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STUDIES IN SESQUITERPENES—XL*

ISOLONGIFOLENE (Part 1): STRUCTURE†‡

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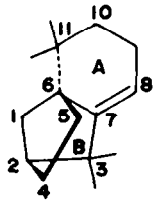
Abstract—Isolongifolene, $C_{15}H_{24}$, an artefact from an acid-catalysed rearrangement of longifolene, is shown to be II.

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

Earlier,[1] evidence has been presented to show that isolongifolene is tricyclic and has a carbon-skeleton different from that of longifolene.

Its PMR spectrum (Fig. 1) shows Me signals (sharp singlets) at 50(3H), 57(6H) and 62(3H) c/s. None of these signals arise from an isopropyl group (J, 6–7 c/s) since they appear in a spectrum, measured at 40 MHZ, at 33(3H), 37·5(6H) and 39·5(3H) c/s, and consequently all the four Me's of isolongifolene must be quaternary. A differential Kuhn–Roth C-Me estimation[2] clearly showed that these four Me's must be located as two $Me_2{=}C{=}C_2$ groups. This is consistent[3,4] with the IR spectra of isolongifolene and isolongifolane, both of which display the symmetrical Me C—H bending vibration as doublets (isolongifolene: 1360, 1380 cm^{-1}; isolongifolane: 1365, 1385 cm^{-1}) consisting of two bands of almost equal intensity.

The only olefinic linkage in isolongifolene must be trisubstituted (UV: ε_{210} 2260, ε_{215} 933, ε_{220} 232; IR: 818 cm^{-1}; PMR: 1 H triplet centred at 305 c/s, J = 4 c/s) and it follows from the multiplicity of the vinyl proton that it must be flanked by a methylene group.

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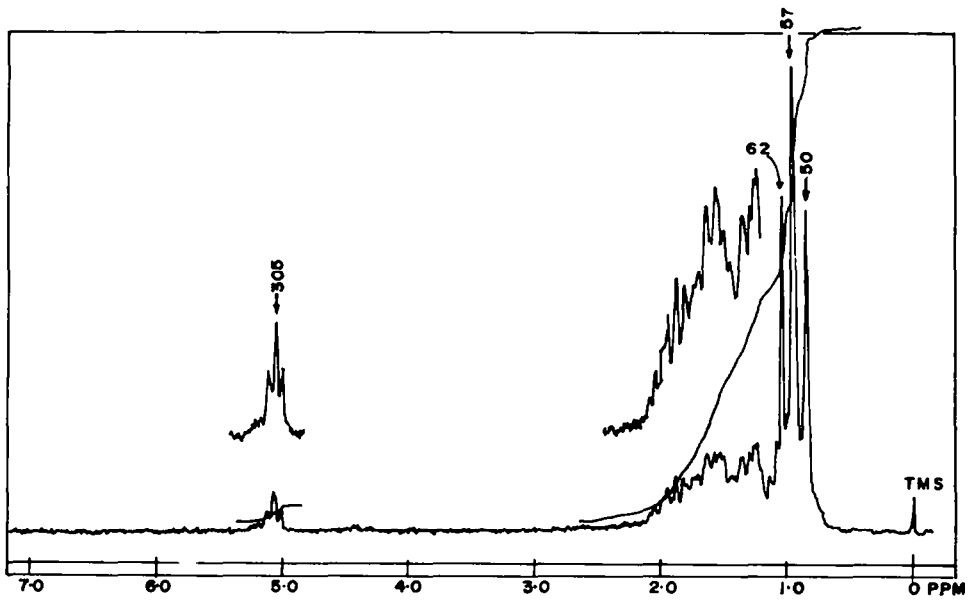


FIG. 1 IR Spectrum of isolongifolene.

Size of ring A. Treatment of isolongifolene with one mole equivalent of perbenzoic acid in benzene at ~0° gave a product, separable by low temperature crystallization into a solid (~8%; m.p. 40·5–41·5°, $[\alpha]_D$ ±0°) and a liquid having essentially identical IR spectra.* The spectral characteristics of the solid ($C_{15}H_{24}O$) compound show that these products represent the required isolongifolene-epoxide (III): PMR: 1 H triplet (J = 3 c/s) centred at 182 c/s[5], no vinyl proton; IR: no C=O or OH absorption, bands at 1244, 917 and 806 cm^{-1} assignable to a 1,2-epoxide.[6]

