Structure of Inuolide,* $C_{22}H_{32}O_9$ (a *cis-cis* Germacranolide from *Inula Indica*)

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Abstract. $M_r = 440.5$, orthorhombic, $P2_12_12_1$, $a = 18.04$ (1), $b = 14.15$ (1), $c = 9.37$ (1) Å, $V = 2392$ Å^3, D_m(flotation) $= 1.217$, $D_x = 1.223$ Mg m^{-3}, $Z = 4$, λ(Cu $K\alpha$) $= 1.5418$ Å; $R = 0.119$ for 695 observed reflections. The molecular structure obtained from the present study is in agreement with that obtained from ^{1}H NMR spectra. The γ-lactone ring adopts an envelope conformation and the cyclodecane ring adopts a distorted chair–boat–chair conformation.

Introduction. A new sesquiterpene lactone isolated from *Inula Indica* L. was characterized as 5β-acetoxy-1β,10α-epoxy-2α,9β-dihydroxy-6α-(2-methylbutyryl-oxy)germacran-8α,12-olide (Nagasampagi, Bhat, Bohlmann & Zdero, 1981) from ^{1}H NMR spectra. As the coupling constants of the H atoms at C(1) and C(2) were found to be too small for their *trans* relationship, it was thought desirable to study the crystal structure of this compound by X-ray single-crystal analysis. The present paper describes the details of this investigation.

Experimental. Cell dimensions were determined with the help of 16 high-angle reflections in zero-layer Weissenberg photographs with the films mounted in Straumanis arrangement.

Crystal 0.3×0.4 mm in cross section, three-dimensional intensity data (*hk0–hk8*) for 695 observed reflections (3107 unique reflections, 2044 unobserved), unfiltered Cu radiation, multiple-film equi-inclination Weissenberg technique; intensities estimated visually using extended spots in higher-layer photographs and corrected for the effect of spot extension; absorption neglected; layerwise scaling of intensities by Wilson's method; unobserved reflections excluded from all calculations.

Initial attempts to solve the structure with *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) were unsuccessful. After a careful survey of several '*E*' maps one seven-atom fragment from one of the '*E*' maps was taken as the known position fragment and input to *MULTAN*, which ultimately gave all the nonhydrogen atoms. Full-matrix least-squares refinement using isotropic temperature factors gave an $R(F)$ value of 0.119; unit weights;

ratio of maximum least-squares shift to error 0.9; no attempt was made to locate the H atoms because of insufficient data; refinement using anisotropic temperature factors was not tried for the same reason; $F(000) = 944$; scattering factors from *International Tables for X-ray Crystallography* (1962); programs *LALS* (Gantzel, Sparks & Trueblood, 1961) and *NRC*-12 (Pippy & Ahmed, 1978) were also used.

Discussion. The atomic parameters with their e.s.d.'s and isotropic temperature factors are given in Table 1,† intramolecular bond lengths and angles in Table 2, and some important torsion angles in Table 3.

Table 1. *Final positional parameters* ($\times 10^4$) *and isotropic thermal parameters, with e.s.d.'s in parentheses*

	x	y	z	U(Å^2)
C(1)	4116 (17)	5152 (24)	8628 (33)	3.5 (7)
C(2)	3736 (15)	5965 (22)	7870 (32)	3.2 (6)
C(3)	4234 (16)	6887 (24)	7600 (32)	3.8 (7)
C(4)	4124 (14)	7690 (19)	8797 (26)	1.7 (6)
C(5)	4628 (15)	7690 (22)	10076 (30)	2.7 (6)
C(6)	4593 (13)	6757 (20)	10967 (26)	1.7 (6)
C(7)	3811 (13)	6618 (17)	11613 (24)	0.8 (5)
C(8)	3690 (13)	5580 (17)	12166 (25)	0.8 (5)
C(9)	3362 (14)	4940 (20)	11031 (29)	2.1 (6)
C(10)	4009 (14)	4670 (20)	9985 (29)	2.1 (6)
C(11)	3597 (14)	7239 (21)	12831 (28)	1.9 (6)
C(12)	3156 (16)	6585 (21)	13817 (31)	2.6 (5)
C(13)	3698 (16)	8145 (24)	13137 (31)	3.7 (7)
C(14)	4676 (14)	4151 (20)	10597 (27)	2.5 (6)
C(15)	4200 (16)	8661 (23)	7954 (35)	3.7 (7)
C(16)	5777 (19)	8497 (26)	9833 (37)	4.0 (8)
C(17)	6580 (18)	8279 (26)	9299 (37)	5.4 (9)
C(18)	5689 (17)	6348 (23)	12104 (33)	3.4 (7)
C(19)	6175 (18)	6609 (24)	13362 (36)	4.4 (8)
C(20)	5842 (18)	6227 (25)	14697 (37)	5.2 (9)
C(21)	6291 (19)	6388 (26)	16109 (39)	6.2 (9)
C(22)	7001 (18)	6137 (25)	13004 (37)	5.5 (9)
O(23)	3716 (9)	4293 (14)	8691 (19)	2.7 (4)
O(24)	3025 (9)	6240 (12)	8533 (17)	1.7 (4)
O(25)	5394 (9)	7696 (13)	9521 (17)	2.1 (4)
O(26)	5521 (12)	9192 (18)	10324 (25)	6.1 (6)
O(27)	5123 (8)	6902 (12)	12145 (16)	0.9 (3)
O(28)	5853 (13)	5773 (19)	11203 (26)	5.8 (6)
O(29)	2769 (10)	6828 (14)	14847 (20)	3.3 (4)
O(30)	3127 (9)	5665 (12)	13312 (16)	1.2 (3)
O(31)	3150 (9)	4107 (12)	11738 (17)	1.7 (4)

