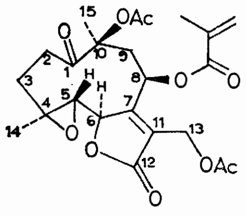
Sesquiterpenoids. Part XIX.[1] *X*-Ray Crystallographic Determination of the Stereochemistry and Conformation of the Germacranolide Glaucolide A †

By **Philip J. Cox * and George A. Sim,** Chemistry Department, University of Glasgow, Glasgow G12 8QQ, Scotland

The stereochemistry of glaucolide A (1), a germacrane sesquiterpenoid lactone, has been defined by *X*-ray crystal-structure analysis. The ten-membered ring, which carries an epoxide function at C(4)–C(5), has a conformation related to those of several other germacrane sesquiterpenoids and to one of the less-stable conformations of cyclodecane. The αβ-unsaturated γ-lactone ring is essentially planar. Crystals are orthorhombic, $a = 9{\cdot}075(6)$, $b = 18{\cdot}901(6)$, $c = 13{\cdot}654(6)$ Å, $Z = 4$, space group $P2_12_12_1$. The structure was solved by direct methods and atomic parameters adjusted by least-squares calculations, which converged to R 6·2% over 1701 reflections measured by diffractometer.

GLAUCOLIDE A is a sesquiterpenoid lactone which was isolated from *V. glauca* (L.) Willd. and twenty-five other species of the genus *Vernonia* (Compositae) found in North and South America.[2] Spectroscopic and chemical results for the sesquiterpenoid indicated the presence of a saturated ten-membered ring and an unusual C(13)-allylic acetate function. We undertook an *X*-ray crystallographic examination of glaucolide A in order to establish the relative stereochemistry of the molecule and the conformation of the ten-membered ring; the stereochemical results obtained have been reported briefly together with a detailed account of the chemical investigations.[3]



(1)

X-Ray measurements were made on an automatic four-circle diffractometer with Mo-K_α radiation and the

---

† Reprints unavailable.

[1] Part XVIII, P. J. Cox and G. A. Sim, *J.C.S. Perkin II*, 1974, 1359.

[2] W. G. Padolina, Ph.D. Thesis, University of Texas at Austin, 1973.

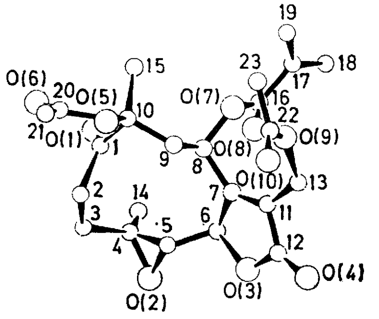
[3] W. G. Padolina, H. Yoshioka, N. Nakatani, T. J. Mabry, S. A. Monti, R. E. Davis, P. J. Cox, G. A. Sim, W. H. Watson, and I. B. Wu, *Tetrahedron*, 1974, **30**, 1161.

crystal structure was elucidated by non-centrosymmetric direct-phasing procedures; subsequent least-squares adjustment of the atomic parameters converged to *R* 6·2% over 1701 independent reflections. The Figure illustrates the atomic arrangement in the molecule and establishes the relative stereochemistry of the germacranolide as (1). Atomic co-ordinates are listed in Table 1 and the thermal parameters in Table 2, while Tables 3—6 list the bond lengths, valency angles, torsion angles, and intermolecular separations.

