The Crystal and Molecular Structure of 21α-Methoxy- Δ^{13}-serraten-3β-ol: the Conformation of the Δ^{13}-Serratene System

By Frank H. Allen,* Olga Kennard† and George M. Sheldrick

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

Crystals of the triterpenoid alcohol 21α-methoxy-Δ^{13}-serraten-3β-ol, $C_{31}H_{52}O_2$, are monoclinic, space group $P2_1$, $a = 6.403$ (2), $b = 31.316$ (9), $c = 7.297$ (2) Å, $\beta = 113.67$ (4)°. The structure has been solved by a direct-phasing technique from diffractometer data and refined to $R = 0.040$. The positions of all 52 H atoms were refined with a novel constraint technique. The analysis establishes the molecular structure and stereochemistry of the alcohol, which were previously unknown. The geometry of the Δ^{13}-serratene skeleton, which contains a cycloheptene C ring, may be accurately defined from results from this study together with those for the bromoindole derivative of 3β-methoxy-Δ^{13}-serraten-21-one [Allen & Trotter, *J. Chem. Soc.* (*B*) (1970), pp. 721–727].

Introduction

A triterpenoid ketone of formula $C_{31}H_{50}O_2$, shown by this analysis to be 21α-methoxy-Δ^{13}-serraten-3-one (I), was isolated from western white spruce (*Picea glauca*, var. *albertiana*) (Kutney & Westcott, 1970; Westcott, 1971). The melting point and spectroscopic characteristics of (I) were found to differ very slightly from those of 3β-methoxy-Δ^{13}-serraten-21-one (II), whose structure was established crystallographically from the

20,21-bromoindole derivative (V) (Allen & Trotter, 1970). The ketones (I) and (II) were reduced to the corresponding alcohols (III) and (IV), and small differences in the mass spectra of these alcohols were analysed (Westcott, 1971). A definite assignment of structure and stereochemistry for (III) was not possible and lack of material prevented further chemical work. We have performed an X-ray analysis of crystals of (III) and shown it to be 21α-methoxy-Δ^{13}-serraten-3β-ol.
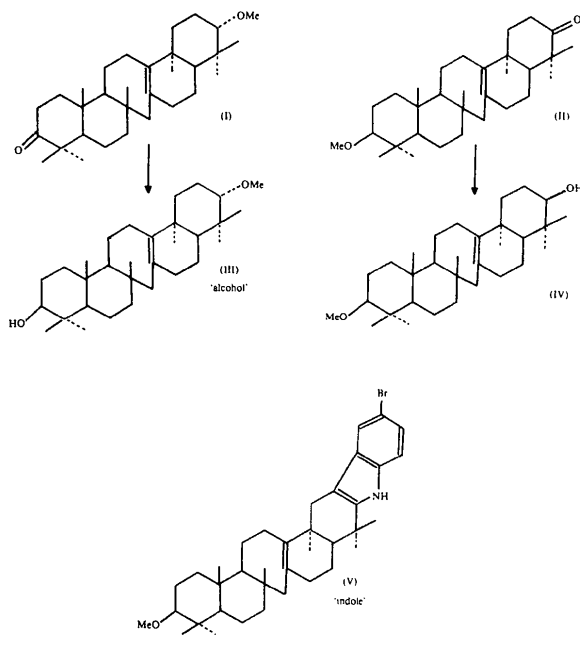
Experimental

Diamond-shaped plates of (III) are colourless and perfectly formed, with **b** perpendicular to the plate and **a** and **c** along the face diagonals. The symmetry and space group were determined by photography, and cell parameters were obtained by least squares from sixteen 2θ values measured on a Picker diffractometer.

Crystal data

21α-Methoxy-Δ^{13}-serraten-3β-ol, $C_{31}H_{52}O_2$, $M_r = 456.8$, monoclinic, $a = 6.403$ (2), $b = 31.316$ (9), $c = 7.297$ (2) Å, $\beta = 113.67$ (4)°, $U = 1340.1$ (4) Å³; $D_m = 1.15 \pm 0.03$ (by flotation), $Z = 2$, $D_x = 1.131$ g cm⁻³; $\mu = 4.4$ cm⁻¹ for Cu $K\alpha$ radiation ($\lambda_{mean} = 1.54178$ Å), $F(000) = 508$. Absent reflexions $0k0$ when k is odd define the space group as $P2_1$ or $P2_1/m$; $P2_1$ was confirmed by the structure analysis.