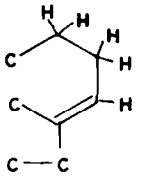
The above solid epoxide on exposure to BF_3-Et_2O was transformed into a saturated ketone (IV; IR: C=O 1715, C$\underline{H}_2$CO 1423 cm^{-1}; semicarbazone, m.p. 207–208°), quantitatively convertible into its epimer (V; IR: C=O 1698, C$\underline{H}_2$CO 1408 cm^{-1}) on filtration through active Al_2O_3. The liquid epoxide on treatment with BF_3-Et_2O behaved in an identical fashion. From the $\nu^{C=O}$ of these ketones it is apparent that the ethylenic linkage in the parent isolongifolene must be located in a cycle higher than 5-membered and in all likelihood a 6-membered ring. Furthermore both these ketones display in their PMR spectra signals in the δ = 2–2·5 region (Experimental) amounting to ≃ 3 H each and assignable[7] to methylene and methine protons flanking the CO function.

Oxidation of isolongifolene with sodium dichromate-acetic acid yielded, besides the saturated ketone IV (~20%, only partly racemic) a mixture (~40%) of two unsaturated ketones (VI, 70%; m.p. 34–35°, $[\alpha]_D$ −210°, semicarbazone, m.p. 226–228°; VII, 30%, m.p. 52–54°, $[\alpha]_D$ −1·8°, semicarbazone, m.p. 218·5–219·5°) separable through their semicarbazones. These two crystalline ketones showed identical UV (λ^{alc}_{max} 245 mμ, ε = 14,000), IR (C=O 1670, C=C 1640 cm^{-1}) and PMR (quaternary

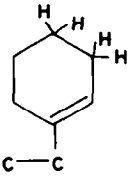
* It will become clear from the sequel that the solid and liquid products are derived respectively from (±)- and (−)-isolongifolene.

Me signals at 59, 62, 65 and 69 c/s; vinylic proton, sharp singlet at 333 c/s) spectra and hence by virtue of their difference in $[\alpha]_D$ must represent the (−) and (±)-modifications of the same unsaturated ketone. This would mean that isolongifolene as obtained by the acid-catalysed rearrangement is partly racemised.* Li-NH_3 reduction of VII, followed by chromic acid oxidation yielded a ketone (VIII; IR: C=O 1715 cm^{-1}) different from either IV or V; this proves that during the chromic acid oxidation of isolongifolene to give the unsaturated ketone, attack had been on the allylic methylene and not on the olefinic bond.[8] This ketone displays the scissoring frequency of the methylene flanking the CO[9] at 1420 cm^{-1}, the intensity of which is almost double that of the corresponding band of IV or V; thus, the keto group in VIII must be flanked by CH_2 groups on either side.

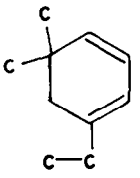
The data presented so far is consistent with the part structure IX.



IX



X



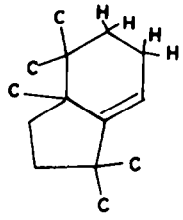
XII

LAH reduction of VI yielded an unsaturated alcohol, readily dehydrated to a conjugated diene (XI; IR: C=C 1650, 1585, 728 cm^{-1}). This diene on catalytic hydrogenation furnished isolongifolane, proving thereby that no skeletal rearrangement took place during its formation. Since, the λ_{max} of conjugated cyclic dienes is dependent on ring-size,[10] the highest value being for a cyclohexa-1,3-diene (λ_{max}^{hexane} 256·5 mμ, ε = 8000 for the unsubstituted cyclohexa-1,3-diene[11]), it became evident from the UV absorption (λ_{max}^{EtOH} 266·5 mμ, ε = 7470) of the diene (XI) that it must be a substituted cyclohexa-1,3-diene and hence, ring A of isolongifolene must be 6-membered. Part structure IX can now be extended to X. The PMR spectrum of the diene (XI) is in complete accord with the diene structure based on X and further requires that carbon 5 must be fully substituted as in XII to account for the spin–spin coupling pattern of the vinyl protons, which show up as a complex 9-line spectrum (total signal strength 3H; 302, 311, 319, 323, 326, 334, 339, 343 and 348 c/s) of the ABC type.

