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ARTICLE *in* JOURNAL OF NATURAL PRODUCTS · MAY 1992

Impact Factor: 3.8 · DOI: 10.1021/np50083a011

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Journal of Natural Products
Vol. 55, No. 5, pp. 626-632, May 1992

A FURTHER C_{15} NONTERPENOID POLYBROMOETHER FROM THE ENCRUSTING SPONGE *MYCALE ROTALIS*

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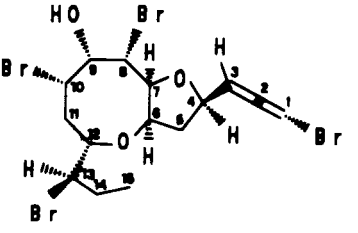
ABSTRACT.—A new cyclic polybrominated C_{15} acetogenin **1** has been isolated from the encrusting sponge *Mycale rotalis*, and its structure has been determined through a combination of spectroscopic and single-crystal X-ray diffraction analyses and simple chemical transformations.

In the course of our systematic studies on Mediterranean organisms, we have investigated the encrusting sponge *Mycale rotalis* Bouterbank (Demospongiae) and isolated rotalins A and B (1), two new diterpenes. More interestingly we found two polybrominated C_{15} acetogenins **2** and **3** (2), typical metabolites of *Laurencia* genus, in the $CHCl_3$ extracts of this animal. We wish to report here that a further investigation of the extractive of *M. rotalis* led us to the isolation of a new cyclic polybrominated metabolite based on a straight C_{15} carbon skeleton.

The structure of the new compound has been established by a combination of spectroscopic methods, including 2D nmr, and some chemical transformations and confirmed by single-crystal X-ray diffraction analysis.

Compound **1** was isolated as an optically active crystalline solid [mp 128–130° (from $CHCl_3$); $[\alpha]^{20}D$ +38.8 (c = 1.3, $CHCl_3$)]. The ei mass spectrum revealed the presence of four bromine atoms in the molecule displaying a cluster of peaks at m/z 564, 566, 568, 570, 572, while the accurate mass measurement established a molecular formula of $C_{15}H_{20}O_3Br_4$ for the new metabolite.

All 15 carbons were observed in the ^{13}C-nmr spectrum of **1** recorded in $CDCl_3$ solution (Table 1), and DEPT experiments demonstrated that 19 protons were attached to



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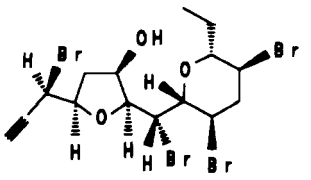

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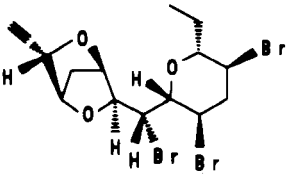

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TABLE 1. ^{1}H- and ^{13}C-nmr Data for Compound **1**.[a]

Position	δ_C[b]	δ_H[c] (mult., *J*)
1	74.0	6.07 (dd, 5.6, 2.1)
2	201.4	
3	103.1	5.56 (dd, 5.6, 5.6)
4	73.7	4.64 (dddd, 5.6, 5.6, 3.6, 2.0)
5	41.1	H_a 2.49 (ddd, 14.6, 5.6, 4.2)
		H_b 2.02 (dd, 14.6, 3.6)
6	70.9	4.50 (bdd, 4.2, 3.4)
7	84.5	4.18 (dd, 9.1, 3.4)
8	54.2	4.31 (d, 9.2)
9	81.3	4.96 (bd, 4.2)
10	55.9	4.35 (bd, 11.5)
11	33.3	H_a 2.95 (ddd, 15.9, 11.3, 11.3)
		H_b 2.49 (dd, 15.9, 3.2)
12	79.9	3.94 (ddd, 11.2, 7.1, 3.2)
13	58.8	3.84 (ddd, 7.1, 7.1, 2.9)
14	29.2	H_a 2.05 (ddq, 14.7, 7.2, 2.9)
		H_b 1.72 (ddq, 14.7, 7.2, 7.2)
15	11.7	1.07 (dd, 7.2, 7.2)
OH		2.71 (bd, 4.2)

[a]^{1}H- and ^{13}C-nmr spectra were recorded in $CDCl_3$ at 270.1 and 67.9 MHz, respectively.

