

Diterpenoid C-Ring Bromoketones.

II. *ent*-3 β -Acetoxy-11 α -bromoisopimar-12-one

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Abstract. C₂₂O₃H₃₅Br, *M*=427. Monoclinic *P*2₁, *a*=10.66 (1), *b*=7.78 (1), *c*=12.94 (1) Å, β =93.4 (1)°, *V*=1071 Å³, *D*_c=1.33 g cm⁻³, *Z*=2, μ (Mo *K* α)=20.6 cm⁻¹. *R*=0.071 for 1053 observed data; Br only anisotropic, 17 H atoms included. Br stands above the mean plane of the C ring, the C(12) keto-O(2) is below the plane.

Introduction. Together with the aromatic diterpene cleistanthol (McGarry, Pegel, Phillips & Waight, 1971), three related diterpenes (Candy, Pakshong & Pegel, 1970) were isolated from the heartwood of *Cleistanthus schlechteri* var. *schlechteri*. Bromination of a tetrahydro derivative yielded an 11-bromo 12-one compound (Fig. 1). To establish the conformation of the C ring, the stereochemistry of the B/C ring junction and the orientation of the Br atom, and to compare the structure with that of the 11-bromo 8(14)-en-12-one derivative (Sommerville & Laing, 1976) the crystal structure was determined.

Suitable crystals were prepared by Mr C. P. Gorst-Allman. Data were collected from a crystal 0.4 × 0.4 × 0.4 mm on a Philips four-circle diffractometer with graphite-monochromated Mo *K* α radiation (λ =0.7107 Å) for θ between 3 and 20°. The ω -2 θ scan mode was used; the scan width was 1.2°, each peak was counted for 60 s and the background counting time was 60 s for each peak. Of 1109 reflexions measured, 1053 were classed as observed, $I > 1.65\sigma(I)$. Three reflexions were used as standards and their intensities were re-measured every hour; no decomposition was detected. The intensities were corrected for Lorentz and polarization effects only. A temperature-sharpened Pat-

erson map gave the coordinates of the Br atom (*y* arbitrarily chosen as 0.25). Subsequent Fourier maps

Table 1. *Atomic coordinates and thermal parameters*

Fractional atomic coordinates and isotropic thermal parameters. All H atoms were assigned *B*=4.0 Å².

