Structure and Absolute Configuration of Florilenalin: *X*-Ray Analysis of 4-*O*-Acetyl-2-*O*-*p*-iodobenzoylflorilenalin

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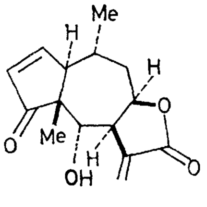
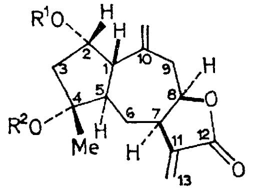
X-Ray single-crystal analysis has established the structure and absolute configuration of (IV), the 4-*O*-acetyl-2-*O*-*p*-iodobenzoyl derivative of florilenalin (II), a cytotoxic guaianolide from *Helenium autumnale* L. Crystals are orthorhombic, space group $P2_12_12_1$ with a = 14·40(2), b = 22·62(3), c = 7·37(1) Å, Z = 4. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations to R 0·086 over 1109 reflections from photographic data. The absolute configuration was established by the anomalous dispersion effect. The cycloheptane ring adopts a chair conformation, the cyclopentane ring is in an envelope form, and the γ-lactone ring is approximately planar.

FLORILENALIN, $C_{15}H_{20}O_4$, a cytotoxic sesquiterpene lactone, was isolated as an oil from Florida *Helenium autumnale* L. by Lee *et al.* during their searches for a convenient source of helenalin (I) for antitumour or cytotoxicity studies. Extensive chemical and spectroscopic investigations led to the assignment of structure (II) with the stereochemistry at C(4) and the *trans* A/B ring-junction being deduced from biogenetic considerations based on the co-occurrence of (I) and (II). We undertook *X*-ray diffraction studies of derivatives of (II) in order to confirm the structure and to define the absolute stereochemistry.[1] Preliminary investigations of florilenalin diacetate (III) showed that the crystals formed as unsuitable very thin plates. The preparation of the 4-*O*-acetyl-2-*O*-*p*-iodobenzyl derivative (IV) provided crystals satisfactory for a diffraction study.



(I)



(II) $R^1 = R^2 = H$
(III) $R^1 = R^2 = Ac$
(IV) $R^1 = p\text{-}IC_6H_4{\cdot}CO$, $R^2 = Ac$

EXPERIMENTAL

Crystal Data.—$C_{24}H_{25}O_6I$, M = 536·4. Orthorhombic, a = 14·40(2), b = 22·62(3), c = 7·37(1) Å, U = 2401 Å^3, D_m = 1·47 (by flotation), Z = 4, D_c = 1·485, $F(000)$ = 1080. Cu-K_α radiation (λ = 1·542 Å), μ = 110 cm^{-1}. Space group $P2_12_12_1$ (D_2^4) from systematic absences: $h00$ when $h \neq 2n$, $0k0$ when $k \neq 2n$, $00l$ when $l \neq 2n$.

Crystallographic Measurements.—Unit-cell dimensions were evaluated from precession photographs taken with Mo-K_α (λ = 0·7107 Å) radiation. Intensity data were recorded by equi-inclination multiple-film Weissenberg photographs (Cu-K_α radiation) of the $hk0$—5 reciprocal lattice levels. The limited data obtained (maximum sinθ 0·89) were estimated visually by comparison with a calibrated intensity scale. Spot-shape and the usual Lorentz and polarization corrections were applied, and 1109 independent observed structure amplitudes were obtained; no correction was made for absorption. Initially, the various layers of data were assumed to be on a common scale; absolute scales were obtained later in the analysis by correlation of $\Sigma|F_o|$ with $\Sigma|F_c|$.

Structure Analysis.—The structure was solved without difficulty by the heavy-atom method. Initial co-ordinates for the iodine atom were derived from the three-dimensional Patterson synthesis and the other non-hydrogen atoms were located in an iodine-phased (R 0·335) three-dimensional electron-density distribution. This model was refined by several cycles of full-matrix least-squares adjustment of the positional and isotropic thermal parameters. Anomalous scattering corrections for the iodine atom were then introduced into the structure-factor calculations in order to establish the absolute stereochemistry. With co-ordinates corresponding to the stereochemistry represented by (IV), R was 0·133 whereas the mirror image gave R

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[1] Preliminary communication, K. H. Lee, T. Ibuka, M. Kozuka, A. T. McPhail, and K. D. Onan, *Tetrahedron Letters*, 1974, 2287.

