Table 3. *Comparison of selected bond distances* (Å), *angles and torsion angles* (°) *in* 4-*ammonio*-3-*hydroxybutanoates*

	(*RS*)-GABOB[a] (ammonio)	(*R*)-Norcarnitine[b] (dimethylammonio)	(*R*)-Carnitine[c] (trimethylammonio)
C3—C4	1·516 (9)	1·510 (2)	1·528 (2)
C4—N	1·477 (8)	1·499 (1)	1·521 (1)
C1—C2—C3	111·4 (6)	116·5 (1)	113·4 (1)
C2—C3—C4	110·8 (5)	110·6 (1)	105·6 (1)
C2—C3—O3	111·1 (5)	111·12 (9)	108·7 (1)
O3—C3—C4	107·0 (5)	106·8 (1)	113·1 (1)
C3—C4—N	109·5 (5)	113·6 (1)	117·3 (1)
C1—C2—C3—C4	−173 (1)	−73·6 (2)	−171·6 (2)
C1—C2—C3—O3	67 (1)	168·0 (1)	66·7 (2)
C2—C3—C4—N	168 (1)	−179·4 (3)	−179·7 (2)
O3—C3—C4—N	−70 (1)	−58·4 (2)	−61·5 (5)

References: (*a*) Tomita *et al.* (1973). (*b*) This work. (*c*) Gandour *et al.* (1985).

(*R*)-Carnitine has significantly different C2—C3—C4, C2—C3—O3 and O3—C3—C4 angles from GABOB and (*R*)-norcarnitine, which have similar values for these parameters. The dimethylammonio group in (*R*)-norcarnitine rotates into a conformation where the H atom on the N atom eclipses O3. The unsubstituted ammonio group in (*RS*)-GABOB can only have an H atom eclipse O3, but the trimethylammonio in (*R*)-carnitine must have a methyl group eclipse. The steric repulsion between methyl and O3 results in larger C3—C4—N and O3—C3—C4 angles but smaller C2—C3—C4 C2—C3—O3 angles. Backbone conformation, C1—C2—C3—C4 and C2—C3—C4—N, in (*RS*)-GABOB and (*R*)-carnitine is *anti, anti*; but in (*R*)-norcarnitine, it is *gauche*$^-$, *anti*. This conformational change results in a larger C1—C2—C3 angle in (*R*)-norcarnitine compared to the other compounds.

Intramolecular interactions control conformation about the C3—C4 bond while intermolecular forces influence conformation about the C2—C3 bond. The '*gauche* effect' of polar bonds O3—C3—C4—N dominates the C3—C4 conformation (see Gandour *et al.*, 1985, and references therein). The C1—C2—C3—C4 torsion angle favors *anti* and *gauche*$^-$ more than *gauche*$^+$ (Gandour *et al.*, 1985; Colucci, Gandour & Mooberry, 1986). Intramolecular hydrogen bonding between hydroxyl and carboxylate in GABOB requires an *anti* conformation for C1—C2—C3—C4. An *anti* conformation occurs in (*R*)-carnitine without intramolecular hydrogen bonding. For (*R*)-norcarnitine, the interactions with water must influence the change to *gauche*$^-$.

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Structure of Heteronemin

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Abstract. (5α,5′α,12β,16β,17aα)-5′,17a-Dihydro-4,4,8-trimethyl-*D*-homoandrostano[17,17a-*c*]furan-5′,12,16-triol 5′,16-diacetate, $C_{29}H_{44}O_6$, $M_r = 488{\cdot}77$, crystallized as a hemiacetonitrile solvate, $C_{29}H_{44}O_6.1/2C_2H_3N$, $M_r = 509{\cdot}20$, monoclinic, *C*2, $a = 36{\cdot}917$ (11), $b = 6{\cdot}289$ (2), $c = 12{\cdot}421$ (2) Å, $\beta = 104{\cdot}51$ (2)°, $V = 2791{\cdot}7$ (11) Å^3, $Z = 4$, $D_x = 1{\cdot}212$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ =

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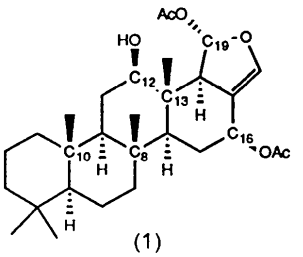
0·793 cm^{-1}, $F(000) = 1108$ for the solvate, $T = 151$ K, $R = 0·056$, $wR = 0·076$ for 2997 observations [$I \geq 3\sigma(I)$]. The sesterterpene was isolated from the marine sponge *Hyrtios erecta*. The structure determination shows a pentacyclic dihydrofuranosesterterpene skeleton with a β-oriented hydroxyl group at C12, β-oriented angular methyls at C8, C10 and C13, a β-oriented acetyl group at C16, and an α-oriented acetyl at C19.