TABLE 1

Fractional atomic co-ordinates with standard deviations in parentheses

Atom	*x*	*y*	*z*
O(1)	0·1551(6)	0·3654(3)	0·2859(4)
O(2)	0·2740(6)	0·2478(3)	−0·0010(4)
O(3)	0·1320(6)	0·1037(3)	0·0328(4)
O(4)	−0·0265(7)	0·0145(3)	0·0083(4)
O(5)	−0·2258(5)	0·3592(2)	0·2473(4)
O(6)	−0·1321(7)	0·4666(2)	0·2830(4)
O(7)	−0·0203(5)	0·1628(2)	0·3531(3)
O(8)	0·2060(6)	0·1193(3)	0·3534(4)
O(9)	−0·2506(6)	0·0845(3)	0·2677(4)
O(10)	−0·4484(7)	0·1099(4)	0·1792(5)
C(1)	0·0464(9)	0·3581(3)	0·2369(6)
C(2)	0·0450(9)	0·3757(4)	0·1275(5)
C(3)	0·1910(9)	0·3622(4)	0·0773(6)
C(4)	0·2501(9)	0·2869(4)	0·0897(5)
C(5)	0·1532(8)	0·2284(4)	0·0602(5)
C(6)	0·1547(8)	0·1567(3)	0·1087(5)
C(7)	0·0307(8)	0·1458(3)	0·1788(4)
C(8)	0·0131(8)	0·1978(3)	0·2621(5)
C(9)	−0·1126(8)	0·2496(3)	0·2405(5)
C(10)	−0·0929(8)	0·3254(3)	0·2830(5)
C(11)	−0·0491(8)	0·0910(3)	0·1486(5)
C(12)	0·0140(9)	0·0630(3)	0·0579(5)
C(13)	−0·1821(9)	0·0526(4)	0·1850(6)
C(14)	0·3750(9)	0·2778(4)	0·1610(6)
C(15)	−0·0885(9)	0·3264(4)	0·3941(5)
C(16)	0·0871(8)	0·1222(4)	0·3901(5)
C(17)	0·0389(9)	0·0824(4)	0·4783(6)
C(18)	0·1274(11)	0·0301(4)	0·5075(6)
C(19)	−0·1064(13)	0·0988(7)	0·5207(9)
C(20)	−0·2331(9)	0·4313(3)	0·2552(5)
C(21)	−0·3795(11)	0·4570(4)	0·2203(6)
C(22)	−0·3856(9)	0·1105(4)	0·2561(6)
C(23)	−0·4420(10)	0·1397(5)	0·3518(7)
H(2A)	0·008(12)	0·426(5)	0·118(7)
H(2B)	−0·042(7)	0·347(3)	0·092(4)
H(3A)	0·264(8)	0·396(3)	0·097(5)
H(3B)	0·174(6)	0·371(3)	0·009(4)
H(5)	0·060(7)	0·241(3)	0·029(4)
H(6)	0·243(7)	0·147(3)	0·137(4)
H(8)	0·108(7)	0·226(3)	0·272(4)
H(9A)	−0·201(7)	0·234(3)	0·270(4)
H(9B)	−0·120(7)	0·256(3)	0·160(5)
H(13A)	−0·251(10)	0·039(4)	0·128(6)
H(13B)	−0·156(8)	0·011(4)	0·196(5)
H(14A)	0·413(7)	0·230(3)	0·152(4)
H(14B)	0·353(7)	0·283(3)	0·227(4)
H(14C)	0·461(9)	0·311(4)	0·137(5)
H(15A)	−0·068(7)	0·368(3)	0·417(4)
H(15B)	−0·008(8)	0·298(4)	0·421(5)
H(15C)	−0·183(7)	0·306(3)	0·415(5)
H(18A)	0·107(8)	0·005(3)	0·562(4)
H(18B)	0·236(9)	0·038(4)	0·485(6)
H(19A)	−0·079(12)	0·155(6)	0·531(8)
H(19B)	−0·197(16)	0·111(7)	0·479(10)
H(19C)	−0·111(9)	0·083(4)	0·574(5)
H(21A)	−0·396(10)	0·446(4)	0·143(6)
H(21B)	−0·384(11)	0·498(5)	0·206(7)
H(21C)	−0·458(10)	0·433(4)	0·262(6)
H(23A)	−0·352(10)	0·172(4)	0·388(6)
H(23B)	−0·471(12)	0·103(5)	0·414(7)
H(23C)	−0·491(8)	0·163(4)	0·339(5)



Atomic arrangement in the molecule of (1)

