Thus, with similar qualitative sets of phospholipids and, especially, of fatty acids, their quantitative compositions in the different varieties of kenaf were different, which is explained by the variety features of the plant. It is possible that this phenomenon is connected with the role of individual phospholipids in metabolic processes.

## EXPERIMENTAL

Solvents were prepared by standard methods [6]. The following solvent systems were used for TLC: 1) chloroform-methanol-ammonia (65:35:5); 2) chloroform-methanol-acetone-acetic acid-water (10:5:4:2:1).

The GLC analysis was performed on a Chrom-4 instrument with a flame-ionization detector. Steel column  $3 \times 2500$  mm filled with 17% of PEGS on Celite 545; column temperature 196-205°C, evaporator temperature 250°C; carrier gas helium.

### SUMMARY

1. The qualitative and quantitative compositions of the phospholipids of two experimental varieties of kenaf have been studied. The phospholipids of the seeds of the kenaf variety Opytnyi-1931 are similar with respect to their set of components and the qualitative composition of the fatty acids of homogeneous classes to the phospholipids of variety Opytnyi-1972, but differ with respect to the amounts of the individual acids.

2. The fatty acid compositions of the lyso-phosphotidylcholines and lyso-phosphotidylinositols of experimental varieties of kenaf seeds have been determined for the first time.

## LITERATURE CITED

- 1. D. Tevekelov, Izv. na Instituta po Khranene, Boig. akad. Nauk, 7, 21 (1968).
- 2. I. Tolibaev, Kh. S. Mukhamedova, and S. T. Akramov, Khim. Prir. Soedin., 559 (1978).
- 3. I. Tolibaev, Kh. S. Mukhamedova, and S. T. Akramov, Khim. Prir. Soedin., 775 (1980).
- 4. I. Tolibaev, Kh. S. Mukhamedova, and S. T. Akramov, Khim. Prir. Soedin., 516 (1982).
- 5. E. Stahl, Thin-Layer Chromatography, 1st English Edition, Springer, Berlin; Academic Press, New York (1965).
- 6. The Preparative Biochemistry of Lipids [in Russian], Moscow (1981).

HYDROXY ACIDS OF THE SEED OIL OF Hippophae rhamnoides

UDC 543.51+547.915:665.31

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With the aid of the mass-spectrometric method and making use of the advantages of an instrument with dual focusing, 25 hydroxy-acid components have been detected in the seed oil of the sea buckthorn, their main representatives being coriolic and dimorphecolic acids. They are accompanied by their homologs: 13hydroxyhexadeca-9,11-dienoic and 9-hydroxypentadeca-10,12-dienoic, and isomers. Ricinoleic acid and its isomer 9-hydroxyoctadec-12-enoic acid and trienoic acids are present in smaller amounts. Four new hydroxy acids have been found in seed oils for the first time: 11-hydroxytridec-9-enoic, 9-hydroxypentadeca-10,12-dienoic, 13-hydroxyhexadeca-9,11-dienoic, and 9,12-dihydroxynonadec-15-enoic.

The possibility of determining the qualitative composition of the total trimethylsilyl (TMS) derivatives of hydroxy acid methyl esters by the mass-spectrometric method without preliminary separation has been demonstrated for the case of the hydroxy acids of cottonseed oil [1]. Here, use was made of the advantages of an instrument with dual focusing, permitting not only the determination of the elementary compositions of characteristic ions but also the establishment of the mass numbers of the parental, including the molecular, ions by

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Fig. 1. Mass spectrum of the total TMS derivatives of the hydroxy acid methyl esters.

the method of defocusing the ion beam in the first field-free space of the mass spectrometer (MD) [2].

In the present work, this approach has been applied to the total hydroxy acids of sea buckthorn seed oil as the first stage before the investigation of the corresponding triacylglycerols.

