Journal of Natural Products
Vol. 58, No. 10, pp. 1581-1586, October 1995

ANTHELIATIN AND ZAHAVINS A AND B, THREE NEW CYTOTOXIC XENICANE DITERPENES FROM TWO SOFT CORALS

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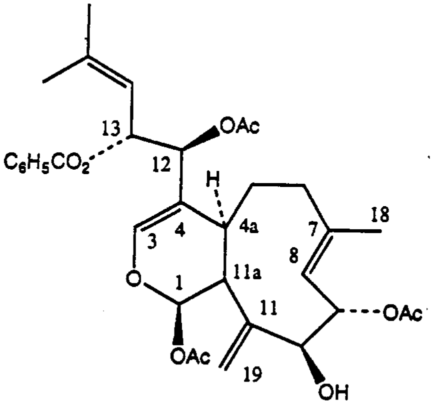
ABSTRACT.—Antheliatin [**1**], zahavin A [**2**], and zahavin B [**3**], three novel xenicane diterpenoids, have been isolated from two Indo-Pacific soft corals, *Anthelia glauca* and *Alcyonium aureum*. The two species belong to different families of reef-inhabiting soft corals. The structures of compounds **1–3** were established on the basis of X-ray and 1D and 2D nmr data.

Marine organisms, especially soft corals, sponges, and tunicates, provide many secondary metabolites that exhibit varying degrees of biological activity (1). Earlier investigations of *Anthelia glauca* Lammarck 1816 (Xeniidae), collected from the entrance to the Gulf of Suez in the northern part of the Red Sea, led to the isolation of xeniculin, xeniolides A and B, 4-isoxeniolide A, 9-desacetylxenicin, 9-acetoacetyl-9-desacetylxenicin, and antheliolides A and B (2–4). Several cembranoids, compounds which are very common in many soft corals (1), were also isolated from *Alcyonium utinomii* (Alcyoniidae) collected from the Gulf of Eilat (5).

Soft corals of the Alcyoniidae and Xeniidae are widespread in many coral reefs. *Anthelia* colonies tend to grow among other soft corals, mainly those of the Xeniidae (6). *An. glauca* is the most common species of the genus and has a wide zoogeographical distribution throughout the Indo-Pacific region (7). *Alcyonium aureum*, found at a depth of between 28 and 36 meters, is a newly described azooxanthellated species collected at Sodwana Bay (8).

As part of our investigation of soft corals (2, 5, 9–13) we were interested in comparing Red Sea soft corals with their Indo-Pacific counterparts. The results of the investigation of two Indo-Pacific soft corals from two different reef-inhabiting families, *An. glauca* (Xeniidae) (14) and *Al. aureum* (Benayahu, 1995, Alcyoniidae) (8), from Sodwana Bay, South Africa, are the subject of this report.

The Sodwana Bay *An. glauca,* in contrast to the Red Sea species, was found to contain a single diterpenoid designated antheliatin [**1**], a crystalline material, mp 165° (MeOH), [α]D +3.5° (c=1.2, $CHCl_3$), 0.2% dry wt. A molecular formula of $C_{33}H_{40}O_{10}$ was established by hrms (M^+ 596.2627; calcd mol wt 596.2622) and ^{13}C-nmr data. Twelve of the fourteen degrees of unsaturation implied by the molecular formula were due



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to four double bonds, three acetates, and one benzoate (Table 1), and the molecule was thus considered bicyclic.

The ir data (3450 cm^{-1}) and the preparation of a monoacetate by microacetylation of **1** (shift of H-10 from δ 4.12 ppm in **1** to δ 5.25 ppm in the monoacetate), confirmed the presence of a secondary hydroxyl function. Interpretation of nmr spectra recorded for **1** (DEPT, COSY, TOCSY, nOe, HMQC, and HMBC, see Table 1) suggested the xenicane structure and more specifically a xenialactol (4,11,12).

Single-crystal X-ray diffraction analysis of **1** confirmed the suggested structure from the nmr spectra and also determined the stereochemistry of C-12 and C-13 (12*S** and 13*R**) as shown in Figure 1.

NOe correlations observed between H-1/H-11a; H-4a/H-8α and H-11a(β); Me-18/H-11a and H-9β; H-9β/H-10α and H-10α/H-19, suggested the "αβ-conformation" (16) in solution, this is, the C-11(19) methylene inclining towards the α direction and Me-18 towards the β direction, as in the solid state (Figure 1).