Intensities were collected on a Picker four-circle automatic diffractometer equipped with a graphite monochromator. The θ–2θ scan technique was employed at a speed of 1° min⁻¹ in 2θ, with background counting for 40 s at the scan limits. The specimen, 0.20 × 0.10 × 0.25 mm, was mounted with **b** parallel to the

* To whom correspondence should be addressed.
† External Staff, Medical Research Council.

φ axis of the goniostat. Of 1729 independent reflexions having $2\theta \leq 110°$, 238 with $I < 3\sigma(I)$ were rejected, where $\sigma^2(I) = S + B + (dS)^2$, and S is the scan count, B the background count corrected to scan time and d a constant included to account for instrumental instability. The value of d was calculated to be 0·023 for this experiment from an analysis of the fluctuation of the S values of three check reflexions. Lorentz and polarization corrections were applied and $|E|$ values derived.

Structure solution and refinement

The structure was solved by weighted multisolution tangent refinement (Germain, Main & Woolfson, 1970) with the 323 reflexions with $|E| \geq 1·30$. Difficulties were experienced in selecting a suitable starting set of reflexions, largely due to the small number of $h0l$ reflexions of high $|E|$. This problem was resolved by the pseudotangent refinement technique, as used in the solution of the testosterone structure (Roberts, Pettersen, Sheldrick, Isaacs & Kennard, 1973). The results of this process were analysed with respect to a listing of Σ_2 triplets to give a starting set of six reflexions (Table 1), where the first three reflexions define the origin and the fourth fixes the enantiomorph.

Weighted tangent refinement was carried out for 12 cycles for each of the 64 possible phase permutations, and the index $R_a = [\Sigma_h g(\alpha - k\langle\alpha^2\rangle^{1/2})^2/\Sigma_h g\alpha^2]^{1/2}$ was calculated. The weights were $w = \tanh|\alpha/2|$, g was set at $\langle\alpha^2\rangle^{-1/2}$, and the scale factor k was chosen to minimize R_a. E maps were calculated for solutions of low R_a. The resulting peak coordinates were used to calculate E values (assuming atomic numbers proportional to peak heights) and a reliability index $R_A = [\Sigma (E_{obs} - kE_{calc})^2/\Sigma (E_{obs})^2]^{1/2}$ was obtained with k chosen to minimize R_A. The best solution had $R_a = 0·219$ and $R_A = 0·298$. Other values of R_a ranged from 0·259 to 0·372, while no other R_A value was less than 0·362. The strongest 32 independent peaks could be assembled to form the skeleton of (III) with only the methyl C(29) missing. A weaker peak (No. 50) did exist in the E map in a chemically sensible position for this atom, a position which was confirmed by a difference map.

Full-matrix least-squares refinement, treating all 33 non-hydrogen atoms isotropically, reduced R to 0·122. The function minimized was $\Sigma w|F_o - kF_c|^2$, where all weights were set to unity. Scattering factors were taken from Cromer & Mann (1968); the y coordinate of C(23) was fixed for origin definition. Anisotropic refinement reduced R to 0·093.

The H positions were calculated with C—C—H angles equal, the methyl group staggered and C—H = 1·0 Å. The methyl groups were then refined as rigid groups, the independent variables consisting of three translations and three rotations. The remaining C—H bonds were constrained so that the C—H vectors remained constant in both magnitude and direction, and the H atoms contributed to the derivative calculation for refinement of the C atom coordinates. Since the idealized geometry was recalculated every third cycle, convergence to idealized geometry was obtained. The hydroxyl H was located in a difference map and allowed to refine subject only to the constraint that O—H = 0·97 Å. Two separate overall isotropic temperature factors for H atoms were refined, one for the methyl, the second for non-methyl. The bonded H atom scattering factor of Stewart, Davidson & Simpson (1965) was employed. Full-matrix refinement following this procedure, with unit weights, reduced R to 0·051. Since the incorporation of all 52 H atoms into the refinement introduced only 29 further independent variables this is a significant improvement over the 'heavy-atom' structure.

