with the *B*, *C* and *D* rings showing minor distortions from ideal geometry. The *E* ring is roughly planar, with C19 displaced furthest from the five-atom least-squares plane.

An intermolecular hydrogen bond is observed between the hydroxyl group at C12, which acts a donor, and the carbonyl oxygen, O28. Associated metrical details are an O12···O28 distance of 2·953 (4) Å, an HO12—O28 distance of 1·96 Å and an angle of 180° at hydrogen. A relatively short intermolecular contact of 3·11 (1) Å between the acetonitrile methyl group carbon, C101, and the acetoxyl carboxyl oxygen, O26 is noted. This contact, which would not exist uniformly in the crystal due to the partial occupancy observed for the acetonitrile, may explain the relatively anisotropic motion of O26 as compared to other atoms in the molecule. Apparent motion of O26 might arise from atomic rearrangement to minimize this contact at sites adjacent to the solvent.

We thank Dr Charles DeBrosse of our Analytical Chemistry Department for helpful discussions on the NMR coupling constants.

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Acta Cryst. (1991). C**47**, 1253–1256

Paucin Methanolate

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(*Received* 3 *October* 1990; *accepted* 18 *December* 1990)

Abstract. 3a*R*-(3aα,4aβ,7α,7aα,8α,9aα)-7-[(6-*O*-Acetyl-β-D-glucopyranosyl)oxy]decahydro-4a,8-dimethyl-3-methyleneazuleno[6,5-*b*]furan-2,5-dione methanol solvate, $C_{23}H_{32}O_{10}.CH_3OH$, $M_r = 500{\cdot}55$, monoclinic, $P2_1$, $a = 10{\cdot}819$ (5), $b = 6{\cdot}591$ (6), $c = 18{\cdot}044$ (8) Å, $\beta = 92{\cdot}91$ (4)°, $V = 1284{\cdot}9$ (11) Å^3, $Z = 2$, $D_x = 1{\cdot}294$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5406$ Å, $\mu = 8{\cdot}198$ cm^{-1}, $F(000) = 536$, $T = 253$ K, $R = 0{\cdot}045$, $wR = 0{\cdot}059$ for 1969 observations, $I \geq 3\sigma(I)$. Paucin was isolated from the plant *Hymenoxys rusbyi* (Asteraceae) and crystallized from methanol. Crystals are isomorphous with those of a previously reported monohydrate. The structure was refined to a better residual. Conformational details are similar when compared to the monohydrate, but not identical. The cycloheptane ring adopts a twist-boat (C_2) conformation. The α-methylene-γ-lactone ring adopts an envelope conformation but with C8 at the flap rather than C7 as observed for the monohydrate. The weakest hydrogen bond from the monohydrate structure is absent in the methanolate, otherwise the hydrogen-bonding pattern is identical in both.

Introduction. Paucin, (1), a pseudoguaianolide β-glucoside, has been isolated previously from species of *Hymenoxys* and *Baileya* (Hertz, Aota, Holub & Samek, 1970); its crystal structure has been determined (Cox & Sim, 1977) as a monohydrated form (PW), and refined to a crystallographic residual of 7·9%. In the course of fractionating plant products from a methylene chloride extract of *Hymenoxys rusbyi*, a compound was isolated which, upon crystallization from methanol, proved to have lattice parameters similar to those of the previously reported paucin monohydrate. However, since paucin is related to a large number of new and known natural-product sesquiterpene lactones and as the known compounds were analyzed under different settings, we undertook the structure determination of

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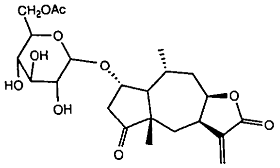
these crystals to identify unequivocally their contents. We found them to contain paucin methanolate (PM).