Size of ring B. In order to determine the size of the ring to which the olefinic linkage of isolongifolene is exocyclic, the saturated ketone (IV) available through the crystalline (±)-expoide appeared a useful starting point. The ketone on Baeyer–Villiger oxidation (perbenzoic acid) gave the required lactone (m.p. 79–80°; IR: C=O 1730 cm^{-1}; PMR: four quaternary Me's, 59, 62, 64·5 and 65·5 cm^{-1}; —CH—O—CO—, 1 H, partly split singlet at 248 c/s) in an excellent yield. The lactone on hydrolysis, followed by CrO_3 oxidation furnished a keto acid, $C_{15}H_{24}O_3$ (XIII; m.p. 107–108°). From the CO stretching frequencies of this keto acid (C=O 1735, 1710 cm^{-1}) and its

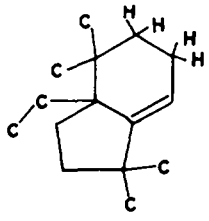
* This conclusion is also in accord with the results of perbenzoic acid oxidation, already described. This point is further discussed under "β-longifolene".

methyl ester (C=O 1732 cm^{-1}) it is clear that XIII must be a cyclopentanone and hence, ring B in isolongifolene must be 5-membered. The keto-function in XIII is highly hindered; thus the compound was recovered unchanged from attempted $NaBH_4$ reduction,[12] Wolff–Kishner reduction[13] or reduction through the thioketal procedure;[14] it also failed to yield a semicarbazone or a 2,4-dinitrophenylhydrazone. No bromination occurred under conditions[15] usually employed for total bromination of α-hydrogens in a ketone and the keto acid was recovered unchanged. Thus, both the positions α to the keto function in XIII, must be fully substituted. In view of the results just discussed, part structure XII can be extended to XIV.

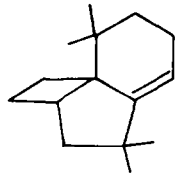


XIV

Structure of isolongifolene. The expression XIV accounts for fourteen out of fifteen C atoms of isolongifolene. Since, isolongifolene has only four quaternary Me's and these are present as two $Me_2C{=}C{=}C_2$ groups, the fifteenth C atom of isolongifolene must be linked to the angular C of XIV, as shown in XV. The expression XV can be extended only to two possible alternatives II and XVI for isolongifolene, which is tricyclic. However, the latter structure (XVI) is ruled out as its genesis from longifolene



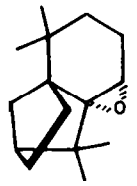
XV



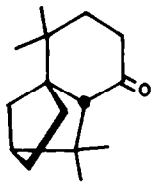
XVI

cannot be rationalized and furthermore would involve a contraction of a 5-membered ring of longifolene into a 4-membered ring, which is considered unlikely. This leaves the unique formulation II for isolongifolene. This structure is vindicated by subsequent degradative and synthetic studies described in the succeeding communications.

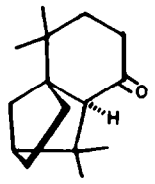
The structures of important products derived from isolongifolene, described above, can now be written:



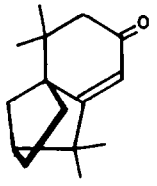
III



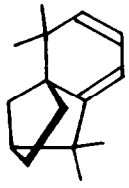
IV



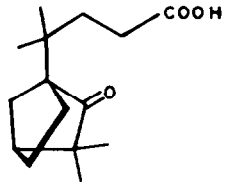
V



VI, VII



XI



XIII

The stereochemistry shown for isolongifolene epoxide (III) follows from the preferred peracid attack from the less-hindered side of isolongifolene, that is from the side opposite to the bimethylene bridge. This stereochemistry is fully borne out from the epoxide ring cleavage reactions, discussed in detail in another communication.[16] The BF_3-induced isomerization of an epoxide is visualized as a one-step concerted process,[17] hence the stereochemistry of the ketone resulting from the BF_3-Et_2O treatment of III should be as shown in IV. Its epimer, resulting from alumina isomerization should then be V.*

"β-*Longifolene.*" Zeiss and Arakawa[18] studied the hydration of longifolene under somewhat different conditions, but ended up with an isomer of longifolene, which these authors termed β-longifolene. β-Longifolene has $[\alpha]_D$ −16·5°, which is quite different from that of isolongifolene ($[\alpha]_D$ −78·1°, EtOH). During the course of present work, when it became apparent that isolongifolene is partially racemized, it appeared that the so-called β-longifolene of Zeiss and Arkawa could, in fact, be only much more racemized isolongifolene. This was fully borne out by a study of a sample of β-longifolene prepared according to the procedure of Zeiss and Arakawa. This product had the same GLC retention time as isolongifolene and the two exhibited identical IR and PMR spectra. As expected, Zeiss and Arakawa's hydrocarbon furnished a much superior yield (~40%) of the solid epoxide III on interaction with perbenzoic acid in benzene. Thus, "β-longifolene" is only much more racemized isolongifolene.