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> (Å ²) |
|---------|-------------|-------------|-------------|----------------------------|
| Br | 0.3685 (2) | 0.25 | 1.2150 (1) | |
| O(1) | 0.1474 (9) | 0.3296 (12) | 0.6577 (7) | 3.37 (21) |
| O(2) | 0.1309 (10) | 0.4876 (17) | 1.3127 (8) | 5.51 (27) |
| O(3) | 0.2539 (11) | 0.0794 (17) | 0.6468 (9) | 5.94 (28) |
| C(1) | 0.2068 (11) | 0.3016 (15) | 0.9471 (8) | 1.90 (28) |
| C(2) | 0.1442 (12) | 0.2699 (24) | 0.8409 (9) | 3.12 (29) |
| C(3) | 0.2125 (12) | 0.3617 (18) | 0.7603 (10) | 2.38 (28) |
| C(4) | 0.2146 (13) | 0.5566 (19) | 0.7741 (10) | 2.78 (30) |
| C(5) | 0.2721 (12) | 0.5888 (18) | 0.8874 (9) | 2.14 (27) |
| C(6) | 0.2904 (13) | 0.7874 (21) | 0.9139 (10) | 3.67 (35) |
| C(7) | 0.3726 (13) | 0.8052 (17) | 1.0168 (10) | 3.09 (32) |
| C(8) | 0.3076 (12) | 0.7156 (19) | 1.1047 (9) | 2.82 (32) |
| C(9) | 0.2942 (12) | 0.5206 (17) | 1.0757 (9) | 1.99 (26) |
| C(10) | 0.2071 (11) | 0.4942 (19) | 0.9746 (9) | 2.15 (26) |
| C(11) | 0.2447 (13) | 0.4195 (19) | 1.1683 (10) | 2.82 (30) |
| C(12) | 0.2255 (13) | 0.5270 (20) | 1.2661 (10) | 3.07 (31) |
| C(13) | 0.3072 (14) | 0.6704 (19) | 1.3003 (11) | 3.19 (33) |
| C(14) | 0.3857 (12) | 0.7276 (24) | 1.2081 (9) | 2.89 (30) |
| C(15) | 0.3925 (14) | 0.6079 (22) | 1.3950 (11) | 3.88 (35) |
| C(16) | 0.4722 (14) | 0.7468 (37) | 1.4490 (11) | 5.45 (35) |
| C(17) | 0.2232 (15) | 0.8219 (22) | 1.3329 (12) | 4.94 (42) |
| C(18) | 0.3078 (14) | 0.6295 (21) | 0.6958 (11) | 3.73 (34) |
| C(19) | 0.0842 (15) | 0.6428 (22) | 0.7490 (11) | 4.02 (35) |
| C(20) | 0.0720 (13) | 0.5551 (19) | 0.9925 (10) | 2.96 (31) |
| C(21) | 0.1805 (15) | 0.1782 (21) | 0.6128 (12) | 4.47 (39) |
| C(22) | 0.0952 (17) | 0.1642 (24) | 0.5067 (13) | 5.79 (45) |
| H(3) | 0.307 | 0.317 | 0.768 | |
| H(5) | 0.357 | 0.533 | 0.886 | |
| H(8) | 0.225 | 0.774 | 1.114 | |
| H(9) | 0.387 | 0.475 | 1.061 | |
| H(11) | 0.161 | 0.373 | 1.140 | |
| H(1.1) | 0.297 | 0.260 | 0.948 | |
| H(1.2) | 0.16 | 0.236 | 1.001 | |
| H(2.1) | 0.054 | 0.316 | 0.840 | |
| H(2.2) | 0.141 | 0.145 | 0.825 | |
| H(6.1) | 0.206 | 0.841 | 0.922 | |
| H(6.2) | 0.33 | 0.845 | 0.857 | |
| H(7.1) | 0.385 | 0.929 | 1.034 | |
| H(7.2) | 0.456 | 0.748 | 1.009 | |
| H(14.1) | 0.41 | 0.848 | 1.220 | |
| H(14.2) | 0.463 | 0.648 | 1.205 | |
| H(15.1) | 0.452 | 0.520 | 1.370 | |
| H(15.2) | 0.338 | 0.557 | 1.447 | |

Anisotropic thermal-motion parameters ($\times 10^4$). The expression is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$.

| | β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} |
|----|--------------|--------------|--------------|--------------|--------------|--------------|
| Br | 226 (3) | 126 (3) | 61 (1) | 151 (7) | 18 (2) | 64 (5) |

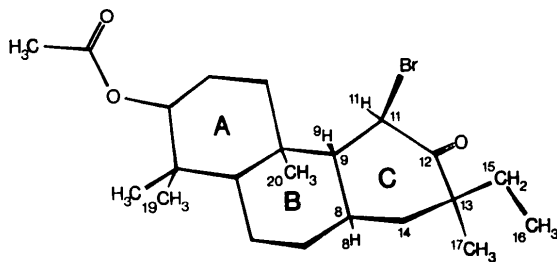


Fig. 1. View of molecule down *x* showing the numbering system.

