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ON THE STRUCTURE OF ISOLONGIFOLENE

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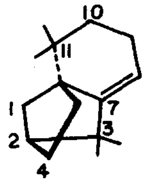
THE isolation of isolongifolene, $C_{15}H_{24}$, an artefact from the acid-catalysed hydration of longifolene (I), has been described previously[1]. We now present evidence which leads to its formulation as (II).

I



II

Isolongifolene is tricyclic and has a carbon-skeleton different from that of longifolene and the necessary evidence for these has been summarised[1]. Its PMR[2]

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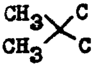
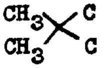
[1] U.Ramdas Nayak and Sukh Dev, Tetrahedron 8,42(1960).

[2] The measurements, unless stated to the contrary, were made on ~20% solution in CCl_4 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.

spectrum showed methyl peaks (sharp singlets) at 50 (3H), 57 (6H) and 62 (3H) cps; that none of these four methyl groups occur as isopropyl group (J ~ 6 cps) was ascertained from a spectrum taken at 40 mc, when these signals showed up at 33, 37.5 and 39.5 cps, and consequently all the four methyls must be quaternary. In the IR both isolongifolene and isolongifolane showed well-resolved doublets (1360 and 1380 cm^{-1};  $\begin{smallmatrix}CH_3 & & C\\ & \times & \\ CH_3 & & C\end{smallmatrix}$) of exactly equal intensity; since the band at lower frequency is considered highly diagnostic of the gem-dimethyl group and its intensity has been used[3] to calculate the number of such systems, one could conclude that the four methyls of isolongifolene are located as two  $\begin{smallmatrix}CH_3 & & C\\ & \times & \\ CH_3 & & C\end{smallmatrix}$ groups. This has been confirmed by differential Kuhn-Roth C-methyl estimation[4].

The only olefinic linkage in isolongifolene must be trisubstituted (ϵ_{210} 2260, ϵ_{215} 933; IR: 819 cm^{-1}; PMR : a triplet centred at 305 cps with area = 1H) and from J-multiplicity (J = 4 cps) of the vinyl proton it must be flanked by a methylene group. Treatment of isolongifolene-α-epoxide[5] (m.p. 40.5 - 41.5°, $\alpha_D \pm 0$) with BF_3-Et_2O

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[3] A.R.H.Cole, D.W.Thornton and D.E.White, Chem. and Ind. 795 (1956).

[4] V.S. Pansare and Sukh Dev, to be published shortly.

[5] This is derived from (±)-isolongifolene.

yielded a ketone (III; b.p. 122°/2 mm, n_D^{27} 1.5005; IR : 1715, 1423 cm^{-1}; semicarbazone m.p. 207-208° dec.) quantitatively convertible into its epimer (IV; b.p. 111-12°/2 mm; IR: 1698, 1408 cm^{-1}). From the $\nu^{C=O}$ of these ketones it is apparent that the ethylenic linkage must be located in a cycle higher than 5-membered and in all likelihood in a six-membered ring.

Oxidation of isolongifolene with sodium-dichromate-acetic acid yielded, besides the saturated ketone (III)[6], a mixture of two unsaturated ketones (V, 70%, m.p. 34-35°, $[\alpha]_D$ -210°, semicarbazone, m.p. 226-28°; VI 30%, m.p. 52-54°, $[\alpha]_D$ -1.8°, semicarbazone, m.p. 218.5-219.5°; total yield ~ 40%), which had identical UV ($\lambda_{max}^{alc.}$ 245 mμ, ε = 14,000), IR (1670, 1640 cm^{-1}) and PMR (sharp methyl signals at 59, 62, 65 and 69 cps; olefinic proton at 333 cps) spectra and must thus represent the (-) and (±)-forms of the unsaturated ketone respectively; this would mean that isolongifolene as obtained by acid-catalysed rearrangement is partially racemised[7]. Li-NH_3 reduction of (VI) followed by chromic acid oxidation yielded a ketone (VII), b.p. 130-35° (bath)/2.5 mm, $\nu^{C=O}$ 1715 cm^{-1}, found to be different from (III) or (IV); this proved that during the chromic acid oxidation to yield the unsaturated ketone, the attack had been on the allylic methylene and not on the

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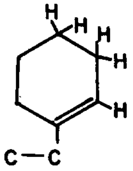
[6] Only partly racemic.

