

I wish to thank Professor M. Sundaralingam for invaluable discussions on this problem and for introducing me to the study of carbohydrates. I also express my thanks to Drs S. T. Rao and J. McAlister for making their computer programs available. This work was supported by grant GM-17378 from the National Institutes of Health of the United States Public Health Service to Professor M. Sundaralingam.

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Acta Cryst. (1982). **B38**, 188–191

Structure and Absolute Configuration of Ajugareptansone A

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(Received 28 November 1980; accepted 27 May 1981)

Abstract

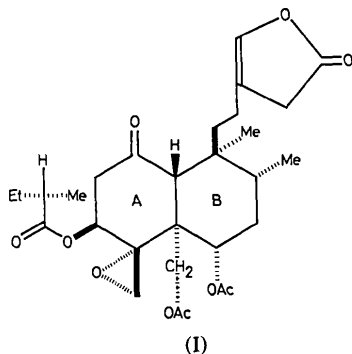
$C_{29}H_{40}O_{10}$, $M_r = 548.6$, is orthorhombic, $P2_12_12_1$, with $a = 16.225(3)$, $b = 11.007(3)$, $c = 16.401(3)$ Å, $Z = 4$, $V = 2929(1)$ Å³, $D_c = 1.24$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å. Ajugareptansone A was isolated from *Ajuga reptans*. The structure was solved by the *MULTAN* method and refined to an R of 0.057 for 3497 reflections. The absolute configuration was determined by the Bijvoet-difference method. The A, B rings adopt a *trans*-fused, chair–chair conformation. The absolute configuration of the title compound is the same as that of other clerodane compounds.

0567-7408/82/010188-04\$01.00

Introduction

The title compound, ajugareptansone A, is isolated from *Ajuga reptans* (Camps, Coll & Cortel, 1981) and has insect antifeedant activity. It is a diterpenoid with a clerodane skeleton (I). It may be compared with its congener ajugareptansin (Camps, Coll, Cortel & Messeguer, 1979; Solans, Miravittles, Declercq & Germain, 1979) which differs in having an (*S*)-(+)-2-methylbutyryloxy group β at C(1) and a hydroxy group β at C(3) and a hexahydroxyfurfuran group β at C(9). In order to determine unambiguously the structure and absolute configuration of the title compound, we have undertaken this X-ray study.

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A colourless prismatic crystal $0.2 \times 0.2 \times 0.3$ mm was used for crystal-data and intensity measurements on a Syntex four-circle diffractometer. This crystal was obtained by recrystallization from methyl acetate and ether solution.

The unit cell was measured by the automatic centring of 15 independent reflections and refinement of the orientation matrix and unit-cell parameters by least squares. Intensities of 3893 reflections in the range $2\theta < 114^\circ$ were collected with Cu K α radiation using the θ - 2θ scan technique. 3497 reflections were considered as 'observed' [$I > 2.5\sigma(I)$]. The observed systematic absences indicated space group $P2_12_12_1$.

Structure solution and refinement

The structure was solved with the *MULTAN* system of computer programs (Main, Woolfson, Lessinger, Germain & Declercq, 1978) and refined using the *SHELX* program system (Sheldrick, 1976). Weighted full-matrix least-squares refinement (including isotropic H atoms in computed positions) converged at $R = 0.057^*$ for all observed reflections ($R = \sum |F_o| - |F_c| / \sum |F_o|$).

The weighting scheme used was $w = [\sigma^2(F) + 0.0006|F_o|^2]^{-1}$, where $\sigma(F)$ was the standard deviation in the observed amplitudes derived from counting statistics.

The absolute configuration was determined by the Bijvoet-difference method. The structure was independently refined with the atoms in both enantiomorphic configurations; the f' and f'' values for C, N and O atoms were those of Cromer & Liberman (1970). 30 reflections with F_c differing significantly at the end of the two refinements were remeasured with great care, all eight reflections equivalent to hkl in the centrosymmetric point group being collected. F_{hkl} was taken as the mean value of F_{hkl} , $F_{\bar{h}\bar{k}\bar{l}}$, $F_{\bar{h}k\bar{l}}$, $F_{h\bar{k}\bar{l}}$ and $F_{\bar{h}\bar{k}l}$ as the mean value of the other four reflections. Table 1

