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THE GLYCERIDE COMPLEX OF THE SEED OIL OF *Onopordum acanthium*

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The fatty acids (FAs) containing epoxide and hydroxy groups that have been isolated from the seed oils of various plants have *a priori* been considered as components of glycerides [1-3]. However, the direct experimental proof of this hypothesis was published elsewhere [4-11]. It has become known that epoxide- and hydroxyl-containing acyl radicals occupy both the 1,3 and the 2 positions in triglycerides (TGs) [3, 6-10] or exclusively the 1,3 positions [11].

In each of the cited papers, information has been published on those individual glycerides that could be isolated. In the present paper we report the isolation and the investigation of a whole series of individual groups of glycerides found simultaneously in the seed oils of *Onopordum acanthium* L. (Scotch cotton-thistle) family Compositae, growing on the northern slopes of the Chatkal range.

The seed oil (100 g) was subjected to column chromatography. This led to the isolation of nine fractions with solvent systems a-g (wt.% on the oil):

a) fraction I (mixture of hydrocarbons, esters, traces of triglycerides) — 0.18;

b) fraction II (triglycerides) — 88.0;

c) fraction III (epoxyacyl triglycerides) — 4.16;

d) fraction IV (oxoacyl triglycerides, about 0.1; free fatty acids and hydroperoxyacyl triglycerides, about 0.1) — 0.40;

e) fraction V (hydroxyacyl triglycerides, 1.58; pentacyclic alcohols) — 1.62;

fraction V' (hydroxyacyl triglycerides) — 3.42;

f) fraction VI (epoxyacyl-hydroxyacyl triglycerides, 0.36; diglycerides, 0.55; free sterols) — 1.21;

g) fraction VII (oxidized triglycerides) — 0.35;

fraction VIII (oxidized triglycerides, hydroxy acids) — 0.18;

fraction IX (monoglycerides) — 0.17.

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The total amount of substances in all the fractions isolated was 99.69%.

Composite fractions of the oils were subjected to rechromatography in a thin layer.

Triglycerides (n-TGs). The substances of fraction II, which were practically transparent in the near ultraviolet (UV), absorbed in the infrared region and give NMR spectra like those of the triglycerides of normal fatty acids (n-FAs).

From the products of the alkaline hydrolysis of the n-TGs we isolated the mixture of FAs. In a thin layer of Silufol, this mixture migrated as one zone (in any of systems **a-g**) like a mixture of 16:0, 18:1, and 18:3 n-FAs. The composition of n-FAs according to GLC of their methyl esters (MEs) was as follows (%): 16:0, 4.3; 18:0, 1.0; 18:1, 26.8; 18:2, 67.9.

From the products of the enzymatic hydrolysis of the n-TGs, by the TLC method in system i we isolated 2-monoglycerides (2-MGs). By mild alkaline hydrolysis the 2-MGs yielded a mixture of n-FAs (Silufol) with the following composition according to the GLC of the MEs (%): 16:0, 0.5; 18:1, 30.7; 18:2, 68.8.

As can be seen from the results obtained, the composition of the FAs of the 2-MGs differed little from the composition of the FAs of the n-TGs. It is obvious that this is due to the random distribution of the acyl radicals between the terminal 1.3 and central 2 positions in the TGs.

In fact, the type composition of the n-TGs found from the results of enzymatic hydrolysis (in mole %; S represents saturated and U unsaturated acyls: SSS, 0.0; SSU, 0.6; SUU, 14.5; UUU, 84.9) corresponds to the typical composition obtained by calculation according to the law of random distribution [12, 13] (in mole %, where S is 5.3% and U 94.7%, the calculation formula being $(S + U)^3 \cdot 10^{-4}$: SSS, 0.0; SSU, 0.8; SUU, 14.2; UUU, 85.0).

