THE HYDROXY ACIDS OF COTTONSEED OIL

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Many plant oils – particularly those of plants of the family Malvaceae – contain hydroxy acids as well as the usual fatty acids [1, 2]. We have investigated the hydroxy acids of the oil of ripe seeds of the cotton plant of variety 108-F. The oil was extracted in the cold with petroleum ether and was then converted into the corresponding methyl esters by transesterification with sodium methoxide. From the total methyl esters of the fatty acids a fraction enriched in hydroxy acid esters (~1%) was isolated by descending column chromatography. The separation was followed chromatographically. By ascending column chromatography two subfractions were isolated from this fraction: esters of epoxy acids (A) and of hydroxy acids (B) ($C_{19}H_{34}O_3$).

The epoxy esters (A) formed a yellow oily liquid giving the characteristic reaction for an epoxy ring with picric acid [1]. Their IR spectrum had absorption bands at 3020 cm^{-1} (–CH=CH–) and at 1250, 830, and 850 cm^{-1}, which are characteristic for the epoxy group.

No absorption was found in the 900-1000 cm^{-1} region. This fraction was transparent in the UV spectrum. The NMR spectrum contained signals (τ scale) at 7.16 ppm (protons of an epoxy ring) and 4.6 ppm (cis-CH=CH group).

By opening the epoxide ring in an acid medium [3], the epoxy esters were converted into dihydroxy derivatives, which, after esterification with diazomethane, were oxidized by the periodate–permanganate method [4]. Two main fragments were obtained: azelaic acid (C_9 dicarboxylic) and caproic acid ($C_{6:0}$). The mass spectrum of the methyl esters of the dihydroxy acids showed the peaks of the molecular ion with M^+ 328 (27.9%), corresponding to an ester of a C_{18} dihydroxy acid with one double bond and also the peaks of ions with m/e 257 (4.7%), 227 (72.1%), 131 (51.2%) 101 (16.2%) and m/e 225 (257 – CH_3OH), m/e 195 (227 – CH_3OH), characterizing the positions of the two hydroxy groups at C_{12} and C_{13} and of the double bond in the Δ^9 position. However, in addition to those mentioned above, the mass spectrum of the mixtures of esters also contained peaks with m/e 217 (9.3%), 187 (86.1%), 155 (187 – CH_3OH), 185 (217 – CH_3OH) which characterize the presence of two hydroxy groups at C_9 and C_{10} and of a double bond in the Δ^{12} position.

To determine the positions of the hydroxy groups, the dihydroxy esters were hydrogenated to complete saturation. The product obtained consisted of a white salve-like substance. It was oxidized by Hilditch's method [5]. The C_8, C_9, C_{11}, and C_{12} dicarboxylic acids were obtained, together with small amounts of the C_7 and C_{10} acids, apparently formed through overoxidation.

Such behavior of the dihydroxy esters and their hydrogenated forms and also the presence in the IR spectrum of the epoxy esters of an absorption band at 3020 cm^{-1} shows that the acids contained one double bond and one epoxide group separated by a methylene link and located between C_9 and C_{13}.

It may be concluded from the results of oxidation that we were dealing with a mixture of isomeric acids. To confirm this assumption the dihydroxy esters were converted into the diacetoxy derivatives the mass spectrum of which was characterized by the peaks of fragments formed by the successive ejection from the molecular ion (M^+ 412; 1%) of acetic acid –m/e 352; 6% ($M^+ - CH_3COOH$) and m/e 292; 7.1% ($M^+ - 2CH_3COOH$) – and of ketene – m/e 310; 100%. No pronounced peaks due to α-cleavage with respect to the acetoxy group were observed.

On the basis of the results obtained, it may be concluded that the ripe seeds of the cotton plant of variety 108-F contain two isomeric epoxy acids – 9,10-epoxyoctadec-cis-12-enoic (I) and 12,13-epoxyoctadec-cis-9-enoic (II) acids:

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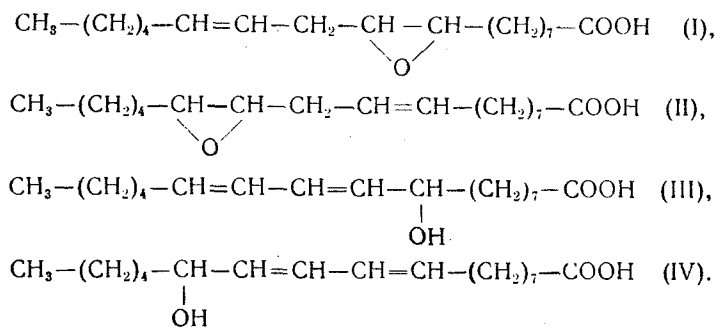

The hydroxy esters (B) consisted of a yellow, oily liquid. Their IR spectrum contained a broad absorption band at 3200-3000 cm^{-1} (OH group) and bands at 950 and 990 cm^{-1} (cis,trans-CH = CH − CH = CH −); the UV spectrum contained a band at 234 nm which is characteristic for a conjugated dienic system; and the NMR spectrum had signals in the 4.8-3.35 ppm region (cis-trans-CH = CH − CH = CH −) (τ scale) and at 5.9 ppm (proton geminal to an OH group). The mass spectrum of the hydroxy esters showed the peaks of the molecular ion M^+ (310) and of ions with m/e 69 (100%) 71, 73, 77, 95, 97, 109, 111, 125, 143, 155, 185, 187. The destructive oxidation of fraction B by the periodate–permanganate method gave caproic acid ($C_{6:0}$) and azelaic acid (C_9-di).

Thus, we are dealing with a mixture of the isomeric acids (III) and (IV).

