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# The Crystal and Molecular Structure of a Diterpenoid, *ent*-Kaurenediol, $C_{20}O_2H_{32}$†

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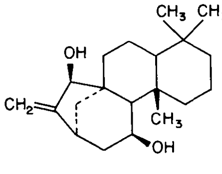
*ent*-Kaurenediol, $C_{20}O_2H_{32}$, isolated from liverwort *Jungermannia sphaerocarpa* was found to have the molecular structure proposed on chemical grounds for a compound obtained from a different species of liverwort. The crystals belong to the space group $P2_12_12_1$ with $a = 10{\cdot}652$ (4), $b = 18{\cdot}376$ (2), $c = 9{\cdot}095$ (3) Å, $Z = 4$. The structure was solved by application of the tangent formula and refined by block-diagonal least squares to $R = 0{\cdot}037$ for 1698 observed reflexions. The molecules are linked by O—H···O hydrogen bonds forming a chain along **c**.

## Introduction

Several derivatives of *ent*-kaurene were obtained from liverwort *Solenostoma triste* (Nees) K. Müll by Connolly & Thornton (1973). On the basis of chemical and spectroscopic evidence they proposed (I) as the structure for the diol, $C_{20}O_2H_{32}$.



(I)

Recently Benešová, Beneš, Châu & Herout (1975) isolated a compound from the liverwort *Jungermannia sphaerocarpa* Hook [syn. *Solenostoma* s. (Hook) Steph.], which appeared to be identical with Connolly & Thornton's material. Professor V. Herout, however, had some doubts about Connolly's assignment and suggested a structure analysis of his crystals. This study has shown that (I) is the correct structure, and that the molecule from the two prementioned sources has the same ring skeleton as (−)-kaur-15-en-19-al which was extracted from the Venezuelan plant *Espeletia weddelii*. The structure of the aldehyde was determined by Karle (1972).

## Experimental

The colourless prisms, crystallized from diethyl ether, were elongated along **c**. Cell dimensions and intensities were measured on a four-circle automatic diffractometer with Cu radiation and a Ni filter. Crystal data are presented in Table 1.

Table 1. *Crystal data*

$C_{20}O_2H_{32}$, F.W. 304·48, m.p. 192–194°C
Space group $P2_12_12_1$, $Z = 4$
$a = 10{\cdot}652$ (4), $b = 18{\cdot}376$ (2), $c = 9{\cdot}095$ (3) Å
$V = 1780{\cdot}27$ Å$^3$
$D_x = 1{\cdot}136$ g cm$^{-3}$
$D_m = 1{\cdot}133$ (by flotation in a toluene and carbon tetrachloride mixture)
$F(000) = 672$, $\mu$(Cu) $= 5{\cdot}55$ cm$^{-1}$

The crystal was cut into a cylinder 0·44 mm in diameter and 0·46 mm in length and mounted along **c***. The cell parameters were calculated from the $2\theta$ values of the high-order axial reflexions. The $\theta/2\theta$ scanning method was used and the $2\theta$ scan ranged from 2·0 to 4·0°. Since the diffractometer was set up for protein data collection, only one background measurement was taken for 10 s at the higher side of the peak. The strong intensities were remeasured with lower current settings and, if necessary, attenuated with an additional thickness of Ni foil. Two standard reflexions, 060 and 510, were monitored at intervals for scaling purposes. Their intensities showed no significant change.

The threshold was taken as a net count of 100 or 10% of the background, whichever was higher (Ahmed, Hall, Pippy & Huber, 1973). 1754 independent reflexions were scanned within $2\theta = 130°$, ($\sin^2\theta_{\max} = 0{\cdot}82$) and of these 1698 were observed above threshold.

The intensities were corrected for Lorentz and polarization factors, but not for absorption. The six highest intensities were corrected for extinction from a plot of $|F_c|/|F_o|$ *vs* net count.

