ALKALOIDS OF *Arundo donax*. IX. CRYSTAL STRUCTURE OF ARUNDAMINE

I. Zh. Zhalolov, B. Tashkhodzhaev, V. U. Khuzhaev, and S. F. Aripova

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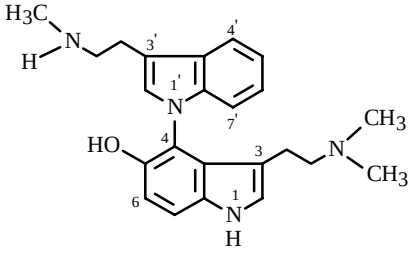
An x-ray structure analysis was performed for the new dimeric alkaloid arundamine isolated from Arundo donax. *Its properties are reported.*

Key words: *Arundo donax*, Poaceae, arundamine, x-ray structure analysis.

In continuation of the study of alkaloids from roots of *Arundo donax* L. (Poaceae) [1], we isolated from the polar fraction of the total bases by column chromatography a new base of formula $C_{23}H_{28}N_4O$, called arundamine (**1**). The structure of **1** was proven by an x-ray structure analysis (XSA). The XSA results indicate that the isolated compound is a dimeric indole alkaloid. The studied crystal is a hydrate (mp 104-105°C) in which the base includes one water molecule, i.e., the crystallographically independent unit has the formula $C_{23}H_{30}N_4O_2$.



1

The structure of **1** from the XSA is shown in Fig. 1. It can be seen that the dimer consists of the two known indole alkaloids dipterin (**A**) [2] and bufotenine (**B**) [3] joined at N1′ and C4 (from **A** and **B**, respectively). The bicyclic aromatic indole nuclei in **1** are planar within ±0.032 Å in **A** and ±0.016 Å in **B**. They are situated practically perpendicular in the crystal (at an angle of 79.7°).

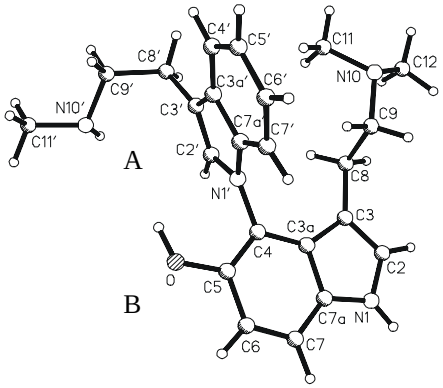


Fig. 1. Structure of arundamine.

S. Yu. Yunusov Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan, Tashkent, fax (99871) 120 64 75. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 67-69, January-February, 2002. Original article submitted December 24, 2001.

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TABLE 1. Bond Lengths (r, Å) and Angles (ω, deg) in **1**