The neutral lipids of the sea buckthorn seed oil were fractionated by column chromatography and thin-layer chromatography. A fraction was isolated that made up 2.7% of the total. neutral lipids. Absorption bands in the IR spectrum at 3200-3600 cm<sup>-1</sup> indicated the presence of hydroxy groups bound by hydrogen bonds. In the PMR spectrum of the fraction, multiplets in the 5.5-5.6 and 6.52 ppm regions, characterized by the protons of esterified  $CH_2 - OH$ groups of glycerol and of CH-OH secondary alcohol groups located in an aliphatic chain. The UV spectrum had an absorption maximum at 234 nm which is characteristic for the -CH = CH - CH =The amount of acids with the conjugated system of double bonds calculated as the CH-group. 18:2 acid from the indices of the UV spectrum was 17.2%. On the basis of literature information [3] and spectral characteristics and chromatographic mobility, this fraction was assigned to the hydroxyacyldiacylglycerols. The hydroxy acids were isolated by the thin-layer chromatography of the reaction mixture obtained after the alkaline hydrolysis of the hydroxyacyldiacylglycerols in solvent system 2. The hydroxy acids were methylated by diazomethane. The hydroxy acid methyl esters were separated by TLC with 20% AgNO<sub>3</sub> in system 1 onto five fractions with  $R_F$  0.6, 0.48, 0.4, 0.3, and 0.2, respectively. To determine the compositions of the components of the total combined hydroxy acids we used the mass spectrometry of their TMS derivatives, which were obtained and purified immediately before analysis.

Figure 1 gives a typical spectrum of the total TMS derivatives of the methyl esters of the hydroxy acids being studied. The presence of the peak of an ion with m/z 311  $(C_{17}H_{31}O_{3}Si)$  (100%), together with the strong peak of a fragment with m/z 382  $(C_{22}H_{42}O_{3}Si)$  permits the assumption that the main components of the total material under consideration were coriolic (13-hydroxyoctadeca-9,10-dienoic) and dimorphecolic (9-hydroxyoctadeca-10,12-dienoic) acids, the spectra of analogous derivatives of which have been given by Kleiman and Spencer [4]. The MD spectra of the ions with m/z 311 and 225 (Fig. 2a,b) confirmed that their main precursor was an ion with m/z 382.

To determine the other components of the mixture, in the spectrum of the total material we selected ions which were analogous by the method of their formation to the ions with m/z 225 (A) and 311 (B) and determined their elementary compositions and recorded their MD spectra. The information obtained permitted the formulas of the monohydroxy acid derivatives to be illustrated in the following way, and was sufficient to determine the structures of the saturated acids. To establish the most probable structures of the unsaturated acids we used the dependences of the fragmentation of the TMS derivatives on the mutual positions of the

TABLE 1. Relative Amounts of Mono- and Dicarboxylic Acids in the Products of the Oxidative Degradation of the Hydroxy Acid Methyl Esters (GLC, %)

	×- x-	Mo	nocarb	arboxylic acids Dicarboxylic acids											
Zone	Amoun the mi ture,	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	C.	C <sub>p</sub>	C <sub>10</sub>	C11	C,	C <sub>5</sub>	C <sub>15</sub>	C <sub>7</sub>	C <sub>8</sub>	C,	C <sub>L</sub> ,
II III IV	10.9 30,4 18.8 21,1	23 5 22.0 11.2	24,6 28,2 42,7 26,8	8,1 8,2 11,5 7,3	10,8 26,2 6,7 7,0	25 5 15 1 12.1 29,0	7,5 22,3 5,0 13,5	  5 2	7,4 tr.	$\frac{-}{-}$ 4.2	4.7 1,2 1,4	9,8 2,2	70,5 6.4 16,2 5,8	17,3 86,2 72,8 86,4	7,5
V Ľ	18,8	12,0 11,4	20,5 28,8	23,6 11,5	5,6	24.1 20.3	14,2 14,1	$\frac{-}{1,0}$	5.6 3 3	3,0 1,5	2,3	2,3	$\frac{23}{18}\frac{0}{2}$	$66.1 \\ 72.4$	0.8



Fig. 2. MD Spectra of the ions with m/z 311(a), 225 (b), and 215 (c).



 $\pi$ -bonds and the TMSO groups found by other authors [4, 6]. We also took into account information that we had obtained on the relative amounts of mono- and dibasic acids in the products of the oxidative degradation of the initial mixture of hydroxy acid methyl esters (Table 1). Oxidative degradation was carried out by a known procedure [5].

Table 2 gives the formulas of the components of the combined hydroxy acids and results confirming them.