(1)

Experimental. Colorless crystals were obtained by slow evaporation from methanol. The data crystal had approximate dimensions 0·40 × 0·30 × 0·20 mm and was mounted on a glass fiber with epoxy cement. Lattice parameters were derived from least-squares refinement of 25 reflections ($30 \le 2\theta \le 35°$) on an Enraf–Nonius CAD-4 diffractometer equipped with graphite monochromator, helium-filled beam tunnels and an FR581 liquid nitrogen cryostat. The only systematic absence was for $0k0$ reflections with $k \neq 2n$. Intensity data ($0 \le h \le 12$, $0 \le k \le 7$, $-21 \le l \le 21$, $2\theta_{\max} = 135°$) were collected in an ω–2θ scan mode using variable speed scans (2·5 to 13·2° min^{-1}). Of the 2634 intensities scanned, 2497 were unique after averaging zonal symmetry equivalents ($R_{\text{int}} =$ 2·0%). Data were corrected for Lorentz and polarization effects but not for absorption. Intensities of three standard reflections ($14\bar{4}$, $4\bar{3}6$, $70\bar{7}$) measured every three hours of exposure (16 times) were unchanged (± 1·2%) during data collection.

Table 1. *Positional parameters and equivalent isotropic temperature factors with e.s.d.'s*

$$B_{\text{eq}} = (8\pi^2/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
OMe	0·8830 (3)	0·262	0·7698 (2)	6·52 (9)
O2′	0·0438 (2)	1·3377 (5)	0·8851 (1)	3·87 (6)
O2	0·2211 (2)	1·2334 (5)	0·7809 (1)	3·49 (5)
O3′	−0·0126 (2)	1·0038 (5)	0·9755 (1)	3·77 (6)
O3	0·0833 (3)	1·7470 (6)	0·4968 (2)	6·06 (8)
O4′	0·2091 (2)	0·7897 (5)	1·0359 (1)	4·36 (6)
O4	0·4675 (3)	1·0786 (6)	0·5944 (2)	6·06 (8)
O5	0·3096 (2)	1·0036 (5)	0·8628 (1)	3·46 (5)
O6′	0·5337 (2)	0·8294 (5)	0·9257 (2)	4·41 (6)
O7′	0·5434 (3)	0·6427 (9)	0·8263 (2)	11·8 (1)
O12	0·0542 (4)	1·7349 (9)	0·3747 (2)	8·8 (1)
CMe	0·7708 (5)	0·358 (1)	0·7597 (4)	9·1 (2)
C1	0·2772 (3)	1·4324 (6)	0·6769 (2)	3·03 (7)
C1′	0·2366 (3)	1·1839 (6)	0·8554 (2)	3·41 (8)
C2′	0·1082 (3)	1·1492 (7)	0·8826 (2)	3·18 (7)
C2	0·3275 (3)	1·3196 (7)	0·7471 (2)	3·19 (7)
C3′	0·1119 (3)	1·0531 (7)	0·9594 (2)	3·38 (6)
C3	0·4143 (4)	1·1579 (7)	0·7199 (2)	4·06 (9)
C4′	0·1954 (4)	0·8699 (7)	0·9620 (2)	3·44 (8)
C4	0·4261 (3)	1·1980 (7)	0·6381 (2)	3·91 (9)
C5′	0·3216 (3)	0·9335 (7)	0·9370 (2)	3·46 (8)
C5	0·3805 (3)	1·4110 (7)	0·6210 (2)	3·39 (8)
C6′	0·4110 (4)	0·7564 (8)	0·9388 (3)	4·52 (9)
C6	0·3391 (8)	1·4403 (8)	0·5378 (2)	4·09 (9)
C7	0·1975 (3)	1·4406 (8)	0·5223 (2)	3·79 (9)
C7′	0·5898 (4)	0·764 (1)	0·8674 (2)	5·2 (1)
C8	0·1287 (4)	1·6169 (8)	0·5579 (2)	4·28 (9)
C8′	0·7095 (4)	0·864 (1)	0·8579 (3)	7·0 (2)
C9	0·2005 (4)	1·7522 (8)	0·6125 (2)	4·33 (9)
C10	0·2314 (4)	1·6503 (7)	0·6880 (2)	3·49 (8)
C11	0·1654 (4)	1·4667 (9)	0·4408 (2)	4·9 (1)
C12	0·0954 (5)	1·657 (1)	0·4303 (2)	6·2 (1)
C13	0·1894 (5)	1·348 (1)	0·3840 (3)	7·6 (2)
C14	0·4933 (4)	1·5466 (8)	0·6391 (3)	4·7 (1)
C15	0·1205 (4)	1·6601 (8)	0·7368 (2)	5·0 (1)

