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The Crystal and Molecular Structure of Hortensenyl *p*-Iodobenzoate

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The structure of hortensenyl *p*-iodobenzoate, $C_{37}H_{53}O_2I$, a derivative of the pentacyclic triterpene hortensenol, was solved using Patterson methods and refined to a weighted $R(F)$ value of 0·038 using absorption-corrected diffractometer data. The molecule is best described as a migrated hopane derivative having a fern-8-enol structure.

Introduction

Hortensenol, $C_{30}H_{50}O$ (m.p. 200–201 °C, $[\alpha]_D = +25{\cdot}5°$), is a pentacyclic triterpene isolated from the light petroleum extract of the leaves of *Evodia hortensis* Forst (*Rutaceae*), a tree native to New Guinea. Professor W. C. Taylor of the University of Sydney kindly provided crystals of the *p*-iodobenzoate derivative of hortensenol for structural elucidation. Fairly good circumstantial chemical evidence existed for the structure of rings *A*/*B*/*C* (Fig. 1) but evidence for the structure of rings *D*/*E* was largely biogenetic. The proposed structure for rings *A*/*B*/*C*/*D* proved to be correct.

Experimental

Weissenberg photographs of a single crystal of hortensenyl *p*-iodobenzoate, $C_{37}H_{53}O_2I$ (m.p. 275–276 °C), showed monoclinic symmetry with systematic absences for reflections of the type $0k0$ with $k \neq 2n$. These observations are consistent with space groups $P2_1$ and $P2_1m$. The acentric polar space group $P2_1$ was favored based on a calculated density requiring two molecules per unit cell and the impossibility of the molecule having the symmetry of the special positions in the space group $P2_1/m$. The cell constants were determined by least-squares refinement of the 2θ(Mo $K\alpha$) values obtained for 14 diffractometer-measured reflections. The preliminary crystal data are summarized in Table 1.

Table 1. *Room-temperature crystal data*

Space group	$P2_1$
Cell constants	$a = 16{\cdot}182\ (8)$ Å
	$b = 7{\cdot}716\ (4)$
	$c = 13{\cdot}857\ (8)$
	$\beta = 105{\cdot}177\ (24)°$
Density	$\varrho_c = 1{\cdot}31$ g cm^{-3}
Absorption coefficient	μ(Mo $K\alpha$) $= 10{\cdot}1$ cm^{-1}

The three-dimensional data were collected on a Picker card-punch-controlled diffractometer equipped with a pulse-height analyzer. The intensities of 2371 reflections to a 2θ value of 55° were measured using Nb-filtered Mo $K\alpha$ radiation. The X-ray source was a standard tube operated at 50 kV and 14 mA with a 3·5° take-off angle. The $\theta/2\theta$ scan mode with a 2° min^{-1} scan rate was used. Two-theta scan ranges were calculated so as to range from 0·7° below $2\theta_1$ to 0·6° above $2\theta_2$. Backgrounds were counted for 20 seconds at each of the scan limits for each reflection.

Four standard reflections were measured periodically during data collection in order to obtain a scale factor for each reflection group and to estimate an instability constant for the diffractometer. The experimental instability constant was found to be 1·5%. The scale factor for each reflection was calculated by linear interpolation from the scale factors for the standard groups bracketing it and ranged between 0·93 and 1·05. The data were corrected for background, coincidence loss, absorption* and the usual Lorentz and polarization effects.

Solution and refinement of the structure

The x and z coordinates of the iodine atom were calculated from the coordinates of the I → I vector in the Harker section of a sharpened, origin-removed Patterson map. Since the space group is polar, the y coordinate of the iodine atom was set at fractional coordinate 0·25 in order to fix an origin. Positions of five of the six carbon atoms in the phenyl ring were located

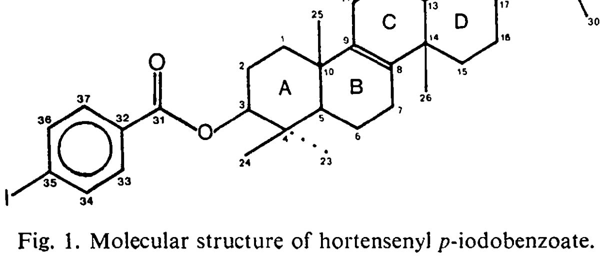

Fig. 1. Molecular structure of hortensenyl *p*-iodobenzoate.