## Structure determination

The structure was solved by direct methods (Karle & Hauptman, 1956). The scale and the overall tempera-

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Table 2. *Fractional coordinates for the carbon and oxygen atoms and vibration tensor components* (Å$^2$) *for the expression* $T=\exp[-2\pi^2(U_{11}a^{*2}h^2+\cdots+2U_{23}b^*c^*kl+\cdots)]$ *and their e.s.d.'s* (*all* × 10$^4$)

| | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $2U_{23}$ | $2U_{13}$ | $2U_{12}$ |
|---|---|---|---|---|---|---|---|---|---|
| C(1) | 4786 (2) | 1453 (1) | 544 (3) | 384 (13) | 477 (14) | 422 (13) | 164 (23) | 92 (23) | 94 (24) |
| C(2) | 5548 (3) | 2143 (1) | 150 (3) | 640 (17) | 482 (14) | 593 (17) | 300 (29) | 356 (32) | 47 (27) |
| C(3) | 5146 (3) | 2818 (1) | 990 (4) | 755 (21) | 462 (15) | 928 (23) | 260 (33) | 512 (40) | 56 (31) |
| C(4) | 5260 (3) | 2689 (1) | 2639 (4) | 758 (21) | 488 (15) | 774 (21) | -206 (31) | 295 (38) | 22 (31) |
| C(5) | 4458 (3) | 2047 (1) | 3182 (3) | 577 (16) | 520 (15) | 577 (17) | -78 (28) | 113 (30) | 210 (28) |
| C(6) | 4813 (2) | 1372 (1) | 2255 (3) | 345 (12) | 467 (14) | 420 (13) | 113 (24) | 113 (23) | 75 (23) |
| C(7) | 4176 (2) | 664 (1) | 2718 (3) | 475 (14) | 542 (15) | 395 (13) | 174 (25) | 260 (24) | 53 (26) |
| C(8) | 4917 (2) | 20 (1) | 2150 (3) | 513 (14) | 445 (12) | 388 (13) | 163 (24) | 212 (27) | 3 (25) |
| C(9) | 5078 (2) | 19 (1) | 456 (2) | 359 (12) | 476 (14) | 379 (13) | 69 (23) | 64 (23) | -24 (22) |
| C(10) | 5501 (2) | 780 (1) | -87 (2) | 298 (10) | 494 (12) | 321 (11) | 135 (23) | -8 (21) | 35 (21) |
| C(11) | 5655 (2) | 793 (1) | -1788 (3) | 464 (14) | 631 (15) | 365 (13) | 226 (26) | 67 (24) | 173 (27) |
| C(12) | 4764 (2) | 297 (2) | -2636 (3) | 541 (17) | 912 (21) | 352 (13) | -80 (29) | -259 (26) | 261 (33) |
| C(13) | 4473 (2) | -426 (2) | -1898 (3) | 459 (14) | 785 (19) | 583 (17) | -337 (33) | -292 (28) | -136 (30) |
| C(14) | 3929 (2) | -274 (1) | -361 (3) | 388 (13) | 619 (17) | 640 (18) | -150 (30) | 56 (28) | -65 (25) |
| C(15) | 6045 (2) | -581 (1) | 15 (3) | 455 (13) | 441 (14) | 417 (13) | 59 (25) | 73 (25) | 28 (22) |
| C(16) | 5663 (2) | -834 (1) | -1497 (3) | 457 (14) | 587 (15) | 570 (16) | -165 (29) | 1 (27) | -118 (27) |
| C(17) | 6235 (3) | -1336 (2) | -2289 (4) | 719 (20) | 884 (22) | 714 (21) | -659 (39) | -11 (37) | 40 (38) |
| C(18) | 3462 (2) | 1539 (1) | -104 (3) | 485 (14) | 725 (19) | 581 (17) | 211 (32) | -65 (30) | 362 (28) |
| C(19) | 4843 (3) | 1908 (2) | 4802 (3) | 1017 (25) | 770 (21) | 498 (17) | -282 (33) | 22 (40) | 287 (39) |
| C(20) | 3058 (3) | 2241 (2) | 3188 (4) | 660 (19) | 730 (19) | 769 (21) | -30 (36) | 434 (37) | 468 (34) |
| O(21) | 6947 (1) | 587 (1) | -2041 (2) | 459 (9) | 766 (12) | 358 (8) | 122 (19) | 206 (16) | 37 (19) |
| O(22) | 7342 (1) | -382 (1) | 118 (2) | 400 (8) | 638 (10) | 393 (8) | 6 (18) | -87 (16) | 175 (16) |

