443. *An Independent Confirmation of the Structure of Geijerene by Physical Methods.*

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The natural hydrocarbon geijerene, $C_{12}H_{18}$, is converted into isogeijerene by the action of potassamide in liquid ammonia. Examination of the ultraviolet, infrared, and nuclear magnetic resonance spectra of these compounds, and examination of the ions produced in the mass spectrometer from geijerene and hexahydrogeijerene permit assignment of the probable structure (VII) to geijerene. Some ancillary evidence provides further support for this structure, which has been independently proved by Sutherland.

The chemistry of geijerene, an optically inactive hydrocarbon, $C_{12}H_{18}$, from the essential oil of *Geijera parviflora* Lindley, was submitted to preliminary investigation by Penfold and Simonsen.[1] They showed it to be a monocyclic triene since it could be hydrogenated to hexahydrogeijerene, $C_{12}H_{24}$. Under milder conditions a tetrahydro-derivative was obtained containing $\geq C{=}CH_2$ since oxidation gave a ketone $C_{11}H_{20}O$. No aromatic compound could be detected after refluxing with selenium.

We began a further investigation in 1954 but, except for the reactions in liquid ammonia mentioned below, we had done little more than repeat the earlier experiments when we learned that Dr. M. D. Sutherland (Queensland) had made considerable progress with degradative work and this aspect was abandoned. We thought, however, that it would be of interest to see how far physical methods could be used to elucidate the structure of geijerene without recourse to chemical evidence relating it to known compounds.

At a stage of our work represented by formula (IV) and with several formulæ including (VII) and (VIII) under our consideration, Dr. Sutherland informed us that he had conclusively determined the structure (VII). We willingly concede priority to him in determination of the structure,[2] but most of the value of the present work is lost unless it is clear that we did in fact independently consider (VII), and we believe that work then in progress would in any case have led us to prefer this formula to the several other possibilities. Dr. Sutherland suggested simultaneous preliminary publication, but the present work could not be suitably condensed.

Ultraviolet Spectra.—Geijerene contains three double bonds which must be unconjugated since it has no selective ultraviolet absorption above 220 mμ. In view of its low molecular weight and cyclic nature we thought that there was a high probability of two double bonds being separated by only $\geq CH-$ or $-CH_2-$. If this were so, then they would become conjugated by the action of potassamide in liquid ammonia.[3] Conjugation in fact took place under these conditions, to give isogeijerene with $\lambda_{max.}$ 244 mμ (ε 8000) corresponding to a new *trans*-diene system. This isomer, or geijerene itself (presumably with preliminary conjugation), was reduced by potassium in liquid ammonia to a dihydroisogeijerene.

Infrared Spectra.—The spectrum of geijerene showed the presence of both $\geq C{=}CH_2$ ($\nu_{max.}$ 898 cm.$^{-1}$) and $-CH{=}CH_2$ ($\nu_{max.}$ 1005, 912 cm.$^{-1}$) groupings. Tetrahydrogeijerene retained the band due to $C{=}CH_2$ ($\nu_{max.}$ 895 cm.$^{-1}$), and the derived ketone, $C_{11}H_{20}O$, had the spectrum of a methyl ketone [3] ($\nu_{max.}$ 1712, 1365 cm.$^{-1}$). Geijerene, therefore, contained $-CH{=}CH_2$ and $-CMe{=}CH_2$ groups, and in accord with this assumption the spectrum of hexahydrogeijerene showed bands due to isopropyl ($\nu_{max.}$ 1392, 1375, 1173, 1155 cm.$^{-1}$) and methyl ($\nu_{max.}$ 1385 cm.$^{-1}$). The nature of the third double bond of geijerene remained uncertain for the moment, as there was no band of comparable strength which could be related to it.

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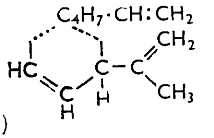
[1] Penfold and Simonsen, *J. Proc. Roy. Soc. N.S.W.*, 1932, **66**, 332.