0·149. This difference is highly significant [2] and indicates that (IV) correctly represents the absolute stereochemistry.

A difference electron-density distribution was evaluated and significant positive regions found at positions calculated for the hydrogen atoms except those on C(14) and C(17) which could not be placed unambiguously. Contributions for the nineteen confirmed hydrogen atoms with fixed positions and B 4·0 Å^2 were included in further least-squares iterations during which the iodine atom was allowed to assume an anisotropic temperature factor. The refinement converged to R 0·086. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21234 (10 pp., 1 microfiche).*

TABLE 1

(*a*) Fractional atomic co-ordinates ($\times 10^4$) and temperature factors, with estimated standard deviations in parentheses

Atom	x	y	z	B/Å^2
C(1)	4547(15)	6337(9)	−2030(31)	3·9(4)
C(2)	5233(16)	6843(11)	−2132(35)	4·6(5)
C(3)	5721(16)	6678(10)	−3896(35)	4·9(5)
C(4)	5722(14)	5993(8)	−4108(30)	3·4(4)
C(5)	5135(12)	5792(7)	−2333(28)	2·4(4)
C(6)	4534(14)	5229(9)	−2668(30)	3·5(4)
C(7)	4257(14)	4920(8)	−924(30)	3·7(4)
C(8)	3557(14)	5272(9)	320(31)	3·5(5)
C(9)	3203(16)	5824(10)	−279(35)	4·4(5)
C(10)	3919(13)	6320(8)	−382(29)	2·9(4)
C(11)	3760(14)	4342(9)	−1317(35)	3·7(4)
C(12)	2878(16)	4350(9)	−316(34)	4·2(5)
C(13)	4017(16)	3895(10)	−2311(35)	4·3(6)
C(14)	5413(18)	5795(11)	−5955(39)	5·9(6)
C(15)	3904(18)	6731(10)	887(39)	5·4(6)
C(16)	6971(17)	5280(10)	−3646(37)	5·2(5)
C(17)	8044(20)	5272(12)	−3474(40)	6·3(7)
C(18)	6173(16)	7294(10)	274(36)	4·8(5)
C(19)	6910(14)	7185(9)	1505(33)	3·9(4)
C(20)	7399(15)	6659(10)	1556(36)	4·5(6)
C(21)	8083(18)	6556(11)	2657(37)	5·0(6)
C(22)	8294(16)	7010(10)	4106(37)	5·0(5)
C(23)	7798(16)	7543(10)	3970(36)	4·8(5)
C(24)	7170(17)	7612(11)	2693(36)	4·9(5)
O(25)	2755(11)	4874(7)	498(22)	5·0(4)
O(26)	2284(11)	3980(7)	−351(24)	5·4(4)
O(27)	6706(10)	5837(6)	−3810(23)	4·4(3)
O(28)	6527(12)	4864(8)	−3579(26)	6·4(4)
O(29)	5925(9)	6793(6)	−705(20)	3·9(3)
O(30)	5803(14)	7775(9)	−37(32)	7·9(5)
I	9297(1)	6869(1)	6094(3)	*

(*b*) Calculated hydrogen atom fractional co-ordinates, labelled according to the carbon atom to which they are bonded

Atom	x	y	z	Atom	x	y	z
H(1)	407	636	−310	H(9β)	296	575	−166
H(2)	490	725	−218	H(13α)	468	389	−299
H(3α)	641	683	−392	H(13β)	368	350	−252
H(3β)	538	688	−506	H(15α)	349	673	208
H(5)	558	571	−123	H(15β)	442	707	91
H(6α)	489	494	−351	H(20)	720	633	64
H(6β)	390	536	−333	H(21)	850	613	279
H(7)	490	484	−28	H(23)	798	788	495
H(8)	389	534	165	H(24)	678	803	272
H(9α)	264	596	49				

* For the iodine atom an anisotropic temperature factor of the form $B \sin^2\theta/\lambda^2 = b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl$ was employed with parameters ($\times 10^5$):

b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
848(9)	281(3)	3566(46)	−125(12)	−1167(44)	−549(26)