[b]$CDCl_3$ as internal reference (77.0 ppm). Carbon multiplicities determined through DEPT experiments. Assignments based on 2D nmr.

[c]Residual $CHCl_3$ as internal reference (7.26 ppm). Coupling constants are given in Hz.

carbon atoms (Me × 1; CH_2 × 3; CH × 10). An ir band at 3446 cm^{-1} revealed that the remaining proton was part of an alcohol functionality which was also indicated by the formation of a monoacetate derivative on treatment with Ac_2O/pyridine. On the other hand, since no carbonyl absorption was present in the ir spectrum, the remaining two oxygen atoms required by the molecular formula of **1** had to be of the ether type. The ^{1}H nmr of **1** recorded in $CDCl_3$ (Table 1) displayed eight resonances for protons geminal to heteroatoms spanned between 3.8 and 5.0 ppm, a methyl triplet at δ 1.07, six other protons resonating in the range 1.6–3.0 ppm belonging to three methylenes (from 2D nmr) and two one-proton signals at δ 6.07 and 5.56 due to the hydrogen atoms belonging to an unsaturated structural moiety. In addition, the ^{1}H spectrum showed in the high field region a broad one-proton signal centered at δ 2.71 assignable to the alcohol hydrogen.

The above data strongly suggested that **1** could be a C_{15} polyhalogenated acetogenin. Resonances at δ 201.4 (-C-) and 103.1 (-CH) in the ^{13}C-nmr spectrum of **1** were tentatively assigned to the two non-halogenated carbons of a bromoallene moiety whose presence was also indicated by the mass spectrum, which exhibited an intense four-peak cluster at *m/z* 447, 449, 451, 453 indicating the facile loss of a C_3H_2Br fragment, and by the ir absorption at 1963 cm^{-1}. This structural subunit is also present in other related metabolites such as laurallene (3), 4-*epi*-laurallene (4), neolaurallene (5,6), kumausallene (7), obtusallene (8,9), microcladallenes A, B, and C (10), okamurallene, deoxyokamurallene, and isookamurallene (11). The lack of other olefinic or carbonyl resonances in the ^{13}C-nmr spectrum of **1** indicated that rings had to account for the remaining two sites of unsaturation in the molecule.

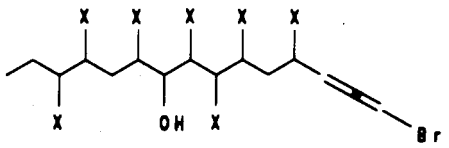
^{1}H-^{1}H COSY-45 and double resonance experiments established that the molecule

consisted of a unique scalar-coupled spin system allowing the identification of the partial structure shown in Figure 1.

Couplings between the alcoholic proton and H-9 and H-8 observed in the ^{1}H-^{1}H COSY spectrum indicated that the hydroxyl function must be attached to C-9.

Comparison of the ^{1}H- and ^{13}C-nmr data of **1** with those of laurallene (3) and 4-*epi*-laurallene (4) suggested that the same 2,6-dioxabicyclo[6.3.0]undecane system was present in **1**, leaving the remaining three bromine atoms linked to C-8, C-10, and C-13.

Support for such a structure came from both one-bond and long-range (via ^2J and ^3J) 2D HETCOR experiments which also allowed the assignment of all carbons in the ^{13}C-nmr spectrum of **1**.



X=O, Br

FIGURE 1. Partial structure for metabolite **1** as deduced from ^{1}H-^{1}H COSY-45 and double resonance experiments.

Further proof for the structure of the metabolite under investigation was provided by the treatment of **1** with Zn/HOAc at 0°. This reaction did not give the expected opening of the bicyclic system. Instead, the sole product obtained was the 1-debromoderivative of **1**, whose structure, inferred from spectral evidence (^{1}H nmr, ^{1}H-^{1}H COSY-45, ir, ms), further supported that of the original metabolite.

