STUDIES IN SESQUITERPENES—XXXV

LONGICYCLENE, THE FIRST TETRACYCLIC SESQUITERPENE*†

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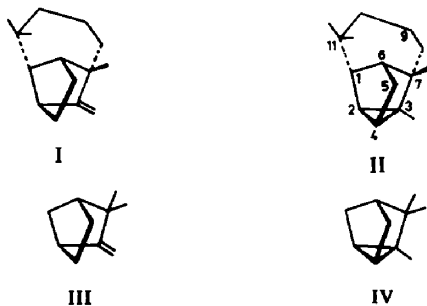
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Abstract—A new sesquiterpene hydrocarbon has been isolated from the essential oil of *Pinus longifolia*, Roxb. and is shown to be the first tetracarbocyclic sesquiterpene; structure II has been assigned to it.

WHILE working on the action of perbenzoic acid on longifolene (I),[1] it was observed that the product always contained minor quantities of a hydrocarbon, different from longifolene. It was surmised that this may be a fully saturated hydrocarbon, which may be a contaminant in the starting longifolene sample. Indeed, it was shown by GLC that this material is present in the starting longifolene sample to the extent of 2–5%. This led to a systematic study of the sesquiterpene portion of the essential oil from the oleoresin of *Pinus longifolia*, Roxb. (Sanskrit: *Sarala*; Hindi: *Chir*), the source of the longifolene sample. We now report the isolation and structure determination of this new hydrocarbon.[2]

The isolation of this compound, which is present in the original essential oil to the extent of 0·7–1% (longifolene content of the essential oil, 10–12%; analyses by GLC), was effected by a combination of fractionation and column chromatography and the product further purified by treatment with perbenzoic acid, which preferentially reacted with olefinic contaminants. This compound is now shown to possess the structure II. As can be seen, this has the same relationship to longifolene as tricyclene (IV) has to camphene (III) and hence we have named it longicyclene.‡ Longicyclene represents the first sesquiterpene to have a well-proven tetracyclic carbon framework.§

I   II

III   IV

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† A preliminary communication appeared in *Tetrahedron Letters* 243 (1963).

‡ The system of adding the prefix *longi* to compounds of monoterpene series, in order to denote the corresponding compounds in the longifolene series, was first introduced in 1954.[3]

§ A tetracyclic structure has been proposed for 'Guerbet's acid', a constituent of the East Indian Sandalwood oil.[4] The evidence, however, is not compelling and a reinvestigation is called for.

Longicyclene ($[\alpha]_D$ $+33 \cdot 6°$, neat) analyses for $C_{15}H_{24}$ and is inert to perbenzoic acid. Its PMR spectrum (Fig. 1) does not show a signal for a vinyl proton.* The possibility of the presence of a tetrasubstituted olefinic linkage in the molecule was ruled out on the basis of end-absorption† in the UV (EtOH): ε_{210} 171, ε_{215} 113, ε_{220} 63 and ε_{225} 38. On the basis of these data, longicyclene, being $C_{15}H_{24}$, must be tetracarbocyclic. In full support of this longicyclene has four quaternary methyls:‡ four sharp 3H singlets at 49, 53, 58 and 60 c/s in the PMR spectrum (Fig. 1).
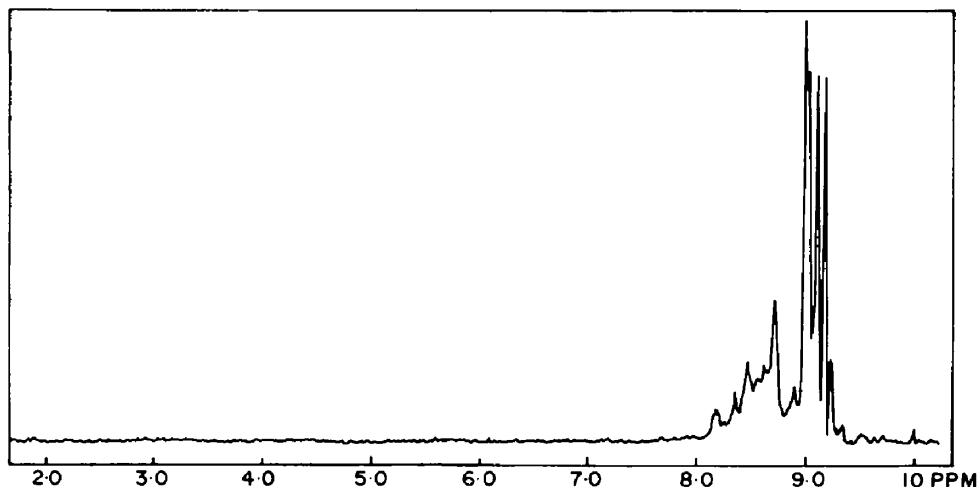

