α-HYDROXYDIENIC ACIDS OF THE SEED OIL OF Artemisia absinthium

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The seed oils of the family Compositae are distinguished by the presence in them of various hydroxy derivatives of fatty acids. Among the α-hydroxydienic acids of seed oils 9-hydroxy- and 13-hydroxyoctadecadienoic acids with conjugated ethylenic bonds in admixture or individually are usually present in the form of spatial and position isomers of three types [1-4]: 9-hydroxy-trans-10, trans-12 (dimorphecolic acid), 9-hydroxy-trans-10, cis-12 (cis isomer of dimorphecolic acid), and cis-9, trans-11 (coriolic acid). A mixture of the two latter isomers has been isolated from the seed oil of Artemisia absinthium, family Compositae, growing in western America [1].

The present paper gives the results of the first investigations of the seed oil of the same species of plant growing in Central Asia (slopes of the western Tien-Shan).

The oil obtained by cold extraction (18%) and the mixture of fatty acids isolated from it (with the separation of the total unsaponifiables) absorbed identically in the UV region of the spectrum (231 nm). The IR region of the spectrum showed the presence of hydroxyls (3600-3000, 1100 cm^{-1}) in the oil and in a mixture of methyl esters of fatty acids, which was confirmed by the paper chromatography and thin-layer chromatography of the mixture of fatty acids (R_f 0.93 on PC, 0.00 on TLC). The latter result was obtained in a layer of silica gel in the light petroleum ether–diethyl ether (9 : 1) system.

After being boiled in glacial acetic acid, the oil and the mixture of fatty acids absorbed in a new region of the spectrum (261, 271, 282 nm) which is characteristic for a conjugated trienic system. This was a proof of the presence of acids with a hydroxy group in the α position to a conjugated system of ethylenic bonds both in the oil and in the mixture of fatty acids.

The combined hydroxy acids (2% of the mixture) isolated from the mixture of fatty acids (and their methyl esters) absorbed in the UV and IR regions of the spectrum in a similar manner to the oil before and after boiling in acetic acid. In the dehydrated combined hydroxy acids an octadecatrienoic acid was detected on a paper chromatogram which, after hydrogenation on the paper, was converted into octadecanoic acid, which confirmed that it contained a straight-chain carbon skeleton of 18 atoms.

The positions of the ethylenic bonds were determined by comparing the products of oxidative degradation by periodate-permanganate of the initial mixture of hydroxy acids with the products of the permanganate oxidation of the hydrogenated mixture of hydroxy acids.

The periodate-permanganate destruction of the initial mixture of hydroxy acids gave caproic ($C_{6:0}$) and azelaic (C_9-di) acids. The fragments obtained showed the presence of an α-hydroxydienic system between carbon atoms 9 and 13.

The combined saturated hydroxy acids were isolated from the hydrogenated oil and the hydrogenated mixture of acids.

The oxidative degradation with permanganate of the combined hydrogenated hydroxy acids gave, on the one hand, pelargonic ($C_{9:0}$) and capric ($C_{10:0}$) acids and azelaic (C_9-di) and suberic (C_8-di) acids, and, on the other hand, valeric ($C_{5:0}$) and caproic ($C_{6:0}$) acids and dodecanedicarboxylic (C_{12}-di) and brassylic (C_{13}-di) acids. The fragments obtained showed that the hydroxyl is present in positions 9 and 13 of two differ-

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ent molecules of α-hydroxydienoic acids, which shows the presence of a mixture of two position isomers: 9-hydroxyoctadeca-10,12-dienoic and 13-hydroxy-octadeca-9,11-dienoic acids. Elementary analyses of the initial and hydrogenated mixtures of hydroxy acids corresponded to the compositions of monohydroxyoctadecadienoic and monohydroxyoctadecanoic acids. Their ratio, calculated from the GLC results of the degradation fragments (mono- and dicarboxylic acids) was 2 : 1, respectively.

The IR spectrum of the mixture of α-hydroxydienoic acids, cm^{-1}: 3600-2500 m, 1280 m, 1710 s, 1175 m ($-COOH$); 2930 s, 1410 m, 1380 m. ($-CH_3$); 2650 s, 1460 m, 730 w. ($-CH_2-$); 1440 m, 1250 m, 1190., 1080 m ($-CH_2COOH$); 1100 m. $\left(-\overset{|}{\underset{|}{C}}-OH\right)$; 1635 m. $\left(-\underset{|}{C}=\underset{|}{C}-\underset{|}{C}=\underset{|}{C}-\right)$; 980, m $\left(\text{trans}-\underset{|}{C}=\underset{|}{C}-\right)$.
As can be seen, the ethylenic bonds of both isomers have only the trans configuration.