Table 3. *Fractional coordinates* (×10$^3$) *and temperature factors of the hydrogen atoms, with e.s.d.'s*

| | $x$ | $y$ | $z$ | $B$(Å$^2$) |
|---|---|---|---|---|
| H(2,1) | 648 (2) | 203 (1) | 45 (3) | 4.6 (0.6) |
| H(2,2) | 550 (3) | 221 (1) | -95 (3) | 6.8 (0.8) |
| H(3,1) | 566 (3) | 322 (1) | 72 (3) | 5.4 (0.7) |
| H(3,2) | 423 (3) | 295 (2) | 77 (3) | 6.8 (0.8) |
| H(4,1) | 618 (3) | 261 (1) | 304 (3) | 6.4 (0.7) |
| H(4,2) | 496 (3) | 315 (1) | 309 (3) | 6.5 (0.7) |
| H(6) | 572 (2) | 131 (1) | 248 (2) | 2.6 (0.5) |
| H(7,1) | 400 (2) | 64 (1) | 378 (3) | 5.3 (0.6) |
| H(7,2) | 330 (2) | 64 (1) | 226 (3) | 4.4 (0.6) |
| H(8,1) | 574 (2) | -1 (1) | 254 (3) | 4.7 (0.6) |
| H(8,2) | 447 (2) | -47 (1) | 240 (3) | 4.0 (0.5) |
| H(10) | 636 (2) | 81 (1) | 31 (2) | 2.0 (0.4) |
| H(11) | 552 (2) | 134 (1) | -212 (3) | 3.6 (0.5) |
| H(12,1) | 510 (3) | 24 (1) | -354 (3) | 7.1 (0.8) |
| H(12,2) | 388 (3) | 58 (1) | -282 (3) | 6.2 (0.7) |
| H(13) | 397 (2) | -72 (1) | -257 (3) | 4.5 (0.6) |
| H(14,1) | 363 (2) | -78 (1) | 28 (3) | 5.3 (0.6) |
| H(14,2) | 330 (2) | 7 (1) | -41 (2) | 3.4 (0.5) |
| H(15) | 602 (2) | -103 (1) | 75 (2) | 3.2 (0.5) |
| H(17,1) | 595 (3) | -144 (2) | -330 (4) | 11.0 (1.1) |
| H(17,2) | 703 (3) | -156 (2) | -179 (4) | 8.6 (0.9) |
| H(18,1) | 289 (2) | 118 (1) | 39 (3) | 5.5 (0.7) |
| H(18,2) | 312 (2) | 203 (1) | 4 (3) | 5.3 (0.6) |
| H(18,3) | 350 (2) | 146 (1) | -124 (3) | 4.8 (0.6) |
| H(19,1) | 432 (3) | 156 (1) | 527 (3) | 6.2 (0.7) |
| H(19,2) | 488 (3) | 240 (1) | 528 (3) | 6.2 (0.7) |
| H(19,3) | 575 (3) | 175 (2) | 494 (4) | 8.3 (0.9) |
| H(20,1) | 297 (3) | 267 (2) | 387 (3) | 7.7 (0.8) |
| H(20,2) | 273 (3) | 243 (2) | 220 (4) | 9.2 (1.0) |
| H(20,3) | 245 (3) | 179 (2) | 351 (3) | 7.8 (0.8) |
| H(21) | 708 (3) | 64 (2) | -301 (4) | 8.6 (0.9) |
| H(22) | 756 (4) | -4 (2) | -61 (4) | 9.8 (1.0) |