Introduction. Heteronemin (1), a pentacyclic dihydrofuranosesterterpene, was first isolated from the marine sponge *Heteronema erecta* (Kazlauskas, Murphy, Quinn & Wells, 1976). These authors, on the basis of spectral data, inferred the stereochemistries of substituents as being α (equatorial) for the C12 hydroxyl and C16 acetoxyl groups, β (axial) for the C8 and C10 methyls and β for the C19 acetoxyl group as well. Subsequently, the ^{13}C NMR spectrum and stereochemistry of heteronemin were the subjects of a publication (Kashman & Rudi, 1977) which concluded that stereochemistry at C19 was ambiguous based on the relatively small (2 Hz) coupling constant, $J_{C18,C19}$. Still later, in a description of new sesterterpenes from a different sponge species, Walker, Thompson & Faulkner (1980) again identified heteronemin with β-stereochemistry for the C19-acetoxyl group.

Yasuda & Tada (1981) isolated heteronemin from the sponge *C. scarlaris* and assigned the stereochemistry of H18 as α, based on a large ^4J value between H18 and H20 in a spin–spin decoupling experiment. Consistent with previous arguments reflecting the ready elimination of acetic acid from (1), and with a small value (1·8 Hz) for ^3J between H18 and H19, these authors assigned the α stereochemistry to the C19 acetoxyl. This latter assignment now seems to be the accepted stereochemistry, as illustrated in a review by Faulkner (1984).

In the course of screening marine natural products for various biological activities, we isolated a compound from a methylene chloride extract of marine sponge *Hyrtios erecta*. Proton NMR data were consistent with previous reports for heteronemin. As the compound crystallized readily and the stereochemical assignment has been the subject of discussion in the literature, we determined the structure by X-ray diffraction from a single crystal.



(1)

Experimental. Colorless crystals were grown by slow evaporation from acetonitrile. The data crystal had approximate dimensions 0·70 × 0·30 × 0·25 mm and was mounted on a glass fiber with epoxy cement. Cell constants were derived from least-squares refinement of the setting angles for 25 reflections ($30 \leq 2\theta \leq 35°$) located using the *SEARCH* routine on an Enraf–Nonius CAD-4 diffractometer equipped with molybdenum source and a graphite monochromator. The *C*-centered condition, *hkl* for $h + k$ odd, was the only apparent systematic absence. Intensity data were collected in an ω–2θ scan mode using variable speed scans (2·5 to 12·4° min^{-1}). Of the 3729 intensities scanned ($0 \leq h \leq 48$, $0 \leq k \leq 8$, $-16 \leq l \leq 16$, $2\theta_{max} = 56°$), 3672 were unique after averaging, $R_{int} = 0·018$. Data were corrected for Lorentz and polarization effects but not for absorption. Intensities of three standard reflections (25,1,3, 24,2,6, 2,0,10) measured after every 3 h of exposure (19 times) showed a non-systematic overall increase of 5·6 (24)%. Temperature control was provided by an Enraf–Nonius FR581 cryostat which is normally constant to within ± 2 K.

The structure was solved using *SHELXS86* (Sheldrick, 1985). The y coordinate of O(12) was fixed to define the origin. Refinement by full-matrix least squares on F minimized the function $\sum w(|F_o| - |F_c|)^2$ where the weights, w, eventually were assigned as $4F_o^2/\sigma^2(I)$ with a $\sigma^2(I)$ defined as $[\sigma^2(I_c) + (0·04I)^2]$. Non-H atoms were refined with anisotropic thermal parameters. H atoms on the steroid nucleus were apparent from difference maps. The hydroxyl H-atom position was taken from such a map while other H-atom positions were calculated based on geometric considerations assuming a C—H bond distance of 1 Å. All H atoms were added as fixed contributors with assigned isotropic temperature factors equal to $1·3 \times B_{iso}$ of the attached atom. Based on bond-distance arguments, the N atom of the acetonitrile was assigned the electron density residual on the twofold axis. The remaining two significant density peaks were assigned as acetonitrile C atoms. Using the Fourier map peak heights as a guide, 1/2 occupancy for the solvent molecule was fixed. Solvent-atom positions were refined with anisotropic thermal parameters, but H-atom positions for the methyl group were omitted. Refinement converged (max. $\Delta/\sigma = 0·04$) to values of the standard crystallographic residuals $R = 0·0563$, $wR = 0·0761$, $S = 2·339$ for 2998 observations with $I > 3\sigma(I)$, 338 variables. A final difference Fourier map showed maximum excursions of +0·823 and −0·249 e Å^{-3}. The largest peak was in the vicinity of the acetonitrile methyl group. Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV), for H from Stewart, Davidson & Simpson (1965), were used as incorporated in a locally

