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Studies on non-traditional oils: I. Detailed studies on different lipid profiles of some *Rosaceae* kernel oils

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RESUMEN

Estudios de aceites no tradicionales: I. Estudios detallados sobre diferentes perfiles lipídicos de aceites de semillas de la familia *Rosaceae*.

Aceites obtenidos de las semillas de albaricoque, melocotón y ciruela, producidos como subproductos de la industria alimenticia conservera, se analizaron mediante cromatografía gaseosa capilar y cromatografía líquida de alta resolución. Se estableció la composición en ácidos grasos de los mono-, di- y triacilgliceroles fraccionados. El ácido oleico osciló desde el 64% al 72% en triacilgliceroles (TAG), mientras que el ácido linoleico lo hizo entre el 17% y el 27%. El perfil de TAG mostró la presencia de OOO (35-42%), LOO (22-28%), LLO (7-16%), LOP y LLS (6-7%), OOP (6-10.4%). En los tres aceites analizados se detectaron campesterol-, 5-estigmasterol-, β-sitosterol-, isofucosterol, 7-estigmasterol y avenasterol. También se determinaron glicósidos de esteroles, mostrando perfiles característicos. El contenido en tocoferoles fue apreciable en todos ellos, siendo el gamma-tocoferol el predominante. Los alfa- y delta-tocoferoles se detectaron en pequeñas cantidades. Los resultados obtenidos pueden usarse para caracterizar estos aceites de semilla y facilitar su diferenciación de otros aceites.

PALABRAS-CLAVE: Aceite de semilla de albaricoque - Aceite de semilla de ciruela - Aceite de semilla de melocotón - Perfil lipídico.

SUMMARY

Studies on non-traditional oils: I. Detailed studies on different lipid profiles of some *Rosaceae* kernel oils.

Kernel oils obtained from apricot, peach and plum, produced as by-products from food canning industry, were analyzed by capillary GC and HPLC. The fatty acid composition of the fractionated mono-, di- and triacylglycerol was elucidated. Oleic acid ranged from 64 to 72% in triacylglycerol (TAG), whereas linoleic acid ranged from 17% to 27%. The TAG profile showed the presence of OOO (35-42%), LOO (22-28%), LLO (7-16%), LOP and LLS (6-7%), OOP (6-10.4%). Campesterol-, 5-stigmasterol-, β-sitosterol-. isofucosterol, 7-stigmasterol and avenasterol were detected in the three analyzed oils. Sterylglycosides were also determined and showed some characteristic profiles. The three kernel oils contained appreciable amounts of tocopherols in which gamma-tocopherol was the predominating one. Alpha-and delta-tocopherols were also present in smaller quantities. Results obtained can be used to characterize these kernel oils and facilitate their differentiation from the other oils.

KEY-WORDS: Apricot seed oil - Lipid profile - Peach seed oil - Plum seed oil.

1. INTRODUCTION

Kernels of apricot, peach and plum, belonging to the family Rosaceae, are produced as by-products in tonnages from food canning industry (1). The kernels are considered as non-traditional potential resources for oils (2).

Previous studies on some Rosaceae kernel oils had been reported by some authors (2,3,4,5,6,7) determining some minor component fatty acids and fatty acid constituents of phospholipids and glycolipids. These oils contained appreciable amounts of oleic and linoleic acids, however linolenic acid was found to be negligibly present.

Tonnages of kernels of peach, apricot and plum are produced from the local food canning industry and their oils have not been fully studied. Peach and apricot kernel oils of the locally cultivated varieties, have been studied by some authors (6,7). Apricot and peach kernel oils had been analyzed only for their fatty acids (6) whereas peach kernel oil had been investigated for their fatty acid and sterol composition (7). Kernel oils of peach and apricot have been used as adulterants or substitutes for some expensive oils particularly, almond oil (8). Therefore, there is a lack of data on the composition of the different lipids of these kernel oils. The objective of this work was to elucidate their fatty acid, triacylglycerol, sterol, sterylglycoside and tocopherol patterns using advanced methods of analysis in order to characterize and possibly to differentiate Rosaceae kernel oils from other vegetable oils.

