.3		0.3	1.2	13.9	24.5	4.6	17.0	0.1	17.5		11.0	3.3	43.3	25.8
LLPo	65.7														
PoLPo	66.2														
OLLn	66.4			8.3	7.1	0.4	0.6		<0.1	2.1		0.7			0.6
LnOPo	66.7														
LLM	66.8					0.6			0.1						0.3
GLnLn	66.8														
OLγLn	67.1														
OLLa	67.2								0.4						
OOC	67.7								0.2						
LnLP	67.8			1.6	6.1		0.2			1.0		0.3			0.2
PLnPo	68.2														
GγLnγLn	68.2														
MLM	68.5	42							0.1						
SLnLn	68.5				0.2										
γLnLP	68.5														
PLLa	68.6								0.2						
OOSt	68.6														
MOLa	68.9								1.1						
POC	69.2								0.3						
SLnγLn	69.2														
SLSt	69.6														
StOP	69.8														
SOCy	69.8								0.1						
SγLnγLn	69.9														
PMLa	70.5								1.7						
SLaLa	70.6								0.4						
LLMo	69.0				0.4	0.1				0.1			0.1	0.1	0.1
LLC15:0	70.3	43													0.1
LnLMa	70.7														
C20:2LL	70.8				0.2	0.1	0.1			0.1				0.1	0.1
OLL	71.8		1.0	7.3	12.9	21.4	16.2	14.3	0.3	22.1	3.1	17.2	13.9	19.8	21.5
GLLn	72.1														
OLPo	72.2										0.4				
OOLn	72.6			13.5	1.2						1.6	0.3			
PoOPo	72.7														
GLγLn	72.8														
LLP	73.1		2.7	1.4	13.3	12.1	6.3	28.7	0.2	16.0	1.2	8.5	4.0	13.6	15.4
OOγLn	73.3														
OLM	73.4		1.2						0.2						
PLPo	73.5														
SLLn	73.8				1.5										
OOLa	73.8								0.7						
LnOP	74.0	44	0.6	3.9	1.7					0.6	0.7	0.3			
PPoPo	74.1														
ALnLn	74.3														
SLγLn	74.5														
γLnOP	74.7														
PLM	74.9		0.7						0.1						
SLLa	75.0								<0.1						
MOM	75.3								0.4						
POLa	75.4								0.7						
PLnP	75.4		0.1	0.4	0.5					0.1					
SOSt	75.9														
PγLnP	76.1														
SMLa	77.0								0.5						
PMM	77.0								0.4						
OLMo	75.6					<0.1	0.1			<0.1			0.1		<0.1
LLMa	76.3	45			0.3	0.3	0.1			0.1		0.1	<0.1	0.1	0.3
MoLP	76.4						0.2						<0.1		
GLL	77.2			<0.1	0.2	0.3	1.2			0.4		0.2		0.5	0.6
OLO	77.9		2.5	15.7	5.3	7.3	14.3	4.8	0.3	10.7	10.0	15.2	20.1	4.8	8.0
C22:1LγLn	78.3														
OOPo	78.3			0.4							2.2				
GOγLn	78.8														
SLL	79.0				2.7	7.1	1.0	1.8	<0.1	1.8		2.1		2.9	5.4
OLP	79.3		9.0	4.4	5.6	6.3	8.1	12.1	0.3	8.7	5.3	9.7	11.8	3.9	8.9
ALLn	79.6														
OOM	79.7		1.7						0.4						
POPo	79.8										0.8				
SOLn	80.0			1.0	0.7						0.1				
BLnLn	80.1														
GγLnP	80.2	46													
ALγLn	80.3														

Table 1 (*Continued*)

