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# *ent*-9(8→15α*H*)*abeo*-17-Norkaur-8(14)-en-16-one

By Tooru Taga, Tsuneyuki Higashi, Hisao Iizuka and Kenji Osaki
*Faculty of Pharmaceutical Sciences, Kyoto University, Kyoto* 606, *Japan*

and Masahito Ochiai and Eiichi Fujita
*Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu* 611, *Japan*

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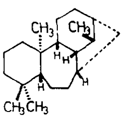
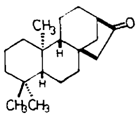
**Abstract.** $C_{19}H_{28}O$, orthorhombic, $P2_12_12_1$, $a = 23 \cdot 69\,(4)$, $b = 8 \cdot 058\,(12)$, $c = 8 \cdot 132\,(12)$ Å, $Z = 4$. The two six-membered rings are in the chair form, and the five-membered ring is in an envelope conformation. All the rings in the moleculre are somewhat distorted. Repulsion between the 1,3 diaxial methyl groups attached to ring *A* results in rotation of the methyl H atoms from the usual staggered position.

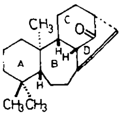
**Introduction.** Two of the authors (MO and EF) carried out a synthesis of *ent*-9(8→15α*H*)*abeo*-kaurane (I). In this synthesis, *ent*-17-norkauran-16-one (II) was allowed to react with thallium trinitrate to afford a rearranged product which was assigned structure III on the basis of spectral and chemical evidence (Fujita & Ochiai, 1976). The present X-ray analysis of compound III provides a confirmation of the structure and also stereochemical evidence for the large strain expected in the structure.



(I)



(II)



(III)

Intensity data were collected on a Rigaku automatic four-circle diffractometer using Cu *Kα* radiation. The structure was solved by trial and error methods based on Patterson maps and *E* maps derived by use of the program *MULTAN* (Germain, Main & Woolfson, 1971). Successive cycles of anisotropic block-diagonal least-squares refinement gave an *R* value of 0·043 for 1571 observed reflexions. H atoms were located from

Table 1. *Fractional atomic coordinates and anisotropic thermal parameters* (×10⁴) *of the non-hydrogen atoms with estimated standard deviations in parentheses*

The temperature factor expression is $T = \exp\,[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

| | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| C(1) | 1630 (2) | 1034 (6) | 4036 (6) | 23 (1) | 121 (8) | 125 (8) | 3 (3) | −7 (3) | 21 (8) |
| C(2) | 1883 (2) | 2276 (7) | 5264 (6) | 34 (1) | 164 (9) | 121 (8) | 7 (3) | −17 (3) | 23 (9) |
| C(3) | 1527 (2) | 3865 (6) | 5297 (6) | 26 (1) | 163 (9) | 136 (8) | −4 (3) | 2 (3) | 18 (9) |
| C(4) | 1455 (2) | 4698 (6) | 3613 (6) | 15 (1) | 144 (8) | 156 (8) | −6 (2) | −5 (2) | −1 (8) |
| C(5) | 1258 (2) | 3377 (5) | 2318 (5) | 12 (1) | 104 (7) | 133 (7) | −5 (2) | −5 (2) | 21 (7) |
| C(6) | 1158 (2) | 4168 (6) | 609 (6) | 20 (1) | 125 (8) | 159 (8) | −7 (2) | −18 (3) | 39 (8) |
| C(7) | 575 (2) | 3654 (6) | −132 (6) | 18 (1) | 132 (8) | 190 (9) | 2 (2) | −22 (3) | 14 (8) |
| C(8) | 552 (2) | 1821 (5) | −441 (6) | 11 (1) | 122 (7) | 176 (9) | 1 (2) | −11 (2) | 21 (8) |
| C(9) | 1315 (2) | 337 (5) | 1183 (5) | 11 (1) | 111 (7) | 126 (7) | 0 (2) | −2 (2) | 9 (7) |
| C(10) | 1606 (2) | 1727 (5) | 2263 (5) | 11 (1) | 119 (7) | 116 (7) | 0 (2) | −1 (2) | 18 (7) |
| C(11) | 1583 (2) | 43 (6) | −534 (6) | 14 (1) | 165 (9) | 128 (8) | 3 (2) | 4 (2) | −14 (8) |
| C(12) | 1256 (2) | −1201 (6) | −1614 (6) | 18 (1) | 160 (9) | 152 (8) | 7 (3) | 1 (2) | −8 (8) |
| C(13) | 612 (2) | −816 (6) | −1644 (6) | 17 (1) | 150 (9) | 165 (9) | −6 (3) | −11 (3) | −12 (8) |
| C(14) | 516 (2) | 1028 (6) | −1871 (6) | 16 (1) | 163 (9) | 159 (9) | −1 (3) | −13 (2) | 16 (8) |
| C(15) | 659 (2) | 598 (5) | 951 (6) | 12 (1) | 112 (7) | 141 (8) | −3 (2) | 1 (2) | 10 (7) |
| C(16) | 438 (2) | −981 (5) | 148 (6) | 12 (1) | 119 (7) | 190 (9) | 0 (2) | −6 (2) | 2 (8) |
| O(17) | 183 (1) | −2095 (4) | 789 (5) | 19 (1) | 147 (6) | 245 (7) | −14 (2) | 2 (2) | 16 (6) |
| C(18) | 981 (2) | 5996 (6) | 3814 (7) | 22 (1) | 148 (9) | 261 (12) | 4 (3) | −12 (3) | −39 (10) |
| C(19) | 1998 (2) | 5649 (6) | 3134 (7) | 21 (1) | 180 (10) | 214 (11) | −25 (3) | −12 (3) | −10 (10) |
| C(20) | 2220 (2) | 1965 (7) | 1659 (6) | 11 (1) | 204 (10) | 185 (9) | −5 (2) | 1 (2) | −13 (9) |

