342 ([m = M^+–AcOH], 22), 327(11), 298(13), 291 ([$m^* = m^2/M^+$], 3), 264(8), ..., 149(100). IR spectrum, ν_{max}, cm^{-1}: 1718 (C=O).

3β-Acetoxy-19,20,21,22,28,29,30-heptanor-18,19-seco(17βH)lupan-18-one (VII). mp 200-203°C; $[\alpha]_{578}^{20}$ +22.0° (c 0.012). Mass spectrum, m/z (%): 388 (M^+, 6), 373(1), 370(3), 332(3), 327(15), 313(7), 285(9), 284(9), 276(6), 264(10), 265(25), 213(11), 204(16), 189(54), 166(79), 151(100), 111(67), 97(63), 95(72), 83(100). IR spectrum, ν_{max}, cm^{-1}: 1722, 1704 (C=O).

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CRYSTAL AND MOLECULAR STRUCTURES OF 4-ACETAMIDO-2,6-DIBROMO-4-HYDROXY-1,2-DIMETHOXYCYCLOHEXA-2,5-DIENE

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UDC 548.737

A complete x-ray investigation has been made of 4-acetamido-2,6-dibromo-4-hydroxy-1,1-dimethoxycyclohexa-2,5-diene, isolated from the marine sponge *Verongia gigantea*. It has been shown that the orientation of the acetamide group in the molecule is stabilized by an intramolecular O–H...O hydrogen bond with the hydroxy group.

Bromine derivatives of tyrosine are known as products of biosynthesis in marine sponges [1]. 4-Acetamido-2,6-dibromo-4-hydroxy-1,1-dimethoxycyclohexa-2,5-diene (I) was first detected in a methanolic extract of the sponge *Verongia fistularis* [2]. In the present paper we give the results of an x-ray structural investigation of this compound carried out with the aim of elucidating stereochemical features of compounds of the type of (I) containing a hydroxy group and an acetamido group in position 4 and differing by the substituents in position 1 (keto group, OMe and OEt groups), not all of which crystallize well (see top of following page).

The spatial structure of the (I) molecule is shown in Fig. 1. The cyclohexane ring in (I) is planar. The deviations of the ring atoms from the mean plane passing through all its

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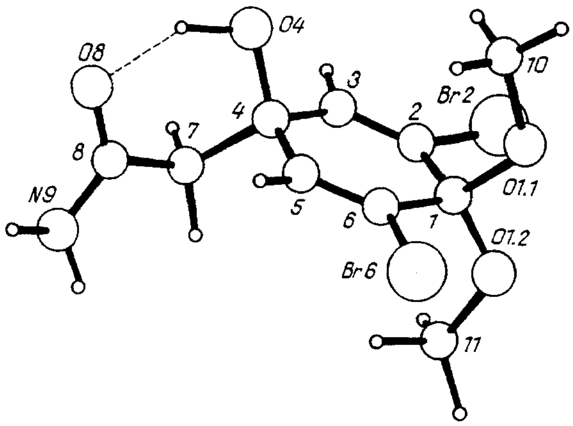
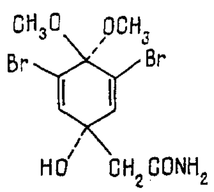


Fig. 1. Spatial structure of molecule I.

TABLE 1. Bond Lengths (Å) and Valence Angles (ω, degrees) in the (I) Molecule

Bond	d	Angle	ω
Br2—C2	1,90 (1)	C1—O1.1—C10	115,5 (6)
Br6—C6	1,924 (8)	C1—O1.2—C11	115,5 (7)
O1.1—C1	1,41 (1)	O1.1—C1—O1.2	101.3 (6)
O1.1—C10	1,45 (1)	O1.1—C1—C2	110,7 (7)
O1.2—C1	1,39 (1)	O1.1—C1—C6	110,9 (8)
O1.2—C11	1,43 (1)	O1.2—C1—C2	113,7 (8)
O4—C4	1,43 (1)	O1.2—C1—C6	113,1 (7)
O8—C8	1,25 (1)	C2—C1—C6	107,2 (7)
C1—C2	1,54 (1)	Br2—C2—C1	112,5 (6)
C1—C6	1,51 (1)	Br2—C2—C3	121,0 (7)
C2—C3	1,29 (1)	C1—C2—C3	126,4 (9)
C3—C4	1,51 (1)	C2—C3—C4	123,5 (8)
C4—C5	1,50 (1)	O4—C4—C3	106.3 (7)
C4—C7	1,56 (1)	O4—C4—C5	107,9 (7)
C5—C6	1,33 (1)	O4—C4—C7	110,8 (6)
C7—C8	1,50 (1)	C3—C4—C5	113,4 (7)
C8—N9	1,32 (1)	C3—C4—C7	109,1 (7)
		C5—C4—C7	109,4 (7)
		C4—C5—C6	120,7 (8)
		Br6—C6—C1	113,0 (6)
		Br6—C6—C5	118,2 (7)
		C1—C6—C5	128,7 (7)
		C4—C7—C8	112,8 (7)
		O8—C8—C7	119.7 (8)
		O8—C8—N9	122,1 (9)
		C7—C8—N9	118,1 (8)