Table 2. *Intramolecular bond lengths (Å) and angles*
(°), *with e.s.d.'s in parentheses*

C(1)–C(2)	1·52 (4)	C(1)–C(10)	1·46 (4)
C(1)–O(23)	1·42 (4)	C(2)–C(3)	1·60 (4)
C(2)–O(24)	1·48 (3)	C(3)–C(4)	1·61 (4)
C(4)–C(5)	1·51 (4)	C(4)–C(15)	1·59 (4)
C(5)–C(6)	1·56 (4)	C(5)–O(25)	1·48 (3)
C(6)–C(7)	1·55 (3)	C(6)–O(27)	1·48 (3)
C(7)–C(8)	1·57 (3)	C(7)–C(11)	1·49 (4)
C(8)–C(9)	1·52 (4)	C(8)–O(30)	1·48 (3)
C(9)–C(10)	1·57 (4)	C(9)–O(31)	1·41 (3)
C(10)–C(14)	1·52 (4)	C(10)–O(23)	1·43 (3)
C(11)–C(12)	1·53 (4)	C(11)–C(13)	1·33 (4)
C(12)–O(29)	1·24 (3)	C(12)–O(30)	1·39 (3)
C(16)–C(17)	1·56 (5)	C(16)–O(25)	1·36 (4)
C(16)–O(26)	1·18 (4)	C(18)–C(19)	1·52 (5)
C(18)–O(27)	1·29 (4)	C(18)–O(28)	1·21 (4)
C(19)–C(20)	1·49 (5)	C(19)–C(22)	1·67 (5)
C(20)–C(21)	1·57 (5)		
C(2)–C(1)–C(10)	135 (3)	C(2)–C(1)–O(23)	116 (3)
C(10)–C(1)–O(23)	60 (2)	C(1)–C(2)–C(3)	116 (2)
C(1)–C(2)–O(24)	113 (2)	C(3)–C(2)–O(24)	110 (2)
C(2)–C(3)–C(4)	113 (2)	C(3)–C(4)–C(5)	119 (2)
C(3)–C(4)–C(15)	105 (2)	C(5)–C(4)–C(15)	110 (2)
C(4)–C(5)–C(6)	114 (2)	C(4)–C(5)–O(25)	107 (2)
C(6)–C(5)–C(25)	103 (2)	C(5)–C(6)–C(7)	111 (2)
C(5)–C(6)–O(27)	105 (2)	C(7)–C(6)–O(27)	108 (2)
C(6)–C(7)–C(8)	112 (2)	C(6)–C(7)–C(11)	117 (2)
C(8)–C(7)–C(11)	105 (2)	C(7)–C(8)–C(9)	112 (2)
C(7)–C(8)–O(30)	105 (2)	C(9)–C(8)–O(30)	107 (2)
C(8)–C(9)–C(10)	107 (2)	C(8)–C(9)–O(31)	106 (2)
C(10)–C(9)–O(31)	107 (2)	C(1)–C(10)–C(9)	122 (2)
C(1)–C(10)–C(14)	117 (2)	C(1)–C(10)–O(23)	59 (2)
C(9)–C(10)–C(14)	118 (2)	C(9)–C(10)–O(23)	110 (2)
C(14)–C(10)–O(23)	116 (2)	C(7)–C(11)–C(12)	104 (2)
C(7)–C(11)–C(13)	134 (3)	C(12)–C(11)–C(13)	122 (3)
C(11)–C(12)–O(29)	127 (3)	C(11)–C(12)–O(30)	112 (2)
O(29)–C(12)–O(30)	120 (2)	C(17)–C(16)–O(25)	104 (3)
C(17)–C(16)–O(26)	131 (3)	O(25)–C(16)–O(26)	125 (3)
C(19)–C(18)–O(27)	107 (3)	C(19)–C(18)–O(28)	124 (3)
O(27)–C(18)–O(28)	129 (3)	C(18)–C(19)–C(20)	109 (3)
C(18)–C(19)–C(22)	105 (3)	C(20)–C(19)–C(22)	113 (3)
C(19)–C(20)–C(21)	117 (3)	C(1)–O(23)–C(10)	62 (2)
C(5)–O(25)–C(16)	114 (2)	C(6)–O(27)–C(18)	114 (2)
C(8)–O(30)–C(12)	107 (2)		

