Crystal and Molecular Structure of Eupaformonin, a Cytotoxic Germacranolide from *Eupatorium formosanum* HAY

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Single-crystal X-ray analysis has established the structure and relative stereochemistry of the title compound (I). The absolute configuration follows from the sign of the Cotton effect of the $n\rightarrow\pi^*$ transition of the α-methylene γ-lactone C=C–C=O chromophore. Crystals are orthorhombic, space group $P2_12_12_1$, $a = 14.28(2)$, $b = 11.52(2)$, $c = 9.68(2)$ Å, $Z = 4$. The structure was solved by direct phase-determining methods and atomic parameters refined by full-matrix least-squares calculations to R 0.093 over 1 437 reflections from photographic data. The $\Delta^{1(10)}$*trans*, Δ^4 *cis*-cyclodecadiene ring is in a chair, boat conformation with the C(4) and C(10) methyl groups oriented *anti*. The anomalous relationship between the sign of the measured Cotton effect of the C=C–C=O chromophore $n\rightarrow\pi^*$ transition for $\Delta^{1(10)}$*trans*, Δ^4 *cis* germacranolide C(6),C(7)-*trans*-fused α-methylene γ-lactones and the position and stereochemistry of the lactone ring fusion is discussed with respect to the preferred cyclodecadiene ring conformation.

EUPAFORMONIN, $C_{17}H_{22}O_5$, a crystalline cytotoxic sesquiterpene lactone was isolated recently from *Eupatorium formosanum* HAY by Lee and co-workers during their searches among Formosan plant sources for potential antitumour or cytotoxic agents.[1] Partial structural information for this new germacranolide having been deduced from spectral data, it was subjected to single-crystal X-ray analysis to define the complete molecular structure and stereochemistry.

EXPERIMENTAL

Crystal Data.—$C_{17}H_{22}O_5$, $M = 306.4$. Orthorhombic, $a = 14.28(2)$, $b = 11.52(2)$, $c = 9.68(2)$ Å, $U = 1\ 598$ Å³, D_m (flotation) $= 1.26$, $Z = 4$, $D_o = 1.274$ g cm⁻³, $F(000) = 656$.

Cu-K_α radiation, $\lambda = 1.542$ Å; $\mu(\text{Cu-}K_\alpha) = 7.8$ 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 $l = 2n$.

Crystallographic Measurements.—Unit-cell dimensions and space group data were obtained from rotation and Weissenberg photographs taken with Cu-K_α radiation and from precession photographs taken with Mo-K_α radiation ($\lambda = 0.7107$ Å).

Three-dimensional intensity data for the $hk0$—9 reciprocal lattice levels were recorded photographically by the equi-inclination multiple-film Weissenberg method using Ni-filtered Cu-K_α radiation and estimated visually by comparison with a calibrated intensity scale. The 1 437

[1] A. T. McPhail, K. D. Onan, K. H. Lee, T. Ibuka, and H. C. Huang, *Tetrahedron Letters*, 1974, 3203.

observed intensity estimates so obtained were corrected for spot-shape variation, Lorentz and polarization effects; absorption was neglected. In the earlier stages of the analysis the various layers were assumed to be on a common scale as each had been given approximately the same exposure time; absolute individual layer scales were derived later by correlation of $\Sigma|F_o|$ with $\Sigma|F_c|$ at the end of the isotropic refinement cycles.

Structure Analysis.—The structure was solved by direct non-centrosymmetric phase-determining methods by use of MULTAN [2] with a total of 257 reflections having $|E| \gtrsim 1.26$

squares refinement of positional and isotropic thermal parameters. A three-dimensional difference map contained significant positive density at positions calculated for hydrogen atoms (assuming C–H 1.05; O–H 1.00 Å), except for those of the C(14) and C(15) methyl groups which could not be located unambiguously. Inclusion of the contributions for 16 hydrogen atoms, all with B 3.5 Å,[2] decreased R to 0.108 and seven further rounds of least-squares adjustment of the carbon and oxygen positional and anisotropic thermal parameters led to convergence at R 0.093.