The extent of racemization in isolongifolene and "β-longifolene" has been computed as follows. The diene (XI) which was prepared from the optically pure αβ-unsaturated

* From models (Dreiding, bicyclo[2,2,1]heptane system improvised), it is hard to see why the equilibrium should be *entirely* in favour of V. The PMR and IR spectra (vide Experimental) of the two ketones are quite distinct to enable detection in a mixture.

ketone (VI) was hydrogenated to give a sample of optically pure (+)-isolongifolane. The optical rotation of this product was compared with that of isolongifolane obtained by hydrogenation of isolongifolene. From the results (Experimental) it follows that isolongifolene must be racemized to the extent of ~30% and thus optically pure isolongifolene should have α_D around $-125°$. "β-longifolene" with $\alpha_D = -24°$ should, thus be racemic to the extent of ~80%.

It has been recently[19] observed that with BF_3-Et_2O, longifolene rapidly isomerizes to isolongifolene. This product, as revealed by its $[\alpha]_D$ $-27°$ is also quite racemized.

Since, it is difficult to visualise any mode of racemization for (−)-isolongifolene,

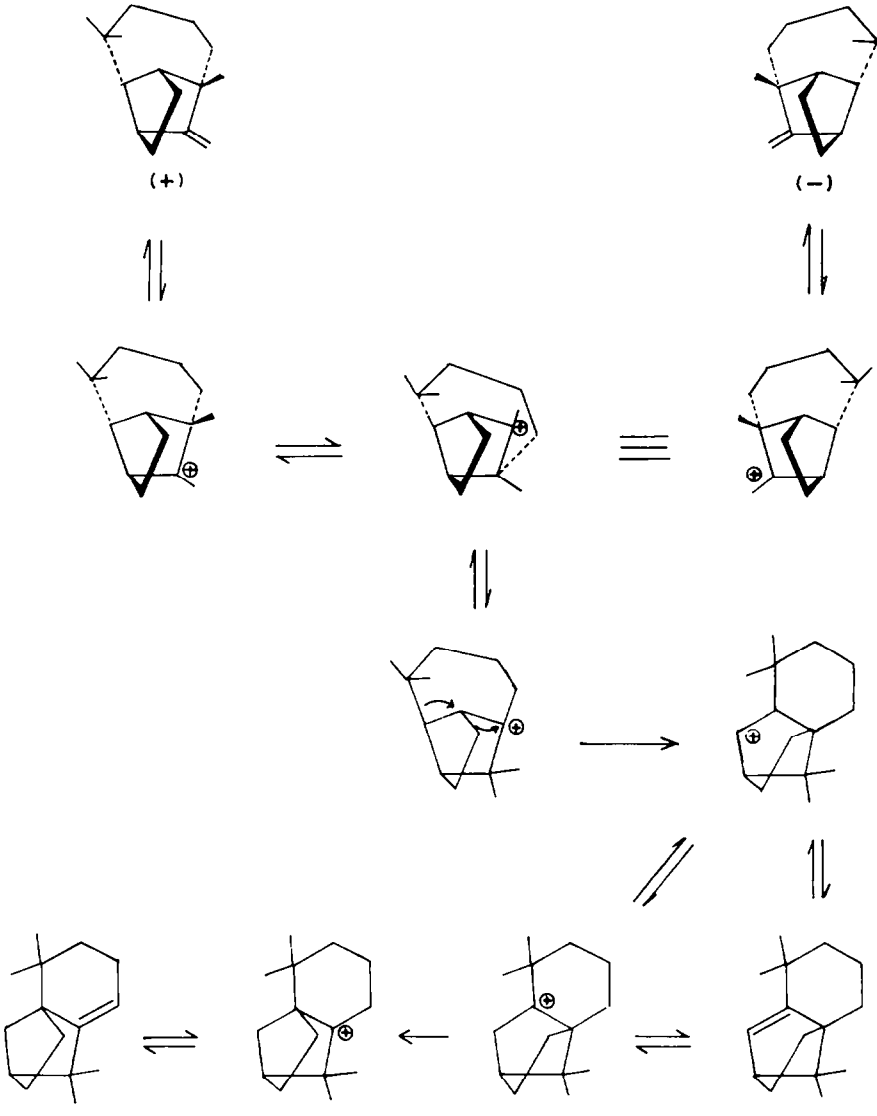


FIG. 2 Racemization and isomerization of longifolene in presence of an acid.

racemization of longifolene (cf. racemization of camphene[20]) must have intercepted the isomerization. Fig. 2[1] very briefly rationalizes the racemization and isomerization of longifolene in terms of classical carbonium ions. A detailed discussion of this mechanism will be presented in another publication describing the results of deuterium incorporation and intermediate interception.

EXPERIMENTAL

All m.ps and b.ps are uncorrected. Light petroleum refers to the fraction b.p. 40–60°. All solvent extracts were finally washed with brine and dried over Na_2SO_4. Optical rotations were measured in $CHCl_3$.

