Sesquiterpenoids. Part XXIV.[1] *X*-Ray Crystallographic Analysis of Paucin Monohydrate, a Pseudoguaianolide Glucoside

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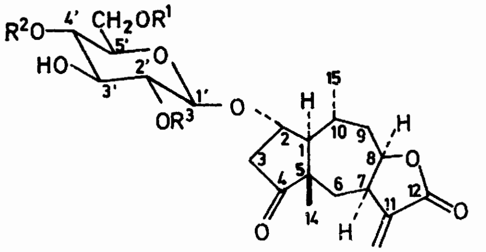
Paucin (1c), a pseudoguaianolide glucoside, has been studied by *X*-ray diffraction and the glucose ring shown to be acetylated at position 6'-*O*. The sesquiterpenoid cycloheptane ring adopts a twist-boat conformation, while the cyclopentanone and α-methylene γ-lactone rings have half-chair and envelope conformations, respectively. The C=C–C=O and C_α–C_β–C_γ–O torsion angles of the α-methylene γ-lactone are −10 and −17°. Crystals of paucin monohydrate are monoclinic, space group $P2_1$, with a = 18.308(4), b = 6.724(2), c = 9.987(4) Å, β = 93.38(4)°, and Z = 2. The crystal structure was elucidated by direct-phasing methods and the atomic parameters were subsequently adjusted by least-squares calculations which converged at R 7.9% over 1 929 diffractometer reflections.

PAUCIN,[2,3] a pseudoguaianolide β-glucoside from *Hymenoxys* and *Baileya* species, is active against P-388 leukaemia in mice.[4] Chemical and spectroscopic investigations led to the structure and stereochemistry shown in (1), though the site of attachment of the acetyl group on the glucose moiety remained in question. We undertook an *X*-ray diffraction investigation to define the constitution of the compound and to obtain details of the molecular conformation.



(1)

a; $R^1 = R^2 = H, R^3 = Ac$

b; $R^1 = R^3 = H, R^2 = Ac$

c; $R^2 = R^3 = H, R^1 = Ac$

The crystal structure of paucin monohydrate was determined by direct-phasing methods and the atomic parameters were adjusted by least-squares calculations. The resultant molecular structure is shown in Figure 1 and the packing of the molecules in the unit cell in Figure 2. Atomic co-ordinates are listed in Table 1, and bond lengths, valency and torsion angles in Tables 2—4.

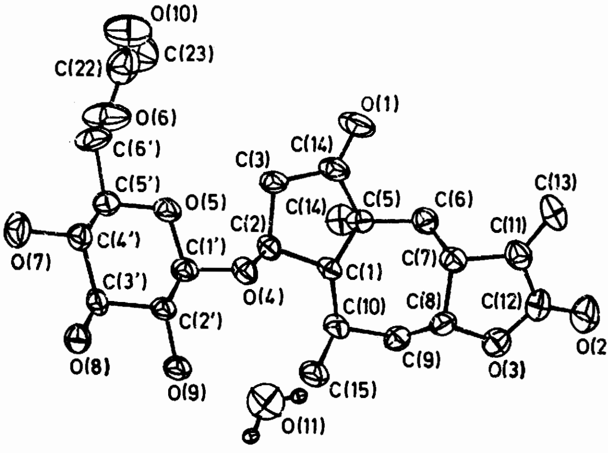


FIGURE 1 Molecular structure of paucin monohydrate

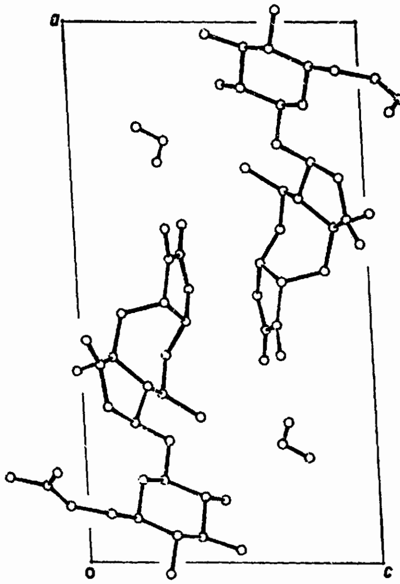
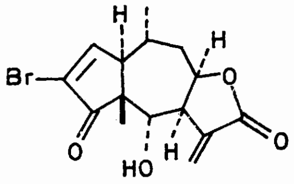


FIGURE 2 Arrangement of molecules in the unit cell

Our results establish that paucin has the constitution and relative stereochemistry (1c); moreover, since treatment of paucin with dilute acid yields D-glucose, it follows that (1c) also represents the absolute stereochemistry of paucin.[3]



(2)

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[1] Part XXIII, P. J. Cox and G. A. Sim, preceding paper.

