## CONCLUSION

The composition and amounts of the phytoglycolipids in the grape and its component elements have been determined. Ten fractions have been isolated and characterized, the main ones being the monogalactosyldiglycerides and the cerebrosides. The predominant carbohydrate component of the phytoglycolipids is galactose (~70%). The fatty acid compositions of the phytoglycolipid fractions have been studied. The structures of the oligosaccharide chains of the ceramide-containing glycolipids have been determined partially.

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# GROUP COMPOSITION OF THE NEUTRAL LIPIDS IN THE OIL OF THE FRUIT OF *Hippophaë rhamnoides*


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The composition of the neutral lipids of the fruit flesh and seeds of two forms of sea buckthorn have been determined. The presence of more than 20 groups of lipids has been shown. The two oils differed in the amounts and compositions of their carotenoids and acyl glycerols and the amounts of alcohols, free fatty acids, and esters.


The oil of the fruit flesh of the sea buckthorn, family Elaeagnaceae, is used for medicinal purposes but its lipids have so far been studied inadequately. The total composition of the seeds and fruit flesh in relation to classes of lipids and the composition of the individual groups of lipids such as waxes, esters of polycyclic alcohols, free alcohols, etc., are unknown.


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TABLE 1. Group Compositions of the Lipids of the Oils of the Fruit of the Sea Buckthorn, Samples I and II (% on the oil)

| Group of lipids | Oil of seeds | | Oil of fruit flesh | |
|---|---|---|---|---|
| | I | II | I | II |
| Carbohydrates | 0,9 | 0,2 | 0,2 | 0,2 |
| Carotenoids | Tr. | Tr. | 1,0 | 0,9 |
| Esters of fatty acids and long-chain alkanols | Tr. | | | |
| " polycyclic alcohols | Tr. | 0,2 | 1,3 | 1,1 |
| " sterols | Tr. | | | |
| " ethanol | | 1,5 | | |
| " methanol | | 0,5 | | |
| Triacylglycerol | 65,0 | 67,0 | 92,0 | 91,0 |
| Tocopherols | 0,2 | 0,2 | 0,3 | 0,3 |
| Fatty acids | 14,4 | 15,4 | 2,1 | 2,6 |
| Epoxyacyldiacylglycerols | 4,7 | 3,9 | | |
| Hydroxyacyldiacylglycerols | 1,7 | 2,7 | | |
| Epoxyacylhydroxyacylmonoacylglycerols | 0,6 | Tr. | | |
| Normal primary alcohols | 0,2 | 0,7 | 0,1 | 1,2 |
| Saturated isoprenols | | | 0,2 | |
| Polycyclic alcohols | | | 0,5 | |
| Sterols | 0,4 | 1,9 | 0,7 | 0,7 |
| Diacylglycerols | 3,0 | 1,6 | 0,8 | 0,9 |
| Monoacylglycerols | 3,1 | 0,7 | Tr. | 0,2 |
| Unidentified | 5,6 | 1,0 | 0,6 | 0,3 |
| Total | 99,8 | 97,5 | 99,8 | 99,4 |

TABLE 2. Composition of the Fatty Acids of the Acyl-Containing Groups of the Lipids, % on the Total

