NEUTRAL LIPIDS OF THE SEED OILS OF *Onopordum olgae* AND *Arcthium tomenthosum*

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A closeness of the compositions of neutral lipids of the seed oils of *Onopordum olgae* and *Arcthium tomenthosum*, family Asteraceae and a difference in the quantitative ratios in the set of hydrocarbons and fatty acids, both the free acids and those acylating glycerol, have been established. Four new groups of oxidized diacylglycerols have been isolated: 1,3- and 1(3),2-hydroxyacylmonoacylglycerols and 1,3- and 1(3),2-epoxyacylmonoacylglycerols.

The seed oils of plants of the family Asteraceae (Compositae) are a rich source of oxidized lipids [1], which have been studied inadequately but are of definite interest as substances fulfilling important biological functions in the organism. The composition of the classes of deposited lipids of the seed oils of the Compositae are considered in publications [2-6] and in the present paper.

The seeds of *Onopordum olgae* were collected in 1976 on the western slopes of Bolshoi Chimgan, and the seeds of *Arcthium tomenthosum* in 1978 in the environs of the village of Poltoratskii, KazSSR.

From each oil we isolated about 16 classes and types of lipids (% on the oil): hydrocarbons (0.1; 0.1, respectively), acyltriterpenols (0.1; tr.); acetyltriterpenols (tr.; tr.), triacylglycerols (84.6; 89.9), epoxyacyldiacylglycerols (5.8; 1.9), hydroxyacyldiacylglycerols (5.5; 1.6), triterpenols (tr.; tr.), epoxyacylhydroxyacylmonoacylglycerols (tr.; tr.), diacylglycerols (1.0; 1.0), sterols (0.5; 1.5), di(hydroxyacyl)monoacylglycerols (0.5; none), epoxyacylmonoacylglycerols (0.2; 0.1), hydroxyacylmonoacylglycerols (none; 0.1), unoxidized free fatty acids (1.0; 1.5), oxidized free fatty acids (tr.; tr.), monoacylglycerols (0.5; 0.1), and unidentified substances (0.2; 3.0).

The results obtained show the isolation of four new groups of oxidized diacylglycerols: 1,3- and 1(3),2-hydroxyacylmonoacylglycerols and 1(3)- and 2-epoxyacylmonoacylglycerols. The IR and NMR spectra confirmed their diacetylglycerol structures. Their migration in a thin layer of adsorbant and the ratio of the numbers of oxidized and unoxidized acyl radicals corresponded to the presence of a single oxidized radical in each of them. The IR and NMR spectra, thin-layer chromatography (TLC), and qualitative reactions of the combined methyl esters of the oxidized fatty acids isolated from them were identical with those given previously [7, 8]. They showed that the normal aliphatic chain of the acyl radicals of the first and second types of lipids contained α-hydroxyoctadecadienic systems appearing as the result of the reduction of the primary products of the peroxide oxidation of 1,4-dienic systems. The same facts showed the presence of isolated epoxide rings and of an ethylenic bond in a normal aliphatic chain of the acyl radicals of lipids of the third and fourth types. Epoxide groups appear as the result of the introduction of hydroperoxide groups of the primary products of peroxide oxidation into 1,4-dienic systems.

The compositions of the fatty acids of the oils and of some lipids isolated from them are given in Table 1.

The trace amounts of mixtures of triterpenols and mixtures of their esterified derivatives were not identified. The hydrocarbons of *O. olgae* proved to be represented by the C_{32}-C_{28} paraffins, with the C_{29} compound present in largest amount, and C_{28}-C_{14} monoenes. The hydrocarbons of *A. tomenthosum* consisted of the C_{32}-C_{28} paraffins, with the C_{30} compound

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TABLE 1. Composition of the Fatty Acids of the Oils and Some Lipids of the Seed Oils of *Onopordum olgae* (I) and *Arctium tomenthosum* (II)