Triacylglycerol	t_R [min]	ECN	Palm	Rapeseed	Soybean	Sunflower	Peanut	Cotton	Coconut	Maize	Olive	Sesame	Almond[a]	Safflower	Grape seed—white
SOγLn	80.7														
PLP	80.9		5.8	0.3	1.6	0.8	1.2	8.1	0.1	2.2	0.4	1.4	0.6	0.7	0.4
SLM	80.9								<0.1						
PPoP	81.3														
POM	81.3		3.9						0.4						
SOLa	81.3								0.2						
SLnP	81.4			0.1	0.3										
SγLnP	82.1														
SMM	83.1								0.2						
SPLa	83.1								0.1						
PPM	83.2		0.5												
OOMo	81.5						0.1				0.2		0.3		
C19:0LL	82.1					<0.1									<0.1
OLMa	82.3	47		<0.1	0.1	<0.1	0.1	0.1		<0.1		0.1	0.1		0.1
MoOP	82.7												0.2		
C23:0LnLn	82.9														
C22:1LL	82.5						0.2							<0.1	
GLO	83.1			0.8	0.1	0.1	1.5	<0.1		0.3	0.1	0.1	0.3	0.2	0.2
C24:1LγLn	83.7														
OOO	84.0		5.3	20.3	1.7	4.1	11.8	1.4	0.2	4.4	39.3	10.2	28.5	1.5	2.1
GLP	84.7				0.2		0.7			0.2					
ALL	84.8				0.2	0.6	0.4	0.2		0.5				0.5	0.3
BLLn	85.1				0.3										
SLO	85.1		1.2	0.6	1.7	3.5	1.2	1.1	<0.1	1.0		3.9	1.4	1.3	3.1
OOP	85.4		20.3	5.5	1.8	1.6	6.3	3.4	0.3	3.8	20.7	6.9	11.5	1.0	2.8
C22:1γLnP	85.5														
BLγLn	85.8	48													
GγLnS	85.9														
SLP	86.6		1.0	0.1	1.0	1.2	0.3	1.3	<0.1	0.4		1.2	0.1	0.4	0.3
ALnP	86.8														
SLnS	86.9														
POP	87.0		24.5	0.4	0.7	0.4	0.9	3.3	0.2	1.0	3.0	1.3	0.5	0.1	0.4
SOM	87.0								<0.1						
SγLnS	87.6														
PPP	88.7		5.3				0.1	0.1		0.1					<0.1
APLa	88.8								0.1						
SPM	88.9								<0.1						
C21:0LL	87.4						<0.1								<0.1
C25:0LnLn	88.3														
OOMa	88.4	49	0.1	0.3	<0.1		0.1					<0.1	0.1		<0.1
SLMa	89.3				<0.1										
MaOP	89.7		<0.1												
C24:1LL	87.9													0.5	
GLG	88.5														
C22:1LO	88.6						0.2								
GOO	89.0			1.4	<0.1	<0.1	1.4			0.1	0.7	0.2	0.1	<0.1	<0.1
C24:1OγLn	89.3														
C22:1LP	89.8														
GLS	89.9														<0.1
BLL	90.0			0.1	0.3	1.5	2.2	0.1		0.1	0.1	0.1		1.3	<0.1
LgLLn	90.2				0.1										
ALO	90.4		<0.1	0.2	0.1	0.3	0.6	0.1	<0.1	0.6	0.1	0.4	0.1	0.3	0.1
GOP	90.4	50	0.1	0.4			0.6		<0.1		0.2				
BOLn	90.6														
C24:1γLnP	90.6														
SOO	90.8		3.0	2.0	0.9	1.6	1.6	0.4	<0.1	0.5	5.9	3.9	2.6	0.5	1.2
LgLγLn	90.9														
ALP	91.8		0.2	<0.1	0.2	0.2	0.2	0.2	<0.1	0.2		0.3		<0.1	<0.1
SLS	91.9			<0.1	0.2	0.5	0.1	0.1	<0.1	0.1		0.3		0.1	0.1
BLnP	92.1														
ALnS	92.2														
SOP	92.3		5.7	0.2	0.2	0.3	0.3	0.7	<0.1	0.1	1.3	1.6	0.2	0.1	0.4
BγLnP	92.8														
SPP	94.4		1.4					<0.1							<0.1
C23:0LL	92.4				0.2	0.1	<0.1							0.1	<0.1
C23:0OLn	93.2	51													
SOMa	95.0														

Table 1 (*Continued*)

Triacylglycerol	t_R [min]	ECN	Palm	Rapeseed	Soybean	Sunflower	Peanut	Cotton	Coconut	Maize	Olive	Sesame	Almond[a]	Safflower	Grape seed—white
C22:1LG	93.1														
C22:1γLnC22:1	93.2														
C24:1LO	93.3			0.2										0.2	
GOG	93.9			<0.1											
C22:1OO	94.0						0.2							<0.1	
C24:1LP	94.6													<0.1	
LgLL	94.9			<0.1	0.1	0.4	1.0	0.1		0.2	<0.1	0.1		0.3	<0.1
C22:1OP	95.3														
BLO	95.5		0.1	0.3	0.2	0.8	2.8	0.1		0.2	0.1	0.1		0.7	<0.1
C24:1γLnS	95.6														
GOS	95.7	52													
LgOLn	95.8														
AOO	96.0		0.2	0.9	0.1	0.1	0.9	<0.1	<0.1	0.3	1.1	0.5	0.1	0.1	0.1
BLP	96.8		<0.1	<0.1	0.1	0.1	1.0	0.1		<0.1		<0.1		0.1	
ALS	96.9			<0.1	0.1	0.1		<0.1		<0.1		0.1		0.1	<0.1
LgLnP	97.1														
BLnS	97.2														
AOP	97.5		0.4	0.1	0.1		0.2	0.1		0.1	0.2	0.2		<0.1	0.1
SOS	97.6		0.4	0.1	0.1	0.2	0.1	0.1		0.1	0.2	0.6		0.1	0.1
APP	99.6		0.2												
SSP	99.7		0.1												
C25:0LL	97.4														
C23:0LO	97.9	53			<0.1	0.1								<0.1	
C21:0OO	98.4										<0.1				
C23:0LP	99.5				<0.1			<0.1							
C22:1LC22:1	97.7													0.1	
C22:1OG	98.7													<0.1	
C24:1OO	98.9			<0.1										<0.1	
C24:1LS	99.9													<0.1	
C26:0LL	100.1				<0.1	<0.1	0.2	<0.1							
C24:1OP	100.3														
C22:1OS	100.5														
LgLO	100.5	54	<0.1	0.1	0.1	0.2	1.6	<0.1	<0.1	0.2	0.1	0.1		0.2	
C26:0OLn	100.7														
BOO	101.0		0.1	0.5	0.1	0.4	2.3	<0.1		0.1	0.5	0.1		0.2	
LgLnS	101.8														
LgLP	101.9		<0.1	<0.1	0.1	0.1	0.4	0.1		0.1		<0.1		<0.1	
BLS	102.0				<0.1	0.1	0.3					<0.1		<0.1	
BOP	102.4		0.1	<0.1	0.1	<0.1	0.4	0.1			<0.1	0.1		<0.1	
AOS	102.6		0.1	<0.1	<0.1	<0.1	0.4				<0.1	0.1		<0.1	<0.1
SSS	104.6														
C25:0LO	102.6	55													
C23:0OO	103.3			<0.1		<0.1	<0.1				0.1			<0.1	
C22:1OC22:1	103.1													0.1	
C24:1OG	103.2														
C24:1OS	104.9														
C26:0LO	105.0						0.3					<0.1			
LgOO	105.5	56	0.1	0.2	<0.1	0.1	1.7	<0.1	<0.1	0.1	0.2	0.1		0.1	
C26:0LP	106.3				<0.1		0.1					<0.1			
LgLS	106.5				<0.1	<0.1	0.1					<0.1		<0.1	
LgOP	106.9		0.1	<0.1	<0.1	<0.1	0.3	<0.1	<0.1	0.1	<0.1	<0.1		<0.1	
BOS	107.0			<0.1	<0.1	<0.1	0.2					<0.1		<0.1	
C25:0OO	107.7	57									<0.1	<0.1			
C23:0OS	109.2														
C26:0OO	109.7	58					0.4				0.1				