The position-species composition of the n-TGs, where S represents the 16:0 + 18:0, O the 18:1, and L the 18:2 acids) was calculated by Coleman's method (mole %):

OSL — 0.2	LOL — 14.0
LSL — 0.2	SLS — 0.4
SOS — 0.2	SLO — 2.6
SOO — 1.2	SLL — 7.1
SOL — 3.2	OLO — 4.2
OOO — 1.9	OLL — 23.1
OOL — 10.3	LLL — 31.4

Of the 18 possible species variants of the n-TGs, only 14 are actually present in the oil.

The monoepoxyacyl TGs (e-TGs) of fraction III have been characterized in an earlier paper [14].

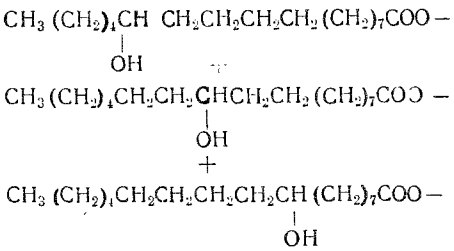
The Monooxoacyl TGs (o-TGs). The sum of the substances of fraction IV was separated by the TLC method in system c. Three zones of substances were obtained, only the first of which gave a positive reaction with 2,4-DNPH [15].

In the IR spectrum of the substances of this zone, attention is attracted by the broadened region of carbonyl absorption (1745 cm^{-1} — ester carbonyl; and 1725 s, 1690 m, 1680 m, 1660 w, and 1590 cm^{-1} w — carbonyl of an α-oxodiene system). This IR and NMR spectra confirm the triglyceride nature of these substances.

From the products of the transesterification of the total oxidized TGs we isolated a mixture of oxidized FAs from which, by the method of descending CC were obtained the MEs of α-oxoctadecadienoic acids (MEs of o-FAs). The presence of an α-oxodiene system in the structure of MEs of the o-FAs (the zone of which on Silufol is stained by 2,4-DNPH) was confirmed by the bathochromic shift of the region of absorption of the oxo group by 13 nm (267 nm in cyclohexane → 280 nm in ethanol). This shift of the absorption with a change in solvent is a well-known characteristic feature of α,β-unsaturated ketones [16-18].

In the products of the periodate-permanganate (Rudloff) degradation of the MEs of the o-FAs we detected a $C_{6:0}$ monocarboxylic fragment — $CH_3(CH_2)_4COO$ — (GLC of the MEs of 125°C) and a $C_{9:0}$ dicarboxylic fragment — $OOC(CH_2)_7COOCH_3$ (GLC of the MEs at 203°C), showing the localization of the α-oxodiene system between the 9th and 13th carbon atoms.

Hydrogenation of the MEs of the o-FAs in the presence of palladium gave the MEs of saturated hydroxy acids. Oxidative degradation of the latter with permanganate (Hilditch) enabled us to establish the presence in the hydrogenation products of three saturated hydroxy isomers:

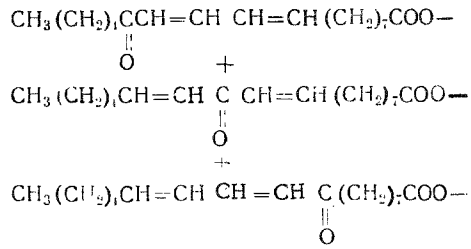


(I)

(II)

(III)

The ratio of the degradation fragments — for example, the monocarboxylic fragments (5:0, 13.8%; 6:0, 34.5%; 7:0, 9.2%; 8:0, 16.7%; 9:0, 20.9%; 10:0, 4.9%) — confirms the presence of the isomer (II), since 9% and 16% are not minute magnitudes that could be due to overoxidation. Consequently, the mixture of MEs of oxooctadecadienoic acids before hydrogenation consisted of the following three isomers:



(IV)

(V)

(VI)

However, the IR and NMR spectra of the o-TGs show the presence in them of only traces of conjugated diene systems. Thus, these facts, as also the absence of the region of absorption of isolated trans bonds, means that the main component of the oxoacyl radicals is 11-oxo-cis,cis isomer (V). The other oxo isomers, obviously and naturally [20], were formed during the process of isolating and separating the MEs of the products of the initial state of oxidation.