Acids		GLC results, % of total												Results of PTLC and calculation, % of the total		
		14:0	14:2	15:0	16:0	16:1[9]	18:0	18:1[9]	18:2[9,12]	18:3[9,12,15]	20:0	22:0	x	Σ unoxidized	epoxy acids	hydroxy acids
Oil																
Total	I	Tr	—	—	7,8	0,7	1,9	32,6	56 6	Tr	0,4	Tr	—	95,6	2,1	2,3
"	II[a]	Tr	—	—	7,7	Tr	2,4	16,3	64,7	8,4	0,5	—	Tr	98,7	0,7	0.6
Unsaturated	I[b]	1,8	—	0,6	71,5	—	20,7	—	—	—	4,5	Tr	—	—	—	—
"	II[c]	—	—	—	56,8	—	36,5	—	—	—	5,8	Tr	—	—	—	—
Triacylglycerols																
Total	I	0,4	—	—	8,0	—	3,7	38,8	48,4	—	0,7	—	—	100	—	—
"	II	0,4	—	—	6,4	—	3,2	19,3	62,4	7,4	0,9	—	—	100	—	—
In position 2	I	—	—	—	1,3	—	—	40,6	58,1	—	—	—	—	100	—	—
"	II	—	—	—	2,1	—	—	25,2	67,2	5,5	—	—	—	100	—	—
Epoxyacyldiacylglycerols																
Total	I	0,4	—	—	7,2	0,6	3,1	32,8	54,6	0,7	0,6	—	—	66,7	33,3	—
"	II	0,8	—	—	8,9	0,9	4,6	21,3	56,8	5,3	1,5	1,4	—	66,7	33,3	—
In position 2	I[d]	0,8	2,2	—	5,3	—	1,5	59,3	30,3	—	—	—	—	66,7	33,3	—
"	II	—	5,0	—	8,9	—	4,3	55,8	22,8	3,2	—	—	—	50,0	50,0	—
Hydroxyacyldiacylglycerols																
Total	I	0,2	—	—	6,9	0,6	2,4	28,2	61,7	—	—	—	—	66,7	—	33.3
"	II	0,8	—	—	8,6	2,2	4,8	20,5	52,6	7,5	1,8	1,2	—	66,7	—	33.3
In position 2	I	—	2,4	—	8,6	1,2	—	65,2	22,6	—	—	—	—	66,7	—	33.3
"	II	1,3	4,2	—	4,8	—	1,5	35,5	47,9	4,2	—	—	0,6	50,0	—	50.0
Diacylglycerols																
Total	I	—	—	—	18,2	7,3	5,5	42,5	25,6	—	0,9	—	—	100	—	—
"	II	—	—	—	8,7	1,4	5,5	23,2	54,6	5,6	1,0	—	—	100	—	—
Epoxyacylmonoacylglycerols																
Total	I	0,8	—	0,8	19,6	7,4	0,2	37,6	26,4	1,2	2,2	2,2	1,6	50,0	50,0	—
"	II	—	—	—	10,4	1,8	4,2	21,2	52,8	6,8	1,6	1,2	—	50,0	50,0	—
Di(hydroxyacyl)monoacylglycerols																
Total	I	1,2	—	0,6	21,3	8,4	0,4	38,4	21,9	1,5	2,7	0,9	2,7	33,3	—	66,7
Hydroxyacylmonoacylglycerols																
"	II	—	—	—	11,2	2,0	3,2	18,6	58,6	5,6	0,8	—	—	50,0	—	50,0
Monoacylglycerols																
Total	I	1,0	—	1,0	10,1	2,0	4,5	29,5	49,0	1,9	1,0	—	—	100	—	—
"	II	—	—	—	6,1	0,9	2,6	22,0	59,0	7,5	1,3	—	—	100	—	—
Free fatty acids																
Unoxidized	I	—	—	—	31,6	4,2	2,6	34,2	26,3	—	—	—	1,1	100	—	—
"	II	—	—	—	16,1	—	3,4	21,7	58,8	—	—	—	—	100	—	—
Oxidized	I	—	—	—	—	—	—	—	—	—	—	—	—	—	—	100
"	II	—	—	—	—	—	—	—	—	—	—	—	—	—	—	100

Note. a) 17:0, tr.; b) 17:0, 0.9%; c) 12:0, 0.9%; d) 12:0, 0.6%.

present in largest amount, the C_{28}-C_{11} monoenes, and traces of C_{18}-C_8 dienes and trienes.

