

An Infra-red Spectroscopic Study of the Structural Relationships of Dextropimaric, Isodextropimaric, and Cryptopimaric Acids

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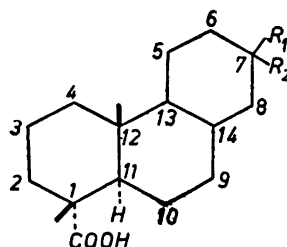


Fig. 1. Ring system numbering of rosin acids. Stereochemical configuration at the carbon atoms 1, 11, and 12 indicated.

Recent mass spectrometric investigations¹ of the structural relations between dextropimaric, isodextropimaric, and cryptopimaric acid have led to the conclusion that dextropimaric acid and cryptopimaric acid can be structurally different only with regard to the orientation of the methyl and vinyl group attached to C₇ (Fig. 1; R₁ = vinyl, R₂ = methyl), whereas the difference between dextropimaric acid and isodextropimaric acid must also involve the geometry of the ring system. In the present study the infra-red spectra of these compounds and their methyl esters have been recorded, and it will be shown that the vinyl group absorption and a skeletal vibration at 8.4 μ exhibit evidence of differences which are in accordance with the above conclusions. Moreover, they show that dextropimaric and isodextropimaric acid are epimeric not only at C₁₃ but also at C₇.

The absorption band due to the $\text{C} \begin{matrix} \text{H} \\ \diagup \\ \text{H} \end{matrix}$ out-of-plane deformation vibration is found at 10.90 μ for dextropimaric acid and at 10.94 μ for both isodextro- and cryptopimaric acid. In the spectra of the methyl esters the same band occurs at 10.92 μ for dextropimaric acid and at 10.98 μ for the other acids. In both cases the band for dextropimaric acid is shifted ca. 0.05 μ towards shorter wavelengths as compared with the (coincident) bands of isodextro- and cryptopimaric acid.

The slightly weaker band at 10 μ due to the $-\text{CH}=\text{}$ out-of-plane deformation of the vinyl group only shows differences within the experimental error of the apparatus.

For the acids in the solid state (in KBr) the position of the vinyl group absorption deviates somewhat from that shown by the acids in solution and by the methyl esters. Again, dextropimaric acid differs from the two others with regard to the $=\text{CH}_2$ out-of-plane vibration, but here the shift is towards longer wavelengths (cf. Table 1). Cryptopimaric acid shows a double band, and the others single maxima with inflexions. The 10 μ band, again, exhibits only differences lying within the experimental error of the apparatus.

These spectral differences indicate that the vinyl group in dextropimaric acid has a different molecular environment, *i. e.* a different stereochemical position, than in isodextro- and cryptopimaric acid. Since surface-film measurements² suggest that the position is quasi-axial for dextropimaric acid and quasi-equatorial for isodextropimaric acid, these absorption differences seem to correspond to axial and equatorial positions of the vinyl group, respectively (see also an earlier infra-red investigation of the solid state spectra of dextro- and isodextropimaric acid³). Spectral differences for substituents in axial and equatorial position are well known in steroid chemistry. For instance, hydroxyl groups⁴, as well as carbonyl groups in the neighbourhood of halogen atoms⁵, exhibit such shifts. Also, the acetate band at 8 μ ^{6,7} is single when the group is in the equatorial position, but splits into several peaks when it is in the axial position.

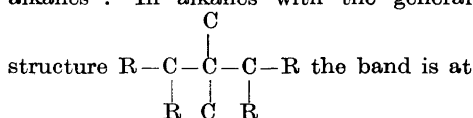
The medium-intensity band at about 8.4 μ is common to the spectra of the CCl_4 solutions of dextro-, isodextro-, and cryptopimaric acids, to the spectra of the esters, and to those of the solid acids in KBr. In

Table 1.

Acid	Skeletal vibration, λ (μ)			RHC=C $\begin{cases} \text{H} \\ \text{H} \end{cases}$ out-of-plane deformation vibration λ (μ)		
	Acid, in CCl ₄ -soln.	Ester, liquid	Acid, in KBr	Acid, in CCl ₄ -soln.	Ester, liquid	Acid, in KBr
Dextropimaric	8.44	8.40; 8.50	8.42	10.90	10.92	— (11.02)* 11.09
Isodextropimaric	8.38	8.39; 8.45	8.39	10.94	11.00	10.88 (11.00) —
Cryptopimaric	8.44	8.40; 8.51	8.45; 8.49	10.94	10.97	10.88 11.02 (11.09)

* Values in parentheses signify inflexions.

each case this band has the same position for dextro- and cryptopimaric acid, but appears at a shorter wavelength in the spectrum of isodextropimaric acid. The numerical values are listed in Table 1. A skeletal vibration in this region occurs for branched-chain alkanes⁹. In alkanes with the general



structure the band is at 8.39–8.44 μ ⁹, *i. e.* it is in the same position as found in our spectra, and it is therefore possible that one of the methyl-substituted carbon atoms (see Fig. 1) in our substances is involved in this vibration. Skeletal vibrations are known to be very sensitive to changes in the immediate environment of the vibrating group. We should therefore have a methyl substituted carbon atom whose environment is the same in dextro- and cryptopimaric acid but different in isodextropimaric acid. This is the case for C₁₂, taking into account the mass spectrometric evidence of different ring fusion between rings B and C in dextropimaric and isodextropimaric acid.

In summary, we can state that the spectral shifts discussed above suggest that dextropimaric and isodextropimaric acid are epimeric at C₇ and C₁₃, while dextropimaric and cryptopimaric acid are epimeric at C₇. These results agree with the conclusions drawn by Bruun, Ryhage, and Stenhagen¹ from mass spectrometric data, and with the chemical evidence recently reported^{10,11}.

Experimental. The apparatus employed is described in Ref.³, and the physical and chem-

ical properties of the acids studied are given in Ref.¹. The wavelength measurements are accurate to $\pm 0.015 \mu$.

Acknowledgements. We are grateful to Mrs. K. Nilsson for the spectrophotometric measurements, and to Mr. L. Ahlquist for assistance in the preparation of material. The visit of one of us (H.B.) to Sweden has made been possible by grants from the Finnish State Commission for Science.

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Received January 15, 1959.