TABLE 2

Thermal parameters

(*a*) Anisotropic parameters * for the oxygen and carbon atoms ($U_{ij} \times 10^3$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	56(4)	59(3)	67(4)	−1(3)	−11(3)	−14(3)
O(2)	66(4)	63(3)	48(3)	−7(3)	18(3)	4(2)
O(3)	68(4)	47(3)	51(3)	14(3)	13(3)	−7(2)
O(4)	87(4)	44(3)	62(3)	3(3)	−4(4)	−19(3)
O(5)	50(3)	32(2)	50(3)	4(2)	−3(3)	−2(2)
O(6)	71(4)	33(3)	87(4)	−2(3)	−20(4)	−9(3)
O(7)	44(3)	36(2)	40(3)	4(2)	7(2)	7(2)
O(8)	49(3)	86(4)	75(4)	16(3)	−1(3)	26(4)
O(9)	47(3)	72(3)	55(3)	−3(3)	1(3)	−3(3)
O(10)	74(2)	107(5)	75(4)	22(4)	−18(4)	3(4)
C(1)	52(5)	27(4)	59(5)	6(4)	−6(5)	−11(4)
C(2)	52(5)	34(4)	45(4)	−4(4)	−3(4)	11(3)
C(3)	68(6)	50(5)	59(5)	−14(4)	8(4)	22(4)
C(4)	50(5)	54(5)	51(4)	−10(4)	12(4)	14(4)
C(5)	45(4)	58(5)	27(3)	8(4)	1(3)	1(3)
C(6)	47(4)	37(4)	36(4)	7(3)	7(4)	0(5)
C(7)	43(4)	31(3)	28(3)	5(3)	0(3)	5(3)
C(8)	44(4)	28(3)	31(3)	3(3)	7(3)	−1(3)
C(9)	47(4)	27(3)	42(4)	12(3)	−2(4)	0(3)
C(10)	51(4)	29(3)	41(4)	11(3)	1(4)	−2(3)
C(11)	52(4)	28(3)	34(4)	15(3)	−10(4)	2(3)
C(12)	56(5)	36(4)	51(4)	19(4)	1(4)	7(3)
C(13)	71(6)	35(4)	71(6)	−2(4)	6(5)	−9(4)
C(14)	55(5)	63(5)	66(6)	7(5)	−9(5)	2(5)
C(15)	71(6)	45(4)	41(4)	4(4)	−7(5)	−11(4)
C(16)	47(4)	41(4)	41(4)	−1(3)	−3(4)	3(3)
C(17)	56(5)	55(5)	55(5)	−13(5)	−15(5)	13(4)
C(18)	92(7)	52(5)	55(5)	1(5)	−11(6)	13(4)
C(19)	92(8)	189(13)	102(9)	48(9)	36(7)	100(9)
C(20)	64(5)	30(3)	50(4)	15(4)	1(4)	1(3)
C(21)	86(7)	40(4)	67(5)	20(5)	−8(5)	4(4)
C(22)	46(5)	43(4)	73(5)	−1(4)	−1(5)	8(4)
C(23)	53(6)	86(6)	85(7)	−6(5)	21(5)	−3(6)

(*b*) Isotropic parameters † ($U \times 10^2$) for the hydrogen atoms

H(2A)	7·8	H(15A)	1·3
H(2B)	1·4	H(15B)	3·4
H(3A)	3·0	H(15C)	1·5
H(3B)	1·1	H(18A)	1·6
H(5)	1·3	H(18B)	4·3
H(6)	1·3	H(19A)	8·9
H(8)	1·2	H(19B)	7·4
H(9A)	1·3	H(19C)	3·8
H(9B)	1·7	H(21A)	5·3
H(13A)	4·5	H(21B)	7·4
H(13B)	2·7	H(21C)	4·8
H(14A)	1·1	H(23A)	6·4
H(14B)	1·8	H(23B)	9·3
H(14C)	3·2	H(23C)	1·6

* In the form: $T = \exp[-2\pi^2\Sigma\Sigma U_{ij}h_ih_ja_i^*a_j^*]$. † Mean σ 1·8 Å^2.

The conformation of the ten-membered ring closely resembles one of the less-favourable conformations derived for cyclodecane by strain-energy minimization calculations[4] (see Table 7). There are also conformational relationships with shiromodiol acetate *p*-bromobenzoate,[5] where the macrocycle contains a double bond at C(1)–C(10) and an epoxide function at C(4)–C(5),

