415. *Biformene.*

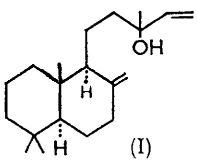
By R. M. Carman and P. K. Grant.

A new diterpene hydrocarbon, named biformene, has been isolated from *Dacrydium biforme* and its structure elucidated as (II).

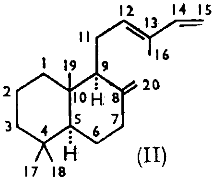
The heartwood extractives of *Dacrydium biforme* contain manool[1] (I), which comprises 90% of the neutral fraction. Reinvestigation of this wood has led to the isolation of a diterpene hydrocarbon for which the name biformene is proposed.

Biformene, obtained by the distillation of the mother-liquors from the recrystallization of manool, and purified by chromatography to constant ultraviolet absorption, is a colourless mobile oil with the formula $C_{20}H_{32}$. It is readily polymerized by heat or atmospheric oxygen. Its ultraviolet and infrared absorption indicated conjugated double bonds, an exocyclic methylene group, a vinyl group, and a *gem*-dimethyl group. On hydrogenation it gave a liquid hydrocarbon $C_{20}H_{38}$ which was saturated (infrared spectrum; ultraviolet end-absorption, $\varepsilon_{2100} < 200$). Biformene therefore has two rings and three double bonds. Reaction with maleic anhydride gave only a resin.

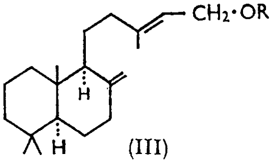
Vapour-phase chromatography of the crude selenium dehydrogenation product of biformene showed the presence of ten compounds, seven of which were identified as substituted naphthalenes by their ultraviolet absorption, the remaining three being substituted phenanthrenes. Addition of authentic materials to the crude dehydrogenation mixture and vapour-phase chromatography of these mixtures indicated three peaks as due to 1,7-dimethylphenanthrene, 1,2,5-trimethylnaphthalene, and 7-isopropyl-1-methylphenanthrene. The first two were isolated and fully characterized. Mixtures of naphthalenes and phenanthrenes have been obtained previously from the bicyclic diterpenes agathic acid,[2] manoyl oxide,[3] and an oxomanoyl oxide derivative,[4] all of which have the carbon skeleton of (I). We have found that dehydrogenation of manool by selenium gives the same ten products, but in different proportions (see p. 2190). Biformene yields 50·6% of naphthalenes and 49·4% of phenanthrenes: manool gives 60·8% and 39·2%, respectively. These figures, together with the rather close correspondence of the yields for each of the ten compounds, suggest that biformene has the same carbon skeleton as manool. Spectral considerations then require biformene to have its three double bonds arranged as in (II).



(I)



(II)



(III)

With this clue we then found that dehydration of manool by acetic acid gave biformene, so proving the carbon skeleton of biformene together with the stereochemistry at positions 5, 9, and 10. The known allyl acetate[5,6] (III; R = Ac), resulting from rearrangement of manoyl acetate, was also isolated; on alkaline hydrolysis this gave the corresponding allyl alcohol (III; R = H). Further proof of the carbon skeleton of biformene was provided when its hydrochloride was found to be identical with the trihydrochloride from manool.[1,7]

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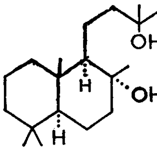
[1] Hosking and Brandt, *Ber.*, 1935, **68**, 1311.
[2] Ruzicka and Hosking, *Helv. Chim. Acta*, 1930, **13**, 1402.
[3] Hosking and Brandt, *Ber.*, 1935, **68**, 37.
[4] Hosking and Brandt, *Ber.*, 1935, **68**, 286.
[5] Büchi and Biemann, *Croat. Chem. Acta*, 1957, **29**, 163.
[6] Ohloff, *Annalen*, 1958, **617**, 134.
[7] Carman, unpublished result.