[2] W. Herz, K. Aota, M. Holub, and Z. Samek, *J. Org. Chem.*, 1970, **35**, 2611; W. Herz, K. Aota, and A. L. Hall, *ibid.*, 1970, **35**, 4117.

[3] T. G. Waddell and T. A. Geissman, *Phytochem.*, 1969, **8**, 2371; *Tetrahedron Letters*, 1969, 515.

[4] W. Herz, K. Aota, A. L. Hall, and A. Srinivasan, *J. Org. Chem.*, 1974, **39**, 2013.

The cycloheptane ring has a conformation which approximates closely to the twist-boat (C_2) form described by Hendrickson,[5] the mean deviation between the torsion angles of the ring and those listed by Hendrickson being only 4°. The approximate C_2 axis of the twist-boat ring passes through C(10) and the midpoint of the bond C(6)–C(7). The related sesquiter-

TABLE 1

Fractional atomic co-ordinates, with standard deviations in parentheses

Atom	*x*	*y*	*z*
O(1)	0.409 8(3)	0.501 6	0.023 5(7)
O(2)	0.625 8(3)	−0.230 4(12)	0.371 1(8)
O(3)	0.505 7(3)	−0.212 4(9)	0.383 5(6)
O(4)	0.224 5(2)	0.361 2(7)	0.290 8(4)
O(5)	0.152 2(2)	0.604 9(7)	0.193 3(5)
O(6)	0.103 0(5)	0.791 0(11)	−0.058 6(7)
O(7)	−0.022 3(3)	0.818 6(10)	0.273 1(5)
O(8)	0.022 7(2)	0.598 7(8)	0.516 8(5)
O(9)	0.115 3(2)	0.273 5(7)	0.472 3(5)
O(10)	0.164 4(5)	1.062 8(12)	−0.099 7(8)
O(11)	0.219 1(3)	0.299 3(12)	0.677 8(7)
C(1)	0.325 4(3)	0.161 6(9)	0.225 9(6)
C(2)	0.257 5(3)	0.279 7(10)	0.176 5(6)
C(3)	0.286 8(4)	0.444 6(10)	0.085 2(7)
C(4)	0.364 7(4)	0.391 0(10)	0.065 4(7)
C(5)	0.378 9(3)	0.177 9(10)	0.110 6(6)
C(6)	0.459 7(3)	0.133 2(11)	0.148 3(6)
C(7)	0.480 4(3)	0.117 2(10)	0.297 8(7)
C(8)	0.445 9(4)	−0.064 7(12)	0.368 3(7)
C(9)	0.382 9(4)	−0.169 7(8)	0.294 0(7)
C(10)	0.311 4(3)	−0.050 2(10)	0.275 1(7)
C(11)	0.561 6(4)	0.075 5(13)	0.321 9(7)
C(12)	0.570 2(4)	−0.135 9(15)	0.359 4(9)
C(13)	0.617 2(4)	0.201 2(16)	0.313 2(10)
C(14)	0.353 0(4)	0.049 9(12)	−0.014 3(7)
C(15)	0.268 9(4)	−0.053 5(12)	0.402 0(8)
C(1′)	0.152 1(3)	0.422 2(9)	0.268 0(6)
C(2′)	0.121 2(3)	0.458 7(9)	0.404 1(6)
C(3′)	0.046 4(3)	0.554 2(10)	0.386 5(7)
C(4′)	0.049 2(3)	0.740 0(10)	0.299 9(7)
C(5′)	0.081 3(3)	0.686 1(10)	0.168 0(7)
C(6′)	0.088 9(5)	0.864 8(12)	0.078 4(8)
C(22)	0.140 7(5)	0.895 4(16)	−0.134 9(9)
C(23)	0.155 5(6)	0.799 9(21)	−0.261 3(10)
H(1)	0.353(3)	0.214(8)	0.303(5)
H(2)	0.223(3)	0.220(8)	0.126(5)
H(3A)	0.255(3)	0.443(12)	0.004(7)
H(3B)	0.280(6)	0.602(21)	0.132(11)
H(6A)	0.476(4)	−0.021(15)	0.104(8)
H(6B)	0.493(6)	0.262(19)	0.119(10)
H(7)	0.470(4)	0.243(14)	0.344(7)
H(8)	0.436(2)	−0.032(8)	0.465(5)
H(9A)	0.396(4)	−0.198(12)	0.202(7)
H(9B)	0.371(5)	−0.270(17)	0.350(10)
H(10)	0.284(3)	−0.103(10)	0.209(6)
H(13A)	0.666(3)	0.179(8)	0.342(5)
H(13B)	0.609(6)	0.348(20)	0.282(10)
H(14A)	0.295(5)	0.051(16)	−0.039(9)
H(14B)	0.356(4)	−0.087(15)	0.010(8)
H(14C)	0.385(4)	0.053(12)	−0.083(7)
H(15A)	0.261(5)	−0.218(18)	0.438(9)
H(15B)	0.219(4)	−0.001(14)	0.381(8)
H(15C)	0.293(4)	0.019(12)	0.467(7)
H(1′)	0.124(4)	0.334(12)	0.215(7)
H(2′)	0.157(4)	0.523(12)	0.469(7)
H(3′)	0.006(3)	0.500(10)	0.341(6)
H(4′)	0.083(3)	0.827(12)	0.350(7)
H(5′)	0.047(3)	0.614(11)	0.115(6)
H(6′A)	0.130(6)	0.933(20)	0.123(10)
H(6′B)	0.048(5)	0.912(15)	0.066(9)
H(O7)	−0.039(4)	0.818(12)	0.370(8)
H(O8)	−0.020(3)	0.601(9)	0.493(5)
H(O9)	0.149(4)	0.285(14)	0.555(7)
H(O11A)	0.259(5)	0.310(21)	0.702(10)
H(O11B)	0.194(4)	0.303(14)	0.767(7)