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* Analytical calculation based on the method of De Meulenaer & Tompa (1965). Program *ABSOR*, a revision of *AGNOST*, as described by Templeton & Templeton (1973). Maximum correction 1·08 × *I*, minimum 1·03 × *I*. All other programs were those of the X-RAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

by manual superposition based on the I → I vector. These five atoms and the iodine atom were used as our initial phasing model. Inital attempts at building a model of the molecule based on F_o and ΔF Fourier syntheses were hindered by the presence of pseudo mirror planes at $y=0{\cdot}25$ and $y=0{\cdot}75$. Nevertheless, a chemically reasonable 40 atom model was found which gave an initial value of $R(F)=0{\cdot}22$.

The initial model was refined using standard least-squares techniques. Carbon, oxygen and iodine scattering factors were those of Doyle & Turner (1968). Scattering factors for hydrogen were from Stewart, Davidson & Simpson (1965). The anomalous dispersion effect was ignored. The quantity minimized was $\sum w(|F_o|-|F_c|)^2$.

After 5 cycles of full-matrix least-squares refinement (anisotropic temperature factor for *I* on the last 3 cycles), $R(F)$ had been reduced to 0·083 on 2059 contributing reflections. A reflection was considered to be observed if $F_o > 2\sigma_{F_o}$. 'Unobserved' reflections were allowed to contribute to the refinement with $F_o \equiv 2\sigma_{F_o}$ if $F_c > 2\sigma_{F_o}$. Unit weights were used in computing the residual. The 'goodness of fit' for this model was 2·1.

At this point the data were corrected for absorption and one cycle of least-squares refinement was attempted using anisotropic temperature factors for all 40 atoms in the model. The matrix was partitioned into 3 non-overlapping blocks along its diagonal with the iodine atom included in the first block. This procedure resulted in nonpositive-definite temperature factors for a number of atoms in the second and third blocks. In order to overcome this difficulty the model was refined using three partial refinement cycles to cover all of the atoms in the molecule. The iodine atom was refined in each of the partial refinement cycles and all temperature factors then behaved normally. Statistical weights defined as $1/\sigma^2_{F_o}$ were used here and in the remainder of the refinement. One cycle of anisotropic refinement over the 40 atoms in the molecule gave $R_w(F)=0{\cdot}07$.

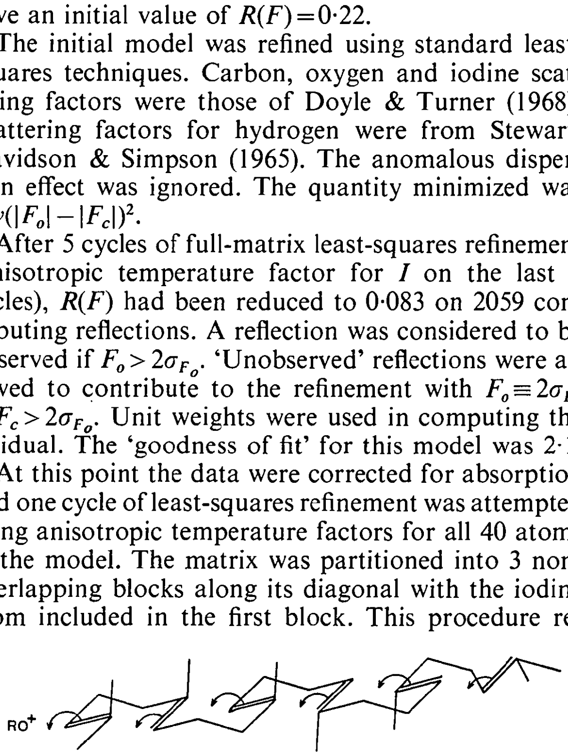

Fig. 2. Cation-induced cyclization of squalene.