Table 1. Comparison of observed and calculated values of $\Delta = (|F_{hkl}| - |F_{\bar{h}\bar{k}\bar{l}}|) / (|F_{hkl}| + |F_{\bar{h}\bar{k}\bar{l}}|)$ for the correct absolute configuration

The 30 reflections with F_c differing significantly at the end of the refinements are used.

hkl	1000 Δ_o	1000 Δ_c	T	hkl	1000 Δ_o	1000 Δ_c	T
282	-13	-16	0.30	1116	15	10	0.16
912	-17	-10	0.24	4101	-12	-12	0.16
714	-7	-9	0.23	663	90*	-24	0.16
258	-51	-21	0.21	1041	24*	-14	0.14
646	12	17	0.21	734	-7	-13	0.14
459	-4	-10	0.21	364	-7	-10	0.14
514	35	28	0.21	828	-48	-23	0.14
643	16	9	0.21	2112	33	17	0.13
1054	-14	-10	0.18	1051	11	13	0.13
561	16	10	0.17	2110	0	19	0.11
913	-29	-16	0.17	275	-34	-12	0.11
613	19	11	0.17	832	6*	-21	0.10
653	-8*	17	0.17	1021	-9*	11	0.10
673	29	17	0.16	334	35	12	0.10
711	53	25	0.16	633	-33	-12	0.07

Table 2. Positional parameters ($\times 10^4$) and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

	x	y	z	B_{eq} (\AA^2)†
C(1)	2875 (2)	5795 (4)	4549 (3)	4.8 (2)
C(2)	3295 (3)	5945 (4)	3740 (3)	6.5 (2)
C(3)	3266 (2)	7220 (4)	3404 (2)	5.3 (2)
C(4)	3430 (2)	8160 (4)	4053 (3)	4.7 (2)
C(5)	2879 (2)	8070 (3)	4796 (2)	4.3 (1)
C(6)	3111 (2)	9018 (3)	5446 (3)	4.7 (1)
C(7)	2755 (3)	8786 (4)	6284 (3)	5.3 (2)
C(8)	3012 (2)	7556 (4)	6617 (2)	5.0 (2)
C(9)	2711 (2)	6507 (3)	6061 (2)	4.5 (1)
C(10)	3039 (2)	6778 (3)	5181 (2)	4.2 (1)
O(11)	2467 (2)	4886 (3)	4687 (2)	6.2 (2)
O(12)	3889 (2)	7296 (3)	2769 (2)	6.6 (2)
C(13)	3685 (3)	7659 (6)	2032 (3)	7.2 (3)
O(14)	2991 (2)	7932 (6)	1839 (3)	10.9 (3)
C(15)	4430 (3)	7775 (6)	1484 (4)	8.2 (3)
C(16)	4332 (5)	6898 (9)	785 (6)	14.1 (4)
C(17)	4442 (5)	9136 (8)	1125 (6)	11.6 (4)
C(18)	4539 (5)	10053 (7)	1750 (6)	10.9 (4)
C(19)	4278 (3)	8706 (5)	4074 (3)	6.4 (3)
O(20)	3596 (2)	9344 (3)	3720 (2)	6.3 (2)
C(21)	1971 (2)	8304 (4)	4540 (3)	5.0 (2)
O(22)	1646 (1)	7222 (2)	4160 (2)	4.9 (1)
C(23)	837 (2)	7021 (5)	4216 (3)	5.6 (2)
O(24)	370 (2)	7723 (4)	4539 (3)	7.9 (2)
C(25)	619 (3)	5798 (5)	3870 (3)	6.9 (3)
O(26)	2819 (2)	10194 (2)	5161 (2)	5.5 (1)
C(27)	3373 (4)	11112 (4)	5118 (3)	5.8 (3)
C(28)	2992 (4)	12229 (4)	4773 (4)	8.3 (3)
C(29)	4075 (2)	11023 (3)	5355 (2)	7.4 (2)
C(30)	2733 (3)	7459 (5)	7517 (3)	6.9 (3)
C(31)	1777 (2)	6378 (4)	6100 (3)	5.0 (2)
C(32)	3079 (2)	5289 (4)	6368 (3)	5.0 (2)
C(33)	4010 (2)	5078 (4)	6287 (3)	5.5 (2)
C(34)	4297 (2)	3875 (4)	6591 (2)	4.8 (2)
C(35)	3853 (3)	2952 (4)	6893 (3)	5.8 (2)
C(36)	4446 (4)	1978 (5)	7121 (3)	7.0 (3)
O(37)	4305 (3)	992 (4)	7427 (3)	10.1 (3)
O(38)	5213 (2)	2355 (3)	6948 (2)	7.2 (2)
C(39)	5175 (3)	3541 (4)	6600 (4)	6.8 (3)