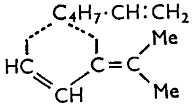
[2] Sutherland, *Chem. and Ind.*, 1959, 1220.

[3] Birch, *J.*, 1947, 1642.

Isogeijerene had lost the $>C{=}CH_2$ band but retained those due to $-CH{=}CH_2$ ($\nu_{max.}$ 1010, 903 cm.$^{-1}$) and showed a strong band probably due to a *cis*-$CH{=}CH-$ group [4] ($\nu_{max.}$ 752 cm.$^{-1}$). From what is known of the type of reaction involved in the production of isogeijerene [3] it was unlikely that more than one double-bond movement occurred, so that the *cis*-$CH{=}CH-$ was present in geijerene and therein related to the $-CMe{=}CH_2$ group as shown in (I). The spectrum of geijerene showed bands at $\nu_{max.}$ 700 and 785 cm.$^{-1}$ which can be ascribed [5] to this *cis*-$CH{=}CH-$ group. Isogeijerene would then contain the structure (II), and this expectation was supported by the presence in dihydroisogeijerene of a trisubstituted double bond ($\nu_{max.}$ 815 cm.$^{-1}$) as well as the vinyl group ($\nu_{max.}$ 1008, 912 cm.$^{-1}$), indicating structure (III).

Since the early work of R. N. Jones and his colleagues [4,6] in the steroid field high-resolution infrared spectroscopy has been employed to a limited extent to distinguish between methylene groups adjacent to, and removed from, unsaturated centres; presumably the two characteristic methyl-group frequencies suffer similar changes due to environment, but this does not appear to have been investigated in detail. Geijerene has five bands in the region 1400—1470 cm.$^{-1}$ ($\nu_{max.}$ 1413, 1436, 1446, 1452, 1460 cm.$^{-1}$) and two in the region 1360—1400 cm.$^{-1}$ ($\nu_{max.}$ 1370, 1375 cm.$^{-1}$) consistent with the presence of three types of methylene and two types of methyl group. This conclusion is to be classed as very highly probable rather than certain, since it is not impossible for a close pair such as the 1446—1452 cm.$^{-1}$ bands to be two components due to one group. In the subsequent discussion the frequency assignments made are based upon the literature previously cited and upon the review by Jones and Sandorfy.[7] An incorrect assignment would not affect the final conclusions which are based on the number of bands observed. One methyl group ($\nu_{max.}$ 1446, 1370 cm.$^{-1}$) is shown in formula (I), the other ($\nu_{max.}$ 1460, 1375 cm.$^{-1}$) is probably in a position not adjacent to a double bond. Formula (I) accommodates two $C{=}CH_2$ which contribute to one band ($\nu_{max.}$ 1413 cm.$^{-1}$) that probably overlaps the weak in-plane CH bending vibration of the *cis*-$CH{=}CH-$ group. The remaining two bands probably correspond to $-CH_2-[C{=}C-]$ ($\nu_{max.}$ 1436 cm.$^{-1}$) and to $-CH_2-$ isolated from unsaturation (ν 1452 cm.$^{-1}$). If we allow the minimum number of groups in each class and take into account the previous deductions, we dispose of eleven carbon atoms and all of the hydrogen atoms in geijerene, and formula (I), can then be expanded to (IV).


(I)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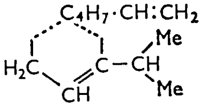
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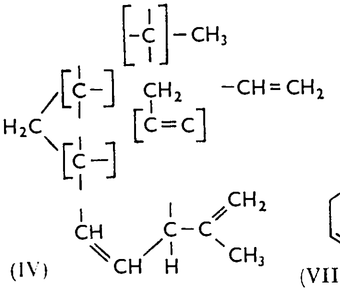
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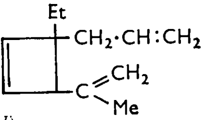
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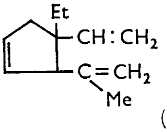
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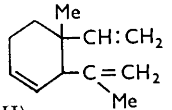
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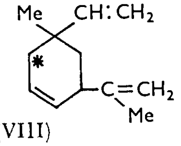
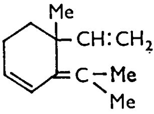

(VIII)


(IX)

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[4] Jones, Cole, and Nolin, *J. Amer. Chem. Soc.*, 1952, **74**, 5662.