The listing of observed and calculated structure factors was examined and four strong low-order reflexions were found to be suffering from secondary extinction. These reflexions were omitted from the next two cycles, when R fell to 0·045. The general effects of secondary extinction were still apparent, however, among the stronger reflexions and an overall isotropic extinction parameter x was refined in the final cycles. The calculated structure factor F^* became $F^* = F(1 - xF^2/\sin\theta)$. In the final cycle, all parameter shifts were less than 0·02 of the corresponding estimated standard deviations and refinement was concluded at $R = 0·040$. Final positional and anisotropic thermal parameters for C and O are in Table 2, final H parameters in Table 3.†

Discussion

The structure of alcohol (III) is shown in Fig. 1 projected down **a**. The pentacyclic Δ^{13}-skeleton has all rings *trans* fused, the hydroxyl group is 3β and the methoxy group is 21α. The structure is drawn with its correct

Table 1. *Reflexions used in the starting set with allowed phases in radians*

h	k	l	φ
−1	0	1	0
−2	3	1	0
−3	2	2	$\pi/4, 3\pi/4$
−4	3	5	$\pi/4, 3\pi/4$
−1	3	3	$\pm\pi/4, \pm3\pi/4$
−4	10	1	$\pm\pi/4, \pm3\pi/4$

Table 2. *Fractional atomic coordinates* $(\times 10^4)$ *and anisotropic thermal parameters* $(\mathring{A}^2 \times 10^3)$ *for non-hydrogen atoms in* (III)

Estimated standard deviations are in parentheses.

$$T = \exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{23}b^*c^*kl + 2U_{13}a^*c^*hl + 2U_{12}a^*b^*hk)].$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	−2359 (7)	3258 (2)	−773 (7)	68 (3)	42 (2)	99 (3)	25 (2)	44 (2)	14 (2)
O(2)	−296 (6)	−1161 (2)	2172 (6)	50 (2)	35 (2)	71 (3)	−8 (2)	23 (2)	−2 (2)
C(1)	−1167 (9)	2105 (2)	−638 (7)	54 (3)	37 (3)	37 (3)	6 (2)	17 (2)	2 (2)
C(2)	−2408 (10)	2532 (2)	−1365 (8)	67 (4)	41 (3)	42 (3)	9 (2)	23 (3)	5 (3)
C(3)	−1126 (9)	2892 (2)	−32 (8)	49 (3)	35 (3)	68 (4)	9 (3)	29 (3)	7 (3)
C(4)	−740 (8)	2832 (2)	2163 (8)	42 (3)	32 (3)	51 (3)	−1 (2)	10 (2)	9 (2)
C(5)	329 (8)	2379 (2)	2838 (7)	33 (2)	33 (3)	44 (3)	−4 (2)	13 (2)	2 (2)
C(6)	905 (9)	2286 (2)	5037 (8)	64 (4)	43 (3)	38 (3)	−8 (2)	6 (3)	16 (3)
C(7)	2595 (9)	1921 (2)	5736 (7)	58 (3)	43 (3)	34 (3)	−5 (3)	1 (2)	9 (3)
C(8)	1788 (8)	1507 (2)	4535 (7)	34 (3)	37 (3)	29 (3)	−1 (2)	5 (2)	1 (2)
C(9)	899 (7)	1607 (2)	2271 (6)	32 (3)	31 (3)	33 (3)	−5 (2)	14 (2)	−5 (2)
C(10)	−827 (8)	1991 (2)	1511 (7)	35 (3)	31 (3)	29 (3)	3 (2)	10 (2)	1 (2)
C(11)	122 (8)	1203 (2)	948 (7)	54 (3)	33 (3)	28 (3)	0 (2)	12 (2)	0 (2)
C(12)	2039 (9)	888 (2)	1163 (7)	71 (3)	34 (3)	39 (3)	4 (2)	30 (3)	5 (3)
C(13)	2770 (8)	587 (2)	2940 (7)	51 (3)	37 (3)	40 (3)	2 (2)	21 (3)	9 (2)
C(14)	3682 (8)	746 (2)	4790 (7)	36 (3)	35 (3)	41 (3)	2 (2)	11 (2)	6 (2)
C(15)	4611 (9)	480 (2)	6639 (7)	54 (3)	43 (3)	41 (3)	0 (2)	3 (2)	2 (3)
C(16)	4712 (9)	5 (2)	6274 (7)	61 (3)	33 (3)	36 (3)	3 (2)	6 (2)	4 (3)
C(17)	2617 (8)	−126 (2)	4426 (7)	41 (3)	35 (3)	28 (2)	1 (2)	13 (2)	6 (2)
C(18)	2621 (8)	104 (2)	2538 (7)	47 (3)	31 (3)	30 (2)	0 (2)	18 (2)	2 (2)
C(19)	405 (8)	−20 (2)	751 (7)	51 (3)	43 (3)	32 (3)	1 (2)	8 (2)	6 (3)
C(20)	94 (9)	−508 (2)	542 (7)	56 (3)	46 (3)	37 (3)	−2 (2)	4 (3)	4 (3)
C(21)	40 (8)	−706 (2)	2400 (7)	44 (3)	30 (3)	51 (3)	−6 (2)	18 (2)	4 (2)
C(22)	2155 (8)	−618 (2)	4297 (7)	47 (3)	32 (3)	38 (3)	1 (2)	17 (2)	1 (2)
C(23)	3957 (8)	1219 (−)	5171 (7)	37 (3)	35 (3)	41 (3)	0 (2)	4 (2)	4 (2)
C(24)	−2967 (10)	2905 (3)	2461 (9)	72 (4)	63 (4)	69 (4)	17 (3)	36 (3)	30 (3)
C(25)	1003 (12)	3174 (2)	3373 (11)	79 (4)	37 (3)	95 (5)	−9 (3)	14 (4)	7 (3)
C(26)	−3164 (8)	1872 (2)	1502 (8)	36 (3)	54 (3)	52 (3)	15 (3)	13 (2)	4 (3)
C(27)	89 (9)	1280 (2)	5220 (8)	51 (3)	66 (4)	44 (8)	14 (3)	25 (3)	8 (3)
C(28)	4666 (9)	−1 (2)	2016 (9)	58 (3)	49 (3)	65 (4)	5 (3)	35 (3)	4 (3)
C(29)	1630 (12)	−750 (2)	6082 (9)	94 (5)	46 (3)	57 (4)	4 (3)	37 (3)	−10 (3)
C(30)	4195 (9)	−885 (2)	4342 (9)	53 (3)	36 (3)	65 (4)	−2 (3)	13 (3)	9 (3)
C(31)	−2603 (10)	−1284 (3)	1082 (11)	54 (4)	62 (4)	94 (5)	−20 (4)	24 (4)	−14 (3)