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$) and anisotropic thermal parameters * ($\times 10^4$), with estimated standard deviations in parentheses

Atom	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	3 881(4)	1 854(6)	3 059(7)	27(2)	61(5)	77(7)	13(6)	−19(8)	15(10)
C(2)	3 279(5)	784(6)	2 990(8)	40(3)	48(4)	126(9)	9(7)	−52(9)	28(11)
C(3)	2 300(4)	1 134(5)	2 462(7)	34(3)	44(4)	76(7)	0(6)	−3(8)	2(10)
C(4)	1 847(4)	2 017(5)	3 354(7)	31(3)	52(4)	67(6)	−8(6)	3(8)	13(10)
C(5)	1 936(4)	3 147(5)	3 122(7)	29(3)	50(4)	73(7)	1(6)	17(8)	−25(9)
C(6)	2 427(4)	3 747(6)	1 959(7)	30(3)	53(4)	81(7)	9(6)	5(8)	7(10)
C(7)	3 185(4)	4 614(5)	2 483(7)	36(3)	42(4)	66(7)	−4(6)	−5(8)	2(9)
C(8)	4 119(4)	4 550(6)	1 699(8)	29(3)	59(5)	105(8)	−12(6)	4(9)	21(12)
C(9)	4 738(4)	3 547(6)	2 185(8)	27(3)	63(5)	114(9)	−9(6)	−19(9)	4(12)
C(10)	4 315(4)	2 347(6)	2 003(7)	25(2)	51(4)	98(8)	17(6)	−25(8)	−36(10)
C(11)	2 694(5)	5 753(6)	2 297(7)	46(3)	47(4)	90(8)	2(7)	54(9)	0(10)
C(12)	1 856(6)	5 588(6)	1 472(7)	62(4)	51(5)	59(7)	28(8)	−13(10)	26(10)
C(13)	2 926(7)	6 797(7)	2 827(12)	61(5)	55(6)	211(15)	−6(9)	7(16)	−38(16)
C(14)	1 332(6)	1 585(7)	4 610(10)	59(4)	69(6)	127(10)	−19(9)	40(12)	16(14)
C(15)	4 356(6)	1 823(7)	562(9)	59(4)	73(6)	83(9)	−1(9)	25(11)	−37(12)
O(16)	1 728(4)	4 452(4)	1 234(5)	43(2)	54(3)	96(6)	20(5)	−8(7)	17(8)
O(17)	1 319(4)	6 283(5)	998(7)	71(3)	69(4)	144(8)	64(6)	−26(9)	29(10)
O(18)	3 904(3)	4 521(5)	278(6)	38(2)	87(4)	95(5)	20(6)	33(7)	45(9)
O(19)	1 773(3)	49(4)	2 453(5)	42(2)	45(3)	109(6)	−6(5)	−39(7)	17(8)
C(20)	983(5)	10(6)	1 743(7)	34(3)	67(5)	60(7)	1(7)	13(8)	−38(11)
O(21)	705(4)	828(5)	1 048(6)	49(3)	85(5)	121(6)	1(6)	−71(7)	26(10)
C(22)	483(6)	−1 115(7)	1 902(10)	45(4)	68(6)	140(11)	−26(8)	−10(11)	0(14)

* In the form $B \sin^2\theta/\lambda^2 = b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl$.

from which a starting set of reflections was selected by the program. An E-map computed from the set of phases

TABLE 2

Fractional atomic co-ordinates ($\times 10^3$) for hydrogen atoms, labelled according to the atom to which they are bonded

Atom	x	y	z
H(1)	387	223	405
H(2α)	320	43	399
H(2β)	358	17	233
H(3)	235	148	143
H(5)	162	378	377
H(6)	274	313	130
H(7)	334	452	355
H(8)	446	528	202
H(9α)	490	367	323
H(9β)	537	357	160
H(13α)	260	761	266
H(13β)	354	694	341
H(18)	453	440	−19
H(22α)	−14	−117	132
H(22β)	36	−123	296
H(22γ)	97	−176	157

having the lowest residual and one of the higher figures-of-merit yielded positions for all 22 non-hydrogen atoms. A structure-factor calculation gave R 0.281 and this was reduced to 0.120 following four cycles of full-matrix least-

* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue.

