ALKALOIDS OF Scopolia tangutica

S. A. Minina, T. V. Astakhova, and D. A. Fesenko

UDC 547.944/945

From the epigeal part of Scopolia tangutica Maxim., grown in the Leningrad oblast under crop conditions, by adsorption column chromatography and selective elution we have isolated two more alkaloids, in addition to hyoscyamine and scopolamine: base I with R_f 0.45 [TLC, Al_2O_3, chloroform-methanol (20 : 1) system] and 0.41 [PC, Filtrak FN-11 paper, butan-1-ol–acetic acid–water (4 : 1 : 5) system] and base (II) with R_f 0.34 and 0.55, respectively.

The molecular weight of base I with the composition $C_{17}H_{21}O_5N$ (M^+ 319) differed by 16 m/e from the molecular weight of scopolamine. We have given some constants of the alkaloid previously [1]. The NMR spectrum of I (CF_3COOH, internal standard TMS) showed the following signals: 7.48 (5H, multiplet, monosubstituted benzene ring), 4.39 (1H, doublet, J = 12 Hz), and 4.84 (1H, doublet, J = 12 Hz) (CH_2 group), and the IR spectrum contained absorption bands corresponding to an ester carbonyl group (1740 cm^{-1}), a benzene nucleus (860 cm^{-1}), and active hydrogen (3510, 3600 cm^{-1}).

The hydrolysis of I by Reimers' method [2] yielded an amino alcohol which was identified as scopoline and an acid $C_9H_{10}O_4$, the constants of which have been published [1]. The NMR spectrum of the acid (CF_3COOH, internal standard TMS) has the signals of the protons of a monosubstituted benzene ring at 7.3-7.7 ppm (5H, multiplet) and also two doublets at 4.21 ppm (1H, J = 12 Hz) and 4.70 ppm (1H, J = 12 Hz) corresponding to a CH_2 group having no protons in the α positions. It follows from this that the acid is α-phenyl-α,β-dihydroxypropionic acid, i.e., it differs from tropic acid by an additional tertiary alcoholic group. This is confirmed by the presence in the IR spectrum of the acid of an additional band at 3620 cm^{-1} in addition to the usual absorption band for tropic acid at 3530 cm^{-1}. Base I has the structure of an ester of scopine (scopoline) with this acid and is identical in structure with anisodine isolated from S. tangutica, growing in China [3].

Base II consisted of white acicular crystals with mp 62-63°C (from benzene), pK_{base} 5.2. IR spectrum cm^{-1}: 700, 742, 760 (benzene nucleus), 3400-3490 (active hydrogen), 1725 (ester carbonyl group). NMR spectrum ($CDCl_3$, internal standard, HMDS ppm): 7.12-7.30 (5H, multiplet, monosubstituted benzene nucleus), 4.95 (1H, triplet, J = 5 Hz, H_3 of a tropane nucleus), 4.30 (1H, quartet, J ~ 8 Hz, J ~ 2Hz, H_6 of a tropane nucleus), 4.11 (1H, triplet, J = 11 Hz, H at the α-C of tropic acid), 2.36 (3H, singlet, $N-CH_3$). The IR and NMR spectra were similar to the spectra of hyoscyamine.

The molecular weight of (II) (M^+ 305) differed from that of hyoscyamine by 16 m/e. The presence in the mass spectrum of (II) of peaks of ions with m/e 261, 140, 96, 95, and 94 shows the α-cleavage of the pyrolidine ring with the subsequent elimination of oxyethylene (peaks of an ion with m/e 261). Such a fragment is characteristic for 6-hydroxyhyoscyamine [4]. The melting point of (II) also agrees with this alkaloid [4].

The acid isolated from II on hydrolysis by Reimer's method [2] was identified as tropic acid from the absence of a depression of the melting point of a mixture; the amino alcohol had R_f 0.12 [PC, Filtrak FN-11 paper, butan-1-ol–acetic acid–water (4 : 1 : 5) system]; melting point of its picrate (from 40% ethanol) 248-249°C. Consequently, II has the structure of 6-hydroxyhyoscyamine, which has been isolated previously from Physochlaina dubia [4] and has been detected chromatographically in S. tangutica growing in China [5].

LITERATURE CITED

1. S. A. Minina, T. V. Astakhova, and N. V. Nazarova, Rast. Res., II, 493 (1975).
2. F. Reimers, Quart. J. Pharm. Pharmacol., 21, 470 (1948).
3. Hsieh, Ching-Hsu, Wang Lin, Liu Yung-Lung, Shang Tian-ming, Hsieh Feng-Chik, and Ke Ta-Lun, K'o Hsueh T'ung Pao, 20, 52 (1975); Ref. Zh. Khim., 22, E64 (1976).
4. R. T. Mirzamatov, V. M. Malikov, K. L. Lutfullin, and S. Yu. Yunusov, Khim. Prirodn. Soedin, 493 (1972).
5. Hsiao Pei-Ken, Hsia Kuang-Cheng, and Ho Li-Vi, Acta Botanica Sinica, 15, 187 (1973).

Leningrad Institute of Pharmaceutical Chemistry. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 712-713, September-October, 1977. Original article submitted March 3, 1977.

 0009-3130/77/1305-0598$07.50