NOEDS experiments failed to give conclusive information on the configuration of all chiral centers of the molecule. Thus, final confirmation of the stereostructure and the absolute configuration of the molecule were obtained by single crystal X-ray diffraction analysis. The two independent molecules contained in the asymmetric unit are presented in Figure 2. Their conformational parameters show a high degree of correspondence. Only the bromoallene side chains show different arrangements owing to packing requirements. The two rings are cis fused. The five-membered ring is close to the envelope form (with C-6 as the out-of-plane atom) in the unprimed molecule and to the

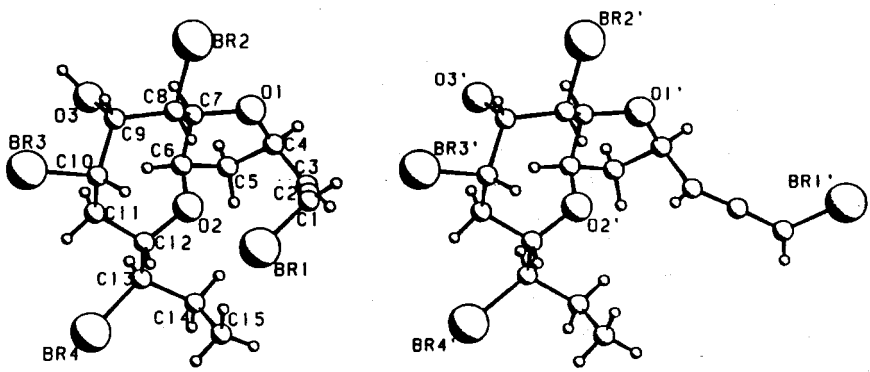


FIGURE 2. Perspective view of the two independent molecules in the correct absolute configuration together with the atom labelling scheme.

half-chair conformation (C-5′ and C-6′ being out of the plane) in the primed molecule. The eight-membered ring displays in both molecules the same conformation with an almost exact C_2 symmetry axis bisecting the opposite O-2–C-6 and C-9–C-10 bonds.

In conclusion we want to mention the occurrence in *M. rotalis* of another minor C_{15} polyhalogenated acetogenin, a very unstable product which readily decomposes. The small quantity and the instability of this compound made it extremely difficult to acquire high-quality spectral data; also, an X-ray diffraction analysis performed on a single crystal obtained from a sample fresh off the hplc did not give conclusive information on the molecule. Nevertheless, studies on the structure determination of this metabolite are still in progress.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—^{1}H- and ^{13}C-nmr spectra were recorded on Bruker WM-270 and WM-400 spectrometers in $CDCl_3$ solutions. ^{1}H-nmr chemical shifts are referenced to the residual $CHCl_3$ signal (7.26 ppm). ^{13}C-nmr chemical shifts are referenced to the solvent ($CDCl_3$, 77.0 ppm). Low resolution mass spectra were determined at 70 eV on an AEI MS 30 mass spectrometer. High resolution mass spectra were recorded on a Kratos MS 50 spectrometer. Fourier transform ir spectra were recorded using a Perkin-Elmer 1760-X Ft-ir spectrophotometer. Optical rotations were measured on a Perkin-Elmer Model 141 polarimeter. Hplc was carried out on a Varian 2510 apparatus equipped with a Waters Associates R403 differential refractometer. Melting points were determined on a Reichert Thermovar type 300429 Kofler hot stage melting apparatus and are uncorrected. Merck Si gel 40 (70–230 mesh) and 60 (230–400 mesh) was used for cc. Tlc analyses were carried out on precoated Si gel F_{254} plates (0.25 thick, Merck).

EXTRACTION OF THE SPONGE AND ISOLATION OF COMPOUND **1**.—The sponge *M. rotalis* was collected in the Stagnone di Marsala lagoon (Sicily) during the spring of 1989. A voucher specimen is on file at our laboratories on the Dipartimento di Chimica Organica e Biologica, Naples. The collected sponge was immediately frozen and transported to Naples. The freshly thawed sponge (46 g, dry wt after extraction) was carefully detached from any accompanying foreign material, cut into pieces, and extracted two times with $CHCl_3$-MeOH (1:1). The combined extracts were evaporated under reduced pressure, leaving an aqueous suspension which was extracted with Et_2O. The dried (Na_2SO_4) Et_2O extract was concentrated in vacuo affording 11.94 g of an oily residue which was fractionated on an open Si gel column (500 g, 4 cm diameter) using CH_2Cl_2 as eluent; 200-ml fractions were collected. Fractions 4–8 (469 mg), eluted slightly before monohydroxylated sterols, contained compounds **2** and **3** along with other minor metabolites. Fractions 21–30 (424 mg), mainly containing compound **1** and sterols, were combined and flash-chromatographed over Si gel eluting with increasing concentrations of Et_2O in petroleum ether. The fractions eluted with petroleum ether-Et_2O (88:12) contained 60 mg of pure **1** which was crystallized from $CHCl_3$. Recrystallization from the same solvent gave suitable crystals for the X-ray analysis.