Triacylglycerol	t_R [min]	ECN	Grape seed—red	Hazelnut[a]	Linseed	Poppy seed[a]	Walnut[a]	Avocado pear	Blackcurrant	Redcurrant	Borage	Cocoa butter	Evening primrose	Kukui oil	Wheat germ
LaCCy	26.5	30													
LaLaCo	27.4														
LaLaCy	33.7	32													
MLaCo	35.0														
StLnSt	38.8									0.1					
LaLCy	40.5														
LaLaC	41.0	34													
MLaCy	41.6														
PLaCo	43.1														
MMCo	43.1														
LnLnSt	43.5									0.8					
γLnLnSt	44.2									0.7					

Table 1 (*Continued*)

Triacylglycerol	t_R [min]	ECN	Grape seed—red	Hazelnut[a]	Linseed	Poppy seed[a]	Walnut[a]	Avocado pear	Blackcurrant	Redcurrant	Borage	Cocoa butter	Evening primrose	Kukui oil	Wheat germ
LaOCy	48.2														
LnLnLn	48.3				14.3		0.8		0.8	1.7				1.9	
LaLaLa	48.6														
MLaC	49.0														
LnLnγLn	49.0								0.9	1.0					
LnLSt	49.4	36							1.6	2.1					
MMCy	49.6														
PLaCy	49.6														
γLnLnγLn	49.7								0.9	0.4					
γLnLSt	50.1								0.8	0.7					
γLnγLnγLn	50.6								0.2	0.1	0.1				
StStP	52.6								0.2	0.1					
LnLLn	54.0				11.9		4.2		3.2	4.9				6.6	1.3
OLCy	54.3														
LnLγLn	54.7								3.6	2.9					
LaLLa	54.8														
LLSt	55.1								1.7	2.1					
LaOC	55.2														
γLnLγLn	55.4								2.0	0.9	3.6		3.4		
PLCy	55.5														
MOCy	55.7	38													
LnOSt	56.1								0.7	1.4					
MLaLa	56.2														
MMC	56.7														
PLaC	56.7														
γLnOSt	56.8								0.5	0.5					
StLnP	57.2								0.6	0.5					
PMCy	57.4														
SLaCy	57.4														
StγLnP	58.0								0.7	0.4					
LnLnC15:0	58.7	39			0.3										
LLLn	59.6		1.0		4.6	2.4	11.6		6.2	7.6				11.0	6.5
LLLa	60.3														
LLγLn	60.4								3.9	3.9	7.4		17.2		
OLC	60.7														
LnOLn	60.8				14.5		1.6		2.7	2.3				5.1	
OOCy	61.5														
LnOγLn	61.6								2.1	2.1					
MLLa	61.8														
OLSt	61.9								1.3	1.7					
LaOLa	62.1														
LnLnP	62.1	40			8.9		1.4		0.8	1.1				1.6	0.6
γLnOγLn	62.3								0.9	0.6	1.3				
MOC	62.4														
γLnLnP	62.8								1.5	0.7					
POCy	63.0														
StLP	63.1								1.5	1.4					
γLnγLnP	63.5								1.4	0.4	2.0		0.7		
PLaLa	63.7														
MMLa	63.7														
SLnSt	63.8								0.1	0.1					
SLaC	64.0														
SγLnSt	64.5									0.1					
LnLMo	63.3	41				0.2									
LnLnMa	65.6				0.1										
LLL	65.3		27.2	2.0	1.0	27.4	16.3	0.4	6.3	6.3	4.7		28.9	7.5	15.3
LLPo	65.7			0.1				0.3							
PoLPo	66.2							0.4							
OLLn	66.4		0.6	0.3	8.1	1.3	8.1	0.6	5.1	7.5				13.6	4.2
LnOPo	66.7							0.4							
LLM	66.8		0.4												
GLnLn	66.8				0.2										
OLγLn	67.1								4.8	4.0	7.9		4.5		
OLLa	67.2														
OOC	67.7														
LnLP	67.8		0.2		4.0	1.1	6.4	0.4	3.8	3.3				6.1	6.6
PLnPo	68.2							0.2							
GγLnγLn	68.2										0.2				
MLM	68.5	42													
SLnLn	68.5				4.3		0.3							0.6	
γLnLP	68.5								5.0	1.4	6.9		6.7		

Table 1 (*Continued*)