Table 3. *Fractional atomic coordinates for the hydrogen atoms* $(\times 10^3)$

The first part of the atom identifier is the number of the bonded carbon. Isotropic thermal parameters refined to $U = 0.053$ $\mathring{A}^2$ for non-methyl hydrogens and 0.092 $\mathring{A}^2$ for methyl hydrogens [H(241)−H(313)].

	x	y	z		x	y	z		x	y	z
H(O1)	−148 (7)	344 (1)	−136 (7)	H(161)	612	−6	606	H(262)	−356	157	107
H(11)	−209	187	−155	H(162)	474	−16	746	H(263)	−434	207	55
H(12)	36	212	−70	H(171)	120	−2	454	H(271)	,−117	148	513
H(21)	−397	251	−136	H(191)	46	10	−50	H(272)	94	119	664
H(22)	−254	259	−276	H(192)	−92	11	95	H(273)	−57	102	437
H(31)	42	290	−7	H(201)	139	−63	29	H(281)	457	−30	152
H(51)	177	241	263	H(202)	−137	−57	−61	H(282)	615	4	319
H(61)	−52	221	521	H(211)	−128	−57	257	H(283)	457	20	93
H(62)	159	255	585	H(231)	482	126	665	H(291)	308	−73	731
H(71)	404	201	564	H(232)	489	133	445	H(292)	109	−105	586
H(72)	290	186	717	H(241)	−430	272	163	H(293)	45	−57	626
H(91)	227	172	210	H(242)	−339	321	219	H(301)	439	−84	306
H(111)	−61	123	−48	H(243)	−254	284	391	H(302)	385	−119	448
H(112)	−103	105	131	H(251)	82	316	467	H(303)	563	−80	549
H(121)	341	106	127	H(252)	61	346	278	H(311)	−263	−160	107
H(122)	152	71	−8	H(253)	262	311	361	H(312)	−304	−118	−31
H(151)	619	58	747	H(261)	−313	191	288	H(313)	−371	−118	163
H(152)	363	52	739								

absolute stereochemistry, derived by analogy with that obtained by anomalous dispersion techniques for the bromoindole derivative (V) (Allen & Trotter, 1970). Throughout this discussion this latter structure (V) will be referred to as the 'indole', while the present structure (III) will be referred to as the 'alcohol'.