FIG. 1 PMR Spectrum of longicyclene.

Longicyclene gives a faint, but a distinct pale yellow color with tetranitromethane, which indicates[7] that one of the rings in the molecule should be 3-membered. The observed value of molecular refractivity (63·37) agrees very well with the value 63·41 calculated§ for $C_{15}H_{24}$ having one 3-membered ring. Though, a cyclopropane ring methylene is readily detected by PMR by virtue of their being abnormally shielded[9] (anisotropy of cyclopropane ring),[10] the ring methine protons are usually not so easily discernible, as they are expected to occur somewhat downfield in the region of C-Me absorption. The PMR spectrum of longicyclene shows a 1H signal (together with another minor signal at 40 c/s) at 46 c/s and, the total area under the Me and the 46 c/s signals equals 14 protons (the average signal area for 1H was determined by taking the total signals area equal to 24H); thus, in all likelihood two cyclopropane ring methine protons are indicated.‖

* Usual range for hydrocarbons is δ = 4·3–5·4 ppm.[5]
† A tetra-alkyl substituted olefinic linkage has ε_{220} 3400–6700.[6]
‡ A hydrocarbon structure, derivable from farnesol, and having *four* quaternary methyls, must necessarily be tetracyclic.
§ Using atomic and group refractivities.[8]
‖ When the spectrum was taken in C_6H_6, there was not any significant relative shift of signals. Tricyclene (in CCl_4) also shows the two cyclopropane ring methine protons, apparently, under the methyl proton (6H) signal at 50 c/s. However, in *cis*-carane the two cyclopropane ring CH signals occur as a complex multiplet between 12–45 c/s.

The above information, coupled with the fact of occurrence of the new hydrocarbon with longifolene, strongly suggested that the new sesquiterpene may as well be the tricyclene analogue (II) of longifolene. This was supported by its IR spectrum (Fig. 2).
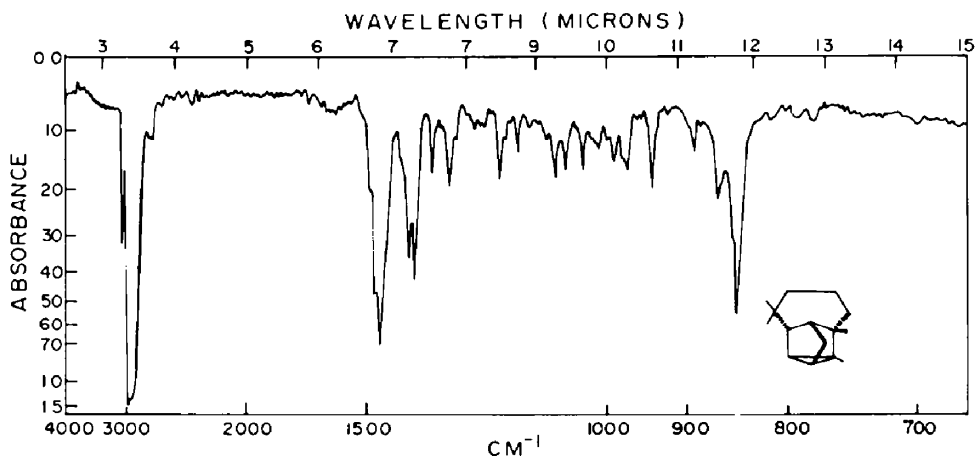

FIG. 2 IR Spectrum of longicyclene.