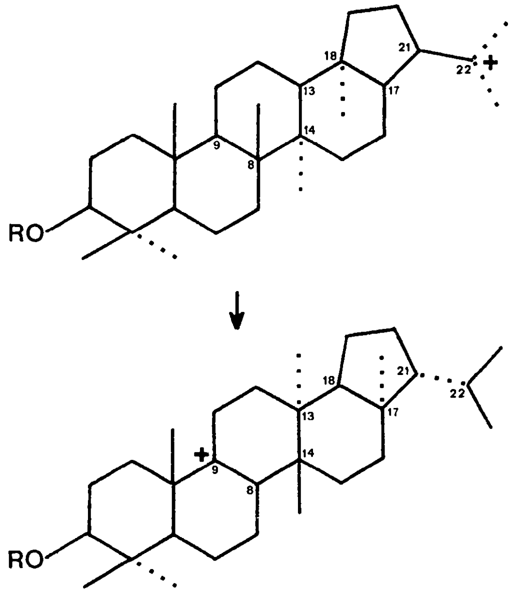

Fig. 3. Methyl group migrations leading to the fernanol structure.

Hydrogen atoms were now introduced in the model. They were placed at calculated positions with isotropic temperature factors equal to the isotropic temperature factors of the atoms to which they were bonded. The hydrogen-atom parameters were not refined but new positions were calculated after one full cycle of refinement. The 93 atom model gave an initial $R_w(F)=0{\cdot}058$.

Two cycles of refinement reduced $R_w(F)$ to 0·041. One partial cycle on all atoms which had any parameter shift more than one standard deviation, along with the atoms to which these were attached, reduced

Table 2. *Positional parameters* (× 10^4) *and their least-squares standard deviations*

	x	y	z
I	−1101·9 (5)	−7500·0	−1964·5 (4)
O(1)	−676 (5)	−6122 (13)	3182 (5)
O(2)	619 (4)	−7090 (10)	3205 (4)
C(1)	1660 (8)	−4882 (16)	5665 (7)
C(2)	1280 (7)	−5069 (16)	4514 (7)
C(3)	938 (7)	−6937 (13)	4303 (6)
C(4)	1592 (6)	−8350 (12)	4651 (6)
C(5)	2049 (6)	−8006 (12)	5786 (7)
C(6)	2696 (10)	−9341 (17)	6275 (9)
C(7)	2953 (9)	−9221 (17)	7380 (10)
C(8)	2998 (5)	−7439 (25)	7806 (5)
C(9)	2732 (9)	−6042 (18)	7229 (11)
C(10)	2422 (8)	−6170 (15)	6056 (8)
C(11)	2822 (7)	−4235 (15)	7639 (7)
C(12)	3187 (6)	−4009 (14)	8776 (7)
C(13)	3065 (6)	−5630 (17)	9359 (6)
C(14)	3463 (6)	−7248 (21)	8931 (6)
C(15)	3410 (6)	−8796 (13)	9576 (7)
C(16)	3863 (8)	−8565 (17)	10679 (8)
C(17)	3552 (6)	−7015 (13)	11157 (7)
C(18)	3537 (7)	−5435 (16)	10479 (8)
C(19)	3362 (7)	−3877 (14)	11069 (8)
C(20)	3860 (7)	−4377 (15)	12156 (7)
C(21)	4174 (7)	−6269 (14)	12132 (7)
C(22)	4262 (7)	−7223 (23)	13139 (7)
C(23)	1109 (7)	−10025 (16)	4569 (7)
C(24)	2216 (6)	−8437 (15)	3997 (7)
C(25)	3152 (8)	−5637 (19)	5666 (8)
C(26)	4414 (5)	−6965 (13)	8932 (5)
C(27)	2083 (7)	−5847 (14)	9178 (7)
C(28)	2674 (6)	−7374 (26)	11370 (6)
C(29)	4921 (8)	−6251 (20)	13967 (8)
C(30)	4487 (9)	−9074 (18)	13133 (8)
C(31)	−163 (6)	−6594 (15)	2762 (7)
C(32)	−351 (7)	−6832 (13)	1647 (6)
C(33)	219 (6)	−7481 (28)	1191 (6)
C(34)	14 (6)	−7697 (25)	152 (6)
C(35)	−786 (7)	−7123 (17)	−399 (6)
C(36)	−1344 (6)	−6452 (14)	27 (6)
C(37)	−1155 (7)	−6227 (15)	1076 (7)