TABLE 2

Bond lengths (Å), with estimated standard deviations in parentheses

O(1)–C(4)	1.204(8)	C(5′)–C(6′)	1.510(10)
O(2)–C(12)	1.199(11)	C(22)–C(23)	1.456(14)
O(3)–C(8)	1.480(9)	C(1)–H(1)	0.96(5)
O(3)–C(12)	1.323(9)	C(2)–H(2)	0.89(5)
O(4)–C(2)	1.432(8)	C(3)–H(3A)	0.97(7)
O(4)–C(1′)	1.394(7)	C(3)–H(3B)	1.17(14)
O(5)–C(5′)	1.416(8)	C(6)–H(6A)	1.17(10)
O(5)–C(1′)	1.438(8)	C(6)–H(6B)	1.11(12)
O(6)–C(6′)	1.491(11)	C(7)–H(7)	0.99(9)
O(6)–C(22)	1.270(12)	C(8)–H(8)	1.01(5)
O(7)–C(4′)	1.421(8)	C(9)–H(9A)	0.98(7)
O(8)–C(3′)	1.428(8)	C(9)–H(9B)	0.91(11)
O(9)–C(2′)	1.427(8)	C(10)–H(10)	0.89(6)
O(10)–C(22)	1.250(13)	C(13)–H(13A)	0.93(5)
C(1)–C(2)	1.531(8)	C(13)–H(13B)	1.04(13)
C(1)–C(5)	1.558(8)	C(14)–H(14A)	1.08(9)
C(1)–C(10)	1.533(9)	C(14)–H(14B)	0.96(10)
C(2)–C(3)	1.551(10)	C(14)–H(14C)	0.92(7)
C(3)–C(4)	1.495(9)	C(15)–H(15A)	1.17(12)
C(4)–C(5)	1.520(9)	C(15)–H(15B)	0.98(8)
C(5)–C(6)	1.536(9)	C(15)–H(15C)	0.91(7)
C(5)–C(14)	1.565(10)	C(1′)–H(1′)	0.93(7)
C(6)–C(7)	1.522(9)	C(2′)–H(2′)	0.99(7)
C(7)–C(8)	1.564(10)	C(3′)–H(3′)	0.93(6)
C(7)–C(11)	1.517(9)	C(4′)–H(4′)	0.97(7)
C(8)–C(9)	1.509(10)	C(5′)–H(5′)	0.93(6)
C(9)–C(10)	1.538(9)	C(6′)–H(6′A)	0.96(11)
C(10)–C(15)	1.527(10)	C(6′)–H(6′B)	0.82(9)
C(11)–C(12)	1.476(13)	O(7)–H(07)	1.04(7)
C(11)–C(13)	1.331(12)	O(8)–H(O8)	0.80(5)
C(1′)–C(2′)	1.522(9)	O(9)–H(O9)	1.01(7)
C(2′)–C(3′)	1.513(8)	O(11)–H(O11A)	0.76(10)
C(3′)–C(4′)	1.523(9)	O(11)–H(O11B)	1.03(7)
C(4′)–C(5′)	1.518(10)		