The second soft coral, the newly described Indo-Pacific soft coral *Al. aureum*, yielded two additional xenicanes designated as zahavins A and B (compounds **2** and **3**), respectively. The structure elucidation of the two was achieved by interpretation of nmr data. The xenicane skeleton of **2**, *m/z* 460.2462, $C_{26}H_{36}O_7$, was unequivocally determined by comparison of the ^{13}C-nmr chemical shifts of the bicyclic system of **2** with those of 9,13-

TABLE 1. Nmr Data for Antheliatin [**1**][a] and Xenicin.

Position	Antheliatin [1]							Xenicin[b]
	δ ^{13}C	δ ^{1}H	m	*J* (Hz)	COSY	HMBC (H to C)	nOe	δ ^{13}C
1	91.9	5.77	d	1.9	11a	3,11a,19,19′	11a	91.7
3	138.3	6.45	s		12			142.6
4	113.4	—				3,4a,5,11a,12		113.5
4a	38.4	2.05	m			1,3,5,5′,6,6′,11a		37.1
5	28.7	2.00	m		4a,5,6,6′	11a		30.5
5′		1.55	m		4a,5′,6,6′			
6	40.8	2.32	br d	12.1	6,5,5′	18,19,19′		40.8
6′		2.10	m		6′,5,5′			
7	137.3	—				5′,18		134.3
8	122.0	5.00	d	9.2	9,18	6,9,10,18	OAc-9	126.2
9	76.9	5.42	d	9.2	8,10	10	10	70.6
10	83.1	4.12	br s		9,OH	9,11a,19,19′	1,9,19′	42.9
11	149.1	—				1,9,10,11a,18		146.5
11a	43.1	2.30	br s		1,19′	19′	1	43.1
12	71.6	5.69	d	4.2		3	3	76.4
13	71.9	5.86	dd	9.3,4.2	12,14			69.8
14	118.5	5.34	dd	9.3,0.9	13,16,17	12,13,16,17		119.6
15	140.8					16,17		140.7
16	18.9	1.79	s		14	14,17		18.9
17	25.9	1.71	s		14	14,16		25.6
18	18.0	1.78	s		8	8	9,11a,13	17.5
19	115.2	4.95	s		19′	10,11a	19′	116.1
19′		4.90	s		11a,19		10,19	
1′	165.6	—				3′,7′,13		
2′	130.1	—				3′,7′		
3′,7′	129.6	7.95	d	7.7	4′,6′	4′,5′,6′		
4′,6′	128.4	7.32	t	7.7	3′,5′	3′,5′,7′		
5′	133.0	7.50	t	7.7	3′,4′	3′,7′		
OAc-1	169.7	—				1, $OCOCH_3$		
	20.1	1.92	s					
OAc-9	170.9					9, $OCOCH_3$		
	20.9	2.05	s					
OAc-12	169.8					12, $OCOCH_3$		
	21.2	2.10	s					

[a] $CDCl_3$; 500 MHz for ^{1}H, 125 MHz for ^{13}C; ^{13}C-nmr resonances assigned by a HMQC experiment.

[b] Data taken from Vanderah *et al.* (4).

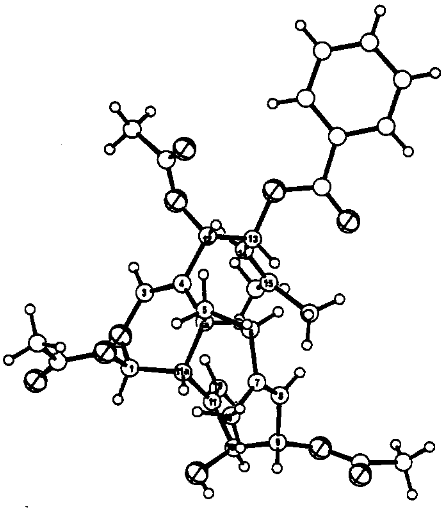


FIGURE 1. ORTEP illustration of **1**.