Saturated monohydroxy acids were represented by two compounds: 10-hydroxy- and 12-hydroxy stearic acids (1 and 2), respectively. Here, as was to be expected [4], the peaks of the M<sup>+</sup> ions were of low intensity. The presence of (1) was confirmed not only by the compositions of the ions A and B of the M<sup>+</sup>  $\rightarrow$  B transition but also by the presence in the total spectrum of a fragment with m/z 169 [6] with the composition  $C_{10}H_{17}O_2Si$  and by the transition  $273^+ \rightarrow 169^+$ . The fact that the mixture also contained the 12-hydroxy isomer (2) was shown by the composition of the ion with m/z 187 and by the detection of the metastable transition  $386^+ \rightarrow 187^+$ .

Five monoenoic acids were found (3-7). The peaks of the M<sup>+</sup> ions of these acids were more appreciable (Fig. 1), but they were all of low intensity. The main component among this group of compounds was ricinoleic acid (3), since this was confirmed not only by the height of the characteristic fragments A and B but also by the presence of an ion with m/z 270 [4]. At the same time, it must be emphasized that all three ions have precursors not characteristic of the spectrum of (3), and, comsequently, may be fragments of hydroxy acids with a different structure, as can be seen from Table 2.

		770			1444+10n-		
Formula, type of compound	car- bon atoms	+ W	Ions, the composi- tion of which were measured	Metastable tran- titions de- tected	al char- acteris- tic peak	No. of C possible tion pr mono-	atoms of e degrada- oducts
<u>Monohydrpxy aeids</u> Saturated							
1. CH <sub>3</sub> (CH <sub>2</sub> ),CH (OTMS ) (CH <sub>2</sub> ) <sub>6</sub> COOCH <sub>3</sub> 2. CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH (OTMS ) (CH <sub>2</sub> ) <sub>10</sub> COOCH <sub>3</sub> Monoenoic	ບ <sup>ື</sup> ່ ເ	386 386	215 (A.), 273 (b.) 169 187 ( A)	M+,B, 273→ <b>16</b> 9 M+ <b>.</b> ,A	169	ບໍ່ບໍ່ ບໍ່ບໍ່	C <sub>9</sub> , <b>C</b> <sub>10</sub> C <sub>11</sub> , <b>C</b> <sub>12</sub>
3. CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH (OTMS ) CH <sub>2</sub> CH=CH (CH <sub>2</sub> ) <sub>7</sub> COOCH <sub>3</sub>	ů	384	187 (A), 299 (B) 270,	M+→A	270	c, c,	ບຶ
4. $CH_3(CH_2), CH=CH (CH_3)_3CH (OTMS ) CH_2 (CH_2)_6-COOCH_3$	C <sub>18</sub>	384	337 227 (A), 259 (B)	<b>м́+</b> +М	230	ບົ	ບ ເ
$6. CH_3CH_3CH_1OHNSCH (OLMS ) C_7H_3COOCH_3$	ບິ ບິ	314 314	173 (A), 257 (B) 157 (A), 255 (B)	M+→A , M+→ B M+→A , M+→ B	1. 1	ບໍ່ ບໍ່ບໍ່	ζ.
7. CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH ( OTMS ) C <sub>8</sub> H <sub>14</sub> COOCH <sub>3</sub> Dienoic	C16	356	187 (A), 271 (B)	M+→A, M+→ B	ł	ບໍ່ດີ ເບີ້	Ŝ
8. $CH_3CH_3CH=CHCH=CHCH ( OTMS .) (CH_3)_{7}COOCH_3$	C <sub>15</sub>	340	1£3 (A), 311 (B)	M+→A, M+→B <sub>E</sub>	1	Č	ن ب
