A TRIENOIC ACID FROM OILS OF PLANTS OF THE FAMILY RANUNCULACEAE

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In a study of the fatty acid composition of the oils from the seeds of all the representatives of the genus **Thalictrum** and also of **Aquilegia karelini**, family **Ranunculaceae**, we detected an unusual trienoic acid [1]. The presence of this acid is confirmed by the determination of the hexabromide number, by the UV spectrogram of the fatty acids subjected to alkaline isomerization, and by gas-liquid chromatograms of the initial mixtures of fatty acids.

Because the hexabromide isolated had mp 145.5–147.5° C, it was clear that the trienoic acid is not α-linolenic acid, the hexabromide of which melts at 178–180° C.

The trienoic acid (in the form of its methyl ester) was isolated preparatively by thin-layer chromatography on silica gel impregnated with silver nitrate. The separating solvent was benzene–diethyl ether (9 : 1). When the chromatogram was run twice, the mixture of fatty acids was separated into six zones. The third zone from the bottom was investigated making use of de Vries and Yurriens' data [2] on the order of separation on a chromatogram of structural and positional isomers of the fatty acids.

The gas-liquid chromatography of this zone gave one peak but the retention time did not coincide with that of ordinary linolenic acid: the peak of this acid issues between the peaks of ordinary linoleic and linolenic acids.

The IR spectrum of this compound showed the presence in it of a transdisubstituted ethylenic bond (sharp absorption band at 970 cm^{-1} [3]). The results of a quantitative determination of the content of trans isomers in this material by comparison with methyl elaidate showed that the trans configuration is a feature of only one of the three double bonds.

The positions of the double bonds in the material isolated were established by microscale periodate-permanganate oxidation [6]. The oxidation products were shown by thin-layer chromatography to contain caproic acid and the monomethyl ester of glutaric acid. On the basis of this it was concluded that the double bond closest to the carboxyl occupies the 5,6-position, and the bond closest to the methyl group the 12,13- position.

The chromatograms showed that among the dicarboxylic acids there are malonic and succinic acid, which can be formed if the central double bond is in either the 9,10- or the 8,9- position:

$$\text{I. } \mathrm{CH_3(CH_2)_4\overset{13}{C}H{=}\overset{12}{C}HCH_2\overset{10}{C}H{=}\overset{9}{C}H(CH_2)_2\overset{6}{C}H{=}\overset{5}{C}H(CH_2)_3COOCH_3.}$$

$$\text{II. } \mathrm{CH_3(CH_2)_4\overset{13}{C}H{=}\overset{12}{C}H(CH_2)_2\overset{9}{C}H{=}\overset{8}{C}HCH_2\overset{6}{C}H{=}\overset{5}{C}H(CH_2)_3COOCH_3.}$$

In order to establish the actual position of the central double bond, the trienoic acid was reduced with hydrazine hydrate, which excluded the possibility of the migration of the double bonds.

The resulting mixture of reduction products was separated into four fractions in a layer of silica gel. The fraction with the lowest R_f value consisted of the unchanged part of the initial substance. The two subsequent fractions with increasing R_f values were oxidized. The oxidation products of these fractions were shown by subsequent analysis in a thin layer of cellulose to contain caproic acid, monomethyl glutarate, and monomethyl azelate, which could arise as the result of the cleavage of a bond between the ninth and tenth carbon atoms. Consequently, the central bond in the trienoic acid under investigation occupies the 9,10- position and therefore structure I is the correct structure for this acid.

In order to establish which of the three double bonds has the transconfiguration, the fatty acids were eluted from the zone with the highest R_f value including those acids that migrated with the solvent front. The gas-liquid chromatography of these fatty acids showed that they contained 3.6% of palmitic, 21.98% of stearic, and 74.12% of octadecenoic acids. The IR spectrum of this fraction contained an absorption band at 970 cm^{-1} which must be ascribed to a monoenoic acid.

Oxidation of this fraction and analysis of the fragments in a thin layer of cellulose showed the pressure in the oxidation products of monomethyl glutarate, which shows that in the octadecenoic acid obtained by the partial hydrogenation of the trienoic acid the double bond with the trans configuration occupies the 5, 6- position. Consequently, in the initial trienoic acid the trans configuration is possessed by the double bond closest to the carboxyl group.

Thus, on the basis of the results given we have definitely established the structure of the octadecatrienoic acid contained in the oils of **Thalictrum** as octadeca-5-trans-9, 12-**dicis-trienoic** acid.

Since octadeca-5-trans-9,**12-dicis-trienoic** acidis present in several oils of plants of the family **Ranunculaceae**, we have proposed to call it "**ranuncelic acid.**"

EXPERIMENTAL

The trienoic acid in the form of its methyl ester was separated preparatively from the mixture of fatty acids in a thin layer of silica gel impregnated with silver nitrate.

The partial reduction of the trienoic acid with hydrazine hydrate was carried out by Aulward and Rao's method [4].

The products of the partial reduction of the trienoic acid were separated in a layer of silica gel impregnated with silver nitrate with two runs of benzene–diethyl ether (9 : 1).

The trans bond in the trienoic acid was determined quantitatively in comparison with methyl elaidate [5]. The presence of 106% of trans bonds was established.

Periodate-permanganate oxidation was carried out by a published method [6] with some modification consisting in the fact that the oxidation was performed not on a plate but in a small flask. The methyl ester of the trienoic acid (5-10 mg) was oxidized by the gradual addition of the recommended oxidizing mixture. The degradation products were extracted with diethyl ether, and the ethereal extracts were then chromatographed.

The monocarboxylic acids and monomethyl esters of dicarboxylic acids obtained in the oxidation were determined in a thin layer of cellulose impregnated with dimethylformamide, using hexane–diethyl ether–dimethylformamide (40 : 20 : 1) as the mobile phase [6].

The dicarboxylic acid fragments were analyzed in a thin layer of unimpregnated cellulose [mobile solvent: ethanol–water–ammonia (50 : 6 : 8)].

The hexabromide of the trienoic acid was obtained as described by Tyutyunnikov [7]; a weighed sample of the trienoic acid was dissolved in a tenfold amount of diethyl ether, the solution was cooled to −15° C and then Br was added in drops until there was a permanent bromine color. The crystals that deposited had mp 145.5–147.5° C. Found, %: Br 62.71. Mol. wt. 723.62 (from the neutralization number). Calculated for $C_{18}H_{30}O_2Br_6$, %: Br 63.26. Mol. wt. 757.9.

CONCLUSIONS

Octadeca-5-trans-9, 12-cis, cis-trienoic acid has been found in the oils of plants of the genera **Thalictrum** and **Aquilegia** and it has been given the name "**ranunculenic acid.**"

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