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ALKALOIDS OF THE CORMS OF Colchicum laetum

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There is limited amount of information in the literature on the alkaloid composition of Colchicum laete Stev. [1-3]. Colchicine has been isolated from the corms of this plant [3]. In order to study its alkaloids, the plant was gathered in the flowering period in September, 1988 in the Apsheron region, Stavropol' krai.

The fresh comminuted corms together with the juice (1.3 kg) were acidified to pH 3-4 with tartaric acid and were extracted with toluene (fraction 1-2.42 g), and they were then made alkaline with ammonia to pH 9-10 and were again treated with toluene (fraction 2-1.68 g). Fraction 3 (1.75 g) was obtained by the chloroform treatment of the meal left after the isolation of fraction 2. Column chromatography was used for the isolation of individual bases.

As a result of the treatment of toluene fraction 1 with petroleum ether and then with ethyl acetate, we isolated base (I) (0.76 g) with the composition $C_{22}H_{25}NO_6$, mp 155-156°C (ethyl acetate), $[\alpha]_D^{20}$ −121° (c 0.879; chloroform), which was identified as colchicine from its physicochemical properties [4], its IR spectrum, and direct comparison with an authentic sample.

The ethyl acetate mother liquor after the separation of base (I) was chromatographed on a column of silica gel with elution by benzene and then by benzene—methanol (9:1) and (1:1). This led to the isolation of base (II) (0.35 g), with the composition $C_{21}H_{23}NO_6$, mp 178-180°C (chloroform), $[\alpha]_D^{20}$ −137° (c 1.0; chloroform). Its UV spectrum showed two maxima, at 243 and 355 nm, and its mass spectrum contained the peak of the M^+ 385 ion, corresponding to a dimethylated colchicine derivative [4-6]. The PMR spectrum of the base taken in deuterochloroform with tetramethylsilane as internal standard contained the signals of three methoxy groups (at 4.10, 3.90, and 3.66 ppm), of an N-acetyl group (1.99 ppm), and of four aromatic protons in the form of singlets at 6.52 and 7.61 ppm (H-3 and H-8), and also doublets at 6.77 and 7.38 ppm, dd, J = 10 Hz (H-11 and H-12). By comparison with literature information, base (II) was identified as 2-demethylcolchicine [5, 6].

The treatment of fraction 2 with acetone led to the precipitation of base (III) (0.24 g), with the composition $C_{21}H_{25}NO_5$, mp 184-186°C (ethanol), $[\alpha]_D^{20}$ −127° (c 1.0; chloroform). Its mass spectrum had the molecular ion M^+ with m/z 371. From these constants it was identical with colchamine [4, 5]. A mixture of the isolated base (III) with an authentic sample of colchamine gave no depression of the melting point.

On a column of Al_2O_3, the acetone mother liquor after the isolation of base (III) yielded base (IV), with the composition $C_{21}H_{21}NO_6$, mp 263-264°C (ethyl acetate), $[\alpha]_D^{20}$ −106° (c 0.68; chloroform). PMR spectrum: 1.96 (NH—CO—CH_3); 3.80 (C-1, OCH_3); 5.98 (O—CH_2—O) and 6.45 (H-4). The mass spectrum contained peaks with m/z 383 (M^+), 355, 340, 312, 296, 281, 265, and 251. A comparison of the results obtained with the literature permitted base (IV) to be identified as cornigerine [5, 7].

Fraction 3 yielded a base (V) having the composition $C_{22}H_{25}NO_6$, mp 183-185°C (ethanol), $[\alpha]_D^{20}$ −304° (c 1.0; chloroform). Its UV spectrum (in alcohol) had maxima at (nm) 224, 266,

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and 337 nm (inflection), and the mass spectrum had peaks of ions with m/z 399 (M^+), 356, and 340. The spectral characteristics agreed with those given in the literature for β-lumicolchicine [8].

Of the bases identified, this is the first time that colchamine, 2-demethylcolchicine, cornigerine, and β-lumicolchicine have been isolated from this plant.

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FORMATION OF DIISOEUGENOL IN THE SYNTHESIS OF ETHYLBIS(4-HYDROXY-3-METHOXYPHENYL)METHANE

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In order to widen the assortment of dimeric models of lignin, we attempted to synthesize ethylbis(4-hydroxy-3-methoxyphenyl)methane from guaiacylpropan-1-ol and guaiacol by the procedure of [1]. Compound (I) with mp 176-177°C (by reprecipitation in hexane from ethereal solution) was obtained in a yield of 44%. According to its mass spectrum, its molecular mass was 328.16817, composition $C_{20}H_{24}O_4$ (MKh 1310, resolving power 10,000, reference substance perfluorokerosine), which did not correspond to ethylbis(4-hydroxy-3-methoxyphenyl)methane ($M = 288$, $C_{17}H_{20}O_4$).

It is known from the literature that (1-hydroxyalkyl)phenols are capable of condensing, with the splitting out of water, in acid and alkaline media, giving dimers and trimers [2-4]. Judging from the molecular mass and composition of the product obtained, dimerization of the initial guaiacylpropan-1-ol had taken place in the acid medium. To check this hypothesis, we performed a reaction under the same conditions but taking only guaiacylpropan-1-ol. As a result, we isolated a substance identical with that obtained previously (I). PMR spectrum of this substance (δ, ppm): 0.78-1.0 (5H, q, 2 CH_3), 1.25-1.75 (2.2 H, m, $-CH_2-$), 2.15-2.5 (1 H, q, $-CH-$ of a five-membered ring), 2.67-3.00 (0.8 H, q, $-CH-$ of a five-membered ring), 3.5-3.87 (6.9 H, m, two intense OCH_3 signals superposed on a 1 H multiplet of a five-membered ring), 5.25-5.5 (2.1 H, d, 2 OH), 6.28-6.8 (4.6 H, m, arom. H). The "value" of one proton was calculated on the basis of the assumption that the total integral corresponded to 24 protons. The spectrum was taken in $CDCl_3$, 0 – HMDS, on a BS 567 A instrument (Tesla, Czechoslovakia) at 100 MHz. The spectrum proved to be identical with that of authentic diisoeugenol [5] also taken at 100 MHz.

We then performed the condensation of guaiacylpropan-1-ol in an acid medium without heating, at room temperature (18-20°C), taking samples for thin-layer chromatography on Silufol plates after predetermined intervals of time. The solvent system was diethyl ether–hexane (4:1 by volume) and the revealing agent was iodine. Without heating, the spot of diisoeugenol appeared on the plate 2 h after the beginning of the reaction. The reaction

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