9. CH <sub>3</sub> C <sub>7</sub> H <sub>12</sub> CH ( <b>_OTMS</b> )C <sub>6</sub> H <sub>10</sub> COOCH <b>3</b> 10. CH <sub>2</sub> (CH3)-CH ( <b>_OTMS</b> ) CH = CHCU=CH (CH3) + COOCU	ບັ້ບ	354	213 (A.), 243 (B.)	$M^+ \rightarrow A, M^+ \rightarrow B$ $M^+ \rightarrow M^+ \rightarrow B$	1	ĵ 	6) (8)
11. $CH_1(CH_2)_{CH}$ ( $Omes$ ) $CH=CHCH=CH$ ( $CH_2)_{COCCH}$	ن ڙ	<b>38</b> 2	19/ (A), 311 (B)	M+M+B	1 20	ບໍ່ ເ ບິ່ ເ	ഗ് v
12. $CH_3(CH_2), CH = CHCH = CHCH (OTHS), (CH_2), COOCH_3$	0"°	382	225(A), 311 (B)	$M^+ \rightarrow A, M^+ \rightarrow B$	292	ڑ ٰٰ ژ	ں ہے ر
13. CH <sub>3</sub> C <sub>7</sub> H <sub>12</sub> CH ( OTMS ) C <sub>8</sub> H <sub>14</sub> COOCH <sub>8</sub>	C <sub>18</sub>	382	213 (A), 271 (B)	$M^+ \rightarrow A, M^+ \rightarrow B$	1	5) )	6 
14. $CH_3G_6H_{10}CH$ ( $OTMS$ ) $C_9H_{16}COOCH_3$	C <sub>18</sub>	382	199 (A), 2.5 (B)	M+→A, M+→B	1		
15. CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH ( OTMS ) C <sub>12</sub> H <sub>20</sub> COOCH <sub>3</sub>	C18	382	325 (B)	M+→ B	1	ີດ, ດີ	C10
16. CH <sub>3</sub> (CH <sub>2</sub> ),CH (OTMC) C <sub>10</sub> H <sub>16</sub> COOCH <sub>3</sub> 17. CH C H, CH (OTMC) C <sub>10</sub> (OCOOCH <sub>3</sub>	C <sub>1</sub>	382	1-7 (A), 297 (B)	W+ → A	]	с", с,	
1. Current to I (OI MC) CAH 12 COOCH3	C <sub>1%</sub>	382	227 (A), 257 (B)	M+.,A, M+.,B	}	•	
Trienoic							
18. CH <sub>3</sub> C <sub>10</sub> H <sub>18</sub> CH ( <b>OTMS</b> ) C <sub>3</sub> H <sub>8</sub> COOCH <sub>3</sub>	C <sub>18</sub>	380	3 0(N <sup>+</sup> ), 253 A)	M <sup>+</sup> →A , 360→290	ł		
19. CH <sub>3</sub> C <sub>3</sub> H <sub>10</sub> CH ( OTMS ) (CH <sub>3</sub> ) <sub>7</sub> COOCH <sub>3</sub>	C <sub>18</sub>	380	223 (A); 259 (B)	M <sup>+</sup> →A, 380 →290	J		ບໍ ບໍ
ZU. CH3C6H8CH (ULTUS ) C9H16COOCH3	C <sub>18</sub>	380	197 (A), 2.5 (B)	<b>A</b> +_+M			ò
Monoenoic dihydroxy acids							
$21.  C_3 H_5 CH$ ( OTMS ) CH ( OTMS ) (CH $_2$ ) $_3 COOCH_3$	C14	416	143, 273	M <sup>+</sup> →273	1	ڻ	ر
22. CH <sub>3</sub> C <sub>3</sub> H <sub>4</sub> CH (OTMS) CH (OTMS) (CH <sub>2</sub> ) <sub>3</sub> COOCH <sub>3</sub>	C <sub>15</sub>	430	157, 273	M+-273	1	•	د. رو راه
23. CH <sub>3</sub> (CH <sub>2</sub> ), CH=CH (CH <sub>2</sub> ) <sub>3</sub> CH (OTMS ) (CH <sub>2</sub> ) <sub>2</sub> CH (OTMS ) (CH <sub>2</sub> ) <sub>7</sub> COOCH <sub>3</sub>	C.,	486	<b>486</b> , 199. 239, 259, 949	360-+270 370 - 916	<b>360</b> 070		0 
$24$ . $C_{23}H_{41}$ ( other ) <sub>2</sub> COOCH <sub>3</sub>	С. <sup>3</sup>	542	+W	0174-017	000 <sup>,</sup> 210		ບໍ ບໍ
Trihydroxy acids							
25. C <sub>18</sub> H <sub>32</sub> (oTMS )3COOCH <sub>3</sub>	C <sub>19</sub>	574	304 (M-2TMS OH)+		484		
		_	_		,		

TABLE 2. Characteristic Ions and Metastable Transitions of the Components of the Combined TMS Derivatives of the Methyl Esters of the Hvdroxy Acids from Sea Buckthorn Oil

