Ajugareptansone B, C$_{24}$H$_{30}$O$_8$, a Disordered Structure

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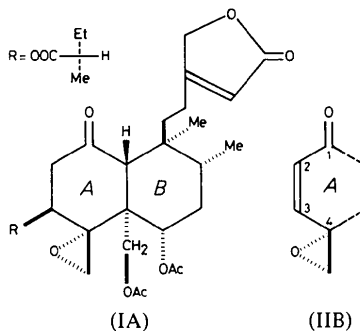
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Abstract. $M_r = 446.5$, orthorhombic, space group $P2_12_12_1$, $a = 10.681$ (8), $b = 9.758$ (7), $c = 21.320$ (13) Å, $Z = 4$, $V = 2222$ (3) Å^3, $D_x = 1.33$ g cm^{-3}, λ(Mo Kα) = 0.71069 Å. Ajugareptansone B was obtained during the isolation of ajugareptansone A. The structure was determined by a Patterson-search method, using the molecular structure of ajugareptansone A as a model, and refined to $R = 0.067$ for 865 observed reflections. The A, B rings adopt a *trans*-fused, half-chair/chair conformation.

Introduction. Camps, Coll & Cortel (1981) have described the isolation and chemistry of two closely related compounds, ajugareptansones A and B, which they obtained from an extract of *Ajuga reptans*, and both of which exhibit a possible insect antifeedant activity. The molecular structure and absolute stereochemistry of ketone A (IA) were determined from their work and an X-ray study (Miravitlles, Solans, Germain & Declercq, 1982).† The present X-ray work has established the stereochemistry (IIB) for the B compound, apart from its absolute configuration. However, as it is now assumed that B is formed from A during the isolation process, we have adopted the chirality of A also for B throughout this communication. Moreover all *trans*-clerodanes of known chirality conform to (IA) (Kato, Munkata & Katayama, 1973; Rogers, Ünal, Williams, Ley, Sim, Joshi & Ravindranath, 1979; Solans, Miravitlles, Declercq & Germain, 1979).

Experimental. Colourless prismatic crystal 0.2 × 0.2 × 0.3 mm, Syntex four-circle diffractometer; unit cell determined by automatic centring of 15 independent reflections followed by refinement of the orientation matrix and unit-cell parameters by least squares; 1891 reflections, $2\theta \leq 47°$, Mo Kα radiation, ω-scan technique; only 865 considered as 'observed' $[I \geq 2.5\sigma(I)]$; no absorption correction applied; observed systematic absences and the statistical distributions of E values indicated that the space group is $P2_12_12_1$; structure solved by Patterson search (Braun, Hornstra & Leenhouts, 1969) with the molecular structure of ajugareptansone A as the search model; refinement with the *SHELX* program system (Sheldrick, 1976) with $w = [\sigma^2(F) + 0.0005F_o^2]^{-1}$. A difference Fourier synthesis showed that the butenolide group is disordered, and a final full-matrix least-squares refinement based on this disordered structure gave a final R value of 0.067† for all observed reflections (the disordered atoms were only refined isotropically and H atoms linked to the non-disordered C atoms were included in the last cycle in computed positions).
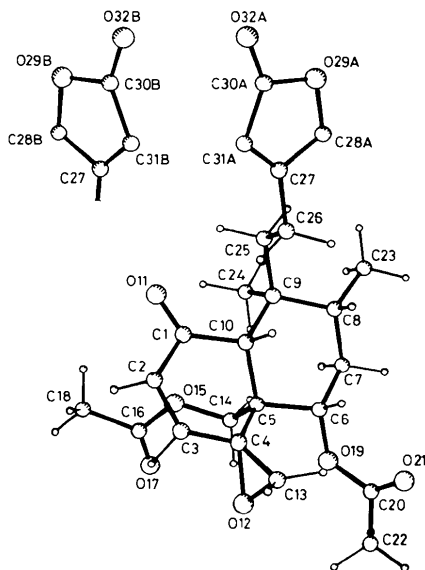

(IA)   (IIB)