[5] Henbest, Meakins, and Wood, *J.*, 1954, 800; Allan, Meakins, and Whiting, *J.*, 1955, 1874.

[6] Jones and Cole, *J. Amer. Chem. Soc.*, 1952, **74**, 5648; Jones and Herling, *J. Org. Chem.*, 1954, **19**, 1252.

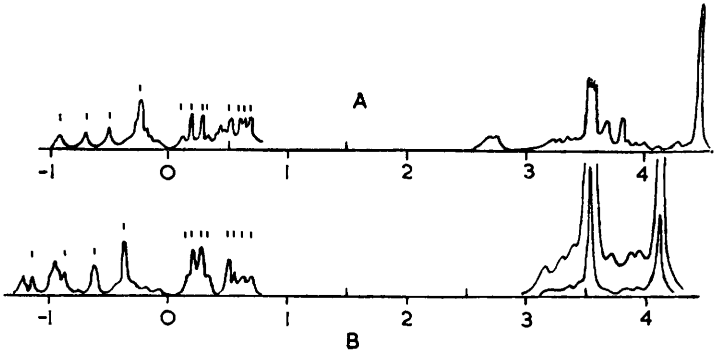
[7] Jones and Sandorfy, " Techniques of Organic Chemistry," Interscience Publ. Inc., New York, 1956, Vol. IX, p. 331.

The remaining carbon atom must be quaternary if all our deductions are correct. The ring can also be four-, five-, or six-membered, so that formulæ of types (V), (VI), (VII), and (VIII) required consideration.

Nuclear Magnetic Resonance Spectra.—The chemical shift scale, σ, quoted below is based on an approximate water zero (see Experimental section). The main correlations between hydrocarbon structures and chemical shifts on this scale have been well summarised by Pople, Schneider, and Bernstein.[8]

The spectrum of geijerene itself (Fig. A) shows twelve lines (marked with vertical strokes) caused by the hydrogens of $CH_2{=}CH{-}[C{\equiv}C_3]$ or $CH_2{=}CH{-}\left[C\begin{smallmatrix}{/\!\!/}C\\ {\backslash}C\end{smallmatrix}\right]$, *i.e.*, of a vinyl group attached to a carbon atom carrying no other hydrogens. This whole pattern of lines is closely similar to, for example, that observed for the vinyl group of 3,3-dimethyl-1-butene by Alexander.[9] A conjugated diene structure is ruled out by the lack of ultraviolet absorption. These three hydrogen atoms have approximate σ values of —0·6, +0·25, and +0·63. The presence of additional olefinic =CH– is shown by bands at σ —0·2, +0·15. The band at σ 2·73 corresponds to one or more hydrogens of the type $[C{=}C]{-}\overset{|}{C}H{-}\left[\overset{|}{\underset{|}{C}}{-}\right]$ or $[C{=}C]{-}\overset{|}{C}H{-}[C{=}C]$. The strong band at σ 3·55 is probably due to CH_2 or Me of the type Me–[C=C]; the fine structure suggests interaction with 2H at the other end of the double bond, *i.e.*, that the grouping $Me{-}\overset{|}{C}{=}CH_2$ is present. The strong band at σ 4·45 corresponds to $Me{-}[C{\equiv}C_3]$. We have already deduced that the vinyl group is attached to a quaternary carbon atom, and since the C_4H_7 residue of (I) can contain only one such carbon atom the molecule must contain $Me{-}C[C_2]{-}CH{=}CH_2$. The remaining complex band-structure in the region 3·2—4·0 corresponds to interacting CH or CH_2 groups in adjacent positions, some of these being adjacent to [C=C] (3·2—3·4).