2. MATERIALS AND METHODS

2.1. Materials

Plum (*Prunus domestica*), apricot (*Prunus armeniaca*) and peach (*Prunus persica*) kernels were obtained from food canning factories, (season 1997) cleaned and dried at 100 °C for 10-12 hrs. The oil was extracted with chloroform-methanol (2/1 v/v) and the oil content was calculated on dry basis (9).

2.2. Methods

2.2.1. *Oil fractionation and fatty acid composition*

2.2.1.1. Chromatographic fractionation of oil

The oil was fractionated into triacylglycerol (TAG) (the predominating fraction) and the minor diacylglycerol (DAG) and monoacylglycerol (MAG) as well as free fatty acids (FFA). Fractionation was conducted with the help of thin-layer chromatography (TLC) using hexane/diethyl ether/formic acid (70/30/1 v/v/v) as developing solvent. The located zones of TAG (R_f = 0.76), DAG (R_f = 0.15), MAG (R_f = 0.01) and FFA (R_f = 0.4) were scraped from the plate and extracted with moistened n-hexane at 50 °C. The hexane solution was dried over anhydrous sodium sulphate and the solvent was distilled off under N_2.

2.2.1.2. Preparation of methyl esters

Each fraction was converted into methyl esters using 5% HCl in methanol and the mixture was refluxed at 70-80 °C for two hours till complete transesterification (10). The reaction was monitored with the help of TLC to ensure the conversion of all MAG, DAG or FFA into methyl esters. TLC was carried out using glass plates (20 x 20 cm) coated with 0.25 mm layer of silica gel G (Merk) and was developed with n-hexane : diethyl ether : acetic acid (80:20:1 v/v/v). The dry plates were subjected to iodine vapour to detect the formed methyl esters and the progress of methylation reaction. After the termination of the reaction, the reaction mixture was transferred to a separating funnel containing diethyl ether to extract the methyl esters. The ether layer was thoroughly washed with distilled water till neutrality and the solution was dried over anhydrous sodium sulphate and filtered. The ether was evaporated under reduced pressure at room temperature using a rotary evaporator apparatus. The methyl esters were placed in 5 ml vials and stored until use at 10 °C.

2.2.1.3. GLC analysis of fatty acid methyl esters

Hewlett-Packard HP 5890-A instrument was used for the analysis of the fatty acid methyl esters. All analysis were conducted by temperature programming using an efficient capillary column under the following operating conditions: column: 0.32 mm x 30 m filled with DB-23 (film thickness, 0.25 μm); column temperature: 150 ~ 230 °C, 3.0 °C/min; injector temperature: 230 °C; detector: flame ionization (FID); carrier gas: N_2, flow rate, 1.3 ml/min and split ratio (100:1). Peaks areas were determined by electronic integrator and percentage composition of fatty acids was automatically calculated. Standard mixture of fatty acids were similarly chromatographed.

2.2.2. *Triacylglycerol*

HPLC (Tosoh, Japan) was used for the direct analysis of triacylglycerol (11,12); 10 μl oil in chloroform (300 mg/ml) was injected under the following conditions: column ODS capcel Pak C_{18} (4.4 x 100 mm); gradient elution with acetonitrile: dichloromethane (starting from 90:10 to 35:65, v/v in 150 min); detector, FID (with moving band, tracor 945).

2.2.3. *Sterols*

Sterols were isolated from the unsaponifiables via preparative silica gel G plates using chloroform: diethyl ether: acetic acid (95:4:1, v/v/v). The isolated sterol mixtures were treated with silylating reagent consisting of three parts of hexamethyl disilazane (HMDS) and one part of trimethyl-chlorosilane (TMCS) with 10 parts of dry pyridine as a solvent. After a reaction period of about 15 min at room temperature, the mixture was directly injected into gas chromatograph (Hewlett-Packard-HP 5890-A). The analysis was conducted under the following operating conditions : column; DB-17 (0.32 mm x 15 m with 0.25 μm coating) at 250 °C; detector, FID at 260 °C; carrier gas, Helium (8.6 ml/min) and split ratio 35:1. The % peak areas were calculated by electronic integrator (10,13).