atoms do not exceed 0.03 Å. The deviations of the Br2 and Br6 atoms from the mean plane of the ring amount to 0.05 and 0.06 Å. The methoxy groups are twisted relative to the plane of the cyclohexane ring in such a way that the O1.1–C1–C2–C3 and O1.2–C1–C6–C5 torsional angles are −116 and −130°, and the deviations of the O1.1 and O1.2 atoms from this plane are −1.12 and 0.95 Å, respectively. The spatial orientation of the acetamide group in the (I) molecule is stabilized by an O4–H...O8 intramolecular hydrogen bond with O...O and H...O distances of 2.63 and 1.64 Å, respectively, and an O4–H...O8 angle of 145°. The C3–C4–C7–C8 and C5–C4–C7–C8 torsional angles are −167 and 68°, respectively, and deviations of the C7, C8, O8, and N9 atoms from the mean plane of the ring are 1.20, 1.10, 0.01, and 2.19 Å, respectively. Among the substituents, because of steric hindrance (the O4...C8 distance is 2.98 Å), the oxygen atoms of the hydroxy group have the greatest deviation from the plane of the ring: −1.25 Å. The bond lengths and valence angles in the molecule are given in Table 1.

TABLE 2. Coordinates of the Nonhydrogen Atoms ($\times 10^4$) and Equivalent Isotropic Thermal Parameters (Å^2 $\times$ 10^3) (the standard deviations are given in parentheses)

Atom	x/a	y/b	z/c	U^*_{eq}
Br2	2391 (1)	3830 (1)	1699 (1)	56 (1)
Br6	2479 (1)	—390 (1)	3993 (1)	42 (1)
O1.1	2496 (7)	1104 (5)	1866 (5)	35 (2)
O1.2	1033 (7)	1602 (5)	3059 (5)	38 (3)
O4	6894 (6)	2863 (5)	3410 (5)	36 (2)
O8	8025 (7)	3042 (6)	5296 (5)	43 (3)
C1	2559 (10)	1726 (8)	2824 (7)	27 (3)
C2	3353 (10)	3010 (8)	2675 (7)	31 (3)
C3	4640 (10)	3506 (7)	3105 (7)	30 (3)
C4	5478 (9)	2903 (7)	3882 (7)	29 (3)
C5	4696 (9)	1670 (7)	4121 (7)	27 (3)
C6	3417 (11)	1105 (7)	3642 (7)	31 (3)
C7	5703 (9)	3626 (7)	4921 (7)	26 (3)
C8	6815 (11)	3244 (7)	5653 (8)	29 (3)
N9	6499 (8)	3180 (7)	6664 (6)	42 (3)

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*Equivalent isotropic U's defined as 1/3 (U_{11} + U_{22} + U_{33}).

The following intermolecular hydrogen bonds were detected in the crystals of compound (I): N9...O1.2' (1/2 − x, 1/2 − y, 1/2 + z) and N9...O4" (3/2 − x, 1/2 − y, 1/2 − z), with N...O distances of 2.95 and 3.04 Å, respectively. In both cases the amino group was the proton donor.

EXPERIMENTAL

Crystals of (I) ($C_{10}H_{13}NO_4Br_2$) were grown from a solution of (I) in ethyl acetate—ethanol (1:1): monoclinic; space group $P2_1/n$; $Z = 4$; $a = 9.060(2)$, $b = 11.665(2)$, $c = 12.734(3)$; $\gamma = 101.68(1)°$; $V = 1317.9(4)$ Å^3; $d_{calc} = 1.87$ g/cm^3. The integral intensities of 1649 independent reflections in the range of 2θ up to 48° were measured on a Syntex P1 automatic diffractometer (Mo Kα radiation, graphite monochromator, $\omega/2\theta$ method of scanning). Corrections for the Lorentz factor and for polarization were introduced in the recalculation of the reflection intensities to structural factors. The structure was determined by the direct method with the use of the SHELXTL programs [3] and was refined by the method of least squares in the full-matrix anisotropic approximation to a value of the discrepancy index of $R = 0.053$ [1513 reflections with $I > 2\sigma(I)$]. The coordinates of the hydrogen atoms were determined from difference syntheses. The positional and thermal parameters of the nonhydrogen atoms are given in Table 2. In the refinement of the structure we used the SHELX-76 packet of programs [4].

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