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1965

SovietRxiv

Abstract

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Chemistry

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STUDY OF THE ALKALOIDS OF *CORYDALIS GORTSCHAKOVII* AND *CORYDALIS PSEUDOADUNCA*

We investigated *C. gortschakovii* and *C. pseudoadunca*, collected in the region of the Zaalai Range by a botanical expedition of the Institute of the Chemistry of Plant Substances under the direction of Candidate of Biological Sciences E. E. Korotkova. For isolation of the total alkaloids, chloroform extraction at room temperature was used.

C. gortschakovii. Extraction was carried out on 2.5 kg of the ground, air-dry aerial part of the plant. Fifteen grams of the ethereal and 2 g of the chloroform total alkaloids were obtained. The ethereal total was divided into phenolic and nonphenolic portions. On treatment with methanol, protopine was obtained from the ethereal nonphenolic total, and from the mother liquor a crystalline base (1.5 g) with m.p. 183-184° (acetone), $(\alpha)_D^{17} = +181^\circ$ (chloroform), containing three methoxyl groups. In the IR spectrum, absorption is observed at 3150 cm^{-1} (OH). The UV spectrum of this base has three maxima, $\lambda_{\max}$ 220, 268, 304 mμ ($\lg\varepsilon$ 4.4, 3.98, 3.6), characteristic of alkaloids of the aporphine type. On acetylation with acetyl chloride at room temperature, an optically inactive O,N-diacetyl product was obtained with m.p. 163.5-164.5° (25% alcohol), IR spectrum: 1645 cm^{-1} (N—Ac), 1770 cm^{-1} ($OCOCH_3$), which confirms that this base belongs to alkaloids of the aporphine type. The methiodide of the O-methyl derivative proved identical with the methiodide of the O-methyl derivative of corydine. In view of the complete identity of the properties both of the base itself and of its derivatives with isocorydine and its corresponding derivatives ([1,2]), we consider that our base and isocorydine are identical.

From the chloroform total of *C. gortschakovii*, on treatment with a methanol—chloroform mixture, a crystalline base was obtained (50 mg) with m.p. 232-234° (decomp., CH_3OH); it contains two methoxyl groups. In the IR spectrum, absorption is observed in the region of 3500 cm^{-1} (OH). According to the UV spectrum of this base ($\lambda_{\max}$ 222, 270, and 360 mμ, $\lg\varepsilon$ 4.4, 3.98, 3.7), it may be assumed that it belongs to alkaloids of the aporphine type with substituent groups in positions 3 and 4.

C. pseudoadunca. Thirty-five kilograms of the ground, air-dry aerial part of the plant were extracted. Three hundred grams of the ethereal and 30 g of the chloroform total alkaloids were obtained. The ethereal total was divided into phenolic and nonphenolic portions. On treatment with methanol, part of the ethereal nonphenolic total crystallized. From the crystalline part of the total, by fractional crystallization from a methanol—chloroform mixture and from acetone, protopine (1 g) was isolated with m.p. 205° (warts from CH_3OH —chloroform) and (5 g) with m.p. 210° (plates from CH_3OH—chloroform), and bases A (15 g), B (10 g), and C (1.7 g).

Base A is a tertiary base with mp 194-195° (CH_3OH—chloroform), $(\alpha)_D^{16} = 112°$ (chloroform); hydrochloride, mp 248-252° (alcohol). In the IR spectrum, absorption is observed at 1750 cm^{-1} (ester group). It contains no methoxy groups and gives positive reactions with gallic acid and phloroglucinol-sulfuric acid for a methylenedioxy group. The UV spectrum has three maxima at λ_{max} 222, 298, and 324 mµ ($\lg\varepsilon$ 4.36, 3.72, 3.68). On oxidation of the alkaloid with dilute nitric acid, a basic product with mp 105-110° (ether) and an acidic product—an aldehydo acid with mp 190-192° (decomp.)—were obtained; the latter was identified as the phthalide, mp 230-232° (aqueous alcohol). The properties of this alkaloid, as well as of the products of its degradation, are close to those of bicuculline and the corresponding products of its degradation ([3]). Thus, base A is bicuculline.