TABLE 3

Intramolecular bonded distances (Å) with standard deviations in parentheses

O(1)–C(1)	1·200(10)	C(5)–C(6)	1·508(10)
O(2)–C(4)	1·459(10)	C(6)–C(7)	1·491(10)
O(2)–C(5)	1·426(9)	C(7)–C(8)	1·513(9)
O(3)–C(6)	1·455(8)	C(7)–C(11)	1·328(9)
O(3)–C(12)	1·362(9)	C(8)–C(9)	1·532(9)
O(4)–C(12)	1·198(9)	C(9)–C(10)	1·556(9)
O(5)–C(10)	1·450(9)	C(10)–C(15)	1·518(10)
O(5)–C(20)	1·368(7)	C(11)–C(12)	1·464(10)
O(6)–C(20)	1·196(9)	C(11)–C(13)	1·493(11)
O(7)–C(8)	1·440(8)	C(16)–C(17)	1·486(11)
O(7)–C(16)	1·338(8)	C(17)–C(18)	1·334(12)
O(8)–C(16)	1·191(9)	C(17)–C(19)	1·474(15)
O(9)–C(13)	1·423(10)	C(20)–C(21)	1·492(12)
O(9)–C(22)	1·330(9)	C(22)–C(23)	1·508(13)
O(10)–C(22)	1·195(11)	C(2)–H(2A)	1·02(9)
C(1)–C(2)	1·530(11)	C(2)–H(2B)	1·08(6)
C(1)–C(10)	1·542(11)	C(3)–H(3A)	0·96(7)
C(2)–C(3)	1·513(12)	C(3)–H(3B)	0·96(6)
C(3)–C(4)	1·530(11)	C(5)–H(5A)	0·97(6)
C(4)–C(5)	1·470(11)	C(6)–H(6)	0·91(6)
C(4)–C(14)	1·504(12)	C(8)–H(8)	1·02(6)
C(9)–H(9A)	0·94(6)	C(18)–H(18B)	1·04(9)
C(9)–H(9B)	1·11(6)	C(19)–H(19A)	1·10(11)
C(13)–H(13A)	1·03(8)	C(19)–H(19B)	1·03(14)
C(13)–H(13B)	0·83(7)	C(19)–H(19C)	0·79(8)
C(14)–H(14A)	0·98(6)	C(21)–H(21A)	1·08(8)
C(14)–H(14B)	0·93(6)	C(21)–H(21B)	0·80(9)
C(14)–H(14C)	1·05(7)	C(21)–H(21C)	1·02(9)
C(15)–H(15A)	0·86(6)	C(23)–H(23A)	1·13(9)
C(15)–H(15B)	0·98(7)	C(23)–H(23B)	1·13(10)
C(15)–H(15C)	0·98(7)	C(23)–H(23C)	0·65(11)
C(18)–H(18A)	0·90(6)		

TABLE 4

Valency angles (deg.), with standard deviations in parentheses

C(3)–C(1)–O(1)	121·8(7)	C(22)–O(9)–C(13)	117·7(6)
C(10)–C(1)–O(1)	119·5(7)	C(11)–C(13)–O(9)	114·3(6)
C(5)–O(2)–C(4)	61·2(5)	O(10)–C(22)–O(9)	122·7(8)
C(3)–C(4)–O(2)	115·4(6)	C(23)–C(22)–O(9)	110·1(7)
C(5)–C(4)–O(2)	58·3(4)	C(23)–C(22)–O(10)	127·1(8)
C(14)–C(4)–O(2)	112·3(7)	C(10)–C(1)–C(2)	118·6(6)
C(4)–C(5)–O(2)	60·5(5)	C(3)–C(2)–C(1)	113·4(6)
C(6)–C(5)–O(2)	118·8(6)	C(9)–C(10)–C(1)	108·1(5)
C(12)–O(3)–C(6)	108·7(5)	C(15)–C(10)–C(1)	112·4(6)
C(5)–C(6)–O(3)	107·8(5)	C(4)–C(3)–C(2)	114·4(7)
C(7)–C(6)–O(3)	104·8(5)	C(5)–C(4)–C(3)	117·4(7)
O(4)–C(12)–O(3)	122·1(7)	C(14)–C(4)–C(3)	116·3(7)
C(11)–C(12)–O(3)	108·4(6)	C(14)–C(4)–C(5)	122·8(6)
C(11)–C(12)–O(4)	129·4(7)	C(6)–C(5)–C(4)	123·5(6)
C(20)–O(5)–C(10)	116·9(5)	C(7)–C(6)–C(5)	113·5(6)
C(1)–C(10)–O(5)	111·6(5)	C(8)–C(7)–C(6)	118·2(5)
C(9)–C(10)–O(5)	100·6(5)	C(11)–C(7)–C(6)	108·7(6)
C(15)–C(10)–O(5)	110·7(6)	C(11)–C(7)–C(8)	133·0(6)
O(6)–C(20)–O(5)	122·9(7)	C(9)–C(8)–C(7)	110·4(5)
C(21)–C(20)–O(5)	110·0(6)	C(12)–C(11)–C(7)	109·3(6)
C(21)–C(20)–O(6)	127·0(6)	C(13)–C(11)–C(7)	135·7(6)
C(16)–O(7)–O(8)	115·8(5)	C(10)–C(9)–C(8)	115·5(6)
C(7)–C(8)–O(7)	111·8(5)	C(15)–C(10)–C(9)	112·8(5)
C(9)–C(8)–O(7)	107·7(5)	C(13)–C(11)–C(12)	115·0(6)
O(8)–C(16)–O(7)	121·8(6)	C(18)–C(17)–C(16)	116·1(8)
C(17)–C(16)–O(7)	112·5(6)	C(19)–C(17)–C(16)	118·4(8)
C(17)–C(16)–O(8)	125·7(7)	C(19)–C(17)–C(18)	125·2(9)

