ALKALOIDS OF *Arundo donax*

THE STRUCTURE OF DONAXARIDINE AND DONAXARINE

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We have investigated the alkaloids of the epigeal part of the plant *Arundo donax* (giant reed), family Gramineae, growing in the territory of the "Subtropik" sovkhoz [communal farm], Shaartuz region, TedhSSR.

From 60 kg of *A. donax* by chloroform extraction we obtained 0.18% of ether-soluble and 0.04% of chloroform-soluble bases. Treatment of the ether-soluble bases with acetone yielded donaxine (I) [1, 2]. By chromatographing the mother liquor from (I) on a column of Al_2O_3 (activity grade II) we obtained the new alkaloid donaxaridine with mp 175-176°C, $[\alpha]_D$ ± 0°, $C_{11}H_{14}N_2O_2$ (II) and the previously isolated donaxarine with mp 218-220°C, $[\alpha]_D$ ± 0°, $C_{13}H_{16}N_2O_2$ (III) [3].

IR spectrum of (II): ν_{max} (cm^{-1}): 3456, 3365 (OH, NH), 1670 (CO—NH—), 1620, 1580, 1500, 760 (1,2-disubstituted benzene ring). The UV spectrum of (II) [λ_{max} 240, 290 nm (log ε 3.82, 3.42)] is similar to the UV spectra of the hydroxyindoles [4]. The NMR spectrum of (II) (in $CDCl_3$, JNM-4H-100 MHz with HMD as δ scale) showed the following signals: multiplets at 2.47 (—CH_2—), 3.17 (—CH_2—), and 6.52-7.08 (4H, aromatic protons), singlet at 2.87 (NH—CH_3), and weakly resolved two-proton signal at 4.59 (2NH). In the mass spectrum of (II) there are peaks of ions with m/e 30, 44, 58, 92, 93, 120 (80%), 130, 135, 146, 147, 149, 188, 206 (100%) M^+. The acetylation of (II) gave N-acetyl-(II)(IV), with mp 185-186°C, M^+ 248 [NMR spectrum 2.10 ppm (3H, N-acetyl)], and the amorphous ON-diacetyl-(II)(V), M^+ 290 [NMR spectrum: 2.0 (O-acetyl), 2.18 ppm (N-acetyl)]. The absence from the NMR spectra of (II) and (V) of signals from geminal protons to hydroxy and acetoxy groups, respectively, showed the tertiary nature of the hydroxy group in (II). In the mass spectrum of (II) the peaks of the ions with m/e 30, 44, and 58 [5] and the displacement of these peaks by one mass unit in the D analog of (II) show that (II) contains a —CH_2—CH_2—NH—CH_3 group. The oxidation of (II) with $KMnO_4$ gave a substance with mp 201°C, identical with isatin (VI) (mixed melting point, IR spectrum [6]. Consequently, (II) is based on a hydroxyindole skeleton and contains a —CH_2—CH_2—NH—CH_3 and an OH group, and donaxaridine has the most probable structure of 3-(β-methylaminoethyl)dihydroxyindole (II).

IR spectrum of (III): ν_{max}, (cm^{-1}): 3310 (NH), 1675 (CO—NH) 1615, 1595, 1500, 760 (1,2-disubstituted benzene ring), 875, 890, 940, 960, 990 (bands of a spiro-condensed ring) [7]. UV spectrum of (III): λ_{max} 246, 297 nm (log ε 3.60, 3.11). The NMR spectrum of (II) had the following signals (ppm): doublet 1.29 (3H—CH—CH_3), triplet at 2.41 (—CH_2—), singlet at 2.88 (>N—CH_3), mulitplet at 3.45 (—CH_2) and 6.56-7.12 (4H, aromatic protons), quartet at 5.43 (H—CH—CH_3), and a weakly resolved one-proton signal at 4.03 NH). The msss spectrum of (III) has the peaks of ions with m/e 58, 118, 119, 130, 133, 146, 174, 189, 232 (100%) M^+.