2.2.4. *Free and acylated sterylglycosides*

The oil sample in chloroform was injected into silica gel cartridge (Sep-Pak, Waters) and the mixed sterylglycosides were eluted with chloroform: methanol (1:1, v/v). The eluted compounds were fractionated with the help of preparative TLC using chloroform: methanol: formic acid (90:15:1, v/v/v) into free sterylglycoside (FSG) and acylated sterylglycoside (ASG). Only ASG was deacylated with alkaline hydrolysis (0.5 N KOH in isopropanol) to obtain FSG. The obtained FSG and the original one were separately converted into their 1-anthroylnitrile derivatives (SG-1-AN).

HPLC was used for the analysis of SG-1-AN under the following conditions: column, ODS Wakosil-5, C_{18} (6.4 x 250 mm); elution: gradient using acetonitrile: dichloromethane (from 50:50 to 68:32, v/v); detector: UV and absorption was measured at 254 nm (14).

2.2.5. *Tocopherols*

HPLC (Tosoh) was used for direct analysis of tocopherols. A sample of 10 µl oil in n-hexane (10% soln.) was injected in HPLC column (silica, YMC-A-012, 6.2 x 150 mm). Elution was isocratic using n-hexane:isopropyl alcohol (100: 0.5, v/v) at flow rate 2 ml/min. Hitachi-650-10S fluorescence detector was used. Spectral absorption was set at excitation and emission wave lengths 295 and 325 nm (13).

3. RESULTS AND DISCUSSION

Dry kernels of plum, apricot and peach contained 32%, 37% and 43% of oil respectively. Therefore, these kernels could be used as potential sources of oils.

3.1. Fatty acid pattern

Table I shows that triacylglycerol (TAG) of peach kernel oil contain lower concentration of palmitic acid compared to those of apricot and plum, whereas apricot kernel oil contains comparatively higher percentage oleic acid (n-9) than the other two oils. Stearic acid in apricot is generally higher than that in plum and peach. Linoleic acid in peach kernel oil is higher than that in the other two oils.

Table I
Fatty acid composition of the fractionated glycerides of the three *Rosaceae* kernel oils determined by GLC

Sample	Content (%)	Fatty acid composition (%)								
		16:0	16:1	18:0	18:1 n-9	18:1 n-7	18:2	18:3	20:0	20:1
Plum										
TAG	99.1	6.0	0.6	2.2	69.4	1.1	20.4		0.2	0.1
DAG	0.5	7.7	—	3.2	63.9	1.6	23.6		—	—
MAG	tr.	—	—	—	—	—	—		—	—
FFA	0.4	18.9	—	6.7	54.8	—	19.6		—	—
Apricot										
TAG	99.1	5.8	0.4	2.7	72.1	0.9	17.8		0.2	0.1
DAG	0.6	10.2	—	3.2	62.7	1.7	22.2		—	—
MAG	tr.	—	—	—	—	—	—		—	—
FFA	0.3	20.6	—	7.9	55.2	—	16.3		—	—
Peach										
TAG	99.3	4.6	0.6	1.3	64.5	1.4	27.3	0.1	0.1	0.1
DAG	0.3	5.5	—	1.5	59.5	2.0	31.5	—	—	—
MAG	tr.	—	—	—	—	—	—	—	—	—
FFA	0.4	12.9	—	4.1	57.1	—	25.9	—	—	—

TAG: Triacylglycerol
DAG: Diacylglycerol
MAG: Monoacylglycerol
FFA: Free fatty acids

In diacylglycerol (DAG) fraction, apricot kernel oil contains higher percentage of palmitic acid than those in the other two oils. On the other hand, the DAG fraction in plum kernel oil contains slightly higher content of oleic acid, whereas DAG in peach kernel oil contains higher amount of linoleic acid than the corresponding fraction in the other two kernel oils.

MAG fraction is found in trace amount in the three kernel oils (Table I). Palmitic, stearic, oleic and linoleic acid were detected in appreciable amounts in the free form.

