LITERATURE CITED

1. H. Schlenk and J. L. Gellerman, J. Am. Oil Chem. Soc., 42, 504 (1965).
2. B. Akermark, Acta Chem. Scand., 21, 589 (1967).
3. G. Bendy, J. Santersson, and L. Tibell, Acta Chem. Scand., 20, 1181 (1966).
4. J. Santersson, Acta Chem. Scand., 21, 1993 (1967).
5. Y. Yamamoto and A. Watanabe, J. Gen. Appl. Microbiol., 20, 83 (1974).
6. E. Kushnir, A. Tietz, and M. Galun, Protoplasma, 97, No. 47 (1978).
7. I. N. Bellman, L. J. De Kok, P. J. C. Kuiper, and P. R. Van Hasselt, Oikos, 35, 321 (1980).
8. V. M. Dembitsky and O. A. Rozentsvet, Phytochemistry, 28, 3341 (1989).
9. V. M. Dembitsky, E. E. Pechenkina, and O. A. Rozentsvet, Phytochemistry, 29, 3417 (1990).

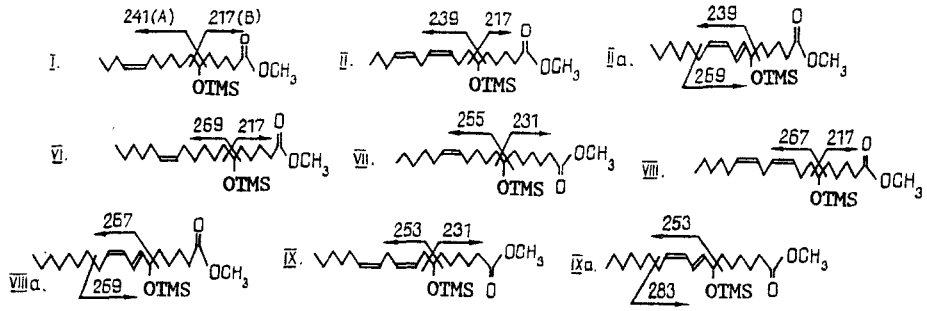
NEW HYDROXY FATTY ACIDS OF Acanthopanax sessiliflorus

D. T. Asilbekova, S. D. Gusakova, and A. I. Glushenkova

UDC 547.915:665.33

The structures of six new hydroxy fatty acids from the hydroxyacyldiacylglycerols of the fruit of Acanthopanax sessiliflorus (Rupr. et amaxim.) Seem. (family Araliaceae have been established as 6-hydroxyhexadeca-12Z-enoic, 6-hydroxyhexadeca-9Z,12Z-dienoic, and the isomeric 6- and 7-hydroxyoctadeca-12-Z-enoic, and 6- and 7-hydroxyoctadeca-9Z,12Z-dienoic acids and their quantitative amounts have been determined with the aid of spectral, chromatographic, and chemical methods of analysis.

We have previously studied the neutral lipids of the fruit of Acanthopanax sessiliflorus (Rupr. et Maxim.) Seem., a medicinal plant of the family Araliaceae [1]. The lipids contained hydroxyacyldicyglycerols (H-TAGs; 0.3% of the weight of the lipids) in which as the main hydroxy acids (HAs) were identified 12-hydroxyoctadecanoic (III) and the isomeric 12(9)-hydroxyoctadeca-9(12)Z-enoic (IV and V) and 9(13)-hydroxyoctadeca-10E,12Z(9Z,11E)-dienoic (X, XI) acids. The minor HAs were not characterized. In the present paper we give the results of a further structural analysis of the unidentified HAs.



When the mixture of methyl esters of the acids (HAMEs) was chromatographed in a thin layer [1], a mixture of overlapping spots was obtained, and of the spots those with the following average R_f values corresponded to known compounds: 0.42 – 12-OH-9Z-18:1; 0.40 – 13-OH-9Z,11E-18:2; 0.38 – 9-OH-10E,12Z-18:2; and 0.35 – 9-OH-12Z-18:1 [2]; three minor spots with R_f 0.33-0.28 belonged to unknown compounds. It was impossible to isolate the minor HAs in the pure form.

Institute of the Chemistry of Plant Substances, Uzbek Academy of Sciences, Tashkent.
Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 616-619, September-October, 1991. Original article submitted December 12, 1990.