TABLE 2

Interatomic distances (Å) and angles (deg.) with estimated standard deviations in parentheses

(*a*) Bond lengths

C(1)–C(2)	1·52(3)	C(11)–C(12)	1·47(3)
C(1)–C(5)	1·51(3)	C(11)–C(13)	1·30(3)
C(1)–C(10)	1·51(3)	C(12)–O(25)	1·34(3)
C(2)–C(3)	1·52(4)	C(12)–O(26)	1·20(3)
C(2)–O(29)	1·45(3)	C(16)–C(17)	1·55(4)
C(3)–C(4)	1·56(3)	C(16)–O(27)	1·32(3)
C(4)–C(5)	1·62(3)	C(16)–O(28)	1·14(3)
C(4)–C(14)	1·50(4)	C(18)–C(19)	1·42(3)
C(4)–O(27)	1·48(2)	C(18)–O(29)	1·39(3)
C(5)–C(6)	1·56(3)	C(18)–O(30)	1·23(3)
C(6)–C(7)	1·52(3)	C(19)–C(20)	1·38(3)
C(7)–C(8)	1·58(3)	C(19)–C(24)	1·36(3)
C(7)–C(11)	1·52(3)	C(20)–C(21)	1·30(4)
C(8)–C(9)	1·42(3)	C(21)–C(22)	1·51(4)
C(8)–O(25)	1·47(3)	C(22)–C(23)	1·41(3)
C(9)–C(10)	1·52(3)	C(22)–I	2·08(3)
C(10)–C(15)	1·32(3)	C(23)–C(24)	1·31(4)

(*b*) Valency angles

C(2)–C(1)–C(5)	104(2)	C(9)–C(10)–C(15)	118(2)
C(2)–C(1)–C(10)	117(2)	C(7)–C(11)–C(12)	107(2)
C(5)–C(1)–C(10)	115(2)	C(7)–C(11)–C(13)	130(2)
C(1)–C(2)–C(3)	99(2)	C(12)–C(11)–C(13)	123(2)
C(3)–C(2)–O(29)	106(2)	C(11)–C(12)–O(26)	127(2)
C(2)–C(3)–C(4)	109(2)	O(25)–C(12)–O(26)	122(2)
C(3)–C(4)–C(5)	101(2)	C(17)–C(16)–O(27)	108(2)
C(3)–C(4)–C(14)	113(2)	C(17)–C(16)–O(28)	123(2)
C(3)–C(4)–O(27)	103(2)	O(27)–C(16)–O(28)	129(2)
C(5)–C(4)–C(14)	120(2)	C(19)–C(18)–O(29)	112(2)
C(5)–C(4)–O(27)	108(2)	C(19)–C(18)–O(30)	127(2)
C(14)–C(4)–O(27)	110(2)	O(29)–C(18)–O(30)	121(2)
C(1)–C(5)–C(4)	101(2)	C(18)–C(19)–C(20)	123(2)
C(1)–C(5)–C(6)	112(2)	C(18)–C(19)–C(24)	120(2)
C(4)–C(5)–C(6)	113(2)	C(20)–C(19)–C(24)	117(2)
C(5)–C(6)–C(7)	113(2)	C(19)–C(20)–C(21)	124(2)
C(6)–C(7)–C(8)	115(2)	C(20)–C(21)–C(22)	118(2)
C(6)–C(7)–C(11)	111(2)	C(21)–C(22)–C(23)	115(2)
C(8)–C(7)–C(11)	104(2)	C(21)–C(22)–I	122(2)
C(7)–C(8)–C(9)	120(2)	C(23)–C(22)–I	122(2)
C(7)–C(8)–O(25)	104(2)	C(22)–C(23)–C(24)	120(2)
C(9)–C(8)–O(25)	107(2)	C(19)–C(24)–C(23)	125(2)
C(8)–C(9)–C(10)	115(2)	C(18)–O(25)–C(12)	113(2)
C(1)–C(10)–C(9)	118(2)	C(4)–O(27)–C(16)	121(2)
C(1)–C(10)–C(15)	124(2)	C(2)–O(29)–C(18)	119(2)

