

Infrared Spectra of Natural Products. Part IV. The Structure of Phyllocladene.*

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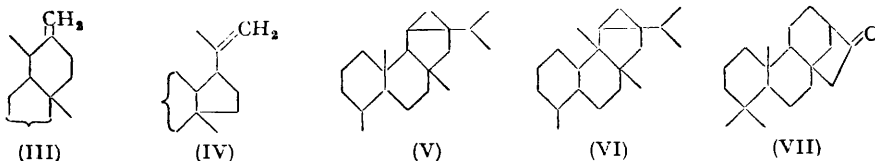
Infrared measurements on phyllocladene (I), a nor-ketone (VII) obtained from it, and *isophyllocladene* (II) lend support to structures put forward by Brandt. For (I) the presence of a vinylidene group attached to a five-membered ring, with one adjacent methylene group, is shown. The methyl-group absorption indicates the presence of one *gem*-dimethyl group and one angular methyl group between two six-membered rings. The trisubstituted double bond and extra methyl group in (II) are confirmed.

THE crystalline diterpene phyllocladene ($C_{20}H_{32}$) was first isolated by Baker and Smith ("The Pines of Australia," p. 419, Technological Museum, Sydney, N.S.W., 1910). Later work on phyllocladene and the related *isophyllocladene* has been summarised by Simonsen and Barton ("The Terpenes," Vol. III, Cambridge University Press, 1952) and by Brandt (*New Zealand J. Sci. Tech.*, 1952, **34B**, 46) who suggested that phyllocladene is represented by (I) and *isophyllocladene* by (II). Although no evidence was given, the *gem*-dimethyl group was placed at $C_{(1)}$ and the angular methyl group at $C_{(12)}$, by analogy with similar diterpenoids of known structure.



We have now measured the infrared spectra of phyllocladene, *isophyllocladene*, and the nor-ketone obtained by oxidation of the former with osmium tetroxide-periodic acid. The results are consistent with the formulæ (I) and (II), although the infrared data do not give all the desired information about the carbon skeleton.

Phyllocladene shows the three characteristic bands of the vinylidene group at 3069 ($=C\begin{matrix} H \\ \diagup \\ H \end{matrix}$ stretching), 1657 ($\epsilon_{max.} = 56$, $C=C$ stretching), and 872 cm^{-1} ($=C\begin{matrix} H \\ \diagup \\ H \end{matrix}$ bending). The relatively high frequency of the $C=C$ stretching vibration indicates that the vinylidene group is attached to a slightly strained ring. It might be compared, for example, with values of 1647 cm^{-1} (Nujol mull) for (III) (Ames, Beton, Bowers, Halsall, and Jones, *J.*, 1954, 1905) and 1640 cm^{-1} (in carbon tetrachloride) for lupeol (IV). Bladon, Fabian, Henbest, Koch, and Wood (*J.*, 1951, 2402) have pointed out that ring strain has the effect of strengthening exocyclic bonds and weakening the cyclic bonds.