Triacylglycerol	t_R [min]	ECN	Grape seed—red	Hazelnut[a]	Linseed	Poppy seed[a]	Walnut[a]	Avocado pear	Blackcurrant	Redcurrant	Borage	Cocoa butter	Evening primrose	Kukui oil	Wheat germ
PLLa	68.6														
OOSt	68.6									2.0					
MOLa	68.9														
POC	69.2														
SLnγLn	69.2								0.2	0.2					
SLSt	69.6								0.2	0.4					
StOP	69.8								0.4	0.4					
SOCy	69.8														
SγLnγLn	69.9								0.3	0.1	0.5		0.1		
PMLa	70.5														
SLaLa	70.6														
LLMo	69.0		0.1			0.2	0.1								
LLC15:0	70.3	43	0.1							0.1					
LnLMa	70.7						0.1			<0.1					
C20:2LL	70.8		0.1			0.1	0.1		0.2	<0.1			0.1		0.1
OLL	71.8		20.7	7.6	2.0	18.5	13.2	3.3	6.7	7.2	7.2		10.4	10.2	13.5
GLLn	72.1								0.2						
OLPo	72.2			0.1				3.4							
OOLn	72.6			0.3	7.9		2.1	1.2	0.9	3.1				5.8	0.5
PoOPo	72.7							0.7							
GLγLn	72.8								0.5		1.4				
LLP	73.1		18.0	2.0	1.1	20.7	10.2	1.9	5.1	3.2	4.8		14.7	4.9	19.8
OOγLn	73.3								1.5	1.9	3.5		0.3		
OLM	73.4														
PLPo	73.5							1.7							
SLLn	73.8				1.7		1.4		0.4	0.9				2.5	
OOLa	73.8														
LnOP	74.0	44			4.2		1.8	1.0	1.3	1.1				2.7	1.8
PPoPo	74.1							0.4							
ALnLn	74.3				<0.1										
SLγLn	74.5								0.8	0.7	2.0		1.1		
γLnOP	74.7								2.3	0.9	3.2		0.4		
PLM	74.9														
SLLa	75.0														
MOM	75.3														
POLa	75.4														
PLnP	75.4		<0.1		0.4	<0.1	0.2	0.2						0.1	0.5
SOSt	75.9								0.1	0.2					
PγLnP	76.1								0.1	<0.1	0.9		0.2		
SMLa	77.0														
PMM	77.0														
OLMo	75.6		<0.1	0.1		0.1									
LLMa	76.3	45	0.2			0.3	0.1		<0.1	<0.1			0.2	<0.1	0.1
MoLP	76.4														
GLL	77.2		0.5		<0.1	0.2	0.2		0.6	0.1	1.8		0.4	0.2	1.4
OLO	77.9		5.9	17.1	2.0	8.0	6.2	10.3	3.7	4.2	3.5		1.3	5.9	5.2
C22:1LγLn	78.3										1.4				
OOPo	78.3			0.3				6.9							
GOγLn	78.8								0.3	<0.1	0.5				
SLL	79.0		5.6		0.3	3.6	2.0		0.9	0.9	2.0		2.6	1.3	1.1
OLP	79.3		8.3	7.0	0.6	7.9	4.0	9.4	2.3	2.0	3.8		1.9	3.8	7.1
ALLn	79.6								0.1						
OOM	79.7														
POPo	79.8			0.1				4.2							
SOLn	80.0				2.6		0.4			0.4				1.2	
BLnLn	80.1				0.1										
GγLnP	80.2	46									0.6				
ALγLn	80.3								0.1		0.2		0.2		
SOγLn	80.7								0.3	0.3	0.9				
PLP	80.9		0.6	0.4	<0.1	1.0	0.6	1.3	0.5	0.1	1.3	1.8	1.3	0.3	4.1
SLM	80.9														
PPoP	81.3							0.5							
POM	81.3														
SOLa	81.3														
SLnP	81.4				0.3		0.1							0.1	
SγLnP	82.1										0.5		0.1		
SMM	83.1														
SPLa	83.1														
PPM	83.2														

Table 1 (*Continued*)