The methyl esters of the α-hydroxydienoic acids were obtained from the oil transesterified with sodium methoxide. The IR spectrum of the methyl esters of the hydroxy acids differs from that given only by the disappearance of the regions of absorption of the carboxy group (3600-2500, 1280, and 1710 cm^{-1}) and by the appearance of a region of absorption of the carbonyl of the ester group (1735 cm^{-1}). At the same time, a region of the absorption of a bound hydroxyl with a maximum at 3450 cm^{-1} was observed, which was concealed in the spectrum of the acids by the region of the absorption of the dimers at the carboxy group.

To determine the nature of the hydrogen bond we obtained the IR spectrum of a dilute solution of the methyl esters of the hydroxy acids in carbon tetrachloride. Under these conditions there was a shift in the region of absorption of the bound hydroxyl (3620 cm^{-1}); this confirmed its α position with respect to the conjugated ethylenic bonds.

NMR spectrum of the mixture of α-hydroxydienoic acids, δ, ppm: 0.9 (3 H), unsymmetrical triplet ($-CH_3$); 1.23 (20 H), unsymmetrical multiplet ($-CH_2-$); 2 (1 H), singlet ($-OH$); 3.5 (1 H), weak multiplet $(-\underset{|}{C}H-)$; 5.15-5.5 ($-CH=CH-$), broad multiplet; and 7.2 (1 H), singlet ($-COOH$). The NMR spectrum of a mixture of the hydrogenated acids differed from that described above by the absence of signals of the olefinic protons and by an increase in the integral intensity of the "methylene rise" to 28 H.

On the basis of the facts given it may be considered that the oil that we investigated contains 9-hydroxyoctadeca-trans,trans-10,12-dienoic (dimorphecolic) acid and 13-hydroxyoctadeca-trans, trans-9,11-dienoic acid (this is the first time that the trans isomer of coriolic acid has been found) in a ratio of 2 : 1.

Thus, in the seed oil of the central Asian Artemisia absinthium we have found spatial isomers of the acids shown to be present in an American sample of the same species of plant, which is probably the result of the influence of the climatic conditions of growth.

EXPERIMENTAL

The IR spectra were taken on a UR-10 instrument in a thin layer and in carbon tetrachloride and the UV spectra on a Hitachi spectrophotometer in hexane at concentrations of 0.1-0.2 mg/ml. The NMR spectra were obtained on a JNM-4H-100/100 MHz instrument at room temperature with concentrations of 5-10% in carbon tetrachloride with HMDS as internal standard (the values of the chemical shifts are given in the δ scale).

The elementary analyses of the compounds corresponded to the calculated figures. Chromatography was performed on type "M" ["slow"] paper of the Leningrad No. 2 mill impregnated with a 10% solution of paraffin oil in benzene; the silica gel of type KSK (150 mesh) was washed with hydrochloric acid, water, acetone, methanol, and chloroform. The composition of the fatty acids was determined by the gas chromatographic method on a UKh-2 chromatograph at 126 and 200°C with a column 2.5-m long. The liquid phase was poly(ethylene succinate) in an amount of 17% on the weight of the solid phase, INZ-600 (60 mesh).

The oil was extracted from the comminuted seeds with light petroleum ether by steeping at room temperature.

The oil was hydrolyzed with 1 N KOH in methanol (100 ml to 10 g of the oil) at room temperature with vigorous shaking for 20-30 min. The methanol was distilled off at a temperature of the water bath not exceeding 40-45°C under the vacuum of a water pump. The unsaponifiables were extracted from an aqueous solution of the potassium salts of the fatty acids with diethyl ether three times (when petroleum ether was used, a stable emulsion was formed). The potassium salts were decomposed with 10-15% sulfuric acid under a layer of diethyl ether.

A concentrate of the hydroxy acids was obtained by distributing 4-9 g of the mixture of acids or their methyl esters between a 10-fold amount of mutually saturated hexane and acetonitrile, and the methyl esters of the hydroxy fatty acids were obtained by the transesterification of the oil with sodium methoxide with stirring for 2 h [5] in a yield of 70%.

The oil and the mixture of acids were exhaustively hydrogenated on an apparatus for liquid-phase hydrogenation at 50°C in ethyl acetate. The catalyst was palladium on a support (aluminum powder) in an amount of 0.5% on the weight of the oil or fatty acids.

The microhydrogenation of the hydroxy acids was performed in the presence of palladium on paper [6] with subsequent chromatography on the same sheet of paper [7].

The destructive oxidation with periodate-permanganate of the α-hydroxydienoic acids was performed by a modification of von Rudloff's method [8] and the destructive oxidation with permanganate of the hydroxyoctadecanoic acids by Hilditch's method [9] in dry acetone.

SUMMARY

From the combined fatty acids of the seed oil of Central Asian Artemisia absinthium (family Compositae) we have isolated a mixture of dimorphecolic and the trans isomer of coriolic acid, found for the first time, in a ratio of 2 : 1.

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