Compound **1**.—Mp 128–130° (from $CHCl_3$); $[\alpha]^{20}D$ +38.8 (c = 1.3, $CHCl_3$); Ft-ir (film) ν max 3446 and 1963 cm^{-1}; ^{1}H and ^{13}C nmr see Table 1; hreims *m/z* $[M]^+$ 563.8149 (calcd for $C_{15}H_{20}{}^{79}Br_4O_3$, 563.8139); lreims *m/z* 564, 566, 568, 570, 572, $[M]^+$ 485, 487, 489, 491, $[M-Br]^+$ 447, 449, 451, 453, $[M-C_3H_2Br]^+$ 429, 431, 433, 435, $[M-C_3H_2Br-H_2O]^+$ 387, 389, 391, $[M-Br-HBr-H_2O]^+$ 349, 351, $[M-C_3H_2Br-H_2O-HBr]^+$ 353, 269, 271, $[M-C_3H_2Br-H_2O-2HBr]^+$ 189, $[M-C_3H_2Br-H_2O-3HBr]^+$.

ACETYLATION OF **1**.—Compound **1** (10 mg) was acetylated overnight at room temperature with pyridine-Ac_2O (2:1) to give a slightly more polar product. The usual workup and purification on a tlc plate [petroleum ether-Et_2O (1:1)] gave 9 mg of the pure acetylderivative: ^{1}H nmr ($CDCl_3$, 270 MHz) δ 6.26 (1H, bs, H-9), 6.09 (1H, dd, J = 5.5 and 1.8 Hz, H-1), 5.55 (1H, dd, J = 5.5 and 5.5 Hz, H-3), 4.66 (1H, m, H-4), 4.55 (1H, bdd, J = 4.9 and 4.9 Hz, H-6), 4.37 (1H, d, J = 9.2 Hz, H-8), 4.33 (1H, bd, J = 10.4 Hz, H-10), 3.98 (2H, overlapped multiplets, H-7 and H-12), 3.89 (1H, ddd, J = 9.8, 7.3 and 3.0 Hz, H-13), 2.85 (1H, ddd, J = 15.9, 11.6 and 11.6 Hz, H_b-11), 2.53 (2H, overlapped multiplets, H_a-11 and H_b-5), 2.05 (2H, overlapped multiplets, H_a-5 and H_b-14), 1.74 (1H, m, H_a-14), 1.08 (3H, dd, J = 7.3 and 7.3 Hz, H_3-15).

TREATMENT OF **1** WITH Zn/HOAc.—To a solution of 7 mg of **1** in 1 ml of EtOH at 0°, 7 mg of Zn dust and 3 ml of HOAc were added. The mixture was stirred for 2.5 h at 0°, Zn was filtered off, and the solvent was evaporated. The residue (two spots on tlc) was separated by hplc on a Hibar LiChrosorb Si-60