TABLE 5

Torsion angles (deg.) *

C(5)–O(2)–C(4)–C(3)	–108
C(5)–O(2)–C(4)–C(14)	116
C(4)–O(2)–C(5)–C(6)	–114
C(12)–O(3)–C(6)–C(5)	–125
C(12)–O(3)–C(6)–C(7)	–3
C(6)–O(3)–C(12)–O(4)	–179
C(6)–O(3)–C(12)–C(11)	3
C(20)–O(5)–C(10)–C(1)	–53
C(20)–O(5)–C(10)–C(9)	–168
C(20)–O(5)–C(10)–C(15)	73
C(10)–O(5)–C(20)–O(6)	6
C(10)–O(5)–C(20)–C(21)	–177
C(16)–O(7)–C(8)–C(7)	67
C(16)–O(7)–C(8)–C(9)	–172
C(8)–O(7)–C(16)–O(8)	5
C(8)–O(7)–C(16)–C(17)	–174
C(22)–O(9)–C(13)–C(11)	114
C(13)–O(9)–C(22)–O(10)	–2
C(13)–O(9)–C(22)–C(23)	178
O(1)–C(1)–C(2)–C(3)	32
C(10)–C(1)–C(2)–C(3)	–143
O(1)–C(1)–C(10)–O(5)	142
O(1)–C(1)–C(10)–C(9)	–108
O(1)–C(1)–C(10)–C(15)	17
C(2)–C(1)–C(10)–O(5)	–42
C(2)–C(1)–C(10)–C(9)	68
C(2)–C(1)–C(10)–C(15)	–167
C(1)–C(2)–C(3)–C(4)	55
C(2)–C(3)–C(4)–O(2)	121
C(2)–C(3)–C(4)–C(5)	55
C(2)–C(3)–C(4)–C(14)	–104
O(2)–C(4)–C(5)–C(6)	107
C(3)–C(4)–C(5)–O(2)	104
C(3)–C(4)–C(5)–C(6)	–149
C(14)–C(4)–C(5)–O(2)	–98
C(14)–C(4)–C(5)–C(6)	9
O(2)–C(5)–C(6)–O(3)	–71
O(2)–C(5)–C(6)–C(7)	174
C(4)–C(5)–C(6)–O(3)	–142
C(4)–C(5)–C(6)–C(7)	102
O(3)–C(6)–C(7)–C(8)	–174
O(3)–C(6)–C(7)–C(11)	2
C(5)–C(6)–C(7)–C(8)	–57
C(5)–C(6)–C(7)–C(11)	120
C(6)–C(7)–C(8)–O(7)	–137
C(6)–C(7)–C(8)–C(9)	103
C(11)–C(7)–C(8)–O(7)	47
C(11)–C(7)–C(8)–C(9)	–72
C(6)–C(7)–C(11)–C(12)	–1
C(6)–C(7)–C(11)–C(13)	179
C(8)–C(7)–C(11)–C(12)	175
C(8)–C(7)–C(11)–C(13)	–6
O(7)–C(8)–C(9)–C(10)	90
C(7)–C(8)–C(9)–C(10)	–148
C(8)–C(9)–C(10)–O(5)	179
C(8)–C(9)–C(10)–C(1)	61
C(8)–C(9)–C(10)–C(15)	–64
C(7)–C(11)–C(12)–O(3)	–2
C(7)–C(11)–C(12)–O(4)	–180
C(13)–C(11)–C(12)–O(3)	179
C(13)–C(11)–C(12)–O(4)	1
C(7)–C(11)–C(13)–O(9)	7
C(12)–C(11)–C(13)–O(9)	–174
O(7)–C(16)–C(17)–C(18)	166
O(7)–C(16)–C(17)–C(19)	–8
O(8)–C(16)–C(17)–C(18)	–13
O(8)–C(16)–C(17)–C(19)	173

* The sign convention used for the torsion angles is such that the sign is negative if an anticlockwise rotation is required of atom (1) to eclipse atom (4) whilst looking down the (2)–(3) bond. Mean σ 0·8°.