TABLE 3

Valency angles (°), with estimated standard deviations in parentheses

C(8)–O(3)–C(12)	112.6(7)	C(1)–C(10)–C(9)	111.6(5)
C(2)–O(4)–C(1′)	115.1(5)	C(1)–C(10)–C(15)	112.5(6)
C(1′)–O(5)–C(5′)	113.2(5)	C(9)–C(10)–C(15)	111.3(6)
C(6′)–O(6)–C(22)	119.7(8)	C(7)–C(11)–C(12)	107.9(6)
C(2)–C(1)–C(5)	105.0(5)	C(7)–C(11)–C(13)	128.2(8)
C(2)–C(1)–C(10)	115.9(5)	C(12)–C(11)–C(13)	123.8(7)
C(5)–C(1)–C(10)	115.2(5)	C(11)–C(12)–O(2)	127.8(8)
C(1)–C(2)–C(3)	104.9(5)	O(2)–C(12)–O(3)	122.5(9)
C(1)–C(2)–O(4)	108.3(5)	C(11)–C(12)–O(3)	109.7(7)
C(3)–C(2)–O(4)	111.8(5)	C(2′)–C(1′)–O(4)	107.5(5)
C(2)–C(3)–C(4)	105.7(5)	C(2′)–C(1′)–O(5)	109.7(5)
C(3)–C(4)–C(5)	109.6(5)	O(4)–C(1′)–O(5)	107.8(5)
C(3)–C(4)–O(1)	125.2(6)	C(1′)–C(2′)–C(3′)	110.2(5)
C(5)–C(4)–O(1)	125.2(6)	C(1′)–C(2′)–O(9)	109.2(5)
C(1)–C(5)–C(4)	100.5(5)	C(3′)–C(2′)–O(9)	109.4(5)
C(1)–C(5)–C(6)	116.3(5)	C(2′)–C(3′)–C(4′)	110.8(5)
C(1)–C(5)–C(14)	112.1(5)	C(2′)–C(3′)–O(8)	107.7(5)
C(4)–C(5)–C(6)	113.7(5)	C(4′)–C(3′)–O(8)	111.6(5)
C(4)–C(5)–C(14)	104.1(5)	C(3′)–C(4′)–C(5′)	108.9(5)
C(6)–C(5)–C(14)	109.2(5)	C(3′)–C(4′)–O(7)	110.6(5)
C(5)–C(6)–C(7)	115.8(5)	C(5′)–C(4′)–O(7)	109.0(5)
C(6)–C(7)–C(8)	114.4(5)	C(4′)–C(5′)–C(6′)	112.2(6)
C(6)–C(7)–C(11)	110.7(5)	C(4′)–C(5′)–O(5)	109.6(5)
C(8)–C(7)–C(11)	101.6(6)	C(6′)–C(5′)–O(5)	107.3(6)
C(7)–C(8)–C(9)	117.5(6)	C(5′)–C(6′)–O(6)	107.8(6)
C(7)–C(8)–O(3)	104.7(5)	C(23)–C(22)–O(6)	114.3(10)
C(9)–C(8)–O(3)	106.1(6)	O(6)–C(22)–O(10)	121.4(9)
C(8)–C(9)–C(10)	115.9(6)	C(23)–C(22)–O(10)	124.2(9)

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[5] J. B. Hendrickson, *J. Amer. Chem. Soc.*, 1961, **83**, 4537.

penoid bromohelenalin (2),[6] on the other hand, has a cycloheptane ring which approximates to a twist-chair form and, indeed, cycloheptane rings in sesquiterpenoids generally adopt conformations resembling twist-chair forms.[7] Recent calculations suggest that the energy difference between the twist-chair and twist-boat forms of cycloheptane is probably small.[8]

