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THE STEREOCHEMISTRY OF ISOPHYLLOCLADENE

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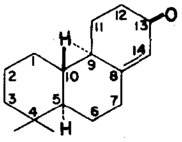
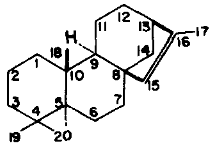
ISOPHYLLOCLADENE has been converted into podocarp-8(14)-en-13-one (I), identical with a sample prepared from manool.[1] Hence isophyllocladene must possess the "normal" trans A/B ring junction, since the reactions employed do not permit the possibility of inversion at these centres. As Djerassi[2] has already pointed out that only one structure possessing this ring fusion is permitted by rotatory dispersion evidence, isophyllocladene must be as depicted in (II).



I



II

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[1] J. R. Hosking, Ber. 69, 780 (1936).

[2] C. Djerassi, M. Cais and C. A. Mitscher, J. Amer. Chem. Soc. 81, 2386 (1959).

Hydroxylation of isophyllocladene with osmium tetroxide gave the known dihydro-15,16-dihydroxyphyllocladene.[3] When this was oxidised with lead tetracetate, 13β-acetyl-8β-aldehydopodocarpane was formed, m.p. 138-140°, $[\alpha]_D$ - 39°. The derived dioxime was dehydrated with acetic anhydride to give the oxime of 13β-acetyl-8β-cyanopodocarpane, m.p. 195-197°, $[\alpha]_D$ - 13°.

The parent ketone was regenerated and subjected to the action of pertrifluoroacetic acid. After hydrolysis of the resulting acetate, 8β-cyano-13-hydroxypodocarpane was produced, m.p. 95-115°. No attempt was made to separate this mixture of 13-hydroxy-isomers, but oxidation with chromium trioxide gave 8β-cyano-13-oxopodocarpane, m.p. 160-161° (with prior melting and resolidification at 153-154.5°), $[\alpha]_D$ + 33°. When this substance was distilled from powdered potassium hydroxide at 120°/0.01 mm, hydrogen cyanide was eliminated, giving podocarp-8(14)-en-13-one, m.p. 64-66°, $[\alpha]_D$ + 45°, λ_{max} (MeOH) 242.5 mμ, ϵ = 16,000. A specimen of the same material prepared from manool had m.p. 64-66°, $[\alpha]_D$ + 49°, λ_{max} (MeOH) 242.5 mμ, ϵ = 16,400. The infra-red spectra of the two samples in CCl_4 were identical. All rotations were measured in chloroform at 18°, and satisfactory analyses have been obtained for all the compounds reported.

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