desacetoxyxenicin previously isolated from *Xenia obscuronata* (12) (Table 2). The complete nmr assignments were achieved from 2D nmr experiments (HMQC, COSY, HMBC). Except for small differences in the chemical shifts of C-3, C-4, and C-4a, due to the different C-4 side-chain (C-12 to C-17), the remaining ^{13}C-nmr chemical shifts for the bicyclic system are in good agreement with the corresponding data found in 9,13-desacetoxyxenicin (12,17). The structure of the side-chain [$-CH(OAc)CH_2CH(OAc)C(CH_3)=CH_2$] was suggested on the basis of its nmr data and particularly the COSY spectrum (Table 2). Due to the conformational mobility of this moiety it was not possible to determine the relative stereochemistry of C-12 and C-14. The small amount of compound available, and its apparent instability, precluded chemical transformations which could shed light on the stereochemistry of C-12 and C-14.

Zahavin B [**3**], *m/z* 476.2411, $C_{26}H_{36}O_8$, is closely related to zahavin A. It possesses the bicyclo[7.4.0]tridecane

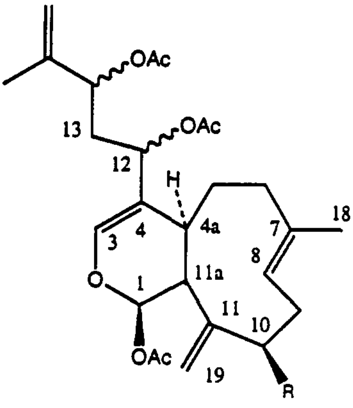
TABLE 2. Nmr Data for Zahavins A [**2**] and B [**3**].[a]

Position	**2**					**3**			9,13-Desacetoxyxenicin[c]
	δ ^{13}C	δ ^{1}H	m(*J*, Hz)	COSY	HMBC	δ ^{13}C	δ ^{1}H	m	δ ^{13}C
1	92.0	5.79	d (2.3)	11a	3,4a,19,19′	92.8	5.79	d (2.3)	91.8
3	137.0	6.33	s		1,12	137.0	6.33	s	140.7
4	117.2				3,12,13,13′	117.1			115.9
4a	37.5	1.90	m		1,3,6,6′	37.7	2.40	m	36.7
5	30.1	1.83	m	4a,5′,6,6′	11a	29.6	1.92	m	30.5
5′.......		1.49	m	4a,5,6,6′			1.60	m	
6	40.2	2.19	m	5,5′,6′	8,18	40.6	2.28	m	40.0
6′.......		1.92	m	5,5′,6			2.05	m	
7	135.6				18	137.3			134.3
8	124.5	5.30	m	9,9′,18	5,18	121.2	5.17	dd (7.2,10.1)	124.3
9	25.2	2.41	m	8,9′,10,10′	8,19′	35.2	2.50	m	25.0
9′.......		2.05	m	8,9,10,10′			2.50	m	
10	35.4	2.00(2H)	m	9,9′,10′	19,19′	76.2	4.67	dd (7.3,2.1)	35.4
11	150.0				1,9,10,10′,19,19′	152.3			151.2
11a	49.5	1.94	m		5,5′,10,10′,19,19′	42.9	2.47	m	49.3
12	68.9	5.28	m		3	68.9	5.34	dd (10.2,4.3)	74.9
13	38.5	1.92	m	13′,14		38.6	1.92	m	31.1
13′......		1.88	m	13,14			1.92	m	
14	73.2	5.16	dd (8.5,3.5)	13,13′	16,16′,17	73.2	5.23	dd (9.3,4.2)	119.0
15	142.9				14,16,17	142.9			135.8
16	112.7	4.91	br s	16′,17	13,13′,14,17	112.8	4.99	s	18.1
16′......		4.84	br t (1.5)	16,17			4.95	s	
17	18.3	1.69	s		16,16′	18.3	1.55	s	25.7
18	16.8	1.69	s	8	8	17.2	1.72	s	16.7
19	113.4	4.23	br s	—	—	113.4	5.06	s	113.1
		4.77	br d (1.1)				5.02	s	
1 OAc ...	(170.1, 21.0, 2.05 s)[b]				$1-CH_3$	(170.0, 21.0, 2.0 s)			
12 OAc ..	(169.8, 21.0, 2.05 s)[b]				$12-CH_3$	(169.8, 21.0, 2.0 s)			
14 OAc ..	(169.7, 21.0, 1.98 s)[b]				$14-CH_3$	(169.0, 21.0, 2.0 s)			

[a] $CDCl_3$; 500 MHz for ^{1}H, 125 MHz for ^{13}C. Carbon resonances assigned by a HMQC experiment.