ture factors ($B=4\cdot2$ Å$^2$) were evaluated by Wilson's (1942) method. The starting set of $E$'s with assigned phases consisted of three origin-defining (780, 072, 0,15,1), one enantiomorph-defining (7,11,0) and two additional reflexions (10,0,6 and 177). Three cycles, of five iterations each, were carried out for different permutations for 87 $|E|$ values $\geq 1\cdot80$. The best trial gave 83 phased $E$'s and $R_K=0\cdot19$. It was then developed by use of the tangent formula, extending gradually the $|E|$ values to 1·40. Out of 257 $E$'s, 244 were thus phased and the final $R_K$ remained at 0·19. The $E$ map showed all the non-hydrogen atoms of the molecule.

The first structure factor calculation for the observed reflexions gave $R=0\cdot21$. A Fourier map allowed us to distinguish the O and C atoms and a few least-squares cycles brought $R$ to 0·11. The H atoms were then located from a difference map.

The refinement was carried out by the block-diagonal approximation, with only the observed reflexions, minimizing $\Sigma\, w(|F_o|-|F_c|)^2$ where $w=1/\{1+[(|F_o|-25)/25]^4\}$ with $0\cdot93\leq|F_o|\leq195\cdot15$. The final $R$ for the observed reflexions was 0·037 and $R_w=[\Sigma\, w(\Delta F)^2/\Sigma\, wF_o^2]^{1/2}$ was 0·035. The final mean shift/e.s.d. for all atoms was 0·12. The maximum shift/e.s.d. was 0·46 for C and O and 0·68 for H atoms. The final difference map showed a residual distribution from $-0\cdot15$ to $+0\cdot12$ e Å$^{-3}$.

The atomic parameters are presented in Table 2, the coordinates of the H atoms in Table 3. Three $|F_o|$ values which were affected by multiple diffraction (052, 220 and 340) were excluded from the final stages of refinement.*

All calculations were carried out with the NRC programs (Ahmed, Hall, Pippy & Huber, 1973). The scattering factors were those of Hanson, Herman, Lea & Skillman (1964) except for H (Stewart, Davidson & Simpson, 1965).

## Discussion

The molecular structure of *ent*-kaurenediol corresponds to the stereochemical structure proposed by Connolly & Thornton (1973), and has the same ring skeleton as (−)-kaur-15-en-19-al (Karle, 1972). It was not possible to establish crystallographically the absolute configuration of the compound under study, but its $[\alpha]_D$ was found by Herout to have the same sign as the material isolated by Connolly & Thornton (1973).

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32039 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The absolute configuration would therefore be the same for both samples, and this is represented in our drawings.