Table 1. *Positional parameters and equivalent isotropic thermal parameters with e.s.d.'s for* (1)

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

	x	y	z	B_{eq} (Å^2)
O12	0·04292 (6)	0·229	0·4784 (2)	2·40 (5)
O16	0·12189 (7)	−0·0597 (5)	0·0843 (2)	2·20 (5)
O19	0·00631 (7)	−0·1670 (5)	0·2883 (2)	2·81 (5)
O20	0·01325 (6)	0·0348 (5)	0·1388 (2)	2·57 (5)
O26	0·1203 (1)	−0·4141 (7)	0·0817 (3)	8·2 (1)
O28	−0·04363 (7)	0·0130 (8)	0·3102 (3)	4·63 (8)
N100	0·000	0·504 (2)	0·000	7·4 (4)
C1	0·16491 [(9)	0·2420 (7)	0·7874 (2)	1·96 (6)
C2	0·1949 (1)	0·2652 (7)	0·8963 (3)	2·31 (7)
C3	0·2300 (1)	0·1432 (7)	0·8920 (3)	2·37 (7)
C4	0·24648 (9)	0·2068 (7)	0·7949 (3)	2·01 (6)
C5	0·21472 (9)	0·1956 (6)	0·6858 (3)	1·67 (6)
C6	0·22746 (8)	0·2408 (7)	0·5797 (3)	1·84 (6)
C7	0·19801 (8)	0·1661 (6)	0·4756 (3)	1·70 (6)
C8	0·15912 (8)	0·2663 (6)	0·4642 (2)	1·49 (5)
C9	0·14865 (8)	0·2381 (6)	0·5776 (2)	1·45 (5)
C10	0·17802 (8)	0·3160 (6)	0·6843 (2)	1·62 (6)
C11	0·10830 (9)	0·3134 (6)	0·5677 (3)	1·91 (6)
C12	0·08109 (8)	0·1757 (6)	0·4845 (3)	1·71 (6)
C13	0·08722 (9)	0·1845 (6)	0·3667 (3)	1·57 (6)
C14	0·12969 (8)	0·1334 (5)	0·3767 (2)	1·51 (6)
C15	0·13799 (9)	0·1218 (6)	0·2607 (3)	1·81 (6)
C16	0·11596 (9)	−0·0612 (6)	0·1945 (2)	1·82 (6)
C17	0·07535 (9)	−0·0319 (6)	0·1902 (3)	1·85 (6)
C18	0·06498 (9)	−0·0005 (6)	0·2985 (3)	1·75 (6)
C19	0·02239 (9)	0·0246 (6)	0·2576 (3)	2·05 (6)
C20	0·04594 (9)	−0·0082 (7)	0·1068 (3)	2·24 (7)
C21	0·2767 (1)	0·0441 (8)	0·7894 (3)	2·99 (8)
C22	0·2653 (1)	0·4255 (7)	0·8167 (3)	2·47 (7)
C23	0·18122 (9)	0·5609 (6)	0·6881 (3)	2·13 (7)
C24	0·16107 (9)	0·4993 (6)	0·4277 (3)	2·05 (6)
C25	0·07434 (9)	0·3990 (6)	0·3102 (3)	2·02 (6)
C26	0·1232 (1)	−0·2498 (7)	0·0358 (3)	2·78 (7)
C27	0·1280 (1)	−0·2299 (9)	−0·0788 (3)	3·52 (9)
C28	−0·0266 (1)	−0·1523 (9)	0·3138 (3)	3·32 (9)
C29	−0·0382 (2)	−0·361 (1)	0·3505 (5)	6·4 (1)
C100	−0·0191 (4)	0·513 (2)	0·0440 (9)	6·1 (3)
C101	−0·0453 (4)	0·509 (4)	0·095 (1)	10·0 (5)

Table 2. *Principal bond distances* (Å) *for* (1)

