Chemistry of Natural Compounds, Vol. 36, No. 5, 2000

ALKALOIDS OF *Arundo donax*. VIII. 3-ALKYLINDOLE DERIVATIVES IN *A. donax*

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UDC 547.944/945

The total bases of Arundo donax *L. contain two alkaloids, bufotenine and 1-methyl-3-aminomethylindole, which were found for the first time in plants.*

Key words: *Arundo donax*, Poaceae, bufotenine, donaxamine.

In continuation of research on the alkaloid composition of *Arundo donax* L. (Poaceae, grasses), which grows in Fergana valley [1], we isolated alkaloid **1** with R_f 0.4 ($CHCl_3$—CH_3OH, 9:1) by chromatographic separation of a mixture of bases from the aerial part on an Al_2O_3 column and rechromatography of some fractions with elution by $CHCl_3$—CH_3OH (100:1).

The IR spectrum of **1** contains absorption bands for active H (3407, 3310 cm^{-1}, OH, NH), an aromatic ring (1625, 1582 cm^{-1}) and absorption bands of di- and trisubstituted aromatic rings in the fingerprint region.

The mass spectrum contains a peak for the molecular ion with *m/z* 204. The base peak with *m/z* 58 corresponds to loss of $CH_2–N(CH_3)_2^+$ from M^+. The second strong peak with *m/z* 146 results from loss of 58 a. m. u. from M^+. The presence of OH group was confirmed by the presence of an ion with *m/z* 187, which is formed from M^+ by loss of 17 a. m. u. $[M - OH]^+$.

The ion with *m/z* 131 arises apparently from M^+ by the loss of $CH_2–CH_2–N(CH_3)_2$ accompanied by migration of one proton. The spectrum also exhibits a peak with *m/z* 160, which arises from loss of $N(CH_3)_2$ from M^+ $[M - 44]^+$. The remaining ions with *m/z* 117, 91, and 77 are formed by cleavage of the indole ring.

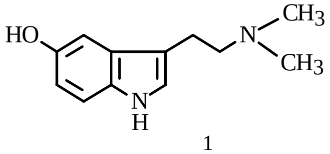
The mass spectrum of the alkaloid (peaks with *m/z* 187 and 131) is consistent with an OH group in the benzene ring of the indole. Its preferred location is on C-5 according to biogenetic principles (analogous to arundinine [4]). This is confirmed by PMR spectra.

The PMR spectrum of **1** in $CDCl_3$ + CD_3OD contains a 6H singlet at 2.34 ppm for the $N(CH_3)_2$ group. There are two symmetric 2H multiplets centered at 2.72 and 2.82 ppm that, in all probability, can be assigned to a $C–CH_2–CH_2$ group bonded to an aromatic ring on one side and to the N atom on the other.

The aromatic region has signals in the range 6.72-7.27 ppm that represent four protons. This part of the PMR spectrum of **1** has four individual signals. Proton H-2 appears as a weakly broadened signal at 6.93 ppm. The three protons of the 6-membered ring form an *ABC*-system typical of this type of substituted benzene ring. Proton H-4 resonates at 7.00 ppm as a doublet with J (H-4,H-6) = 2.3 Hz. Proton H-6 appears as a doublet of doublets at 6.78 ppm [J(H-4,H-6) = 2.3 Hz and J(H-6,H-7) = 8.5 Hz]. Finally, the doublet for H-7 [J(H-6,H-7) = 8.5 Hz] is observed at 7.19 ppm. A broad singlet for the NH group is located at 8.59 ppm.

The acetate of **1** was prepared using acetic anhydride in pyridine. The PMR spectrum of **1** acetate has a distinct 3H singlet for protons of the methyl ester at 2.25 ppm. Thus, the O-acetate was obtained.

The spectral properties described above suggest the structure **1**, which is the alkaloid bufotenine [5, 6]. This is isolated by us for the first time from *A. donax* at this location.