UV spectra were taken on a Perkin–Elmer spectrophotometer, model 350, in 95% EtOH. IR spectra were recorded as smears (liquids) or nujol mulls (solids), unless stated to the contrary, on a Perkin–Elmer Infracord, model 137E. PMR spectra were taken in 10–20% soln in CCl_4 with TMS as the internal standard, on a Varian A-60 spectrometer; signals are recorded in c/s relative to TMS as zero.

Analytical GLC was run on "Aerograph", model A-350-B, using a 150 cm × 5 mm column packed with 20% stationary phase on Chromosorb W (60–80 mesh) with H_2 as carrier gas.

Alumina used for chromatography was made neutral by the HNO_3 method[22] and graded according to Brockmann.[23]

Isolongifolene

(i) *By Bertram–Walbaum reagent.*[24] Longifolene[1] (550 g) gl AcOH (2200 ml) and 50% (v/v) H_2SO_4aq (38·5 ml) were mixed and kept at room temp (~25°) for 8 days. The reaction mixture, which was heterogenous in the beginning became homogeneous after 2 days. The brown reaction mixture was poured into water (2 l.) the organic layer separated and the aqueous phase extracted with ether (100 ml × 4). The combined organic extracts were washed neutral with water and dried. The solvent was flashed off and the residue fractionated to get a hydrocarbon fraction (b.p. 106–120°/7 mm, 365 g, $[\alpha]_D$ −74·8°) and a hydrated fraction[1] (b.p. 120–145°/7 mm, 213 g, $[\alpha]_D$ +14°). The hydrocarbon fraction, representing crude isolongifolend was precisely refractionated to get pure isolongifolene (recovery ~80%, b.p. 105–106°/6 mm 95°/3 mm), the α_D (neat) of the product varied, as the fractionation proceeded, from −86·7 to −90·5°. Unless stated to the contrary; isolongifolene employed for various experiments was obtained by this method.

(ii) *According to the procedure of Zeiss and Arakawa.*[18] Longifolene (100 g) was treated with a mixture of AcOH (500 ml), water (700 ml) and conc H_2SO_4 (200 ml) and the reaction mixture stirred on a water bath (inside temp 85°) for 14 days. The product was worked up as above to give a brown liquid, which was distilled, finally over Na to give "β-longifolene": b.p. 100°/4 mm, α_D −24·0 (neat).

(iii) *By the action of* BF_3-Et_2O*. To longifolene (100 g) in gl AcOH (500 ml), $BF_3.Et_2O$ (5 ml) was added at room temp (~25°) and the reaction mixture left for 20 min when all longifolene had been consumed (TLC, $AgNO_3$-SiO_2 gel[26]; solvent: 10% C_6H_6 in hexane). The reaction mixture was, then, worked up essentially as described under (i). The crude product (101·5 g) was fractionated to give: (a) isolongifolene, b.p. 94–95°/3 mm, $[\alpha]_D$ −27°, yield 63 g; (b) intermediate cut, b.p. 94–100°/1·5 mm, 4 g; (c) acetate mixture, b.p. 130–134°/1·5 mm, 33 g.

Use of C_6H_6 instead of AcOH in the above experiment gave isolongifolene in a yield of ~95% ($[\alpha]_D$ −24°).

Isolongifolene epoxide (III)

To isolongifolene (24·48 g, 0·12 mole), dissolved in dry benzene (50 ml), cooled to 0°, was added dropwise a benzene soln (300 ml, precooled to 5°) of perbenzoic acid (PBA, 16·56 g, 0·12 mole) during 10 min. At the end of 6·5 hr at 0–5°, the reaction was almost complete (iodometric titration) and, was worked up by extraction with 10% $NaHCO_3$aq (100 ml × 3). The organic layer was dried and the solvent removed (water–bath/suction) to yield an almost colourless liquid residue (24·5 g). Dilution of this material with hexane (20 ml), followed by chilling in dry-ice–acetone (−78°) gave a small quantity of solid, which was separated by inverse cold filtration and recrystallized thrice from hexane at low temp to furnish III (1·63 g) as a white crystalline powder, m.p. 40·5–41·5°, $[\alpha]_D$ ±0°; PMR spectrum: quaternary methyls: 45, 55, 55 and 65 c/s. (Found: C, 82·4; H, 11·3. $C_{15}H_{24}O$ requires: C, 81·8; H, 11·0%). Solvent removal from the combined filtrates gave a liquid, which was distilled: b.p. 102–112°/1·7 mm.