| Group of lipids | Sample | Seed oil | | | | | | | Oil of the fruit flesh | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 14:0 | 16:0 | 16:1 | 18:0 | 18:1 | 18:2 | 18:3 | 14:0 | 16:0 | 16:1 | 17:0 | 18:0 | 18:1 | 18:2 | 18:3 |
| Triacylglycerols: total | I | — | 16,8 | 19,7 | 1,4 | 18,6 | 28,9 | 14,6 | 0,2 | 37,2 | 49,9 | — | — | 12,1 | 0,6 | — |
| | II | — | 7,5 | 2,5 | 2,5 | 18,9 | 43,4 | 25,2 | — | — | — | — | — | — | — | — |
| Position 2 | I | — | 19,9 | 18,8 | 4,8 | 18,8 | 23,0 | 14,7 | — | 2,8 | 71,7 | — | — | 21,1 | 4,4 | — |
| " | II | 0,4 | 22,3 | 5,0 | 5,5 | 19,7 | 31,2 | 15,9 | — | — | — | — | — | — | — | — |
| Methyl and ethyl esters | I | 0,2 | 10,3 | 19,3 | 0,6 | 13,0 | 34,9 | 21,7 | — | — | — | — | — | — | — | — |
| Free fatty acids | I | — | 21,9 | 11,0 | 3,9 | 25,0 | 27,9 | 10,3 | — | 30,4 | 46,9 | — | 0,8 | 16,8 | 3,0 | 2,1 |
| | II | 0,4 | 28,2 | 21,6 | 2,3 | 13,8 | 21,6 | 12,1 | — | — | — | — | — | — | — | — |
| Epoxyacyldiacylglycerols | I | — | 13,8 | 6,9 | 2,4 | 20,1 | 39,3 | 17,5 | — | — | — | — | — | — | — | — |
| " | II | — | 7,3 | 2,4 | 1,8 | 15,9 | 43,8 | 28,8 | — | — | — | — | — | — | — | — |
| Hydroxyacyldiacylglycerols | I | — | 29,6 | 18,5 | Tr. | 21,9 | 21,9 | 8,1 | — | — | — | — | — | — | — | — |
| " | II | — | 9,7 | 5,3 | 0,6 | 21,8 | 45,3 | 17,3 | — | — | — | — | — | — | — | — |
| Diacylglycerols | II | — | 7,9 | 4,8 | 2,0 | 18,3 | 42,3 | 24,7 | 0,2 | 26,6 | 34,1 | — | 2,8 | 25,3 | 11,0 | — |
| Monoacylglycerols | II | — | 12,2 | 9,3 | 1,7 | 18,9 | 38,1 | 19,8 | — | — | — | — | — | — | — | — |
| Esters of fatty acids and polycyclic alcohols | II | — | 25,7 | 19,5 | 3,3 | 28,0 | 22,3 | 1,2 | — | 29,0 | 9,1 | 4,7 | 8,9 | 33,5 | 12,7 | — |

The present paper gives a comparative analysis of the group compositions of the main neutral lipids of the oil of the fruit flesh and the oil of the seeds of the sea buckthorn growing in the Ukrainian SSR in the flood plains of the rivers Paltau (sample I) and Zeravshan (sample II) (Table 1).

The oils were fractionated by column chromatography and thin-layer chromatography.

The hydrocarbons, according to the results of TLC and GLC and comparison with known samples and of IR, PMR, and mass spectrometry consisted of a group of homologous alkanes with trace amounts of alkenes, which were concentrated in one of the fractions reacting with iodine in a thin layer of silica gel.

In the oil of the fruit flesh of samples I and II we detected mainly the $C_{21}$-$C_{37}$ paraffins, the $C_{13}$-$C_{27}$ monoenes, and the $C_{13}$-$C_{20}$ dienes, trienes, and tetraenes. The ratio of the main paraffinic components in sample II determined by the GLC method was (% on the total): $C_{19}$ — 0.5; $C_{20}$ — 0.8; $C_{21}$ — 0.7; $C_{22}$ — 0.3; $C_{23}$ — 2.8; $C_{24}$ — 0.7; $C_{25}$ — 18.7; $C_{26}$ — 0.9; $C_{27}$ — 28.6; $C_{28}$ — 0.4; $C_{29}$ — 37.3; $C_{31}$ — 8.3. The $C_{31}$ and $C_{29}$ components were anteisoparaffins according to GLC and MS.

The seed oils of samples I and II contained the $C_{15}$-$C_{37}$ paraffins with small amounts of the $C_9$-$C_{28}$ monoenes and $C_9$-$C_{20}$ dienes, trienes, and tetraenes.

