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LIPIDS OF THE SEEDS OF *Securinega suffruticosa*

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The lipid composition of the seeds of *Securinega suffruticosa* (*Euphorbiaceae*) has been studied, and eight classes of lipids have been identified with a predominance of triacylglycerols; the fatty acid compositions and structures of the triacylglycerols have been determined. Among the hydroxy acids of the hydroxyacylglycerols 13 components belonging to saturated, monoenic, and dienic acids of the C_{17}, C_{18}, and C_{20} series have been identified; 12-hydroxyheptadecanoic and 12-hydroxyeicosanoic acids are new.

The family Euphorbiaceae include 280 genera and 8000 species, the genera *Euphorbia*, *Croton*, and *Phyllanthus* being the most widespread. Some indices of the total lipids and of the fatty acids have been determined for the seeds of more than 58 species of *Euphorbiaceae* [1]. There is no information in the literature on *Securinega suffruticosa* (Pall.) Rend., but it is known [2] that this plant contains alkaloids which serve as a basis for the creation of medicinal preparations used in hypotension, afflictions of the nervous system, and chronic alcoholism [2].

We have investigated the seed lipids of the Far Eastern species *S. suffruticosa* introduced into the Tashkent Botanical Garden. The total lipids were separated by column chromatography on silica gel into individual classes of compounds. The lipids were identified by their chromatographic mobilities in TLC in comparison with model samples, from the results of chemical transformations, and from their IR, UV, and mass spectra. The lipid composition is given below (% by weight): hydrocarbons 0.2; triacylglycerols (TAGs) 95.0; free fatty acids (FFAs) 1.0; sterols 0.6; total diacyl- and hydroxyacyldiacylglycerols (DAGs and HAGs) 2.6; monoacylglycerols (MAGs) 0.1; polar lipids (PLs) 0.5. Thus, the seed lipids of *S. suffruticosa* consist of a total of eight classes with a predominance of TAGs.

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The fatty acid composition of the lipids is given below (GLC, wt.-%):

Acid	Total lipids	TAGs	FFAs	HAGs* DAGs	MAGs	PLs
14:0	Tr.	Tr.	—	—	—	0.6
16:0	4,9	5,0	26,0	7,7	12,7	12,2
18:0	2,3	3,0	13,5	3.8	6,3	5,4
18:1	8,0	9,0	19,9	8.8	14,2	12.3
18:2	20,9	24.0	20.7	34.3	26 0	29,0
18:3	63,9	59,0	19,9	45.4	40 8	40,5
Σ sat	7,2	8.0	39.5	11,5	19,0	18,2
Σ unsat	92,8	92,0	60,5	88,5	81,0	81,8

*The composition of the unoxidized fatty acids is given.

As we see, in all the lipids of *S. suffruticosa* apart from the FFAs the main unsaturated acid is the 18:3 representative. It is present in the largest amount in the TAGs. A considerable amount of 18:3 acid has been reported from the lipids of the seeds of many species of *Euphorbiaceae* [1].

The structures of the TAGs were determined by stereospecific analysis. The results obtained on the distribution of the acids over the three positions of the TAG molecule are given below (GLC, mol-%):

Acid	TAGs	Position *sn-1*	*sn-2*	*sn-3*
16:0	5,4	10,6	0,6	5 0
18:0	2,9	5,6	—	3,1
18:1	8,9	13,7	2,5	10 5
18:2	23 8	25,5	27,2	18,7
18:3	59,0	44,6	69,7	62,7

According to these results, in the TAGs of *S. suffruticosa* the saturated acids mainly esterify the sn-1 position of the molecule, while the distribution of the unsaturated acids is such that the largest amount of the 18:2 acids esterifies the sn-2 and sn-1 positions, the largest amount of the 18:3 acids the sn-2 and sn-3 positions with a predominance of these acids in the sn-2 position, and the 18:1 acids are distributed between the sn-1 and sn-3 positions with the bulk in the sn-1 position.

The distribution of the 18:3 acids must be regarded as one of the distinguishing features of the structure of the TAGs of this species, since in the other plant families studied the 18:3 acids are concentrated in the extreme positions of the TAG molecules [3].