Triacylglycerol	t_R [min]	ECN	Grape seed—red	Hazelnut[a]	Linseed	Poppy seed[a]	Walnut[a]	Avocado pear	Blackcurrant	Redcurrant	Borage	Cocoa butter	Evening primrose	Kukui oil	Wheat germ
OOMo	81.5			0.4											
C19:0LL	82.1		<0.1												
OLMa	82.3	47	0.1	0.1		0.1	<0.1		<0.1	<0.1					
MoOP	82.7			0.1				<0.1							
C23:0LnLn	82.9				<0.1										
C22:1LL	82.5										1.5				0.3
GLO	83.1		0.1	0.1	<0.1	0.1	0.1	<0.1	0.3	0.1	1.2		0.1	0.1	0.6
C24:1LγLn	83.7										0.7				
OOO	84.0		1.5	31.8	1.8	1.8	2.2	23.7	1.2	1.6	3.3	0.7	0.3	2.5	1.7
GLP	84.7										0.9				0.6
ALL	84.8		0.3			0.3	0.5		0.1	0.1	0.1		0.6		0.3
BLLn	85.1				<0.1										
SLO	85.1		2.7	1.2	0.1	1.6	1.3		0.7	0.5	1.3	0.7	0.4	1.1	0.3
OOP	85.4		2.5	18.5	1.2	1.5	1.2	20.2	0.9	0.8	2.2	3.9	0.2	1.9	2.7
C22:1γLnP	85.5										0.6				
BLγLn	85.8	48									0.2		0.1		
GγLnS	85.9										0.2				
SLP	86.6		0.4	0.5	0.1	0.4	0.3		0.1	0.1	0.8	1.9	0.4	0.2	0.3
ALnP	86.8				<0.1										
SLnS	86.9				0.1										
POP	87.0		0.9	1.8	0.2	0.4	0.2	4.2	0.2	0.1	0.6	16.6	0.1	0.3	1.2
SOM	87.0														
SγLnS	87.6										0.2				
PPP	88.7		<0.1					0.2		<0.1		0.1			0.1
APLa	88.8														
SPM	88.9														
C21:0LL	87.4		<0.1										<0.1		
C25:0LnLn	88.3				<0.1										
OOMa	88.4	49	<0.1	0.3	<0.1			<0.1							
SLMa	89.3														
MaOP	89.7											0.4			
C24:1LL	87.9										0.8		<0.1		0.2
GLG	88.5										0.2				
C22:1LO	88.6										0.7				0.2
GOO	89.0		<0.1	0.4	<0.1	<0.1	<0.1	0.3	0.1	<0.1	0.8			0.1	0.2
C24:1OγLn	89.3										0.4				
C22:1LP	89.8														0.1
GLS	89.9		<0.1				<0.1				0.4				
BLL	90.0		<0.1			<0.1	<0.1		0.1		0.4		0.3		0.1
LgLLn	90.2				<0.1										
ALO	90.4		0.1	0.2		0.1	0.1		0.1	<0.1	0.1		0.1	<0.1	0.1
GOP	90.4	50						0.3			0.5				0.2
BOLn	90.6				0.1										
C24:1γLnP	90.6										0.3				
SOO	90.8		1.0	5.4	0.8	0.4	0.4	1.0	0.3	0.4	1.6	4.4	<0.1	0.6	0.2
LgLγLn	90.9												<0.1		
ALP	91.8		<0.1		<0.1	0.1	0.1		<0.1		0.1		0.1	<0.1	<0.1
SLS	91.9		0.1		<0.1	<0.1	0.1		<0.1	<0.1	0.1	1.2	0.1	<0.1	<0.1
BLnP	92.1				<0.1										
ALnS	92.2				<0.1										
SOP	92.3		0.6	1.3	0.1	0.2	<0.1	0.3	0.1	0.1	0.6	36.4	<0.1	0.2	0.2
BγLnP	92.8										0.1				
SPP	94.4		<0.1									0.9			
C23:0LL	92.4								<0.1				<0.1		
C23:0OLn	93.2	51			<0.1										
SOMa	95.0											0.6			
C22:1LG	93.1												<0.1		
C22:1γLnC22:1	93.2										0.1		<0.1		
C24:1LO	93.3										0.5				0.1
GOG	93.9														<0.1
C22:1OO	94.0										1.0		<0.1		<0.1
C24:1LP	94.6										0.6				0.1
LgLL	94.9		<0.1			<0.1			<0.1		0.1		0.1		0.1
C22:1OP	95.3										0.6				
BLO	95.5		<0.1		<0.1			0.1	<0.1				0.1		0.1
C24:1γLnS	95.6										0.1				
GOS	95.7	52									0.2				<0.1
LgOLn	95.8				<0.1										
AOO	96.0		<0.1	0.4	<0.1		<0.1	0.2	<0.1	<0.1	0.1	0.2	0.1	<0.1	<0.1
BLP	96.8										<0.1		<0.1		0.1

Table 1 (*Continued*)

Triacylglycerol	t_R [min]	ECN	Grape seed—red	Hazelnut[a]	Linseed	Poppy seed[a]	Walnut[a]	Avocado pear	Blackcurrant	Redcurrant	Borage	Cocoa butter	Evening primrose	Kukui oil	Wheat germ
ALS	96.9		<0.1		<0.1						<0.1		<0.1		
LgLnP	97.1				<0.1										
BLnS	97.2				<0.1										
AOP	97.5		0.1	<0.1				<0.1			0.1	0.9	<0.1	<0.1	<0.1
SOS	97.6		0.1	0.1	0.1			<0.1		<0.1	0.1	23.5	<0.1	<0.1	<0.1
APP	99.6														
SSP	99.7											1.6			
C25:0LL	97.4												<0.1		<0.1
C23:0LO	97.9	53													
C21:0OO	98.4														
C23:0LP	99.5												<0.1		
C22:1LC22:1	97.7												0.1		
C22:1OG	98.7										0.3		<0.1		
C24:1OO	98.9										<0.1				<0.1
C24:1LS	99.9										0.1				
C26:0LL	100.1												<0.1		<0.1
C24:1OP	100.3										0.1				
C22:1OS	100.5										0.3				
LgLO	100.5	54			<0.1			0.1			0.1		<0.1		0.1
C26:0OLn	100.7				<0.1										
BOO	101.0				<0.1			0.1			0.1		<0.1		<0.1
LgLnS	101.8				<0.1										
LgLP	101.9										<0.1		<0.1		0.1
BLS	102.0										<0.1	0.1			
BOP	102.4				<0.1						<0.1	0.7			<0.1
AOS	102.6		<0.1		<0.1						<0.1	1.9			
SSS	104.6											0.7			
C25:0LO	102.6	55						<0.1							
C23:0OO	103.3														
C22:1OC22:1	103.1										0.1		0.1		
C24:1OG	103.2										0.1				
C24:1OS	104.9										0.2				
C26:0LO	105.0														<0.1
LgOO	105.5	56			<0.1			0.1			0.1	0.1	<0.1		<0.1
C26:0LP	106.3														<0.1
LgLS	106.5										<0.1		<0.1		
LgOP	106.9							<0.1			<0.1	0.3			<0.1
BOS	107.0										<0.1	0.4			
C25:0OO	107.7	57						<0.1							
C23:0OS	109.2											<0.1			
C26:0OO	109.7	58						0.1							

[a] Data from ref. [25].