Base B is a tertiary base with mp 131-132° (CH_3OH), $(\alpha)_D^{18} = 63°$ (chloroform); picrate, mp 148-153° (alcohol), picrolonate, mp 219-220° (alcohol), methiodide, mp 204-206° (CH_3OH); it contains two methoxy groups and gives positive reactions with gallic acid and phloroglucinol-sulfuric acid for a methylenedioxy group. In the IR spectrum, absorption is observed at 1760 cm^{-1} (ester group); the UV spectrum has a maximum at λ_{max} 298 mµ ($\lg\varepsilon$ 3.94) and a minimum at λ_{min} 264 mµ ($\lg\varepsilon$ 3.07). On oxidation with dilute nitric acid, hydrastinine and an acid with mp 176-178° (H_2O) were obtained; the acid was identical with hemipinic acid (mixed melting point of the acids and their anilides and IR spectra of the acids). On the basis of the data obtained, it may be assumed that base B is the dextrorotatory form of the known alkaloid hydrastine. However, although a number of authors indicate that on oxidation of alkaloids of the narcotine type and, in particular, hydrastine ([4], [5]) with dilute nitric acid an aldehydo acid is obtained, in our case hemipinic acid is obtained. The dextrorotatory form of hydrastine was obtained by resolving *dl*-hydrastine into optical antipodes ([6]).

Base C is an optically inactive tertiary base with mp 197-203° (CH_3OH—chloroform); hydrochloride, mp 250-252° (aqueous alcohol). On oxidation with dilute nitric acid, hydrastinine and an aldehydo acid were isolated. Oxidation of the latter with potassium permanganate in alkaline medium gave a dicarboxylic acid with mp 197-198° (H_2O). The anhydride of the acid, mp 167-169° (ether —acetone), proved to be identical with the anhydride of 3,4-methylenedioxy-1,2-benzenedicarboxylic acid obtained from bicuculline. Thus, base C is *dl*-bicuculline.

Structural formula

Figure 1: Structural formula

On evaporation of the phenolic ether fraction, 10 g of a crystalline base were obtained with mp 247-252° (butanol—pyridine), 247-252° (alcohol), $(\alpha)_D^{21} = -391°$ (CH_3OH); diethyl ether, mp 164-166° (alcohol). The UV spectrum has a maximum at λ_{max} 288 mµ ($\lg\varepsilon$ 4.74). On acetylation with acetic anhydride in pyridine, an O,O-diacetyl derivative with mp 191-193° (ether—benzene), 193-195° (CH_3OH—ether) was obtained. By methylation of the phenolic base with methyl iodide in alkaline medium, the methiodide of the O,O-dimethyl derivative with mp 243-246° (H_2O) was obtained. On heating the latter with ethanolamine at 160-170°, the dimethyl ether was obtained with mp 177-179° (alcohol), $(\alpha)_D^{21} = -300°$ (chloroform); hydrochloride, mp 216-219° (alcohol—ether), bromohydrate, mp 223-226° (CH_3OH). All the properties of the dimethyl ether agree well with those of corypalline (Ia). The known alkaloid of the tetrahydroprotoberberine type, coreximine ([7], [8]) (Ib), containing two phenolic hydroxyl and two methoxy groups, has mp 262° (chloroform—alcohol), $(\alpha)_D$ rotates to the left; diethyl ether, mp 131°. Since our base and coreximine and their

The diethyl ethers have different melting points; thus, it is evident, one may consider them nonidentical, and we propose the name **coramine** for the base.

$$\begin{array}{ll} \text{Ia.} & R_1 = R_2 = R_3 = R_4 = \text{CH}_3 \\ \text{Ib.} & R_2 = R_3 = \text{H}, \quad R_1 = R_4 = \text{CH}_3. \end{array}$$

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Received
7 XII 1964

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Note: Figure translations are in progress. See original paper for figures.