When in the above experiment, the so-called "β-longifolene" was employed, the crude product (32·8 g

* Experiment carried out by Dr. R. R. Sobti of this laboratory.

from 30·1 g of "β-longifolene") on cooling to ~0°, crystallized *en masse*. The solid oxide, m.p. 38–39° (13·5 g, 41·5%) was isolated from this material by three recrystallizations from hexane at low temp (dry ice).

Rearrangement of isolongifolene oxide to ketone IV

(i) *Rearrangement of (±)-epoxide.* The solid oxide (0·5 g) in dry benzene (25 ml) was mixed with freshly distilled BF_3-Et_2O (0·4 ml) and left aside, protected from moisture, at room temp (~25°) for 24 hr. The reaction mixture was then diluted with ether (20 ml), washed with water (10 ml), $NaHCO_3$ aq (10 ml), water (10 ml × 2) and dried. Solvent was removed and the residue distilled: b.p. 122°/2 mm, $n_D^{26.5}$ 1·5005, $[\alpha]_D \pm 0$; IR spectrum: distinguishing band at 1100 cm^{-1}, absent in the spectrum of epimer V; PMR spectrum: quaternary Me's at 59, 61, 73 and 73 c/s; —CH—C(=O)—, 1H singlet at 123 c/s. (Found: C, 81·6; H, 11·0. $C_{15}H_{24}O$ requires: C, 81·8; H, 11·0%).

The *semicarbazone* (pyridine method) was recrystallized from aqueous EtOH to give white micro needles, m.p. 207–208° (dec). (Found: N, 15·5. $C_{16}H_{27}ON_3$ requires: N, 15·15%).

The 2,4-*dinitrophenylhydrazone* prepared *via* the above semicarbazone by the H_2SO_4 method, was crystallized from aqueous EtOH-pyridine to give silky orange needles, m.p. 243–244° (dec). (Found: N, 13·6. $C_{21}H_{28}O_4N_4$ requires: N, 14·0%).

(ii) *Rearrangement of total oxide mixture.* The total PBA-isolongifolene oxidation product (mixture of racemic and optically-active III; 10 g) in benzene (100 ml) was isomerized with BF_3-Et_2O (2 ml) as above. The product (8·4 g) thus obtained, had, b.p. 117°/1·6 mm, $[\alpha]_D$ +9·2° (neat) and its IR spectrum was completely superimposable on that of the ketone described under (i) above.

The *semicarbazone* prepared from this material had a final m.p. of 212° (dec) and is evidently derived from the (+)-isomer. Its mixed m.p. with the semicarbazone, described under (i) was 210–212°. (Found: N, 15·4. $C_{16}H_{27}ON_3$ requires: N, 15·15%).

The 2,4-*dinitrophenylhydrazone*, likewise showed a higher m.p. 248–249°.

Epimerization of ketone IV *to ketone* V

Ketone IV ($[\alpha]_D$ +9·2°; 0·58 g) in light petroleum (50 ml) was adsorbed in a column of Al_2O_3 (grade II; 30 g, 10 × 2·5 cm) and allowed to remain for 20 hr. Elution with light petroleum (50 ml × 2) gave little material. Further elution with ether (300 ml) and removal of solvent from the eluate gave V (0·4 g): b.p. 111–112°/2 mm, n_D^{34} 1·4925, $[\alpha]_D$ −36·2° (*c*, 4·9%); IR spectrum: distinguishing band at 1280 cm^{-1}, v.v. weak in the spectrum of the epimer IV; PMR spectrum: quaternary Me's at 54, 57, 60 and 70 c/s; —CH—C(=O)—, 1H singlet at 129 c/s.

Sodium dichromatic-acetic acid oxidation of isolongifolene

Isolongifolene (40 g), crystalline sodium dichromate (120 g) and gl AcOH (650 ml) were mixed and the soln stirred at 55–60° for 8 hr. The reaction mixture was then treated with EtOH (80 ml) to destroy the excess of oxidant and the resulting green soln diluted with water (1 l.). The organic phase was separated and the aqueous layer extracted with benzene (60 ml × 4). The organic extracts were combined, washed with water and then separated into acidic (gummy, negligible, rejected) and neutral (oil, 38 g) parts in the usual way.

The neutral product, from four such experiments, was combined and fractionated: *Fraction* 1 (18·6 g): b.p. 90–94°/3 mm, n_D^{25} 1·4965; *Fraction* 2 (28·5 g): b.p. 110–117°/2 mm, n_D^{25} 1·5000; *Fraction* 3 (49·2 g): b.p. 124–129°/2 mm, n_D^{25} 1·5180; *Fraction* 4 (4·4 g): b.p. > 130°/2 mm, n_D^{25} 1·5139.

Fraction 1 was essentially unchanged isolongifolene (b.p. IR). Fraction 4 was not studied further.