MS (Table 2) to compare their FA profiles in individual samples. Analyzed samples are composed almost exclusively by FAs with 16 (palmitic and palmitoleic acids) and 18 (stearic, oleic, linoleic, linolenic, gamma-linolenic and stearidonic acids) carbon atoms with the total concentration in samples from 97.01% in palm oil to 99.82% in kukui oil. The lower concentrations of C16 and C18 FAs have been observed only in borage (91.86%) and peanut (90.81%) oils with higher concentration of FAs with long acyl chains (C20 and longer) and coconut oil (23.45%) with well-known high content of short-chain FAs (C6:0 to C14:0). The most abundant FAs present in all analyzed samples are palmitic acid (C16:0) with concentration from 5.76% in redcurrant oil to 40.57% in palm oil, stearic acid (C18:0) from 0.46% in avocado oil to 34.51% in cocoa butter, oleic acid (C18:1) from 7.66% in evening primrose oil to 73.85% in olive oil, linoleic acid (C18:2) from 1.89% in cocoa butter to 73.96% in safflower oil and arachidic acid (C20:0) from 0.03% in coconut oil to 1.05% in cocoa butter.

3.5. Nutritional parameters of analyzed plant oils

Physical and nutritional properties of plant oils are given by FA composition in TGs. Various contents of saturated and unsaturated FAs in TG mixtures result in their different melting points under room temperature (oils vs. fats), oxidation stability, digestion or relation to the harmful low-density lipoprotein (LDL) cholesterol. The average composition of FAs can be expressed by average parameters calculated from TG composition in individual samples (Table 3). Values of calculated average parameters can be compared with values of relevant parameters of FAs, i.e. ECN = 16, CN = 18 and DB = 1 for oleic acid (C18:1), etc. For example, aECN = 15.88, aCN = 17.76 and aDB = 0.94 for olive oil correspond to the high content of oleic acid with 18 CNs and 1 DB, in fact with the total content of oleic acid 73.85%. Other example of aECN = 14.21, aCN = 17.82 and aDB = 1.81 for evening primrose oil corresponds to the high content of linoleic acid with 18 CNs and 2 DBs, in fact with the total content of linoleic acid 67.49%. aECN values of analyzed samples range from 14 to 16 with several exceptions. Coconut oil with aECN = 12.10 is typical by high content of short-chain FAs with the low ECN value. Lower aECN values of linseed (aECN = 13.68), redcurrant (13.82) and blackcurrant (13.91) oils are caused by high content of linolenic acid (ECN = 12) or linolenic and gamma-linolenic (ECN = 12) acids in case of blackcurrant and redcurrant oils. In contrast, the higher value of cocoa butter (aECN = 16.72) results from the high content of stearic acid with ECN = 18. Plant oils are composed predominantly by FAs

Table 2
Relative concentrations [%] of individual fatty acids in analyzed plant oils calculated from HPLC/APCI-MS of triacylglycerols with their response factors (RF)

Fatty acid	Symbol	CN:DB	RF	Palm	Rape	Soybean	Sunflower	Peanut	Cotton	Coconut	Maize	Olive	Sesame	Almond[a]	Safflower	Grape seed—white
Caproic	Co	6:0	134.76							1.37						
Caprylic	Cy	8:0	74.44							15.60						
Capric	C	10:0	17.62							3.70						
Lauric	La	12:0	6.04							37.05						
Myristic	M	14:0	2.77	2.36			0.18			18.80						0.08
–	C15:0	15:0	1.75													0.03
Palmitoleic	Po	Δ9–16:1	1.33		0.13							1.10				
Palmitic	P	16:0	1.32	40.57	6.51	11.66	7.69	9.47	22.12	7.33	11.95	11.75	10.86	9.47	6.60	9.40
Margaroleic	Mo	Δ9–17:1	0.81			0.12	0.06	0.12			0.04	0.08		0.23	0.02	0.05
Margaric	Ma	17:0	0.81	0.03	0.09	0.13	0.11	0.08	0.02		0.04		0.05	0.09	0.03	0.12
Stearidonic	St	Δ6,9,12,15–18:4	0.23													
α-Linolenic	Ln	Δ9,12,15–18:3	0.40	0.23	12.87	12.52	0.14	0.27		0.01	1.73	0.77	0.63			0.60
γ-Linolenic	γLn	Δ6,9,12–18:3	0.29													
Linoleic	L	Δ9,12-C18:2	0.57	10.26	19.21	51.76	61.52	35.63	57.27	2.20	55.99	8.53	41.52	27.03	73.96	63.20
Oleic	0	Δ9-C18:1	1.00	41.36	57.67	19.18	22.94	43.50	18.15	10.73	27.41	73.85	40.91	61.65	15.15	22.21
Stearic	S	18:0	0.61	4.59	1.46	3.41	5.15	1.94	1.93	3.18	1.44	2.57	4.95	1.43	1.86	3.69
–	C19:0	19:0	0.49				<0.01									0.01
–	C20:2	Δ11,14–20:2	0.36			0.05	0.03	0.04			0.02				0.04	0.04
Gadoleic	G	Δ9–20:1	0.36	0.05	0.97	0.16	0.15	1.90	0.01	<0.01	0.34	0.34	0.16	0.04	0.25	0.28
Arachidic	A	20:0	0.40	0.38	0.45	0.32	0.49	0.92	0.25	0.03	0.65	0.49	0.59	0.06	0.40	0.25
–	C21:0	21:0	0.39					0.02				0.01				0.01
Erucic	C22:1	Δ13–22:1	0.42					0.22							0.12	
Behenic	B	22:0	0.46	0.07	0.40	0.42	1.14	3.49	0.15		0.16	0.28	0.19		0.95	0.02
–	C23:0	23:0	0.40		0.02	0.08	0.06	0.03	0.01			0.04			0.05	<0.01
Nervonic	C24:1	Δ15–24:1	0.40		0.08										0.33	
Lignoceric	Lg	24:0	0.40	0.10	0.14	0.18	0.33	1.99	0.08	<0.01	0.23	0.16	0.13		0.24	0.01
–	C25:0	25:0	0.39									0.01	<0.01			
Cerotic	C26:0	26:0	0.39			0.01	0.01	0.38	0.01			0.02	0.01			