[7] Further discussed under "β-longifolene".

olefinic linkage. Lithium aluminium hydride reduction of (V) yielded an unsaturated alcohol, readily dehydrated to a conjugated diene (VIII; n_D^{30} 1.5058, $[\alpha]_D$ -479°; IR : $\nu^{c=c}$ 1650, 1585, $\delta^{=CH}$ 728 cm^{-1}); catalytic hydrogenation of (VIII), furnished isolongifolane, proving thereby that no skeletal rearrangement is involved in its formation. The UV absorption of the diene (λ_{max}^{EtOH} 266.5 mμ; ε, 7471) is clearly that of a cyclohexadiene (Calcd. 256 + 10 mμ). Thus, the olefinic linkage of isolongifolene must be located in a six-membered ring. Furthermore, since the intensity of the 1420 cm^{-1} band (bending frequency of the methylene group flanking the carbonyl[8,9]) in the IR spectrum of VII, is almost double that of the corresponding band of III and IV, the keto group in VII must be flanked by CH_2 groups on either side. Taking into account, all the data presented so far, the part structure (IX) can now be written for isolongifolene:



IX

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[8] R.N.Jones and A.R.H. Cole, J.Amer.Chem.Soc. 74, 5648 (1952); R.N.Jones, A.R.H. Cole and B. Nolin, ibid. 74, 5662 (1952).

[9] C.S. Barnes, D.H.R. Barton, A.R.H. Cole, J.S.Fawcett and B.R. Thomas, J. Chem. Soc. 573 (1953).

This is fully supported by the PMR spectrum of the diene (VIII), which showed a complex 9 line spectrum (302, 311, 319, 323, 326, 334, 339, 343 and 348 cps) accounting for three vinyl protons coupled in an ABC pattern.

The saturated ketone (III) on further oxidation with perbenzoic acid furnished a lactone[5] (X; m.p. 79-80°, $\nu^{C=O}$ 1730 cm^{-1}), which could also be directly prepared from isolongifolene by the action of two moles of the peracid in $CHCl_3$. The lactone on hydrolysis followed by chromic acid oxidation furnished a keto acid , $C_{15}H_{24}O_3$, (XI; m.p. 107-108°). The keto acid could also be obtained directly from the saturated ketone (III) by oxygenation in the presence of potassium tert-butoxide. From the carbonyl stretching frequencies of the keto acid ($\nu^{C=O}$ 1735, 1710 cm^{-1}) and its methyl ester ($\nu^{C=O}$ 1732 cm^{-1}), XI must be a cyclopentanone. The keto function in XI is highly hindered: thus the compound was recovered unchanged from attempted $NaBH_4$ reduction[10], Wolff-Kishner reduction[11] or reduction by the thioketal procedure[12]; it also failed to yield a semicarbazone or a 2,4-dinitrophenylhydrazone. No bromination took

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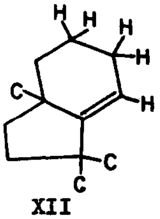
[10] H.C. Brown, O.H.Wheeler and K. Ichikawa, Tetrahedron **1**, 214 (1957).

[11] D.H.R. Barton, D.A.J. Ives and B.R. Thomas, J. Chem. Soc. 2056 (1955).

