X-Ray Crystal and Molecular Structure of the *p*-Bromobenzoate Derivative of the Sesquiterpene (±)-Cyclobazzanene Obtained in the Formic Acid-catalysed Reaction of (+)-Bazzanene

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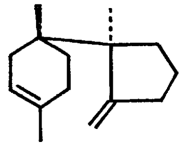
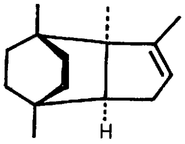
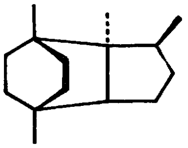
Summary The bicyclic sesquiterpene (+)-bazzanene (I) was treated with formic acid to give the tricyclic sesquiterpene (±)-cyclobazzanene (II), which was shown to be a racemate of the novel sesquiterpene (II) by *X*-ray diffraction analysis of the *p*-bromobenzoate derivative.

WE reported in the preceding communication the absolute configuration of (+)-bazzanene (I) isolated from the leafy liverwort *Bazzania pompeana*,[1] and we report here elucidation, by *X*-ray analysis, of the structure of (±)-cyclobazzanene (II), a novel sesquiterpene hydrocarbon obtained in the formic acid-catalysed reaction of (+)-bazzanene.


(I)


(II)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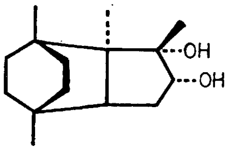
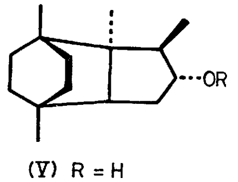

(IV)


(V) R = H

(VI) R = COC$_6$H$_4$Br-*p*

When (+)-bazzanene, containing both an *exo*-methylene group and a trisubstituted double bond, was heated with formic acid (88%) on a water bath for 2 h and the resulting mixture was chromatographed on AgNO$_3$-impregnated silica gel with hexane as eluent, cyclobazzanene (II), C$_{15}$H$_{24}$ (M^+ 204); $[\alpha]_D$ 0°, was obtained, optically inactive, in 65% yield. Its i.r. and ^{1}H n.m.r. spectra showed the presence of one trisubstituted double bond bearing a methyl group [ν 822 cm^{-1}; δ 1·63 (3H, br. s) and 5·28 (1H, m)] together with three tertiary Me groups [ν 1378 and 1368 cm^{-1}; δ 0·67, 0·79, and 0·99 (each 3H, s)]; catalytic hydrogenation over PtO$_2$ in AcOH afforded the saturated dihydro-derivative (III), C$_{15}$H$_{26}$ (M^+ 206); $[\alpha]_D$ 0°.† Oxidation (OsO$_4$) gave the glycol (IV), C$_{15}$H$_{26}$O$_2$ (M^+ 238); m.p. 96—97 °C; $[\alpha]_D$ 0°, the off-resonance ^{13}C n.m.r. spectrum of which showed 4 singlets (δ 83·8, 50·0, 31·5, and 31·4) attributed to 1 tertiary carbinyl and 3 quaternary carbons, 2 doublets (δ 78·8 and 53·0) assigned to 1 secondary carbinyl and 1 methine carbon, 5 CH$_2$ triplets (δ 37·1, 34·9, 33·0, 32·3, and 27·8), and 4 Me quartets (δ 26·9, 24·4, 23·6, and 21·0).‡ These results show that cyclobazzanene is a tricyclic sesquiterpene hydrocarbon containing 3 tertiary Me groups and 1 trisubstituted double bond bearing an Me group.

For the structure determination cyclobazzanene was converted into cyclobazzanenol (V), C$_{15}$H$_{26}$O (M^+ 222); $[\alpha]_D$ 0°, by hydroboration, and the *p*-bromobenzoate (VI), C$_{22}$H$_{29}$BrO$_2$ (M^+ 404 and 406); m.p. 66—68 °C; $[\alpha]_D$ 0°, was prepared by reaction with *p*-bromobenzoyl chloride in dry pyridine. The benzoate afforded colourless triclinic

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† The i.r., ^{1}H n.m.r., and mass spectra of all new compounds (III)—(VI) were consistent with the proposed structures. Optical rotations were measured in CHCl$_3$ solutions and i.r. and ^{1}H n.m.r. spectra in CCl$_4$ solutions.

‡ ^{13}C N.m.r. spectra were determined in CDCl$_3$ solution; δ values are given in p.p.m.

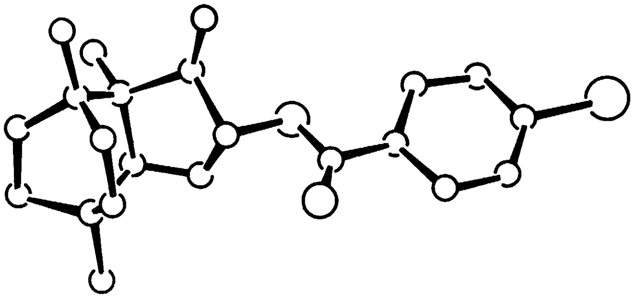

FIGURE. A perspective view of the structure of the *p*-bromobenzoate (VI).

crystals from hexane–EtOAc. *Crystal data:* $a = 13{\cdot}29(1)$, $b = 11{\cdot}83(1)$, $c = 7{\cdot}84(1)$ Å; $\alpha = 116{\cdot}3(2)$, $\beta = 81{\cdot}7(2)$, $\gamma = 111{\cdot}8(2)^\circ$, space group $P\bar{1}$, $D_c = 1{\cdot}31$, $D_m = 1{\cdot}31$ g cm^{-3} (in $ZnCl_2$), $Z = 2$. A total of 2135 independent reflexions was obtained by visual estimation of equi-inclination Weissenberg photographs (*hk*0—*hk*5 and *h*0*l*) with Ni—K_α (λ 1·6591 Å) radiation.

The position of bromine atom was determined from a sharpened Patterson map, and successive use of Fourier and difference Fourier techniques enabled the structure to be assigned. Refinement of structural parameters by block-diagonal least-squares, using anisotropic thermal parameters, led to a current *R*-value of 0·120.§ The structure of the *p*-bromobenzoate (VI) is in the Figure.¶ Accordingly, the parent hydrocarbon (±)-cyclobazzanene has the structure (II) which is represented by one optical isomer of the racemic mixture.

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§ All computations were carried out using a HITAC 8700 computer at Hiroshima University, using the UNICS programs of the Crystallographic Society of Japan (1965) and slightly modified forms.

¶ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] A. Matsuo and S. Hayashi, preceding communication.