(*c*) Intermolecular distances $<3{\cdot}7$ Å

O(30) ··· C(13$^{\mathrm{III}}$)	3·21	C(21) ··· O(27$^{\mathrm{V}}$)	3·65
C(21) ··· O(28$^{\mathrm{II}}$)	3·39	O(25) ··· C(11$^{\mathrm{I}}$)	3·66
C(23) ··· O(26$^{\mathrm{IV}}$)	3·41	O(25) ··· C(12$^{\mathrm{I}}$)	3·67
C(26) ··· C(6$^{\mathrm{I}}$)	3·57	O(26) ···· C(1$^{\mathrm{I}}$)	3·67
C(15) ··· O(26$^{\mathrm{I}}$)	3·63	C(17) ··· O(28$^{\mathrm{II}}$)	3·67

Roman numeral superscripts refer to the following transformations of the co-ordinates of Table 1:

I $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$
II $\frac{3}{2} - x, 1 - y, \frac{1}{2} + z$
III $1 - x, \frac{1}{2} + y, -\frac{1}{2} - z$
IV $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
V $x, y, 1 + z$

Atomic scattering factors used in all the structure-factor calculations were those for iodine, carbon, and oxygen from ref. 3 with that of iodine corrected for anomalous scattering [4] of Cu-K_α radiation. For hydrogen, the

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue.

[2] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

[3] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[4] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

scattering factor of ref. 5 was used. The weighting scheme used in the least-squares calculations [$\sqrt{w} = 1$ for $|F_o| \leqslant 30{\cdot}1$ and $\sqrt{w} = 30{\cdot}1/|F_o|$ for $|F_o| > 30{\cdot}1$] showed no systematic dependence on $\langle w\Delta^2\rangle$ when analysed in ranges of $|F_o|$. Final atomic co-ordinates and temperature factors appear in Table 1; interatomic distances and valency angles in Table 2, and torsion angles in Table 3. Displacements of selected atoms from various mean planes are in Table 4.

TABLE 3

Torsion angles (deg.) *

C(5)–C(1)–C(2)–C(3)	49	C(1)–C(5)–C(6)–C(7)	−87
C(5)–C(1)–C(2)–O(29)	−62	C(4)–C(5)–C(6)–C(7)	160
C(10)–C(1)–C(2)–C(3)	178	C(5)–C(6)–C(7)–C(8)	68
C(10)–C(1)–C(2)–O(29)	67	C(5)–C(6)–C(7)–C(11)	−174
C(2)–C(1)–C(5)–C(4)	−48	C(6)–C(7)–C(8)–C(9)	3
C(2)–C(1)–C(5)–C(6)	−168	C(6)–C(7)–C(8)–O(25)	122
C(10)–C(1)–C(5)–C(4)	−178	C(11)–C(7)–C(8)–C(9)	−119
C(10)–C(1)–C(5)–C(6)	62	C(11)–C(7)–C(8)–O(25)	0
C(2)–C(1)–C(10)–C(9)	178	C(6)–C(7)–C(11)–C(12)	−127
C(5)–C(1)–C(10)–C(9)	−59	C(6)–C(7)–C(11)–C(13)	54
C(2)–C(1)–C(10)–C(15)	4	C(8)–C(7)–C(11)–C(12)	−3
C(5)–C(1)–C(10)–C(15)	127	C(8)–C(7)–C(11)–C(13)	178
C(1)–C(2)–C(3)–C(4)	−31	C(7)–C(8)–C(9)–C(10)	−68
O(29)–C(2)–C(3)–C(4)	84	O(25)–C(8)–C(9)–C(10)	175
C(1)–C(2)–O(29)–C(18)	−136	C(7)–C(8)–O(25)–C(12)	3
C(3)–C(2)–O(29)–C(18)	117	C(9)–C(8)–O(25)–C(12)	131
C(2)–C(3)–C(4)–C(5)	3	C(8)–C(9)–C(10)–C(1)	80
C(2)–C(3)–C(4)–C(14)	132	C(8)–C(9)–C(10)–C(15)	−105
C(2)–C(3)–C(4)–O(27)	−109	C(7)–C(11)–C(12)–O(25)	5
C(3)–C(4)–C(5)–C(1)	27	C(7)–C(11)–C(12)–O(26)	177
C(3)–C(4)–C(5)–C(6)	146	C(13)–C(11)–C(12)–O(25)	−176
C(14)–C(4)–C(5)–C(1)	−98	C(13)–C(11)–C(12)–O(26)	−4
C(14)–C(4)–C(5)–C(6)	22	C(11)–C(12)–O(25)–C(8)	−5
O(27)–C(4)–C(5)–C(1)	134	O(26)–C(12)–O(25)–C(8)	−178
O(27)–C(4)–C(5)–C(6)	−106	C(17)–C(16)–O(27)–C(4)	176
C(3)–C(4)–O(27)–C(16)	171	O(28)–C(16)–O(27)–C(4)	−6
C(5)–C(4)–O(27)–C(16)	64	C(19)–C(18)–O(29)–C(2)	−175
C(14)–C(4)–O(27)–C(16)	−68	O(30)–C(18)–O(29)–C(2)	1