Bond	r	Angle	ω	Angle	ω
O1-C5	1.368(3)	C2-N1-C7a	108.3(2)	N1-C2-C3	111.4(3)
N1-C2	1.365(4)	C2-C3-C3a	105.7(2)	C2-C3-C8	124.7(3)
N1-C7a	1.371(4)	C3a-C3-C8	129.6(3)	C4-C3a-C7a	117.6(2)
C2-C3	1.368(4)	C4-C3a-C3	135.5(2)	C7a-C3a-C3	106.9(2)
C3-C3a	1.433(4)	C5-C4-C3a	120.2(3)	C5-C4-N1′	118.3(3)
C3-C8	1.50(4)	C3a-C4-N1′	121.5(2)	O1-C5-C4	123.8(2)
C3a-C4	1.409(4)	O1-C5-C6	115.9(2)	C4-C5-C6	120.2(3)
C3a-C7a	1.421(4)	C7-C6-C5	121.6(3)	C6-C7-C7a	118.1(3)
C4-C5	1.384(4)	N1-C7a-C7	130.0(3)	N1-C7a-C3a	107.7(2)
C4-N1′	1.430(3)	C7-C7a-C3a	122.2(3)	C3-C8-C9	112.6(2)
C5-C6	1.408(4)	N10-C9-C8	116.5(2)	C11-N10-C12	110.4(2)
C6-C7	1.365(4)	C11-N10-C9	113.5(2)	C12-N10-C9	112.4(2)
C7-C7a	1.398(4)	C7′a-N1′-C2′	107.4(2)	C7′a-N1′-C4	125.2(2)
C8-C9	1.532(4)	C2′-N1′-C4	127.3(2)	C3′-C2′-N1′	111.1(2)
C9-N10	1.465(3)	C2′-C3′-C3a	106.4(2)	C2′-C3′-C8′	126.3(3)
N10-C11	1.455(4)	C3′a-C3′-C8′	127.2(2)	C4′-C3′a-C7′a	118.5(3)
N10-C12	1.460(4)	C4′-C3′a-C3′	134.3(3)	C7′a-C3′a-C3′	107.1(2)
N1′-C7′a	1.383(3)	C5′-C4′-C3′a	118.8(3)	C4′-C5′-C6′	121.8(3)
N1′-C2′	1.387(3)	C7′-C6′-C5′	120.9(3)	C6′-C7′-C7′a	117.3(3)
C2′-C3′	1.350(4)	N1′-C7′a-C7′	129.3(2)	N1′-C7′a-C3′a	108.0(2)
C3′-C3′a	1.437(4)	C7′-C7′a-C3′a	122.7(2)	C3′-C8′-C9′	114.8(2)
C3′-C8′	1.503(4)	N10′-C9′-C8′	114.1(2)	C11′-N10′-C9′	112.0(2)
C3′a-C4′	1.398(4)				
C3′a-C7′a	1.407(4)				
C4′-C5′	1.381(4)				
C5′-C6′	1.393(4)				
C6′-C7′	1.379(4)				
C7′-C7′a	1.396(4)				
C8′-C9′	1.514(4)				
C9′-N10′	1.461(4)				
N10′-C11′	1.456(4)				

TABLE 2. H-Bonds in **1**

D-H...A	d(D...A), Å	d(D-H), Å	d(H...A), Å	<(DHA), deg
O1-H...Ow	2.68	0.96	1.83	145
Ow-H...N10′	2.86	0.98	1.93	157
N10′-H...Ow (-X+3/2, Y+1/2, -Z+1/2)	3.02	0.87	2.19	159
N10′-H...O1 (-X+3/2, Y+1/2, -Z+1/2)	3.19	0.87	2.54	131
Ow-H...N10 (-X+1/2, Y-1/2, -Z+1/2)	2.73	0.88	1.86	168

D - donor, A - acceptor.

The aromaticity of the indole nuclei (conjugation) in **A** and **B** is evident in the short N1–C2 [1.365(4) Å], N1–C7a [1.371(4) Å], and N1′–C2′ [1.383(3) Å], N1′–C7a′ [1.387(3) Å] bonds compared with the analogous N1′–C4 [1.430(3) Å] bond that is not conjugated because of the perpendicular orientation of the planes of the two indole nuclei. Atoms N10 and N10′ have the tetrahedral configuration. This can be observed in Fig. 1 and from the bond angles (Table 1).

The packing in the structure of **1** indicates that the molecules form H-bonds of the type O–H...O and O–H...N that involve the water of solvation. Furthermore, the crystal includes intermolecular H-bonds of these types. Table 2 contains the geometric parameters of these bonds.

TABLE 3. Atomic Coordinates ($\times 10^4$) and Equivalent Thermal Parameters U_{eq} ($Å^2 \times 10^3$) in **1**

