solution was made up to 1000 ml. Then, for each experiment, a suitable amount of adsorbent was taken and was covered with 100 ml of the solution. The mixture was stirred for 10-15 min and was left overnight, after which the adsorbent was separated off by filtration, and the solvent was distilled off. The gossypol residue so isolated was washed with petroleum ether and dried, and the purity of the gossypol was determined by titration with Fehling's solution [9].

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LIPIDS OF THE SEEDS OF Cynoglossum officinale

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The compositions of the lipids and fatty acids of the seeds of Cynoglossum officinale, family Boraginaceae have been established. The bulk of the lipids consisted of neutral compounds (95.2%), while the amounts of glycolipids and phospholipids were 3.1 and 1.7%, respectively. Among the fatty acids, in addition to the usual components, acids characteristic for the Boraginaceae family have been found: 18:3 (6, 9, 12), 18:3 (9, 12, 15), 18:4 (6, 9, 12, 15), 20:1 (11), 22:1 (13), and 24:1 (15).

The family Boraginaceae includes about 100 genera and more than 2000 species of plants growing over the whole of the terrestrial globe. In the USSR 350 species have been found [1]. There is information in the literature on a study of the composition of the fatty acids (FAs) of the lipids of the seeds of about 40 species of plants of this family [2-5] but the class composition of the lipids of plants of the Boraginaceae family has not been investigated.

A feature of the FAs of representatives of the Boraginaceae family is the presence of the 18:4 (6, 9, 12, 15) acid, the amount of which in the seed lipids reaches 17%. In addition, in plants of this family the 18:3 (6, 9, 12) acid (γ-linolenic acid) and high-molecular-mass acids of the even series from 20:1 to 26:1 have been detected. In spite of the fact that the latter acids and γ-linolenic acid have been found separately in representatives of other families [6-8], the uniqueness of the Boraginaceae family consists in the simultaneous presence of all the above-mentioned acids in the seed lipids.

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We have investigated the neutral lipids (NLs), glycolipids (GLs), and phospholipids (PLs) of the seeds of Cynoglossum officinale L. (common hound's tongue). The yield of NLs, GLs, and PLs were (% on the weight of the seeds) 21.6, 0.76, and 0.4, respectively. The neutral lipids were studied in more detail.

The sums of the NLs was separated into individual classes by CC on silica gel followed by the separation of the mixed fractions by preparative TLC. The lipids were identified on the basis of their spectral characteristics, chemical transformations, qualitative reactions, and their mobilities in a thin layer of silica gel in comparison with model specimens.

As a result of the separation the following set of components was revealed (% by weight): hydrocarbons – 0.2; esters of alcohols and fatty acids – 0.2; triacylglycerols (TAGs) – 94.6; free fatty acids (FFAs) – 0.5; diacylglycerols (DAGs) + aliphatic alcohols + triterpenols – 1.1; DAGs + sterols – 2.3; and monoacylglycerols (MGs) – 0.1. The bulk of the lipids (more than 98%) consisted of acylglycerols (TAGs, DAGs, and MAGs).

The composition of the FAs isolated from the total lipids (Table 1) was studied in the following way. The total FAs in the form of methyl esters (MEs) were separated by CC on argentized silica gel according to their degree of saturation [5]. As a result, six zones of substances (I-VI) with different R_f values on argentized silica gel in a thin layer in system 1 were obtained:

Zone	I	II	III	IV	V	VI
R_f	0,81	0,70	0,63	0,47	0,15	0,03
% by weight	8,1	14,1	32,0	28,7	14,1	3,0

The MEs of each zone were analyzed by GLC and, where necessary, by mass spectrometry and UV spectroscopy.

By GLC, in the MEs of the FAs of zone I we detected 91% of the 16:0 acid and 9% of the 18:0 acid, and the mass spectrum contained the peaks of the molecular ions and the corresponding fragments of acids of the 10:0–20:0 22 and 24:0 series.

The MEs of the FAs of zone II consisted of high-molecular-mass monoenic components (GLC, %): 20:1 – 26.5; 22:1 – 61.4; 24.1 – 12.1. Because of its small amount in the mixture, the ME of the 26:1 acid could be detected only mass-spectrometrically (M^+ 408).

The positions of the double bonds in the FAMEs were established by oxidative degradation with the periodate-permanganate reagent. The monocarboxylic 9:0 and the dicarboxylic 11:0, 13:0, and 15:0 acids were detected in the degradation products by GLC. The results obtained showed the position of the double bond and C-11 in the 20:1 acid, at C-13 in the 22:1 acid, and at C-15 in the 24:1 acid.