$R_w(F)$ to 0·040. It also reduced the shift to error ratio to less than one standard deviation for all atoms except C(26). One final partial cycle on C(26) reduced its shift to error ratios to below one standard deviation. New hydrogen-atom positions were calculated to give the final molecular model. This model gave a final $R_w(F)=0{\cdot}038$ for 1738 observed reflections. The final standard deviation of an observation of unit weight was 2·22. The final atomic coordinates and thermal parameters are given in Tables 2 and 3 respectively.[*][†]

Table 4. *Interatomic distances* (Å) *and their estimated standard deviations*

C(1)—C(2)	1·559 (14)	C(14)–C(26)	1·555 (13)
C(1)—C(10)	1·566 (17)	C(15)–C(16)	1·524 (14)
C(2)—C(3)	1·544 (16)	C(16)–C(17)	1·516 (17)
C(3)—C(4)	1·508 (14)	C(17)–C(18)	1·535 (16)
C(3)—O(2)	1·478 (10)	C(17)–C(21)	1·568 (13)
C(4)—C(5)	1·576 (11)	C(17)–C(28)	1·550 (15)
C(4)—C(23)	1·499 (16)	C(18)–C(19)	1·522 (17)
C(4)—C(24)	1·526 (15)	C(19)–C(20)	1·559 (14)
C(5)—C(6)	1·497 (16)	C(20)–C(21)	1·549 (16)
C(5)—C(10)	1·547 (15)	C(21)–C(22)	1·550 (16)
C(6)—C(7)	1·482 (18)	C(22)–C(29)	1·542 (16)
C(7)—C(8)	1·490 (22)	C(22)–C(30)	1·474 (22)
C(8)—C(9)	1·344 (21)	C(31)–O(1)	1·189 (14)
C(8)—C(14)	1·551 (10)	C(31)–O(2)	1·311 (11)
C(9)—C(10)	1·574 (18)	C(31)–C(32)	1·506 (12)
C(9)—C(11)	1·498 (18)	C(32)–C(33)	1·343 (16)
C(10)–C(25)	1·480 (20)	C(32)–C(37)	1·414 (13)
C(11)–C(12)	1·541 (12)	C(33)–C(34)	1·401 (12)
C(12)–C(13)	1·530 (14)	C(34)–C(35)	1·392 (14)
C(13)–C(14)	1·589 (17)	C(35)–C(36)	1·308 (16)
C(13)–C(18)	1·547 (13)	C(35)–I	2·114 (8)
C(13)–C(27)	1·551 (14)	C(36)–C(37)	1·416 (13)
C(14)–C(15)	1·506 (17)		

Table 3. *Thermal parameters* ($\times 10^3$) *and their least-squares standard deviations*