The least-squares weighting scheme used [$\sqrt{w} = 1$ for $|F_o| \leqslant 12.5$ and $\sqrt{w} = 12.5/|F_o|$ for $|F_o| > 12.5$] showed no systematic dependence of $\langle w\Delta^2 \rangle$ when analysed in ranges of $|F_o|$. Scattering factor curves used in the structure-factor calculations for carbon and oxygen were from ref. 3, and for hydrogen from ref. 4.

Final atomic positional and anisotropic thermal parameters are given in Table 1. Calculated hydrogen atom positions are in Table 2. Observed and calculated structure amplitudes are listed in Supplementary Publication No. SUP 21609 (10 pp., 1 microfiche).*

RESULTS AND DISCUSSION

The results of the X-ray analysis establish that eupaformonin has the constitution and relative stereochemistry represented by (I). The solid-state conformation and atom numbering scheme are shown in Figure 1. Interatomic distances and angles are in Tables 3 and 4.

Eupaformonin is a representative of the $\Delta^{1(10)}$*trans,-* Δ^4*cis*-germacradiene class of sesquiterpenes, sub-group 'heliangolides'.[5] Before the isolation of eupaformonin

[2] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

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

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

[5] D. Rogers, G. P. Moss, and S. Neidle, *J.C.S. Chem. Comm.* 1972, 142.

all previously known authentic members of this sub-group were various helianginol (II) esters which con-sequently all possessed a 3β-oxygen function and a

a *trans*-oriented precursor after (or during) the oxidation which introduces these functions. The presence of a 3α-acetate group and the still extant 1(10)-*trans*-double

TABLE 3

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses

(a) Bond lengths

C(1)–C(2)	1.508(9)	C(8)–C(9)	1.533(10)
C(1)–C(10)	1.324(9)	C(8)–O(18)	1.410(9)
C(2)–C(3)	1.542(9)	C(9)–C(10)	1.524(9)
C(3)–C(4)	1.485(9)	C(10)–C(15)	1.521(11)
C(3)–O(19)	1.463(7)	C(11)–C(12)	1.451(11)
C(4)–C(5)	1.332(9)	C(11)–C(13)	1.353(11)
C(4)–C(14)	1.506(11)	C(12)–O(16)	1.346(8)
C(5)–C(6)	1.496(9)	C(12)–O(17)	1.202(10)
C(6)–C(7)	1.561(9)	O(19)–C(20)	1.322(8)
C(6)–O(16)	1.467(8)	C(20)–O(21)	1.227(9)
C(7)–C(8)	1.536(9)	C(20)–C(22)	1.491(11)
C(7)–C(11)	1.502(9)		

(b) Valency angles

C(2)–C(1)–C(10)	125.8(6)	C(9)–C(8)–O(18)	114.0(6)
C(1)–C(2)–C(3)	108.4(5)	C(8)–C(9)–C(10)	115.1(5)
C(2)–C(3)–C(4)	112.5(5)	C(1)–C(10)–C(9)	119.2(6)
C(2)–C(3)–O(19)	104.1(5)	C(1)–C(10)–C(15)	123.7(6)
C(4)–C(3)–O(19)	111.6(5)	C(9)–C(10)–C(15)	117.0(6)
C(3)–C(4)–C(5)	122.3(6)	C(7)–C(11)–C(12)	109.6(5)
C(3)–C(4)–C(14)	117.0(6)	C(7)–C(11)–C(13)	128.5(7)
C(5)–C(4)–C(14)	120.5(6)	C(12)–C(11)–C(13)	121.8(7)
C(4)–C(5)–C(6)	128.7(6)	C(11)–C(12)–O(16)	109.5(6)
C(5)–C(6)–C(7)	112.2(5)	C(11)–C(12)–O(17)	130.5(7)
C(5)–C(6)–O(16)	107.4(5)	O(16)–C(12)–O(17)	120.0(7)
C(7)–C(6)–O(16)	105.7(5)	C(6)–O(16)–C(12)	111.6(5)
C(6)–C(7)–C(8)	114.2(5)	O(19)–C(20)–O(21)	122.3(6)
C(6)–C(7)–C(11)	101.5(5)	O(19)–C(20)–C(22)	112.7(6)
C(8)–C(7)–C(11)	112.8(5)	O(21)–C(20)–C(22)	125.0(7)
C(7)–C(8)–C(9)	112.7(6)		
C(7)–C(8)–O(18)	107.2(5)		