* For sign convention see W. Klyne and V. Prelog, *Experientia*, 1960, **16**, 521.

TABLE 4

Displacements (Å) of atoms from mean planes through various groups of atoms; atoms not included in the derivation of the plane are italicized

Plane (*a*)	C(2) −0·01, C(3) 0·02, C(4) −0·02, C(5) 0·01, *C(1) 0·71*
Plane (*b*)	C(7) −0·01, C(7) 0·00, C(11) 0·00, C(12) −0·04, C(13) 0·02, O(25) 0·03, O(26) 0·01
Plane (*c*)	C(4) 0·02, C(16) 0·00, C(17) 0·02, O(27) −0·03, O(28) −0·01
Plane (*d*)	C(2) 0·03, C(18) −0·03, C(19) 0·03, O(29) −0·03, O(30) 0·00
Plane (*e*)	C(19) −0·03, C(20) −0·02, C(21) 0·05, C(22) −0·04, C(23) 0·00, C(24) −0·04, *C(18) −0·08, I −0·10*

RESULTS AND DISCUSSION

The *X*-ray analysis establishes unequivocally that (IV) represents the structure and absolute stereochemistry of 4-*O*-acetyl-2-*O*-*p*-iodobenzoylflorilenalin from which it follows that florilenalin is correctly represented by (II). The conformation of (IV) in the crystal and the atom numbering scheme are shown in Figure 1. Thus, florilenalin is a guaianolide with a *trans* A/B ring-fusion and a *cis*-fused γ-lactone.

The twist chair (C_2) form of cycloheptane is more stable than the chair (C_s) form by *ca.* 2 kcal mol^{-1}, and *cis,trans*-fusion of 5-membered rings is restricted to certain positions in each of these conformations.[6] In (IV), the relative positions of the ring fusions are compatible with those allowed for either the twist-chair form in which C(7) is the axis carbon or the chair form with the mirror plane passing through C(1). The torsion angles for (IV) ($\omega_{1,5}$ 62, $\omega_{5,6}$ −87, $\omega_{6,7}$ 68, $\omega_{7,8}$ 3, $\omega_{8,9}$ −68, $\omega_{9,10}$ 80, and $\omega_{10,1}$ −59°) clearly demonstrate that the B ring approximates a chair conformation in which the values are close to those derived by Hendrickson[7] (64, −84, 66, 0, −66, 84, and −64°). That the chair form is favoured over the twist-chair form here may be ascribed to the presence of a centre of unsaturation at C(10) one consequence of which is removal of two unfavourable diaxial H···H transannular interactions involving the C(5) and C(8) α-hydrogen atoms. The mean endocyclic valency angle in the cycloheptane ring (115°) lies in the normal range, *e.g.*