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I	115·8 (6)	85·7 (5)	30·7 (3)	−16·9 (9)	6·2 (3)	−1·8 (7)
O(1)	50 (6)	172 (10)	39 (4)	51 (6)	7 (4)	−9 (5)
O(2)	40 (4)	57 (7)	23 (3)	5 (4)	−2 (3)	−2 (4)
C(1)	103 (11)	45 (9)	39 (6)	1 (9)	−9 (7)	−7 (6)
C(2)	88 (10)	55 (9)	45 (7)	11 (8)	3 (6)	−5 (7)
C(3)	68 (8)	46 (10)	21 (5)	−5 (6)	8 (5)	6 (5)
C(4)	41 (7)	37 (7)	21 (5)	−7 (6)	6 (5)	−2 (5)
C(5)	29 (7)	27 (10)	24 (5)	10 (6)	0 (5)	1 (5)
C(6)	92 (12)	37 (9)	27 (7)	11 (8)	2 (7)	5 (6)
C(7)	56 (10)	30 (8)	25 (7)	22 (7)	4 (6)	−4 (6)
C(8)	39 (6)	40 (7)	25 (4)	6 (10)	2 (4)	−1 (10)
C(9)	35 (8)	44 (9)	39 (8)	−19 (7)	3 (6)	−14 (7)
C(10)	50 (8)	29 (8)	22 (6)	−4 (7)	−4 (6)	3 (6)
C(11)	76 (9)	44 (8)	28 (6)	−2 (7)	−4 (6)	15 (6)
C(12)	50 (8)	45 (8)	35 (6)	−2 (7)	−4 (5)	3 (6)
C(13)	27 (6)	16 (6)	33 (5)	−6 (5)	2 (5)	1 (5)
C(14)	37 (6)	38 (9)	32 (4)	1 (8)	8 (4)	3 (7)
C(15)	28 (7)	31 (7)	36 (6)	−3 (6)	4 (5)	−6 (6)
C(16)	52 (9)	53 (9)	31 (7)	16 (8)	14 (6)	−4 (7)
C(17)	28 (7)	29 (10)	31 (6)	0 (6)	2 (5)	0 (5)
C(18)	37 (8)	41 (9)	31 (7)	−8 (7)	12 (6)	−8 (6)
C(19)	42 (8)	44 (8)	47 (7)	−1 (7)	11 (6)	−8 (7)
C(20)	50 (9)	50 (9)	42 (7)	−23 (7)	16 (6)	−16 (6)
C(21)	39 (8)	44 (8)	38 (6)	−13 (7)	4 (5)	−3 (6)
C(22)	46 (7)	69 (12)	30 (5)	−2 (9)	4 (5)	−10 (8)
C(23)	59 (8)	67 (9)	26 (5)	−6 (8)	−9 (5)	−16 (6)
C(24)	39 (7)	83 (10)	38 (6)	21 (7)	−1 (5)	−12 (6)
C(25)	77 (10)	128 (14)	50 (7)	−64 (10)	6 (7)	−17 (9)
C(26)	41 (6)	66 (11)	36 (5)	0 (6)	8 (4)	−3 (5)
C(27)	58 (8)	50 (8)	44 (6)	6 (7)	19 (6)	2 (6)
C(28)	41 (6)	56 (8)	40 (5)	−15 (10)	4 (5)	7 (10)
C(29)	81 (10)	120 (13)	31 (6)	−19 (10)	−2 (7)	−3 (8)
C(30)	99 (11)	80 (11)	36 (7)	21 (10)	13 (7)	20 (7)
C(31)	24 (7)	74 (9)	36 (6)	14 (6)	2 (5)	−5 (6)
C(32)	48 (7)	48 (9)	21 (5)	13 (6)	11 (5)	0 (5)
C(33)	48 (7)	78 (8)	31 (5)	19 (12)	1 (5)	−2 (13)
C(34)	55 (7)	71 (10)	35 (5)	28 (10)	17 (5)	−9 (9)
C(35)	61 (7)	35 (10)	22 (5)	13 (7)	10 (5)	4 (6)
C(36)	58 (8)	57 (8)	25 (5)	25 (7)	−3 (5)	10 (5)
C(37)	45 (8)	67 (9)	42 (6)	13 (7)	11 (6)	3 (7)

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[*] It was pointed out by a referee that $\sigma(y)$ for atoms near $y/b=0{\cdot}75$ is large (by a factor $\sim 1{\cdot}8$) compared to that of other atoms. Analysis of the least-squares process for refinement on $|F|$ has shown that (in $P2_1$) as $y_J \rightarrow y_{\rm I}$, $(\partial|F|/\partial y_J)^2{}_{hkl} \rightarrow 0$ systematically for those reflections for which $\varphi_{hkl} \rightarrow \varphi_{{\rm I}_{hkl}}$. Since I tends to dominate the phases, especially of the strong reflections, this effect causes the affected diagonal sums of the *LS* matrix to be abnormally small. Thus the corresponding terms in the inverse matrix, and the derived $\sigma(y)$'s, are large.

