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THE CONSTITUTION OF THE DITERPENES, PHYLLOCLADENE, MIRENE, KAURENE, CRYPTOMERENE AND CUPRESSENE

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THE earlier literature on the diterpenes has been adequately reviewed.[1]

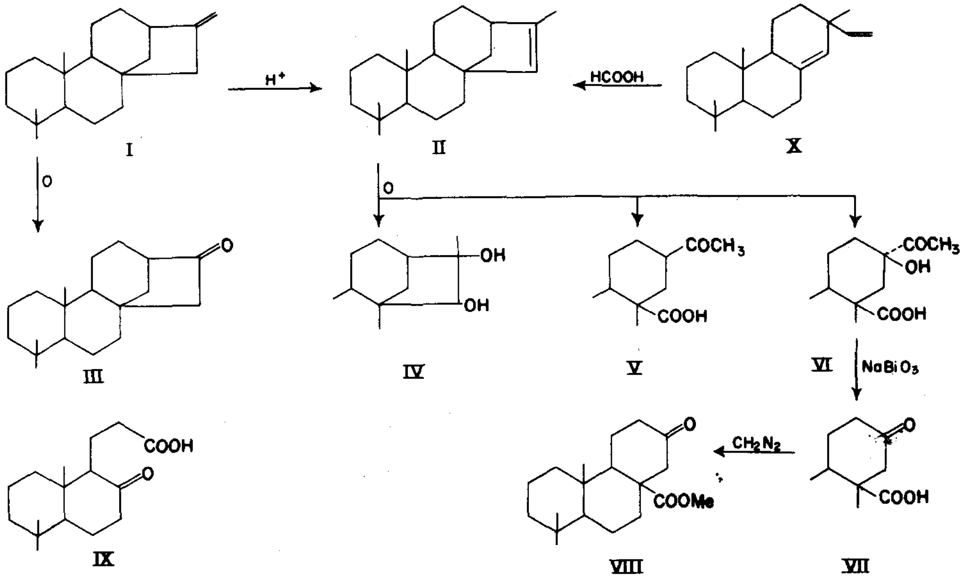
Phyllocladene.

Continuing the earlier work of Brandt,[2] stepwise degradation of phyllocladene has confirmed the structure of rings C and D of his proposed formula (I) for this diterpene,[3] although up till now, no direct chemical proof has been given for the constitution of rings A and B, including the position of the angular methyl group (see, however, the following papers). Many new compounds have been obtained but those having a bearing on the configuration are included in the following flow-sheet:

[1a] J. L. Simonsen and D. H. R. Barton, The Terpenes Vol. III, p. 334. Cambridge University Press (1952); [b] D. H. R. Barton, Quart. Rev. **3**, 36 (1949).

[2] C. W. Brandt, New Zealand J. Sci. Tech. **34** B, 46 (1952).

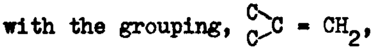
[3] Cf. also W. Bottomley, A. R. H. Cole and D. E. White, J. Chem. Soc. 2624 (1955).



The properties of the previously prepared compounds (III), (IV), (V) and (VII)[2] have been confirmed. The compound, m.p. 215°, however, considered by Brandt[2] to have the constitution (IX), has the structure (VI) since it forms a λ-lactone, m.p. 175-176° (Found: C, 75.15; H, 9.9. $C_{20}H_{30}O_3$ requires C, 75.4; H, 9.5; infra-red bands at 1761 and 1706 cm^{-1}) and is oxidized by sodium bismuthate to the ketoacid (VII), identified by mixed m.p. and identical infra-red spectra. Esterification of (VII) with diazomethane yields the ketoester (VIII), m.p. 153-155.5 (Found: C, 74.8; H, 9.8. $C_{19}H_{30}O_3$ requires C, 74.5; H, 9.9).

The infra-red spectrum of the ketoester (VIII) indicates a carbonyl group in a six-membered ring (strong band at 1721 cm^{-1})[4] while its behaviour to hydrolysis supports a sterically-hindered carboxyl group.