In literature sources there is information only on the detection of seed oils of the natural (?) 9-oxo- and 13-oxooctadecadienoic acids [17, 18].

Monohydroperoxyacyl TGs (HOO-TGs). The second zone of substances isolated by the TLC method by system c from fraction IV consisted exclusively of free FAs (Silufol, system c, model FAs 16:0 + 18:1 + 18:2). The third zone contained triglycerides (IR spectrum) revealing active oxygen on Silufol plates under the action of the thiocyanate reagent [19]. The HOO-TGs liberate iodine instantaneously even from a neutral solution of potassium iodide and after treatment with formaldehyde decolorize an alkaline solution of Methylene Blue [20]. All the qualitative reactions were performed in comparison with blank experiments and in experiments with the n-TGs.

The simultaneous presence of HOO-TGs and o-TGs is an additional indirect confirmation of the presence of HOO-TGs in the oil, since HOO groups are unstable and can decompose with the formation of oxo groups [20]. Furthermore, hydroperoxides accumulating in the animal organism are reduced by enzymes or by other natural compounds to hydroxy groups. Consequently, it is not surprising that considerably larger (more than 10 times) amounts of hydroxyacyl triglycerides were detected in the oil.

Monohydroxyacyl TGs (h-TGs). The mixture of substances of fraction V' was detected by its IR, NMR, and UV spectra (233 nm), which were identical with the spectra of the HOO-TGs but it gave no reaction with thiocyanate for the presence of active oxygen.

Glycerol was isolated from the water soluble products of transesterification and the products of the alkaline hydrolysis of the h-TGs. It was identified from its mobility in a thin layer of silica gel on Silufol plates (systems j, k, l) and by reactions with silver nitrate and with iodine vapor. From its IR spectrum, which was identical with the spectrum of a sample of authentic glycerol, we obtained a shift in the signals of the hydroxylic protons of 4.79 → 5.33 ppm in the presence of trifluoroacetic acid (TFA).

In the ether-soluble products of the two reactions we detected (TLC, systems c, f) the MEs of n-FAs, and the MEs of h-FAs, n-FAs, and h-FAs. The reaction products were separated by the CC method (systems c, f). In this way we isolated: the total MEs of the n-FAs, the composition of which according to GLC, was as follows (%): 14:0, 0.4; 16:0, 6.8; 18:0, 0.9; 18:1, 22.8; 18:2, 69.1; the sum of the MEs of the h-FAs, which, according to the results of UV, IR, and NMR spectroscopy, were identical with the MEs of α-hydroxyoctadecadienoic acids that we have isolated from the seed oil of common wormwood [21]; the sum of the n-FAs, the composition of which corresponds to that given above from the GLC results after methylation with diazomethane; and the sum of the h-FAs, after treatment of which with diazomethane the MEs of the h-FAs were obtained (Silufol, system f).

The weight ratio between the sum of the n-FAs (or the MEs of the n-GAs) and the sum of the h-FAs (or the MEs of the h-FAs), about 2:1, as found by the TLC method (gravimetrically) shows that in the h-TGs only one acyl radical is oxidized. Hence, the fatty-acid composition of the h-TGs calculated for ∿33.3% of h-FAs is as follows, %: 14:0, 0.3; 16:0, 4.5; 18:0, 0.6; 18:1, 15.2; 18:2, 46.1; h-18:2, 33.3.

From the products of the enzymatic hydrolysis of the h-TGs we isolated by the TLC method in systems i the hydroxyacyl and acyl 2-monoglycerides (2-h-MGs and 2-n-MGs) in a weight ratio of 1:7. The composition of the n-FAs of the 2-n-MGs according to the results of mild alkaline hydrolysis and the GLC of the MEs of the n-FAs was (%): 18:1, 22.2; 18:2, 77.8. The fatty-acid composition of the total 2-MGs calculated on the basis of their ratio was as follows (%): 18:1, 19.5; 18:2, 68.0; h-18:2, 12.5.

