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ALKALOIDS OF *Veratrum nigrum*

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The alkaloids of *Veratrum nigrum* L. [1] have been studied inadequately. There are reports on the dynamics of the accumulation of the combined alkaloids in various organs according to the vegetation stage of the plant [2], of a preliminary chromatographic separation of the combined alkaloids separated from the epigeal and hypogeal parts [3], and of the isolation of jervine, germerine, and veratroylzygadenine [4]. In view of this, we have undertaken the study of the composition of the alkaloids of this species of *Veratrum*.

From the combined alkaloids isolated by treating the roots with rhizomes, by the method described for *Veratrum lobelianum* Bernh. [5], we have isolated by chromatography on a column of cellulose [6] two alkaloids with R_f 0.40 (I), and 0.47 (II) (chloroform, saturated formamide; type "M" ["slow"] paper of the Volodarskii paper mill, impregnated with a 1:2 solution of formamide in ethanol).

Alkaloid (I), mp 191-192°C (benzene), $[\alpha]_D^{22}$ −16° (c 0.6 pyridine). IR spectrum (KBr): 1740, 1250 cm^{-1} (ester C=O). The UV spectrum of a sulfuric acid solution of the alkaloid taken 24 h after its dissolution (λ_{max} = 250, 290, 370, 540 nm) had a region at 360 nm of coincidence with the spectrum taken after 1.5 h (the amino alcohol protoverine [7]). In the hydrolysis products of the alkaloid, paper chromatography [8] showed the presence of substances analogous to the hydrolysis products of deacetylprotoveratrine A (III), which we have isolated from *Veratrum lobelianum* Bernh. [9]: the amino alcohol protoverine (butan-1-ol − CH_3COOH − H_2O (4:1:5)), acetic acid, (l)-α-methylbutyric acid, and (d)-α-hydroxy-α-methylbutyric acid (butan-1-ol − 1.5 N aqueous ammonia (1:1)). The methanolysis [10] of (I) converted it into dideacetylprotoveratrine A (IV) [11].

The results of analysis show that the alkaloid (I) is deacetylprotoveratrine A [9]. This is the first time that it has been isolated from *Veratrum nigrum* L.

Alkaloid (II), mp 202-204°C (benzene), $[\alpha]_D^{20}$ −7° (c 0.88; pyridine). IR spectrum (KBr); 1738, 1250 cm^{-1}. A sulfuric acid solution of the substance had a spectrum in the UV and visible regions taken 24 h after dissolution (λ_{max} 246, 315, 406, 528 nm) that did not coincide with the spectrum taken after 1.5 h (amino alcohol germine) [7]. The products of the alkaline hydrolysis of (II) [8] were shown by paper chromatography with "markers" to contain the amino alcohol germine (butan-1-ol − CH_3COOH − H_2O (4:1:5)), (l)-α-methylbutyric acid, and (d)-α-hydroxy-α-methylbutyric acid. According to the scheme of determining the positions of acyl groups in *Veratrum* esters [12], the acids found must occupy position 3 and 15 of the germine, respectively.

The results of analysis permit the conclusion that the alkaloid (II) isolated is germerine. This is the first time that it has been isolated from raw material growing on the territory of the USSR.

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PREPARATION OF OPTICALLY ACTIVE PROLINE

SYNTHESIS AND RESOLUTION OF CYCLO(N-PANTOYL-DL-PROLINE)

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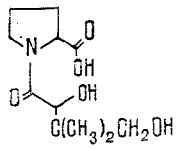
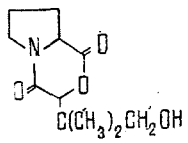
In spite of the fact that a whole series of chemical and fermentation methods has been proposed for the resolution of DL-proline [1, 2], the search for new simpler and cheaper methods is of undoubted interest because of the importance of L-proline for the pharmaceutical and foodstuffs industries. Recently, a convenient method has been proposed for resolving some DL-α-amino acids into optical antipodes by their conversion into N-D- and N-L-pantoyl derivatives [3]; however, the resolution of DL-proline has not been reported. In studying the reaction of D-pantolactone with L-proline we have found that, in addition to the formation of the oily N-D-pantoyl-L-proline (I), a well-crystallizing compound is formed, which has been identified as cyclo(N-D-pantoyl-L-proline) (II). In this connection, by using the difference in the solubilities of the enantiomers of (II) we have studied the possibility of the preparative separation of racemic proline by means of the reaction with D-pantolactone.



I



II

Condensation of the sodium salt of DL-proline with D-pantolactone in boiling methanol with subsequent chromatography on KU-2 cation-exchange resin (H^+ form) and extraction of the aqueous eluates with chloroform yielded a mixture of diastereomeric cyclo(N-D-pantoyl-L- and -D-proline)s. Crystallization of this mixture from ether led to the isolation in optically pure form of cyclo(N-D-pantoyl-L-proline) with mp 118-120°C, $[\alpha]_D^{20}$ −68° (c 2; MeOH) (identical with the substance obtained by the reaction of D-pantolactone with L-proline) in a yield of ~10%. The enantiomer of (II) is readily hydrolyzed by boiling with 5 N hydrochloric acid giving L-proline with $[\alpha]_D^{20}$ −55° (c 0.6; 5 N HCl) [1]. Thus, we have succeeded in performing the resolution of DL-proline into antipodes by using D-pantolactone as resolving agent.

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