Table 3. *Torsion angles for inuolide (e.s.d.'s ~4°)*

Ten-membered cyclodecane ring

C(1)–C(2)–C(3)–C(4)	96	C(6)–C(7)–C(8)–C(9)	91
C(2)–C(3)–C(4)–C(5)	–92	C(7)–C(8)–C(9)–C(10)	–77
C(3)–C(4)–C(5)–C(6)	59	C(8)–C(9)–C(10)–C(1)	99
C(4)–C(5)–C(6)–C(7)	64	C(9)–C(10)–C(1)–C(2)	–2
C(5)–C(6)–C(7)–C(8)	–165	C(10)–C(1)–C(2)–C(3)	–117

Five-membered γ-lactone ring

C(7)–C(8)–O(30)–C(12)	23	C(11)–C(7)–C(8)–O(30)	–25
C(8)–O(30)–C(12)–C(11)	–14	C(29)–C(12)–C(11)–C(13)	–11
O(30)–C(12)–C(11)–C(7)	–2	C(6)–C(7)–C(11)–C(13)	–40
C(12)–C(11)–C(7)–C(8)	16		

Side chains

O(30)–C(8)–C(9)–O(31)	54	C(15)–C(4)–C(5)–O(25)	67
O(31)–C(9)–C(10)–C(14)	53	O(25)–C(5)–C(6)–O(27)	–65
C(14)–C(10)–C(1)–O(23)	–105	C(6)–O(27)–C(18)–O(28)	–4
O(23)–C(1)–C(2)–O(24)	–60		

From the present study, on stereochemical considerations, the H atoms attached to C(1) and C(2) are *cis* to each other. The stereochemistry at all other centres remains unchanged as compared with ¹H NMR

studies and the compound should be represented as 5β-acetoxy-1α,10α-epoxy-2α,9β-dihydroxy-6α-(2-methylbutyryloxy)germacran-8α,12-olide (Fig. 1). We name the present compound inuolide.

Fig. 2 shows the molecule projected along [100]. There are two intermolecular hydrogen bonds between O(24) and O(31) (2·75 Å), and O(29) and O(31) (2·76 Å). There is one short OH···O intramolecular contact between O(31) and O(30) (2·65 Å).

The valency angles of the ten-membered ring are in the range 107–135° (mean 116°). The large deviations of the valency angles from the tetrahedral value of 109° indicate a considerable amount of angular strain (Cox & Sim, 1974); the largest such deviation is found at C(10) and C(1) where the epoxide ring is fused to the ten-membered ring. The following three groups of four atoms form good planes: C(9),C(10),C(1),C(2); C(10),C(1),C(5),C(6); and C(2),C(4),C(7),C(9).

The C(1)···C(5) transannular separation in inuolide is 3·95 Å, which shows the absence of transannular interactions as the cyclodecane ring is saturated.

