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Received June 2, 1958.

Mass Spectrometric Evidence Regarding the Structural Relations between Dextropimaric, *Iso*dextropimaric, and Cryptopimaric Acids *

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A study of the mass spectra of the methyl esters of rosin acids, performed with a high-mass, high-resolution mass spectrometer with heated inlet system [1], has provided new evidence regarding the structural relations between dextropimaric acid, *iso*dextropimaric acid, and cryptopimaric acid [2].

The mass spectrum of the methyl ester of cryptopimaric acid (Fig. 1a) is strikingly similar to that of the methyl ester of dextropimaric acid (Fig. 1b). The base peak of the spectra is at *m/e* 121, and strong peaks occur at *m/e* 316 (molecular peak), 180, 181, 241, 257, and 301. The methyl ester of *iso*dextropimaric acid gives a quite different mass spectrum (Fig. 1c) that has the base peak at *m/e* 241 and strong peaks at *m/e* 316 (molecular peak), 256, 257, 287, and 301.

We interpret these results as showing that dextropimaric acid and cryptopimaric acid can be structurally different only with regard to the orientation of the methyl and vinyl groups attached to C7, and that dextropimaric acid and *iso*dextropimaric acid must be different with regard to the geometry of the ring system. The opinion of Wenkert [3] that the two last mentioned acids differ in the configuration at C13 is thus supported by the present evidence: As the proposed stereochemical difference at C7 [4] has recently been confirmed [5] it follows that the acids are stereochemically different both at C7 and C13.

The above conclusions seem to tally with monolayer [6] and infrared absorption [7-9] data.

Experimental. The cryptopimaric acid used had $[\alpha]_D^{12} - 21.7°$ and m.p. 160—162°.** Because of the small amount of material, the optical rotation was not checked by us. Keimatsu *et al.*[2] give m.p. 159—161° and $[\alpha]_D^{17.5} - 18.99°$ (in ethanol). The sample of dextropimaric acid had m.p. 207—208°, $[\alpha]_D^{25} + 70° \pm 3°$ ** (ethanol, micro tube), and the *iso*dextropimaric acid m.p. 160°, $[\alpha]_D^{25} \pm 0.00°$ ** in ethanol. The acids were converted into methyl esters by means of fresh diazomethane in ether solution. The mass spectra were run on 0.5 mg samples with the inlet system kept at a temperature of 200°.

Acknowledgements. We are indebted to Prof. H. Inamura, Government Forest Experiment Station, Meguro, Tokyo, for a sample of cryptopimaric acid, to Dr. R. V. Lawrence, Naval Stores Research Station, United States Department of Agriculture, Olustee, Florida, for dextro- and *iso*dextropimaric acids, and to Dr. O. Jeger, Institute of Organic Chemistry, Eidg. Technische Hochschule, Zürich, for dextropimaric acid. The two samples of dextropimaric acid gave identical infrared absorption spectra.

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** Determined by us.

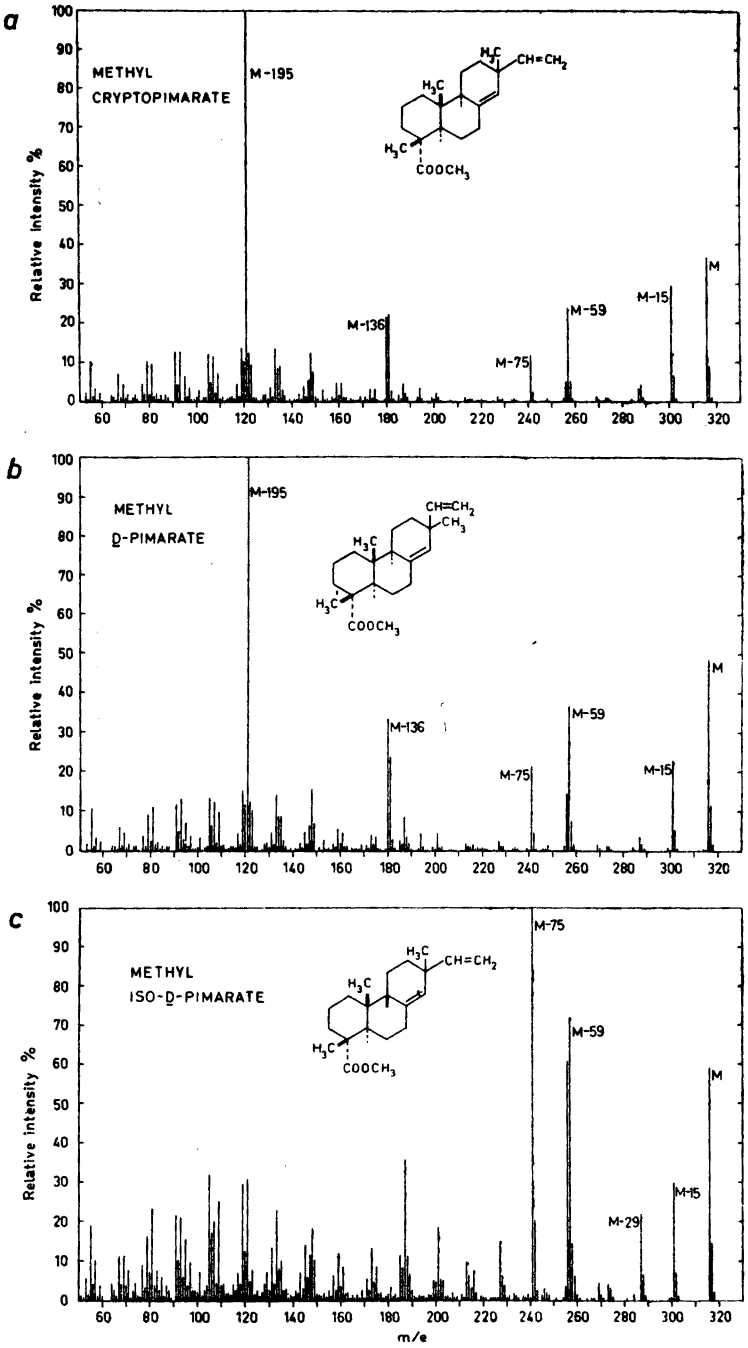
a
METHYL
CRYPTOPIMARATE
M-195
M-136
M-75
M-59
M-15
M
b
METHYL
D-PIMARATE
M-195
M-136
M-75
M-59
M-15
M
c
METHYL
ISO-D-PIMARATE
M-75
M-59
M-29
M-15
M
Relative intensity %
m/e