Table 2. *Interatomic distances (Å) and angles (°), and least-squares plane*

| Some intramolecular bond lengths (± 0.01 Å) | | | |
|--|------|-------------------|------|
| C(22)–C(21) | 1.60 | C(11)–C(12) | 1.54 |
| C(21)–O(3) | 1.16 | C(12)–C(13) | 1.47 |
| C(21)–O(1) | 1.37 | C(13)–C(14) | 1.56 |
| O(1)–C(3) | 1.48 | C(14)–C(8) | 1.54 |
| C(18)–C(4) | 1.57 | C(11)–Br | 1.94 |
| C(19)–C(4) | 1.56 | C(12)–O(2) | 1.24 |
| C(7)–C(8) | 1.53 | C(13)–C(15) | 1.56 |
| C(8)–C(9) | 1.57 | C(13)–C(17) | 1.55 |
| C(10)–C(20) | 1.55 | C(15)–C(16) | 1.52 |
| C(9)–C(11) | 1.55 | | |
| Bond angles associated with ring C ($\pm 1^\circ$) | | | |
| C(7)–C(8)–C(9) | 107 | C(9)–C(11)–Br | 109 |
| C(10)–C(9)–C(11) | 111 | C(12)–C(11)–Br | 104 |
| C(7)–C(8)–C(14) | 112 | C(11)–C(12)–O(2) | 115 |
| C(9)–C(8)–C(14) | 108 | C(13)–C(12)–O(2) | 122 |
| C(8)–C(9)–C(11) | 110 | C(12)–C(13)–C(15) | 108 |
| C(9)–C(11)–C(12) | 115 | C(14)–C(13)–C(15) | 112 |
| C(11)–C(12)–C(13) | 124 | C(15)–C(13)–C(17) | 110 |
| C(12)–C(13)–C(14) | 109 | C(12)–C(13)–C(17) | 108 |
| C(13)–C(14)–C(8) | 111 | C(13)–C(15)–C(16) | 115 |
| Some intramolecular non-bonded distances (Å) | | | |
| C(20)···C(19) | 3.23 | Br····C(1) | 3.80 |
| C(20)···O(2) | 4.19 | O(1)····C(19) | 2.81 |
| C(20)···C(17) | 5.05 | O(1)····C(18) | 2.92 |
| C(20)···C(13) | 4.67 | | |

Least-squares plane of the form $Ax + By + Cz = D$ where A , B and C are the direction cosines of the normal to the plane referred to the orthogonal crystallographic axes. The deviations in Å of the most relevant atoms from the plane are given in square brackets.

Atoms defining the plane

C(8), C(9), C(11), C(12), C(13), C(14)

| A | B | C |
|-------|--------|-------|
| 0.860 | -0.484 | 0.159 |

[C(8) -0.44, C(9) 0.13, C(11) 0.19, C(12) -0.26, C(13) 0.00, C(14) 0.38, C(7) -0.30, C(10) -0.71, C(15) 1.15, C(17) -1.30, Br 2.03, O(2) -0.91]

yielded the coordinates of the lighter atoms. The structure was refined by block-diagonal least squares with only Br anisotropic; 17 H atoms bonded directly to the main skeleton were included in the structure factor calculations. The final R was 0.071 for 1053 observed

data.* Weighting was proportional to $1/\sigma(F)$. Scattering factors for neutral atoms were used (*International Tables for X-ray Crystallography*, 1962); that of Br was corrected for anomalous dispersion. Final positional and thermal parameters are given in Table 1, with estimated standard deviations in parentheses; bond lengths and angles are in Table 2.

Discussion. Rings A and B are near perfect chairs. Ring C is not planar and is a badly distorted chair. Br and C(15) are above the mean plane of ring C ; the keto-O(2) and C(17) are below the mean plane. The torsion angles are Br–C(11)···C(13)–C(15) 16, Br–C(11)–C(12)–O(2) 99, O(2)–C(12)–C(13)–C(17) 41, C(10)–C(9)–C(11)–C(12) 126, C(10)–C(9)–C(11)–Br 118, C(8)–C(9)–C(11)–Br 118, H(9)–C(9)–C(11)–H(11) 125, Br–C(11)–C(9)–H(9) 0, C(20)–C(10)–C(9)–H(9) 178°. The Br atom is *trans* to C(20) and exactly *cis*-eclipses H(9). Important non-bonded distances are Br···C(1) 3.80, C(19)···C(20) 3.23, C(17)···C(20) 5.05, C(20)···O(2) 4.19 Å. All bond lengths and angles are normal; the non-bonded contacts between the methyl groups show no large compression strains. The acetate and ethyl groups are ordered and a difference map shows no trace of solvent of crystallization.

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* A table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31787 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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