Below we give the position-species composition of the h-TGs calculated by Coleman's method, where S represents the 14:0 + 16:0 + 18:0, O the 18:1, and L the 18:2 fatty acids and H the hydroxy-FAs (mole %):

1(3)-h-TGs (87.5%)		2-h-TGs (12.5%)	
SOH — 2.8	OLH — 15.8	SHS — 0.3	OHO — 0.6
SLH — 9.7	LOH — 12.2	SHO — 0.8	OHL — 3.6
OOH — 4.5	LLH — 42.5	SHL — 2.3	LHL — 4.9

The results obtained show that the α-hydroxyoctadecenoyl group is present predominantly in one of the extreme (1,3) positions in the triglycerides.

The epoxyhydroxydiacyl TGs (eh-TGs) were isolated from the combined substances of fraction VI by the TLD method using system h (zone 1). They gave a reaction with picric acid showing the presence of epoxide groups. In the near UV they absorbed at 233 nm.

The NMR and IR spectra of the eh-TGs showed the simultaneous presence in the glyceride molecule of two functional groups — epoxide and hydroxyl.

In the ether-soluble product of the transesterification of the eh-TGs three zones of substances were detected which migrated (Silufol, systems c, f) as the MEs of n-FAs, MEs of e-FAs, and MEs of h-FAs. Each of the three components was isolated by the TLC method in system c in a ratio of 1:1:1. The composition of the MEs of the n-FAs according to GLC was (%): 14:0, 0.6; 16:0, 8.4; 18:0, 2.3; 18:1, 26.5; 18.2, 62.2.

From the results obtained it is possible to calculate the fatty-acid composition of the eh-TGs (%): 14:0, 0.2; 16:0, 2.8; 18:0, 0.8; 18:1, 8.8; 18:2, 20.7; e-18:1, 33.3; h-18:2, 33.3.

The NMR spectra of the MEs of the e-FAs and the MEs of the h-FAs correspond to the structures of the MEs of vernolic or coronaric and coriolic acids [22].

Glycerol was detected in the water-soluble products of the mild alkaline hydrolysis of eh-TGs in the same way as described above.

On enzymatic hydrolysis of the eh-TGs we obtained three types of MGs — 2-n-MGs, 2-e-MGs, and 2-h-MGs (Silufol, system i), which confirmed the absence of an acyl radical with mixed functional groups and shows that not all the epoxy- and hydroxyacyl radicals were present in the 1 and 3 positions in the TGs. The ratio of the three types of MGs was about 8:1:1.

The FA composition of the 2-n-MGs, according to the results of hydrolysis and the subsequent GLC of the MEs of the n-FAs was (%): 18:1, 29.9; 18:2, 70.1. If we take into account

the ratio of the three types of 2-MGs, their fatty acid composition must correspond to the following (%): 18:1, 23.9; 18:2, 56.1; e-18:1, 10.0; h-18:2, 10.0.

The position-species composition of the eh-TGs calculated by Coleman's method, where S represents the 14:1 + 16:0 + 18:0, O the 18:1, L the 18:2, E the e-18:1, and H the h-18:2 acids, is as follows (mole %):

1,3(3,1)-eh-TGs (80%)	1(3),2-eh-TGs (10%)	1(3),2-he-TGs (10%)
HOE — 23.9	SHE — 1.1	SEH — 1.1
HLE — 56.1	OHE — 2.7	OEH — 2.7
	LHE — 6.2	LEH — 6.2

Diglycerides (DGs). Zones 2 and 3 isolated in the rechromatography of fraction VI by the TLC method (system h) had IR and NMR spectra corresponding to the spectra of 1,3 and 1,2-DGs. Since each type of DG contains, as impurity, a small amount of its isomer (according to the NMR spectra), the combined isomers were subjected to mild alkaline hydrolysis. Only the n-FAs were detected in ether-soluble products of alkaline hydrolysis (Silufol, systems c, f). After the acids had been methylated with diazomethane, GLC showed the following composition of the FAs (%): 16:0, 7.7; 18:0, 2.2; 18:1, 54.4; 18:2, 35.7.