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The position of the double bond in the molecule of the monoenoic hydroxy acid (4) was less easy to show. The mass numbers of ions A and B in the spectrum of the hydroxy acid (4) indicate the position of the C=C bond at the hydrocarbon end and that it is separated from the CH(OTMS) group by not less than one CH<sub>2</sub> group. The presence in the spectrum of the mixture of a weak peak of a fragment with m/z 230 is not a sufficient basis for determining this acid in octadec-12-enoic. In the hexadecenoic hydroxy acid (7), the double bond is located between the C-OH group and the carboxylic end of the molecule. Two of the acids are of the short-chain (C<sub>13</sub>) type. In both, the  $\pi$ -bond is located between the CH-OH and COOH groups, and on the basis of the mass numbers of fragments A and B compound (6) can be determined as 12-hydroxytridec-9-enoic acid.

The group of dienic monohydroxy acids (8-17) is the most widely represented. The molecular peak of the  $C_{18}$  acids (m/z 382) has a high intensity. It has been reported that coriolic (11) and dimorphecolic (12) acids are most common in a mixture. An additional indication confirming the high concentration of the acid (11) is the peak of an ion with m/z 130 having the composition  $C_6H_{14}$ OSi. However, the defocusing of this ion led to precursors uncharacteristic for the spectrum of (11). Consequently, this ion is formed by a complex multistage mechanism.

The presence in the spectrum of the mixture of a strong peak with m/z 183 homologous to the ion with m/z 225, together with the revelation of a parental ion with m/z 340 for fragments with m/z 183 and 311 indicates the presence in the mixture of 9-hydroxypentadeca-10,12-enoic acid (8), which is analogous to dimorphecolic acid (12).

The amount of the  $C_{16:2}$  hydroxy acids is substantial, its molecular peak with m/z 354 having an intensity of about 10% rel. An analysis of the metastable transitions led to two compounds with this molecular weight. One of them is 13-hydroxyhexadeca-9,11-dienoic acid (10). In the molecule of the 8-hydroxy acid (9),  $\pi$ -bonds are present on both sides of the -CH-OH group, but their positions have not been established. Three  $C_{18:2}$  hydroxy acids have been characterized similarly; a 10-hydroxydecadienoic acid (13), an 11-hydroxyoctadecadienoic acid (14), and a 9-hydroxyoctadecadienoic acid (17). Two other acids are apparently analogs of coriolic acid (10) with hydroxy groups at C-14 (15) or at C-12 (16).

The spectrum of the mixture (Fig. 1) well shows the peaks of  $(M - TMSOH)^+$  ions with m/z 292 and 290. These are formed in the breakdown of the M<sup>+</sup> ions of the trienic monohydroxy acids (18-20). The positions of the hydroxy groups and of the  $\pi$ -bonds in the molecules of these compounds have not been determined. With a rise in the temperature of the experiments, weak peaks of ions appeared in the > 400 amu region of the mass spectrum of the total TMS derivatives which, on the basis of various items of information, can be considered as the molecular and fragmentary ions of the TMS derivatives of dihydroxy acids. The detection of the metastable transitions 416<sup>+</sup>  $\rightarrow$  273<sup>+</sup> and 430<sup>+</sup>  $\rightarrow$  273<sup>+</sup> permits us to consider that the C<sub>14</sub> and C<sub>15</sub> dihydroxy acids (21 and 22) are present in the mixture. A check on the elementary compositions of the ions with m/z 143 and 157 gave grounds for assuming that they were  $\alpha$ -dihydroxy acids. The compositions of the ions with m/z 486 (C<sub>26</sub>H<sub>54</sub>O<sub>4</sub>Si<sub>2</sub>) and 542 (C<sub>30</sub>H<sub>62</sub>· O<sub>4</sub>Si<sub>2</sub>) permitted them to be regarded as the M<sup>+</sup> ions of derivatives of longer-chain hydroxy acids.