The structure was solved using *SHELXS*86 (Sheldrick, 1985). The y coordinate of OMe was held fixed to define the origin. Refinement by full-matrix least squares minimized the function $\sum w(|F_o| - |F_c|)^2$ where the weight, w, was eventually assigned as $4F_o^2/\sigma^2(I)$ with $\sigma^2(I)$ defined as $[\sigma^2(I_c) + (0{\cdot}04F_o)^2]$. Non-H atoms were refined with anisotropic thermal parameters. H-atom positions, suggested from difference Fourier maps, were held fixed along with thermal factors calculated as $1{\cdot}3 \times B_{\text{iso}}$ of the C or O atoms to which they were attached. An extinction coefficient refined in the latter stages to $2{\cdot}292\,(1) \times 10^{-6}$. In the final least-squares cycle no parameter shifted relative to its e.s.d. A final difference Fourier map showed residuals of ±0·199 e Å^{-3}. Standard crystallographic residuals upon convergence were $R = 0{\cdot}0453$, $wR = 0{\cdot}059$ with GOF = 1·533 for 316 variables and 1969 observations, $I \ge 3\sigma(I)$. Neutral atom scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV) were used as incorporated in the locally modified version of the Enraf–Nonius *SDP-Plus* (Frenz, 1987) which was the source of all programs. All metrical values are calculated based on coordinates in Table 1,* which represent the results after refinement against the data with $I \ge 3\sigma(I)$. A refinement using all 2332 data not flagged as weak in a prescan gave $R = 0{\cdot}055$, $wR = 0{\cdot}062$.

Discussion. The structure of paucin as found in the methanolate structure is displayed as Fig. 1. Principal bond distances are listed in Table 2. Overall stereochemistry was assigned in accord with that previously determined for PW (Cox & Sim, 1977). The paucin molecule in the PM structure adopts a conformation quite similar to that observed in PW, but there are some differences. Valency angles in the PM cycloheptane ring cover a broader range (110·3–118·3°) than in PW but the average of 114·5° is the same within experimental error. As in PW, the cycloheptane ring of paucin in PM adopts a twist-boat conformation which most closely depicts the C_2 barrier form as described by Hendrickson (1961). The $\sum_2$ values, which provide a measure of the deviation from idealized symmetry, are 10 for

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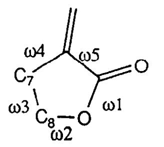
* Lists of structure factors, anisotropic thermal parameters, bond angles, bond distances and angles involving H atoms and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53851 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Principal bond distances* (Å) *with e.s.d.'s*

OMe—CMe	1·375 (6)	C2′—C3′	1·522 (4)
O2′—C2′	1·426 (4)	C2—C3	1·518 (5)
O2—C1′	1·386 (4)	C3′—C4′	1·507 (5)
O2—C2	1·446 (4)	C3—C4	1·511 (5)
O3′—C3′	1·429 (4)	C4′—C5′	1·518 (4)
O3—C8	1·462 (5)	C4—C5	1·514 (5)
O3—C12	1·350 (5)	C5′—C6′	1·515 (5)
O4′—C4′	1·435 (4)	C5—C6	1·557 (5)
O4—C4	1·215 (4)	C5—C14	1·534 (5)
O5—C1′	1·429 (4)	C6—C7	1·544 (4)
O5—C5′	1·416 (4)	C7—C8	1·539 (5)
O6′—C6′	1·443 (4)	C7—C11	1·504 (5)
O6′—C7′	1·312 (5)	C7′—C8′	1·469 (6)
O7′—C7′	1·187 (6)	C8—C9	1·513 (6)
O12—C12	1·193 (5)	C9—C10	1·542 (5)
C1—C2	1·544 (4)	C10—C15	1·525 (5)
C1—C5	1·549 (4)	C11—C12	1·473 (7)
C1—C10	1·536 (5)	C11—C13	1·325 (7)
C1′—C2′	1·514 (4)		

Table 3. *Sesquiterpene α-methylene-γ-lactone-ring torsion angles* (°) *in* 7,8-*fused systems*