The glycerides of fractions VII and VIII, after the elimination of the free hydroxy acids in the form of the MEs by the TLC method in system c, gave IR and NMR spectra identical with those of the eh-TGs with the exception of the presence of a band at 995 cm^{-1} in the region of the absorption of trans,trans-conjugated ethylenic bonds. In the ether-soluble products of the mild alkaline hydrolysis of the glycerides of each of the above-mentioned fractions n-FAs, e-FAs, and h-FAs were detected in the form of their MEs (Silufol, system f). The glycerides of the two fractions differed by the fatty-acid compositions of the MEs of the n-FAs (GLC, %): fraction VII — 14:0, 0.7; 16:0, 7.7; 18:0, 2,2; 18:1, 24.3; 18:2, 65.1; fraction VIII — 16:0, 39.4; 18:0, 7.8; 18:1, 45.8; 18:2, 7.0.

The monoglycerides (MGs) of fraction IX had IR and NMR spectra qualitatively similar to the spectra of the mixture of isomeric DGs. Mild alkaline hydrolysis of the MGs gave only n-FAs (Silufol) the composition of which, according to GLC, was as follows (%): 16:0, 6.0; 18:0, 0.8; 18:1, 19.8; 18:2, 73.4.

Glycerol was identified by the method described above in the water-soluble hydrolysis products.

EXPERIMENTAL

The IR spectra were taken on a UR-10 instrument in a film, and the NMR spectra on a JNM-4H-100/100 MHz instrument (10-12% solutions in carbon tetrachloride with MHDS as internal standard), δ scale.

Oxoacyl Triglycerides. IR spectrum, cm^{-1}: 3015 m, 1635 w (—CH=CH—); 2960 s, 1380 m ($—CH_3$); 2930 s, 2860 s, 1465 m, 730 m ($—CH_2—$); 1745 s, 1420 m, 1245 m, 1170 s (—OCOR); 1725 s, 1690 m, 1660 w, 1590 w (>C=O).

NMR spectrum, ppm: t 0.86 ($—CH_3$, m 1.26 ($—CH_2—$), m 1.55 ($—CH_2CH_2COO—$), superposed m 2.01 ($—CH_2CH=$ and $—CH_2CH_2CH=$), t 2.22 ($—CH_2COO—$), m 2.68 ($=CHCH_2CH=$), m 4.12 ($—CH_2OCOR$), m 2.68 ($=CHCH_2CH=$), m 4.12 ($—CH_2OCOR$), m 5.10 (>CHCOR) m 5.23 (—CH=CH—).

Hydroperoxyacyl Triglycerides. IR spectrum: 3550-3480 m (—OOH); 3010 m, 1635 w, 990 and 950 m (—CH=CH—), 2965 s, 2870 s, 1380 m ($—CH_3$); 2930 s, 2860 s, 1465 m ($—CH_2—$); 1745 s, 1420 m, 1245 s, 1170 s (—OCOR); 1070 s [—CH(O—)—]; 855 w (—OO—).

NMR spectrum, ppm: t 0.86 ($—CH_3$), m 1.26 ($—CH_2—$), m 1.55 ($—CH_2CH_2COO—$); m 2.00 ($—CH_2$·CH= and $CH_2CH_2CH=$), t 2.22 ($—CH_2COO—$); m 2.68 ($=CHCH_2CH=$), m 3.51 [—CH(O—)—], m 4.12 ($—CH_2OCOR$), m 5.10 (>CHOCOR); m 5.24 (—CH=CH—) s 2-6, (—OOH, shift to the 7-8 region in the presence of TFA).