* Lists of structure factors, anisotropic thermal parameters and H-atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36100 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† $B_{eq} = \frac{1}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

compares the observed and calculated values of $\Delta = (|F_{hkl}| - |F_{\bar{h}\bar{k}\bar{l}}|) / (|F_{hkl}| + |F_{\bar{h}\bar{k}\bar{l}}|)$ for the correct absolute configuration whose atomic parameters are given in Table 2. The absolute configuration of the molecule is shown in Fig. 1 with the atom numbering (*PLUTO*, Motherwell & Clegg, 1978). It can be seen from Table 1 that the signs of Δ_c and Δ_o are the same for the twelve reflections with highest T [$T = w^{1/2} ||F_c(hkl)| - |F_o(hkl)||$], and for most of the others, but there are five contradictions in the reflections with $[||F_o(hkl)| + |F_o(\bar{h}\bar{k}\bar{l})|/2 < 9.0]$ among the 30 reflections. These five are denoted by asterisks in Table 1.

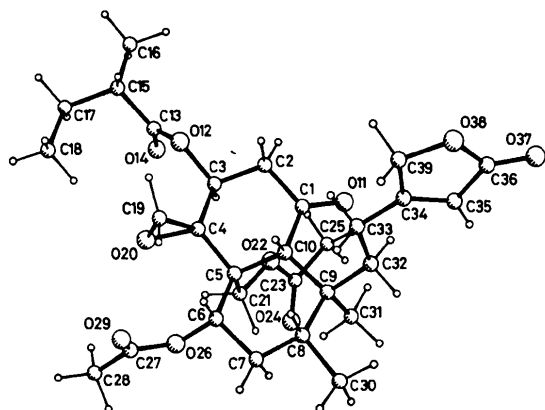


Fig. 1. A view of the molecule with the atomic numbering. [Ring A is defined by C(1), C(2), C(3), C(4), C(5) and C(10), and ring B by C(5), C(6), C(7), C(8), C(9) and C(10).]

The absolute configuration of ajugareptansone A is the same as that of ajugareptansin *p*-bromobenzoate (Solans, Miravittles, Declercq & Germain, 1979), clerodendrin A *p*-bromobenzoate chlorhydrin (Kato, Munkata & Katayama, 1973), 3-epicyaroptin and clerodin (Rogers, Ünal, Williams, Ley, Sim, Joshi & Ravindranath, 1979).

Discussion

The bond lengths, bond angles and some torsion angles are shown in Fig. 2 and Table 3.

Table 3. Torsion angles ($^{\circ}$)

E.s.d.'s are in the range 0.4–1.0 $^{\circ}$.