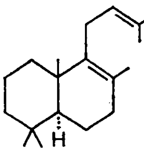
The ready dehydration of manool to biformene allowed the possibility that biformene is not present in the wood, but is an artefact of the working-up. The ultraviolet spectrum of an extract of the wood obtained by spectroscopically pure iso-octane at room temperature showed a strong inflexion at 2280 Å which is assigned to biformene, on a band with a maximum at 2320 Å. Chromatography over alumina indicated that both these bands were due to non-polar hydrocarbons. The optical density of the 2280 Å band corresponded to approximately 0·06% of biformene in the wood.

A similar hydrocarbon (V) was postulated by Ruzicka *et al.*[8] as a hypothetical, first-stage, dehydration product in the acetylation of sclareol (IV). Conformational analysis requires modification of this structure to (II), since the elimination of water from the 8α-hydroxyl group of sclareol demands *trans*-elimination,[9] resulting in an exocyclic 8-methylene group. That the exocyclic double bond does not isomerize to the endocyclic position under these conditions is demonstrated by the isolation of the allyl alcohol (III; R = H) and manool from sclareol.[6] Büchi and Biemann [5] reported the presence of a triene containing a conjugated diene system as an impurity formed on hydrolysis of sclareol diacetate and on dehydration of sclareol with acetic anhydride; from the infrared (not quoted) and ultraviolet spectra ($\lambda_{\text{max.}}$ 2280 Å; log ε 4·08) the hydrocarbon was considered to be a mixture of (II) and (VI).

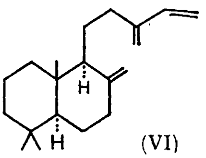
By acetylation and subsequent hydrolysis of sclareol, Ohloff [6] obtained a bicyclic triene, sclarene, which he formulated as (VI) and characterized as a dihydrochloride, m. p. 123—125°. Its physical constants closely resembled those of biformene but its infrared spectrum showed considerable C–O stretching in the 1050—1150 cm.$^{-1}$ region. When we repeated Ohloff's work we obtained the same products but in different yields, notably 30% of the bicyclic triene and 28% of epimanoyl oxide as against 47% and 6·4% respectively reported by Ohloff. The infrared spectrum of our liquid hydrocarbon from sclareol was identical with that of biformene and contained no C–O stretching absorption; and it gave the same saturated trihydrochloride as was prepared from manool, and not an unsaturated dihydrochloride.



(IV)



(V)



(VI)

Structure (II) is assigned to biformene in preference to Ohloff's formula (VI) for the following reasons. Structure (II), with the more stable trisubstituted double bond, should be formed in preference to (VI), which may in fact revert to (II) under acid conditions. The ultraviolet maximum at 2280 Å supports a disubstituted rather than a monosubstituted diene system [it should be noted, however, that ocimene, with a similar diene system, exhibits anomalous ultraviolet absorption [10] ($\lambda_{\text{max.}}$ 2350 Å; log ε 4·22)]. Finally, the nuclear magnetic resonance spectrum of biformene supports structure (II). The vinyl region of the spectrum (3·0—6·0τ) had an integrated area corresponding to six protons which is in accord with structure (II), whereas (VI) requires seven protons. Two single proton peaks, at 5·25 and 5·50 τ, can be assigned to the two different exocyclic methylene protons;[11] these are unsplit, but broad, indicating that the coupling constants $J_{20,20'}$, $J_{7,20}$, and $J_{9,20}$ are approximately zero. A triplet (relative area $\frac{1}{4}:\frac{1}{2}:\frac{1}{4}$ proton) centred at 3·36 τ ($J_{12,11}$ = 9·6 c./sec.) is assigned to the proton at $C_{(12)}$ while the $C_{(14)}$- and $C_{(15)}$-protons occur as a multiplet of eleven peaks (each of area approximately $\frac{1}{4}$ proton) between 3·68 and 5·07 τ. In addition, the spectrum showed four methyl peaks, at 9·18, 9·13, 9·13,