A full list of bond lengths and angles for the alcohol is given in Tables 4 and 5. Values for the indole are also given for that part of the Δ^{13}-skeleton where direct comparisons are valid, namely the rings A, B, C, D and C(19), C(20), C(29), C(30) of ring E. The alcohol structure is much more accurate (mean e.s.d.'s 0·007 Å and 0·4° for parameters involving C and O) than the indole (mean e.s.d.'s 0·02 Å, 1·3°, $R = 0·09$); despite this, values of distances and angles in rings $A–D$ all agree to within 3σ (indole). In particular, the mean dif-

ference between intra-annular angles in these rings is only 1·2°; the mean difference between bond lengths in the ring system is 0·023 Å. Both these figures represent 1σ (indole) or 3σ (alcohol).
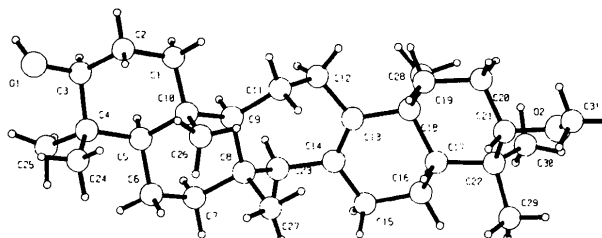
Fig. 1. Perspective view of one molecule of the alcohol viewed down a.

Table 4. *Bond lengths* (Å) *for the alcohol* (III) *together with comparable* (*see text*) *values for the indole* (V)

All C—H distances were constrained to 1·00 Å. The O(1)—H(O1) distance was constrained to 0·97 Å.

	(III)	(V)		(III)	(V)		(III)	(V)
C(1)—C(2)	1·536 (7)	1·537	C(8)—C(23)	1·561	1·553	C(16)—C(17)	1·527 (6)	1·480
C(1)—C(10)	1·536 (6)	1·531	C(8)—C(27)	1·542 (7)	1·560	C(17)—C(18)	1·556 (6)	1·537
C(2)—C(3)	1·501 (8)	1·527	C(9)—C(10)	1·576 (6)	1·583	C(17)—C(22)	1·566 (6)	1·559
C(3)—C(4)	1·531 (8)	1·506	C(9)—C(11)	1·547 (6)	1·522	C(18)—C(19)	1·543 (7)	1·602
C(3)—O(1)	1·443 (6)	–	C(10)—C(26)	1·539 (7)	1·534	C(18)—C(28)	1·539 (7)	1·564
C(4)—C(5)	1·568 (7)	1·536	C(11)—C(12)	1·534 (7)	1·583	C(19)—C(20)	1·540 (7)	–
C(4)—C(24)	1·543 (8)	1·609	C(12)—C(13)	1·516 (7)	1·509	C(20)—C(21)	1·504 (7)	–
C(4)—C(25)	1·542 (8)	1·584	C(13)—C(14)	1·334 (7)	1·361	C(21)—C(22)	1·523 (7)	–
C(5)—C(6)	1·524 (7)	1·524	C(13)—C(18)	1·536 (7)	1·525	C(21)—O(2)	1·440 (6)	–
C(5)—C(10)	1·543 (6)	1·605	C(14)—C(15)	1·491 (7)	1·480	C(22)—C(29)	1·527 (7)	1·564
C(6)—C(7)	1·514 (7)	1·573	C(14)—C(23)	1·504 (7)	1·485	C(22)—C(30)	1·540 (7)	1·572
C(7)—C(8)	1·535 (7)	1·581	C(15)—C(16)	1·517 (7)	1·532	O(2)—C(31)	1·421 (6)	–
C(8)—C(9)	1·548 (6)	1·552						

Table 5. *Valency angles* (°) *for the alcohol* (III) *together with comparable* (*see text*) *values for the indole* (V)

H—C—H angles constrained to 109·47°. C—C—H angles range from 100·2–116·3°. The angle C(3)—O(1)—H(O1)= 105·9°.