The probable structure of the dihydroxy acid (23) is shown by the following facts: a metastable transition at  $360^+ \rightarrow 270^+$  indicating the loss of a TMSOH molecule was recorded. If we take as a basis the fact that the ion with m/z 270 has the same structure as the TMS derivative of methyl ricimoleate (3), one of the TMSO grops is located at C-12 and the other closer to the methoxycarbonyl group. The C-9 position is the most likely, since it does not contradict the structure of the ion with m/z 270. The breakdown of the TMS derivative of such a dihydroxy acid should form an ion of type A with m/z 329, which, on the elimination of one TMSOH molecule, should lead to a fragment with m/z 239 having the composition  $C_{14}H_{27}OSi$ , all the more since an ion of this composition, and also the  $329^+ \rightarrow 239^+$ transition has been detected. Other fragments that may be formed from  $M^+$  (23) (m/z 199, 259) are characteristic of the spectra of the acids included in Table 2. We may also mention that the ion with m/z 270 can, as shown in the scheme, break down with the loss of a  $C_4H_7$  particle, which leads to a daughter ion with m/z 215 ( $C_{11}H_{23}O_2Si$ ). This fragment makes up about 50% of the total height of the ions with a mass number of 215, and the 270 $^+$ ightarrow 215<sup>+</sup> transition in the MD spectrum is characterized by a distinct metastable peak (Fig.2c). Compound (24) is a  $C_{23-1}$  dihydroxy acid. An ion with m/z 574 decomposing with the successive elimination of two TMS-OH molecules (ions with m/z 484 and  $394 - C_{23}H_{42}O_{3}Si$ ) may be regarded as the M<sup>+</sup> ion of the trihydroxy acid (25).



The structure of the total material contains weak peaks of fragments which, judging from their compositions, were formed from acids with even longer chains. For example, an ion with m/z 567 has the composition  $C_{35}H_{71}O_3Si$ .

Table 2 gives the number of C atoms of the most probable products of the degradation of compounds (1-23) (apart from the cases where the positions of the  $\pi$ -bonds are unknown). We may note that among the monocarboxylic acids a C<sub>6</sub> acid is encountered the most frequently, and among the dicarboxylic acids a C<sub>9</sub> acid. These facts agree well with the maximum amounts of these acids in the mixture (bottom line of Table 1). Thus, the spectrum of zone (11) shows the largest amount, among all the zones, of derivatives of coriolic and dimorphecolic acids, which is in harmony with the greatest contribution of this zone to the total (30.4%). The maximum distribution of the C<sub>6</sub> acids among the monocarboxylic acids and the C<sub>9</sub> acids among the dicarboxylic acids also corresponds to the structures of acids (11) and (12). The large amount of the C<sub>8</sub> monocarboxylic acids in this zone is reflected in the spectrum by an increase in the intensity of the peak of an ion with m/z 215, which is characteristic for the 10-hydroxy acid (1). In the spectrum of zone (III) the peaks of the ions A with m/z 187 and 173 characteristic of acids (1, 3, 5, and 16) have the greatest intensity. The predominant distribution of caproic acid (C<sub>6</sub>) in zone (III) is in harmony with this, and the contribution of C<sub>5</sub> acids is also considerable.

The main characteristic of the spectrum of zone (IV) is its enrichment with the M<sup>+</sup> peaks of trienic acids. At the same time, only the high intensity of the peak of an ion with m/z259 confirms the presence of one of the trienic acids that we have found, (19). A consequence of this may be the fairly high contribution of the C<sub>6</sub> monocarboxylic acids (26.8%) in zone (IV). In order to explain the maximum content of the C<sub>9</sub> acids in this zone (29.0%), it may be assumed that it was enriched with the dienic hydroxy acid (13). In the spectrum of zone (IV), the peaks of ions with m/z 213 and 271, which are characteristic for this acid, are some of the strongest.

Thus, the main hydroxy acids in sea buckthorn seed oil are coriolic and dimorphecolic, and these are accompanied by their homologs: 13-hydroxyhexadeca-9,11-dienoic and 9-hydroxypentadeca-10,12-dienoic and isomers with respect to the positions both of the double bonds and of the hydroxyl (13-17). Ricinoleic acid and its isomer, 9-hydroxyoctadec-12-enoic, and also trienoic acids are present in smaller amount. Di- and trihydroxy acids are also present in small amounts.

Dimorphecolic acid has been detected in many seed oils of plants of the family <u>Compositae</u>. Coriolic acid has been found in the seed oils of the families <u>Compositae</u>, <u>Coriaraceae</u>, and <u>Polygonaceae</u> [7]. Ricinoleic acid and its isomers have been found in the seed oils of plants of the families <u>Euphorbiaceae</u>, <u>Cruciferae</u>, and <u>Apocyanaceae</u>. 10-Hydroxystearic acid has been found together with ricinoleic in the surface waxes of he leaves of <u>Rosmarinus officinalis</u> [6]. 8-Hydroxyhexadecanoic acid has been isolated from <u>Lycopodium combinatum</u> [8].