From the results of the GLC of the paraffins of sample I (% on the total: $C_{29}$ — 44.6; $C_{28}$ — 1.6; $C_{27}$ — 15.4; $C_{26}$ — 1.9; $C_{25}$ — 22.1; $C_{24}$ — 0.9; $C_{23}$ — 2.1; $C_{22}$ — 3.3; $C_{21}$ — 4.0; $C_{20}$ — 2.9; $CL_9$ — 1.1), it can be seen that hydrocarbons with an odd number of carbon atoms predominated quantitatively in the seed oil.

The carotenoids of the seed oils, which amounted to 48 mg-% in sample I, were separated by column chromatography on silica gel in solvent systems a-1. From the nature of their absorption in the visible region of the spectrum [1], in a mixture with lipids, which are transparent in this region of the spectrum, we found β-carotene (425, 450, 472 nm) — 10.6 mg-%; 5,8-dihydro-5',8'-epoxy-β-carotene (405, 426, 450 nm) — 32.9 mg-%; and 3,3'-dihydroxy-5,5',8,8'-tetrahydro-5,8,5',8'-diepoxy-β-carotene (379, 399, 423 nm) — 4.5 mg-%. In the fruit flesh of samples I and II there were about 1000 and 900 mg-% of carotenoids, respectively. The compositions of these components in sample I have been studied previously [2].

Tocopherols were present in fairly large amounts in the seed oils I and II — about 200 mg-%, which corresponds to figures published previously [3]. It is considered that 33-55 mg-% of tocopherol is sufficient to protect an oil from autooxidation [4]. In view of this, these oils should be resistant to oxidation. In the seed oils, just as in the oil of the fruit flesh [2], they consisted of a mixture of α-, γ-, and δ-tocopherols [3, 4].

Chlorophylls *a* and b, which were found in trace amounts in individual fractions of the seed oils from their characteristic absorption in the visible region of the spectrum [5], did not change the yellow coloration of these oils.

The esters of alcohols and fatty acids from the corresponding fractions of the oils of the seeds of sample I and of the fruit flesh of samples I and II which were difficult to separate chromatographically, were recrystallized from acetone. The mass spectra of the esters from each sample showed the presence of identical molecular ions with m/z 746 ($C_{38}$ + 18:0), 732, 718, 704, 690, 676, 674, 662, 648, 646, 634, 620 ($C_{26}$ + 16:0), 592, 578, 564, 562, 560, 550, 536 534, 522, 508 ($C_{18}$ + 16:0) (the values of the most intense ions are underlined).

The esters of the seed oil and the oil of the fruit flies of sample II were hydrolyzed with alkali. The alcohols were isolated from an aqueous solution of the hydrolysis products with diethyl ether. The TLC of the alcohols isolated from the esters of the oils of the seeds and of the flesh in solvent system j were identical.

The alcohols from the esters of the seed oil of sample II were separated preparatively in a thin layer of silica gel in the same solvent system into three zones of substances with $R_f$ 0.41, 0.25, and 0.12. The first two zones were poorly separated, and therefore we determined the ratio of the weights of the sum of the first two zones and the last. On the basis that the esters made up 0.2% of the total lipids (Table 1), they amounted to 0.12 and 0.08%, respectively.

In the group of alcohols with $R_f$ 0.41, from a comparison of the mass spectra of the esters and of the substances from the top zone of the chromatogram we detected the $C_{38}$-$C_6$ normal primary alkanols. The detection of alcohols of low molecular mass solely from the spectrum of the alcohols isolated from the esters was difficult for two reasons: In the first place, being water-soluble, they can pass into diethyl ether only because of their mutual solubility with the high-molecular-mass alcohols, and, in the second place, the identification of molecular ions having low masses is difficult because of the superposition of the hydrocarbon fragments.

In the combined alcohols the main representatives were the seven components of the even series $C_{16}$-$C_{28}$.

Among the alcohols with $R_f$ 0.25 there were polycyclic components with molecular masses of 426, 440, and 454, and in the group of alcohols with $R_f$ 0.12 there were sterols with molecular masses of 414, 412, and 400 (mass spectrometry).