Fraction 2 (2 g) was treated with semicarbazide hydrochloride (2 g) in aqueous pyridine and alcohol and, the derivative (1·45 g, m.p. 188–205°) collected after 24 hr. Recrystallization from aqueous EtOH gave pure semicarbazone (1·22 g) m.p. 202–203° (dec). The semicarbazone (1·0 g), oxalic acid (3 g), heptane (15 ml) and water (20 ml) were mixed up and refluxed with stirring for 4 hr. The regenerated ketone was isolated in the usual manner: b.p. 125–126°/3 mm, n_D^{24} 1·4987 yield, 0·6 g. The IR spectrum of this ketone is superimposable on that of ketone IV described earlier.

Isolation of αβ-unsaturated ketones VI *and* VII. Fraction 3 (15 g) was treated with semicarbazide hydrochloride (12 g), water (24 ml) and pyridine (12 ml) and sufficient alcohol to make the reaction mixture homogeneous. After several hr at room temp the semicarbazone (19 g, m.p. 212–227°) was collected. This was refluxed for 0·5 hr with pyridine (15 ml) and EtOH (150 ml), cooled (room temp) and the insoluble part

(15·7 g, m.p. 226–231°) collected. This material was again refluxed for 15 min with pyridine (125 ml) and EtOH (125 ml) and, after cooling the *insoluble semicarbazone* (12·31 g, m.p. 228–231°) collected. The two filtrates were separately concentrated at ~50°/30 mm to ~30 ml each and the solids (1·32 g, m.p. 215–217°, and 2·2 g, m.p. 217–219°, respectively from the first and second filtrate) collected and mixed. This semicarbazone will be referred to as the more *soluble semicarbazone.*

The insoluble semicarbazone (12·3 g), oxalic acid (36 g), heptane (180 ml) and water (380 ml) were mixed and refluxed with stirring for 9 hr. The regenerated ketone was isolated from the reaction mixture in the usual manner and distilled to give pure VI (8·52 g): b.p. 142–144°/4·5 mm, m.p. 34–35° (EtOH), $[\alpha]_D$ −210·1° (*c*, 1·9%). (Found: C, 82·8; H, 10·0. $C_{15}H_{22}O$ requires: C, 82·51; H, 10·16%). *Semicarbazone*, m.p. 226–228° (Found: N, 15·26. $C_{16}H_{25}ON_3$ requires: N, 15·27%). 2,4-*Dinitrophenylhydrazone*, fine red needles, m.p. 200–201°. (Found: N, 14·1. $C_{21}H_{26}O_4N_4$ requires: N, 14·0%).

The more soluble semicarbazone (4·7 g) was also treated with aqueous oxalic acid, as above, to furnish, after distillation pure VII (3·6 g): b.p. 143–144°/4·5 mm, m.p. 52–54° (EtOH), $[\alpha]_D$ −1·8° (*c*, 1·1%). (Found: C, 82·7; H, 10·1. $C_{15}H_{22}O$ requires: C, 82·51; H, 10·16%). *Semicarbazone*, m.p. 218·5–219·5°. (Found: N, 15·0. $C_{16}H_{25}ON_3$ requires: N, 15·27%). 2,4-*Dinitrophenylhydrazone*, fine red needles, m.p. 195·5–196·5°. (Found: N, 14·1. $C_{21}H_{26}O_4N_4$ requires: N, 14·0%).

Li-NH_3 *Reduction of ketone* VII *and oxidation of resulting product to give* VIII

The racemic unsaturated VII (1·0 g) in dry ether (60 ml) was added dropwise with stirring to a soln of Li (0·2 g) in liquid ammonia (300 ml) during 15 min. After stirring for another 45 min, EtOH (25 ml) was added to the still blue soln and then ammonia was allowed to evaporate. Water (175 ml) was added to the residue and the product taken up in ether (20 ml × 5). This was concentrated to *ca.* 20 ml and then filtered to remove an ether insoluble impurity (40 mg). Removal of solvent from the filtrate gave a waxy solid (0·95 g; IR: 3279, 1695, 1404 and 1028 cm^{-1}) which (0·85 g) was dissolved in AcOH (6 ml) and directly oxidized with chromic acid (0·8 g dissolved in 2 ml of water and 8 ml AcOH) at room temp (25°) for 12 hr. Usual work up gave ketone VIII (0·55 g): b.p. 136–138°/5 mm. This was converted into its *semicarbazone*, m.p. 234–235° (pyridine-EtOH). (Found: C, 69·9; H, 10·1. $C_{16}H_{27}ON_3$ requires: C, 69·27; H, 9·81%). Pure ketone was regenerated from the semicarbazone by the aqueous oxalic acid-heptane method:[25] b.p. 130–135° (bath)/2·5 mm; IR spectrum: 1715, 1420, 1389, 1370, 1302, 1256, 1175, 1085 and 934 cm^{-1}. (Found: C, 82·1; H, 11·4. $C_{15}H_{24}O$ requires: C, 81·76; H, 10·98%).