(250 × 4 mm) column [eluent *n*-hexane–EtOAc (85:15)] to give 2 mg of unreacted **1** and 4 mg of the 1-debromoderivative which showed the following spectral features: Ft-ir (ν max) 3441 and 1957 cm^{-1}; ^1H nmr ($CDCl_3$) δ 5.38 (1H, ddd, J = 6.8, 6.8, and 6.8 Hz, H-3), 4.95 (1H, bs, H-9), 4.81 (2H, AB system further coupled, J_{AB} = 11.0 Hz, H_a-1 and H_b-1), 4.43 (2H, overlapped multiplets, H-4 and H-6), 4.34 (1H, bd, J = 11.3 Hz, H-10), 4.29 (1H, d, J = 9.1 Hz, H-8), 4.06 (1H, dd, J = 9.2 and 3.6 Hz, H-7), 3.91 (1H, ddd, J = 11.2, 7.5 and 3.3 Hz, H-12), 3.84 (1H, ddd, J = 7.8, 7.5 and 2.9 Hz, H-13), 2.93 (1H, ddd, J = 15.9, 11.3 and 11.3 Hz, H_a-11), 2.69 (1H, bd, J = 4.8 Hz, O*H*-9), 2.51 (2H, overlapped multiplets, H_b-11 and H_a-5), 2.08 (1H, ddq, J = 14.7, 7.2, 2.8 Hz, H_a-14), 1.97 (1H, ddd, J = 13.9, 5.8, 1.1 Hz, H_b-5), 1.73 (1H, ddq, J = 14.7, 7.8, 7.2 Hz, H_b-14), 1.07 (3H, dd, J = 7.2, 7.2 Hz, H_3-15); lreims *m/z* 486, 488, 490, $[M]^+$ 492, 447, 449, 451, 453 $[M-C_3H_3]^+$ 429, 431, 433, 435 $[M-C_3H_3-H_2O]^+$ 407, 409, 411, $[M-Br]^+$ 389, 391, 393, $[M-Br-H_2O]^+$ 349, 351, 353 $[M-C_3H_3-H_2O-HBr]^+$ 271, 273 $[M-C_3H_3-H_2O-2Br]^+$ 269, 271 $[M-C_3H_3-H_2O-2HBr]^+$ 191, $[M-C_3H_3-H_2O-2Br-HBr]^+$ 189, $[M-C_3H_3-H_2O-3HBr]^+$.

X-RAY ANALYSIS[1].—Crystal data and relevant details of the structure determination are presented in Table 2. The final atomic parameters are given in Table 3.

TABLE 2. Crystal Data.

Crystal dimensions, mm	0.08 × 0.23 × 0.37
Formula	$C_{15}H_{20}O_3Br_4$
Formula wt	567.96
Space group	$P2_12_12_1$
a, Å	8.508(1)
b, Å	14.108(4)
c, Å	31.534(5)
V, $Å^3$	3785(1)
Z	8 (2 mols per asymmetric unit)
D_x, g/cm^3	1.99
λ Cu Kα, Å	1.5418
θ_{max} (°)	75
Absorption coefficient (μ), cm^{-1}	105.8
No. indep. refl.	3434
No. refl. above 3σ (I)	2376
No. variables	397
R	0.049
R_w	0.064
R^- (inverted structure)	0.052
R^-_w (inverted structure)	0.069

As the crystals, obtained by evaporation of a $CHCl_3$ solution, suffer a severe degradation in the X-ray beam, a first crystal was used only to select out of a total 3434 independent reflections 2376 ones, which, having $I_o > 3(I_o)$, were taken as observed and re-collected on a second crystal. The data collection was done at room temperature with the ω/θ scan technique on an Enraf-Nonius CAD4 diffractometer on line with a VAX 750 computer. Four monitoring reflections showed a crystal decay of about 13% at the end of the data collection. In addition to the usual corrections for Lorentz and polarization factors, a linear correction for the crystal decay and an empirical correction for the absorption effects according to North *et al.* (12) were applied. The structure was solved by direct methods using the program MULTAN80 (13). The refinement of the positional and anisotropic thermal parameters for the non-hydrogen atoms was carried out by full-matrix least-squares procedure, minimizing the quantity $W(\Delta F)^2$ with $W = 1/\alpha^2(F_o)$. The H atoms were generated at their expected positions and included but not refined in the last refinement cycles with an isotropic thermal parameter slightly larger than the B_{eq} of the carrier atoms. The H atom of the hydroxyl group of the unprimed molecule was detected in the Fourier difference map. It forms an H-bond with O-1′ of the asymmetric unit at $0.5+x$, $1.5-y$, $1.0-z$. H-bond parameters are: O-3 . . . O-1′ 2.75 Å, H . . . O-1′ 1.85 Å, angle O-3-H . . . O-1′ 158°. The H atom of the hydroxyl group of the primed molecule forms no H-bond and was not localized.

[1]Atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre and can be obtained on request from Dr. Olga Kennard, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.