Fatty acids were isolated from the water-soluble products of the hydrolysis of the esters of the oils of the seed and of the fruit flesh of sample II after the potassium salts had been decomposed with acid (Table 2). In the fatty acids of the esters of the seed oil the pairs of acids 16:0 and 16:1, and 18:1 and 18:2, predominated, and in the oil of the flesh 16:0 and 18:1 acids.

The trace amounts of $C_{33}$-$C_{27}$ primary n-alkanols must correspond to the same amounts of esters with molecular masses of 746, 732, 718, 704, 690, and 662. Consequently, the molecular ions of the last four esters owe their appearance in the spectrum to the following pairs of esters of polycyclic alcohols and fatty acids: $C_{32} + C_{18:1}$ (traces), $C_{31} + C_{18:1}$ $C_{30} + C_{18:1}$, and $C_{30} + C_{16:1}$ (traces).

The group of molecular ions with m/z 676, 674 (tr.), and 662 (tr.) can be assigned only to esters of sterols having molecular masses of 414, 412 (tr.), and 400 (tr.) with the 18:2 acid, and the group of peaks with molecular masses of 648, 646 (tr.), and 634 (tr.) to esters of the same sterols with the 16:1 acid. Reckoning them as 0.08% (on the total lipids), about 40% of the 0.2% of total acids must be due to sterol esters. This corresponds to an amount of the 18:2 and 16:1 acids found in the esters of the seed oils of 41.8% on the total amount of acids (Table 2).

The other peaks of the molecular ions of the esters correspond mainly to the palmitates and stearates of saturated alkanols. The esters of alkanols and polycyclic alcohols of the seed oil of sample II amounted to about 60% of the total esters taking them as 0.12% of the total lipids containing 0.2% of esters. This is close to the amount of oleic and saturated acids — 57% on the total acids (Table 2) — in the esters of this oil.

Thus, in the seed oil of the sea buckthorn, the three groups of alcohols are esterified with fatty acids in basically different ways: the alkanols predominantly with palmitic acid, which corresponds to literature information relating to the waxes of a number of plants [6], the pentacyclic alcohols with oleic acid, and the sterols in almost equal degree with linoleic and palmitoleic acids (22.3 and 19.5%, Table 2).

The methyl and ethyl esters of the fatty acids were isolated from the seed oil of sample II. They migrated in a thin layer of silica gel and on GLC in a manner identical to that of the corresponding markers: The methyl esters were obtained by the diazomethane treatment of the fatty acids of cottonseed oil and the ethyl esters were synthesized by acid ethanolysis from the triacylglycerols of the same oil. The retention times of the ethyl esters were only slightly greater than those of the methyl esters and mixed samples showed no differences even when these esters were present in equimolar amounts. However, in the PMR spectrum of the sum of natural and synthetic esters isolated, in addition to the usual signal from methyl and ethyl esters and the singlet of the methoxy protons from the first group of esters, there was also a quartet of methylene protons and a triplet of methyl protons of the ethoxy group from the second group. By comparing the integral intensities of the three-proton singlet of the methoxy groups and the two-proton quartet of the ethoxy groups we found the ratio between the amounts of methyl and ethyl esters in the natural mixture as 3:1. We calculated the amounts of these components in the oil on this basis (Table 1).

The composition of the methyl esters obtained after the hydrolysis of the combined natural esters and the diazomethane methylation of the fatty acids isolated from them is given in Table 1.

The mass spectrum of the total natural esters confirmed that they consisted of the ethyl esters — m/z 88 (100%) — and the methyl esters — m/z 74 (100%) — of the same fatty acids.

The free alcohols of the fruit flesh of samples I were separated by TLC in solvent system k into zones of substances with $R_f$ 0.25 and 0.51 after recrystallization from acetone (0.8 and 0.7%, Table 1).

Among the alcohols of the first zone (fraction 1) sitosterols with a molecular mass of 414, together with trace amounts of components having molecular masses of 412, 400, and 426, were detected by mass spectrometry. The component with a molecular mass of 426 corresponded — according to TLC and to GLC with a RRT of 1.3 (relative to β-sitosterol) — to citrostadienol [7]. No polycyclic diols with a molecular mass of 442 were detected.