(c) Intermolecular separations $\leqslant 3.60$ Å

O(18) · · · O(21$^{\mathrm{I}}$)	2.90	C(5) · · · C(22$^{\mathrm{III}}$)	3.56
O(17) · · · C(22$^{\mathrm{II}}$)	3.35	C(1) · · · O(17$^{\mathrm{IV}}$)	3.58
C(9) · · · O(21$^{\mathrm{I}}$)	3.50	O(18) · · · C(20$^{\mathrm{I}}$)	3.60
C(8) · · · O(21$^{\mathrm{I}}$)	3.52	O(18) · · · C(22$^{\mathrm{I}}$)	3.60

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

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

TABLE 4

Torsion angles (°)

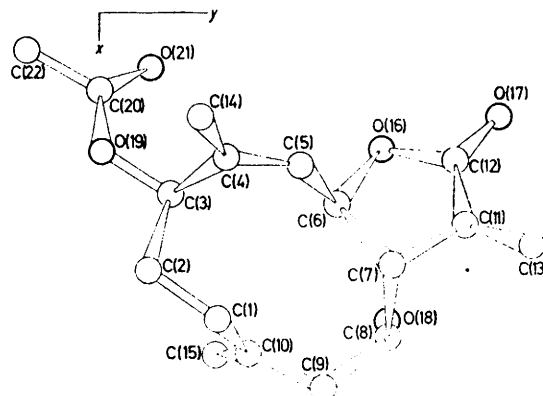|			
C(10)–C(1)–C(2)–C(3)	−80	C(6)–C(7)–C(8)–C(9)	−80
C(2)–C(1)–C(10)–C(9)	168	C(6)–C(7)–C(8)–O(18)	46
C(2)–C(1)–C(10)–C(15)	−7	C(11)–C(7)–C(8)–C(9)	165
C(1)–C(2)–C(3)–C(4)	−58	C(11)–C(7)–C(8)–O(18)	−69
C(1)–C(2)–C(3)–O(19)	−179	C(6)–C(7)–C(11)–C(12)	−12
C(2)–C(3)–C(4)–C(5)	92	C(6)–C(7)–C(11)–C(13)	165
C(2)–C(3)–C(4)–C(14)	−84	C(8)–C(7)–C(11)–C(12)	111
O(19)–C(3)–C(4)–C(5)	−152	C(8)–C(7)–C(11)–C(13)	−72
O(19)–C(3)–C(4)–C(14)	33	C(7)–C(8)–C(9)–C(10)	61
C(2)–C(3)–O(19)–C(20)	−164	O(18)–C(8)–C(9)–C(10)	−62
C(4)–C(3)–O(19)–C(20)	75	C(8)–C(9)–C(10)–C(1)	−96
C(3)–C(4)–C(5)–C(6)	4	C(8)–C(9)–C(10)–C(15)	79
C(14)–C(4)–C(5)–C(6)	179	C(7)–C(11)–C(12)–O(16)	6
C(4)–C(5)–C(6)–C(7)	−124	C(7)–C(11)–C(12)–O(17)	−173
C(4)–C(5)–C(6)–O(16)	120	C(13)–C(11)–C(12)–O(16)	−172
C(5)–C(6)–C(7)–C(8)	135	C(13)–C(11)–C(12)–O(17)	9
C(5)–C(6)–C(7)–C(11)	−103	C(11)–C(12)–O(16)–C(6)	4
O(16)–C(6)–C(7)–C(8)	−108	O(17)–C(12)–O(16)–C(6)	−177
O(16)–C(6)–C(7)–C(11)	14	C(3)–O(19)–C(20)–O(21)	3
C(5)–C(6)–O(16)–C(12)	108	C(3)–O(19)–C(20)–C(22)	−176
C(7)–C(6)–O(16)–C(12)	−12		

FIGURE 1   Molecular conformation and atom numbering scheme of eupaformonin

bond in eupaformonin indicate that the biosynthetic stage at which *trans–cis*-isomerization occurs may equally well precede the oxidation stage.