Dehydroisolongifolene (XI)

The levorotatory unsaturated VI (4·0 g) in ether (100 ml) was reduced with LAH_4 (0·3 g) suspended in ether (40 ml), in the usual fashion, the reaction mixture being worked up with 2% Rochelle salt soln (100 ml). The resulting crude alcohol (3·98 g) was dehydrated by distilling it in presence of freshly fused $KHSO_4$ (0·8 g). The product was purified by filtration of its hexane soln through a column of Al_2O_3/I. The pure diene was obtained as a colourless liquid: b.p. 77°/1·3 mm, n_D^{30} 1·5058, $[\alpha]_D$ −479·4° (*c*, 0·11%); PMR spectrum: four quaternary Me's at 53, 62 and 66 c/s. (Found: C, 89·06; H, 10·76. $C_{15}H_{22}$ requires: C, 89·04; H, 10·96%).

Isolongifolane

(i) *From isolongifolene.* This sample was prepared from isolongifolene with $\alpha = -88{\cdot}4°$, by the procedure already described.[1] The product had $[\alpha]_D^{30}$ +3·24 (*c*, 3·3%). PMR spectrum: four quaternary Me's at 51, 51, 51 and 57 c/s.

(ii) *From dehydroisolongifolene.* The pure (−)-diene (0·16 g) in AcOH (8 ml) was catalytically reduced over pre-reduced Adam's PtO_2 catalyst (20 mg) at 27°/710 mm, when the 2 mole equiv of H_2 had been absorbed during 5 hr and further absorption ceased. The usual work up gave a product, which was filtered through $AgNO_3$-SiO_2 gel[26] (21 cm × 0·6 cm) and distilled to give a liquid (0·12 g) with $[\lambda]_D^{30}$ +4·68 (*c*, 2·75%). Its IR spectrum was superimposable on that of product, described under (i).

Baeyer–Villiger oxidation of ketone IV

The saturated IV (1·0 g) in $CHCl_3$ (5 ml) was treated at room temp (25°) with a $CHCl_3$ soln of PBA (2 mole equiv; 23 ml containing 1·27 g of PBA) for 48 hr when TLC monitoring (solvent system: 2% EtOAc in C_6H_6) showed almost complete transformation. The reaction mixture was washed with KOH aq (2·5%; 25 ml × 4), brine and dried. Removal of solvent furnished a waxy solid (1·05 g), which was crystallized from light petroleum at 0° to give colourless needles (0·32 g), m.p. 79–80°, $[\alpha]_D$ ±0° (*c*, 11%). (Found: C, 75·71; H, 10·13. $C_{15}H_{24}O_2$ requires: C, 76·22; H, 10·24%).

Hydrolysis of lactone and oxidation to the keto acid (XIII)

The above solid lactone (1·0 g) was hydrolysed with KOH aq (3 g KOH in 5 ml of water and 20 ml of EtOH) by refluxing for 3 hr. Usual work up with ether gave the crude hydroxy acid as a colourless gum (1·01 g). This was taken up in acetone (10 ml) and treated, at room temp, with Jones reagent[27] (2·67 g of CrO_3 in 2·3 ml H_2SO_4 and 4·0 ml H_2O, and the total volume made to 10 ml with more H_2O) till an orange colour persisted (2 ml). After 3 hr at room temp (27°), the reaction mixture was diluted with water (50 ml) and extracted with ether (50 ml × 3). The solvent extract was washed with brine, dried and free of solvent to give the crude keto acid as a solid (0·9 g) which was recrystallized from light petroleum to furnish white flakes (0·45 g), m.p. 107–108°; PMR spectrum: four quaternary Me's, 12 H signal at 60 c/s, with shoulders at 60·5 and 61 c/s; UV spectrum: λ_{max}^{EtOH} 292 mμ, $\varepsilon = 21$. (Found: C, 71·57; H, 9·91; Neut. Equiv. 256. $C_{15}H_{24}O_3$ requires: C, 71·39; H, 9·52%; Neut. Equiv. 252).

The *methyl ester* (CH_2N_2 method) was distilled to give a colourless liquid: b.p. 143–147°/1·7 mm, n_D^{30} 1·4771. (Found: C, 72·50; H, 9·80. $C_{16}H_{26}O_3$ requires: C, 72·14; H, 9·84%).

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