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STRUCTURE OF ISOMERISTOTROPIC ACID

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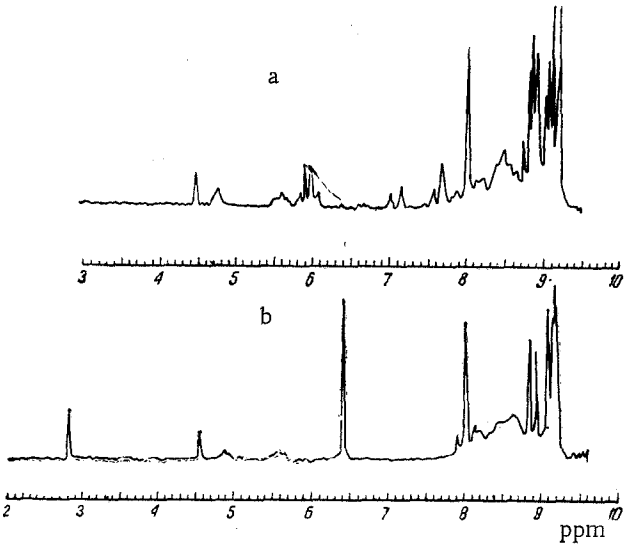
Isomeristotropic acid, which we have isolated from Meristotropis triphylla Fisch. et Mey [1] apparently has the empirical formula $C_{30}H_{44}O_4$ * since, according to a mass spectroscopic analysis, the molecular weight of the methyl ester of this acid is 482.

To elucidate the structure of isomeristotropic acid, we eliminated the keto group from it by reducing the methyl ester by the well-known Wolf-Kizhner method, obtaining a deoxo acid $C_{30}H_{46}O_3$ with mp 276.5-277.5° C. The latter was converted into the acetate of the methyl ester $C_{33}H_{50}O_4$, with mp 230-233° C, the IR spectrum of which, like those of isomeristotropic acid and its derivatives, had a maximum at λ 282 mμ (log ε 3.6-3.9) which is characteristic for a homoannular diene.

By oxidizing the acetate of methyl deoxoisomeristotropate with selenium dioxide we obtained a substance with mp 218-220° C and with maxima in the UV spectrum at λ 258, 250, and 242 mμ (log ε 4.18, 4.36, 4.39). This substance gave no depression of the melting point in admixture with the acetate of methyl deoxomeristotropate and evidently arose as the result of the isomerizing action of the selenium dioxide. In addition to this substance, the acetate of the methyl ester of the 9(11), 13(18)-diene-12, 19-dione derivative of deoxomeristotropic acid with mp 230-231° C was obtained [2].

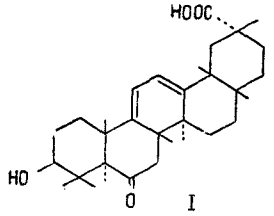


NMR spectrum of the acetate of ethyl isomeristotropate (a) and ethyl deoxoisomeristotropate (b) (at 100 MHz).

The results given above showed that the positions of the carboxyl and hydroxyl in isomeristotropic acid are the same as in meristotropic acid. We assumed that the ketone groups in isomeristotropic and meristotropic acids also occupy the same positions. In actual fact, when methyl isomeristotropate was reduced with lithium aluminum hydride, a triol $C_{30}H_{48}O_3$ with mp 247-249° C was obtained which, on acetylation, gave a triacetate $C_{36}H_{54}O_6$ with mp 202-205° C.

When the triacetate was heated with selenium dioxide in acetic acid solution, a product $C_{36}H_{54}O_6$ with mp 242-244° C was obtained which was identical in composition, melting point, and UV and IR spectra with the triacetate obtained previously from meristotropic acid. A mixture of these two substances gave no depression of the melting point. The experiment showed that the positions of all the functional groups in meristotropic and isomeristotropic acids are the same.

The NMR spectrum of the acetate of ethyl isomeristotropate (figure, a) has signals (7.8 and 7.4) that are not present in the NMR spectrum of the acetate of methyl deoxoisomeristotropate (figure, b). The signals in the NMR spectrum of isomeristotropic acid are apparently connected with the $-CH-CO-CH_2-$ group, which determines the position of the CO group at C_6. Thus, the most probable structure for isomeristotropic acid is (I).



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* The analyses of the acid and its derivative given earlier agreed better with the formation $C_{32}H_{48}O_4$. However, as a mass spectroscopic determination of the molecular weight of methyl isomeristotropate has shown, the figures for the C and H contents of a number of substances are 0.2-0.5% too high.

Experimental

Reduction of methyl isomeristotropate. A solution of 0.5 g of the substance in 20 ml of ethanol was treated with 20 ml of 85% hydrazine hydrate and 5 ml of diethylene glycol and the resulting mixture was heated for 8 hr. Then 1 g of caustic potash was added, the ethanol, water, and excess of hydrazine hydrate were distilled off, and heating was continued at 200° C for another 5 hr. At the end of the reaction water was added, and the precipitate was filtered off, washed, dried, and recrystallized from ethanol. Mp 276.5–277.5° C. IR spectrum: 1715 cm^{-1} (CO group of a carboxyl); UV spectrum: λ_{max} 282 mμ (log ε 3.93).

Found, %: C 78.92, 78.97; H 10.52, 10.66. Calculated for $C_{30}H_{46}O_3$, %: C 79.26; H 10.2.