TABLE 3. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) of the Non-hydrogen Atoms with the e.s.d.'s in Parentheses of Compound **1**.

	x	*y*	*z*	B_{eq}[a]
Br-1	−0.0866(3)	1.0087(2)	0.9178(1)	11.20(8)
Br-2	0.2957(2)	1.2220(1)	0.80668(5)	5.91(4)
Br-3	0.4033(3)	0.8477(1)	0.78968(5)	6.23(4)
Br-4	0.4337(4)	0.74361(1)	0.95481(6)	11.06(8)
O-1	0.328(1)	1.2248(6)	0.9044(3)	5.1(2)
O-2	0.332(1)	1.0194(6)	0.9224(3)	5.2(2)
O-3	0.564(1)	1.0470(7)	0.8208(3)	4.6(2)
C-1	−0.047(3)	1.139(1)	0.9314(6)	8.8(5)
C-2	0.080(2)	1.167(1)	0.9524(5)	6.9(4)
C-3	0.204(2)	1.193(1)	0.9714(5)	6.4(4)
C-4	0.351(2)	1.219(1)	0.9492(4)	5.5(4)
C-5	0.478(2)	1.146(1)	0.9558(5)	5.7(4)
C-6	0.464(2)	1.081(1)	0.9166(5)	5.5(4)
C-7	0.423(2)	1.152(1)	0.8828(4)	4.0(3)
C-8	0.327(2)	1.116(1)	0.8466(4)	4.3(3)
C-9	0.400(1)	1.033(1)	0.8214(4)	3.7(3)
C-10	0.355(2)	0.932(1)	0.8373(4)	4.2(3)
C-11	0.435(2)	0.896(1)	0.8767(5)	4.3(3)
C-12	0.359(2)	0.919(1)	0.9183(4)	5.2(4)
C-13	0.434(2)	0.881(1)	0.9565(4)	5.8(4)
C-14	0.348(4)	0.914(2)	0.9962(6)	16(1)
C-15	0.185(5)	0.888(3)	1.003(1)	26(2)
Br-1′	0.3461(4)	0.7527(2)	0.11690(8)	10.93(8)
Br-2′	−0.0430(2)	0.4210(1)	0.29884(5)	5.40(3)
Br-3′	0.1886(2)	0.5106(1)	0.45286(5)	5.35(3)
Br-4′	0.7740(2)	0.6314(2)	0.40901(6)	6.63(4)
O-1′	0.258(1)	0.4806(7)	0.2490(3)	4.8(2)
O-2′	0.438(1)	0.5760(6)	0.3163(2)	4.0(2)
O-3′	0.238(1)	0.3682(6)	0.3714(3)	4.7(2)
C-1′	0.488(2)	0.720(1)	0.1597(5)	6.4(4)
C-2′	0.440(2)	0.667(1)	0.1917(5)	6.2(4)
C-3′	0.394(2)	0.618(1)	0.2244(5)	5.7(4)
C-4′	0.397(2)	0.511(1)	0.2300(4)	5.6(4)
C-5′	0.534(2)	0.478(1)	0.2602(4)	4.6(3)
C-6′	0.451(2)	0.479(1)	0.3028(4)	4.3(3)
C-7′	0.282(2)	0.445(1)	0.2912(4)	3.9(3)
C-8′	0.156(2)	0.480(1)	0.3193(4)	4.2(3)
C-9′	0.171(2)	0.457(1)	0.3671(4)	4.5(3)
C-10′	0.249(2)	0.535(1)	0.3954(4)	4.0(3)
C-11′	0.434(2)	0.535(1)	0.3932(4)	4.2(3)
C-12′	0.500(2)	0.598(1)	0.3578(4)	4.3(3)
C-13′	0.678(2)	0.597(1)	0.3544(4)	5.0(3)
C-14′	0.745(2)	0.662(1)	0.3192(5)	6.2(4)
C-15′	0.690(2)	0.765(1)	0.3191(6)	7.6(5)

[a] $B_{eq} = 4/3\Sigma_i\Sigma_j\beta_{ij}a_i \cdot a_j$.

The peaks in the final difference electron density were within 0.6 e Å^{-3}. The absolute configuration was determined on the basis of Hamilton's test (14) on the conventional and weighted R and R_w indices for the two enantiomorphous structures. Atomic scattering factors and anomalous dispersion corrections were taken from *International Tables for X-ray Crystallography* (15).

ACKNOWLEDGMENTS

This work was supported by the Ministero della Pubblica Istruzione, Italy. Mass spectral data were provided by the Servizio di Spettrometria di Massa del CNR e dell'Università di Napoli. Throughout the

crystallographic work the equipment of the Centro di Metodologie Chimico-fisiche dell'Università di Napoli was used. The assistance of the staffs is gratefully acknowledged.

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Received 9 September 1991