Fig. 1. View of the molecule, showing the orientations of the disordered butenolide group (from which H atoms have been omitted).
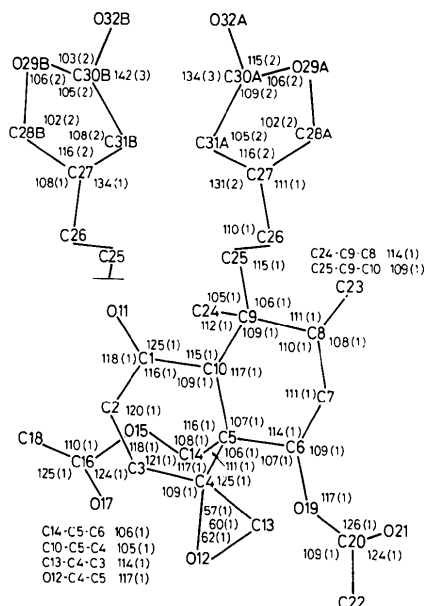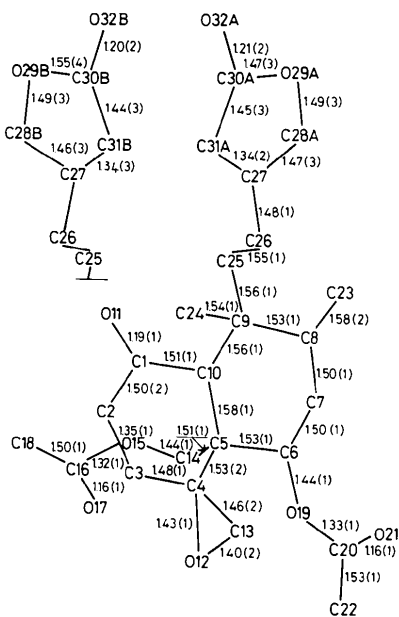

Fig. 3. Bond angles in degrees.

Fig. 2. Bond lengths in Å.

Fig. 1 shows the molecule with atom numbering (*PLUTO*, Motherwell & Clegg, 1978) and Table 1 the atomic coordinates with standard deviations. Bond lengths, bond angles and selected torsion angles are shown in Figs. 2, 3, and Table 2 (deposited), respectively.

Table 1. *Atomic coordinates* $(\times 10^4)$ *with standard deviations in parentheses and equivalent isotropic temperature factors* (Å^2)

	x	y	z	$B_{eq}*/B_{iso}$
C(1)	3200 (13)	4320 (19)	954 (7)	4·64
C(2)	3284 (16)	5707 (20)	1258 (8)	6·71
C(3)	2279 (16)	6252 (17)	1557 (9)	6·87
C(4)	1072 (12)	5504 (20)	1598 (9)	6·48
C(5)	856 (13)	4315 (17)	1137 (7)	4·43
C(6)	−204 (13)	3394 (17)	1376 (6)	4·22
C(7)	−250 (13)	2003 (16)	1067 (7)	4·42
C(8)	952 (13)	1217 (16)	1163 (8)	5·37
C(9)	2051 (13)	1970 (17)	848 (6)	4·36
C(10)	2099 (11)	3434 (16)	1150 (7)	4·49
O(11)	4053 (8)	3951 (13)	629 (5)	6·66
O(12)	72 (14)	6479 (15)	1667 (10)	11·50
C(13)	404 (25)	5697 (31)	2193 (11)	11·67
C(14)	446 (12)	4835 (19)	499 (7)	5·78
O(15)	1529 (8)	5399 (13)	185 (5)	6·53
C(16)	1368 (18)	6436 (19)	−205 (8)	6·05
O(17)	398 (13)	6829 (16)	−370 (6)	9·72
C(18)	2615 (15)	6952 (23)	−431 (9)	9·20
O(19)	−1371 (8)	4098 (11)	1266 (4)	5·05
C(20)	−2230 (15)	4053 (19)	1720 (8)	5·01
O(21)	−2142 (10)	3496 (14)	2203 (6)	7·54
C(22)	−3370 (12)	4909 (15)	1520 (6)	5·37
C(23)	765 (15)	−276 (18)	886 (8)	7·74
C(24)	1965 (13)	2025 (19)	123 (6)	5·60
C(25)	3296 (12)	1201 (17)	1000 (7)	5·53
C(26)	3654 (15)	1110 (19)	1707 (7)	7·77
C(27)	4799 (14)	273 (18)	1792 (6)	4·79
C(28A)	4530 (32)	−1200 (37)	1732 (18)	6·24
O(29A)	5715 (22)	−1830 (23)	1962 (10)	6·67
C(30A)	6600 (23)	−698 (33)	2072 (13)	2·70
C(31A)	5958 (31)	601 (35)	1994 (16)	5·77
O(32A)	7655 (21)	−1030 (28)	2214 (12)	7·57
C(28B)	5887 (31)	1088 (37)	1607 (16)	6·30
O(29B)	6947 (22)	143 (26)	1748 (12)	7·87
C(30B)	6359 (31)	−1247 (38)	1950 (18)	4·95
C(31B)	5033 (32)	−989 (36)	2014 (17)	5·70
O(32B)	7218 (20)	−1852 (23)	2194 (10)	6·46