In the MEs of zone III the main component detected was the 18:1 species, with the 16:1 and 20:1 species in trace amounts, while in the MEs of zone IV that of the 18:2 acid was detected.

TABLE 1. Fatty-Acid Compositions of the Acyl-Containing Lipids

Acid	Lipids						
	total	TAGs	FFAs	DAGs*	MAGs	GLs	PLs**
14:0	0,1	0,2	0,6	1,0	0,7	Tr.	1,4
16:0	7,5	6,3	9,4	7,7	9,8	8,4	19,7
16:1 (9)	0,1	0,1	0,2	Tr.	Tr.	1,5	2,7
18:0	0,3	0,2	0,6	1,1	0,2	2,5	4,5
18:1 (9)	32,4	33,5	36,5	31,1	36,1	28,3	18,6
18:2 (9,12)	29,8	30,0	24,2	34,8	29,5	29,0	31,2
18:3 (6,9,12)	8,2	8,9	3,2	10,1	5,7	6,5	5,3
18:3 (9,12,15)	5,6	6,3	2,7	6,4	4,8	3,8	1,3
18:4 (6,9,12,15)	3,0						
20:1 (11)	4,2	7,1	8,7	3,9	4,8	5,6	2,7
22:1 (13)	7,5	6,5	12,9	1,0	8,6	8,2	3,2
24:1 (15)	1,2	1,0	1,0	Tr.	Tr.	6,2	5,2
Σ monoenes	45,4	41,0	51,6	32,1	44,7	44,2	29,7

In addition to those mentioned, the following were detected: *10:0–0.9; 12:0–1.0; 17:0–1.0%.
**10:0–0.3; 12:0–0.6; 15:0–1.2; 17:0–1.8%.

Fragments of the oxidative degradation of the MES of zone III were the 9:0 monocarboxylic acid and the 9:0 dicarboxylic acid while those of the MEs of zone IV were the 6:1 monocarboxylic and the 9:0 dicarboxylic acid. These facts permitted the conclusion that the double bonds in the 18:1 and 18:2 acids were located in the same way as in ordinary oleic (at C-9) and linoleic (at C-9,12) acids.

The MEs of zone V were transparent in the UV spectrum and, according to GLC, consisted of two components: the 18:3 (6, 9, 12) – γ-linolenic acid – 58.2%, and the 18:3 (9, 12, 15) – α-linolenic acid – 41.8%. The positions of the bonds were confirmed by the products of oxidative degradation: among the monocarboxylic acids the 6:0 species and among the dicarboxylic acids the 6:0 and 9:0 acids were detected.

A gas-liquid chromatogram of the MEs of zone VI revealed one peak coinciding in its retention time with the 20:1 acid. The UV spectrum of the substance likewise revealed no adsorption of conjugated ethylenic bonds. In the mass spectrum of the MES we found M^+ 290 and the peaks of fragments corresponding to the ME of an 18:4 acid in which the double bonds were, according to the literature, located at C-6, -9, -12, and -15 [2].

We identified the FAs of the individual classes of lipids on the basis of the information on the FA composition of the total lipids given above (see Table 1). It can be seen from the table that the bulk of the total acids consisted of monoenoic components (40-50%). Polyenoic fatty acids were detected in all the classes of lipids.

Thus, it has been established that in the NLs of the seeds of common hound's tongue the whole complex of unusual FAs that this characteristic for representatives of the Boraginaceae family is present simultaneously.

In the mass spectrum of the hydrocarbons we found M^+ ions from 282 to 450, from 280 to 448, from 278 to 446, from 276 to 444, and from 274 to 442, corresponding to saturated, monoenoic, dienoic, trienoic, and tetraenoic components of the C_{20}–C_{32} series and the M^+ ions from 314 to 440 corresponding to pentaenoic components of the C_{23}–C_{32} series.

Esters of fatty acids and alcohols were also identified mass-spectroscopically, as described in [9, 10]. The spectrum contained the peaks of the $(RCO)^+$ and $(RCO - 1)^+$ fragments for the 14:0, 16:0, 18:0, 18:1, 18:2, 20:0, 20:1, 22:1, and 24:1 acids, and also the peaks of the ions of aliphatic alcohols, sterols, and triterpenols the composition of which was analogous to that of the components isolated from the lipids in the free form, which is given below. The aliphatic alcohols included the following saturated components (GLC, %): C_{18}–0.5; C_{20}–1.0; C_{21}–0.8; C_{22}–0.6; C_{23}–0.5; C_{24}–3.9; C_{25}–tr., C_{26}–52.1; C_{27}–0.5; C_{28}–38.7; C_{29}–tr., C_{30}–0.6.