3.2. Triacylglycerol pattern

Eleven TAG molecular species were determined in the three kernel oils, at various amounts (Table II). Kernel oils, were free of linolenate (X), no TAGs including this acid were detected. LLL, in peach kernel oil is in higher percentage than the other two oils. LLO constitutes 16.0% in peach kernel oil which is markedly higher than that in plum (9.6%) and apricot (7.6%). LOO is the major TAG component of the three kernel oils, but peach contains higher

percentage (28.5%) than that in plum kernel oil (23.9%) and apricot kernel oil (22.0%). LLS is incompletely separated from LOP and the two peaks were calculated as one. Thus, the LLS-LOP constitute 7.1, 6.9 and 6.3% for plum, apricot and peach, respectively. OOO is the second major TAG component that amounts to 42.9, 43.8 and 35.6% in plum, apricot and peach respectively, showing a comparatively lower amount in peach kernel oil. In apricot kernel oil, OOP is higher (10.4%) than that in plum (8.6%) and peach kernel oil (6.0%), whereas, OOS is present at levels of 3.1, 4.6 and 1.4% in plum, apricot and peach kernel oils, respectively.

It seems that each oil exhibits very characteristic TAG pattern that can differentiate one oil from the other. Thus, peach exhibits higher LLL, LLO, LOO and lower OOO, whereas apricot shows a markedly higher amount of OOP.

Table II

Triacylglycerol profiles of the three *Rosaceae* kernel oils determined by HPLC

Molecule species	Plum	Apricot	Peach
LLL	1.4	1.1	3.1
LLO	9.6	7.6	16.0
LLP	1.5	1.0	1.6
LOO	23.9	22.0	28.5
LLS / LOP	7.1	6.9	6.3
LPP	0.2	0.2	0.2
OOO	42.9	43.8	35.6
LOS	1.5	2.2	1.2
OOP	8.6	10.4	6.0
POP	0.2	0.2	0.1
OOS	3.1	4.6	1.4

X: Linolenic
L: Linoleic
O: Oleic
P: Palmitic
S: Stearic

3.3. Tocopherols pattern

Tocopherol content of plum kernel oil was distinctly higher than that of apricot and peach kernel oils (Table III). Plum, apricot and peach kernel oils contained 710, 430 and 520 ppm respectively. These oils were rich in gamma-tocopherol containing 85.5%, 93.5% and 97.7% respectively. However, alpha-and delta-tocopherols were detected in minor amounts. Beta-tocopherol was not detected in the three oils. Based on the tocopherol patterns of the three kernel oils, it can be denoted that these three oils are highly resistant to autoxidation due to the presence of gamma-tocopherol in high percentage. The later exhibits high antioxidant activity (15).

3.4. Sterols pattern

GLC analysis of the sterol's TMS using capillary column gives different sterol patterns for the three kernel oils (Table IV). Plum kernel oil contained higher amount of campesterol compared to the other two kernel oils. However 7-stigmasterol was detected in apricot kernel oil at a concentration of 1.8% which was higher than that in peach kernel oil (1.0%). In plum kernel oil it was detected in trace amount. Peach kernel oil contained comparatively higher amount of isofucosterol than the other two oils. Therefore, the three oils can be differentiated one from the other by the higher campesterol content in plum kernel oil, the higher 7-stigmasterol in apricot and finally the higher isofucosterol in peach kernel oil.

3.5. Sterylglycoside profiles of FSG and ASG

Sterylglycosides were present in the kernel oils as non esterified (FSG) and esterified (ASG) forms (Table V). The total amounts of these compounds was 150, 170 and 155 ppm for plum, apricot and peach kernel oils respectively. The FSG fractions of the kernel oils were present at lower levels than that of the ASG. Only apricot kernel oil contained 0.6% avena-SG and 3.5% 7-stigma-SG which is unique in this respect (Table V). In plum kernel oil, isofuco-SG and campe/stigma-SG were determined in higher concentrations than in the other two oils. Peach kernel oil showed SG patterns of FSG with lower amount of campe-/stigma-SG than the other two oils.Peach kernel oil showed SG patterns of FSG with lower amount of campe-/stigma-SG than the other two oils. Therefore, the FSG patterns of the three oils can be used for their differentiation. The ASG fraction of plum, apricot and peach kernel oils was 131, 129 and 104 ppm respectively. In FSG and ASG fractions of plum kernel oil, the isofuco-SG and campe-/stigma-SG were present in higher amounts than in the other two kernel oils. It should be noted that SG's, as minor lipid components, have received the interest of some authors (13,14,16). They seem to be sterol carriers in plant tissue of the seeds (17). According to our findings, SG patterns of the three kernel oils are more decisive for differentiating and recognizing these three kernel oils.