Nuclear magnetic resonance spectrum of (A) *geijerene and* (B) *isogeijerene.*



In isogeijerene the 12-line vinyl pattern remains (Fig. B) although the quartet of the lone C=CH is shifted to ~ —0·73. Olefinic CH additional to the vinyl group gives rise to doublet bands centred near —1·1 and a broad band near —0·3. The very strong and sharp band at 3·55 corresponds to Me–[C(C)=C] and because of its strength probably two such groups are present, as in $Me_2C{=}C$. The strong band at 4·15 indicates one Me of the type $Me{\cdot}[C{\equiv}C_3]$. The same comments as for geijerene apply to the broad bands in the region 3·1—4·0.

There is nothing in the above deductions to contradict the conclusions drawn from the infrared spectra. In addition, they seem to rule out any formula containing an angular

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[8] Pople, Schneider, and Bernstein, " High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, 1959, Ch. 11.

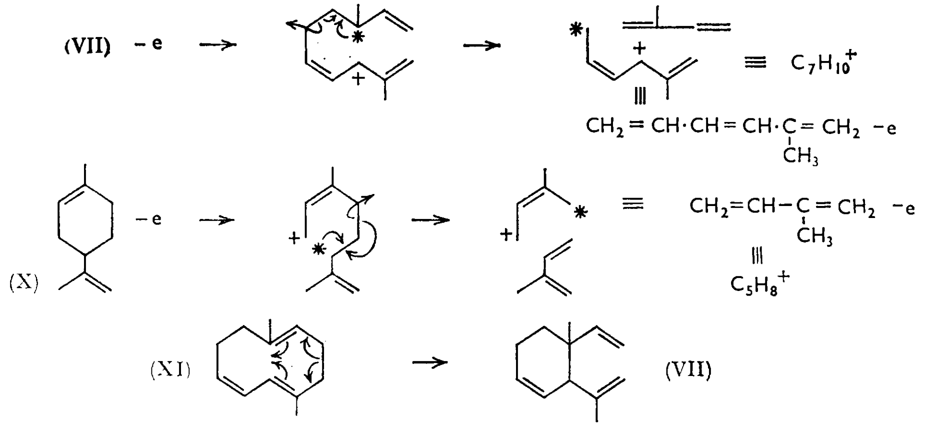
[9] Alexander, *J. Chem. Phys.*, 1958, **28**, 358.

ethyl group; the remaining possibilities (VII) and (VIII) fit the data very well. The olefinic CH band in geijerene at —0·2 is probably due to –CH=CH– and that in the region 0·5 to the C=CH$_2$ function of the MeC(C)=CH$_2$ group.

The structure (IX) also fits well the spectrum of isogeijerene; the group Me$_2$C=C shows up particularly well. The fact that the Me·[C=C$_3$] and –CH=CH$_2$ (vinyl) bands are both shifted considerably when compared with the spectrum of geijerene indicated that the ring substituents were probably adjacent, as in (VII), rather than separated, as in (VIII). The doublet of olefinic CH bands at —0·95 and —1·2 are probably caused by the =CH– of the –CH=CH– group which is adjacent to the conjugated double bond; the main separation is probably caused by strong spin–spin interaction with the other –CH=, and weak long-range coupling with the nearer of the two –CH$_2$– groups could give rise to the unresolved triplet contours. Resonance of the other –CH= of the –CH=CH– would be expected to be more widely split, both by strong interaction with the immediately adjacent –CH$_2$– group and by strong interaction with =CH– at the other end of the double bond.