$$* B_{eq} = \tfrac{8}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \, \mathbf{a}_i \cdot \mathbf{a}_j.$$

Discussion. The two positions which are randomly occupied by the butenolide group are in very good approximation related by reflection across the plane C(25)C(26)C(27). The two groups, which are planar [maximum deviations: C(30*A*) −0·04 (3); C(30*B*) −0·06 (4) Å], are mutually inclined at approximately 30°; the torsion angles are C(25)−C(26)−C(27)−C(28) −76 (2) (A), 76 (2)° (B); C(25)−C(26)−C(27)−C(30) 114 (2) (A), 107 (2)° (B).

The torsion angles around the C(5)−C(14) bond are similar to those formed in ajugareptansone A, but they are twisted 107 and 102°, respectively, with respect to the angles observed in the ajugareptansin *p*-bromobenzoate. In the two ketones O(15) lies very close to C(1) and relatively close to several other atoms of ring *A* (Table 3, deposited).

The double bond C(2)−C(3) reduces the torsion angle C(1)−C(2)−C(3)−C(4) to 0 (3)°, and the other endocyclic torsion angles in rings *A*,*B* show that each ring approximates closely to twofold symmetry about the lines joining the midpoints of bonds C(2)−C(3), C(5)−C(10), C(7)−C(8). A view along the 'diad' axis in ring *A* is given in Fig. 4* and this shows ring *A* to be in a half-chair conformation and ring *B* in a fairly regular chair conformation. The two 'diad' axes are inclined at 12·5°. This arrangement differs slightly from that in ketone A due to the extra space available to O(15) as a result of the double bond in B. The short intramolecular distances are similar to those observed by Miravitlles *et al.* (1982) in ajugareptansone A or Solans *et al.* (1979) in ajugareptansin *p*-bromobenzoate and Paul, Sim, Hamor & Robertson (1962) in clerodin bromolactone.

The packing of the molecules in the cell is shown in Fig. 5. The shortest intermolecular distances differ from those observed in other compounds isolated from *Ajuga reptans*; in our case these distances are C(13)−O(32*A*^{i}) 2·96 (4) and O(17)−C(28*A*^{ii}) 3·11 (4) Å [where (i) = 1 − *x*, *y* + ½, ½ − *z*, and (ii) = *x* − ½, ½ − *y*, −*z*].

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* Deposited. See previous footnote.
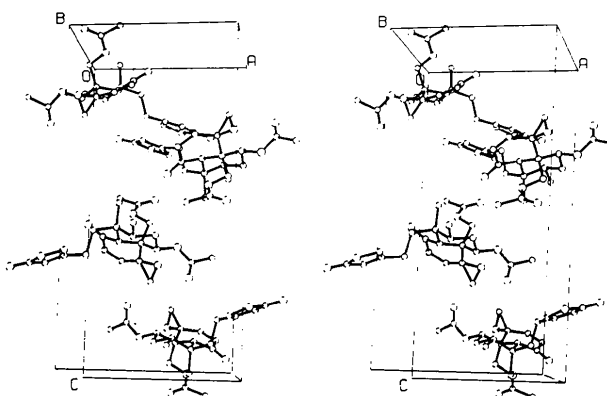
Fig. 5. Stereoscopic view of the packing in the cell.

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