Fig. 1

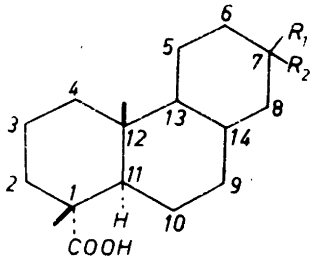

Fig. 2. Ring system numbering of rosin acids. Stereochemical configuration at carbon atoms 1, 11, and 12 indicated.

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Received June 12, 1958.

Reactions between Quinones and Carbonyl Compounds Catalysed by Aluminium Oxide

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In the course of studies on the oxidation of 2,6-dimethoxyphenol with sodium periodate [1], an attempt was made to separate, by chromatography on a column of aluminium oxide, a benzene solution of the previously unknown 3,8-dimethoxy-1,2-naphthoquinone (I) and 2,6-dimethoxy-*p*-benzoquinone (III). By irrigation with benzene, compound III was eluted while a red compound, assumed to be the naphthoquinone I, remained strongly adsorbed on the upper part of the column. This latter material was eluted with acetone and from the eluate two crystalline products were obtained. One of those was the expected naphthoquinone I; the other was a yellow substance. This indicated that an unexpected transformation of I had taken place either during the adsorption or during the elution step. To clarify this question, the following investigations were carried out.

When an acetone solution of the pure naphthoquinone I (m. p. 196°) was boiled for a few minutes in the presence of aluminium oxide the red solution became yellow, and from it yellow crystals (m. p. 142°) were obtained in a yield of 90 %. (In the absence of aluminium oxide a reaction did not occur and acetone was then a very suitable recrystallization solvent for I.) Analysis of the substance indicated that it might be an addition product formed from equimolar amounts of acetone and compound I. Ultra-violet and infrared absorption data, and the fact that on reduction the substance was converted into a compound having the properties of an α-naphthol with a free *p*-position, all suggested that the addition product might be the *o*-naphthoquinol of structure II.

2,6-Dimethoxy-*p*-benzoquinone (III) when heated in acetone solution in the presence of aluminium oxide also yielded an apparently similar type of addition product having m. p. 154°. Spectrographic examination of this compound, and its reduction to a phenol, to which the structure of 3,5-dimethoxy-4-acetonylphenol could be ascribed, indicated that the acetone addition compound of III was a *p*-quinol of structure IV.

Since the formation of the quinols II and IV involves a reaction of the aldol condensation type, it appeared possible that it might have been catalysed by traces of alkali present in the commercial aluminium oxide. This is improbable, however, as the catalytic effect of the aluminium oxide preparation was retained even after its thorough treatment with dilute hydrochloric acid (followed by washing with water). Thus, neutral aluminium oxide would appear to act as a catalyst of the reactions described.

Other ketones, for example methyl ethyl ketone, were also found to add to the quinones I and II in the presence of aluminium oxide.

Addition of acetone and of other ketones to tetrachloro-*o*-quinone has been reported by Schenck *et al.*[2] to be catalysed by dry