[b] May be interchanged.

[c] Data taken from Groweiss and Kashman (12).



2 R=H
3 R=OH

system and the same side-chain. Zahavin B, however, carries an additional secondary hydroxyl group at C-10 (δ_C 76.2; δ_H 4.67 (dd), J=7.3 and 2.1 Hz). The location of this group was proposed mainly on the basis of the following CH correlations, deduced from an HMBC experiment: C-8/H-10; C-10/H-19; C-11a/H-19 as well as from COSY correlations, i.e., H-10/9,9′ and H-8/9,9′. In addition, the chemical shifts of C-9 and C-11a also supported the C-10 location of the OH-group; if the OH group were at C-9 the resonance of C-10 should be at approximately 46 ppm as in xenicin, and not at 35.2 ppm. The upfield shift of 6 ppm of C-11a, to 42.9 ppm, due to a strong γ-effect of the 10-OH group, is in good agreement with the latter position. Zahavin B [**3**] is unstable under both mild base and mild acid conditions, and it decomposed readily under acetylation conditions (Ac_2O, pyridine, CH_2Cl_2) or in $CDCl_3$ solution.

The conformation of the bicyclic system of **3** and the stereochemistry of the secondary hydroxyl group were determined from nOe difference measurements. An nOe correlation between Me-18 and H-11a (β) and H-6 (β) (δ_H 2.28) determined the conformation of the Me-18 group to be on the same side as H-11a (β). The latter nOe's together with the measurable proton coupling constants, require the $\Delta^{11(19)}$ double bond to be in the α orientation. Thus, **3** has the same "αβ-conformation" (15,16) as antheliatin. Another nOe between H-19 (α) and H-10 determined the α configuration for H-10 and thus the β-configuration for the 10-OH group. The latter configuration is also in full agreement with the above-mentioned γ-effect of the alcohol on C-11a.

Xenicanes, which were once thought to be characteristic of the genus *Xenia*, have already been found in the closely related genus *Anthelia* (2,3). However, the discovery of xenicanes in *Alcyonium*, belonging to the different family Alcyoniidae, is of special interest. Despite the similarities in the diterpenes of *An. glauca* and *Al. aureum*, they represent opposing biological traits. The distinct systematic differences and barriers between *An. glauca* and *Al. aureum* challenge the possibility of using their secondary metabolites for taxonomic purposes. The biosynthetic mechanism producing the chemical resemblance between these two species is still awaiting further study.

All three new compounds [**1**–**3**] were cytotoxic towards P-388 mouse leukemia, A-549 human lung carcinoma, MEL-28 human melanoma, and HT-29 human colon carcinoma cell lines, with IC_{50} values of 1 μg/ml for almost all tumor cells; for **1** towards the HT-29 system, the IC_{50} value was found to be 0.1 μg/ml.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Ir spectra were recorded on a Nicolet 205 Ft-ir spectrophotometer. Lrms were recorded on a Finnigan-4021 mass spectrometer. Hrms were taken on a VG70 VSEQ instrument. ^1H- and ^{13}C-nmr spectra were recorded on Bruker AMX-360 and ARX-500 spectrometers. All chemical shifts are reported with respect to TMS (δ=0). Optical rotations were measured on a Perkin-Elmer model 141 polarimeter using a 1-cm microcell.

ANIMAL MATERIAL.—The soft coral *Anthelia glauca* was collected in Sodwana Bay, South Africa, in May 1994, by divers using scuba. A voucher (TASA 293) is deposited in the Zoological Department at Tel Aviv University. *Alcyonium aureum* was collected in Sodwana Bay, South Africa, in May 1994 by divers using scuba. A voucher (TASA 217) is deposited in the Zoological Department at Tel Aviv University.

