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9,11-Secogorgost-5-en-9-one-3β,11-diol, a Marine Steroid from the Sea Whip *Pseudopterogorgia hummelinkii*

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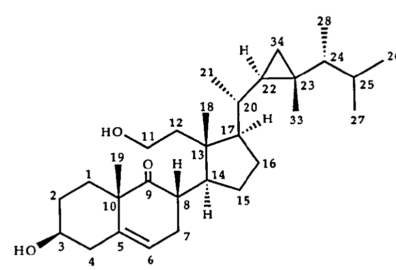
Abstract

The title steroid [(22*R*,23*R*,24*R*)-22,23-methylene-23,24-dimethyl-9,11-secocholest-5-en-9-one-3β,11-diol, $C_{30}H_{50}O_3$], was isolated from *Pseudopterogorgia hummelinkii*, a Caribbean gorgonian. The cyclopropane ring in the side chain of this molecule, a feature very unusual in terrestrial steroids, has been found in several other marine steroids. The molecular structure is potentially very flexible because of the oxidative cleavage of ring *C*, but the two independent molecules in the crystal have quite similar overall conformations. The observed conformational differences correlate with dissimilar participation of the hydroxyl and carbonyl groups of each molecule in hydrogen bonding, which is entirely intermolecular. The crystal structure was solved by direct methods, but only with great difficulty.

Comment

Marine organisms with restricted mobility have evolved a variety of chemical defenses. Novel sterols, with structures having few or no terrestrial counterparts (Djerassi & Silva, 1991), might be among these, although their functions are not well established. As part of a continuing study of bioactive metabolites from marine invertebrates, we investigated the sea whip *Pseudopterogorgia hummelinkii*, a gorgonian octocoral collected in the Caribbean off the coast of Belize. Broadly speaking, the genus *Pseudopterogorgia* is the most highly chemically defended of all Caribbean gorgonians (Pawlik, Burch & Fenical, 1987).

The major polar secondary metabolite of *P. hummelinkii* is 9,11-secogorgost-5-en-9-one-3β,11-diol, (I). Compound (I) was isolated from this gorgonian by homogenization and solvent extraction, followed by chromatography of the crude extract on silica gel. X-ray analysis confirmed the structure proposed on the basis of spectral evidence, primarily NMR.



(I)

Compound (I) was first isolated by Spraggins (1970) from *Pseudopterogorgia americana* (Gmelin). The relationship of (I) to gorgosterol (Hale *et al.*, 1970; Ling, Hale & Djerassi, 1970), which is found in a relatively high proportion in the same species, was unambiguously demonstrated and its absolute configuration determined by an X-ray crystal structure analysis of the prepared 3-(*p*-iodobenzoyl)-11-acetate derivative (Enwall *et al.*, 1972). Our analysis is of the native unsubstituted molecule. The structure is a 9,11-secosteroid (ring *C* opened), and has a cyclopropane ring in the side chain, a structural feature unusual for terrestrial steroids but found in a significant number of marine steroids. The cleavage of ring *C* is an oxidative one: C9 is transformed to a carbonyl group and C11 to a primary alcohol.

Gorgosterol was the first sterol shown to have alkyl substitution at C22 and C23 and the first shown to have a cyclopropane ring in the side chain. The crystal structure of a hydrate of gorgosterol was determined by Hu, Huang, Shi, Li & Di (1990). Marine sterols closely related to gorgosterol include acanthasterol, the Δ^7 isomer, isolated from the echinoderm sea star *Acanthaster planci* L. (Gupta & Scheuer, 1968; Sheikh, Djerassi & Tursch, 1971), 23-desmethylgorgosterol, isolated from *Gorgonia flabellum* L. and *Gorgonia ventilina* L. (Schmitz & Pattabhiraman, 1970), and clavisterol A, which differs from 23-desmethylgorgosterol only by having terminal methyl and ethyl rather than dimethyl moieties on C25, a compound isolated from the Chinese soft coral *Clavularia viridis* (Su, Zhong & Zeng, 1991). 9,11-Secosteroids closely related to (I) include the 24β-hydroxylated derivative 9,11-secogorgost-5-en-9-one-3β,11,24β-triol, isolated from *Pseudopterogorgia americana* (Gmelin) collected from coral reefs off the Florida Keys (Haertle, 1971; Musmar, 1983; Musmar & Weinheimer, 1990), 24-methylene-9,11-secocholest-5-en-9-one-3β,11-diol and 24-methyl-9,11-secocholest-5-en-9-one-3β,11-diol, both from a soft coral, *Sinularia* sp., collected at Feather Reef, Queensland, Australia (Kazlauskas, Murphy, Ravi, Sanders & Wells, 1982).