Evidence from the spectra of geijerene and isogeijerene was, therefore, strongly in favour of formula (VII) for the former. This was also supported by evidence of the hindered nature of the –CMe=CH$_2$ group in geijerene, as shown by its resistance to hydrogenation, and of the acetyl group in the ketone from tetrahydrogeijerene, as shown by its slow reaction with semicarbazide and failure [1] to lead to the bromoform reaction.

Mass Spectra.—Examination of the mass spectra (at 70 ev) of geijerene and hexahydrogeijerene confirmed the formulæ as $C_{12}H_{18}$ and $C_{12}H_{24}$, respectively, by peaks at the appropriate masses, small isotope peaks being obtained one unit higher. Structurally the most significant peaks are those of large mass number, probably due to rupture of only one bond.[10] Saturated molecules are cleaved at the most highly substituted centres, an ethyl radical being lost in preference to a methyl; unsaturated molecules are cleaved at " allylic " bonds. Hexahydrogeijerene gave $C_{10}H_{19}^+$ as the most abundant heavy fragment. It must arise by loss of C_2H_5 from the quaternary carbon atom. At about one-third of this abundance was the ion $C_9H_{17}^+$, probably produced by loss of the isopropyl group. Ions of the groups C_7, C_8, and C_{11} were almost negligible in amount. The most abundant fragment was $C_6H_{11}^+$, and although explanations can be advanced to account for this no unequivocal structural conclusions could be drawn.



The most abundant fragment from geijerene larger than C_7 was $C_{11}H_{17}^+$ corresponding to loss of CH_3^-; only a trace of $C_{10}H_{15}^+$ was formed. This contrast with the hexahydrogeijerene results indicated the absence of an angular ethyl group in geijerene itself, but the presence of an allylic methyl group. The only major peaks (70 ev) corresponded to

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[10] Field and Franklin, " Electron Impact Phenomena," Academic Press Inc., New York, 1957.

$C_6H_7^+$ and $C_7H_{10}^+$, and at 8 ev the former was greatly reduced and the latter greatly preponderant. The presence in the latter of an even number of hydrogen atoms indicated the loss of a molecule rather than a radical. Its formation was explicable on the basis of formula (VII) by the fissions shown above. Each arrow indicates the movement of one electron. Both fragments of the fission, the isoprene molecule and $C_7H_{10}^+$, should be stable, the latter representing the conjugated triene $CH_2{=}CH{-}CH{=}CH{-}CMe{=}CH_2$ minus one electron. An analogous observation was the production of $C_5H_8^+$ from limonene[11] (X).

The mass spectra indicated, therefore, the presence of allylic methyl, but not ethyl, in geijerene, and the presence of ethyl in hexahydrogeijerene, presumably generated by hydrogenation of $-CH{=}CH_2$. These observations and the production of $C_7H_{10}^+$ were explicable on the basis of either formula (VII) or (VIII) and were, therefore, in accord with our previous conclusions.

That a reasonably firm conclusion can be reached on the physical evidence cited was due partly to the relatively low molecular weight of geijerene and partly to the fact that no CH function is exactly duplicated anywhere in the molecule.

The optical inactivity of geijerene is unexpected in view of the presence of two asymmetric centres. By analogy with Ohaloff's results[12] on the conversion of a ten-membered ring compound, germacrone, into an elemane derivative merely by heat, it is possible that the precursor of geijerene is the analogous compound (XI). Geijerene could possibly be an artefact produced during prolonged rectification of the essential oil. Biogenetically geijerene is probably a sesquiterpene which has lost an isopropyl group.

EXPERIMENTAL

General Remarks.—Infrared spectra were taken on a Perkin-Elmer instrument model 21 (double-beam, double-pass sodium chloride prism) for CS_2 solutions, or on a model 112G (single-beam, double reflection grating) for CCl_4 solutions, as appropriate. Mass spectra were measured by means of a Metrovic Ms 2 instrument. Nuclear magnetic resonance spectra were measured by use of a Varian V-4300 spectrometer at 40 Mc. sec.$^{-1}$ for carbon tetrachloride solutions. The measurements were actually made against a benzene external standard. This resonance was in turn calibrated against cyclohexane as internal standard in carbon tetrachloride. The latter is given the value of $+3{\cdot}9$ on the " water " scale: $\sigma = 10^6\Delta(H - H_r)/H_r$ ($r = H_2O$); for conversion to the tetramethylsilane internal standard scale (τ scale)[13] add 4·66 to all σ values.