Hydroxyacyl Triglycerides. IR spectrum, cm^{-1}: 3550-3480, 3010, 2965, 2930, 2870, 2860, 1745, 1635, 1465, 1420, 1380, 1245, 1170, 1070, 990, 950, 730. NMR spectrum, ppm: t 0.86; m 1.26; m 1.55; m 2.00; t 2.22; m 2.68, m 3.51, m 4.12, m 5.10, m 5.24, s 2-6 (7-8 with TFA).

Epoxyhydroxydiacyl Triglycerides. IR spectrum, cm^{-1}: 3550-3450 m (—OH); 3010 m; 660 w (—CH=CH—); 2960 s, 2880 s, 1380 m ($—CH_3$); 2930 s, 2860 s, 1465 m, 730 m ($—CH_2—$);

1745 s, 1420 m, 1245 s, 1170 s (—OCOR); 1110 s, [—CH(O—)—]; 990 and 950 m (—CH=CH—) 845 and 830 m (epoxide ring).

NMR spectrum, ppm: t 0.86 ($—CH_3$), m 1.30 ($—CH_2—$), m 1.55 ($—CH_2CH_2COO—$), m 2.01 ($—CH_2$·CH= and $—(CH_2CH_2CH=)$, t 2.24 ($—CH_2COO$), superposed m's 2.68 and 2.70 ($=CHCH_2CH=$ and the protons of a cis-epoxide ring, the signals being shifted in the presence of TFA by 2.90 and 2.65), m 3.50 [—CH(O—)—], m 4.11 ($—CH_2OCOR$), m 5.1 (>CHOCOR), m 5.23 (—CH=CH—), s 0.7-2.0 (—OH, shift into the 7.50 region in the presence of TFA).

Diglycerides (1,3 and 1,2-DGs). IR spectrum of 1,3-DGs, cm^{-1}: 3500 m (—OH); 3015 m, 1660 w (—CH=CH—); 2960 s, 2875 s, 1380 m ($—CH_3$); 2930 s, 2860 s, 1465 m, 730 m ($—CH_2—$), 1745 s, 1420 m, 1245 s, 1170 s (—OCOR s [—CH(O—)—]. The IR spectrum of the 1,2-DGs was identical with that given above with the exception of the low intensity of the band at 1060 cm^{-1}.

NMR spectrum of the 1,3-DGs, ppm: t 0.86 ($—CH_3$), m 1.28 ($—CH_2—$), m 1.55 ($—CH_2CH_2COO—$), t 1.96 ($—CH_2CH=$ and $—CH_2CH_2CH=$), m 2.24 ($—CH_2COO—$), m 2.67 ($-CHCH_2CH=$), superposed m's 4.12 and 4.01 [$—CH_2OCOR$, —CH(OH)—]; m 5.24 (—CH=CH—), s 8.72 (—OH with TFA).

Characteristic chemical shifts in the NMR spectrum of the 1,2-DGs, ppm: d 3.55 ($—CH_2OH$), m 4.12 ($—CH_2OCOR$), m 4.90 [>CHOCOR)—], c 8.30 (—OH with TFA).

Sum of the Monoglycerides. IR spectrum, cm^{-1}: 3400, 3010, 2960, 2930, 2880, 2860, 1745, 1660, 1465, 1420, 1380, 1240, 1170, 1120, 1100, 1040, 980, 730.

NMR spectrum, ppm: t 0.86, m 1.26, m 1.55, d 2.00, t 2.23, m 2.67, d 3.76, superposed m's 3.97, m 5.10, m 5.24, s 3.60 (—OH, disappears with TFA).

Gas—liquid Chromatograms. These were obtained on a UKh-2 instrument under the following conditions: 15% of Reoplex 400 on Chromaton N-AW-HMDS, copper column with an internal diameter of 4 mm and a length of 2.5 m.

Extraction of the Oil. The seeds were comminuted in an electric mill and were covered with hexane and the mixture was infused at room temperature for 1-2 h. The process was repeated 4-6 times.

Column Chromatography. For the separation of the oil into its individual fractions column chromatography was performed on silica gel L 100/250 μ, the dimensions of the column of adsorbent being 3 × 55 cm.