Elucidation of the biosynthesis of these marine metabolites has been notoriously difficult, but two points are worth noting here. Some gorgonian metabolites, gorgosterol and 23-desmethylgorgosterol in particular, have been shown to originate from the symbiotic zooxanthellae associated with these soft corals (Withers, Kokke, Fenical & Djerassi, 1982), so the ultimate producer of compound (I) is uncertain. In gorgosterol, the extra C atom, C34, forming the cyclopropane ring has been claimed to originate from methionine (Bonini, Kinnel, Li, Scheuer & Djerassi, 1983).

Since the crystal structure of (I) contains two molecules in the asymmetric unit and the molecular structure has the potential for great flexibility, it is interesting to compare molecules *a* and *b*. The two independent molecules assume remarkably similar conformations overall, including the side chain (see Figs. 1 and 2). Significant differences affecting the gross molecular shape exist at only two points: (i) the torsion angle around the C8—C14 bond connecting ring *B* to ring *D* (C9—C8—C14—C13 is +144.6 and +158.8° in molecules *a* and *b*, respectively), and (ii) the hydroxyl oxygen O(11), oriented very differently in molecules *a* and *b* (O11—C11—C12—C13 is −174.4 and +81.8° in molecules *a* and *b*, respectively). Except for the difference in the hydroxyl oxygen O11, corresponding halves of the two molecules fit on each other rather closely, but the halves are related to each other differently within each molecule because of the different torsion angles around C8—C14.

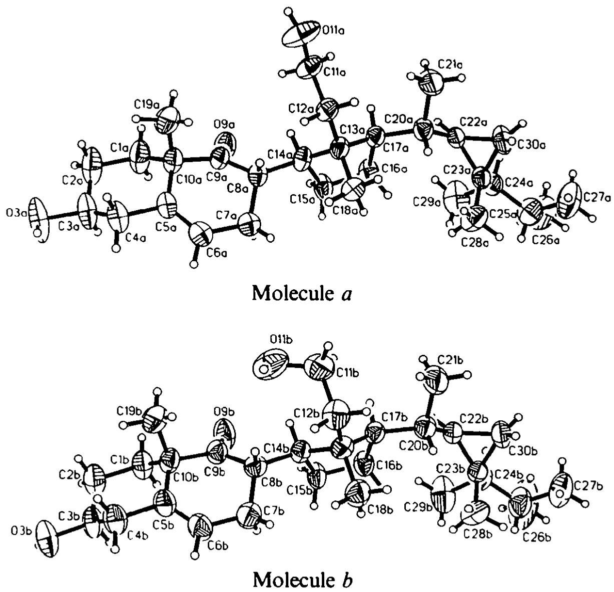


Fig. 1. View of compound (I) showing molecule *a* and molecule *b*, with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary radii.

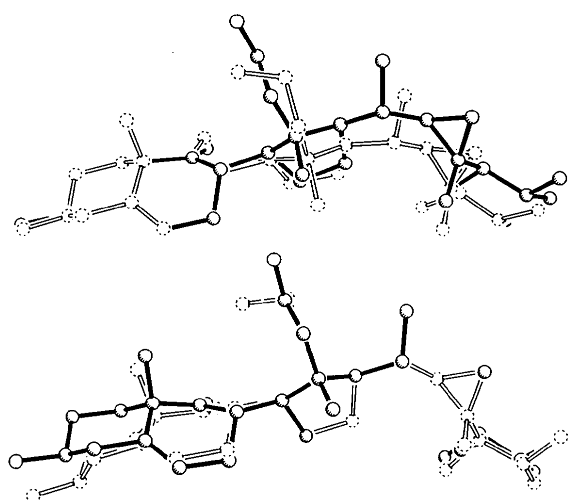


Fig. 2. Overlap diagram showing the least-squares fits of selected corresponding atoms in molecules *a* (solid bonds) and *b* (open bonds); the top view shows C1–C10 and the bottom view C13–C17, C20, C22, C23 and C24.