The compound, though completely transparent in the 6 μ region, shows a clear band at 3049 cm^{-1}, assignable to the C—H stretching of the cyclopropane ring. It has been suggested[11] that only those cyclopropane derivatives which have a ring methylene group display absorption in this region. However, it was noticed in connection with another investigation that tricyclene (IV) which does not have a cyclopropane ring methylene, does show a distinct peak at 3045 cm^{-1} and other workers[12] find this to be a general characteristic of compounds with a tricyclene or isotricyclene system. These authors report a rather strong band at $\sim$845 cm^{-1} as being characteristic of a tricyclene system and our new sesquiterpene, indeed, displays a strong peak at 840 cm^{-1}. Furthermore in the near IR, longicyclene (CCl$_4$) shows a band at 1·640 μ (ε 0·72), just like a similar absorption of tricyclene (CCl$_4$, 1·650 μ, ε 1·13) assignable to the first overtone of cyclopropane ring C—H stretching, in such systems.[13]

Finally, conformation of structure II was achieved by its chemical correlation with longifolene, in different ways.

On interaction with HCl in dry ether, longicyclene yielded (+)-longibornyl chloride (V), the product of the HCl–longifolene reaction,[14,*] though in a lesser yield than that obtainable from longifolene.†

On treatment with cupric acetate in AcOH at reflux (22 hr), longicyclene underwent isomerization to a mixture of hydrocarbons (yield 85–95%), shown by a combination of GLC and the IR spectrophotometery to contain, besides isolongifolene[16] (15%) and longicyclene (29%), 51% of longifolene (I). Under identical conditions, longifolene

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* cf. Action of HCl on tricyclene to give isobornylchloride.[15]

† Longicyclene is unsymmetrical unlike tricyclene and thus two different secondary chlorides (resulting from the camphyl → bornyl type rearrangement) can result from this. This might explain the rather unsatisfactory yield of the longibornyl chloride.

yielded a product consisting (GLC, IR) of longicyclene (24%), isolongifolene (19%) and longifolene (55%). Thus, under these conditions* longifolene and longicyclene get interconverted, in all likelihood through the longibornyl cation (VI).

V a : R = Cl
V b : R = Br
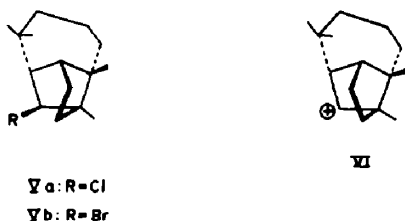
In view of the above results, the fate of the longibornyl cation, generated from longibornyl bromide (Vb), has been investigated. In conformity with the results of the earlier investigators,[17] refluxing longibornyl bromide in buffered (CaCO$_3$) 80% aq–EtOH yielded only pure (GLC) longifolene. However, when the bromide was treated with aqueous ethanolic KOH, the product consisted of longicyclene (26%) and longifolene (74%).†‡ Since longifolene has been synthesized,[19] this conversion constitutes, in a formal sense, a synthesis of longicyclene (II).§

The isolation of longicyclene (II) from nature assumes importance, as it represents an alternate pathway for the stabilization of longibornyl cation (VI), the species implicated[21–23] in the biogenesis of longifolene (I). The occurrence of longifolene and longicyclene in the same plant is biogenetically significant and may be compared with the fate of longibornyl cation (from longibornyl bromide and aq ethanolic KOH) discussed earlier.

EXPERIMENTAL

All m.ps and b.ps are uncorrected. Pet. ether refers to the fraction b.p. 40–60°. All solvent extracts were dried over Na$_2$SO$_4$.

IR spectra were taken on a Perkin–Elmer infracord model 137E. UV and NIR spectra were measured on a Perkin–Elmer spectrophotometer, model 350. All PMR spectra were taken in 10–20% soln in CCl$_4$ with TMS as the internal standard, on a Varian Associates A-60 spectrometer; peaks are reported in c/s from TMS.