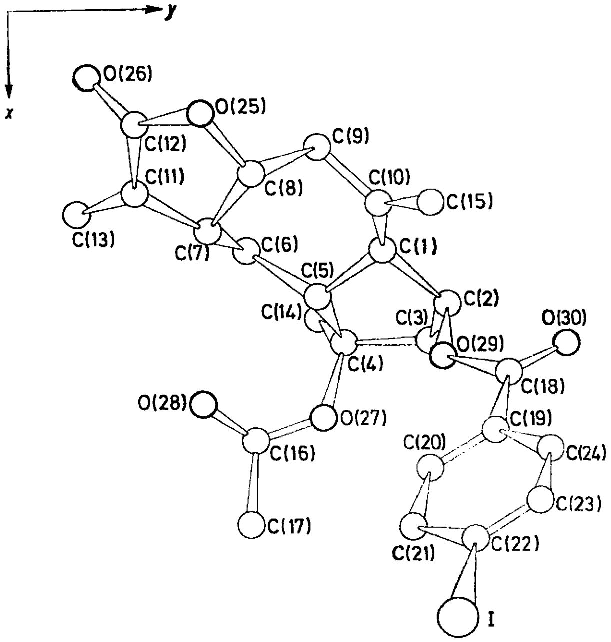

FIGURE 1 Molecular conformation and atom numbering scheme

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[5] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[6] J. B. Hendrickson, *Tetrahedron*, 1963, **19**, 1387.

[7] J. B. Hendrickson, *J. Amer. Chem. Soc.*, 1967, **89**, 7036.

116° in bromogeigerin,[8] bromohelenalin,[9] and bromomexicanin E,[10] 114° in bromoisotenulin.[11]

In the γ-lactone ring the mean internal valency angle is 108° and accordingly the ring is planar. This contrasts with the more frequently encountered approximate half-chair conformations of the *cis*-fused α-methylene lactone rings in some other sesquiterpenes where the carbon atoms C(7) and C(8) are displaced significantly to opposite sides of the mean plane through the C–CO–O atoms, *e.g.* 0·45 and 0·17 Å (calculated from co-ordinates of ref. 10) in bromohelenalin, 0·20 and 0·26 Å (calculated from co-ordinates of ref. 11) in bromomexicanin E, 0·12 and 0·24 Å in an oxide from helenalin.[12,13]

The cyclopentane ring adopts an envelope conformation with C(1) 0·71 Å from the mean plane through the other four ring atoms. The mean endocyclic valency angle (103°) is slightly smaller than in the corresponding ring of deacetyldihydrogaillardin *p*-bromobenzoate[14] (104·5°), where a similar *trans* A/B junction is present but C(2), the out-of-plane atom, is displaced to a smaller extent, 0·61 Å. The greater degree of puckering found in (IV) is required to increase the C(15) $\cdots$ O(29) distance from *ca.* 2·5 Å as measured on a Dreiding molecular model to a more acceptable value of 3·14 Å.