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0009-3130/00/3605-0528$25.00

TABLE 1. PMR Spectrum of **2**

Signal	Proton	Chem. shift, ppm	SSCC (J, Hz)
A	H-4	7.49	7.5 (H-5); 1.1(H-6), 0.9 (H-7)
B	H-5	7.23	7.5 (H-4); 7.0 (H-6), 0.8 (H-7)
C	H-6	7.18	1.1 (H-4); 7.0 (H-5), 7.2 (H-7)
D	H-7	7.74	0.9 (H-4); 0.8 (H-5), 7.2 (H-6)

Signals *ABCD* were assigned to H-4-H-7 using the nuclear Overhauser effect with saturation of the N–CH_3 signal and complete saturation of the H-7 signal.

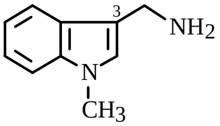
Further separation of the total alkaloids of *A. donax* on an Al_2O_3 column with elution by $CHCl_3$—CH_3OH (30:1) isolated **2** with mp 178-179°C and R_f 0.25 in $CHCl_3$—CH_3OH (9:1), which we call donaxamine.

The IR spectrum exhibits absorption bands of active H (3160 cm^{-1}) and an aromatic ring (1618 and 1578 cm^{-1}).

The PMR spectrum of **2** in CD_3OD has a well resolved aromatic portion in the range 7.14-7.78 ppm and two singlets. A 2H singlet at 4.83 ppm belongs to a methylene whereas a 3H singlet at 2.94 ppm comes from an N-methyl group. A singlet at 7.64 ppm in the aromatic region is readily identified as belonging to the olefinic proton H-2. The remaining four 1H signals form a completely resolved *ABCD*-system.

Saturation of the 3H singlet at 2.94 ppm clearly displays a nuclear Overhauser effect (12-15%) for one of the aromatic protons, the signal of which appears at 7.74 ppm and, therefore, belongs to H-7. If the signal for H-7 is completely saturated, the *ortho*-constants of H-6 and the small constants for the signals of the remaining two aromatic protons disappear. According to the SSCCs, these signals can be unambiguously assigned to H-4 and H-5, which indicates that the N–CH_3 group is located in the indole ring.

The data suggest that the alkaloid isolated by us is a 3-alkylderivative of N-methylindole. A synthetic analog of this compound has been reported [2, 3]. However, we have isolated it from a plant for the first time.



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EXPERIMENTAL

IR spectra were recorded on a Perkin—Elmer model 2000 Fourier-spectrometer in KBr pellets; mass spectra, on an MX-1310 spectrometer equipped with direct-sample probe into the ion source. PMR spectra were obtained on a UNITY-400+ (Varian) NMR spectrometer in CD_3OD and $CDCl_3$ with TMS internal standard.

Neutral Al_2O_3 (100/160 µm) was used for column chromatography. TLC was performed on plates with Al_2O_3 (5/40 µm) in system 1 ($CHCl_3$—CH_3OH, 9:1).

Isolation and Separation of Total Alkaloids from *A. donax*. Ground aerial parts (5 kg) of the plant were extracted with ethanol in a percolator. Five extractions were performed. The combined alcohol extracts were concentrated. Traces of alcohol were removed under vacuum. Such treatment produced the total alkaloids (23 g, 0.46% of the air-dried mass of starting material).

The alkaloids were placed on an Al_2O_3 column that was eluted successively with hexane, ether, $CHCl_3$, and $CHCl_3$—CH_3OH. The $CHCl_3$—CH_3OH fractions were rechromatographed on an Al_2O_3 column with elution by $CHCl_3$ and $CHCl_3$—CH_3OH mixtures. The $CHCl_3$—CH_3OH (100:1) eluates contained **1**, R_f 0.40 (TLC, Al_2O_3, system 1). The $CHCl_3$—CH_3OH eluates (30:1) contained **2**, mp 178-179°C, R_f 0.25 (TLC, Al_2O_3, system 1).

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