the difference synthesis and included in the refinement assuming an isotropic temperature factor of 3·2 Å$^2$. The final structural parameters are listed in Tables 1 and 2.* A perspective view of the molecule and the crystal packing are shown in Figs. 1 and 2 respectively. The bond lengths and angles for the non-hydrogen atoms are given in Fig. 3.

Table 2. *Fractional atomic coordinates* (×10$^3$) *of the hydrogen atoms with estimated standard deviations in parentheses*

| | *x* | *y* | *z* |
|---|---|---|---|
| H(1*A*) | 123 (2) | 73 (6) | 434 (6) |
| H(1*B*) | 188 (2) | −9 (6) | 404 (6) |
| H(2*A*) | 235 (2) | 249 (6) | 504 (6) |
| H(2*B*) | 190 (2) | 173 (6) | 644 (6) |
| H(3*A*) | 170 (2) | 474 (6) | 614 (6) |
| H(3*B*) | 109 (2) | 361 (6) | 578 (6) |
| H(5) | 86 (2) | 305 (6) | 279 (6) |
| H(6*A*) | 151 (2) | 389 (6) | −26 (6) |
| H(6*B*) | 118 (2) | 551 (6) | 77 (6) |
| H(7*A*) | 50 (2) | 429 (6) | −124 (6) |
| H(7*B*) | 21 (2) | 406 (6) | 62 (6) |
| H(9) | 138 (2) | −78 (6) | 191 (6) |
| H(11*A*) | 199 (2) | −45 (6) | −37 (6) |
| H(11*B*) | 163 (2) | 114 (6) | −107 (6) |
| H(12*A*) | 133 (2) | −239 (6) | −129 (6) |
| H(12*B*) | 140 (2) | −115 (6) | −273 (6) |
| H(13) | 41 (2) | −156 (6) | −248 (6) |
| H(14) | 48 (2) | 149 (6) | −309 (6) |
| H(15) | 46 (2) | 88 (6) | 209 (6) |
| H(18*A*) | 88 (2) | 677 (6) | 290 (6) |
| H(18*B*) | 106 (2) | 678 (6) | 476 (6) |
| H(18*C*) | 58 (2) | 548 (6) | 427 (6) |
| H(19*A*) | 200 (2) | 593 (6) | 189 (6) |
| H(19*B*) | 235 (2) | 507 (7) | 354 (6) |
| H(19*C*) | 201 (2) | 666 (6) | 362 (6) |
| H(20*A*) | 226 (2) | 249 (6) | 51 (6) |
| H(20*B*) | 239 (2) | 86 (6) | 164 (6) |
| H(20*C*) | 244 (2) | 280 (6) | 237 (6) |

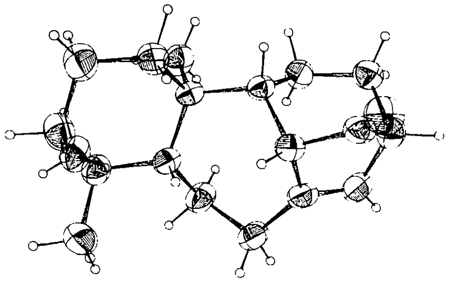


Fig. 1. Perspective view of the molecule.