TABLE 4

Torsion angles (°) *

C(12)–O(3)–C(8)–C(7)	12	C(1)–C(5)–C(6)–C(7)	−11
C(12)–O(3)–C(8)–C(9)	137	C(4)–C(5)–C(6)–C(7)	105
C(8)–O(3)–C(12)–O(2)	177	C(14)–C(5)–C(6)–C(7)	−139
C(8)–O(3)–C(12)–C(11)	−1	C(5)–C(6)–C(7)–C(8)	67
C(1′)–O(4)–C(2)–C(1)	−162	C(5)–C(6)–C(7)–C(11)	−179
C(1′)–O(4)–C(2)–C(3)	83	C(6)–C(7)–C(8)–O(3)	102
C(2)–O(4)–C(1′)–O(5)	−75	C(6)–C(7)–C(8)–C(9)	−15
C(2)–O(4)–C(1′)–C(2′)	167	C(11)–C(7)–C(8)–O(3)	−17
C(1′)–O(5)–C(5′)–C(4′)	63	C(11)–C(7)–C(8)–C(9)	−135
C(1′)–O(5)–C(5′)–C(6′)	−175	C(6)–C(7)–C(11)–C(12)	−105
C(5′)–O(5)–C(1′)–O(4)	−178	C(6)–C(7)–C(11)–C(13)	76
C(5′)–O(5)–C(1′)–C(2′)	−61	C(8)–C(7)–C(11)–C(12)	17
C(22)–O(6)–C(6′)–C(5′)	−150	C(8)–C(7)–C(11)–C(13)	−162
C(6′)–O(6)–C(22)–O(10)	−3	O(3)–C(8)–C(9)–C(10)	176
C(6′)–O(6)–C(22)–C(23)	175	C(7)–C(8)–C(9)–C(10)	−68
C(5)–C(1)–C(2)–O(4)	−150	C(8)–C(9)–C(10)–C(1)	47
C(5)–C(1)–C(2)–C(3)	−30	C(8)–C(9)–C(10)–C(15)	−80
C(10)–C(1)–C(2)–O(4)	82	C(7)–C(11)–C(12)–O(2)	171
C(10)–C(1)–C(2)–C(3)	−159	C(7)–C(11)–C(12)–O(3)	−11
C(2)–C(1)–C(5)–C(4)	38	C(13)–C(11)–C(12)–O(2)	−10
C(2)–C(1)–C(5)–C(6)	161	C(13)–C(11)–C(12)–O(3)	169
C(2)–C(1)–C(5)–C(14)	−72	O(4)–C(1′)–C(2′)–O(9)	−68
C(10)–C(1)–C(5)–C(4)	166	O(5)–C(1′)–C(2′)–O(9)	175
C(10)–C(1)–C(5)–C(6)	−70	O(4)–C(1′)–C(2′)–C(3′)	172
C(10)–C(1)–C(5)–C(14)	56	O(5)–C(1′)–C(2′)–C(3′)	55
C(2)–C(1)–C(10)–C(9)	168	O(9)–C(2′)–C(3′)–O(8)	64
C(2)–C(1)–C(10)–C(15)	−66	C(1′)–C(2′)–C(3′)–O(8)	−176
C(5)–C(1)–C(10)–C(9)	45	O(9)–C(2′)–C(3′)–C(4′)	−173
C(5)–C(1)–C(10)–C(15)	171	C(1′)–C(2′)–C(3′)–C(4′)	−53
O(4)–C(2)–C(3)–C(4)	128	O(8)–C(3′)–C(4′)–O(7)	−65
C(1)–C(2)–C(3)–C(4)	11	C(2′)–C(3′)–C(4′)–O(7)	175
C(2)–C(3)–C(4)–O(1)	−164	O(8)–C(3′)–C(4′)–C(5′)	175
C(2)–C(3)–C(4)–C(5)	14	C(2′)–C(3′)–C(4′)–C(5′)	55
O(1)–C(4)–C(5)–C(1)	146	O(7)–C(4′)–C(5′)–O(5)	−179
O(1)–C(4)–C(5)–C(6)	21	C(3′)–C(4′)–C(5′)–O(5)	−58
O(1)–C(4)–C(5)–C(14)	−98	O(7)–C(4′)–C(5′)–C(6′)	62
C(3)–C(4)–C(5)–C(1)	−32	C(3′)–C(4′)–C(5′)–C(6′)	−178
C(3)–C(4)–C(5)–C(6)	−157	O(5)–C(5′)–C(6′)–O(6)	73
C(3)–C(4)–C(5)–C(14)	84	C(4′)–C(5′)–C(6′)–O(6)	−166

* The mean standard deviation of the torsion angles is 0.8°. An angle is positive when a clockwise rotation is required of atom (1) to eclipse atom (4) whilst looking down the (2)–(3) bond.