The cyclodeca-1,5-diene ring adopts a chair-boat conformation (III) in which the methyl groups are *anti* with respect to the ring plane. The ring is characterized
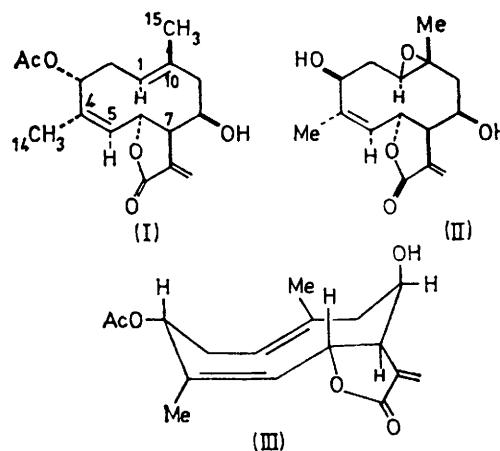
by endocyclic torsion angles $\omega_{1,2}$ −80, $\omega_{2,3}$ −58, $\omega_{3,4}$ 92, $\omega_{4,5}$ 4, $\omega_{5,6}$ −124, $\omega_{6,7}$ 135, $\omega_{7,8}$ −80, $\omega_{8,9}$ 61, $\omega_{9,10}$ −96, and $\omega_{10,1}$ 168°, which lie close to the corresponding values in dihydroheliangine: −88, −46, 80, −4, −122, 149, −80, 58, −84, and 163° (calculated from the co-ordinates of ref. 7 with the signs reversed to conform to the same absolute stereochemistry). In both compounds the small value around the *cis*-double-bonds ($\omega_{4,5}$) is close to the unstrained value of 0°. In contrast there is a significant departure from 180° at the *trans*-double-bonds ($\omega_{10,1}$) reflecting their more strained nature. The values in eupaformonin (168°) and dihydroheliangine (163°) are

[6] S. Gnecco, J. P. Poyser, M. Silva, P. G. Sammes, and T. W. Tyler, *Phytochemistry*, 1973, **12**, 2469.
[7] N. Nishikawa, K. Kamiya, A. Takabatake, H. Oshio, Y. Tomjie, and I. Nitta, *Tetrahedron*, 1966, **22**, 3601.

1(10)-epoxide group.[1] This consistent oxidation pattern led to speculation [6] that the Δ⁴*cis*-bond might arise from

similar in magnitude to those at *trans*-double-bonds in other germacranolide sesquiterpenes; *e.g.* 167 in shiromodiol acetate *p*-bromobenzoate,[8] 163 in elephantol *p*-bromobenzoate,[9] and —163° in dihydromikanolide.[10] The C(2)–C(1)–C(10)–C(15) torsion angle (—7°) indicates that the distortion in (I) results from approximately equal contributions from a true twist about the C(1)–C(10) double-bond and departure from planar trigonal bonding at C(10). Although the C(1) ··· C(4) and C(1) ··· C(5) transannular separations (2.92 and 3.15 Å) in eupaformonin are distinctly short, the two double bonds of the *trans,cis*-cyclodeca-1,5-diene ring are not oriented in such a manner as to produce significant π–π interaction of the type encountered in the *trans,trans*-cyclodeca-1,5-diene rings of, *e.g.* pregeijerine[11] or eupatolide.[12]

The α-methylene γ-lactone ring is *trans*-fused at C(6), C(7) and the ring adopts a very flattened half-chair (C_2) conformation (mean valency angle 107.6°, $\Sigma|\omega|$ 48°) with C(6) and C(7) displaced by 0.08 and 0.16 Å to opposite sides of the least-squares plane through C(11), C(12), O(16), and O(17).