EXTRACTION AND ISOLATION.—Freshly collected *An. glauca* was immediately frozen at −25°. The freeze-dried coral, a single animal (5 g), was then extracted with EtOAc to give brown gum (90 mg). The gum was chromatographed first over a Sephadex LH-20 column eluted with MeOH-$CHCl_3$-hexane (1:1:2) and then over Si gel eluted with hexane-EtOAc (1:1) to afford antheliatin [**1**] (10 mg). Freeze-dried *Al. aureum*, a single animal (9 g), was extracted with EtOAc to give a yellowish gum (155 mg). The gum was chromatographed first over a Sephadex LH-20 column eluted with MeOH-$CHCl_3$-hexane, 1:1:2) and then several times over Si gel columns eluted with hexane-EtOAc (8:2) to afford zahavins A [**2**] and B [**3**].

TABLE 3. Atomic Coordinates and Equivalent Isotropic Thermal Parameters of **1**.

Atom	*x/a*	*y/b*	*z/c*	U_{eq}[a]
C-1	−0.3088 (5)	0.4440 (5)	0.6879 (3)	0.0557 (19)
O-1a	−0.4220 (3)	0.3751 (4)	0.6275 (2)	0.0663 (14)
C-1b	−0.5233 (7)	0.4344 (9)	0.5612 (5)	0.1051 (34)
O-1c	−0.5182 (8)	0.5429 (7)	0.5480 (4)	0.1527 (32)
C-1d	−0.6324 (9)	0.3512 (16)	0.5041 (10)	0.1632 (62)
O-2	−0.2267 (4)	0.4700 (3)	0.6346 (2)	0.0600 (14)
C-3	−0.1507 (5)	0.3744 (5)	0.6237 (3)	0.0525 (19)
C-4	−0.1285 (4)	0.2727 (4)	0.6747 (3)	0.0415 (16)
C-4a	−0.1814 (4)	0.2502 (4)	0.7558 (3)	0.0390 (17)
C-5	−0.2737 (5)	0.1402 (4)	0.7415 (4)	0.0510 (21)
C-6	−0.2568 (5)	0.0765 (4)	0.8387 (4)	0.0567 (20)
C-7	−0.2705 (5)	0.1662 (4)	0.9131 (4)	0.0498 (20)
C-7a	−0.4101 (5)	0.1884 (6)	0.9100 (5)	0.0705 (24)
C-8	−0.1650 (4)	0.2275 (4)	0.9672 (3)	0.0467 (18)
C-9	−0.1612 (4)	0.3429 (5)	1.0201 (3)	0.0497 (18)
O-9a	−0.0308 (3)	0.3565 (4)	1.0969 (2)	0.0677 (15)
C-9b	−0.0123 (7)	0.2970 (6)	1.1806 (4)	0.0663 (23)
C-9c	0.1279 (8)	0.3039 (7)	1.2511 (5)	0.1041 (32)
O-9d	−0.1036 (5)	0.2440 (5)	1.1938 (3)	0.0949 (22)
C-10	−0.1794 (4)	0.4575 (4)	0.9543 (3)	0.0471 (17)
O-10a	−0.3153 (3)	0.4957 (4)	0.9234 (2)	0.0617 (13)
C-11	−0.1455 (4)	0.4417 (4)	0.8639 (3)	0.0431 (17)
C-11a	−0.2433 (4)	0.3680 (4)	0.7801 (3)	0.0417 (15)
C-11b	−0.0373 (5)	0.4905 (5)	0.8587 (4)	0.0566 (20)
C-12	−0.0346 (4)	0.1804 (4)	0.6606 (3)	0.0441 (17)
O-12a	−0.0206 (4)	0.1996 (3)	0.5674 (2)	0.0555 (14)
C-12b	−0.0493 (6)	0.1081 (7)	0.5029 (4)	0.0691 (26)
O-12c	−0.0769 (7)	0.0099 (5)	0.5197 (4)	0.1114 (29)
C-12d	−0.0276 (10)	0.1501 (9)	0.4116 (5)	0.1120 (39)
C-13	0.1036 (5)	0.1874 (5)	0.7390 (3)	0.0546 (19)
C-14	0.1780 (6)	0.2995 (6)	0.7387 (5)	0.0753 (27)
C-15	0.2466 (6)	0.3669 (8)	0.8181 (8)	0.1126 (40)
C-16	0.2608 (9)	0.3377 (10)	0.9205 (7)	0.1499 (52)
C-17	0.3183 (9)	0.4804 (9)	0.8045 (11)	0.1864 (76)
O-18	0.1772 (3)	0.0862 (4)	0.7176 (2)	0.0599 (14)
C-19	0.2664 (5)	0.0275 (5)	0.7916 (3)	0.0488 (20)
O-19a	0.2837 (4)	0.0485 (4)	0.8757 (2)	0.0614 (15)
C-20	0.3364 (5)	−0.0659 (5)	0.7578 (4)	0.0504 (19)
C-21	0.4283 (5)	−0.1388 (6)	0.8264 (4)	0.0671 (23)
C-22	0.4963 (7)	−0.2275 (7)	0.7978 (6)	0.0906 (34)
C-23	0.4708 (8)	−0.2438 (8)	0.7000 (7)	0.1040 (41)
C-24	0.3818 (9)	−0.1767 (10)	0.6327 (6)	0.1230 (41)
C-25	0.3153 (8)	−0.0858 (7)	0.6606 (4)	0.0937 (35)