	(III)	(V)		(III)	(V)		(III)	(V)
C(2)—C(1)—C(10)	113·3 (4)	113·7	C(8)—C(9)—C(10)	115·8 (4)	117·5	C(18)—C(17)—C(22)	118·1 (4)	116·0
C(1)—C(2)—C(3)	111·0 (4)	109·2	C(8)—C(9)—C(11)	112·9 (4)	114·1	C(17)—C(18)—C(19)	107·7 (4)	108·6
C(2)—C(3)—C(4)	113·7 (4)	113·6	C(10)—C(9)—C(11)	113·6 (4)	111·2	C(17)—C(18)—C(13)	108·0 (4)	111·7
C(2)—C(3)—O(1)	108·9 (4)	–	C(1)—C(10)—C(5)	107·1 (4)	106·7	C(17)—C(18)—C(28)	115·0 (4)	113·5
C(4)—C(3)—O(1)	109·3 (4)	–	C(1)—C(10)—C(9)	109·2 (4)	109·3	C(19)—C(18)—C(13)	112·1 (4)	108·2
C(3)—C(4)—C(5)	107·9 (4)	108·2	C(1)—C(10)—C(26)	108·2 (4)	108·9	C(19)—C(18)—C(28)	108·7 (4)	107·4
C(3)—C(4)—C(24)	111·0 (4)	111·3	C(5)—C(10)—C(9)	106·7 (3)	105·0	C(28)—C(18)—C(13)	105·4 (4)	107·2
C(3)—C(4)—C(25)	106·8 (5)	108·8	C(5)—C(10)—C(26)	114·4 (4)	114·4	C(18)—C(19)—C(20)	111·9 (4)	–
C(5)—C(4)—C(24)	113·6 (4)	115·7	C(9)—C(10)—C(26)	111·1 (4)	112·1	C(19)—C(20)—C(21)	111·7 (4)	–
C(5)—C(4)—C(25)	108·9 (4)	108·8	C(9)—C(11)—C(12)	114·8 (4)	112·4	C(20)—C(21)—C(22)	114·2 (4)	–
C(24)—C(4)—C(25)	108·3 (5)	104·4	C(11)—C(12)—C(13)	116·5 (4)	114·3	C(20)—C(21)—O(2)	111·2 (4)	–
C(4)—C(5)—C(6)	113·2 (4)	113·1	C(12)—C(13)—C(14)	119·6 (4)	120·1	C(22)—C(21)—O(2)	108·8 (4)	–
C(4)—C(5)—C(10)	118·4 (4)	116·7	C(12)—C(13)—C(18)	118·3 (4)	118·1	C(21)—C(22)—C(17)	108·1 (4)	–
C(6)—C(5)—C(10)	111·3 (4)	109·7	C(14)—C(13)—C(18)	121·9 (4)	121·7	C(21)—C(22)—C(29)	107·9 (4)	–
C(5)—C(6)—C(7)	109·7 (4)	108·6	C(13)—C(14)—C(15)	124·1 (4)	122·6	C(21)—C(22)—C(30)	111·0 (4)	–
C(6)—C(7)—C(8)	114·5 (4)	112·9	C(13)—C(14)—C(23)	121·7 (4)	121·4	C(17)—C(22)—C(29)	108·4 (4)	108·5
C(7)—C(8)—C(9)	109·5 (4)	111·1	C(15)—C(14)—C(23)	114·1 (4)	115·8	C(17)—C(22)—C(30)	113·2 (4)	113·2
C(7)—C(8)—C(23)	105·2 (4)	105·2	C(14)—C(15)—C(16)	114·8 (4)	114·6	C(29)—C(22)—C(30)	108·1 (5)	104·8
C(7)—C(8)—C(27)	108·9 (4)	109·4	C(15)—C(16)—C(17)	109·5 (4)	110·1	C(8)—C(23)—C(14)	119·3 (4)	119·7
C(9)—C(8)—C(23)	109·7 (4)	108·6	C(16)—C(17)—C(18)	110·1 (4)	111·9	C(21)—O(2)—C(31)	114·0 (4)	–
C(9)—C(8)—C(27)	115·8 (4)	114·7	C(16)—C(17)—C(22)	113·3 (4)	114·0			
C(23)—C(8)—C(27)	107·3 (4)	107·9						