In the stereotype composition of the TAGs of *S. suffruticosa*, the UUU and SUU types predominate (76.9% and 14.7% by weight, respectively), the amount of SSU being 0.1%, of SUS 1.3%, of UUS 6.7%, and of USU 0.3%; the SSS and USS types are absent. This composition is typical for plant TAGs enriched with 18:3 acids [3].

Characteristic for the Euphorbiaceae family is the presence of a broad spectrum of unusual fatty acids with one or two hydroxy groups and epoxide groups and with two or three conjugated double bonds. At the present time, more than 10 unusual fatty acids have been detected in various species of Euphorbiaceae [4].

In view of this, we have investigated the structure of the hydroxy acids present in the HAGs. The fraction containing the HAGs was subjected to mild alkaline hydrolysis, and the fatty acids (FAs) in the form of their methyl esters (MEs) were separated by preparative GLC in system 1 into the MEs of unsaturated FAs (UFAMEs, R_f 0.9) and MEs of hydroxy fatty acids (HFAMEs, R_f 0.4). On plates coated with silica gel impregnated with 10% of $AgNO_3$ in system 2, the HFAMEs were separated according to their degree of unsaturation into two spots corresponding in their mobilities to saturated acids with α-hydroxydienoic acids (R_f 0.4) and to hydroxymonoenoic acids (R_f 0.35; the main group quantitatively).

In the mass spectrum of the TMS derivatives of the UFAMEs there was a series of M^+ peaks in the m/z region of 320-340 and ions of the $(M - 15)^+$, $(M - 31)^+$, and $(M - 47)^+$ types, which correspond to saturated, monoenoic, and dienoic, monohydroxy acids of the C_{17} and C_{18} series and their C_{20} saturated isologs. The spectrum contained no M^+ ion corresponding to derivatives of C_{17} saturated hydroxy acids. The peaks of the ions of the C_{18} isologs had the greatest intensity. For this series of acids and for the C_{20} hydroxy acids there were fragments showing the loss of 90 mass units by M^+.

Fragments formed on the cleavage of bonds in the allyl position to the TMSO—CH_2 group [6] and also rearranged ions with m/z 230, 244, 270, and 272 corresponded to the molecular ion.

From the set of characteristic fragments [6-8], it was decided that the components of the mixture of hydroxy acids included the C_{18} 9-hydroxy-10,12-dienoic acid; the C_{18} 13-hydroxy-9,11-dienoic acid (traces); the C_{18} 12-hydroxy-9-monoenoic (ricinoleic) acid and its 9-hydroxy-12-monoenoic isomer and a C_{17} 12-hydroxymonoenoic acid; and the saturated C_{18} 9-hydroxy and 10-hydroxy acids. Another isomer of ricinoleic acid — a C_{18} 10-hydroxymonoenoic acid that we had detected previously in the lipids of *Gossypium hirsutum* [6] but with an unestablished position of the double bond — was assigned on the basis of fragments with m/z 213, 273, and 244 and in the light of the rule for the decomposition of TMS derivatives of unsaturated hydroxy fatty acids [8] and the laws of their biosynthesis [9] to 10-hydroxyoctadeca-12-enoic acid.

In addition to these known hydroxy acids, from the peaks of ions of appreciable intensity with m/z 173, 187, 272, and 301 it was concluded that the 9-hydroxy-17:0, 12-hydroxy-17:0, 12-hydroxy-18:0, and 12-hydroxy-20:0 acids were present among the components. No fragmentary ions corresponding to a given position of the hydroxy group in the chains of the C_{17} and C_{20} acids were detected in the spectrum. It was impossible to establish a probable structure for the hydroxy-17:2 acid.

12-Hydroxyoctadecanoic acid has been detected previously in the lipids of the fungus *Claviceps purpurea* [10], but 12-hydroxyheptadecanoic and 12-hydroxyeicosanoic acids are new.

It must be mentioned that weak peaks of ions containing no Si with m/z 310, 279 (310 — 31), and 239, which are characteristic for the decomposition of oxo acids [11], were observed in the spectrum.

On a gas-liquid chromatogram of the TMS derivatives, four peaks were obtained. A peak with C_{sp} 4.2 min (82%) corresponded to C_{sp} of a model sample of the analogous derivatives of ricinoleic acid, while the other peaks were assigned to C_{17} hydroxy acids (C_{sp} 2.8 min, 0.6%), to saturated C_{18} hydroxy acids (C_{sp} 4.8 min, 14%), and to hydroxyeicosanoic acid (C_{sp} 6.8 min, 3.4%) [12].