[†] A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31541 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

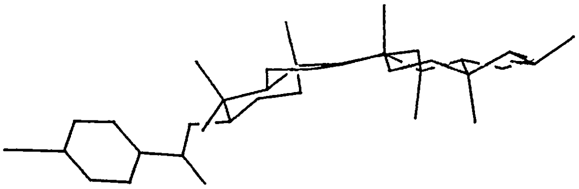

Fig. 4. Side view of hortensenyl *p*-iodobenzoate.

Discussion

Hortensenol may best be described as a migrated hopane derivative having a fern-8-enol structure. This structure is new as a natural product but has been reported as an acid-isomerization/demethylation product of arundoin, one of five pentacyclic triterpenoids found in the rhizomes of *Imperata cylindrica* by Nishimoto, Ito, Natori & Omoto (1968).

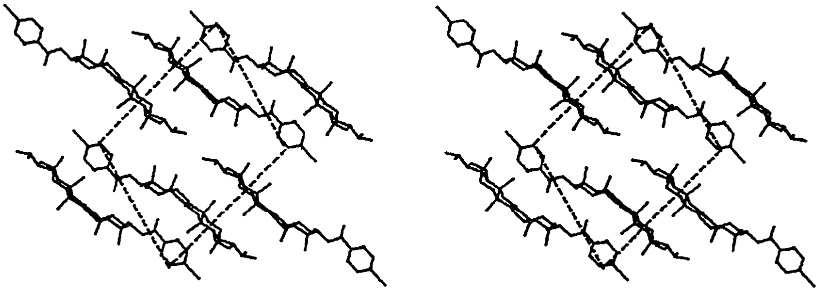

Fig. 5. Stereo packing diagram. Projection along **b**.