The conformation of the ten-membered ring is a distorted chair–boat–chair. The torsion angles agree well with the theoretical values for the chair–boat–chair and to some extent to the twist-chair–boat–chair form of the cyclodecane ring (Hilderbrandt, Wieser & Montgomery, 1973). Though it seems reasonable to argue that the large deviations for these values from ideal
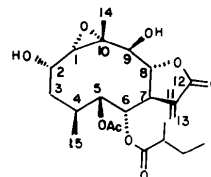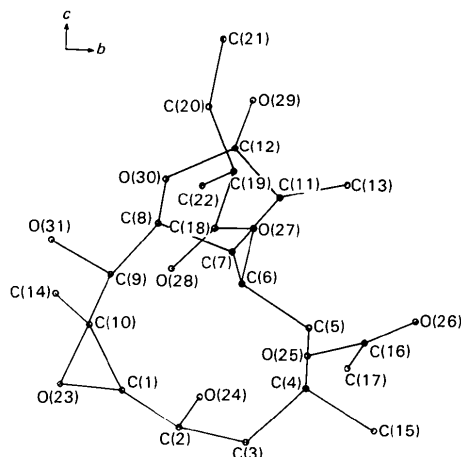

Fig. 1. The stereochemistry of inuolide

Fig. 2. A view of a molecule of inuolide projected along [100].

values of a chair–boat–chair conformation may be due to the large side groups attached at these sites, there is a striking resemblance between the torsion-angle values for inuolide and scorpioidine (Drew, Hitchman, Mann & Lopes, 1980) where there are no large side groups attached to the corresponding sites. The torsion angles are also comparable to those of 1,3,5,7-tetraoxa-9-aza-8-cyclodecanone (Kobelt & Paulus, 1973), epoxy-ineupatorolide and ineupatolide (Baruah, Sharma, Thyagarajan, Herz, Govindan & Blount, 1980).

The γ-lactone ring is *trans*-fused to the ten-membered ring at C(7) and C(8) and assumes an envelope form with C(8) as the flap, about 0·4 Å away from the plane of the other atoms of the lactone ring.

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Structure of Methyl 5,6,7,8,9-Pentaacetoxy-2-amino-4-nitromethyl-D-*glycero*-L-*gluco*-2-nonene-3-carboxylate, $C_{22}H_{32}N_2O_{14}$

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Abstract. $M_r = 548\cdot5$, orthorhombic, $P2_12_12_1$, $a = 14\cdot270$ (2), $b = 18\cdot743$ (2), $c = 10\cdot309$ (1) Å, $V = 2757\cdot3$ (6) Å^3, $Z = 4$, $D_x = 1\cdot32$, $D_m = 1\cdot30$ Mg m^{-3}, λ(Cu $K\alpha$) $= 1\cdot542$ Å, $\mu = 0\cdot95$ mm^{-1}, $F(000) = 1160$, $T = 300$ K. Final $R = 0\cdot074$ for 1848 observed reflections. The configurations of the chiral centres C(8), C(7), C(6), C(5) and C(4) are R, S, R, S and S, respectively, that is D-*glycero*-L-*gluco*. The molecule has an intramolecular hydrogen bond between the N and O atoms of the amino and carbonyl groups respectively, showing a chelate structure. Packing of the molecules is governed by van der Waals contacts.

Introduction. Open-chain sugar nitro-olefins [poly-acetoxy-1-nitroalk-1-enes, $NO_2.HC=CH.(CHOAc)_4.CH_2OAc$ and O-protected 2-C-glycosyl-1-nitroethylenes, $R.NH.C(CH_3)=CH.O_2R'$] are attractive as potential starting materials for the synthesis of functionalized, branched-chain sugars and C-

(polyhydroxyalkyl) and C-glycosylheterocyclic compounds derived from them. Gómez-Sánchez, Mancera, Rosado & Bellanato (1980) reported an easy way to obtain 3-(pentaacetoxypentyl)pyrrole derivatives by Michael-type addition of 3-(alkylamino)crotonic esters to pentaacetoxy-1-nitrohept-1-enes and further cyclization of the adducts.

$$R.NH.C(CH_3)=\underset{|}{C}.COOR'$$
$$NO_2.CH_2.C^*H.(CHOAc)_4.CH_2OAc$$
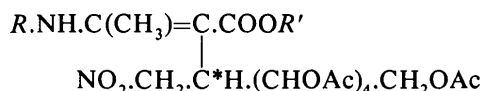
These compounds are intermediates in the synthesis of 3-(pentaacetoxypentyl)pyrroles, substances which have aroused interest as precursors of C-glycosylpyrroles. A new chiral centre is found (marked with an asterisk) and two diastereoisomers could result, although only one has been isolated. The configuration of these derivatives could not be established from chemical and spectroscopic considerations.