Thus, the mixture of monohydroxy acids in the lipids of *S. suffruticosa* consists of not less than 13 components, among which ricinoleic acid predominates, with accompanying isomers having the double bond in the $\Delta^{12,13}$ position and the hydroxy group at C-9 or C-10. A hydroxypentadecenoic acid is structurally similar to ricinoleic aicd, and the positions of the OH groups in the saturated C_{17}, C_{18}, and C_{20} components are analogous to that in ricinoleic acid and its isomers.

The structural characteristics mentioned are also observed in the hydroxyhepta- and hydroxyoctadecenoic acids of similar qualitative composition present in the seed lipids of *Gossypium hirsutum* (family Malvaceae), although the plant species under consideration belong to different families [6].

It is known that the seed lipids of *Ricinus communis* (family Euphorbiaceae) contain 80-90% of ricinoleic acid with the 9,10-dihydroxy acid as impurity [13]. According to our results, obtained by chromato-mass spectrometry, in some samples of castor oil there are also trace amounts of the 10-hydroxy-18:0 acid and of a hydroxy-17:0 acid. A plant dehydrogenase desaturating the 12-hydroxy-18:0 acid in the $\Delta^{9,10}$ position has also been described [14]. In view of all these facts, the minor hydroxyheptadecenoic acid and the hydroxyhepta- and hydroxyoctadecanoic acids of the *S. suffruticosa* lipids can be considered as intermediates of the biosynthesis of ricinoleic acid.

EXPERIMENTAL

UV spectra were taken on a Hitachi spectrometer in hexane and mass spectra on a MKh-1303 spectrometer at an ionization energy of 40 eV. The conditions of chromato-mass spectrometry were described in [6].

Gas-liquid chromatography was performed on a Chrom-4 chromatograph with a flame-ionization detector and a stainless-steel column filled with Chromaton N-AW-DMCS with 15% of Reoplex-400, and also with 17% of ethylene succinate for the MEs of the unsaturated fatty acids; and Chromaton N-AW-DMCS with 5% of SE-30 for the TMS derivatives of the hydroxy acid MEs. The column was 4 mm in diameter and 2.5 m long; the temperature was 198°C or, for the MEs of the

TMS-acids, 220°C; the rate of flow of the carrier gas (helium) was 0.62 kg/cm^2 [sic], of H_2 60, and of air 0.6 liters/min; and the chart speed was 0.5 cm/min.

TLC on Silufol and silica gel was performed as described in [6] using the following systems: 1) diethyl ether–hexane (5:5); and 2) benzene–chloroform–diethyl ether (50:50:2.5).

The oil was extracted from the ground seeds five times with hexane at room temperature.

The column chromatography of the total lipids was performed as described in [15].

The stereoanalysis of the triacylglycerols was performed as described in [16], and alkaline hydrolysis as in [5].

The TMS derivatives of the hydroxy acids were obtained by the method of Gunstone and Schuler [17].

Mass spectrum: m/z 414, 386, 384, 382, 372, 370, 368 M^+; 399, 371, 369, 367, 357, 355, 353 $(M-15)^+$; 383, 355, 353, 351, 341, 339, 337 $(M-31)^+$; 367, 339, 337, 335, 325, 323, 321 $(M-47)^+$; 324, 296, 294, 292 $(M-90)^+$.

SUMMARY

1. The lipids of *S. suffruticosa* seeds consist of eight classes: Normal linolenic-acid-rich triacylglycerols predominate, these being accompanied by hydroxyacyldiacylglycerols.

2. The distribution of fatty acid over the sn-1 and sn-3 positions of the TAGs is unsymmetrical, and the main types of TAGs are triunsaturated and sn-2,3-diunsaturated-sn-1-saturated.

3. In the hydroxy fatty acids, 13 components have been identified, of which 12-hydroxyheptadecanoic and 12-hydroxyeicosanoic acids are new. The hypothesis has been expressed that hydroxyheptadecenoic and hydroxyhepta- and hydroxyoctadecanoic acids may be precursors in the biosynthesis of ricinoleic acid.

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