In the mass spectrum of the fraction of aliphatic alcohols, in addition to the peaks of the $(M - 18)^+$ ions relating to the above-mentioned components, we detected the M^+M^+ ions with m/z 426, 428, and 440 and major fragments with m/z 189, 203, 207, and 218, corresponding to triterpene alcohols. In the sterols, 91% of β-sitosterol (M^+ 414) and 9% of stigmasterol (M^+ 412) were detected by GLC and spectrometry.

On analyzing the GLs by TLC on silica gel in system 2, the following components were revealed: digalactosyldiacylglycerols (R_f 0.32), monogalactosyldiacylglycerols (R_f 0.80), esters of sterol glycosides (R_f 0.90), and sterol glyclosides (R_f 0.60), with the latter predominating.

Among the classes of PLs, two-dimensional GLC in systems 3 and 4 revealed five components the quantitative ratio of which it was possible to place visually in the series: phosphatidylcholines > phosphatidylinositols > phosphatidylethanolamines > phosphatidic acids > N-acylphosphatidylethanolamines.

The FAs of the GLs and PLs are shown in Table 1. It can be seen from the facts presented that the FA components of the GLs, which included more than 40% of monoenoic components, were close to those of the NLs, while the FAs of the PLs were enriched with saturated acids (29.5%).

EXPERIMENTAL

The UV spectra of the MEs were taken on a Hitachi spectrophotometer in hexane, and the mass spectra on a MKh-1310 instrument at an energy of the ionizing electron of 40/50 eV and a temperature of the ionization chamber of 100/80°C. GLC was conducted on a Chrom-41

instrument with a flame-ionization detector. A 4 × 2000 nm column filled with PEGSon Chromaton W and a 4 ×2000 mm column with 5% of SE-30 on Chromosorb W were used.

The FAMEs were analyzed on a column containing PEGS. The column temperature for the FAMEs and the MEs of dicarboxylic acids was 198°C, and for the MEs of low-molecular-mass acids it was 132°C. Aliphatic alcohols and sterols were chromatographed on SE-30 at 280°C.

The seeds were gathered from plants grown in an experimental plantation of the South Urals reservation (Bashkiriya) in the period of full ripeness (September).

The neutral lipids were extracted from the previously comminuted seeds with hexane by steeping at room temperature.

The sum of the glyco- and phospholipids was isolated from the residual meal by extraction with chloroform–methanol (2:1). The extract was freed from carbohydrates by washing with a 0.5% solution of $CaCl_2$ (aqueous) followed by chromatography on a column of Molselekt G-25. The lipids were eluted by chloroform–methanol–water (90:10:1).

The separation of the PLs and GLs was achieved by CC on silica gel L 100/250. The residual NLs were eluted by chloroform, the GLs by acetone, and the PLs by methanol.

The CC of the neutral lipids was also conducted on silica gel. Elution of the classes of Nls was carried out with hexane containing gradually increasing concentrations of diethyl ether (0, 10, 20, 30, 40, 50, and 100%), and preparative GLC was conducted on silica gel L 5/40 with 13% of gypsum [11].

The CC of the sum of the MEs was conducted on silica gel with the addition of 20% of $AgNO_3$ as described in [5]. The separation of the MEs according to their degree of unsaturation was monitored by GLC on silica gel with the addition of 13% of gypsum and 20% of $AgNO_3$.

Solvent systems: 1) hexane–benzene–diethyl ether (6:4:1); 2) acetone–benzene–water (91:30:8); 3) chloroform–methanol–ammonia (65:35:5); 4) chloroform–methanol–acetic acid–acetone–water (20:10:4:8:2).

The GLs were identified with α-naphthol, and the PLs with ninhydrin and with the Vas'kovskii and Dragendorff reagents [12].

The alkaline hydrolysis of the acyl-containing lipids and the oxidation of the FAMEs with von Rudloff's periodate-permanganate reagent were carried out as described in [11, 13]. FAs were methylated with diazomethane in diethyl ether.

Esters of the FAs and Alcohols. Mass spectrum (100, 40 eV, 0.5 mA), m/z: 211, 239, 267, 265, 263, 295, 293, 321, 349 $(RCO)^+$; 210, 238, 266, 264, 262, 294, 292, 320, 348 $(RCO - 1)^+$ for the acyl moiety; 252, 280, 308, 336, 364, 392 $(M - 18)^+$ for the aliphatic alcohols; 396, 394 $(M - 18)^+$, 273, 255, 213 for the sterols; and 422, 410, 408 $(M - 18)^+$, 218, 207, 203, 189 for the triterpenols.

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