The valency angles in the cycloheptane ring of paucin are in the range 111.6—117.5°, mean 115.2°. Similar mean values characterize the cycloheptane rings in other sesquiterpenoids, *e.g.* 115.6 in bromohelenalin,[6] 115.1 in euparotin bromoacetate,[7] 115.4 in bromodihydroisophotosantonic lactone acetate,[9] and 115.9° in bromogeigerin [10] and bromomexicanin-E.[11]

The α-methylene γ-lactone ring has an envelope (C_s) conformation, with C(7) constituting the flap. Because of the *cis*-ring-junction, the cycloheptane torsion angle C(6)–C(7)–C(8)–C(9) (−15°) and the lactone torsion angle C(11)–C(7)–C(8)–O(5) (−17°) have nearly identical values. Both have the same sign as the C=C–C=O torsion angle (−10°) and these results may be pertinent to the negative $n \rightarrow \pi^*$ Cotton effect of the α-methylene γ-lactone chromophore.[7,12] The cyclopentanone ring displays a half-chair (C_2) conformation, in which the local-symmetry axis passes through C(10) and the mid-point of C(6)–C(7).

The magnitudes of the torsion angles in the glucose ring of paucin range from 53 to 63°, mean 58°, the smallest angle being associated with the C(2′)–C(3′) bond and the largest with C(5′)–O(5). The same pattern is found in α-D-glucose monohydrate,[13] where the torsion angles about these bonds are −50 and 61°. The largest valency angle in the glucose ring is at O(5) in both paucin (113.2°) and α-D-glucose monohydrate (113.1°). The valency angle of the bridging oxygen atom O(4) in paucin is 115.1°. The relative orientation of the glucose and sesquiterpenoid moieties in paucin is defined by the torsion angles C(2)–O(4)–C(1′)–C(2′) (167°) and C(1)–C(2)–O(4)–C(1′) (−162°).

The water molecule participates in three hydrogen bonds, O(11)H$^{\rm III}\cdots$O(10) 2.95, O(11)H$^{\rm IX}\cdots$O(2) 2.92, and O(11)$\cdots$HO(9) 2.72 Å. The other hydrogen bonds in the crystal structure are O(7)H$\cdots$O(8$^{\rm V}$) 2.82 and O(8)H$\cdots$O(9$^{\rm V}$) 2.79 Å. The shorter intermolecular separations in the crystal are listed in Table 5.

TABLE 5

Intermolecular separations (<3.65 Å)

O(9) $\cdots$ O(11)	2.72	O(8) $\cdots$ O(8$^{\rm V}$)	3.47
O(8) $\cdots$ C(23$^{\rm I}$)	3.47	O(8) $\cdots$ C(3′$^{\rm V}$)	3.47
O(11) $\cdots$ C(23$^{\rm I}$)	3.62	O(7) $\cdots$ O(10$^{\rm VI}$)	3.49
O(1) $\cdots$ C(9$^{\rm II}$)	3.55	O(8) $\cdots$ C(4′$^{\rm VII}$)	3.34
O(10) $\cdots$ C(2$^{\rm II}$)	3.48	O(1) $\cdots$ C(6$^{\rm VIII}$)	3.15
O(10) $\cdots$ C(14$^{\rm II}$)	3.51	O(1) $\cdots$ C(11$^{\rm VIII}$)	3.55
O(10) $\cdots$ O(11$^{\rm III}$)	2.95	O(1) $\cdots$ C(13$^{\rm VIII}$)	3.63
O(11) $\cdots$ C(22$^{\rm IV}$)	3.64	O(2) $\cdots$ O(11$^{\rm IX}$)	2.92
O(11) $\cdots$ C(23$^{\rm IV}$)	3.62	O(2) $\cdots$ C(15$^{\rm IX}$)	3.61
O(7) $\cdots$ O(8$^{\rm V}$)	2.82	O(3) $\cdots$ C(17$^{\rm IX}$)	3.38
O(7) $\cdots$ O(9$^{\rm V}$)	3.16	O(3) $\cdots$ C(8$^{\rm IX}$)	3.50
O(8) $\cdots$ O(9$^{\rm V}$)	2.79	O(3) $\cdots$ C(11$^{\rm IX}$)	3.55

