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ALKALOIDS OF *Arundo donax*.
IV. DONAXANINE — A NEW PYRROLIDINE ALKALOID FROM *Arundo donax*

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The new pyrrolidone alkaloid donaxanine, $C_{12}H_{14}N_2O_2$, has been isolated from Arundo donax. *Its structure has been shown by chemical transformations and a study of its IR, mass, and PMR spectra as spiro[(N-methylpyrrolidin-2-one)-3,4'-(3',1'-benzoxazine).*

We have previously [1] reported the isolation of alkaloids of the pyrrolidine series from the epigeal part of *Arundo donax* L. (environs of the village of Kumkishlak, Kashkadar'inskaya province).

Continuing the study of the alkaloids of this plant, we have isolated a new base differing in its physicochemical parameters and spectral characteristics from known alkaloids of this series; it has been called donaxanine (**1**).

Donaxanine has the composition $C_{12}H_{14}N_2O_2$ (HRMS 218.1055). It crystallizes well from chloroform, is sparingly soluble in benzene, ether, and hexane, and is readily soluble in acetone and chloroform. The IR spectrum of (**1**) showed absorption bands of active hydrogen in the 3305 cm^{-1} region (NH), of an amide carbonyl at 1678 cm^{-1}, of the asymmetric stretching vibrations of a C–O–C bond at 1283 cm^{-1}, and of the deformation vibrations of an aromatic ring in the 854, 798, 746, and 731 cm^{-1} regions.

The mass spectrum of (**1**) had the peaks of the molecular ion (M^+ 218) and of fragmentary ions with *m/z* 190 (M^+ − 28), 160 (M^+ − 58), and others (see the Experimental section). The peak with the maximum intensity was that with *m/z* 190.

A comparison of the mass spectrum of donaxanine with that of donaxarine, isolated previously from the same plant [1], gave grounds for the assumption that donaxanine is apparently a demethylated derivative of donaxarine.

In the PMR spectrum of (**1**) there were two two-proton multiplets at 2.32 and 3.20 ppm due to the H-4 and H-5 protons of a pyrrolidine nucleus. A three-proton singlet characteristic of an N-methyl group was observed at 2.72 ppm. Aromatic protons appeared in the 6.62-7.20 ppm region (4H, m, Ar-H). The protons of the methylene group of the oxazine ring were distinguished by their nature. These protons are magnetically nonequivalent and appeared at 4.73 and 5.51 ppm in the form of two one-proton doublets of doublets (J = 7.5 Hz and J = 5 Hz). The large constant (7.5 Hz) is geminal, and the small one results from an NH proton and disappeared on the addition of trifluoroacetic acid through the occurrence of rapid exchange. In these circumstances, the signals of the methylene group were simplified and were now found in the form of two one-proton doublets. A one-proton signal corresponding to an NH group was found at 4.70 ppm.

When (**1**) was acetylated with acetic anhydride in pyridine, an oily monoacetyl derivative of donaxanine, (**2**), was obtained, as was shown by its mass and IR spectra. The IR spectrum of acetyldonaxanine showed an additional absorption band of an amide carbonyl (1687 cm^{-1}). The mass spectrum of acetyldonaxanine showed the peak of the molecular ion with *m/z* 260 and the peaks of other ions formed by the fragmentation of the molecular ion (see the Experimental section).

All the spectral characteristics of donaxanine, and also a comparison with those of the alkaloids donaxarine and donaxaridine [1] showed the pyrrolidine nature of the alkaloid, upon which basis the following structure is proposed for (**1**):

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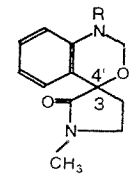

1. R=H
2. R=Ac

The structure proposed for (1) has been confirmed by its synthesis from donaxaridine and formaldehyde. The synthetic donaxanine was identical with the natural substance according to its R_f values in TLC, a mixed melting point with an authentic specimen, and its IR spectrum. Thus, donaxanine has the structure of spiro[(N-methylpyrrolidin-2-one)-3,4′-(3′,1′-benzoxazine).

EXPERIMENTAL

General Observations. The chromatographic separation of the total alkaloids was carried out on columns of alumina (Brockmann activity grade II). For TLC we used the benzene–methanol (9:1) system. IR spectra were taken on a Perkin-Elmer model 2000 spectrometer, using tablets with KBr; mass spectra on an MKh-1310 spectrometer (EI source); and PMR spectra on a Tesla BS 567 A instrument.

Isolation of Donaxanine (1). The isolation and preliminary separation of the total alkaloids has been described in [1]. When the ether fraction of the alkaloids was eluted with chloroform, a fraction enriched with donaxanine was obtained. This fraction was rechromatographed on a column of alumina, and elution with ether–chloroform (1:1) gave 0.04 g of chromatographically pure donaxanine (1) with R_f 0.78 (TLC, Al_2O_3).

Donaxanine (1). $C_{12}H_{14}N_2O_2$, mp 162-164° (acetone). IR spectrum (KBr, cm^{-1}): 3305, 2286, 1678, 1610, 1468, 1283, 854, 798. Mass spectrum (EI, 70 eV), *m/z* (%): 219 (5), 218 (35), 203 (1), 200 (3), 191 (11), 190 (100), 189 (13), 161 (5), 160 (30), 159 (8), 158 (8), 148 (5), 147 (44), 146 (55), 145 (5), 144 (5), 133 (50), 132 (33), 130 (33), 120 (5), 119 (16), 118 (16), 117 (27), 106 (5), 105 (22), 104 (27), 103 (5), 96 (5), 78 (16), 77 (27)

PMR spectrum (C_5D_5N, ppm): 2.32 (m, 2H, CH_2), 2.72 (s, 3H, NCH_3), 3.20 (m, 2H, CH_2), 4.73 (d, 1H, J = 7.5 Hz, H-2′), 5.51 (d, 1H, J = 7.5 Hz, H-2′), 4.70 (br.s, 1H, NH), 6.62-7.20 (m, 4H, Ar-H).

Acetyldonaxanine (2). A mixture of 0.02 g of donaxanine, 1 ml of acetic anhydride, and 0.3 ml of pyridine was kept at room temperature until the substance had passed into the solvent completely (3 days). The reaction mixture was evaporated under vacuum, the residue was dissolved in 5 ml of water, and the solution was made alkaline with ammonia and extracted with chloroform. After elimination of the solvent, the oily N-acetyldonaxanine (2) remained, with R_f 0.85 (TLC, Al_2O_3).

IR spectrum (KBr, cm^{-1}): 1689, 1665, 1595, 1455, 1110.

Mass spectrum (EI, 70 eV), *m/z* (%): 260 (M^+ 20), 217 (33), 190 (100), 160, 146, 133, 130, 105.

Synthesis of Donaxanine (Condensation of Donaxaridine with Formaldehyde). A mixture of 0.03 g ($1.4 \cdot 10^{-4}$ mole) of donaxaridine, 3 ml of methanol, and 1 ml ($1.3 \cdot 10^{-2}$ mole) of formaldehyde was heated in the water bath for 2 h. The solvent was driven off, and the residue was treated with acetone. This gave crystals of donaxanine with mp 162-164°C (acetone), R_f 0.88 (TLC, Al_2O_3).

REFERENCE

1. V. U. Khuzhaev, B. Tashkhodzhaev, and S. F. Aripova, Khim. Prir. Soedin., 720 (1995) [preceding paper in this issue].