Table 5. *Bond angles (°) and their estimated standard deviations*

C(10)-C(1)—C(2)	111·1 (1·0)
C(1)—C(2)—C(3)	107·8 (0·9)
C(2)—C(3)—C(4)	115·3 (0·8)
C(2)—C(3)—O(2)	106·3 (0·8)
C(4)—C(3)—O(2)	107·4 (0·8)
C(3)—C(4)—C(5)	107·8 (0·8)
C(3)—C(4)—C(23)	106·9 (0·8)
C(3)—C(4)—C(24)	111·1 (0·8)
C(5)—C(4)—C(23)	108·7 (0·7)
C(5)—C(4)—C(24)	112·9 (0·7)
C(23)-C(4)—C(24)	109·3 (0·8)
C(4)—C(5)—C(6)	115·2 (0·9)
C(4)—C(5)—C(10)	116·6 (0·8)
C(6)—C(5)—C(10)	109·8 (0·9)
C(5)—C(6)—C(7)	113·5 (1·1)
C(6)—C(7)—C(8)	116·0 (1·0)
C(7)—C(8)—C(9)	122·0 (0·9)
C(7)—C(8)—C(14)	116·5 (1·2)
C(9)—C(8)—C(14)	121·2 (1·5)
C(8)—C(9)—C(10)	122·0 (1·2)
C(8)—C(9)—C(11)	122·5 (1·2)
C(10)-C(9)—C(11)	115·0 (1·0)
C(1)—C(10)-C(5)	106·0 (0·9)
C(1)—C(10)-C(9)	109·0 (1·0)
C(1)—C(10)-C(25)	109·2 (1·0)
C(5)—C(10)-C(9)	107·8 (0·9)
C(5)—C(10)-C(25)	117·7 (1·1)
C(9)—C(10)-C(25)	106·9 (1·0)
C(9)—C(11)-C(12)	117·8 (0·9)
C(11)-C(12)-C(13)	112·3 (0·8)
C(12)-C(13)-C(14)	109·0 (0·8)
C(12)-C(13)-C(18)	110·6 (0·8)
C(12)-C(13)-C(27)	105·7 (0·7)
C(14)-C(13)-C(18)	108·0 (0·7)
C(14)-C(13)-C(27)	110·6 (0·8)
C(18)-C(13)-C(27)	112·9 (0·8)
C(8)—C(14)-C(13)	108·2 (0·9)
C(8)—C(14)-C(15)	115·7 (1·2)
C(8)—C(14)-C(26)	103·5 (0·7)
C(13)-C(14)-C(15)	108·1 (0·8)
C(13)-C(14)-C(26)	112·7 (1·0)
C(15)-C(14)-C(26)	108·7 (0·8)
C(14)-C(15)-C(16)	114·5 (0·9)
C(15)-C(16)-C(17)	113·8 (0·9)
C(16)-C(17)-C(18)	108·2 (0·9)
C(16)-C(17)-C(21)	117·0 (0·8)
C(16)-C(17)-C(28)	111·6 (1·0)
C(18)-C(17)-C(21)	98·0 (0·8)
C(18)-C(17)-C(28)	113·0 (1·0)
C(21)-C(17)-C(28)	108·4 (0·8)
C(13)-C(18)-C(17)	117·5 (0·9)
C(13)-C(18)-C(19)	120·2 (0·9)
C(17)-C(18)-C(19)	105·9 (0·9)
C(18)-C(19)-C(20)	101·7 (0·9)
C(19)-C(20)-C(21)	107·6 (0·8)
C(20)-C(21)-C(17)	103·0 (0·7)
C(20)-C(21)-C(22)	112·4 (1·0)
C(17)-C(21)-C(22)	119·3 (1·0)
C(21)-C(22)-C(29)	108·8 (1·2)
C(21)-C(22)-C(30)	114·8 (1·0)
C(29)-C(22)-C(30)	110·6 (1·0)
C(3)—O(2)—C(31)	119·5 (0·8)
O(1)—C(31)-O(2)	124·9 (0·8)
O(1)—C(31)-C(32)	124·1 (0·8)
O(2)—C(31)-C(32)	110·8 (0·9)
C(31)-C(32)-C(33)	123·3 (0·8)
C(31)-C(32)-C(37)	116·3 (0·9)
C(33)-C(32)-C(37)	120·4 (0·8)
C(32)-C(33)-C(34)	121·4 (0·9)
C(33)-C(34)-C(35)	117·5 (1·1)
C(34)-C(35)-C(36)	122·1 (0·8)
C(34)-C(35)-I	117·3 (0·8)
C(36)-C(35)-I	120·5 (0·7)
C(35)-C(36)-C(37)	121·6 (0·9)
C(36)-C(37)-C(32)	116·9 (1·0)

The bond lengths, bond angles and ring dihedral angles are given in Tables 4, 5 and 6 respectively. The average C–C bond distances between various types of atoms in the rings are 1·538 Å for sp^3-sp^3 atoms, 1·528 Å for sp^3-sp^2 atoms, and 1·344 Å for sp^2-sp^2 atoms. As expected, the longest bonds are between highly substituted carbon atoms [*e.g.* C(13)–C(14) 1·589 Å, C(4)–C(5) 1·576 Å and C(17)–C(21) 1·568 Å].