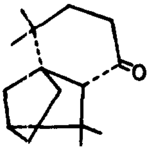
[12] L.F. Fieser, J. Amer. Chem. Soc. **76**, 1945 (1954).

place under the conditions[13] usually employed for total bromination of α-hydrogens in a ketone and the keto acid was recovered unchanged. All these experiments yielded the valuable information that there are no hydrogens α to the keto function, and thus the part structure IX can now be expanded to XII:

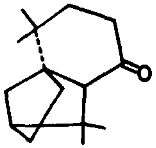


XII

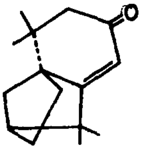
Taking into consideration the fact that isolongifolene is an acid-catalysed rearrangement product from longifolene (I) only structure (II), consistent with the above described facts, can be advanced for it. The structures of important products derived from isolongifolene, described above, can now be written:



III or
IV



IV or
III



V, VI

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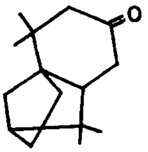
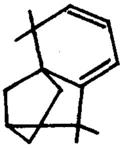
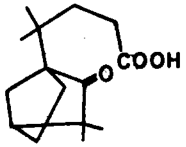
[13] T.R.Govindachari, B.R. Pai, K.K. Purushothaman and S. Rajadurai, *Tetrahedron* **12**, 105 (1961).



VII



VIII



XI

Further confirmatory evidence in favour of structure (II) was obtained as follows:

As anticipated the diene (VIII) did not yield any aromatic derivative on heating with Se at 320-330° (20 hr). However, on dehydrogenation over 10% Pd-C in the vapour phase[14] at 450 ± 10°, isolongifolene yielded a mixture of naphthalenes (23%). Of these, three have been identified as indicated in Table 1, while the structure of the fourth is uncertain, though from its PMR spectrum it is certainly a dimethyl ethylnaphthalene and by the application of certain empirical rules[15] the structure indicated in Table 1 appears very likely. The formation of these products fits eminently (CHART 1) the structure (II) arrived at earlier by other methods. Furthermore, the fact that all the derived naphthalenes carry a methyl group in the α-position is a proof for the presence of a methyl group at C_{11}. This fact together with the previous deductions

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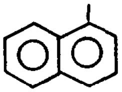
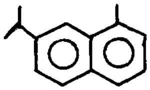
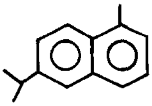
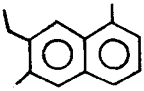
[14] Sukh Dev, J. Indian Chem. Soc. **32**, 325 (1955).

[15] B.A. Nagasampagi, R.C. Pandey, V.S. Pansare, J.R. Prahlad and Sukh Dev, Tetrahedron Letters

Table 1: Dehydrogenation Products of Isolongifolene

No.	Yield (%)	M.p.of TNB* complex	$\lambda_{max}^{heptane}$ in mμ, (ε x 10^{-2})	PMR signals for aliphatic protons	Identified as
1	8	150-51°	-	-	
2	68	108-09°	224 (560)$^+$ 228 (816) 273 (48)$^+$ 279 (51) 290 (38)$^+$ 305 (8)$^+$ 312 (2.4)$^+$ 318 (2.5)	CH_3- 158 CH_3 CH_3 77,84	
3	3	123-24°	222.5 (670)$^+$ 227 (843) 273 (50)$^+$ 278 (52.5) 288 (40)$^+$ 304 (6) 311 (3.8) 318 (4.4)	CH_3- 156 CH_3 CH_3 76,83	 By synthesis
4	7	124-25°	225 (670)$^+$ 230.5 (880)$^+$ 273 (47)$^+$ 282 (51)$^+$ 293 (35)$^+$ 317 (2.6)$^+$ 322 (1.8)$^+$	CH_3- 146 CH_3- 158 $CH_3 \cdot CH_2$- 71,78,85 CH_3 CH_2- (155),163, 170, 178	 ?

*trinitrobenzene.

$^+$Shoulder.