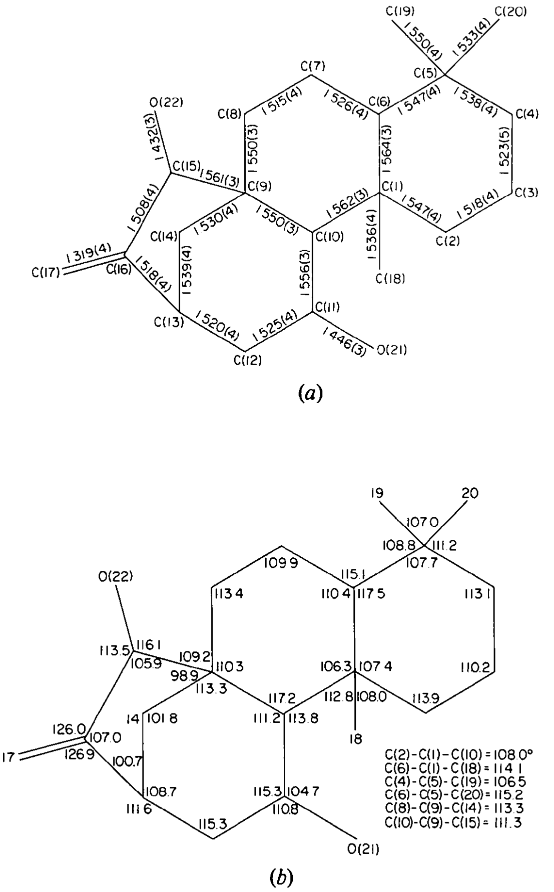

Fig. 1. (*a*) Bond lengths (Å) of *ent*-kaurenediol with their e.s.d.'s. (*b*) Valency angles (°). The e.s.d. is ≤0·3°.

The bond lengths and angles, not corrected for thermal vibration, are shown in Fig. 1. The $C(sp^3)$—$C(sp^3)$ lengths range from 1·515 to 1·564 Å (mean 1·540 Å). The longest bonds are associated with the fully substituted C(1) and C(9). The two bonds adjoining the C(16)—C(17) double bond are, as expected, appreciably shortened to 1·508 and 1·518 Å. The C=C is 1·319 Å and the C—O are 1·446 and 1·432 Å. All these values are in agreement with those given in *Molecular Structures and Dimensions* (1972), since the estimated standard deviations are considered to be somewhat underestimated. The C—H bonds vary from 0·89 to 1·14 Å (mean 1·01 Å). The C—C—H and H—C—H angles are in the range 99·6–117·4° (mean 109·2°).

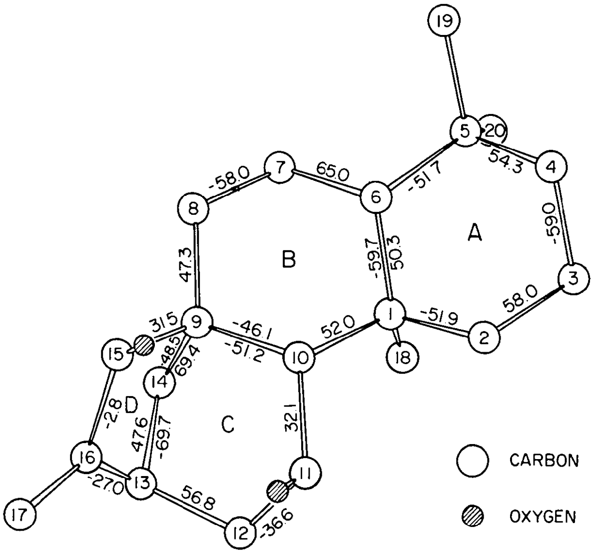

Fig. 2. Torsional angles (°).

Table 4. *Mean planes:* $lX + mY + nZ = p$

(*a*) Parameters referred to Cartesian coordinates in Å

| | $l$ | $m$ | $n$ | $p$ | $\chi^2$ |
|---|---|---|---|---|---|
| Ring *A* | −0·8314 | 0·4536 | −0·3209 | −3·1782 | 33·2 |
| Ring *B* | −0·8209 | −0·3095 | −0·4799 | −5·2325 | 208·0 |
| Ring *C* | 0·9262 | −0·3366 | −0·1696 | 4·9444 | 237·5 |
| Ring *D* | 0·5651 | 0·7046 | −0·4292 | 2·8946 | 112·9 |

(*b*) Deviations from the mean planes (Å)

| Ring *A* | $\Delta$ | Ring *B* | $\Delta$ | Ring *C* | $\Delta$ | Ring *D* | $\Delta$ |
|---|---|---|---|---|---|---|---|
| C(1) | −0·007 | C(1) | −0·016 | C(9) | −0·016 | C(9) | 0·008 |
| C(2) | 0·008 | C(10) | 0·016 | C(10) | 0·013 | C(15) | −0·014 |
| C(4) | −0·008 | C(7) | 0·017 | C(12) | −0·021 | C(16) | 0·018 |
| C(5) | 0·007 | C(8) | −0·017 | C(13) | 0·024 | C(13) | −0·012 |
| C(3)* | 0·681 | C(6)* | −0·740 | C(11)* | 0·419 | C(14)* | −0·743 |
| C(6)* | −0·598 | C(9)* | 0·582 | C(14)* | −0·843 | C(17)* | 0·022 |

* Identifies atoms excluded from the calculation.

