Tetrahedron Letters No. 4, pp. 243-246, 1963. Pergamon Press Ltd.
Printed in Great Britain.

LONGICYCLENE, THE FIRST TETRACYCLIC SESQUITERPENE

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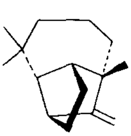
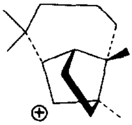
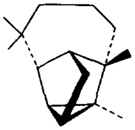
(Received 7 November 1962)

The vapour phase chromatography (VPC) of the higher boiling portion of Indian turpentine oil (from *Pinus longifolia*, Roxb.) revealed that the material contains, besides longifolene (I), the chief component, a number of other constituents, though in much smaller proportion. We now report the isolation and structure determination of another sesquiterpene from this source. As will be clear from what is described below, this compound has the same relationship to longifolene as tricyclene has to camphene and hence we have named it longicyclene.


(I)


(II)


(III)

A pure sample of longicyclene was obtained by a combination of fractional distillation and chromatography and further purified by treatment with perbenzoic acid, which preferentially reacted with olefinic contaminants (chiefly longifolene). It analyzed for $C_{15}H_{24}$ (Found: C, 88.2; H, 12.29. $C_{15}H_{24}$ requires C, 88.2; H, 11.9%) and had: b.p. 82°/2 mm, n_D^{30} 1.4888, d_4^{30} 0.9307, M_D 63.37, $[\alpha]_D$ + 33.6°(neat).

Its proton magnetic resonance (PMR) spectrum* did not show any vinyl protons. The possibility of the occurrence of a tetrasubstituted olefinic linkage in the molecule was ruled out on the basis of end absorption of the compound in the ultraviolet region: ϵ_{210} 171, ϵ_{215} 113, ϵ_{220} 68 ϵ_{225} 38 in alcohol. On the basis of these data, longicyclene $C_{15}H_{24}$, should be a fully saturated tetracyclic sesquiterpene. This is consistent with its inertness to perbenzoic acid.

Longicyclene gives a faint but distinct pale yellow colour with tetranitromethane, which indicated[1] that one of the rings in the molecule may be three-membered. The observed value of molecular refractivity (63.37) agrees very well with the value (63.41) calculated for a $C_{15}H_{24}$ hydrocarbon containing a cyclopropane ring. The presence of such a ring was borne out from its PMR spectrum: besides displaying four unsplit peaks at 49, 53, 58 and 60 cps (due to four quaternary methyl groups) it showed another peak (1H) at 45.8 cps ascribable to a cyclopropane ring proton[2]; the total area under the methyl and the 45.8 cps peak equalled fourteen protons, thus revealing the presence of another cyclopropane ring proton under the methyl peaks; thus the presence of a cyclopropane ring with two ring protons was indicated.

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[*] The spectrum was taken on a 20% solution in carbon tetrachloride on a Varian A-60 High Resolution NMR Spectrometer, with tetramethylsilane as an internal reference. The values are reported in cycles/sec., from tetramethylsilane as zero. We are grateful to Prof.Bates for the measurements.

[1] D.H.R.Barton, J.Chem.Soc. 1444 (1951)

[2] L.M.Jackman, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, p.52, Pergamon Press, London (1959)
S.Forsen and T.Norin, Acta Chem.Scand. **15**, 592 (1961)

At this stage it was strongly suspected on account of its occurrence with longifolene, that the new hydrocarbon may as well be the tricyclene analogue (III) of longifolene. This was supported by its infrared spectrum. The compound, though completely transparent in the double bond region, showed a clear band at 3049 cm^{-1} due to the C-H stretching of the cyclopropane ring. It has been suggested[3] that only those cyclopropane derivatives which have a methylene group incorporated in the ring display absorption in this region. However, it was noticed in connection with another investigation that tricyclene, which does not have a $-CH_2$ group in its three-membered ring, does show a distinct peak at 3045 cm^{-1} and in a recent paper[4] this has been found to be a general characteristic of compounds with a tricyclene or isotricyclene system. These authors have described a rather strong band at 845 cm^{-1} as being characteristic of a tricyclene system and our new sesquiterpene displays a strong peak at 840 cm^{-1}.

Final proof for the structure (III) could be obtained as follows: On treatment with cupric acetate in acetic acid at reflux (22 hrs) longicyclene underwent isomerisation to a mixture of hydrocarbons which was shown by a combination of VPC and infrared spectroscopy to contain besides isolongifolene[5] (15%) and longicyclene (29%), 51% of (+)-longifolene (I).

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[3] A.R.H.Cole, J.Chem.Soc. 3807 (1954)

[4] M.Hanack and H.Eggensperger, Liebigs Ann. **648**, 1 (1961)

[5] U.R.Nayak and Sukh Dev, Tetrahedron **8**, 42 (1960)

The occurrence of longicyclene (III) in Nature assumes importance as it represents an alternate pathway for the stabilisation of longibornyl cation (II), the suggested[6,7] species in the biogenesis of longifolene.

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[6] G.Ourisson, Bull.Soc.Chim. 895 (1955)

[7] J.B.Hendrickson, Tetrahedron 7, 82 (1959)