The overall shape of the Δ^{13}-skeleton is very similar in both compounds. Fig. 2 shows the two molecules viewed along the C(13)—C(14) double bond. The Δ^{13}-serratene skeleton in both cases has a shallow S shape caused by 1,3 methyl–methyl interactions on both faces of the molecule. There are two such interactions across the A and B rings between the methyl groups C(24) and C(26), and between C(26) and C(27); the skeleton is convex towards these C–methyl vectors. In an ideal all-chair conformation for rings A and B, these vectors should be parallel, but in the alcohol we obtain angles of 23·8 and 22·8° between vector pairs (Fig. 2a), while values in the indole are slightly larger at 24·5 and 25·2°. These distortions allow the methyl–methyl distances to range from 3·26–3·35 Å and the two closest H—H approaches in the alcohol, where H atoms were located, are 2·12 and 2·20 Å. The 1,3 interactions cause one of the intra-annular angles at the 2-carbon position (i.e. the ring C between the two C-methyl vectors) to expand significantly from its minimum-energy value of 111·6° (Hendrickson, 1967; Bucourt & Hainaut, 1965). The angles involved in both skeletons are C(4)—C(5)—C(10) and C(10)—C(9)—C(8), which are 117 and 118° in the indole, and 118·4 and 115·8° in the alcohol.

The reverse bend of the skeleton is caused by a similar 1,3 methyl–methyl interaction between C(28) and C(30) across the E ring on the opposite face of the molecule. The methyl–methyl separations (3·31 and 3·32 Å in indole and alcohol respectively) are identical, while the closest H—H approach is 2·07 Å in the alcohol. However, the angle between the two C–methyl vectors required to gain this separation is much larger in the indole (33·2°) than in the alcohol (24·5°). This is due to the indole fusion at the 20,21 position which yields a sofa-form cyclohexane ring rather than the chair-form cyclohexane in the free skeleton of the alcohol. Once again the intra-annular angle in the E ring at the 2-carbon position [C(18)—C(17)—C(22)] is expanded significantly to 116 (indole) and 118·1° (alcohol).
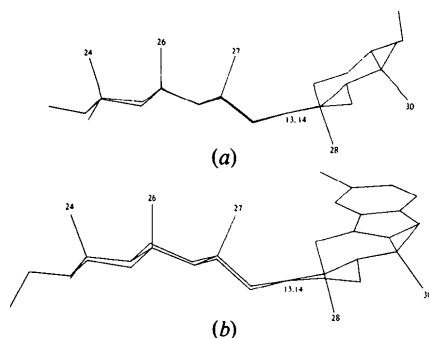
Intra-annular torsion angles in the five rings of the Δ^{13}-serratene skeletons are compared in Table 6. The chair-form A and B rings are somewhat distorted in both molecules by the 1,3 methyl–methyl interactions described above. Torsion angles vary from 45–68° in the indole and from 48–63° in the alcohol. The mean

Table 6. *Intra-annular torsion angles in the pentacyclic* Δ^{13}-*serratene skeleton in the alcohol* (III) *and the indole* (V)

Comparisons with results of minimum-energy calculations are denoted HE (Hendrickson, 1967) and BH (Bucourt & Hainaut, 1965).

Ring A

	(III)	(V)	HE
C(1)—C(2)	−58·7	−59·0	−54·4
C(2)—C(3)	57·8	60·1	54·4
C(3)—C(4)	−51·3	−55·9	−54·4
C(4)—C(5)	49·8	52·1	54·4
C(5)—C(10)	−50·4	−50·5	−54·4
C(10)—C(1)	52·7	52·6	54·4

Ring B

	(III)	(V)	HE
C(5)—C(6)	−62·5	−67·7	−54·4
C(6)—C(7)	57·3	57·7	54·4
C(7)—C(8)	−49·5	−45·3	−54·4
C(8)—C(9)	48·5	45·5	54·4
C(9)—C(10)	−53·5	−53·1	−54·4
C(10)—C(5)	59·0	63·3	54·4

Ring C

	(III)	(V)	HE
C(8)—C(9)	−63·2	−66·3	−63·8
C(9)—C(11)	66·1	68·9	63·8
C(11)—C(12)	−81·1	−81·7	−83·5
C(12)—C(13)	63·2	66·2	66·1
C(13)—C(14)	−1·6	−6·0	0·0
C(14)—C(23)	−64·6	−62·2	−66·1
C(23)—C(8)	81·1	81·0	83·5

