

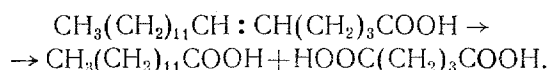
A NEW OCTADECENOIC ACID

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In the oils of plants of the genus *Thalictrum* (meadowrue), family Ranunculaceae, that we have studied, an acid was found which, when the mixture of fatty acids isolated from them was subjected to chromatography, occupied a position between stearic and palmitic acids. The chromatogram was obtained by A. T. Astvatsatur'yan's method [2] using twofold development with a mixture of solvents: 90% acetic acid-85% formic acid (3:1) and 98% acetic acid-85% formic acid (3:1).

The same acid was detected still more clearly on a chromatogram of the solid fatty acid fraction isolated by Grossfeld's method [3, p. 544] and it disappeared from the chromatogram of a hydrogenated mixture of the fatty acid, which shows its unsaturation. On a chromatogram of the fatty acid fraction isolated by Bertram's method, this acid is absent and in its place the spot of tridecanoic acid appears which is not on any of the other chromatograms. Its appearance can be due only to the oxidative decomposition of the acid the spot of which occupies the position between those of stearic and palmitic acids. Consequently this presumably has the structure of a Δ^5 -isoleic acid



Since the qualitative fatty acid compositions of a number of the oils of plants of the genus *Thalictrum* that we have studied, as determined by means of paper and gas-liquid chromatography, are completely identical, we carried out our investigation of the nature and structure of the new acid on one of the oils of *Thalictrum minus* (low meadowrue).

We detected octadec-5-enoic acid in five species of *Thalictrum*—*minus*, *sultanabadense*, *flavum*, *foetidum*, and *simplex* (low, Sultanabad, yellow, fetid, and slimtop meadowrues). This acid has also been found by Canadian scientists in two other species of plants [4, 5] of the same genus—*Thalictrum polycarpum* and *venulosum* (sierra and veiny meadowrues). Since this acid is present in the oils of at least seven species of the genus *Thalictrum*, it may be considered, together with morphologic characteristics, as a chemical-physiological classification index of plants of the genus *Thalictrum*. Consequently we propose to give the trans isomer of octadec-5-enoic acid the name of thalictric acid.

Experimental

To isolate the acid, we subjected the mixture of acids from the oil to low-temperature crystallization [6]; a solution of the acids in dichloroethane (1:60) was kept at -30°C for 6 hr; the liquid phase was sucked off through a suction filter, the precipitate was washed with dichloroethane cooled to the same temperature, and the wash-liquor was added to the main filtrate. The combined filtrates were again subjected to freezing out at -30°C for 4 hr. The additional amount of precipitate obtained was added to the original crystallizate.

The fatty acids obtained in this way had a faint yellowish color. For purification, they were dissolved in a small amount of acetone and were frozen out twice more at -30°C for 4 hr. The crystals so obtained were white.

From the solid fatty acid fraction so obtained the monoenoic acids were isolated by Bertram's mercury (II) acetate adduct method [3, p. 49] without methylation or by the method of Jantzen and Andreas [7] after the methylation of the mixture. The solid monoenoic acid fraction obtained in this way was recrystallized several times from 70% ethanol until the product had a constant mp of $39-40^\circ\text{C}$. After this, the IR spectrum was recorded; it clearly showed an absorption band at 970 cm^{-1} indicating the trans configuration of the double bond [8]. A quantitative determination of the amount of trans isomers in this preparation was carried out by comparison with methyl elaidate [9]. The presence of 96% of trans bonds was established. Since the relative error of this method is $\pm 10\%$ and its sensitivity is 5%, we may consider that a fairly pure preparation of a monoenoic acid with the trans configuration of the double bond had been isolated.

In order to establish definitively the position of the double bond in this acid, it was oxidized by the periodate-permanganate method of Lemieux and von Rudloff [10] as modified by Bagby et al. [4], for which purpose the acid was previously converted into the methyl ester. The mixture of fragments obtained by degradative oxidation was analyzed by gas-liquid chromatography; the maximum peaks corresponded to the tridecanoic acid among the monocarboxylic acids and to glutaric acid among the decarboxylic acids. This definitely confirmed that we are dealing with an octadec-5-enoic acid.

We have obtained two derivatives of this acid; 5,6-dihydroxystearic acid (by Zaitsev oxidation) and 5,6-dibromostearic acid. The dihydroxystearic acid had mp $89.5-90.5^\circ\text{C}$.

Found, %: C 68.60; H 11.45; mol. wt. 315.31 (from the neutralization number). Calculated for $C_{18}H_{36}O_4$, %: C 68.35; H 11.39; mol. wt. 316.47.

This derivative contains two asymmetric carbon atoms and, as was to be expected, it proved to be optically inactive, since it consisted of a racemic mixture of the two antipodes.

The dibromostearic acid had mp 48–48.5° C.

Found, %: Br 34.45; mol. wt. 442.96 (from the neutralization number). Calculated for $C_{18}H_{34}O_2Br_2$, %: Br 36.14; mol. wt. 442.28.

Conclusions

It has been shown that the fatty oils of five species of *Thalictrum* contain trans-octadec-5-enoic acid. This acid may be regarded as a chemico-physiological classification index of plants of the genus *Thalictrum*.

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