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# Structure of Alnusenone (*D*:*B*-Friedoolean-5-en-3-one)

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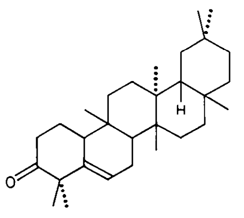
**Abstract.** $C_{30}H_{48}O$, $M_r = 424{\cdot}71$, triclinic, $P1$, $a = 7{\cdot}338\,(1)$, $b = 14{\cdot}856\,(1)$, $c = 6{\cdot}267\,(1)$ Å, $\alpha = 97{\cdot}10\,(1)$, $\beta = 113{\cdot}60\,(1)$, $\gamma = 93{\cdot}20\,(1)°$, $Z = 1$, $D_x = 1{\cdot}10$ Mg m$^{-3}$, $\mu$(Cu $K\alpha$) = 4·9 cm$^{-1}$. The structure was refined by a block-diagonal least-squares method. The final $R$ value was 0·037 for 1904 reflexions. The *cis* fusion at the *D*/*E* junction and the axial $\alpha$-methyl group at C(13) cause the *D* and *E* rings to be in the twist-boat and boat conformations respectively.

**Introduction.** Alnusenone (*D*:*B*-friedoolean-5-en-3-one, I), a naturally occurring triterpene (Chapon & David, 1953), was isolated from *Trogopterum Faeces* (Akamatsu, 1970).



(I)

Prismatic crystals were obtained from an acetone–methanol solution at room temperature. Oscillation and Weissenberg photographs indicated the crystal to be triclinic. As the compound is optically active, the space group should be $P1$. A crystal, 0·4 × 0·5 × 0·65 mm, was mounted on a Rigaku automated four-circle diffractometer. The unit-cell dimensions were determined by least-squares refinement of $2\theta$ values for 22 high-angle reflexions.

Intensity data were collected on the diffractometer by the use of Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1{\cdot}54184$ Å), with an $\omega/2\theta$ scanning technique ($2\theta \le 122°$). Five reference reflexions showed no significant intensity deterioration during the course of data collection. Corrections were made for Lorentz and polarization factors, but not for absorption. A total of 1904 independent reflexions were obtained, of which 7 reflexions had zero intensities [$I \le \sigma(I)$]. The standard deviations were estimated by the equation $\sigma^2(F_o) = \sigma_P^2(F_o) + qF_o^2$; here $\sigma_P(F_o)$ was evaluated by counting statistics and $q$ ($1{\cdot}689 \times 10^{-5}$) was derived from the variations of the monitored reflexions.

Many peaks corresponding to cyclohexane rings appeared on an $E$ map calculated with *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). One of the least-squares trials among several possible models gave a promising low $R$ value,

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though its convergence was slow. The subsequent weighted Fourier synthesis revealed all the atoms. The atomic parameters were refined by the block-diagonal least-squares method; the quantity minimized was $\sum w(|F_o| - |F_c|)^2$, with $w = 1/\sigma^2(F_o)$. When the $R$ value reached 0·084, a difference synthesis revealed all the H atoms. The refinement was terminated when the maximum shift of parameters for H atoms was less than $0{\cdot}65\sigma$. The final $R$ value was 0·037 for 1904 reflexions. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The final positional and thermal parameters are listed in Table 1.*

Table 1. *Final positional and equivalent isotropic thermal parameters*

$B = 8\pi^2 \sum(U_1 + U_2 + U_3)/3$, where $U_1$, $U_2$, and $U_3$ are the principal components of the mean-square displacement matrix **U**. Values in angle brackets are anisotropicity defined by $[\sum (B - 8\pi^2 U_i)^2/3]^{1/2}$. The e.s.d.'s in round brackets refer to last decimal places.

| | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| C(1) | −0·3167 (4) | 0·4494 (2) | 0·0408 (5) | 3·8 ⟨11⟩ |
| C(2) | −0·3644 (5) | 0·5165 (2) | 0·2106 (6) | 4·5 ⟨13⟩ |
| C(3) | −0·1889 (4) | 0·5481 (1) | 0·4446 (5) | 3·6 ⟨12⟩ |
| C(4) | 0·0205 (4) | 0·5469 (1) | 0·4485 (5) | 3·25 ⟨91⟩ |
| C(5) | 0·0372 (4) | 0·4518 (1) | 0·3333 (4) | 2·86 ⟨74⟩ |
| C(6) | 0·2165 (4) | 0·4245 (2) | 0·3727 (5) | 3·6 ⟨12⟩ |
| C(7) | 0·2482 (4) | 0·3327 (2) | 0·2729 (5) | 3·6 ⟨13⟩ |
| C(8) | 0·0571 (3) | 0·2654 (1) | 0·1788 (4) | 2·47 ⟨48⟩ |
| C(9) | −0·1244 (3) | 0·3093 (1) | 0·0163 (4) | 2·61 ⟨49⟩ |
| C(10) | −0·1546 (4) | 0·3917 (1) | 0·1747 (4) | 2·79 ⟨43⟩ |
| C(11) | −0·3125 (3) | 0·2393 (1) | −0·0805 (4) | 2·80 ⟨81⟩ |
| C(12) | −0·2835 (3) | 0·1440 (1) | −0·1755 (4) | 2·58 ⟨75⟩ |
| C(13) | −0·1145 (3) | 0·1017 (1) | 0·0076 (4) | 2·12 ⟨26⟩ |
| C(14) | 0·0850 (3) | 0·1667 (1) | 0·0868 (4) | 2·38 ⟨51⟩ |
| C(15) | 0·2535 (4) | 0·1307 (2) | 0·2891 (4) | 3·17 ⟨102⟩ |
| C(16) | 0·2344 (4) | 0·0272 (2) | 0·2846 (5) | 3·5 ⟨13⟩ |
| C(17) | 0·1083 (3) | −0·0349 (1) | 0·0480 (4) | 2·58 ⟨52⟩ |
| C(18) | −0·0901 (3) | 0·0049 (1) | −0·1033 (4) | 2·18 ⟨34⟩ |
| C(19) | −0·2768 (3) | −0·0637 (1) | −0·1648 (5) | 2·83 ⟨66⟩ |
| C(20) | −0·2687 (4) | −0·1615 (1) | −0·2717 (5) | 2·95 ⟨58⟩ |
| C(21) | −0·0710 (4) | −0·1963 (2) | −0·1176 (6) | 3·9 ⟨12⟩ |
| C(22) | 0·0546 (4) | −0·1287 (2) | 0·1020 (5) | 3·5 ⟨9⟩ |
| C(23) | 0·1776 (5) | 0·5731 (2) | 0·7037 (5) | 4·6 ⟨17⟩ |
| C(24) | 0·0440 (5) | 0·6206 (2) | 0·3031 (6) | 4·5 ⟨16⟩ |
| C(25) | −0·0965 (5) | 0·3440 (2) | −0·1920 (5) | 4·0 ⟨13⟩ |
| C(26) | −0·1722 (4) | 0·0933 (1) | 0·2174 (4) | 2·80 ⟨51⟩ |
| C(27) | 0·1510 (4) | 0·1689 (2) | −0·1181 (5) | 3·2 ⟨9⟩ |
| C(28) | 0·2416 (4) | −0·0514 (2) | −0·0884 (6) | 3·8 ⟨12⟩ |
| C(29) | −0·4460 (5) | −0·2224 (2) | −0·2756 (7) | 4·9 ⟨24⟩ |
| C(30) | −0·2887 (5) | −0·1654 (2) | −0·5255 (5) | 4·6 ⟨14⟩ |
| O(1) | −0·2163 (4) | 0·5731 (1) | 0·6190 (4) | 5·5 ⟨17⟩ |

**Discussion.** Molecules lie approximately on the (011) plane. All intermolecular distances are greater than those expected from van der Waals contacts.

Fig. 1 shows a stereoscopic view of the alnusenone molecule, which was drawn with the *TSD:XTAL* program (Takenaka & Sasada, 1980).

The least-squares planes of carbonyl and double-bond moieties are listed in Table 2,* together with deviations of atoms from them. Of the two methyl groups attached to C(4), C(23) is closer to the plane. The double-bond part is planar with maximum deviation of 0·013 Å for C(6). The dihedral angle between these planes is 48·2 (1)°.

Bond lengths and angles except those for H atoms are shown in Fig. 2. They are in good agreement with those for related compounds (Fowell, Melson & Smith, 1978).

Endocyclic torsion angles are shown in Fig. 3. The conformations of rings *A*, *B*, *C*, *D*, and *E* are twist-boat, half-chair, chair, twist-boat, and boat respectively.

Average endocyclic torsion and bond angles of ring *C* are 52·7 and 112·1° respectively, which are close to the normal values 54·9 and 111·4° reported for the chair form of cyclohexane (Bastiansen, Fernholt, Seip, Kambara & Kuchitsu, 1973).

Because of the boat forms of the *D* and *E* rings, some short intramolecular contacts are observed: C(27)···H(151)† 2·44 (3), C(28)···H(181) 2·46 (3),

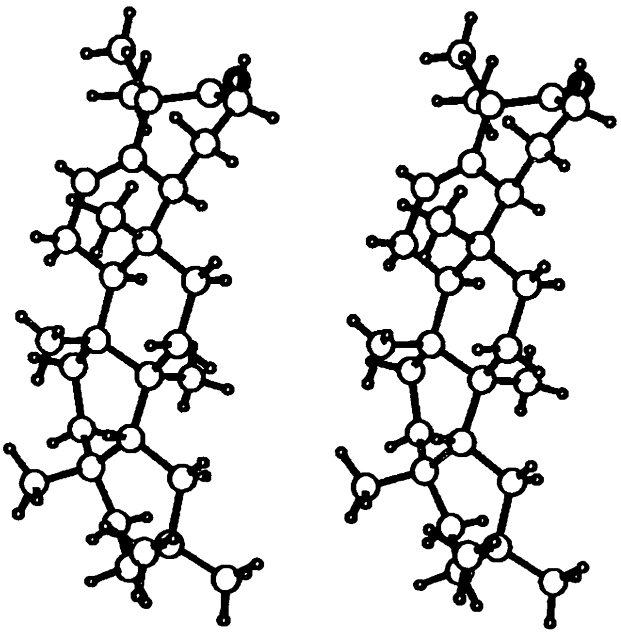

Fig. 1. Stereoscopic view of the alnusenone molecule.