Thin—Layer Chromatography. To rechromatograph the composite fractions we used glass plates (18 × 24 cm) with a layer of silica gel L 5/40 μ fixed with 3% of gypsum (8 g of adsorbent per plate). The eluates obtained from the columns and from the thin layers were monitored on Silufol plates.

Solvent Systems. Hexane—ether: **a** — 10:0; **b** — 9:1; **c** — 8:2; **d** — 7:3; **e** — 6:4; **f** — 5:5; **g** — 0:10; **h** — 4:6; **i** — 1:9; 2% ammonia—methanol: **j** — 2:3; chloroform—methanol: **k** — 85:15; isopropanol—25% ammonia—water: **l** — 7:1:2.

Enzymatic Hydrolysis. The enzymatic hydrolysis of the glycerides with pancreatic lipase was performed in an ammonia buffer solution (100 ml of 1 M ammonium chloride and 2-3 ml of 1 M ammonia; pH 8.0) at 37°C for 30 min with stirring. The ratio of the components taking part in the reaction was: 1 g of glycerides, 7 ml of buffer, 0.5 ml of a saturated solution of bile acids, 0.6 g of lipase. The reaction was stopped with 4 N hydrochloric acid. The hydrolysis products were extracted with diethyl ether, the extract was washed with water to neutrality, dried over sodium sulfate, and filtered, and the ether was distilled off. The hydrolyzate was kept in a vacuum-drying chest at 40°C for 3 h.

Alkaline Hydrolysis. The alkaline hydrolysis of the glycerides (10 g) was carried out with a 1 M solution of caustic potash in methanol (100 ml) at room temperature, the reaction mixture being shaken vigorously for 20 min and then left in a dark place for 12 h.

Mild Alkaline Hydrolysis. Mild alkaline hydrolysis of the glycerides (10 g) was carried out at 37°K in a 0.1 M solution of caustic soda in methanol (100 ml) for an hour.

Transesterification. This was performed with methanol in the presence of catalytic amounts of sodium methanolate.

Hydrogenation. The process was catalyzed by palladium on aluminum (1:1) at 50-60°C in ethyl acetate in an amount of 5% of metal referred to the mixture being hydrogenated.

SUMMARY

The complex mixture of glycerides of a seed oil containing oxidized acyl radicals in the triglycerides (10 groups of glycerides) has been separated for the first time. New groups of monohydroxyacyl triglycerides (oxoacyl, ∿0.1% of the oil, and hydroperoxyacyl, ∿0.1%) and di(oxyacyl)triglycerides (epoxacyl-hydroxyacyl, ∿0.36%) have been detected and isolated.

A new α-oxodienoic acid has been found for which the following structural formula is proposed as the most probable: 11-oxooctadeca-cis-9,cis-12-dienoic acid.

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THE STEREOCHEMISTRY OF TERPENOID COUMARINS

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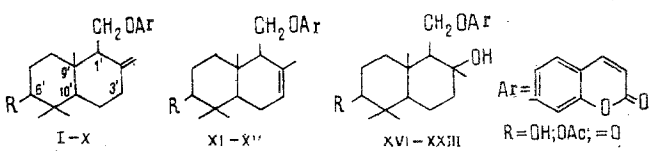
From plants of the genera *Ferula* and *Coladonia* have been isolated a number of terpenoid coumarins with an exocyclic methylene group at C_2' (farnesiferol A series) (I-X) [1-10], with an endocyclic double bond at C_2'-C_3' (conferol series) (XI-XV) [11-16], and with a hydroxy group C_2' (samarcandin series) (XVI-XXIII) [17-24] in the bicyclofarnesyl residue, and their relative configurations have been demonstrated.



Absolute configurations have been put forward for representatives of the coumarins of the farnesiferol A series — farnesiferol A (I) and gummosin (II) [7-9]. On the basis of the results of a study of spectra using paramagnetic shift reagents (PSRs) the trans linkage of

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