 0009-3130/91/2705-0542$12.50

TABLE 1. Hydroxy Acids of the Lipids of Acanthopanax sessiliflorus

Hydroxy acid	Amount, %	Molecular ions and breakdown of fragments of the TMS*					
		M^+	$[M-15]^+$	$[M-31]^+$	$[M-47]^+$	A†	B†
I.6-OH-12Z-16:1	4,4	356 (1,5)	341 (3,9)	325 (3,0)	309 (5,8)	241 (9,7)	217 (9,7)
II.6-OH-9Z, 12Z-16:2	13,1	354 (6,0)	339 (4,4)	323 (4,2)	307 (1,7)	239 (16,0)	
III.12-OH-18:0			371 (2,7)	355 (3,1)	339	187 (18,5)	301 (12,6)
IV.9-OH-12Z-18:1	13,2					227 (17,4)	259 (16,6)
V. 12-OH-9Z-18:1		384 (4,4)	369 (3,3)	353 (3,0)	337 (5,7)	187	299 (4,5)
VI.6-OH-12Z-18:1						269 (4,5)	217
VII. 7-OH-12Z-18:1	4,9					255 (5,5)	231 (10,3)
VIII. 6-OH-9Z, 12Z-18:2						267 (10,3)	217
IX. 7-OH-9Z, 12Z-18:2	12,4					253 (11,2)	231
X. 9-OH-10E, 12Z-18:2		382(17,9)	367 (3,5)	351 (4,4)	335 (2,7)		
XI. 13-OH-9Z, 11E-18:2	47,5					225 (43,7)	311 (23,2)
Unidentified	4,5						

*Intensity relative to m/z 73 (100%).
†A) the $CH_3...CHOTMS-$ fragment; B) the $-CHOTMS...COOCH_3$ fragment.

Information on the structure and components of minor HAs was obtained from the results of the GLC analysis of the total HAMEs on a nonpolar phase and of their TMS derivatives on a polar phase, and also by the mass-spectrometric analysis of the latter.

As a result of GLC analysis on a nonpolar phase three spots were detected on the chromatogram, one of which with a relative retention time (RT with respect to 16:0) of 1.75 corresponded to a HAME with 16 carbon atoms. The amount of this component in the HAMEs was ~18%. Another peak, belonging to a C_{18} HAME, was partially separated into two components with RRTs of 2.67 and 2.97 (~72%), which showed the presence of isomers in which the hydroxy group was located close to the carboxy group.

When the TMS derivatives of the HAMEs were chromatographed on a polar phase, three peaks were obtained: a main peak (RRT 2.75) with two inflections (RRTs 2.45 and 3.04; 82.5%) belonged to poorly resolved isomers and isologues of derivatives with 18 carbon atoms; the other two peaks corresponded to derivatives of C_{16} monoenic (RRT 1.60; 4.4%) and dienic (RRT 2.18; 13.1%) HAMEs.

In the mass spectrum of the TMS derivatives of the HAMEs, the region of high masses contained the peaks of the molecular ions M^+ and of the $[M-15]^+$, $[M-31]^+$, and $[M-47]^+$ fragments of C_{18} and C_{16} monoenic and dienic HAs. For the saturated HA, M^+ ions with the loss of 15, 31, and 47 mass units were observed.

The mass numbers and intensities of the peaks of the main fragments in the spectrum corresponded to the known 12-OH-18:0 (III, Table 1), 9(12)-OH-12Z(9Z)-18:1 (IV and V), and 9(13)-OH-10E,Z(9Z,11E)-18:2 (X and XI) acids [1]. According to the UV spectrum, the amount of the isomeric OH-18:2 acids with conjugated double bonds was 47.5% of the weight of the HAMEs. Of the two isomeric hydroxydienoic acids, the 9-OH-10E, 12Z-18:2 compound (m/z 225, 47%) predominated [4].

In addition to those mentioned above, the mass spectrum contained the peaks of a fragment B with m/z 217 formed as the result of the fragmentation of a derivative with a hydroxy group at the sixth carbon atom; those of fragments A with m/z 241 of the derivative of the 6-OH-16:1 acid (I) and with m/z 239 of two possible 6-OH-16:2 isomers (II and IIa). Fragments with m/z 267 and 269 were present which, in association with the ion having m/z 217, corresponded to the derivative of the ME of the 6-OH-18:1 acid (VI) and of two possible

isomeric 6-OH-18:2 acids (VIII and VIIIa). Ions with m/z 231, 255, and 253 revealed the structures of the 7-OH-18:1 acid (VI) and of possible isomeric 7-OH-18:2 acids (IX and IXa). The choice of the isomer of the hydroxydienoic acid was made on the basis of the results of the oxidative cleavage of the HAME.