Geijerene.—The essential oil obtained by steam-distillation of the foliage of *Geijera parviflora* Lindley was fractionated and the geijerene isolated as previously described.[14] It quickly deteriorated in air but was readily purified by percolation in pentane through alumina followed by distillation; it had b. p. 81—82°/14 mm., n_D^{23} 1·4910. It showed only end-absorption below 220 mμ.

Hexahydrogeijerene was prepared as previously described.[1]

Only one substance could be detected by vapour-phase chromatography of either geijerene or hexahydrogeijerene.

The mass spectrum of geijerene (70 ev) showed the following peaks >8% of largest peak (relative peak heights in parentheses): 27 (10·5); 39 (15·5); 41 (14·5); 77 (15·8); 79 (100); 91 (12·7); 93 (15); 94 (63); 147 (8·0); parent peak 162 (3·3).

The mass spectrum of hexahydrogeijerene (70 ev) showed the following peaks >10% of largest peak (relative peak heights in parentheses): 27 (17·7); 29 (20); 39 (14); 41 (52·5); 43 (30); 55 (69); 56 (19); 57 (40); 67 (11); 69 (81); 70 (42); 71 (17); 81 (11·5); 83 (100); 97 (18); 125 (14); 139 (38); parent peak 168 (4·35).

Isogeijerene.—Geijerene (1 g.) in ether (1·5 ml.) was added to potassamide (from potassium, 1 g.) in liquid ammonia (50 ml.), and the resulting crimson solution stirred for 15 min. Ethanol (3 ml.) was slowly added, followed by water, and the resulting *isogeijerene* separated and distilled

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[11] Friedman and Wolf, *J. Amer. Chem. Soc.*, 1958, **80**, 2424.

[12] Ohaloff, *Angew. Chem.*, 1959, **71**, 162.

[13] Tiers, *J. Phys. Chem.*, 1958, **62**, 1151.

[14] Penfold, *J. Proc. Roy. Soc. New South Wales*, 1930, **64**, 279.

as a colourless oil, b. p. 87°/15 mm., n_D^{23} 1·52313, $\lambda_{max.}$ (in EtOH) 244 mμ (ε 8000) (Found: C, 88·6; H, 11·0. $C_{12}H_{18}$ requires C, 88·9; H, 11·1%).

Dihydroisogeijerene.—In separate experiments geijerene and isogeijerene (1 g.) in ether (5 ml.) were added to a solution of potassium (1 g.) in liquid ammonia (100 ml.). The solutions changed from red to blue and finally became colourless. *Dihydroisogeijerene*, isolated in the usual way, was a colourless oil, b. p. 80°/13 mm., showing only end-absorption in the ultraviolet spectrum (Found: C, 87·4; H, 12·1. $C_{18}H_{20}$ requires C, 87·8; H, 12·2%).

Apotetrahydrogeijerene.—Hydrogenation of geijerene over 2% palladium–strontium carbonate ceased after uptake of 2 mols.[1] Ozonolysis of the tetrahydrogeijerene was carried out as previously described.[1] The semicarbazone of the product was formed slowly, unchanged ketone being detectable even after 1 hour's heating on the steam-bath with an excess of semicarbazide acetate in aqueous methanol. The semicarbazone formed colourless plates, m. p. 167—168° (lit.,[1] 163—164°) (Found: C, 64·3; H, 9·7. Calc. for $C_{12}H_{23}N_3O$: C, 64·0; H, 10·3%). The ketone was regenerated from this derivative by steam-distillation from N-sulphuric acid for spectral examination.

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