---

[4] J. D. Dunitz, *Perspectives in Structural Chem.*, 1968, **2**, 1.

[5] R. J. McClure, G. A. Sim, P. Coggon, and A. T. McPhail, *Chem. Comm.*, 1970, 128.

and dihydromikanolide,[6] the ten-membered ring of which contains a double bond at C(4)–C(5) and two epoxide functions at C(1)–C(10) and C(2)–C(3). Although these germacrane rings have related conformations, corresponding torsion angles are associated with different bonds, *e.g.* the bond C(7)–C(8) in shiromodiol and dihydromikanolide plays the same role as C(1)–C(2) in (I) (Table 7).

TABLE 6

Intermolecular contacts <3·85 Å

$C(18) \cdots O(3^{I})$	3·36	$C(21) \cdots C(18^{III})$	3·73
$C(18) \cdots O(4^{I})$	3·72	$C(13) \cdots O(1^{VII})$	3·57
$C(23) \cdots O(4^{II})$	3·62	$O(6) \cdots O(3^{VIII})$	3·61
$C(18) \cdots C(12^{I})$	3·76	$O(6) \cdots O(4^{VII})$	3·32
$C(19) \cdots O(1^{III})$	3·48	$O(8) \cdots O(6^{VII})$	3·50
$C(5) \cdots O(2^{IV})$	3·56	$C(7) \cdots O(6^{VII})$	3·55
$C(9) \cdots O(2^{IV})$	3·43	$C(11) \cdots O(6^{VII})$	3·02
$C(21) \cdots O(3^{IV})$	3·64	$C(12) \cdots O(6^{VII})$	3·03
$C(3) \cdots O(4^{V})$	3·66	$C(13) \cdots O(6^{VII})$	3·31
$C(21) \cdots O(4^{IV})$	3·44	$C(16) \cdots O(6^{VII})$	3·80
$C(18) \cdots O(6^{VI})$	3·60	$C(21) \cdots O(8^{VIII})$	3·59
$C(3) \cdots O(10^{V})$	3·76	$C(21) \cdots O(10^{IX})$	3·56
$C(12) \cdots C(3^{IV})$	3·74	$C(18) \cdots C(2^{VII})$	3·79
$C(23) \cdots C(15^{III})$	3·77	$C(22) \cdots C(21^{X})$	3·61
$C(20) \cdots C(18^{III})$	3·55		

Roman numeral superscripts refer to the following transformations of the atomic co-ordinates:

(I) $\frac{1}{2} - x, -y, \frac{1}{2} + z$
(II) $-\frac{1}{2} - x, -y, \frac{1}{2} + z$
(III) $-\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$
(IV) $-\frac{1}{2} + x, \frac{1}{2} - y, -z$
(V) $\frac{1}{2} + x, \frac{1}{2} - y, -z$
(VI) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$
(VII) $-x, -\frac{1}{2} + y, \frac{1}{2} - z$
(VIII) $-x, \frac{1}{2} + y, \frac{1}{2} - z$
(IX) $-1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
(X) $-1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$

TABLE 7

Endocyclic torsion angles (deg.) for some ten-membered rings

	(I)	(II)		(III)	(IV)
ω(1)–(2)	66	112	ω(5)–(6)	102	101
ω(2)–(3)	−3	−49	ω(6)–(7)	−57	−44
ω(3)–(4)	55	86	ω(7)–(8)	103	104
ω(4)–(5)	−163	−151	ω(8)–(9)	−148	−154
ω(5)–(6)	116	79	ω(9)–(10)	61	50
ω(6)–(7)	−2	57	ω(10)–(1)	68	63
ω(7)–(8)	−90	−129	ω(1)–(2)	−143	−134
ω(8)–(9)	73	53	ω(2)–(3)	55	62
ω(9)–(10)	57	64	ω(3)–(4)	55	53
ω(10)–(1)	−153	−166	ω(4)–(5)	−149	−159

(I) Dihydromikanolide (ref. 6), (II) shiromodiol acetate *p*-bromobenzoate (ref. 5), (III) glaucolide A(1), (IV) cyclodecane: less-favourable conformation (ref. 4).