GLC was carried out on a Perkin–Elmer Vapour Fractometer model 154D, using H$_2$ as the carrier gas and a 2 meter × 5 mm column packed with 20% diethylene glycol polysuccinate on Chromosorb W.

Al$_2$O$_3$ used for column chromatography was made neutral by the HNO$_3$ method and graded according to Brockmann.

* Both camphene and tricyclene on treatment with Cu(OAc)$_2$ in AcOH yield a product of essentially similar composition and having isobornyl acetate as the major component and traces of the two hydrocarbons.

† cf. The action of NaOAc in AcOH on longibornyl chloride, when the product obtained (96%) consisted of longifolene (80%), longicyclene (8%) and isolongifolene (~12%).[18]

‡ By the dehydrohalogenation (methanolic-KOH) of "liquid hydrochlorides", formed during the hydrochlorination of longifolene, Naffa and Ourisson,[14] obtained a hydrocarbon fraction, containing as one of the components a compound, considered to be a tricyclene-type isomer, in a poor yield.

§ A projected conversion of longicamphor into longicyclene by the camphor hydrazone → tricyclene route[20] could not be carried out, due to the failure of longicamphor to react with hydrazine, under a variety of conditions.

Isolation of longicyclene

The "Secondary residue"* (13 l.), after a preliminary drying (Na$_2$SO$_4$) was fractionated on a Pod-bielniak column† (press 3 mm, reflux ratio 1:10) and the first two 300 ml cuts (b.p. 83–84°/3 mm, n^{30} 1·4800–1·4885) were combined for the isolation of longicyclene,[2] which was present (GLC: temp 130°, press. 15 psi) to the extent of ~ 18%. This mixture (50 g) was chromatographed over Al$_2$O$_3$/I (35 cm × 8 cm). The material (37 g) eluted with pet. ether (8 × l.) consisted only of sesquiterpene hydrocarbons. This material (35 g) in CHCl$_3$ (30 ml) was cooled to −10° and a similarly chilled·CHCl$_3$ soln of perbenzoic acid (46 g; 610 ml of 1·104N), to which had been added EtOH (60 ml), was rapidly added to this. The reaction mixture was left aside at 0–5° for 60 hr and then worked up by extraction with 10% Na$_2$CO$_3$ aq (4 × 125 ml), washing with brine and drying. The solvent was removed and the residue (39·3 g) chromatographed over Al$_2$O$_3$/II (28 cm × 7 cm): pet. ether (3 × 500 ml) eluted pure longicyclene (5·5 g); later pet. ether eluates were contaminated with longicamphenilone and, the still later eluates (pet. ether–C$_6$H$_6$; C$_6$H$_6$, etc.) contained other products of oxidation of longifolene.[1]

The above material was distilled over Na to give a product (5·0 g) of > 98% GLC purity: b.p. 82°/2 mm, n_D^{30} 1·4888, d_4^{20} 0·9307, M_D 63·37. (Found: C, 87·98; H, 11·95. C$_{15}$H$_{24}$ requires: C, 88·16; H, 11·84%).

Reaction with hydrogen chloride

Longicyclene (136 mg) in dry ether (5 ml) was chilled (−10°) and the soln saturated with dry HCl. After keeping the reaction mixture overnight (16 hr) in the cold, the light pink soln was diluted with ether (40 ml), washed with water, brine and dried. The solvent was removed under suction to get a somewhat viscous liquid (164 mg), which failed to crystallize. (However, its IR spectrum was very similar to that of longibornyl chloride, except for a few extra peaks in the 1000–1140 cm^{-1} region). On seeding its methanolic soln with a speck of authentic longibornyl chloride, a white solid (40 mg, m.p. 52–55°) readily separated, which was recrystallized (MeOH) to give colorless needles (25 mg), m.p. 59–60°, mixed m.p. with an authentic sample of (+)-longibornyl chloride (m.p. 59–60°)[14] remained undepressed. IR spectrum (nujol) (completely superimposable on that of an authentic sample): st. absorptions at 730, 796, 807, 855 cm^{-1}.