Thus, the results obtained have shown that the seed oils of two species of Compositae belonging to different genera of plants of this family have very similar compositions of the deposited lipids. A difference is observed only in the quantitative ratio of the homologs of the hydrocarbons and fatty acids in both the free acids and those acylating glycerol, produced in the seeds.

EXPERIMENTAL

The isolation of the oils, their separation into the individual components, the identification and purity checking of the latter with the aid of TLC, all types of spectral analyses, the hydrolysis of the acyl-containing lipids, the methylation of the fatty acids, the gas–liquid chromatography and separation of the methyl esters of these fatty acids according to their degree of unsaturation, oxidative degradation at the positions of the ethylenic bonds in the methyl esters of the monoenic, dienic, and trienic acids, and enzymatic hydrolysis of the acylglycerols were all carried out by methods described previously [7-11].

Hydrocarbons. Mass spectrum of the combined hydrocarbons of *O. olgae* (165°C, 40 V), molecular ions (rel.%), C_n, where n is the number of carbon atoms. Paraffins: 450(0.1), C_{32}; 436(0.3), C_{31}; 422(0.4), C_{30}; 408(1.9), C_{29}; 394(0.3), C_{28}; monoenes: 392(0.6), C_{28}; 378(0.9), C_{27}; 364(1.2), C_{26}; 350(1.2), C_{25}; 336(1.4), C_{24}; 322(1.5), C_{23}; 308(1.2), C_{22}; 294(1.5), C_{21}; 280(1.5), C_{20}; 266(1.8), C_{19}; 252(1.8), C_{18}; 238(1.8), C_{17}; 224(2.4), C_{16}; 210(2.1), C_{15}; 196(3.3), C_{14}.

Mass spectrum of the combined hydrocarbons of *A. tomenthosum* (180°C, 40V), molecular ions (rel. %), C_n. Paraffins: 450(0.1), C_{32}; 436(0.1), C_{31}; 422(3.0), C_{30}; 408(0.1), C_{29}; 394(2.0), C_{28}; monoenes: 392(0.5), C_{28}; 378(0.6), C_{27}; 364(0.68), C_{26}; 350(1.0), C_{25}; 336(1.2), C_{24}; 322(1.5), C_{23}; 308(1.6), C_{22}; 294(1.8), C_{21}; 280(1.9), C_{20}; 266(2.0), C_{19}; 254(2.1), C_{18}; 240(2.3), C_{17}; 226(2.1), C_{16}; 212(2.3), C_{15}; 198(3.2), C_{14}; 184(4.5), C_{13}; 170(6.3), C_{12}; 166(6.1), C_{11}; dienes: 252 (tr.), C_{18}; 100 (tr.), C_8; trienes: 250 (tr.), C_{18}; 98 (tr.), C_8.

Di(hydroxyacyl)monoacylglycerols. The IR and NMR spectra correspond to the spectra of triacylglycerols [10, 11]. In a thin layer of silica gel they had R_f 0.55 in system 1 hexane–ether (4:6). The ratio of the number of oxidized and unoxidized acyl radicals was 2:1. Characteristic signals of these glycerols and of the methyl esters of the combined oxidized fatty acids isolated from them by mild alkaline hydrolysis are: 3550-3450 cm^{-1}, s (–OH), and 950 and 985 cm^{-1}, m (IR spectrum, ν_{max}^{film}) and a broad complex multiplet, m, 6-5.2 ppm (NMR, δ; cis,trans-conjugated double bonds).

The 1,3- and 1(3),2-hydroxyacylmonoacylglycerols were partly separated by column chromatography. NMR, δ, ppm: for the 1,3- isomer signals detected were s 4.03 (>CHOH), m 4.1 ($-CH_2OCOR$, 4 H); for the 1(3),2- isomer – m 5.1 (>CHOCOR), d 3.67 ($-\underline{CH_2}OH$), m 4.1 ($-CH_2OCOR$). IR spectrum, ν_{max}^{film}, cm^{-1}: 1100 m and 1060 m (secondary and tertiary alcohol groups, respectively), 950 and 985 m (cis,trans-conjugated dienic bonds), and 3550-3450 m (bound –OH).