Donaxarine forms a N-acetyl derivative with M^+ 274. The saponification of (II) gave a substance with mp 175-176°C identical with donaxaridine (II). When donaxaridine (II) was condensed with acetaldehyde, (III) was formed. The condensation of (II) with acetaldehyde apparently takes place with the formation of a tetrahydro-1,3-oxazine ring [8, 9]. Thus, for donaxarine we can propose the structure of oxindole-3-spiro-6'-(2',3'-dimethyltetrahydro-1',3'-oxazine) (III).

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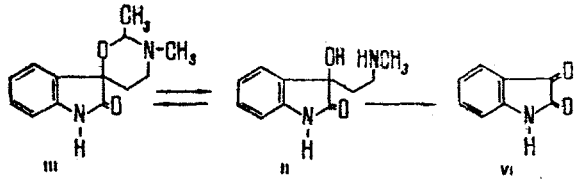

III II VI

LITERATURE CITED

1. A. P. Orekhov and S. S. Nopkina, Ber., 68, 436 (1935).
2. A. P. Orekhov and S. S. Nopkina, Zh. Obshch. Khim., 7, 673 (1937).
3. J. Madinhaveita, Nature, 139, 27 (1937).
4. A. H. Beckett, R. W. Daidlay, and I. Walker, Tetrahedron, 24, 6093 (1968); C. B. Hudson and A. V. Robertson, Aust. J. Chem., 20, 1511 (1967).
5. G. Budzikiewicz, C. Djerassi, and D. Williams, Interpretation of Mass-Spectra of Organic Compounds, Holden-Day, San Francisco (1964).
6. G. Adam, K. Schreiber, and J. Tomko, Tetrahedron Lett., 24, 2815 (1968).
7. A. Chatterjee and S. Bose, J. Indian Chem. Soc., 31, 17 (1954).
8. A. R. Kon and J. Roberts, J. Chem. Soc., 978 (1950).
9. Heterocyclic Compounds [in Russian], Vol. 6, Moscow (1960), p. 437.

CONFIGURATION OF l-CYCLOPROTOBUXINE-C

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We have previously reported the isolation of the new alkaloid l-cycloprotobuxine-C with mp 195-197°C, $[\alpha]_D$ − 62°, $C_{27}H_{48}N_2$ (I), and we concluded that it was the levorotatory form of cycloprotobuxine-C (II) [1-3]. However, a comparison of (I) with an authentic sample of (II) (kindly given to us by J. Tomko, Bratislava) showed a difference in their physicochemical properties. Consequently, (I) is not the antipode of (II).

The mass-spectrometric decomposition of (I) takes place similarly to that of (II) but differs in the intensities of the peaks of the ions. In both (I) and (II) the maximum peak is that of the ion with m/e 72. On comparing the chemical shifts of the protons of the secondary and tertiary methyl groups in the NMR spectra of (I) and (II), a downfield displacement of the signal of the protons from the 18-CH_3 group in (I) by 4 Hz was found [4]. Such a displacement is connected with a configurational difference of the C_{20} asymmetric center and in (I), probably, the $N(CH_3)_2$ at C_{20} has the β orientation. A study of the rates of saponification of buxaline-C, baleabuxidine [5-7], and the N-acetyl derivative of (I) showed that buxaline-C (III) and baleabuxadine (IV) are readily hydrolyzed [(III) has a 3β-N-acetyl group and (IV) a 3β-N-isobutyryl group), while the N-acetyl and N-benzoyl derivatives of (I) do not undergo acid or alkaline hydrolysis under various reaction conditions. Such an inhibition of saponification is observed only when the N-acyl group at C_3 has the α-axial orientation (examined on models of (I) and (II)]. Consequently, in (I) the NH—CH_3 group at C_3 has the α-axial orientation.

On the basis of the facts given, it may be considered that the alkaloid (I) is a stereoisomer of (II) and has the most probable structure and configuration of 20β-dimethylamino-4,4,14α-trimethyl-3α-methylamino-9β,19-cyclo-5α-pregnane:

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