Ring D

	(III)	BH	(V)	BH
C(13)—C(14)	0·9	0	−6·5	0
C(14)—C(15)	−7·0	0	−8·6	−15
C(15)—C(16)	37·6	28	42·1	45
C(16)—C(17)	−63·2	−56	−61·2	−62
C(17)—C(18)	55·6	54	46·0	45
C(18)—C(13)	−25·0	−27	−11·9	−15
	'Sofa'		'Half-chair'	

Ring E

	(III)	BH	(V)	BH
C(17)—C(18)	−50·9	−58	−61·7	−56
C(18)—C(19)	53·1	56	50·6	54
C(19)—C(20)	−58·6	−56	−21·3	−27
C(20)—C(21)	57·6	57	−4·6	0
C(21)—C(22)	−50·4	−58	−1·0	0
C(22)—C(17)	49·0	59	35·1	28
	'Chair'		'Sofa'	

Fig. 2. (a) The alcohol viewed along the C(13)—C(14) double bond. (b) The indole viewed along the C(13)—C(14) double bond.
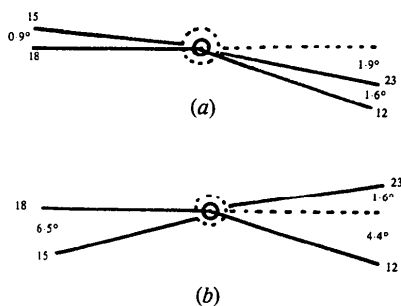
Fig. 3. (a) Newman projection down the C(13)—C(14) double bond in the alcohol. (b) Newman projection down the C(13)—C(14) double bond in the indole.

The D and E rings, although geometrically comparable to a certain extent (Tables 4 and 5), differ markedly in their conformations due to the 20,21 indole fusion. The figures in Table 6, shown compared with theoretical values of Bucourt & Hainaut (1965), indicate that the two cyclohexane rings in the indole are half-chair and distorted sofa respectively. In the free skeleton of the alcohol the cyclohexene D ring is a distorted sofa while the E ring is a chair.

The molecules of the alcohol pack in a head-to-tail arrangement along **b**. The closest intermolecular contacts between screw-related molecules (denoted *) are O(1)—O(2*) at 2·89 and O(1)—C(31*) at 3·54 Å; these values are close to the corresponding van der Waals sums.

values of 55·2° (indole) and 54·3° (alcohol) are close to theoretical predictions (54·4°, Hendrickson, 1967), and deviations from the mean for individual angles follow a similar pattern in both structures.

The seven-membered C ring, which makes this skeleton unique, adopts an almost perfect chair form in both structures. Minimum-energy preferred values for this conformation (Hendrickson, 1967) are also given in Table 6. The mean deviations from the theoretical results are 3·1° (indole) and 2·0° (alcohol); the mean deviation between the two structures is 2·4°. C(8), C(11), C(12) and C(23) forming the 'seat' of the chair are accurately coplanar in both structures. C(13) and C(14) average 1·03 Å above this plane and C(9) averages 0·72 Å below. The tetra-substituted double bond C(13)—C(14) is not strictly planar in either structure, as can be seen in the Newman projections in Fig. 3. The out-of-plane distortions are not identical in the two structures, presumably a result of differences in ring-fusion strain between the alcohol and the indole, where rings D and E are conformationally quite different. Another feature in this ring is the systematic expansion of the angle C(8)—C(23)—C(14) to 118·7° in the indole and 119·3° in the alcohol; this is a result of the introduction of a seven-membered ring in the pentacyclic triterpene skeleton.

References

ALLEN, F. H. & TROTTER, J. (1970). J. Chem. Soc. (B), pp. 721–727.

BUCOURT, R. & HAINAUT, D. (1965). Bull. Soc. Chim. Fr. pp. 1366–1378.

CROMER, D. T. & MANN, J. B. (1968). Acta Cryst. A24, 321–324.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1970). Acta Cryst. B26, 275–285.

HENDRICKSON, J. B. (1967). J. Amer. Chem. Soc. 89, 7036–7046.

KUTNEY, J. P. & WESTCOTT, N. D. (1970). Private communication.

ROBERTS, P. J., PETTERSEN, R. C., SHELDRICK, G. M., ISAACS, N. W. & KENNARD, O. (1973). J. Chem. Soc. Perkin II, pp. 1978–1984.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). J. Chem. Phys. 42, 3175–3187.

WESTCOTT, N. D. (1971). Thesis, Univ. of British Columbia, Vancouver.