Table 6. *Ring dihedral angles*

Ring		Angle (°)
A	C(10)-C(1)—C(2)—C(3)	+61·3 (1·3)
A	C(1)—C(2)—C(3)—C(4)	−58·6 (1·2)
A	C(2)—C(3)—C(4)—C(5)	+52·1 (1·1)
A	C(3)—C(4)—C(5)—C(10)	−52·0 (1·2)
A	C(4)—C(5)—C(10)-C(1)	+55·8 (1·2)
A	C(5)—C(10)-C(1)—C(2)	−59·5 (1·3)
B	C(10)-C(5)—C(6)—C(7)	+60·3 (1·5)
B	C(5)—C(6)—C(7)—C(8)	−35·2 (1·7)
B	C(6)—C(7)—C(8)—C(9)	+7·1 (1·8)
B	C(7)—C(8)—C(9)—C(10)	−5·0 (1·9)
B	C(8)—C(9)—C(10)-C(5)	+28·6 (1·7)
B	C(9)—C(10)-C(5)—C(6)	−54·3 (1·3)
C	C(14)-C(8)—C(9)—C(11)	−3·4 (1·8)
C	C(8)—C(9)—C(11)-C(12)	−3·6 (1·8)
C	C(9)—C(11)-C(12)-C(13)	−23·5 (1·4)
C	C(11)-C(12)-C(13)-C(14)	+54·4 (1·0)
C	C(12)-C(13)-C(14)-C(8)	−59·2 (1·1)
C	C(13)-C(14)-C(8)—C(9)	+34·7 (1·4)
D	C(18)-C(13)-C(14)-C(15)	+54·6 (1·0)
D	C(13)-C(14)-C(15)-C(16)	−57·9 (1·1)
D	C(14)-C(15)-C(16)-C(17)	+56·7 (1·3)
D	C(15)-C(16)-C(17)-C(18)	−48·7 (1·2)
D	C(16)-C(17)-C(18)-C(13)	+51·4 (1·2)
D	C(17)-C(18)-C(13)-C(14)	−55·2 (1·2)
E	C(21)-C(17)-C(18)-C(19)	−49·1 (1·0)
E	C(17)-C(18)-C(19)-C(20)	+35·8 (1·0)
E	C(18)-C(19)-C(20)-C(21)	−7·7 (1·2)
E	C(19)-C(20)-C(21)-C(17)	−21·8 (1·1)
E	C(20)-C(21)-C(17)-C(18)	+41·8 (1·0)

Rings *A* and *D* take slightly distorted chair conformations. The distortion is primarily a result of nonbonded 1,3 diaxial repulsions between the angular methyl groups. The distance between the methyl carbon atoms C(24) and C(25) is 3·24 Å while the distance between C(27) and C(28) is 3·16 Å. These distances may be compared to 2·52 Å, the distance expected for 1,3 diaxial methyl groups on a ring having an undistorted chair conformation. Rings *B* and *C* take on half-chair conformations as a result of the double bond between atoms C(8) and C(9). Both *A*/*B* and *C*/*D* ring junctions are *trans*-fused. Atoms C(5) and C(13) have the same relative orientation forcing both ends of the molecule to be on the same side of the central C(8)–C(9) double bond, and giving a pronounced curvature to the molecule as a whole. Ring *E* has a slightly distorted envelope conformation. Rings *C*/*D*/*E* are in the *anti* arrangement, the *D*/*E* junction being *trans*-fused.

The relative stereochemistry of hortensenol is easily understood in terms of the biogenesis of migrated hopane derivatives. The α,β relationships among the methyl groups are established during initial stages of cation-induced cyclization of squalene [see, *e.g.* Richards & Henderickson (1964) and Fig. 2]. Both hydrogen atoms and methyl groups then migrate along the C(9)–C(8)–C(14)–C(13)–C(18)–C(17)–C(21)–C(22) chain in a concerted fashion, inverting the configuration at each of these atoms (Fig. 3). It is this series of Wagner–Meerwein-type rearrangements that gives C(13) the same orientation as C(5) and thus produces the curved nature of the molecule as a whole. Elimination of the hydrogen atom at C(8) then leaves the fern-8-enol structure.

A side view of the molecule is in Fig. 4 while Fig. 5 is a packing diagram.

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