Fatty acid	Symbol	CN:DB	Grape seed—red	Hazelnut[a]	Linseed	Poppy seed[a]	Walnut[a]	Avocado pear	Blackcurrant	Redcurrant	Borage	Cocoa butter	Evening primrose	Kukui oil	Wheat germ
Caproic	Co	6:0													
Caprylic	Cy	8:0													
Capric	C	10:0													
Lauric	La	12:0													
Myristic	M	14:0	0.13												
–	C15:0	15:0	0.03		0.08					0.03					
Palmitoleic	Po	Δ9–16:1		0.20				6.52							
Palmitic	P	16:0	10.50	10.60	6.90	10.95	8.67	16.75	9.23	5.76	10.97	27.03	9.02	7.29	16.52
Margaroleic	Mo	Δ9–17:1	0.03	0.18		0.16	0.04	0.01							
Margaric	Ma	17:0	0.10	0.10	0.04	0.12	0.07	0.01	0.03	0.03		0.32	0.06	0.01	0.02
Stearidonic	St	Δ6,9,12,15–18:4							3.54	5.32					
α-Linolenic	Ln	Δ9,12,15–18:3	0.61	0.19	52.32	1.68	16.59	1.32	15.80	20.10				25.56	8.06
γ-Linolenic	γLn	Δ6,9,12–18:3							13.73	9.20	18.41		13.04		
Linoleic	L	Δ9,12-C18:2	65.07	17.61	15.89	66.05	52.69	13.48	37.86	36.34	35.42	1.89	67.49	39.36	54.85
Oleic	0	Δ9-C18:1	19.36	67.83	20.82	18.58	19.34	60.98	17.29	21.20	22.88	34.58	7.66	24.95	17.81
Stearic	S	18:0	3.63	2.91	3.65	2.10	2.19	0.46	1.52	1.86	4.18	34.51	1.71	2.66	0.76
–	C19:0	19:0	0.01												
–	C20:2	Δ11,14–20:2	0.05			0.04	0.02		0.07	0.02			0.04		0.05
Gadoleic	G	Δ9–20:1	0.24	0.18	0.11	0.12	0.15	0.20	0.73	0.09	3.37		0.17	0.13	1.11
Arachidic	A	20:0	0.21	0.20	0.06	0.17	0.24	0.07	0.16	0.05	0.28	1.05	0.36	0.04	0.21
–	C21:0	21:0	0.01										0.01		
Erucic	C22:1	Δ13–22:1									2.53		0.15		0.21
Behenic	B	22:0	0.02		0.09	0.01	<0.01	0.06	0.03		0.35	0.45	0.16		0.12
–	C23:0	23:0			0.01				<0.01			0.01	0.02		
Nervonic	C24:1	Δ15–24:1									1.49		0.01		0.13
Lignoceric	Lg	24:0	<0.01		0.03	0.02		0.10	0.01		0.12	0.16	0.09		0.10
–	C25:0	25:0			<0.01			0.02					<0.01		0.01
Cerotic	C26:0	26:0						0.02					0.01		0.04

[a] Data processed from ref. [25].

Table 3
Number of identified triacylglycerols and fatty acids, average parameters, the relative concentration of essential fatty acids [%] (linoleic and linolenic acids) and of saturated (Sat), monounsaturated (Mono) and polyunsaturated (Poly) fatty acids [%] in all analyzed oils calculated from NARP-HPLC/APCI-MS results