C(10)–C(1)–C(2)–C(3)	–43	C(7)–C(8)–C(9)–C(10)	54
C(2)–C(1)–C(10)–C(5)	51	C(7)–C(8)–C(9)–C(31)	54
O(11)–C(1)–C(10)–C(9)	5	C(30)–C(8)–C(9)–C(31)	54
C(1)–C(2)–C(3)–C(4)	42	C(30)–C(8)–C(9)–C(32)	–62
C(2)–C(3)–C(4)–C(5)	–54	C(3)–C(9)–C(10)–C(5)	–51
O(12)–C(3)–C(4)–C(19)	–17	C(31)–C(9)–C(10)–C(1)	–62
O(12)–C(3)–C(4)–O(20)	47	C(31)–C(9)–C(10)–C(5)	71
C(3)–C(4)–C(5)–C(10)	60	C(32)–C(9)–C(10)–C(1)	56
C(3)–C(4)–C(5)–O(21)	–63	C(8)–C(9)–C(32)–C(33)	–68
C(19)–C(4)–C(5)–C(6)	23	C(10)–C(9)–C(32)–C(33)	48
O(20)–C(4)–C(5)–C(6)	–45	C(3)–O(12)–C(13)–O(14)	0
O(20)–C(4)–C(5)–C(21)	73	O(12)–C(13)–C(15)–H(15)	–2
C(4)–C(5)–C(6)–O(26)	74	O(14)–C(13)–C(15)–C(16)	–66
C(10)–C(5)–C(6)–C(7)	–48	O(14)–C(13)–C(15)–C(17)	51
C(21)–C(5)–C(6)–C(7)	75	C(13)–C(15)–C(17)–C(18)	63
C(21)–C(5)–C(6)–O(26)	–45	C(21)–O(22)–C(23)–O(24)	3
C(4)–C(5)–C(10)–C(1)	–56	C(6)–O(26)–C(27)–O(29)	–5
C(6)–C(5)–C(10)–C(9)	47	C(32)–C(33)–C(34)–C(35)	2
C(21)–C(5)–C(10)–C(1)	64	C(39)–C(34)–C(35)–C(36)	0
C(21)–C(5)–C(10)–C(9)	–72	C(35)–C(34)–C(39)–O(38)	–1
C(4)–C(5)–C(21)–O(22)	78	C(34)–C(35)–C(36)–O(38)	0
C(10)–C(5)–C(21)–O(22)	–41	C(35)–C(36)–O(38)–C(39)	0
C(5)–C(6)–C(7)–C(8)	58	C(36)–O(38)–C(39)–C(34)	1
C(6)–C(7)–C(8)–C(9)	–60		

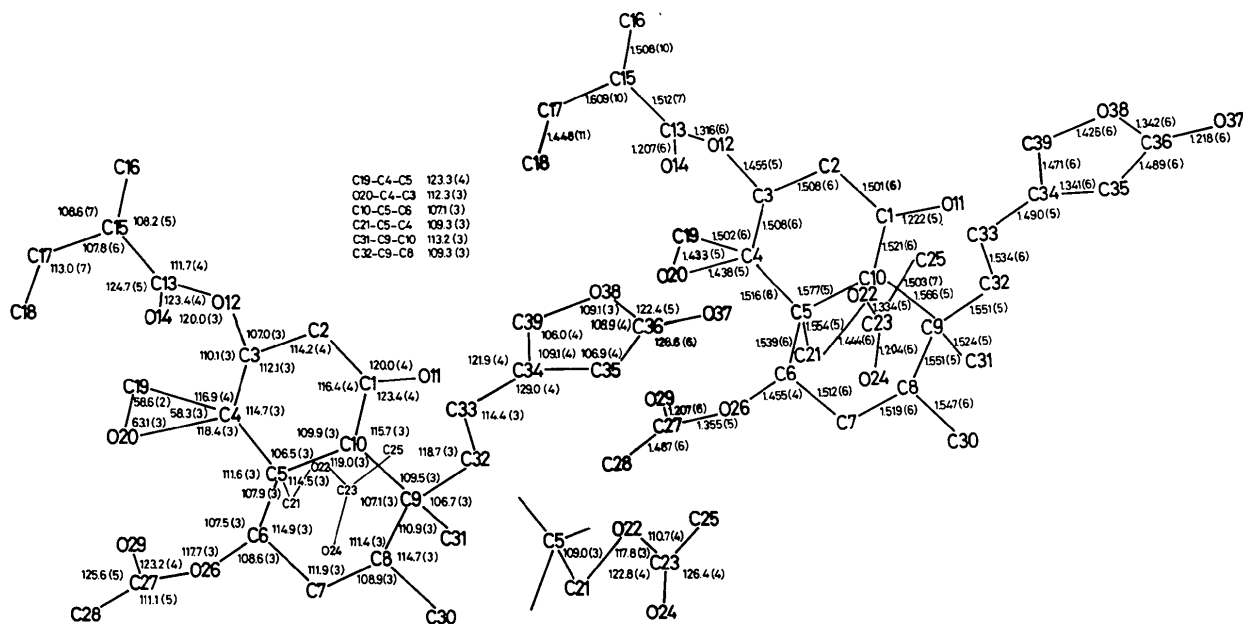


Fig. 2. Bond lengths (\AA) and angles ($^{\circ}$).