Within the relatively rigid *A–B* ring system, a further noticeable conformational difference exists: the carbonyl C9—O9 group points out of the ring system at slightly different angles in the two molecules. This is correlated with the torsional difference around C8—C14 mentioned above and connected with significant variations in the conformation of ring *B* as a whole. The relevant torsion angles for molecules *a* and *b* are given in Table 3.

Clearly the largest differences arise from different twists about the bonds C8—C9 and C9—C10. This difference in ring conformation, leading to different carbonyl orientations, and the other differences, in the relative orientation of the two halves of the molecule and the direction of hydroxyl oxygen O11, probably arise from the hydrogen bonding interactions among the molecules in the crystal.

In both molecules, ring *D* (which is not fused to any other ring) assumes an envelope conformation, with the quaternary atom C13 as the point of the flap. Torsion angles in ring *D* for molecules *a* and *b* are given in Table 3.

There are four independent hydrogen bonds, all intermolecular, forming isolated chains. These hydrogen-bonded chains, which connect molecules along the **a** direction, are indicated in the crystal packing diagram (Fig. 3; see also Table 4).

Each molecule *b* serves as the terminus of one chain and the start of another. While hydroxyl O atoms O3*b*, O3*a* and O11*a* both donate and accept hydrogen bonds, the hydroxyl atom O11*b* only donates. The carbonyl O atom O9*b* accepts a hydrogen bond, but the carbonyl O atom O9*a* does not. This differing involvement of the O atoms in the hydrogen-bonding scheme correlates with all the significant conformational differences between molecules *a* and *b*.

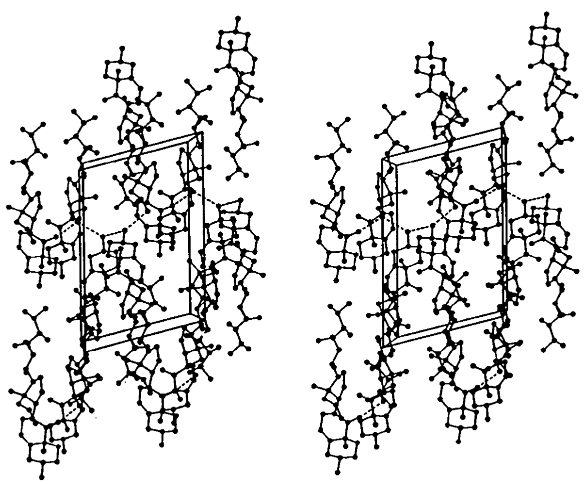


Fig. 3. Stereoscopic crystal packing diagram, viewed down the *b* axis. The *c* axis is vertical. Hydrogen bonds are indicated by dashed lines.

Experimental

Compound (I) was extracted from the sea whip *Pseudopterogorgia hummelinkii* and crystals were prepared by slow evaporation from dichloromethane–isooctane solution. D_m was measured by flotation in a hexane–carbon tetrachloride mixture. The absolute stereochemistry was assumed to correspond to that found earlier by Enwall *et al.* (1972) for a different organismal source of the same molecule.

Crystal data

$C_{30}H_{50}O_3$
$M_r = 458.73$
Monoclinic
$P2_1$
$a = 11.186$ (1) Å
$b = 15.064$ (3) Å
$c = 17.281$ (5) Å
$\beta = 103.90$ (2)°
$V = 2826.7$ Å^3
$Z = 4$
$D_x = 1.078$ Mg m^{-3}
$D_m = 1.077$ (5) Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 15.39$–$22.48°$
$\mu = 0.486$ mm^{-1}
$T = 296$ K
Block
0.25 × 0.21 × 0.20 mm
Colorless