Atom	x	y	z	U_{eq}
O1	6408(2)	1125(1)	3059(2)	36(1)
N1	7602(2)	4297(2)	2179(2)	33(1)
C2	6414(3)	4573(2)	1703(2)	33(1)
C3	5487(3)	3969(2)	1629(2)	29(1)
C3a	6144(3)	3262(2)	2106(2)	27(1)
C4	5773(3)	2455(2)	2316(2)	27(1)
C5	6687(3)	1915(2)	2822(2)	28(1)
C6	7996(3)	2167(2)	3121(2)	32(1)
C7	8398(3)	2943(2)	2937(2)	33(1)
C7a	7471(3)	3490(2)	2433(2)	27(1)
C8	4081(3)	4071(2)	1138(2)	31(1)
C9	3144(3)	4246(2)	2004(2)	31(1)
N10	1758(2)	4381(2)	1599(2)	34(1)
C11	1088(3)	3650(2)	1161(3)	41(1)
C12	1586(3)	5042(2)	800(2)	38(1)
N1′	4444(2)	2183(1)	2065(2)	26(1)
C2′	3837(3)	1932(2)	1054(2)	29(1)
C3′	2597(3)	1672(2)	1134(2)	29(1)
C3′a	2383(3)	1758(2)	2267(2)	27(1)
C4′	1305(3)	1631(2)	2857(2)	32(1)
C5′	1429(3)	1822(2)	3960(2)	34(1)
C6′	2601(3)	2123(2)	4498(2)	33(1)
C7′	3682(3)	2256(2)	3940(2)	31(1)
C7′a	3550(3)	2075(2)	2822(2)	26(1)
C8′	1656(3)	1329(2)	222(2)	34(1)
C9′	1721(3)	413(2)	91(2)	36(1)
N10′	3038(2)	104(2)	-33(2)	37(1)
C11′	3030(3)	-767(2)	-253(3)	49(1)
O1w	4788(2)	50(1)	1953(2)	36(1)

EXPERIMENTAL

Isolation of Arundamine. Ground roots (5 kg) of *Arundo donax* L. collected at the termination of growth were wetted with dilute ammonia solution. After standing (2 h) they were extracted with $CHCl_3$. The extracts were condensed and worked up to give total alkaloids (10.4 g) that were separated over a column of alumina. The eluents were mixtures of C_6H_6—$CHCl_3$ and $CHCl_3$—CH_3OH in various ratios (polar fractions). Separate fractions of $CHCl_3$—CH_3OH eluates afforded arundamine (0.24 g), R_f 0.3 TLC, Al_2O_3, $CHCl_3$—CH_3OH (9:1), mp 104-105°C.

X-ray Structure Analysis. Crystals of formula $C_{23}H_{30}N_4O_2$ (**1**) were grown from an ethanol solution. A transparent single crystal at 110 K was selected. The crystals are monoclinic: a = 10.211(3), b = 16.420(7), c = 12.272(5) Å, β = 96.30(9)°, V = 2045.1(1) $Å^3$, d_{calc} = 1.281 g/cm^3, absorption coefficient μ = 0.83 cm^{-1}, space group $P2_1/n$, Z = 4. Intensities of 3518 independent reflections (R_{int} = 0.044) were measured on an automated Bruker SMART 1K CCD (Mo Kα-radiation, λ = 0.71 Å, graphite monochromator, ω-scanning, $2\theta_{max}$ = 50°) diffractometer. Absorption corrections were applied semi-empirically using the SADABS program [3].

The structure was solved by direct methods using the program set SHELXTL PLUS 5.0 [5]. Nonhydrogen atoms were refined by anisotropic full-matrix least-squares methods (over F^2). Positions of H atoms were found from a difference Fourier synthesis and refined with fixed isotropic thermal parameters $U_{iso} = nU_{eq}$, where n = 1.5 for methyls and 1.2 for others and U_{eq} is the equivalent isotropic thermal parameter of the corresponding C, N, or O atom. The final agreement factors are $R_1(F)$ = 0.1042, $wR_2(F^2)$ = 0.1928 and GOF = 0.95 over all independent reflections [$R_1(F)$ = 0.0736, $wR_2(F^2)$ = 0.1724 calculated over 2241 reflections with $I > 2\sigma(I)$] included in the final refinement cycle.

Atomic coordinates in **1** and equivalent thermal parameters appear in Table 3.

The XSA was performed at the Institute of Organoelement Compounds of the Russian Academy of Sciences (Moscow) by L. A. Lysenko and M. Yu. Antipin.

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