

The Ethylenic Bond in Dihydroabietic Acid

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The position of the double bond in the isomeric dihydroabietic acids has not been established. The suggested sites are Δ 7, 8(14), 9(14) and 13 (Fig. 1)**. For two dihydroabietic acids prepared by partial hydrogenation of abietic acid, the α - and β -dihydroabietic acids of Lombard^{5,6}, Simonsen and Barton⁷ have proposed the position 9(14) and 13, respectively. This proposal is supported by the recent molecular rotation studies of Klyne⁸.

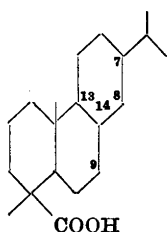


Fig. 1.

Trisubstituted ethylenic bonds ($R_1R_2C=CHR_3$) can generally be distinguished from the tetrasubstituted bonds ($R_1R_2C=CR_3R_4$) by infrared absorption measurements by means of the C—H out-of-plane deformation vibrations in the spectra of the former. Complex molecules studied by this method are triterpenes (Ruzicka, Jeger *et al.*^{9,10} and a number of sterols (Hirschmann¹¹). For sterols the absorption band occurs at a wavelength of 12.5μ . In the present study, the infrared absorption in this range has been recorded for dihydroabietic acid and for several other abietic and pimaric acids of known structure. The aim has been to determine whether the infrared spectrum of dihydroabietic acid shows the band in question or not. A negative result would suggest that the double bond is tetrasubstituted, *i. e.*

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** For reviews, see *e. g.* Refs. 1-4.

the position is at 13; however, this would not be fully conclusive in view of the frequently weak and varying intensity of the band. A positive result would imply without reservation that the double bond is of the trisubstituted type, *i. e.* it would be situated somewhere else in the molecule.

Experimental. The infrared absorption spectra were recorded with a double beam spectrophotometer (built by Dr. M. Skogh) of the type described by Hornig, Hyde and Adcock¹². The samples were prepared by the potassium bromide technique, the tablets were 0.8 mm thick and 13 mm in diameter, and contained 3—3.2 mg of the acid per 300 mg of potassium bromide.

The samples of the dihydro-, tetrahydro- and dehydroabietic acids and *isodextropimaric acid* were obtained from the Research Laboratory of Hercules Powder Company, Wilmington, Delaware. According to Dr. C. G. Harris of that laboratory, the dihydroabietic acid had been prepared by partial hydrogenation of abietic acid and was a mixture of isomeric acids, but otherwise pure. M. p. 133.8—136.8, $[\alpha]_D^{20} + 19^\circ \pm 2^\circ$. Tetrahydroabietic acid, m. p. 149.4—152.4, $[\alpha]_D^{20} + 11^\circ \pm 2^\circ$; dehydroabietic acid, m. p. 173.3—174.6, $[\alpha]_D^{20} + 66^\circ \pm 1^\circ$; *isodextropimaric acid*, m. p. 162.9—164.9, $[\alpha]_D^{20} 0^\circ$.

The dextropimaric acid was obtained from Dr. O. Jeger at the Eidg. Techn. Hochschule, Zürich.

The abietic acid was obtained in the form of its butylamine salt from Dr. E. Back of the Swedish Forest Products Research Laboratory, Stockholm. Before use, the acid was liberated from its salt with an aqueous boric acid solution. M. p. 170.2—172.7, $[\alpha]_D^{20} - 104^\circ \pm 1^\circ$.

The melting points were determined by the capillary method (diameter of the capillary tubes 1 mm). The values were corrected. The optical rotations in absolute alcohol (0.01 g per ml) were measured with a Lippich polarimeter.

For monolayer data relating to the same samples of rosin acids, see Ref. 13.

Results. The infrared absorption spectra of the rosin acids for the range $12-13 \mu$ are shown in Fig. 2. There is a band at 12.5μ in the spectrum of dihydroabietic acid (a). The two pimaric acids have a trisubstituted ethylenic bond at 8(14) and the corresponding band is evident in the spectra. For *isodextropimaric acid* (b), the band is of a relatively high intensity,

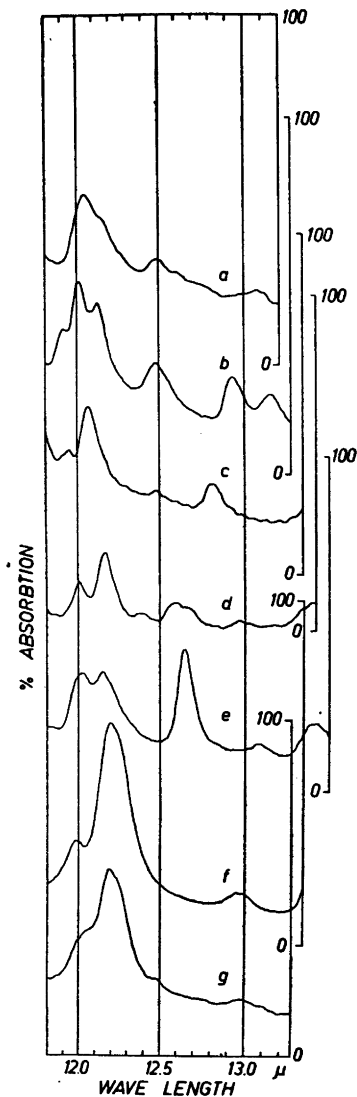


Fig. 2.

while that for dextropimaric acid (c) is of much lower intensity. The band is not evident in the spectrum of the fully saturated tetrahydroabietic acid (d), in the spectrum of the abietic acid (e) with conjugated double bonds or in the spectrum of

the hydroaromatic dehydroabietic acid (f). In a mixture containing equal parts of the last mentioned and dihydroabietic acid (g) the band at 12.5 μ is still observed.

Discussion. The evidence presented above strongly suggests that the dihydroabietic acid studied contains a tri-substituted ethylenic bond. If we assume provisionally that the sample is a mixture of Lombard's α - and β -acids (cf. Refs. 7,8), the appearance of the band in the spectrum of the mixture in spite of the strong background absorption implies that the α -acid content in the sample is relatively high. This conclusion is supported by the optical rotation value of the sample; a comparison with the values for Lombard's α - and β -acids (-26° and $+128^\circ$, respectively) points to a concentration of about 70 %.

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