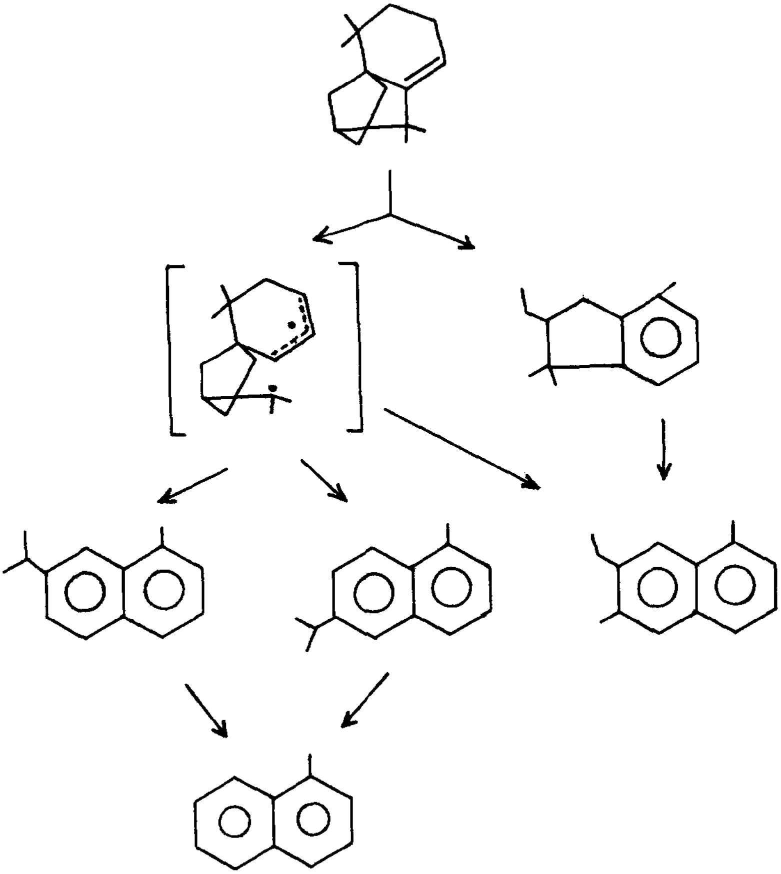
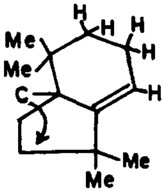
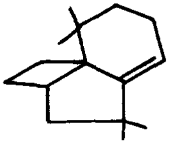


CHART 1.

about the nature of the methyl groups in isolongifolene, help extend the systematically derived part structure (XII) to (XIII). Since isolongifolene is tricyclic and has only four methyl groups, XIII can be extended only to two possible



XIII



XIV

alternatives (II) and (XIV) for isolongifolene. However, the latter structure stands ruled out as its genesis from longifolene cannot be rationalised and furthermore would involve a contraction of a five-membered ring of longifolene into a four-membered ring, which is considered unlikely. This leaves us with the unique formulation (II) for isolongifolene.

The possible mechanism of isomerisation of longifolene (I) to isolongifolene (II) will be discussed in the fuller communication.

"<u>β-Longifolene</u>"

The so-called "β-longifolene" of Zeiss and Arakawa[16] has been found to have the same infrared spectrum as isolongifolene. However since "β-longifolene" has a lower specific rotation (-23°) as compared to that of isolongifolene (-85°), the former must have been racemised to a greater extent. This has been confirmed by the preparation of the solid epoxide (m.p.40.5°-41.5°), which has been shown to be derived from (±)-isolongifolene, in much superior yields from "β-longifolene".

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[16] H.H.Zeiss and M.Arakawa, J.Amer.Chem.Soc. 76,1653(1954).

Since, it is difficult to visualise any mode of racemisation for (-)-isolongifolene, racemisation of longifolene must have intercepted the isomerisation. A fuller discussion of these ideas will be incorporated in the detailed paper.