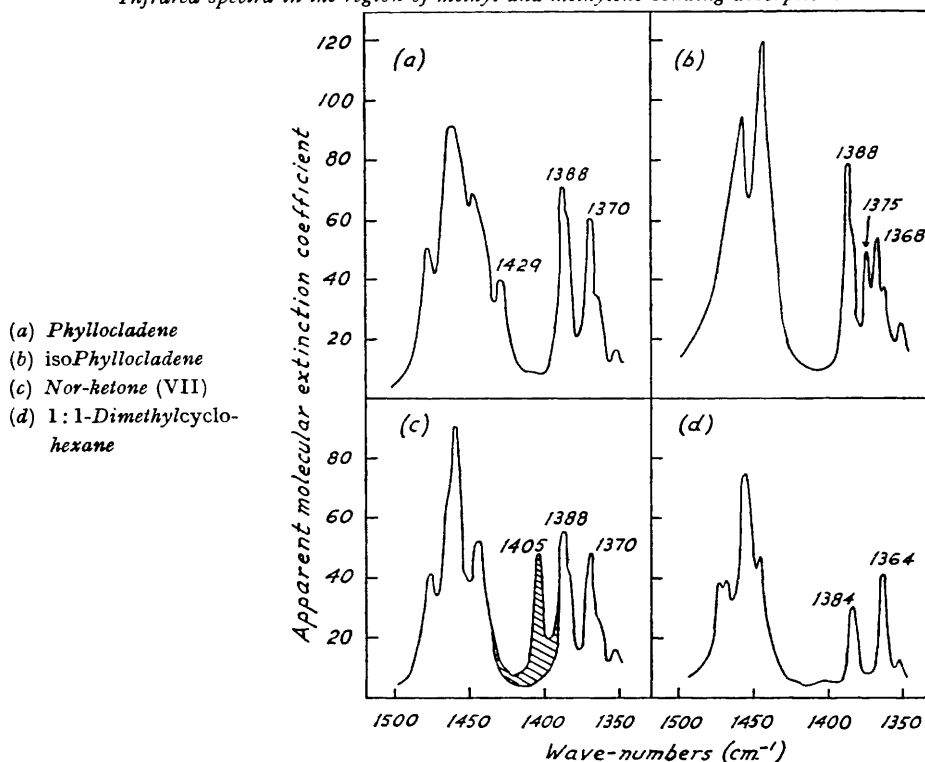
Phyllocladene has no band at 3040 cm^{-1} (Cole, *J.*, 1954, 3807), indicating that it has no methylene group in a three-membered ring as would be required by the structures (V) or (VI) suggested for α -dihydrophyllocladene by Soltys (*Monatsh.*, 1929, **53-54**, 175).

The nor-ketone (VII, if I is correct) shows a carbonyl band at 1742 cm^{-1} , proving conclusively that in phyllocladene the vinylidene group is attached to a five-membered ring. Furthermore, there is a band at 1405 cm^{-1} in the region of methyl and methylene bending absorption (see Fig.). This must be due to one or two methylene groups adjacent

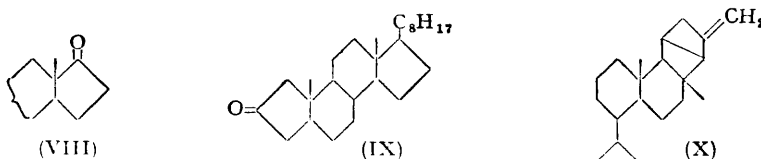
* Part III, *J.*, 1954, 3810.

to the carbonyl group (Jones and Cole, *J. Amer. Chem. Soc.*, 1952, **74**, 5648). A quantitative measurement of the area under the band (see p. 2626) shows that there is one methylene group adjacent to the carbonyl. The shaded portion corresponds to an area of 330 units [cf. 320 for 17-oxoandrostan-3 β -yl acetate (VIII; 1407 cm^{-1}) which has one adjacent methylene group, and 620 for Δ -norcholestanone (IX; 1410 cm^{-1}) which has two (Barnes,

Infrared spectra in the region of methyl and methylene bending absorption.

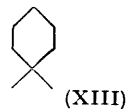
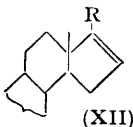


Barton, Cole, Fawcett, and Thomas, *J.*, 1953, 571)]. The carbonyl frequency eliminates the possibility of the four-membered ring structure (X) suggested by Uota (*J. Dept. Agric. Kyushu Imp. Univ.*, 1937, **5**, 118, quoted by Brandt, *loc. cit.*) for phyllocladene.



isoPhyllocladene has bands at 3037 (C-H stretching), 1635 ($\epsilon_{\text{max.}} = 18$, C=C stretching), and 825 cm^{-1} , all of which are characteristic of a trisubstituted double bond. The marked decrease in intensity of the C=C stretching absorption due to the increase in symmetry of the double bond on isomerisation from phyllocladene should be noted. The fairly high intensity of the band at 3037 cm^{-1} and the relatively low frequency of the C=C stretching band are due to the presence of considerable strain in the five-membered bridged ring [cf. 1645 cm^{-1} for 1:4:4-trimethylcyclopentene (XI; A.P.I. "Catalogue of Infrared Spectra," Serial No. 213) which has very little strain, and 1621–1630 cm^{-1} for Δ^{16} -steroids (XII; Jones and Herling, *J. Org. Chem.*, 1954, **19**, 1252) in which the five-membered ring is quite strained. The region of methyl absorption (1350–1400 cm^{-1}) due to bending vibrations (Jones and Cole, *loc. cit.*) is shown in the Figure.