The deoxo acid was heated with 5% methyl sulfate for 3 hr. The resulting methyl ester, without purification, was boiled in the presence of acetic anhydride and acetic acid for 5 hr. The acetate of methyl deoxoisomeristotropate was isolated in the usual way, mp 230–232° C (from ethanol). IR spectrum: 1735, 1260 cm^{-1} (ester group); UV spectrum: λ_{max} 282 mμ (log ε 3.6).

Found, %: C 77.48, 77.64; H 10.13, 10.16. Calculated for $C_{33}H_{50}O_4$, %: C 77.58; H 9.86.

Oxidation of the acetate of methyl deoxoisomeristotropate. A solution of 0.8 g of the substance in 100 ml of acetic acid was treated with 0.8 g of freshly-prepared selenium dioxide and the mixture was heated in the water bath for 28 hr. Then it was filtered, the filtrate was diluted with water, and the precipitate was dried and chromatographed on inactive alumina with elution by means of a mixture of benzene and diethyl ether (1 : 1). The first three 10-ml fractions of the eluate showed a single spot on a plate of inactive alumina with chloroform elution, mp 218–220° C (from ethanol). IR spectrum: 1730 and 1260 cm^{-1} (ester groups), UV spectrum: λ_{max} 258, 250, 242 mμ (log ε 4.18, 4.36, 4.39). This substance exhibited no depression of the melting point in admixture with the acetate of methyl deoxomeristotropic acid. On further elution of material from the column, a product was isolated with mp 230–231° C (from a mixture of diethyl and petroleum ethers), $[\alpha]_D$ -165° (c 1; chloroform). IR spectrum: 1730 cm^{-1}, 1710, 1700, 1660, 1620, 1585, 1255 cm^{-1}; UV spectrum: λ_{max} 278 mμ (log ε 4.43).

Found, %: C 73.2, 73.02; H 8.66, 8.50. Calculated for $C_{33}H_{46}O_6$, %: C 73.5; H 8.6.

The substance gave no depression of the melting point in admixture with the acetate of the methyl ester of the 9(11),13(18)-diene-12,19-dione derivative of deoxomeristotropic acid (epicatonic acid).

The triol from methyl isomeristotropate, and its triacetate. A solution of 0.4 g of methyl isomeristotropate in 30 ml of tetrahydrofuran was treated with 0.42 g of lithium aluminum hydride. The mixture was heated in the water bath for 8 hr. After the usual working up, a triol with mp 247–249° C (from a mixture of benzene and diethyl ether) was obtained. IR spectrum: 3400 cm^{-1}, broad (OH group); no maxima in the keto group region. In the IR spectrum, the maximum was at 282 mμ (log ε 3.98).

Found, %: C 78.65, 78.80; H 10.65, 10.70. Calculated for $C_{30}H_{48}O_3$, %: C 78.89; H 10.59.

A mixture of 0.35 g of the triol, 5 ml of acetic anhydride, and 0.2 g of sodium acetate was boiled for 5 hr. Then 10 ml of water was added to the mixture and it was heated and diluted with water, the precipitate was filtered off, dried, and dissolved in chloroform, and the solution was filtered through alumina (activity II), mp 202–205° C (from diethyl ether). IR spectrum: 1740, 1260 cm^{-1} (ester groups), no hydroxy group. UV spectrum: λ_{max} 282 mμ (log ε 3.6).

Found, %: C 74.06, 74.04; H 9.56, 9.59. Calculated for $C_{36}H_{54}O_6$, %: C 74.18; C 9.34.

Oxidation of the triacetate. A solution of 0.2 g of the substance (mp 202–205° C) in 15 ml of acetic acid was heated with 0.2 g of selenium dioxide and was treated under the same conditions as the acetate of methyl deoxomeristotropate. The product obtained was purified by chromatography through alumina (activity II) in chloroform. The 1-st fraction contained a substance with mp 242–244° C (from ethanol), $[\alpha]_D$–39° (c 3; chloroform). IR spectrum: 1740, 1260 cm^{-1} (ester groups); UV spectrum: λ_{max} 258, 250, 242 mμ (log ε 4.22, 4.4, 4.36).

Found, %: C 74.23, 74.17; H 9.41, 9.38. Calculated for $C_{36}H_{54}O_6$, %: C 74.18; H 9.34.

The substance gave no depression of the melting point in admixture with the triacetate from meristotropic acid.

Other substance were isolated in small amount and have not been studied.

The microanalyses were carried out by E. A. Sokolova, the IR spectra were recorded by T. V. Bukreeva, and the NMR spectra were recorded and interpreted by A. I. Kol'tsov and Yu. N. Sheinker on a spectrometer with a resolving capacity of 40 and 100 MHz. The mass spectroscopic determination of the molecular weight of methyl isomeristotropate was performed by Dr. Dolejš (Czechoslovakia).

Conclusions

It has been established that the positions of the functional groups (COOH, CO, and HO) in isomeristotropic and meristotropic acids are the same. The probable structure of isomeristotropic acid corresponds to Formula (I).

REFERENCES

1. N. P. Kir'yalov and G. S. Amirova, KhPS [Chemistry of Natural Compounds], 1, 311, 1965.
2. N. P. Kir'yalov and G. S. Amirova, KhPS [Chemistry of Natural Compounds], **4**, 60, 1968.

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