The C(14) and C(15) carbon atoms carried by C(4) and C(10) in these sesquiterpenoids are *cis* and lie on the α-face of the macrocycle. Conformational similarities also exist, of course, among germacrane sesquiterpenoids in which the C(14) and C(15) carbon atoms are *cis* and β.[7]

The C–C(sp^3)–C valency angles of the ten-membered ring are in the range 108·1—123·5°, mean 114·5°, the largest deviations from the tetrahedral value being found at the epoxide function where C(3)–C(4)–C(5) is 117·4° and C(4)–C(5)–C(6) is 123·5°.

The αβ-unsaturated γ-lactone is essentially planar, the largest endocyclic torsion angle being 3°.

EXPERIMENTAL

Crystal Data.—$C_{23}H_{28}O_{10}$, $M = 464·5$. Orthorhombic, $a = 9·075(6)$, $b = 18·901(6)$, $c = 13·654(6)$ Å, $U = 2341·8$ Å^3, $D_m = 1·29$, $Z = 4$, $D_c = 1·31$, $F(000) = 984$. Space group $P2_12_12_1$ (D_2^4). Mo-K_α radiation, $\lambda = 0·7107$ Å; μ(Mo-K_α) = 1·12 cm^{-1}.

Crystallographic Measurements.—Initial values for the cell dimensions, obtained by photographic procedures, were subsequently adjusted by a least-squares analysis of the angular settings of 12 reflections measured on a Hilger and Watts computer-controlled four-circle diffractometer at θ(Mo-K_α) *ca.* 16°. For intensity measurements the octants *hkl* and $h\bar{k}l$ were surveyed in the range $\theta < 27°$ by means of θ—ω scans which consisted of forty steps of 0·02° s^{-1} in θ with background counts for 15 s at each end of the scan range. The intensities of 2895 independent reflections were obtained, of which 1701 had $I > 3\sigma(I)$. No correction for absorption was applied.

Structure Analysis.—The crystal structure was determined by direct phasing procedures which form part of the '*X*-Ray '72' series of programmes. $|E|$ Values were derived from the intensities, on the basis of an overall isotropic temperature factor B 3·56 Å^2, and Σ2 relationships were generated for the 339 reflections with $|E| \geqslant 1·5$. The initial set of phases consisted of three to define the origin[8] and one the enantiomorph, together with two phases to which values of $\pm\pi/2$ were given.* This procedure gave four possible starting sets of six phases for input to the 'Tangen' programme, which then generated phase sets characterized[9] by values of R_K 0·24 and 0·33—0·35. An E map derived from the phases with the lowest value of R_K yielded positions for all 33 carbon and oxygen atoms.

The initial structure-factor calculation gave R 33·5%, and three cycles of full-matrix least-squares refinement with isotropic thermal parameters lowered R to 11·4%. Subsequent calculations with anisotropic thermal parameters reduced R further to 9·2%, at which stage a difference electron-density distribution revealed the sites of all the hydrogen atoms. The hydrogen atoms were then included in the least-squares calculations with isotropic thermal parameters and convergence was reached at R 6·2%. Since $\langle w\Delta^2 \rangle$ was approximately constant over various ranges of $|F_o|$ and sinθ, a unit weighting scheme ($w = 1$) was retained throughout the analysis.

We thank Dr. T. J. Mabry for a supply of (1) and the S.R.C. for a grant which enabled us to purchase the diffractometer.

[4/1722 *Received, 16th August*, 1974]

---

* These are listed together with final observed and calculated structure factors in Supplementary Publication No. SUP 21199 (14 pp., 1 microfiche). See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue.

[6] P. J. Cox and G. A. Sim, *J.C.S. Perkin II*, 1974, 1355.

[7] F. H. Allen and D. Rogers, *J. Chem. Soc.* (*B*), 1971, 257; A. T. McPhail and G. A. Sim, *J.C.S. Perkin II*, 1972, 1313.

[8] H. Hauptman and J. Karle, *Acta Cryst.*, 1956, **9**, 45.

[9] J. Karle and I. L. Karle, *Acta Cryst.*, 1966, **21**, 849.