The alcohols of the second zone of substances ($R_f$ 0.51) were acetylated with acetic anhydride in pyridine. The acetates of the alcohols were separated by preparative TLC/$Ag^+$ in solvent system m into four zones of substances with $R_f$ 0.65, 0.60, 0.55, and 0.50 (fractions 2-5, respectively). The weight ratio between them was 4.8:16.9:24.3:54.2. The components of each zone were identified from the results of GLC, mass spectroscopy, and PMR. The acetates of the $C_{20}$ and $C_{25}$ saturated isoprenols were detected in fraction 2 in trace amounts and 100%. The ratio of the integral intensities of the methyl and methylene protons corresponded to a structure of the saturated isoprenols with the general formula

$$H[CH_2CHCH_2CH_2]_n OH.$$
$$CH_3$$

The absence from the mass spectrum of unusual molecular ions and the difference in the RRT [6] of the only two alcohols — with 20 and 25 carbon atoms — permitted one of them to the assigned to phytanol ($C_{20}$, mol. mass 298) and the other to its saturated "isoprenologue" ($C_{25}$, mol. mass 368). The presence of iso branching was confirmed by a doublet of the corresponding methyl groups superposed on the triplet of the other methyl groups.

In the following fractions the same alcohol acetates in a ratio of 94.5 and 5.5% (13.7% of the total) were present together with derivatives of the $C_{33}$-$C_6$ homologues of primary saturated alcohols of normal structure (86.3% of the total). Among them nine homologues predominated quantitatively (% on the total): $C_{18}$ — 2.1; $C_{19}$ — 0.3; $C_{20}$ — 0.6; $C_{21}$ — 0.5; $C_{22}$ — 2.4; $C_{23}$ — tr.; $C_{24}$ — 27.8; $C_{25}$ — 5.6; $C_{26}$ — 60.7. As in the majority of mixtures of n-alkanols of natural origin [8], the main alcohols were the $C_{26}$ and $C_{24}$ compounds. Traces of β- and α-amyrins (RRTs 0.95 and 1.15 with respect to β-sitosterol acetate here and below) were detected in the same fraction. Fraction 4 also contained the saturated $C_{25}$ and $C_{20}$ isoprenols in a ratio of 82.0 and 5.2%. The remaining 12.8% was represented by an unidentified component with RRT 1.64.

The ratio between the amounts of free aliphatic and polycyclic alcohols was calculated on the basis of the results obtained (Table 1). As can be seen, in the total amount of free alkanols — 0.3% — more than half consisted of saturated isoprenols, among which the $C_{25}$ homologue predominated.

Fraction 5 contained only the monoacetate ($M^+$ 482) of a pentacyclic alcohol ($M^+$ 440) with an RRT of 1.27 and an mp of 117-119°C corresponding to 24-methylenecycloartanol [7, 9].

Acylglycerols were identified as described in [10]. It can be seen from Table 1, that in contrast to the oils of the fruit flesh the seed oils contained, besides those mentioned above, about 6% of three groups of oxidized triacylglycerols — epoxyacyldiacylglycerols, hydroxyacyldiacylglycerols, and epoxyacylhydroxyacylmonoacylglycerols. In addition, the total amount of partial esters of glycerol in the seed oil was twice as much as in the oil of the fruit flesh (2.5% as compared with 1%). The amount of free fatty acids in the seed oil was almost seven times more than in the oil of the flesh (15% as compared with 2%).

The fatty acids of the triacylglycerols of the oil of the fruit flesh contained fatty acids that were resistant to oxidation by lipoxygenase.