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[8] Ruzicka, Engel, and Fischer, *Helv. Chim. Acta*, 1938, **21**, 364.
[9] Barton, Campos-Neves, and Cookson, *J.*, 1956, 3500.
[10] O'Connor and Goldblatt, *Analyt. Chem.*, 1954, **26**, 1726.
[11] Dev, *Tetrahedron*, 1960, **9**, 1.

and 8·27 τ: the three highest of these correspond to the unsplit 17-, 18-, and 19-methyl groups, while the peak at 8·27 τ must be due to an allylic methyl group,[12] thus confirming structure (II). The last peak is also broad, owing to secondary coupling with protons across the double bond.

It is proposed that the name biformene be given to the hydrocarbon of structure (II) while the name sclarene be reserved for the hydrocarbon (VI).

EXPERIMENTAL

M. p.s are corrected. Ultraviolet spectra were measured for iso-octane solutions. Alumina, B.D.H. grade " for chromatographic adsorption analysis," and light petroleum (b. p. 60—80°) were used unless otherwise stated.

Isolation of Biformene.—(*a*) Distillation of the neutral fractions of an acetone extract of *D. biforme* gave manool, b. p. 150—153°/0·3 mm. Distillation of the residue obtained from the mother-liquors from the recrystallization of manool gave a mobile straw-coloured oil, b. p. 140—145°/0·5 mm. Repeated chromatography on alumina from light petroleum gave *biformene*, n_D^{20} 1·5257, d_4^{20} 0·952, $[\alpha]_D^{20}$ +12·2° (*c* 14% in iso-octane) (Found: C, 87·4; H, 11·4. $C_{20}H_{32}$ requires C, 88·2; H, 11·8%), $\nu_{max.}$ (film) 1596 (C:C·C:C), 3079, 1786, 1644, and 888 (exocyclic CH_2=), 3034 infl., 990, 905 infl. (C:CH_2), 1388 and 1366 (*gem*-Me_2), also 1413 cm.$^{-1}$, $\lambda_{max.}$ 2280 Å (ε 15,300) (C:C·C:C). Redistillation resulted in decomposition. It was necessary to store biformene under a vacuum to minimize polymerization.

(*b*) *D. biforme* chips (10·4 g.) were treated with iso-octane (50 ml.) for 90 hr. at 20°. The extract, filtered and diluted to 10 times its volume, had $\lambda_{max.}$ 2320 Å (O.D. 0·82), $\lambda_{infl.}$ 2280 Å (O.D. 0·73). The extracted material, recovered at 20° and chromatographed over alumina from iso-octane, gave on elution with iso-octane a fraction still absorbing at 2280 and 2320 Å.

Synthesis of Biformene.—Manool (6·03 g.) in acetic acid (50 c.c.) was refluxed for ¾ hr. Chromatography on alumina from light petroleum gave, on elution with light petroleum, biformene (1·64 g.), n_D^{20} 1·5235, d_4^{20} 0·950 (Found: C, 88·45; H, 12·0%), $\nu_{max.}$ (film) 1642, 1592, 990, 905sh, and 890 cm.$^{-1}$, $\lambda_{max.}$ 2280 Å (ε 12,500). Further elution with light petroleum–ether (10 : 1) gave the allyl acetate (III; R = Ac) (2·3 g.), purified by distillation (bath-temp. 170°/0·15 mm.), n_D^{20} 1·5063 (lit.,[6] 1·5071) (Found: C, 79·3; H, 10·9. Calc. for $C_{22}H_{36}O_2$: C, 79·5; H, 10·9%), $\nu_{max.}$ (film) 1745 and 1232 (OAc), 1670 (CH:C), 3095, 1645, 889 (>C:CH_2) cm.$^{-1}$. Elution with light petroleum–ether (1 : 2) gave unchanged manool (1·23 g.).