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* Lists of structure factors, anisotropic thermal parameters of C and O atoms, atomic parameters of H atoms, atomic deviations from the least-squares planes through carbonyl and double-bond moieties (Table 2), bond lengths and angles including all atoms, and short intramolecular distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36166 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* See deposition footnote.

† H(151) designates the H atom attached to C(15). The last digit indicates the number of H atoms attached to the same C atom.

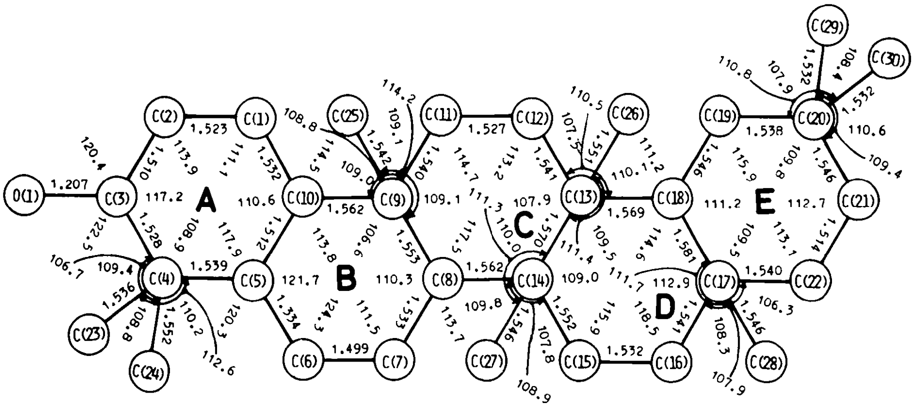

Fig. 2. Bond lengths (Å) and angles (°) involving non-H atoms, their standard deviations being 0·003–0·005 Å and 0·2–0·4° respectively.

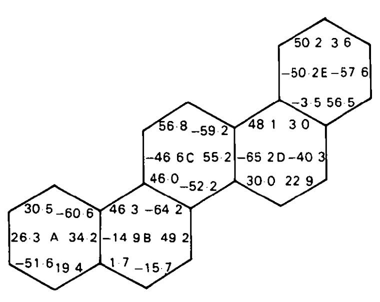

Fig. 3. Endocyclic torsion angles (°). The average standard deviation is 0·3°.

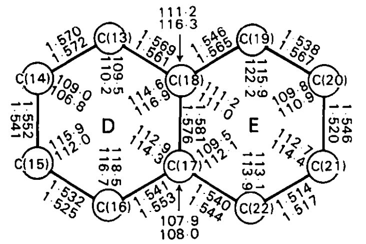

Fig. 4. A comparison of bond lengths and angles of *D* and *E* rings between alnusenone (above) and campanulin (below; Mo, 1977). The standard deviations in bond lengths and angles of campanulin are 0·003–0·005 Å and 0·2–0·3° respectively.

C(26)···H(162) 2·78 (4), C(29)···H(212) 2·49 (4), and C(30)···H(211) 2·45 (4) Å, corresponding to 1,2-diaxial interactions and bow–stern repulsions. In ring *A*, on the other hand, the $sp^2$ character of C(3) and C(5) makes the ring flat and releases the bow–stern repulsion: C(24)···H(12) 2·92 (4) and H(12)···H(241) 2·17 (5) Å. Inspection of a Dreiding model reveals that repulsion between the *β*-methyl group at C(4) and the hydrogen at C(6) may prevent the ring taking a chair form.

The *cis* fusion at rings *D* and *E* forces the *D* ring to take a twist-boat and the *E* ring a boat conformation, C(13) and C(16) of the *D* ring, and C(19) and C(22) of the *E* ring, being the bow and stern. This feature is similar to that found in epifriedelinol (Laing, Burke-Laing, Bartho & Weeks, 1977). On the other hand, the corresponding rings are chairs in campanulin (Mo, 1977). This difference in ring conformations may be explained by the relative magnitudes of 1,2-diaxial and bow–stern repulsions in the present alnusenone or epifriedelinol, and of repulsion between the axial *α*-methyl group C(26) at C(13) and the *α*-methyl group at C(19) of the *E* ring in campanulin. Some short intramolecular contacts are also found in the chair forms of the *D*/*E* rings in campanulin. Fig. 4 shows a comparison of bond lengths and angles of *D* and *E* rings between alnusenone and campanulin. The repulsions mentioned above mainly affect the bond angles; in particular, the angles C(15)—C(16)—C(17) 118·5 (3)° in alnusenone and C(18)—C(19)—C(20) 122·2 (2)° in campanulin are both unusually large. Thus *cis* fusion of *D* and *E* rings causes the large distortion at the *D* ring for boat–boat forms and at the *E* ring for chair–chair forms.

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