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

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

EXPERIMENTAL

Crystal Data.—$C_{23}H_{32}O_{10},H_2O$, $M = 486.52$. Monoclinic, $a = 18.308(4)$, $b = 6.724(2)$, $c = 9.987(4)$ Å, $\beta = 93.38(4)°$, $U = 1\,227$ Å^3, $D_c = 1.31$ g cm^{-3}, $Z = 2$, $F(000) = 520$. Space group $P2_1$ (C_2^2). Mo-K_α radiation, $\lambda = 0.710\,7$ Å; μ(Mo-K_α) = 1.13 cm^{-1}.

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[6] Mazher-ul-Haque and C. N. Caughlan, *J. Chem. Soc.* (*B*), 1969, 956.

[7] A. T. McPhail and G. A. Sim, *Tetrahedron*, 1973, **29**, 1751.

[8] D. F. Bocian, H. M. Pickett, T. C. Rounds, and H. L. Strauss, *J. Amer. Chem. Soc.*, 1975, **97**, 687.

[9] J. D. M. Asher and G. A. Sim, *J. Chem. Soc.*, 1965, 1584.

[10] J. A. Hamilton, A. T. McPhail, and G. A. Sim, *J. Chem. Soc.*, 1962, 708.

[11] Mazhar-ul-Haque and C. N. Caughlan, *J. Chem. Soc.* (*B*), 1967, 355.

[12] W. Stöcklin, T. G. Waddell, and T. A. Geissman, *Tetrahedron*, 1970, **26**, 2397; A. F. Beecham, *ibid.*, 1972, **28**, 5543

[13] E. Hough, S. Neidle, D. Rogers, and P. G. H. Troughton, *Acta Cryst.*, 1973, **B29**, 365.

Crystallographic Measurements.—Final values of the cell dimensions were obtained by least-squares analysis of the θ, ϕ, and χ angles of twelve reflections, measured with Mo-K_α radiation, at θ *ca*. 16°, on a Hilger and Watts four-circle diffractometer controlled by a PDP 8 computer. For the intensity measurements the reflections with indices hkl and $\bar{h}kl$ were surveyed in the range $\theta \leqslant 28°$ by θ—ω scans consisting of 35 0.02° steps of 2 s, with background counts at each end of the scan range. Of 3 196 independent intensities accumulated, 1 929 had $I > 3\sigma(I)$. No absorption correction was applied.

Structure Analysis.—The crystal structure was elucidated by direct phase-determining procedures based on the '*X*-Ray '72' series of programs.[14] Σ_2 relationships were generated for 319 reflections with $|E| \geqslant 1.60$. Three reflections were assigned phases of 0° to define the origin, another reflection was initially set at 90° to define the enantiomorph, and three further reflections were given initial phases of $\pm 90°$ (see Supplementary Publication). The eight starting sets generated phases characterized by R_K 0.21 and 0.24—0.32, and an E map derived from the phases with the lowest value R_K yielded positions for all but one of the carbon and oxygen atoms. A structure-factor calculation gave R 27.7% and a difference-Fourier synthesis yielded the position of the remaining carbon atom.

Least-squares adjustment of the positional and anisotropic thermal parameters of the carbon and oxygen atoms converged at R 11.4%, at which stage examination of the difference electron-density distribution revealed the majority of the sites of the hydrogen atoms. The hydrogen atoms were included in the structure analysis with isotropic vibration parameters and the subsequent calculations converged at R 7.9%, R' 9.4%. A final difference-Fourier synthesis failed to reveal the C(23)-methyl hydrogen atoms.

The weighting function used in the calculations was of the form $w = AB$, where $A = 1$ if $\sin\theta > 0.306$, $A = \sin\theta/0.306$ if $\sin\theta \leqslant 0.306$, and $B = 1$ if $|F_0| < 10$, $B = 10/|F_0|$ if $|F_0| > 10$. Observed and calculated structure factors, thermal parameters, and the eight starting sets are listed in Supplementary Publication No. SUP 21841 (19 pp., 1 microfiche).*

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* See Notice to Authors No. 7, in *J.C.S. Perkin II*, 1976, Index issue.

[14] '*X*-Ray' Program System, University of Maryland Report TR 192, version of June 1972.