O12—C12	1·433 (3)	C8—C9	1·562 (3)
O16—C16	1·440 (3)	C8—C14	1·571 (3)
O16—C26	1·345 (3)	C8—C24	1·541 (3)
O19—C19	1·436 (3)	C9—C10	1·566 (3)
O19—C28	1·335 (3)	C9—C11	1·538 (3)
O20—C19	1·429 (3)	C10—C23	1·545 (3)
O20—C20	1·389 (3)	C11—C12	1·519 (3)
O26—C26	1·198 (4)	C12—C13	1·536 (3)
O28—C28	1·209 (4)	C13—C14	1·574 (3)
N100—C100	1·00 (1)	C13—C18	1·548 (3)
C1—C2	1·525 (3)	C13—C25	1·540 (3)
C1—C10	1·550 (3)	C14—C15	1·548 (3)
C2—C3	1·519 (4)	C15—C16	1·526 (3)
C3—C4	1·533 (3)	C16—C17	1·498 (3)
C4—C5	1·556 (3)	C17—C18	1·502 (3)
C4—C21	1·529 (4)	C17—C20	1·308 (3)
C4—C22	1·534 (4)	C18—C19	1·535 (3)
C5—C6	1·533 (3)	C26—C27	1·483 (3)
C5—C10	1·548 (3)	C28—C29	1·483 (5)
C6—C7	1·540 (3)	C100—C101	1·29 (2)
C7—C8	1·541 (3)		

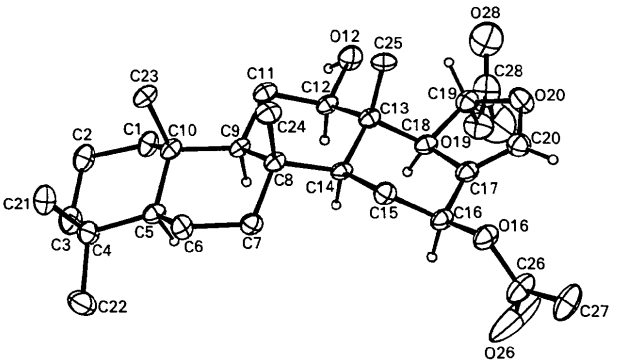


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of heteronemin. Thermal ellipsoids are drawn at the 50% probability level. H atoms are displayed as spheres of arbitrary size; many H atoms have been omitted for clarity.

modified version of the Enraf–Nonius *SDP-Plus* (Frenz, 1987) which was the source of all programs. Refinement using all data not flagged as weak in a prescan (3443 observations) gave $R = 0{\cdot}064$, $wR = 0{\cdot}078$. It is these latter data which are tabulated in the structure-factor listings although all metrical values are calculated based on coordinates in Table 1,* which were obtained from refinement against data with $I \geq 3\sigma(I)$.

Discussion. The structure of heteronemin is displayed as Fig. 1. Principal bond distances are listed in Table 2. Overall stereochemistry was assigned assuming β-orientation for the methyl group at C10. Relative to this assignment, the methyls at C8 and C13 also are β-oriented as is the hydroxyl at C12. The acetoxyl group at C16 is also β-oriented while that at C19 is α-oriented. The hydrogens at C18 and C19 adopt a *cisoid* orientation one to another, and the H20—C18—C19—H21 torsion angle is 105°. Such a torsion angle would be predicted from the Karplus relationship to give rise to a J coupling of approximately 2·6 Hz. This value is consistent with the 2·2 Hz value reported by Kazlauskas *et al.* (1976) as well as the 2·05 Hz value which we observed in acetone solution. Coupling constants are known to deviate from the idealized Karplus equation depending particularly on the electronegativity of adjacent substituent atoms (Haasnoot, DeLeuw & Altona, 1980). Experimental error in coupling constant measurement and digital resolution of the spectra combined would lend further consistency to these observations. The small coupling constant was interpreted by Kazlauskas *et al.* (1976) as indicative of a *trans* relationship for the protons; however, a much larger coupling of 10 Hz or more would be expected for such an orientation.

The *A*/*B*, *B*/*C* and *C*/*D* ring junctions are all *trans*. All six-membered ring conformations are half-chairs

* Lists of structure factors, anisotropic thermal parameters, bond angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53608 (30 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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.

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Paucin Methanolate

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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 = 500·55, monoclinic, $P2_1$, a = 10·819 (5), b = 6·591 (6), c = 18·044 (8) Å, β = 92·91 (4)°, V = 1284·9 (11) Å^3, Z = 2, D_x = 1·294 g cm^{-3}, λ(Cu $K\alpha$) = 1·5406 Å, μ = 8·198 cm^{-1}, F(000) = 536, T = 253 K, R = 0·045, wR = 0·059 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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