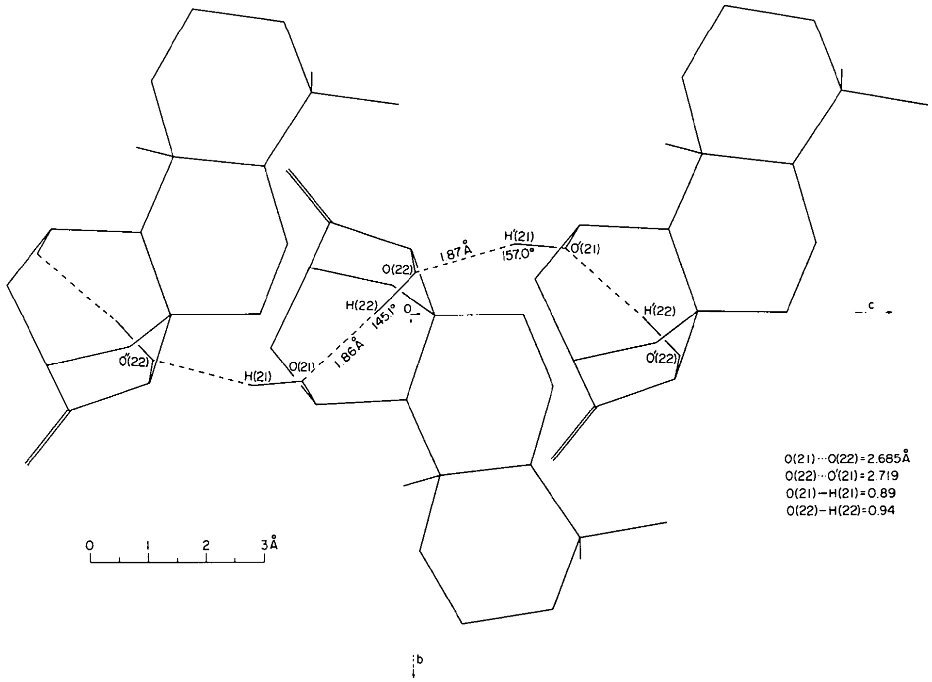

Fig. 3. Projection along the *a* axis showing the hydrogen bonds between three neighbouring molecules.

The mean planes, calculated for four atoms of each of the rings, are listed in Table 4. None of these sets of atoms can be regarded as coplanar, as indicated by their $\chi^2$ values. The torsion angles are presented in Fig. 2, where the signs are according to the convention of the IUPAC–IUB Commission on Biochemical Nomenclature (1970). Rings *A* and *B* are in a slightly distorted chair conformation, with ring *B* having more distortion because of the presence of the fully substituted C(9). Ring *C*, also of chair form, is appreciably flattened at C(11), the distance of C(11) from the mean plane of C(9), C(10), C(12) and C(13) being only 0·42 Å. Ring *D* has the envelope conformation.

The molecular conformation is such that the intramolecular van der Waals contacts are maintained close to or above their expected values, except for an intramolecular hydrogen bond O(21)···H(22)–O(22) and a rather short H(7,2)···H(18,1) contact of 1·93 Å. The intramolecular distances C(18)···C(20), C(18)···C(14) and C(18)···C(12) are 3·288, 3·378 and 3·527 Å respectively. The intramolecular hydrogen bond combines with an intermolecular hydrogen bond O(22)···H'(21)–O'(21) to form a continuous spiral along **c** (Fig. 3, where the pertinent dimensions of these bonds are presented). The molecules of one spiral have no contacts shorter than van der Waals with those of the adjacent spirals.

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