The ratio of the numbers of oxidized and unoxidized acyl radicals in the molecule was 1:1. In a thin layer of silica gel, the R_f value in system 1 was 0.4. For the IR spectrum of the methyl esters of the fatty acids forming the oxidized radical there were characteristic signals in the regions of 3550-3450 cm^{-1}, m (–OH), and 950 and 985 cm^{-1}, m, and in the NMR spectrum of the same esters there was a signal at 5.2-6 ppm δ (cis,trans-conjugated ethylenic bonds).

1,3- and 1(3),2-Epoxyacylmonoacylglycerols. The indices of the IR and NMR spectra of this type of disubstituted glycerols and of the methylated fatty acids from the oxidized acyl radical obtained from them differed from the preceding ones only by the absence of the group and of cis,trans-conjugated ethylenic bonds and by the presence of the absorption of the bonds (830 and 850 cm^{-1}, m) and of the resonance of the protons (2.71 ppm, δ) of an epoxide ring.

The ratio of the numbers of oxidized and unoxidized acyl radicals was 1:1. In a thin layer of silica gel in system 1, migration was characterized by R_f 0.6.

SUMMARY

The compositions of the neutral lipids of the seed oils of *Onopordum olgae* and *Arctium tomenthosum*, family Asteraceae, have been studied. The closeness of the compositions of the lipids and a difference in the quantitative ratios in the sets of hydrocarbons and fatty acids, both the free acids and those acylating glycerol, have been established. Four new groups of oxidized diacylglycerols have been isolated.

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TRIACYLGLYCEROLS OF OITICICA OIL

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The composition of the triacylglycerols (TAGs) of oiticica oil has been studied by enzymatic hydrolysis with pancreatic lipase. It has been established that the majority of TAGs of the 96 types present have a mixed character. The four main types make up 60% of the total TAGs and the remainder consist of minor components. A high content of TAGs with octadeca-9,11,13-trienoic acids (including licanic) in the extreme positions has been detected.

A source of oiticica oil is formed by the seeds of the tree *Licania rigida* (family Rosaceae) growing in Brazil, Mexico, and Central America [1]. The oil belongs to the group of tung-like drying oils [2, 3]. Because of its high film-forming capacity, this oil is widely used for modifying alkyd resins [4].

The physicochemical indices [5] and fatty-acid composition [6] of oiticica oil have been studied. In view of the presence of licanic acid in oiticica oil in an amount of 74-82%, it is considered that it consists mainly of glycerides of licanic acid, which are responsible for its high film-forming properties [3]. In the present work we consider the composition of the triacylglycerols of oiticica oil studied by the method of enzymatic hydrolysis with pancreatic lipase. The results of a determination of the fatty-acid compositions of the initial triacylglycerols (TAGs), of the 2-monoacylglycerol fraction of the oil (MGs), and also of the enrichment and selectivity factors (EF and SF) [7] are given in Table 1.

As can be seen from Table 1, α-eleostearic, β-eleostearic, and licanic acids, which are highly unsaturated, have low values of the selectivity factor and mainly esterify the primary hydroxy groups of the glycerol.

TABLE 1. Fatty-Acid Compositions of the Triacylglycerols and 2-Monoacylglycerols of Oiticica Oil

Acid	Amounts of the acid in the fractions		Enrichment factor	Selectivity factor
	TAGs	MGs		
Palmitic	3,2	4,7	1,47	0,70
Stearic	4,2	3,5	0,83	0,39
Oleic	9,4	18,9	2,01	0,96
Linoleic	3,6	10,6	2,94	1,40
α-Eleostearic	5,3	0,0	0,00	0,00
β-Eleostearic	2,8	0,0	0,00	0,00
Licanic	71,5	62,3	0,87	0,41

*Deceased.

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