From measurements of the sign of the Cotton effect of the α-methylene γ-lactone chromophore $n \rightarrow \pi^*$ transition in a number of sesquiterpene lactones, Stöcklin *et al.*[13] demonstrated that, with a few exceptions, the sign of the Cotton effect could be correlated with the position and stereochemistry of the ring fusions. Particularly relevant to the present study was their conclusion that *trans* ring fusions at C(6), C(7) generally gave rise to a negative Cotton effect but an anomalous result was obtained for helianginol (II) which, like eupaformonin, is a $\Delta^{1(10)}$*trans*,Δ^4*cis*-germacradiene. Subsequently, Beecham[14] suggested that the sign of the Cotton effect of the α-methylene γ-lactone chromophore is determined by the C=C–C=O group chirality, knowledge of which permits determination of the absolute configuration of the molecule under consideration. The c.d. curve of eupaformonin exhibits a positive Cotton effect with a maximum at 264 nm, a result which although in conflict with Stöcklin *et al.*'s proposals, may be used to assign the absolute configuration. Eupaformonin represented by formulation (I) has a C=C–C=O torsion angle of 9° and consequently to accord with Beecham's conclusions (I) must represent the absolute configuration which places the C(7) substituent in a β-orientation in common with all previously established absolute stereochemistries for germacranolides from higher plants. The breakdown of the Stöcklin *et al.* rule when applied to eupaformonin (and helianginol) may now be explained by comparing the results of the present study with those for eupatolide (IV) which obeys the rule. Major differences in the cyclodecadiene ring conformations in

eupaformonin and eupatolide[12] arise because of their differing configurations at the C(4)–C(5) double bond. In eupaformonin there is a significant enlargement of the
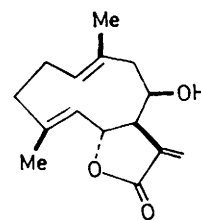
(IV)

cyclodeca-1,5-diene C(5)–C(6)–C(7)–C(8) torsion angle (135°) from that of 90° in eupatolide with concomitant change in magnitude and sign of the O–C(6)–C(7)–C(11) torsion angle in the γ-lactone ring [14° in (I), —27° in (IV), see Figure 2] which approximates to a half-chair conformation in both compounds. It has been noted previously[15] that the sign of the exocyclic α-methylene γ-lactone ring C=C–C=O torsion angle is paired with that of the endocyclic torsion angle about the C(6), C(7) bond; a like result holds true here also. Thus, the change in magnitude of the cyclodeca-1,5-diene torsion angle produces a change in the chirality of the C=C–C=O chromophore and consequently a change in the sign of the Cotton effect. For ideal tetrahedral geometry at the C(6) and
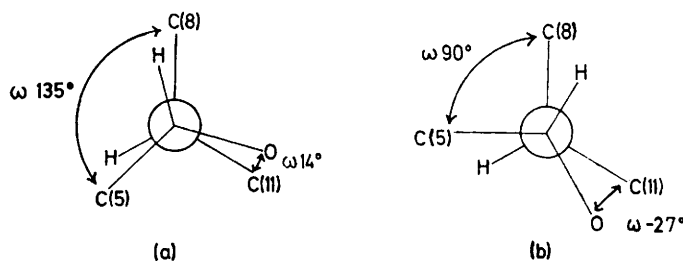

FIGURE 2 Newman projections along the C(6)–C(7) bonds in (a) eupaformonin, and (b) eupatolide, illustrating the relationship between the magnitude of the cyclodeca-1,5-diene C(5)–C(6)–C(7)–C(8) torsion angle and the sign of the γ-lactone O–C(6)–C(7)–C(11) torsion angle at a C(6), C(7)-*trans* ring fusion

C(7) atoms, this sign change will occur when the endocyclic cyclodeca-1,5-diene torsion angle has a value of 120°. In this region the sign of the Cotton effect will be particularly sensitive to small deviations from ideal geometry and anomalous results will be likely but when the torsion angles depart significantly from 120° the relationship shown in Figure 2 should hold true.

At the planar acetate ester group the C(2)–C(3)–O(19)–C(20) and C(4)–C(3)–O(19)–C(20) torsion angles (—164 and 75°) imply that the C(20)–O(19)–C(3)–H(3) torsion angle must lie close to —45°. This value accords with

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

[9] A. T. McPhail and G. A. Sim, *J.C.S. Perkin II*, 1972, 1313.

[10] P. J. Cox, G. A. Sim, J. S. Roberts, and W. Herz, *J.C.S. Chem. Comm.*, 1973, 428.