The butenolide moiety is planar with bond lengths similar to those obtained in ring *D* of ajugareptansin *p*-bromobenzoate (Solans, Miravittles, Declercq & Germain, 1979).

The main differences between ajugareptansin *p*-bromobenzoate and the title compound occur in the torsion angles about the C(5)–C(21) bond and in the conformation of the *cis*-decalin group. The substituents at C(21) are twisted 102° with respect to the torsion angle obtained in ajugareptansin *p*-bromobenzoate, thus producing several short intramolecular distances between O(22) and the atoms of cyclohexane ring *A* (Table 4).

Despite the carbonyl function at C(1), rings *A* and *B* of the *cis*-decalin group (Fig. 3) have chair forms instead of the skew-boat and chair forms found in ajugareptansin *p*-bromobenzoate. The present conformation is similar to those obtained in clerodin bromolactone (Paul, Sim, Hamor & Robertson, 1962) and in epicaryoptin (Rogers, Ünal, Williams, Ley, Sim, Joshi & Ravindranath, 1979). The two rings are *trans*-fused, with *trans* torsion angles of 167 (3) and –176 (3)°.

Table 4. Selected intramolecular distances (Å)

C(1)···O(22)	2.617 (4)	O(11)···C(31)	3.053 (6)
C(2)···O(22)	3.100 (5)	O(11)···C(32)	2.964 (6)
C(3)···O(14)	2.721 (6)	O(12)···C(19)	2.718 (6)
C(3)···O(22)	2.906 (4)	O(12)···O(20)	2.782 (5)
C(4)···O(22)	3.078 (4)	O(20)···O(26)	2.837 (5)
C(6)···O(29)	2.709 (5)	C(21)···O(26)	2.694 (5)
C(10)···O(22)	2.855 (4)	C(30)···C(31)	3.037 (7)
O(11)···O(22)	3.022 (4)	C(30)···C(32)	3.094 (7)

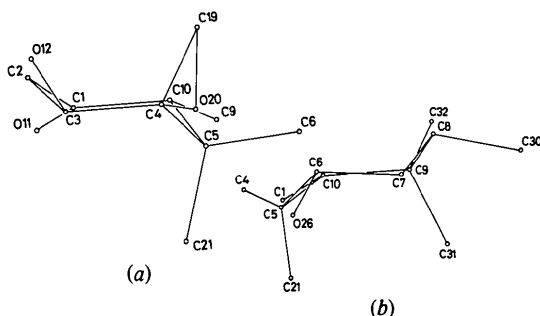


Fig. 3. Atom deviations from mean planes of (a) ring *A*, and (b) ring *B*.

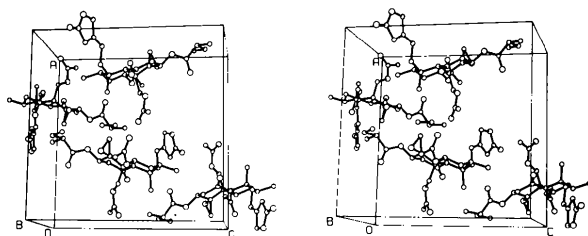


Fig. 4. Stereoscopic view of the packing in the cell.

These two differences produce variations in the distances, bond angles and torsion angles of the *cis*-decalin group in the two natural products isolated from *Ajuga reptans*. The other bond distances and angles have the expected values and are similar in the two compounds.

The short intramolecular distances are similar to those reported by Paul, Sim, Hamor & Robertson (1962) in clerodin bromolactone and by Solans, Miravittles, Declercq & Germain (1979) in ajugareptansin *p*-bromobenzoate. In the present structure there are the additional short O(22)···C distances of ring *A*.

The packing of the molecules in the cell is illustrated in Fig. 4. The only short intermolecular distance O(11)···C(28¹) = 3.049 (6) Å (*i* = *x*, *y* – 1, *z*) has a counterpart between different atoms [C(31) and O(20)] in ajugareptansin *p*-bromobenzoate.

We thank Drs F. Camps, J. Coll and A. Cortel for providing the samples and for discussions. We also thank Professor D. Rogers for reading the manuscript and for valuable discussions.

The present work is part of a wider research project supported by the Government through the Comisión Asesora de Investigación Científica y Técnica; JPD is indebted to the Fonds National de la Recherche Scientifique for a research fellowship.

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