Data collection

Siemens *R3m/V* diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4186 measured reflections
4028 independent reflections
3602 observed reflections [$F > 4\sigma(F)$]

$R_{int} = 0.0217$
$\theta_{max} = 58°$
$h = -12 \rightarrow 11$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 18$
3 standard reflections monitored every 50 reflections intensity decay: ±2.6%

Refinement

Refinement on F
$R = 0.0529$ (all data)
$wR = 0.0674$ (all data)
$S = 1.1313$
4028 reflections
650 parameters
$w = 1/[\sigma^2(F) + 0.0025F^2]$
$(\Delta/\sigma)_{max} = 0.34$

$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C1*a*	0.2965 (4)	0.8002	0.5981 (3)	0.077 (2)
C2*a*	0.2832 (4)	0.7642 (6)	0.5141 (3)	0.087 (2)
C3*a*	0.1827 (4)	0.6959 (6)	0.4942 (2)	0.077 (2)
O3*a*	0.1756 (3)	0.6619 (5)	0.4147 (2)	0.100 (2)
C4*a*	0.0609 (4)	0.7335 (6)	0.5031 (2)	0.065 (2)
C5*a*	0.0738 (3)	0.7718 (5)	0.5859 (2)	0.052 (1)
C6*a*	0.0053 (4)	0.7442 (5)	0.6341 (2)	0.061 (1)
C7*a*	0.0149 (5)	0.7800 (5)	0.7172 (3)	0.069 (2)
C8*a*	0.0744 (3)	0.8725 (5)	0.7269 (2)	0.046 (1)
C9*a*	0.1913 (3)	0.8602 (5)	0.6996 (2)	0.048 (1)
O9*a*	0.2926 (2)	0.8615 (5)	0.7456 (2)	0.063 (1)