Structure	Junction	ω1	ω2	ω3	ω4	ω5	ω6*
I	*cis*	−7	11	−10	6	0	−10
II	*cis*	−1	12	−17	17	−11	−2
III†	*cis*	0 7	−3 4	4 1	−4 −5	3 8	6 5
IV	*cis*	−7	13	−13	9	−1	−2
V	*cis*	12	−32	38	−32	14	15
VI	*cis*	13	−29	33	−26	9	8
VII	*cis*	9	−30	38	−33	16	17
XIII	*cis*	−12	26	−28	21	−7	−9
IX	*cis*	−11	21	−22	16	−4	−9
X	*cis*	−5	3	0	−3	5	−4
XI	*cis*	−5	8	−7	5	0	−3
XII	*trans*	1	−13	19	−18	11	9
XIII†	*trans*	11 4	−23 −19	24 24	−18 −22	5 12	8 11
XIV	*trans*	11	−21	23	−17	5	6

* ω6 is the torsion angle about C11-C12 defined by the α-methylene and β-keto groups.

† Two crystallographically independent molecules. I Paucin methanolate, this work; II Paucin monohydrate, Cox & Sim (1977); III Psilotropin, Emerson, Asdjodi, Ratnapala, Subramanian & Seff (1990); IV Hymenoxon, Pettersen & Kim (1976); V Helenalin, Watson & Kashyap (1990); VI Helenalin, Fronczek, Ober & Fischer (1987); VII Bromohelenalin, Haquc & Caughlan (1969); VIII Bromomexicanin-E, Haque & Caughlan (1967); IX Helenalin oxide, McPhail & Onan (1975*a*); X Florilenalin, McPhail & Onan (1975*b*); XI Autumnolide, Von Dreele, Pettit, Cragg & Ode (1975); XII Mexicanin I, Watson & Kashyap (1990); XIII Geigerinin; Bloszyk *et al.* (1989); XIV Diacetylspathulin; Inayama, Ohkura & Iitaka (1977).

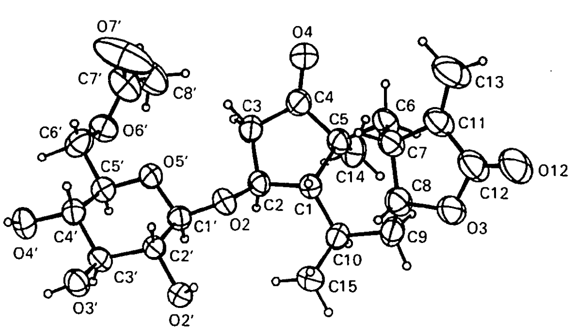


Fig. 1. *ORTEP* (Johnson, 1976) drawing of paucin in PM. Thermal ellipsoids are shown at the 50% probability level, H atoms as small spheres of arbitrary size.

Table 4. *Hydrogen-bonding interactions in paucin methanolate*

	(Å)	(°)	Symmetry operations*
OMe—O12	2·733 (5)	177	(ii) 121
HOMe—O12	1·82		
O2′—OMe	2·691 (4)	179	(i) 110
HO2′—OMe	1·79		
O3′—O2′	2·780 (4)	172	(ii) 012
HO3′—O2′	1·97		
O4′—O3′	2·839 (4)	170	(i) 012
HO4′—O3′	1·92		

* Symmetry operators: (i) x, y, z; (ii) $-x, \frac{1}{2}+y, -z$. Translations are along x, y and z respectively.

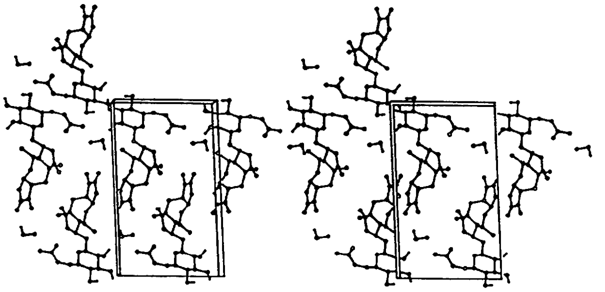


Fig. 2. Unit-cell drawing for paucin methanolate. The *a* and *c* axes are shown horizontally and vertically, respectively. All atoms are drawn as small spheres of arbitrary size. Only H atoms involved in hydrogen-bonding interactions are included.