**Discussion.** Six-membered rings *A* and *C* are in a distorted chair form. Torsional angles for the ring *A* (49·3–59·8°) and for the ring *C* (45·9–77·1°) deviate largely from the idealized value for the chair form. Seven-membered ring *B* is also distorted owing to repulsion between the H atoms on C(5) and C(15). The internal bond angles at C(5), C(9) and C(10) are significantly larger than the normal tetrahedral angle.

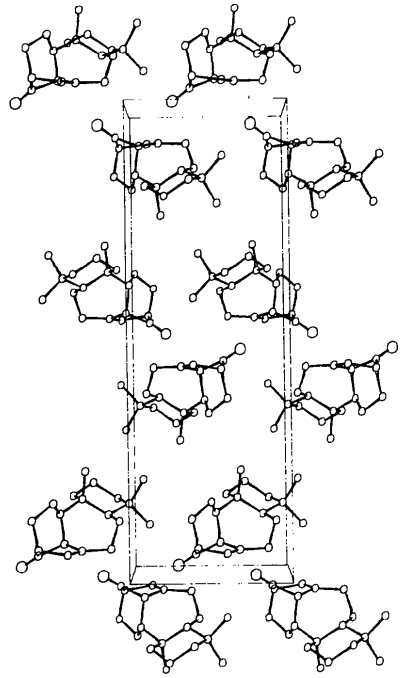


Fig. 2. Crystal packing. Axes for the unit cell are *a*↓, *b*→, and *c* is out of the page.

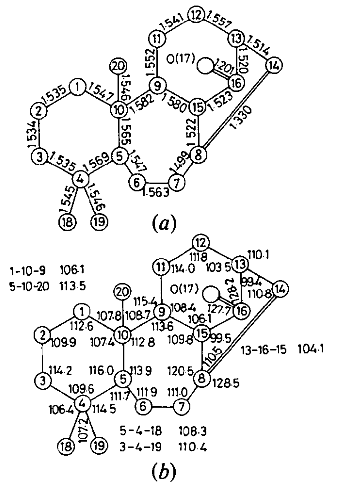


Fig. 3. (*a*) Bond lengths (standard deviations range from 0·006 to 0·007 Å). (*b*) Bond angles (standard deviations range from 0·4 to 0·5°).

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32131 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Least-squares planes and atomic deviations*

The planes are defined by $Ax + By + Cz + D = 0$ where $x$, $y$ and $z$ are in Å along the axes $a$, $b$ and $c$. An asterisk indicates an atom not used in the plane calculation.

| | | | |
|---|---|---|---|
| $A =$ | −0·8634 | $A =$ | −0·9905 |
| $B =$ | 0·4616 | $B =$ | −0·0654 |
| $C =$ | −0·2037 | $C =$ | 0·1208 |
| $D =$ | 1·2841 | $D =$ | 1·4961 |
| Atom deviations (Å) | | Atom deviations (Å) | |
| C(7)* | 1·489 | C(7) | −0·059 |
| C(8)* | 0·905 | C(8) | 0·061 |
| C(13) | 0·001 | C(13) | −0·059 |
| C(14)* | 0·920 | C(14) | 0·046 |
| C(15) | 0·001 | C(15) | 0·011 |
| C(16) | −0·002 | C(16)* | 0·534 |
| O(17) | 0·001 | O(17)* | 1·255 |
| H(14)* | 1·372 | H(14)* | −0·008 |

The single bond C(7)–C(8) (1·499 Å) is shortened by resonance with the adjacent double bond C(8)–C(14). Five-membered ring *D* has an envelope conformation. The C(16) atom deviates from the plane of the other four atoms. The least-squares plane through C(13), C(15), C(16) and O(17) makes a dihedral angle of 33·8° with that through C(7), C(8), C(13), C(14) and C(15) (Table 3). The strain in ring *D* is evidenced by the fact that the internal bond angles at C(8), C(14) and C(16) are much smaller than the normal $sp^2$-hybridization angle (120°). Repulsion between the 1,3 diaxial methyl groups attached to ring *A* causes the significantly greater bond angles 114·5° for C(5)–C(4)–C(19) and 113·5° for C(5)–C(10)–C(20), resulting in the C(19)–C(20) distance of 3·24 Å. A similar structural feature has been observed in (−)-kaur-15-en-19-al (Karle, 1972) and in phyllocladan-15-yl bromoacetate (Brown & Hall, 1976). In the present case, the three methyl H atoms on C(19) are rotated about the C(4)–C(19) bond from the staggered position, while the methyl H atoms on C(20) are in the usual staggered position. The shortest H–H approach between these methyl groups is 2·08 Å.

There are no intermolecular approaches likely to influence the molecular structure.

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## References

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