C10*a*	0.1750 (3)	0.8399 (5)	0.6111 (2)	0.052 (1)
C19*a*	0.1458 (5)	0.9286 (6)	0.5655 (3)	0.079 (2)
O11*a*	0.0420 (3)	1.1829 (5)	0.6985 (2)	0.089 (1)
C11*a*	0.0838 (4)	1.1141 (5)	0.7538 (2)	0.058 (1)
C12*a*	−0.0260 (3)	1.0602 (5)	0.7626 (2)	0.047 (1)
C13*a*	−0.0037 (3)	0.9834 (5)	0.8230 (2)	0.042 (1)
C18*a*	−0.1264 (3)	0.9363 (5)	0.8145 (2)	0.055 (1)
C14*a*	0.0980 (3)	0.9182 (5)	0.8094 (2)	0.048 (1)
C15*a*	0.1245 (4)	0.8594 (5)	0.8837 (2)	0.057 (1)
C16*a*	0.1025 (4)	0.9188 (5)	0.9508 (2)	0.054 (1)
C17*a*	0.0547 (3)	1.0094 (5)	0.9123 (2)	0.043 (1)
C20*a*	−0.0244 (3)	1.0643 (5)	0.9562 (2)	0.048 (1)
C21*a*	−0.0209 (5)	1.1634 (5)	0.9368 (3)	0.075 (2)
C22*a*	0.0108 (3)	1.0554 (5)	1.0472 (2)	0.045 (1)
C23*a*	−0.0476 (3)	0.9955 (5)	1.0980 (2)	0.047 (1)
C34*a*	−0.0772 (5)	1.0924 (5)	1.0914 (3)	0.067 (2)
C33*a*	−0.1448 (4)	0.9295 (6)	1.0593 (3)	0.072 (2)
C24*a*	0.0366 (3)	0.9663 (5)	1.1777 (2)	0.054 (1)
C28*a*	0.1246 (5)	0.8939 (6)	1.1666 (3)	0.095 (2)
C25*a*	−0.0342 (5)	0.9393 (6)	1.2406 (3)	0.077 (2)
C26*a*	0.0512 (6)	0.9200 (7)	1.3215 (3)	0.115 (3)
C27*a*	−0.1297 (6)	1.0068 (7)	1.2506 (3)	0.103 (3)
C1*b*	0.7663 (4)	0.8858 (6)	0.4705 (2)	0.067 (2)
C2*b*	0.7522 (4)	0.9411 (6)	0.5422 (3)	0.079 (2)
C3*b*	0.6384 (4)	0.9977 (5)	0.5208 (2)	0.065 (2)
O3*b*	0.6246 (3)	1.0516 (5)	0.5865 (2)	0.081 (1)
C4*b*	0.5250 (4)	0.9414 (5)	0.4930 (3)	0.065 (2)
C5*b*	0.5373 (3)	0.8851 (5)	0.4220 (2)	0.058 (1)
C6*b*	0.4583 (4)	0.8915 (6)	0.3518 (3)	0.069 (2)
C7*b*	0.4727 (5)	0.8451 (6)	0.2772 (3)	0.086 (2)
C8*b*	0.5520 (3)	0.7625 (5)	0.2949 (2)	0.050 (1)
C9*b*	0.6683 (3)	0.7870 (5)	0.3583 (2)	0.053 (1)
O9*b*	0.7696 (3)	0.7730 (5)	0.3487 (2)	0.078 (1)
C10*b*	0.6522 (3)	0.8278 (5)	0.4352 (2)	0.053 (1)
C19*b*	0.6434 (5)	0.7480 (6)	0.4900 (3)	0.084 (2)
O11*b*	0.5778 (4)	0.5563 (5)	0.3432 (2)	0.098 (2)
C11*b*	0.5249 (5)	0.5207 (6)	0.2660 (3)	0.079 (2)
C12*b*	0.4350 (4)	0.5816 (5)	0.2134 (3)	0.066 (2)
C13*b*	0.4859 (3)	0.6557 (5)	0.1686 (2)	0.050 (1)
C18*b*	0.3733 (4)	0.7101 (6)	0.1232 (3)	0.069 (2)
C14*b*	0.5839 (3)	0.7142 (5)	0.2239 (2)	0.046 (1)
C15*b*	0.6361 (4)	0.7702 (5)	0.1663 (2)	0.058 (1)
C16*b*	0.6242 (4)	0.7116 (5)	0.0916 (2)	0.055 (1)
C17*b*	0.5636 (3)	0.6246 (5)	0.1099 (2)	0.044 (1)
C20*b*	0.5015 (3)	0.5679 (3)	0.0362 (2)	0.051 (1)
C21*b*	0.5017 (6)	0.4685 (5)	0.0592 (3)	0.082 (2)
C22*b*	0.5640 (3)	0.5756 (5)	−0.0329 (2)	0.048 (1)
C23*b*	0.5216 (3)	0.6323 (5)	−0.1075 (2)	0.048 (1)
C34*b*	0.5012 (5)	0.5338 (5)	−0.1109 (3)	0.067 (2)
C33*b*	0.4104 (4)	0.6926 (6)	−0.1145 (3)	0.075 (2)
C24*b*	0.6208 (4)	0.6663 (5)	−0.1463 (2)	0.061 (1)
C28*b*	0.6873 (6)	0.7472 (6)	−0.1031 (3)	0.099 (2)
C25*b*	0.5739 (6)	0.6856 (6)	−0.2365 (3)	0.088 (2)
C26*b*	0.6742 (9)	0.7139 (9)	−0.2740 (4)	0.176 (5)
C27*b*	0.4985 (8)	0.6123 (7)	−0.2826 (3)	0.125 (3)

Table 2. *Selected geometric parameters* (Å, °)