Plant	Number of TGs/FAs	Major TGs (>5%)	aECN	aCN	aDB	Essential FAs [%]	Sat [%]	Mono [%]	Poly [%]
Oil palm	41/11	POP,OOP,OLP,PLP,SOP,OOO,PPP	15.85	17.07	0.61	10.49	48.10	41.41	10.49
Rape	55/13	OOO,OLO,OOLn,OLLn,OLL,OOP	15.20	17.91	1.36	32.08	9.07	58.85	32.08
Soybean	66/14	LLL,LLP,OLL,LLLn,LnLP,OLP,OLO	14.59	17.79	1.60	64.28	16.21	19.46	64.33
Sunflower	50/16	LLL,OLL,LLP,OLO,SLL,OLP	14.97	17.90	15.16	61.66	15.16	23.15	61.69
Peanut	60/16	OLL,OLO,OOO,OLP,LLP,OOP	15.69	18.05	1.18	35.90	18.32	45.74	35.94
Cotton	38/11	LLP,LLL,OLL,OLP,PLP	14.93	17.55	1.31	57.27	24.57	18.16	57.27
Coconut palm	85/13	MLaCy,LaLaCy,PLaCy,LaOCy	12.10	12.36	0.13	2.21	87.06	10.73	2.21
Maize	46/12	OLL,LLL,LLP,OLO,OLP	14.90	17.78	1.44	57.72	14.4	27.79	57.74
Olive	37/15	OOO,OOP,OLO,SOO,OLP	15.88	17.76	0.94	9.30	15.33	75.37	9.30
Sesame	49/12	OLL,OLO,LLL,OOO,OLP,LLP,OOP	15.29	17.79	1.25	42.15	16.78	41.07	42.15
Almond[a]	25/8	OOO,OLO,OLL,OLP,OOP	15.49	17.80	1.15	27.03	11.05	61.92	27.03
Safflower	55/14	LLL,OLL,LLP	14.67	17.94	1.63	73.96	10.13	15.87	74.00
Grape vine white	46/17	LLL,OLL,LLP,OLP,OLO,SLL	14.81	17.81	1.50	63.80	13.62	22.54	63.84
Grape vine red	46/16	LLL,OLL,LLP,OLP,OLO,SLL	14.77	17.78	1.51	65.68	14.64	19.63	65.73
Hazel[a]	30/10	OOO,OOP,OLO,OLL,OLP,SOO	15.70	17.77	1.04	17.80	13.81	68.39	17.80
Linseed (Flax)	63/13	LnOLn,LnLnLn,LnLLn,LnLnP,OLLn,OOLn	13.68	17.86	2.09	68.21	10.86	20.93	68.21
Opium poppy[a]	33/12	LLL,LLP,OLL,OLO,OLP	14.67	17.77	1.55	67.73	13.37	18.86	67.77
Walnut[a]	43/11	LLL,OLL,LLLn,LLP,OLLn,LnLP,OLO	14.34	17.82	1.74	69.28	11.17	19.53	69.30
Avocado pear	44/14	OOO,OOP,OLO,OLP,OOPo	15.57	17.52	0.97	14.80	17.49	67.71	14.80
Blackcurrant	77/14	OLL,LLL,LLLn,OLLn,LLP,γLnLP	13.91	17.82	1.94	53.66	10.98	18.02	71.00
Redcurrant	78/12	LLLn,OLLn,OLL,LLL	13.82	17.88	2.00	56.44	7.73	21.29	70.98
Borage	88/11	OLγLn,LLγLn,OLL,γLnLP	14.90	17.98	1.56	35.42	15.90	30.27	53.83
Cacao	25/9	SOP,SOS,POP	16.72	17.47	0.37	1.89	63.53	34.58	1.89
Evening primrose	61/17	LLL,LLγLn,LLP,OLL,γLnLP	14.21	17.82	1.81	67.49	11.44	7.99	80.57
Kukui nut tree	38/8	OLLn,LLLn,OLL,LLL,LnLLn,LnLP,OLO,OOLn,LnOLn	14.25	17.85	1.80	64.92	10.00	25.08	64.92
Wheat germ	61/15	LLP,LLL,OLL,OLP,LnLP,LLLn,OLO	14.67	17.70	1.51	62.91	17.78	19.26	62.96

[a] Data processed from ref. [25].

with 18 CNs which also correspond to aCN ranging from 17.40 to 18.00 in plant oils. Exceptions are found for coconut oil (aCN = 12.10) with the high content of short-chain FAs, palm oil (aCN = 17.07) with the high content of palmitic acid or peanut oil (aCN = 18.05) with the higher content of long-chain FAs from C20 to C24. The content of saturated and unsaturated FAs in samples is a valuable nutritional parameter in human diet. In analyzed samples, aDB range from 0.9 to 1.9 except for highly saturated coconut (aDB = 0.13), cacao butter (0.37) and palm (0.61) oils or highly unsaturated blackcurrant oil (1.94), redcurrant oil (2.00) and linseed oil (2.09).

Other important nutritional parameters of analyzed plant oils are expressed by the sums of essential, saturated, monounsaturated and polyunsaturated FAs (Table 3). FAs with DBs positions Δ12 and Δ15 (ω3 and wω6 FAs) are essential for human and have to be obtained by food, therefore their content in plant oils correlates with the nutritional value of these oils. The sum of essential FAs in most samples is found in the wide interval from 10 to 70%, except for 1.89% in cacao butter, 2.21% in coconut oil, 9.3% in olive oil and 73.96% in highly essential safflower oil. The sum of saturated FAs in analyzed plant oils ranges from 10 to 25% in common plant oils except 7.73% in redcurrant oil, 9.07% in rapeseed oil or highly saturated oils with 48.10% of saturated FAs in palm oil, 63.53% in cocoa butter and 87.06% in coconut oil. In analyzed samples, the sum of monounsaturated FAs is in the range from 15 to 65% except for 7.99% in evening primrose oil, 10.73% in coconut oil, 67.71% in avocado oil, 68.39% in hazelnut oil and 75.37% in olive oil. The sum of polyunsaturated FAs range from 10 to 70% in samples except for 1.89% in cocoa butter, 2.21% in coconut oil, 9.30% in olive oil, 70.98% in redcurrant oil, 71.00% in blackcurrant oil, 74.00% in safflower oil and 80.57% in evening primrose oil.

4. Conclusions

This work reports the quantitation of TGs in 26 plant oils important in food, nutrition and cosmetic industries according to the ref. [4]. The APCI-MS quantitation is based on the use of response factors calculated according to the calibration slopes of standards of individual single-acid TGs. This method is based on optimized NARP-HPLC separation providing the highest separation selectivity, as demonstrated by the fact that the number of positively identified TGs in our works is significantly higher than reported by others including two-dimensional separations. This is the first case when both intact TGs identification/quantitation and total/average FA profiles are reported and compared with the assessment of nutritional parameters of individual plant oils. Chromatograms are used as fingerprints (i.e. qualitative aspect) of individual oils in contrast to Table 1 showing precise quantitative composition including low abundant TGs. Table 2 presents quantitative results of FAs identified in TGs, while Table 3 summarizes average parameters to explored obtained data from different points of view.

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