The monocarboxylic acids from oxidative degradation consisted (mole %, GLC) of the 4:0 (9.6), 6:0 (81.8), and 7:0 (9.3) species; no other monocarboxylic acids were present. The set of dicarboxylic acids included (mole %, GLC): 2:0 (tr.), 3:0 (tr.), 4:0 (4.8), 6:0 (26.2), 7:0 (27.8), 9:0 (36.5), 11:0 (tr.), 12:0 (0.2), and an unidentified component (4.5).

The formation of the 6:0 and 7:0 monocarboxylic and the 3:0, 4:0, 9:0, 11:0, and 12:0 dicarboxylic acids confirmed the structure of the known HAs. Butyric acid, 4:0, the 6:0 and 7:0 dicarboxylic acids, and the increased amount of 6:0 monocarboxylic acid are explained by the breakdown of the HAs (I), (II), and (VI-IX) in which, in the case of the monoenic acids, the double bond is located at the 12th carbon atom and in the case of the dienic acids there are double bonds at the 9th and 12th carbon atoms.

The results obtained showed that different positions of the double bonds and the OH groups in the HAMEs investigated are unlikely. The absence of the 9:0 and 8:0 monocarboxylic acids among the oxidation fragments excludes structures (VIII) and (IXa); the structure of the HA (IIa) is also doubtful, since the 7:0 monocarboxylic acid is a product of the oxidative degradation of the 12-OH-18:0 and 12-OH-9-18:1 acids, as well.

The IR spectrum of the HAMEs lacked a well-defined band characteristic for an isolated trans —CH=CH— group. The behavior of the HAMEs and their derivatives in GLC was also evidence in favor of the cis configuration of the double bond [5] in all the new HAs isolated.

Earlier, a HA with an OH group at the sixth carbon atom — namely, 6-hydroxyoctadeca-7,9-diynoic acid — was detected in the bark of the roots of Paramacrolobium caeruleum (family Fabaceae), while among the unsubstituted acids of this plant the main one was octadeca-7,9-diynoic [6]. The synthesis of HAs having hydroxy groups at the 6th and 7th carbon atoms is apparently connected biogenetically with the synthesis of octadec-6Z-enoic acid, which is the main specific unsubstituted acid A. sessiliflorus [1] and of other species of Araliaceae, Umbelliferae, Garryaceae, and Cornaceae [7].

EXPERIMENTAL

UV spectra were taken on a Hitachi spectrophotometer in heptane; IR spectra on a UR-10 instrument in a film; and mass spectra on a MKh-1303 mass spectrometer with an ionizing voltage of 40 V, a collector current of 50 μA, and a temperature of the ionization chamber of 160°C.

GLC analysis was carried out on a Chrom-4 chromatograph (Czechoslovakia) with a flame-ionization detector using a stainless steel column (4 × 2500 mm) filled with, as a polar phase, Chromaton N-AW-DMCS impregnated with 17% of ethylene succinate, and a column (4 × 1200 mm) filled with, as a nonpolar phase, Chromaton NAW-DMCS impregnated with 5% of SE-30. The HAMEs were analyzed at 200°C, and their TMS derivatives at 198°C.

The preparation of the HAMEs from the H-TAGs of the fruit of A. sessiliflorus and the conditions of TLC have been described in [1].

The periodate-permanganate degradation of the HAMEs was carried out as described in [8] at KIO_4:$KMnO_4$:HAME ratio of 10.7:0.1:0.5 by weight.

LITERATURE CITED

1. D. T. Asilbekova, S. D. Gusakova, and A. I. Glushenkova, Khim. Prir. Soedin., 760 (1985).
2. L. J. Morris and D. M. Wharry, J. Chromatogr., 20, 27 (1965).
3. A. P. Tulloch, J. Am. Oil Chem. Soc., 41, 833 (1964).
4. R. Kleiman and G. F. Spencer, J. Am. Oil Chem. Soc., 50, 31 (1973).
5. E. G. Perkins, T. P. McCarthy, M. A. O'Brien, and F. A. Kummerow, J. Am. Oil Chem. Soc., 54, 279 (1977).
6. A. D. Patil, J. A. Chan, P. Löis-Flamberg, R. J. Meyer, and J. W. Westley, J. Nat. Prod., 52, 153 (1989).
7. R. Kleiman and G. Spencer, J. Am. Oil Chem. Soc., 59, 29 (1982).
8. S. D. Gusakova, I. I. Vinokurov, and A. U. Umarov, Khim. Prir. Soedin., 288 (1981).