Table III
Tocopherol composition of the three *Rosaceae* kernel oils determined by HPLC

Sample	Total ppm	Tocopherol composition (%)			
		Alpha-Tocopherol	Beta-Tocopherol	Gamma-Tocopherol	Delta-Tocopherol
Plum	710	11.0	—	85.5	3.5
Apricot	430	5.0	—	93.5	1.5
Peach	520	Trace	—	97.7	2.3

Table IV
Sterol patterns of the three *Rosaceae* kernel oils determined by GLC

Sample	Content (%)	Sterol composition (%)					
		Campesterol	Stigmasterol	B-sitosterol	Isofucosterol	7-stigmasterol	Avenasterol
Plum	0.32	5.5	0.9	87.4	6.2	Trace	—
Apricot	0.35	4.0	0.9	87.8	5.5	1.8	—
Peach	0.37	4.1	—	84.4	10.5	1.0	—

Table V
Sterylglycoside profiles of the three *Rosaceae* kernel oils determined by HPLC

Sample	SG type	Content ppm	Sterylglycoside composition (%)				
			Avena-SG	Isofuco-SG	Campe/stigma-SG	7-stigma-SG	B-sito-SG
Plum	FSG	19	—	6.0	3.9	—	90.1
	ASG	131	—	4.8	4.0	—	91.2
Apricot	FSG	41	0.6	4.7	2.5	3.5	88.7
	ASG	129	—	2.9	2.8	—	94.3
Peach	FSG	51	—	4.4	1.9	—	93.7
	ASG	104	—	3.3	2.9	—	93.8

SG: Sterylglycoside
FSG: Free sterylglycoside
ASG: Acylated sterylglycoside

In the light of the different lipid compositions of the three Rosaceae oils in comparison with some common oils, the following observation can be pointed out:

Rosaceae oil TAG are rich in oleic acid which ranges from 64.5 to 72.1%. They also contain linoleic acid at amounts similar to that in rape seed oil, however cottonseed and sunflower oils contain appreciably higher amounts of linoleic acid (17,18).

Concerning the TAG profiles, OOO is the predominating TAG in the three Rosaceae oils, however cottonseed, sunflower oils contain very lower amounts, whereas rapeseed contains reasonable amounts. On the other side, LLL in these three kernel oils is lower than in cottonseed and sunflower oils, whereas rapeseed oil contains very little amount of this TAG. LOP in the three kernel oils is present in amounts lower than in cottonseed and sunflower oils but is similar to that of rapeseed (17,18).

The three kernel oils show very characteristic tocopherol patterns in which gamma-tocopherol is the predominating one. On the other side, the common seed oils are either rich in alpha-tocopherol (sunflower) or in gamma-tocopherol (corn oil). However, in cottonseed and rapeseed oil the ratios of alpha to gamma-tocopherol are 1:1 and 1:5 respectively (17).

7-Stigmasterol is generally present in lower amounts in apricot, peach and plum kernel oils respectively in comparison to sunflower oil (17). The

presences of characteristic sterol in common oils can help differentiate them from Rosaceae oil.

In contrast to some common seed oils (cottonseed and rapeseed oils), Rosaceae kernel oils are characterized by having low total sterylglycoside contents. In addition, free sterylglycosides of the kernel oils are present in comparatively lower levels than those of the acylated ones, which is not the case with the two common oils (17).

It can be concluded that from the different lipid profiles of the analyzed Rosaceae oils, it is possible to detect any one of them, if it is mixed with other oil. Particularly apricot and peach oils are sold as adultrants or substitutes for almond oil.

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