To confirm the proposed structures the hydroxy esters were hydrogenated to complete saturation and oxidized by the permanganate method. In addition, they were converted into the acetoxy derivative, the mass spectrum of which showed that, as in the case of the analogous epoxy acid derivative, the main decomposition of the molecule was associated with the elimination of an acetic acid molecule.

The results obtained confirmed the proposed structures of the hydroxy acids.

The fragments from the oxidation of the saturated hydroxy ester (C_{10}-di and $C_{8:0}$) apparently show the presence in the mixture of a 11-hydroxyoctadeca-9,12-dienoic acid, as well. However, its formation may be due to the isomerization unavoidably accompanying hydrogenation.

EXPERIMENTAL

The oil was extracted from the ripe seeds by three treatments with petroleum ether (40-60°C). Transesterification was performed with sodium methoxide (0.5%) at 40°C for 4 h.

The fraction enriched in hydroxy esters was isolated by descending chromatography in a column of KSK silica gel (100 mesh). The methyl esters of the unoxidized ordinary fatty acids were eluted with petroleum ether, and those of the hydroxy acids by diethyl ether. The latter were separated by ascending column chromatography in the hexane–diethyl ether (8 : 2) system.

The epoxy esters were acetylated by dissolving a weighed sample in a small amount of freshly distilled acetic anhydride (2-3 ml per 70 mg) and adding 2-3 drops of trifluoroacetic acid. The mixture was left at room temperature in the dark for two days and was then left under a draught to eliminate the bulk of the acetic anhydride.

Saponification of the Diacetoxy Compound. The diacetoxy compound obtained (4 ml) was dissolved in 5 ml of methanol, 0.2-0.3 g of KOH was added, and the mixture was boiled under reflux for 1 h. After this, the ethanol was distilled off, water was added, and the mixture was shaken with ether to remove unsaponifiable substances. The aqueous solution was acidified with 15% sulfuric acid and extracted with ether. The ethereal extract was washed with water and dried over sodium sulfate, and the solvent was driven off in a rotary evaporator.

Acetylation of the Hydroxydienic Esters. A weighed sample of the esters was dissolved in a small amount of freshly distilled acetic anhydride, and 2-3 drops of pyridine was added. After two days, the mixture was left under a draught to eliminate the acetic anhydride. Then it was transferred to a separatory funnel containing ice acidified with 2-3% sulfuric acid, and extracted three times with ether. The ethereal extract was washed with water and dried over sodium sulfate, and the solvent was eliminated in a rotary evaporator.

Hydrogenation was carried out in ethyl acetate at room temperature with a palladium catalyst.

SUMMARY

It has been established that the oil of the ripe seeds of the cotton plant of variety 108-F contains 9,10-epoxyoctadec-cis-12-enoic (I) and 12,13-epoxyoctadec-cis-9-enoic (II) acids. In addition, 9-hydroxyoctadeca-cis,trans-10,12-dienoic (III) and 13-hydroxyoctadeca-cis,trans-9,11-dienoic (IV) acids, found previously in other oils, have been detected.

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NEW TERPENOID COUMARINS FROM Ferula tadshikorum

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Ferula tadshikorum M. Pimem. – a species separated [1] from the close species F. foetidissima – is one of the species of the genus Ferula L. that is widely distributed in Central Asia. Ferula tadshikorum is endemic to southern Tadzhikistan, southern Uzbekistan, and eastern Turkmenia. A qualitative comparison of extracts of the two species (TLC on Silufol) has shown [2] that they differ in chemical composition.

From an acetone extract of the fruit of F. tadshikorum we have isolated two new coumarin derivatives – $C_{24}H_{30}O_4$, mp 68-70°C, Rf 0.35 (I), and $C_{26}H_{32}O_6$, liquid, Rf 0.25 (II), which we have called, respectively, tadzhiferin and tadzhikorin. Both compounds are unbelliferone derivatives (characteristic UV spectra).

The IR spectrum of (I) (Fig. 1a) has two bands in the region of OH stretching vibrations – a narrow band at 3520 cm^{-1} and a broad band at 3300 cm^{-1}, and at the same time the carbonyl band is split into two components – 1730 and 1707 cm^{-1}. The spectrum of a solution of (I) in dioxane has only one hydroxy band (3500 cm^{-1}) and one carbonyl band (1746 cm^{-1}). Thus, the splitting of the bands in the IR spectrum taken in paraffin oil arises through the formation of a hydrogen bond between the OH and C = O groups in the crystalline state; in dioxane solution there is no such bond, and there is no splitting of the bands. Consequently, tadzhiferin is an ether of umbelliferone and a sequesterpene alcohol the residue of which contains a free hydroxyl.

The structure of the terpenoid residue is determined unambiguously from the NMR spectrum of (I) (Fig. 2a). In addition to the signals of a 7-monosubstituted coumarin nucleus, the spectrum contains the signals of four methyl groups on double bonds, three methylene groups with double bonds in the α position, a $-CH_2-O-Ar$ group, three vinyl protons, the proton of a hydroxy group, and one proton geminal to the hydroxyl. The assignment of the latter signal was confirmed by its downfield shift by 1.19 ppm on acetylation. It follows from the empirical formula of the terpenoid residue ($C_{15}H_{25}O-$) and the presence of three double bonds in it that it has a linear structure. The use of the double-resonance and INDOR methods enabled the positions of the individual structural elements in this chain to be determined unambiguously. The signals of all the methyl groups in the spectrum are broadened as the result of allyl interaction with vinyl protons. Under conditions of double resonance at an H_2 frequency corresponding successively to the resonance of the vinyl protons, a contraction of the signals of the methyl groups and an increase in their peak intensity was observed. At the same time, irradia-

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