<u>Kaurene.</u>

The reactions of this diterpene agree with its formulation as a stereoisomer of phyllocladene (I). Chemically it behaves in an almost identical manner. Selenium dehydrogenation yields both retene and pimanthrene. Hydrogenation affords isomeric α[1]- and β-dihydrokaurene, m.p. 51-52° (Found: C, 87.6; H, 12.5. $C_{20}H_{34}$ requires C, 87.5; H, 12.5) while ozonization gives formaldehyde and a norketone, m.p. 113-115° [Found: C, 82.4; H, 10.5. $C_{19}H_{30}O$ requires C, 83.15; H, 11.0; 2:4-dinitrophenylhydrazone, m.p. 243-244° (Found: C, 66.0; H, 7.5; N, 12.5. $C_{25}H_{34}O_4N_4$ requires C, 66.05; H, 7.5; N, 12.3)] both reactions consistent with the grouping,  $\genfrac{}{}{0pt}{}{C}{C}\!>\!C = CH_2$, supported by the infra-red spectrum (strong band at 876 cm^{-1}), while the spectrum of the norketone shows that the carbonyl group is in a five-membered ring (strong band at 1745 cm^{-1})[4]. Kaurene may be isomerized with acids to isokaurene, containing the group,  $\genfrac{}{}{0pt}{}{C}{C}\!>\!C = C\!<\!\genfrac{}{}{0pt}{}{H}{C}$ (band at 820 cm^{-1}), which on hydrogenation yields α-dihydrokaurene. This is analogous to the exocyclic - endocyclic double bond shift in the isomerization of phyllocladene into isophyllocladene (II).

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[4] L. H. Bellamy, <u>The Infra-red Spectra of Complex Molecules</u> (2nd Ed.), p. 132. Methuen, London (1958).

[5] K. Nishida and H. Uota, <u>J. Agric. Chem. Soc. Japan</u> <u>7</u>, 157 (1931).

Cryptomerene.

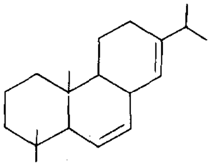
This has been shown (mixed melting point and infra-red spectrum) to be identical with isokaurene. The so-called λ-kaurene of Nishida and Uota[5] formed by the action of alcoholic sulphuric acid on kaurene or alcoholic potash on kaurene hydrochloride is, however, the corresponding alcohol, (Found: C, 82.7; H, 11.3. $C_{20}H_{34}O$ requires C, 82.7; H, 11.8) which with dry hydrogen chloride forms kaurene hydrochloride.

Mirene.

The infra-red spectrum of this diterpene is almost identical with that of phyllocladene and only varies at some points in the intensity of the bands. This evidence agrees with its being stereoisomeric with phyllocladene (I). As already recorded, it forms a monohydrochloride and a dihydro derivative different from α- and β-dihydrophyllocladene and α- and β-dihydrokaurene. Consistent with its having the group, $\begin{matrix}C\\C\end{matrix}\!\!>C = CH_2$, it forms a norketone, m.p. 98-99° (Found: C, 83.3; H, 10.5. $C_{19}H_{30}O$ requires C, 83.15; H, 11.0), similar to (III) by oxidation. Isomerization by heating with glacial acetic acid yields isophyllocladene.

Cupressene.

Owing to the small amount of this compound available no further constitutional work has yet been carried out. The infra-red spectrum exhibits strong bands at 823 and 743 cm^{-1}, consistent with the groups, $\begin{matrix}C\\C\end{matrix}\!\!>C = C\!<\!\begin{matrix}H\\C\end{matrix}$ and $\begin{matrix}H\\C\end{matrix}\!\!>C = C\!<\!\begin{matrix}H\\C\end{matrix}$. The ultra-violet spectrum indicates the absence of conjugation. Both bands are absent in the tetrahydroderivative which shows no absorption in the 220 mμ region, indicating its saturated character.[6] As previously reported, attempted dehydrogenation with palladium-charcoal isomerized it to isophyllocladene, but it was stable to alcoholic sulphuric acid. A check on the infra-red spectrum of the material used showed the absence of any appreciable amount of isophyllocladene. On these and biogenetic grounds cupressene has been assigned the provisional formula (XI), although there are a number of alternative structures.



XI

Rimuene.

The evidence for its structure as (X) has recently been summarized.[7]

Assistance in this work is acknowledged in the following paper.

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[6] P. Bladon, H. B. Henbest and G. W. Wood, J. Chem. Soc. 2737 (1952).

[7] L. H. Briggs, B. F. Cain and J. K. Wilmshurst, Chem. & Ind. 599 (1958).