The allyl acetate (1 g.) in 5% ethanolic potassium hydroxide (20 c.c.) was refluxed for 1 hr. Chromatography on alumina from light petroleum gave, on elution with light petroleum–ether (1 : 2) the allyl alcohol (III; R = H) which, purified by distillation (bath-temp. 180°/0·15 mm.), had n_D^{20} 1·5203 (lit.,[6] 1·5220), $\nu_{max.}$ (film) 3415 (OH), 1670 (CH:C), 1000 br (C–O), 3095, 1646, 887 (>C:CH_2) cm.$^{-1}$.

Sclareol (5 g.) was heated with acetic anhydride (5 g.) and acetic acid (5 g.) for 6 hr. (yield 4·81 g.) and then with alcoholic potassium hydroxide[6] (yield 4·57 g.). Chromatography on alumina from light petroleum gave biformene (1·47 g., 30%) on elution with light petroleum. Further elution with light petroleum–ether (30 : 1) gave colourless needles of epimanoyl oxide (1·41 g., 28%), m. p. and mixed m. p. 94—95° (from aqueous acetone).

Hexahydrobiformene.—Biformene (4·8 g.) in cyclohexane was hydrogenated (50°/100 atm.) over Raney nickel (activity W 2) for 12 hr. Chromatography on alumina from light petroleum gave a colourless oil (3·7 g.; ε_{2100} 1110). This oil, in light petroleum, was extracted with concentrated sulphuric acid (3 × 20 c.c.), washed with sodium carbonate and then water, chromatographed, and distilled (105°/0·02 mm.) to give *hexahydrobiformene*, n_D^{20} 1·4918, d_4^{20} 0·908, α_D^{20} +10·6° (homog.) (lit.,[6] 1·4922, 0·910, +44·1°) (Found: C, 86·5; H, 13·85. $C_{20}H_{38}$ requires C, 86·25; H, 13·75%). The infrared spectrum showed only C–C and C–H absorption. The ultraviolet spectrum had end-absorption only (ε_{2100} 190).

Dehydrogenation of Biformene.—Biformene (1·5 g.) was heated with selenium for 46 hr. at 310—320°. A benzene extract of the product was filtered through a Celite column and evaporated. The residue was filtered in light petroleum through a short alumina column. Vapour-phase chromatography (helium gas, 1 m. column of 15% silicone oil on chromosorb; 190°)

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[12] Jackman, " Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p. 58.

gave ten peaks (see Table). The peak at 1·35 is probably due to 7-ethyl-1-methylphenanthrene since the ultraviolet spectrum of this material was superimposable (as regards wavelengths) on that of pimanthrene.

Chromatography of the crude hydrocarbons (370 mg.) on alumina from light petroleum gave an oil (205 mg.); its 1,3,5-trinitrobenzoate, on repeated recrystallization gave 1,2,5-trimethylnaphthalene 1,3,5-trinitrobenzoate as yellow needles, m. p. 155—158° (lit.,[13] 158—159°) [Found: C, 59·0; H, 4·3; N, 10·9%; *M* (ref. 14), 378. Calc. for $C_{19}H_{17}N_3O_6$: C, 59·5; H, 4·5; N, 11·0%; *M*, 383]. Regeneration of the hydrocarbon on alkaline alumina gave 1,2,5-trimethylnaphthalene as plates (from aqueous ethanol), m. p. 29° (lit.,[2] 31—32°), $\lambda_{max.}$ 3240, 3154, 3092, 2944, 2886, 2780, 2308 Å (log ε 3·06, 2·84, 3·14, 3·73, 3·88, 3·80, 4·98) with infl. at 2992, 2968, 2834, 2685, 2588, 2250, 2177, 2138 Å (log ε 3·68, 3·70, 3·80, 3·59, 3·33, 4·51, 4·38) (this spectrum shows greater resolution than that reported in the literature [15]), $\nu_{max.}$ (film) 1601, 1515, 1442, 1414, 1381, 813, 791, 741 cm.$^{-1}$. The picrate, red needles from aqueous ethanol, had m. p. 136° (lit.,[13] 137—138°). Further elution of the hydrocarbon column with light petroleum gave a crystalline fraction (143 mg.), purified by sublimation (60°/0·02 mm.) and recrystallization from aqueous ethanol, to give 1,7-dimethylphenanthrene, m. p. 78—81° undepressed on admixture with pimanthrene (m. p. 82°) (recorded m. p. range from 75° [16] to 86° [17]). Its trinitrobenzoate (m. p. 155—158°) did not depress the m. p. of an authentic sample (m. p. 161°). The ultraviolet spectrum agreed with that reported.[18]