[a] U_{eq} is one third of the trace of the orthogonalized U_{ij} tensor.

Antheliatin [**1**].—Crystalline; mp 165° (MeOH); $[\alpha]^{20}D$ +3.5° (c=1.2, $CHCl_3$); ir (neat) ν max 3485, 2950, 1740, 1710, 1451 cm^{-1}; nmr data, see Table 1; hreims m/z 597.2707 (MH^+, $C_{33}H_{41}O_{10}$) (calcd 597.2700).

Zahavin A [**2**].—A viscous oil (30 mg; R_f 0.7, EtOAc-hexane, 1:1); $[\alpha]^{20}D$ +7.3° (c=1.8, $CHCl_3$); ir (neat) ν max 2950, 1740, 1372, 1238 cm^{-1}; ^1H- and ^{13}C-nmr data, see Table 2; hreims m/z 461.2546 (MH^+, $C_{26}H_{37}O_7$) (calcd 461.2540).

Zahavin B [**3**].—A viscous oil (5 mg; R_f 0.65); $[\alpha]^{20}D$ +4.8° (c=0.7, $CHCl_3$); ir (neat) ν max 3460, 2925, 1743, 1372, 1238 cm^{-1}; nmr data, see Table 2; hreims m/z 477.2493 (MH^+, $C_{26}H_{37}O_8$) (calcd 477.2489).

X-RAY CRYSTALLOGRAPHY OF **1**[1].—The X-ray diffraction measurements of **1** were carried out at room temperature (ca. 298° K) on an automated CAD4 diffractometer equipped with a graphite monochromator, using MoKα (λ=0.7107 Å) radiation. Intensity data were collected out to $2\theta=50°$ by the ω-2θ scan mode with a constant scan speed of 4°/min. Possible deterioration of the analyzed crystal was tested by detecting periodically the intensities of three standard reflections from different zones of the reciprocal space, and was found to be negligible during the experiment. A total of 2840 unique reflections with positive intensities was recorded. No corrections for absorption or secondary extinction effects were applied. Crystal data: $C_{33}H_{40}O_{10}$, formula weight 596.67, monoclinic, space group $P2_1$, a=10.728(5), b=11.113(6), c=14.662(5) Å, β=111.22(3)°, V=1629.5 $Å^3$, Z=2, D_{calcd}=1.216 $g.cm^{-3}$, F(000)=636, μ(MoKα)=0.84 cm^{-1}. For atomic coordinates, see Table 3.

The structure was solved by direct methods (SHELXS-86) (19), and refined by full matrix least-squares (SHELXL-93) (20), including the positional and anisotropic thermal parameters of the non-hydrogen atoms. The final refinement, based on F^2, converged at R=0.059 for 2193 observations having $F_o>4\sigma(F_o)$ and R=0.074 for all 2840 data. The hydrogen atoms were introduced in calculated positions, the methyls being treated as rigid groups. The hydroxyl H-atom was located from difference-Fourier maps. At convergence, the peaks and troughs of the final difference density maps did not exceed 0.23 and −0.32 $e.Å^{-3}$, respectively.

ACKNOWLEDGMENTS

We are grateful to PharmaMar SA, Madrid, Spain for the bioassays and for financial support.

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Received 29 November 1994

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[1] Hydrogen coordinates, thermal parameters, bond distances and angles, and observed and calculated structure factors have been deposited with the Cambridge Crystallographic Data Centre and can be obtained upon request from Dr. Olga Kennard, University Chemical Laboratory, 12 Union Road, Cambridge CB2 1EZ, UK.