Action of cupric acetate in acetic acid

(i) *On longicyclene.* Longicyclene (0·5 g), cupric acetate (0·1 g) and gl. AcOH (10 ml) were refluxed (22 hr), the greenish blue reaction mixture, diluted with water (60 ml), extracted with pet. ether (3 × 15 ml), washed with brine and dried. The solvent was removed and the product (0·47 g) in pet. ether filtered through a column of Al$_2$O$_3$/I, which was eluted with pet. ether. The product (0·38 g) was distilled to give a liquid (0·31 g): b.p. 109–110°/7 mm, n_D^{30} 1·4955, $[\alpha]_D$ +10·8° (c, 5% in EtOH). GLC (temp 160°, press 15 psi) showed three components: longicyclene (29%, RRT = 1), isolongifolene (15%, RRT = 1·1) and longifolene (51%, RRT = 1·3).

(ii) *On longifolene.* Longifolene (0·5 g) was treated exactly as above to give after the same work-up 0·3 g of a product: b.p. 120°/12 mm, $[\alpha]_D$ +4·5° (c, 4·7% in EtOH). GLC showed longicyclene (24%), isolongifolene (19%) and longifolene (55%).

(iii) *On camphene.* Reaction with camphene (0·5 g) was carried out exactly, as under (i) and the crude product (0·41 g) directly distilled (no chromatography): b.p. 115°/20 mm, yield 0·31 g. The IR spectrum of this material was very similar to that of isobornyl acetate: strong bands at 1727, 1639, 1235, 1185 and 877 cm^{-1}. GLC (temp 160°, press 15 psi) showed essentially one peak (RRT = 1·074, bornyl acetate, RRT = 1) with traces of hydrocarbons.

(iv) *On tricyclene.* Reaction with 0·5 g tricyclene, as above, gave essentially identical product.

Dehydrobromination of longibornyl bromide.

(i) *Buffered aqueous ethanol.* Pure longibornyl bromide[14] (m.p. 69–70°, 1·9 g), EtOH (40 ml), water (10 ml) and CaCO$_3$ (1·5 g) were mixed and the whole refluxed for 22 hr. The reaction mixture was diluted with water (150 ml), extracted with ether (3 × 40 ml), and the extracts washed with brine and dried. The

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* 'Secondary residue' represents the less steam-volatile part of the turpentine oil from *Pinus longifolia.* The crude oil, as first obtained by the steam-distillation of the oleoresin, is subjected to a second steam-distillation to separate the more steam-volatile and the less steam-volatile portions. The product was supplied by The Indian Turpentine and Rosin Co., Bareilly, U.P. (India).

† Model No. 3730, Podbielniak, Chicago, USA.

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solvent was removed and the product (1·25 g) distilled: b.p. 114°/9 mm, $[\alpha]_D$ +42·6° (neat). GLC indicated >99% purity and IR spectrum was superimposable on that of an authentic sample.

(ii) *Ethanolic* KOH. A mixture of longibornyl bromide (5·7 g) and KOH (4 g dissolved in 5 ml water) and EtOH (40 ml) was refluxed (24 hr) and worked up by extraction with pet. ether as above. The crude product was distilled to give a colorless liquid (3·86 g, 95%): b.p. 108–110°/8 mm. GLC (temp 130°, press 15 psi) showed two peaks with RRT of 1 and 1·34 in the ratio 26:74 respectively. IR spectrum: longifolene 3021, 1653, 877 cm^{-1}; longicyclene 840 cm^{-1}.

The above product (3·06 g) in benzene (3 ml) was cooled in an ice-bath and treated with a cooled soln of perbenzoic acid (2·07 g) in benzene (42 ml) and the mixture set aside at ∼5° for 48 hr and then worked up as described earlier. The product (3·18 g) was chromatographed over Al$_2$O$_3$/I, as detailed earlier to give 0·61 g of GLC pure material: b.p. 98°/4 mm, n_D^{30} 1·4892, $[\alpha]_D$ +24·6° (c, 19·5% in CHCl$_3$) identified (GLC, IR, PMR) as longicyclene.

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