	Molecule *a*	Molecule *b*
C1—C2	1.522 (7)	1.533 (9)
C1—C10	1.551 (6)	1.546 (8)
C2—C3	1.502 (10)	1.502 (8)
C3—O3	1.450 (6)	1.434 (8)
C3—C4	1.517 (8)	1.505 (8)
C4—C5	1.517 (7)	1.524 (8)
C5—C6	1.327 (7)	1.322 (5)
C5—C10	1.512 (8)	1.520 (8)
C6—C7	1.513 (7)	1.508 (8)
C7—C8	1.536 (10)	1.516 (10)
C8—C9	1.504 (6)	1.532 (5)
C8—C14	1.548 (6)	1.540 (7)
C9—O9	1.218 (4)	1.203 (5)
C9—C10	1.526 (5)	1.512 (7)
C10—C19	1.546 (10)	1.548 (10)
O11—C11	1.412 (9)	1.427 (7)
C11—C12	1.510 (8)	1.496 (9)
C12—C13	1.537 (8)	1.543 (9)
C13—C18	1.520 (7)	1.549 (7)
C13—C14	1.563 (8)	1.545 (7)
C13—C17	1.574 (5)	1.559 (6)
C14—C15	1.529 (7)	1.524 (8)
C15—C16	1.531 (8)	1.544 (8)
C16—C17	1.555 (9)	1.543 (10)
C17—C20	1.538 (7)	1.552 (7)
C20—C21	1.533 (11)	1.549 (11)
C20—C22	1.533 (5)	1.527 (6)
C22—C23	1.512 (8)	1.524 (7)
C22—C34	1.492 (7)	1.500 (7)
C23—C34	1.495 (11)	1.499 (11)
C23—C33	1.507 (8)	1.521 (8)
C23—C24	1.534 (5)	1.517 (7)
C24—C28	1.513 (10)	1.526 (10)
C24—C25	1.545 (7)	1.549 (6)
C25—C26	1.520 (7)	1.486 (12)
C25—C27	1.515 (11)	1.498 (12)
C2—C1—C10	112.8 (3)	113.1 (4)
C1—C2—C3	111.1 (4)	110.7 (4)
C2—C3—O3	109.1 (5)	111.8 (4)
C2—C3—C4	111.2 (6)	111.0 (6)
O3—C3—C4	112.4 (3)	109.2 (4)
C3—C4—C5	110.7 (3)	109.8 (4)
C4—C5—C6	122.3 (5)	121.9 (5)
C4—C5—C10	115.2 (4)	115.6 (3)
C6—C5—C10	122.4 (4)	122.3 (5)
C5—C6—C7	124.4 (6)	124.4 (5)
C6—C7—C8	110.9 (5)	112.7 (4)
C7—C8—C9	103.9 (5)	107.6 (6)
C7—C8—C14	118.6 (4)	117.6 (4)
C9—C8—C14	112.0 (3)	111.4 (3)
C8—C9—O9	122.4 (3)	121.6 (4)
C8—C9—C10	115.8 (3)	117.8 (3)
O9—C9—C10	121.7 (4)	120.5 (4)
C1—C10—C5	108.5 (5)	109.0 (6)
C1—C10—C9	108.9 (3)	108.4 (4)
C5—C10—C9	109.0 (4)	112.0 (3)
C1—C10—C19	110.1 (4)	111.4 (4)
C5—C10—C19	112.8 (4)	110.9 (4)
C9—C10—C19	107.3 (5)	105.1 (6)
O11—C11—C12	108.5 (4)	113.8 (6)
C11—C12—C13	118.0 (3)	118.3 (4)
C12—C13—C18	106.9 (3)	106.6 (4)
C12—C13—C14	112.1 (3)	113.3 (3)
C18—C13—C14	111.4 (6)	112.4 (6)
C12—C13—C17	116.1 (5)	116.1 (6)
C18—C13—C17	111.3 (3)	109.9 (3)
C14—C13—C17	99.1 (3)	98.6 (3)
C8—C14—C13	116.7 (3)	119.8 (3)
C8—C14—C15	118.1 (6)	117.2 (6)
C13—C14—C15	103.8 (3)	103.8 (3)
C14—C15—C16	105.3 (6)	105.1 (5)
C15—C16—C17	106.8 (4)	105.5 (4)
C13—C17—C16	102.8 (5)	102.7 (5)
C13—C17—C20	117.7 (3)	119.3 (3)
C16—C17—C20	116.1 (4)	115.6 (4)
C17—C20—C21	111.6 (4)	110.5 (4)
C17—C20—C22	115.0 (4)	113.6 (4)
C21—C20—C22	107.1 (5)	107.5 (5)
C20—C22—C23	127.4 (4)	126.6 (4)
C20—C22—C34	117.1 (4)	117.8 (4)
C23—C22—C34	59.7 (4)	59.4 (4)
C22—C23—C34	59.5 (4)	59.5 (4)
C22—C23—C33	120.1 (3)	119.0 (4)
C34—C23—C33	119.2 (4)	118.3 (4)
C22—C23—C24	115.8 (3)	116.8 (3)
C34—C23—C24	115.2 (5)	115.9 (5)
C33—C23—C24	115.5 (6)	115.7 (6)
C22—C34—C23	60.8 (4)	61.1 (4)
C23—C24—C28	111.7 (4)	112.1 (5)
C23—C24—C25	113.5 (3)	113.6 (4)
C28—C24—C25	111.0 (6)	110.4 (6)
C24—C25—C26	112.5 (5)	112.6 (5)
C24—C25—C27	113.5 (6)	114.1 (7)
C26—C25—C27	109.1 (5)	111.6 (6)