PM and 8 for PW. Individual torsion angles in the cycloheptane ring agree within ±6°. The α-methylene-γ-lactone ring adopts an envelope conformation, as in the monohydrate, but with C8 at the flap instead of C7. In the reduced temperature structure of PM this ring displays less distortion from an idealized envelope conformation. Torsion angle comparison for this lactone ring with that in other 7,8-fused systems is afforded by the values collected in Table 3. The largest differences between rings are found in the endocyclic torsion angles ω4 and ω5 (11°) as well as in the exocyclic torsion for the α-methylene-β-keto orientation (8°). Represented amongst this series are all of the general conformations expected to arise along the pathway of pseudorotational motions for this ring system, including both envelopes (I,II,IV,XII), the planar (III,X-XI) and half-chair forms (V-IX,XIII-XIV).

Hydrogen-bonding interactions (Table 4) in the PM structure involve all possible donors, as was true for PW. The hydrogen-bonding pattern involving the solvent molecule is quite similar to that observed for the monohydrate in that the acceptor of a hydrogen bond from methanol is the γ-lactone carbonyl oxygen, O12, and the methanol accepts a hydrogen bond from the glucosidic oxygen, O2′. In addition, glucosidic oxygens O3′ and O4′ donate to the same hydroxyls as in PW. The difference in hydrogen-bond pattern between the two structures involves the lack of a second H atom on methanol to act as a donor to the acetyl carbonyl oxygen, O7′. Interestingly, this missing interaction is the weakest, by distance criteria, of all the hydrogen bonds in PW and the acetyl oxygen displays a considerable wagging motion in the PM structure, reflecting its lack of constraint by the additional hydrogen bond. As may be seen in the unit-cell drawing, Fig. 2, the acetyl group sits in a cavity formed by the glucose ring and the paucin skeleton. As a result of the crystal packing, and in the absence of the second hydrogen-bonding interaction, the acetyl carbonyl group has a considerable space in which to flex.

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Structure of the *Z* Isomer of 5-(2-Chlorobenzylidene)-2,3-dihydroimidazo[2,1-*b*]thiazol-6(5*H*)-one

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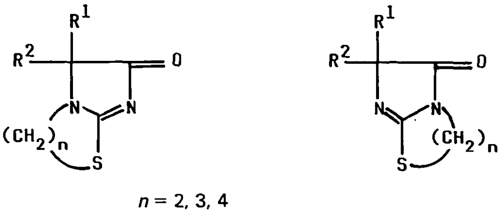
(*Received* 12 *June* 1990; *accepted* 4 *October* 1990)

Abstract. $C_{12}H_9ClN_2OS$, $M_r = 264\cdot73$, orthorhombic, $Pbca$, $a = 21\cdot881\,(3)$, $b = 14\cdot619\,(2)$, $c = 7\cdot118\,(1)$ Å, $V = 2276\cdot8\,(5)$ Å^3, $Z = 8$, $D_x = 1\cdot544$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1\cdot54178$ Å, $\mu = 43\cdot77$ cm^{-1}, $F(000) = 1088$, final $R = 0\cdot040$ for 887 observed reflections with $F > 6\sigma(F)$ (of 1249 unique data). The molecule is in the *Z* configuration and adopts a non-planar conformation with the two planar rings (benzene and thiohydantoin) forming an angle of 34·2 (2)°. Molecular-mechanics calculations indicate that it is not a minimum-energy conformation.

Introduction. Searching for new compounds influencing the central nervous system we have examined annelated 2-thiohydantoin derivatives of types (1), (2), (3) and (4). The derivatives of 5,5-diphenyl-2-thiohydantoin (DPTH) [(1) and (2)] have shown sedative properties while the derivatives of 5-benzylidene-2-thiohydantoin [of type (4)] possessed analgesic, anxiolytic, antidepressant and anticonvulsive properties (Kolasa, Kleinrok, Pietrusiewiez, Czechowski, Kieć-Kononowicz & Zejc, 1989).



$n = 2, 3, 4$

(1) $R^1 = R^2 = \text{Ph}$ (2)

(3) $R^1 = R^2 =$ (un)substituted benzylidene (4)

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