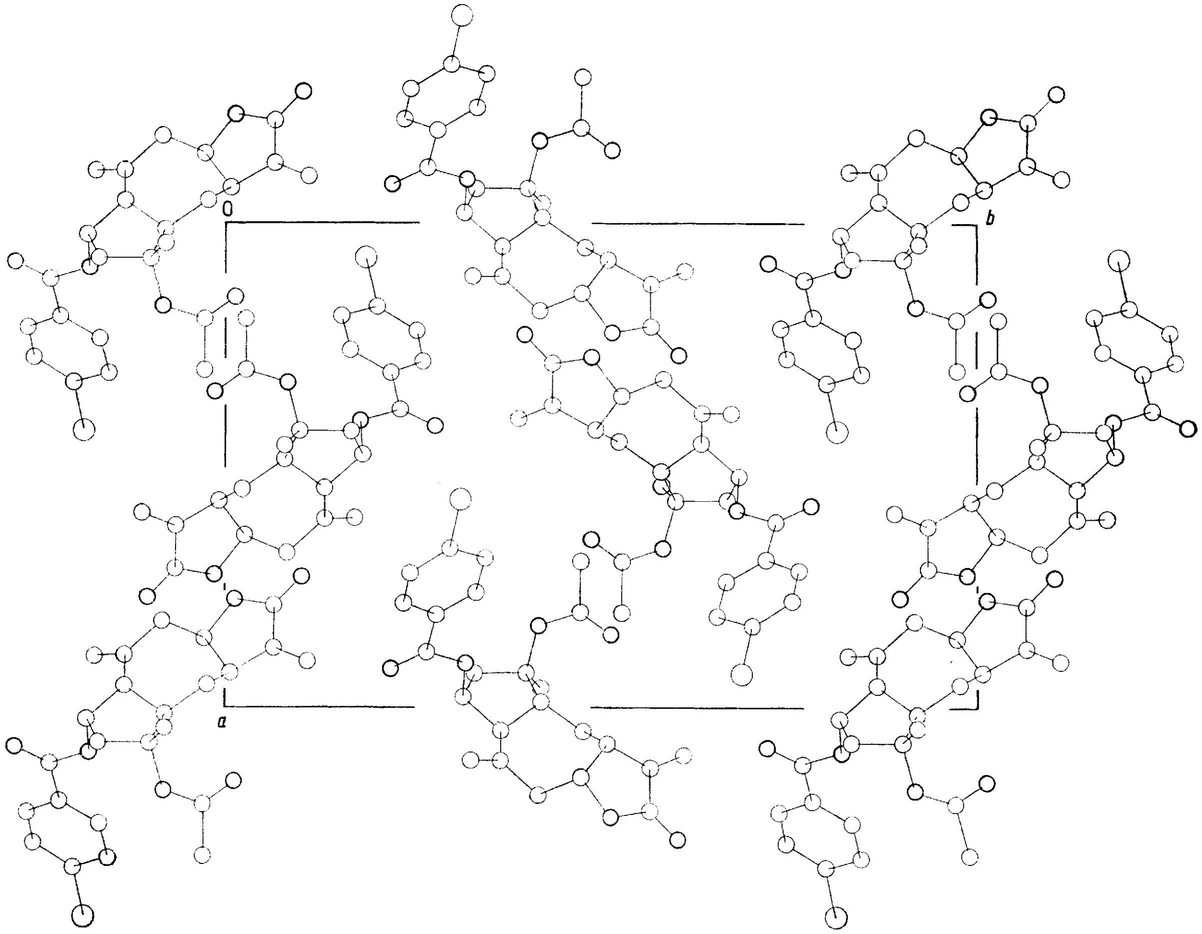

FIGURE 2 The crystal structure, viewed in projection along the *c* axis

The C–CO–O–C atoms of both ester groups are planar, as expected. At the acetate group the nearly equal magnitude of the C(5)–C(4)–O(27)–C(16) and C(14)–C(4)–O(27)–C(16) torsion angles (64 and −68°), indicates that the acetate C=O group approximately bisects the C(5)–C(4)–C(14) angle. At the *p*-iodobenzoate the C(3)–C(2)–O(29)–C(18) and C(1)–C(2)–O(29)–C(18) torsion angles (117 and −136°) indicate that the C=O bond lies close to *syn*-planar with the C(2)–H(2) bond as is

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

[9] Mazhar-Ul-Haque and C. N. Caughlan, *J. Chem. Soc.* (*B*), 1969, 956.

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

[11] Mazhar-Ul-Haque, D. Rogers, and C. N. Caughlan, *J.C.S. Perkin II*, 1974, 223.

[12] A. T. McPhail, K. D. Onan, K. H. Lee, H. Furukawa, S. H. Kim, and C. Piantadosi, *Tetrahedron Letters*, 1973, 46.

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customary in secondary esters,[15] the small rotation (*ca.* 9°) being in direction away from C(15). The *p*-iodobenzoate ester is not completely planar; the dihedral angle between the plane of C(18)—(24), I and the C(2), C(18), C(19), O(29), O(30) plane is 10°, and the iodine and C(18) atoms are displaced by small amounts to the same side of the C(19)—(24) plane. We ascribe these small effects to crystal-packing forces.

The mean lengths of chemically equivalent bonds are satisfactorily close to accepted values:[16] C(sp^3)–C(sp^3) 1·53, C(sp^3)–C(sp^2) 1·53, C(sp^2)–C(sp^2) 1·45, C(sp^2)=C(sp^2) 1·31, C(ar)–C(ar) 1·38, C(sp^3)–O 1·47, C(sp^2)–O 1·35, C=O 1·19, and C(ar)–I 2·08 Å.

The arrangement of molecules in the crystal as viewed along the *c* axis is illustrated in Figure 2. The shorter intermolecular separations listed in Table 2 all involve oxygen atoms and none is abnormal.

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