Table 3. *Selected torsion angles* (°)

	Molecule *a*	Molecule *b*
Within the six-membered ring *B*		
C10—C5—C6—C7	3.2	−1.0
C5—C6—C7—C8	21.5	24.4
C6—C7—C8—C9	−52.0	−47.6
C7—C8—C9—C10	67.1	54.9
C8—C9—C10—C5	−43.8	−33.1
C6—C5—C10—C9	6.5	4.7
Involving ring *B* substituents		
C4—C5—C6—C7	179.8	173.2
C6—C7—C8—C14	−177.0	−174.3
C14—C8—C9—O9	20.0	3.7
C7—C8—C9—O9	−109.1	−126.6
O9—C9—C10—C5	132.4	148.4
O9—C9—C10—C19	−105.0	−91.1
C8—C9—C10—C1	−162.1	−153.4
O9—C9—C10—C1	14.2	28.1
C6—C5—C10—C1	125.0	124.6
Within the five-membered ring *D*		
C17—C13—C14—C15	45.8	46.9
C13—C14—C15—C16	−31.4	−30.1
C14—C15—C16—C17	3.9	0.8
C15—C16—C17—C13	24.8	28.4
C14—C13—C17—C16	−42.6	−45.8

Table 4. *Hydrogen-bond distances* (Å)

O11*b*···O3*b*^{i}	2.815	O3*a*···O11*a*^{iii}	2.750
O3*b*···O3*a*^{ii}	2.790	O11*a*···O9*b*^{ii}	2.788

Symmetry codes: (i) $1 - x, y - \frac{1}{2}, 1 - z$; (ii) $1 - x, \frac{1}{2} + y, 1 - z$; (iii) $-x, y - \frac{1}{2}, 1 - z$.

This crystal structure proved notably difficult to solve with direct methods. Phase development from small starting sets (*MULTAN*88; Debaerdemaeker, Germain, Main, Refaat, Tate & Woolfson, 1988) was unsuccessful, using either the statistically weighted tangent formula (Hull & Irwin, 1978) (various parameter choices, total of 1276 starting points) or the Sayre equation tangent formula (Debaerdemaeker, Tate & Woolfson, 1985) (various parameter choices, total of 1888 starting points). The algorithms in *SHELXTL-Plus* (Sheldrick, 1990), which use random starting values for all phases and weighted tangent formula phase development, also failed (21 different parameter combinations tried, total of 45 350 starting points). The structure was finally solved, using *MULTAN*88, only when random starting values for all phases were assigned (*RANTAN*; Yao, 1981) and phases were developed using the Sayre equation tangent formula (*SAYTAN*), with both 'big' and 'zero' quartets included (Debaerdemaeker, Tate & Woolfson, 1988). Various parameter combinations were tried; a total of 5112 starting points were used. The final successful parameter combination solved the structure from starting point 2761; this was recognized from the figures of merit (ABSFOM 0.966, PSIZERO 0.775, RESID 16.82, CFOM 2.926) and so the program stopped.

The parameter 0.0025 in the weighting scheme was found to give the most uniform distribution of the variance S as a function of $|F|$.

H-atom positions were determined using a riding model, with CH_3 groups as rigid bodies. One isotropic U was assigned for the CH_3 H atoms, another for the other H atoms.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1102). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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