## EXPERIMENTAL

The isolation of the oils, the recording of the spectra, and the performance of PC and TLC have been described previously [2, 10]. Gas-liquid chromatograms were obtained on a Chrom-4 instrument (for the hydrocarbons: metal column; 150 × 0.4 cm, 5% of SE-30 on Chromaton N-AW-DMCS; column temperature 240°C; evaporator temperature 290°C; carrier gas helium at a rate of flow of 100 ml/min; for the fatty acid methyl esters: 250 × 0.4 cm; 15% of Reoplex on Chromaton N-AW-DMCS; column temperature 204°C; carrier gas helium and hydrogen at a rate of flow of 70 ml/min); and for the alcohol acetates a Chrom-41 instrument (glass column, 250 × 0.3 cm; 5% of SE-30 on Chromaton N-AW-DMCS; column temperature 255°C; carrier gas nitrogen). Solvent systems: hexane—ether: a — (10:0); b — (9.5:0.5); c — (9:1); d — (8.5:1.5); e — (8:2); f — (7.5:2.5); g — (7:3); h — (6.5:3.5); i — (6:4); j — (5:5); k — (4:6); l — (1:9). Chloroform—carbon tetrachloride: m — (5:5). Hexane—benzene: n — (6:4). Hexane—ethyl acetate: o — (4:1).

The alkaline hydrolysis of the esters was performed in the boiling water bath for 6 h with a 1 N ethanolic solution of caustic potash taken in a ratio to the sample of 10:1.

The free alcohols of fraction 2: PMR, ppm: coincident d and t 0.86; s 1.28 (methylene); m 2.25 (methine). The ratio of the integral intensities of the $CH_3$, $CH_2$, and CH signals was 1:2:0.33 = 18:36:5 ($C_{25}$).

IRS, $cm^{-1}$: 1385-1375, doublet, gem-dimethyl group.

## CONCLUSION

The presence of more than 20 groups of lipids in the oils of the fruit flesh and seeds of the sea buckthorn has been shown.

In the seed oil of the sea buckthorn, unlike the fruit flesh, there are three types of oxidized triacylglycerols with an increased amount of the products of incomplete esterification of glycerol and free fatty acids.

It has been shown that 80% of the carotenoids of the oil are epoxy derivatives of β-carotene.

In the seed oil, three groups of alcohols — alkanols, sterols, and triterpenols — are esterified by fatty acids in different ways.

Two saturated "isoprenologues," $C_{20}$ and $C_{25}$, have been detected in the oil of the fruit flesh.

In one of the samples of seed oils, combined methyl and ethyl esters of fatty acids have been found.

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## SPECTRAL CHARACTERISTICS OF C-METHYLFLAVONES


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A study has been made of natural C-methylflavones and their dealkylated analogues: 5-hydroxy-4',7-dimethoxy-7-methylflavone (noreucalyptin); 4',5,7-trihydroxy-6-methylflavone; 5-hydroxy-4',7-dimethoxy-6,8-dimethylflavone (eucalyptin); 4',5-dihydroxy-7-methoxy-6,8-dimethylflavone (sideroxylin); 4',5,7-trihydroxy-6,8-dimethylflavone; 4',5,6-trihydroxy-3-methoxy-8-methylflavone (silpin) and 3,4',5,6-tetrahydroxy-8-methylflavone.


Among natural flavonoids, C-methylated compounds form a fairly small group, and it is characteristic that the C-methylation of the flavonoid molecule takes place only in positions 6 and (or) 8 [1].

We have studied the properties of the following C-methylflavones: 5-hydroxy-4',7-dimethoxy-6-methylflavone, which for brevity we shall call noreucalyptin (II), 5-hydroxy-4',7-dimethoxy-6,8-dimethylflavone (eucalyptin, III), 4',5-dihydroxy-7-methoxy-6,8-dimethylflavone (sideroxylin, IV), and 4',5,6-trihydroxy-3-methoxy-8-methylflavone (silpin, VI). In the course of our study of these compounds, we have performed their dealkylation by heating with pyridine hydroxychloride, as in the conversion of silpin (VI) into demethylsilpin (VII) [2]. In this way, from noreucalyptin we obtained methylapigenin (II), and from eucalyptin and sideroxylin the same product, a dimethylapigenin (V).


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