9-Hydroxytridecanoic, 10-hydroxyhexadecadienoic, 8-hydroxyhexadecadienoic, 10-11-dihydroxytetradecenoic, 10,11-dihydroxypentadecenoic, and 14-hydroxyoctadecadienoic acid have not previously been detected in seed oils. The structures of these acids could not be established definitively, since because of the wealth of components it was difficult to determine the positions of the double bonds unambiguously from the products of oxidative degradation.

11-Hydroxytridec-9-enoic, 9-hydroxypentadeca-10,12-dienoic, 13-hydroxyhexadeca-9,11-dienoic, and 9,12-dihydroxynonadec-15-enoic acids are new and this is the first time that they have been detected in seed oils.

# EXPERIMENTAL

The mass spectra of the total TMS derivatives and of individual fractions were taken on a MKh 1310 instrument with direct introduction of the sample at a temperature of the ionization chamber and of the evaporator bulb of 80°C using an ionizing voltage of 50 V and a collector current of 40  $\mu$ A. The elementary compositions of the ions were measured at R = 10,000 with an accuracy of 5  $\cdot 10^{-6}$ , the standard being perfluorokerosine. Defocusing:  $\epsilon$ , H = const; scanning of U from 2.0 to 4.8 kV at the rate of 0.1 kV/sec; chart speed 5 mm/sec.

The lipids were isolated from the seeds by extraction with hexane at room temperature. The hydroxyacyldiacylglycerols were isolated as described in [9].

Thin-layer chromatography was performed on Chemapol type 5/40 silica gel in the systems: 1) chloroform-benzene-diethyl ether (50:50:15); and 2) hexane-diethyl ether (6.5:3.5).

Alkaline hydrolysis was performed with a 0.1 M solution of KOH in methanol with stirring by a magnetic stirrer at 37°C for an hour. The methyl esters of the hydroxy acids were silylated according to [10]. The silylation products were purified by preparative TLC on silica gel in the solvent system hexane-diethyl ether (9:1).

The GLC analysis of the methyl esters of the mono- and dicarboxylic acids was carried out on a Chrom-41 instrument with a flame-ionization detector using a  $2.5 \times 4$  mm column filled with 17% of ethylene succinate on Chromaton NAV-DMCS at 198°C for the dicarboxylic acids and 132°C for the low-molecular-weight acids.

### SUMMARY

In sea buckthorn seed oil 25 hydroxy acid components have been detected by the mass-spectrometric method, the main ones being coriolic and dimorphecolic acids.

Four new hydroxy acids have been found in seed oils for the first time: 11-hydroxytridec-9-enoic, 9-hydroxypentadeca-10,12-dienoic, 13-hydroxyhexadeca-9,11-dienoic, and 9,12-dihydroxynonadec-15-enoic.

#### LITERATURE CITED

- 1. S. G. Yunusova, S. D. Gusakova, and Ya. V. Rashkes, Khim. Prir. Soedin., 436 (1981).
- 2. D. S. Smith, C. Djevossi, K. H. Maurer, and U. Rapp, J. Am. Chem. Soc., <u>96</u>, 3482 (1974). 3. C. R. Smith, R. V. Madrigal, and R. D. Plattner, Biochim. Biochim. Biophys. Acta, 572,
- 314 (1979).
- 4. R. Kleiman and S. F. Spencer, J. Am. Oil Chemists' Soc., <u>50</u>, 31 (1973).
- 5. S. D. Gusakova, A. L. Markman, and A. U. Umarov, Maslozhir. Prom-st', No. 4, 21 (1969).
- 6. C. H. Brieskorn and L. Kabelits, Phytochem., 10, 3195 (1971).
- 7. R. C. Badami and K. B. Patil, Progr. Lipid Res., 19, 119 (1980).
- 8. P. Pohl and H. Wagner, Fette, Seifen, Anstrichmittel, 9, 541 (1972).
- 9. H. T. Ul'chenko, É. I. Gigienova, K. L. Seitanidi, and A. U. Umarov, Khim. Prir. Soedin., 699 (1978).
- 10. F. D. Gunstone and H. R. Schuler, Chem. Phys. Lipids, 15, 198 (1975).