Dehydrogenation of Manool.—Manool (3 g.) was dehydrogenated with selenium as described for biformene. Vapour-phase chromatography gave ten peaks (see Table). Admixture of the dehydrogenation product with that from biformene and chromatography of the resultant mixture gave only the same ten peaks. Chromatography of the crude hydrocarbon fraction (630 mg.) on alumina from light petroleum gave an oil (440 mg.) from which 1,2,5-trimethylnaphthalene, m. p. 29°, was obtained as described above, giving one peak on vapour-phase chromatography at a relative retention time (pimanthrene = 1) of 0·27. The picrate had m. p. 135°. Further elution with light petroleum gave crystals (185 mg.), m. p. 79° (from aqueous ethanol), identified as 1,7-dimethylphenanthrene through the trinitrobenzoate (m. p. 158°), picrate (m. p. 129—130°, lit., 126°,[17] 132° [19]), and the ultraviolet spectrum.

Relative retention time (1,7-dimethylphenanthrene = 1)	Compound	Yield (%) from biformene	Yield (%) from manool
0·13	A substituted naphthalene	2·0	2·4
0·16	A substituted naphthalene		
0·24	1,2,5-Trimethylnaphthalene	12·1	13·5
0·49	A substituted naphthalene	0·2	0·2
0·65	A substituted naphthalene	0·3	0·4
0·73	A substituted naphthalene	0·4	0·5
1·00	1,7-Dimethylphenanthrene	12·3	9·5
1·10	A substituted naphthalene	1·9	2·2
1·35	A substituted phenanthrene	2·8	1·9
1·70	7-Isopropyl-1-methylphenanthrene	1·4	0·9
		33·4	31·5

Biformene Trihydrochloride.—Biformene (0·8 g.), suspended in glacial acetic acid, was shaken while dry hydrogen chloride was passed in at 20°. The solution became red after 90 min. Water was added after 6 hr. and the emulsion extracted with light petroleum. The yellow oil (660 mg.) crystallized. Repeated recrystallization from light petroleum gave the trihydrochloride as colourless needles, m. p. 123°, undepressed on admixture with manool trihydrochloride or with sclareol trihydrochloride, m. p. 125° (Found: C, 62·7; H, 9·4; Cl, 27·7. Calc. for $C_{20}H_{35}Cl_3$: C, 62·9; H, 9·2; Cl, 27·9%), ε_{2100} 175. The infrared spectrum (KBr) was completely superimposable on that of manool trihydrochloride or sclareol trihydrochloride, ν(major) 839, 740 cm.$^{-1}$.

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[13] Ruzicka, Baumgarten, and Prelog, *Helv. Chim. Acta*, 1949, **32**, 2057.
[14] Godfrey, *Analyt. Chem.*, 1959, **31**, 1087.
[15] Heilbronner, Fröhlicher, and Plattner, *Helv. Chim. Acta*, 1949, **32**, 2479.
[16] Galik, Petrů, and Kuthan, *Tetrahedron*, 1959, **7**, 223.
[17] Brandt, *J. N. Z. Science Technol.*, 1952, **34***B*, 46.
[18] Heilbronner, Däniker, and Plattner, *Helv. Chim. Acta*, 1949, **32**, 1723.
[19] Haworth, Letsky, and Marvin, *J.*, 1932, 1784.

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