[11] P. Coggon, A. T. McPhail, and G. A. Sim, *J. Chem. Soc. (B)*, 1970, 1024.

[12] A. T. McPhail and K. D. Onan, *J.C.S. Perkin II*, 1975, 1798.

[13] W. Stöcklin, T. G. Waddell, and T. A. Geissman, *Tetrahedron*, 1970, 26, 2397.

[14] A. F. Beecham, *Tetrahedron*, 1972, 28, 5543.

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

those of −37 and −46° at the secondary ester groups of deacetyldihydrogaillardin *p*-bromobenzoate [16] and bromogaillardin,[16] and provides further evidence that the favoured geometry at secondary esters is that where the C=O group is *syn*-oriented with the C–H bond.[17]

illustrated in Figure **3**, and shorter intermolecular separations are reported in Table **3**. Eupaformonin molecules are linked by O(hydroxy)···O(carbonyl) hydrogen bonds, O···O 2.90 Å, around the 2_1 screw axis along the *a* direction.
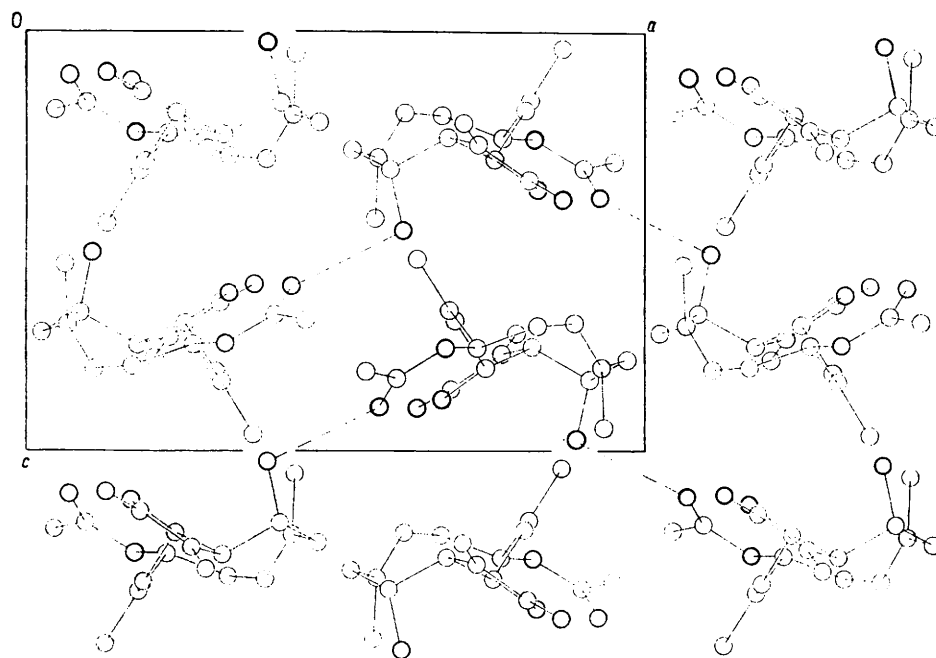
FIGURE 3   Crystal structure of eupaformonin viewed in projection along the *b* axis; O–H···O hydrogen bonds are denoted by broken lines

The means of chemically equivalent bonds compare well with accepted values [18] and none of the individual lengths departs significantly from the corresponding mean: $C(sp^3)$–$C(sp^3)$ 1.543(10), $C(sp^3)$–$C(sp^2)$ 1.504(11), $C(sp^2)$–$C(sp^2)$ 1.451(11), $C(sp^2)$=$C(sp^2)$ 1.336(11), $C(sp^3)$–O(R) 1.465(7), $C(sp^3)$–O(H) 1.410(9), $C(sp^2)$–O 1.334(18), and C=O 1.215(10) Å.

The crystal structure in projection along the *b* axis is

[16] T. A. Dullforce, G. A. Sim, and D. N. J. White, *J. Chem. Soc.* (*B*), 1971, 1399.

[17] A. McL. Mathieson, *Tetrahedron Letters,* 1965, 4137; C. Chothia and P. Pauling, *Nature,* 1970, **226,** 541.
[18] *Chem. Soc. Special Publ.,* No. 11, 1958; No. 18, 1965.