In the spectrum of 1 : 1-dimethylcyclohexane (XIII) the *gem*-dimethyl group gives bands at 1384 and 1364 cm^{-1} with an intensity ratio of 0.75 : 1. It will be noticed that in the methyl region of phyllocladene the bands at 1388 and 1370 cm^{-1} have a ratio of intensity of approximately 1.2 : 1, and there is a suggestion of a shoulder at 1385 cm^{-1} . This means that there are two bands contributing to the upper peak, and near 1385—1388 cm^{-1} is just the expected frequency for an angular methyl group between two six-membered rings (Jones and Cole, *loc. cit.*).



A similar intensity ratio is found for the methyl bands of the nor-ketone (VII) and for *isophyllocladene*, while in the spectrum of the latter the extra band at 1375 cm^{-1} is due to the methyl group produced by the isomerisation of the double bond (cf. 1375 cm^{-1} for methylcyclopentane, A.P.I. "Catalogue, etc.," Serial No. 511). The small band at 1429 cm^{-1} in the spectrum of phyllocladene is due to the methylene group adjacent to the vinylidene double bond (Jones and Cole, *loc. cit.*), and disappears on isomerisation to *isophyllocladene*.

EXPERIMENTAL

The sample of phyllocladene was kindly supplied by Professor A. J. Birch from H. G. Smith's collection of compounds. After recrystallisation from methylene chloride-methanol it melted at 96°.

Oxidation of Phyllocladene with Osmium Tetroxide-Periodic Acid.—Osmium tetroxide (0.16 g.) was added to phyllocladene (58 mg.) in ether (5 ml.). After 24 hr. benzene (10 ml.), ethanol (10 ml.), mannitol (1 g.), potassium hydroxide (1 g.), and water (10 ml.) were added. The mixture was refluxed for 6 hr., and continuously extracted with ether (5 hr.) after addition of water (30 ml.). Evaporation of the ether gave a glycol (35 mg.), m. p. 165—167°. To the crude glycol (35 mg.) in ethanol (18 ml.) and water (4 ml.), periodic acid (0.2 g.) in water (2 ml.) was added, and the solution was set aside for 26 hr. Addition of water, evaporation of ethanol, and cooling gave the nor-ketone, m. p. 86—95°. This was chromatographed on alumina (activity I-II) in light petroleum. The solid from the first fraction, after sublimation at 50°/0.2 mm., had m. p. 93—95°.

isophyllocladene.—This was prepared from phyllocladene by using alcoholic sulphuric acid as described by Brandt (*loc. cit.*). After recrystallisation from ethanol it melted at 107.5—109°.

1 : 1-Dimethylcyclohexane.—This was prepared from dimedone semicarbazone as described by Seibert (*Chem. Ber.*, 1947, 80, 494), except that a glass flask instead of a copper vessel was used. After two distillations over sodium, it boiled at 117—118°, n_D^{20} 1.4250.

The infrared spectra were measured on a Grubb-Parsons Spectrometer, Model S.3.A., equipped with a Perkin-Elmer thermocouple, light chopper, and No. 81 amplifier. All measurements in the range 1300—3200 cm^{-1} were made with a calcium fluoride prism and solutions in carbon tetrachloride, and for the range 650—1300 cm^{-1} a double-pass sodium chloride system and carbon disulphide solutions were used. The absorption cell was 1.3 mm. in thickness.

For quantitative measurements the apparent molecular extinction coefficient $\epsilon = [\log_{10}(T_0/T)]/cl$ (Ramsay, *J. Amer. Chem. Soc.*, 1952, 74, 72) was employed. With the resolving power available in our spectrometer, these values do not differ from the true molecular extinction coefficients by more than 2—3%. When determining the area of the band due to the methylene group adjacent to the carbonyl of (VII) a true graphical separation of overlapping bands was not carried out, but approximately the same proportion of the area was integrated as in the earlier publication (Barnes *et al.*, *loc. cit.*).

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