

Thus, *dl*-peganin, vasicinone, and deoxyvasicinone have been obtained from *Peganum nigellastrum*.

#### LITERATURE CITED

1. L. K. Safina, Harmel Peganum [in Russian], Alma-Ata (1977).
2. S. Yu. Yunusov, Alkaloids [in Russian], Tashkent (1974), p. 169.

#### ALKALOIDS OF *Berberis integerrima*

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Continuing the separation of the combined alkaloids of the leaves of *Berberis integerrima* Bge. [1], we have isolated a phenolic base (I) with mp 125–126°C (benzene),  $[\alpha]_D^{+57}$  (c 0.2; ethanol). Methylation of (I) with diazomethane yielded glaucine. According to its mass and NMR spectra, (I) must contain two hydroxy and two methoxy groups. A direct comparison of (I) with isoboldine [2] showed their identity.

A phenolic base (II) with mp 192–193°C,  $[\alpha]_D^{+90}$  (c 0.16; CHCl<sub>3</sub>) gave a crystalline hydrochloride with mp 204–205°C. The UV spectrum [ $\lambda_{\text{max}}^{\text{ethanol}}$  222, 282, 306 nm (log  $\epsilon$  4.49, 4.04, 4.06)] characterized (II) as a 1,2,9,10-substituted aporphine. The mass spectrum coincided with that of thalicmidine (III). The NMR spectra of (II) and (III) differed by the signal of the N-methyl group: in (II) it was displaced downfield to 3.08 ppm. The facts given above permit (II) to be identified as thalicmidine N-oxide [3]. In actual fact, the reduction of (II) with Zn/HCl or NaBH<sub>4</sub> yielded (III). Oxidation of the latter with hydrogen peroxide gave (II).

Another phenolic base (IV) was isolated in the form of an oil with  $[\alpha]_D^{+20.6}$  (c 0.06; ethanol). UV spectrum:  $\lambda_{\text{max}}^{\text{ethanol}}$  230 nm (shoulder), 285 nm (log  $\epsilon$  4.09, 3.76). Mass spectrum: m/e 329 (M<sup>+</sup>), 192 (100%), 178, 137. The NMR spectrum taken in CDCl<sub>3</sub> showed signals in the form of singlets from a N-CH<sub>3</sub> group (2.39 ppm), two OCH<sub>3</sub> groups (3.76 ppm), five aromatic protons in the form of three singlets at 6.24, 6.45, and 6.61 ppm, and two one-proton doublets at 6.51 and 6.68 ppm. This enabled (IV) to be assigned to the benzyltetrahydroisoquinoline bases. The benzyl and the isoquinoline moieties of (IV) contain hydroxy and methoxy groups. When (IV) was methylated with methyl iodide in an alkaline medium, a methiodide was obtained with mp 217–218°C, which was identified as the methiodide of laudanosine by comparison with an authentic sample. Consequently, (IV) contains substituents in positions 3', 4', 6, and 7.

The mutual arrangement of the hydroxy and methoxy groups was determined with the aid of proton-proton double resonance from the results of measurements of the intramolecular NOE. According to these results, the positions of the hydroxy and methoxy groups in (IV) correspond to reticuline [4].

The detection of reticuline among the protoberberine, aporphine, and bisoclaurine alkaloids of the barberry is interesting from the biogenetic point of view: it shows that in the barberry biogenesis probably takes place by the route as has been shown by experiments with labeled atoms for *Hydrastis canadensis* [5].

An alkaloid (V) was isolated in the form of an amorphous substance. It formed a crystalline hydrochloride with mp 228–229°C. The UV spectrum of (V) [ $\lambda_{\text{max}}^{\text{ethanol}}$  223, 271, 306 nm (log  $\epsilon$  4.39, 3.95, 3.96)] is characteristic for aporphine alkaloids with substituents in positions 1, 2, 10, and 11. The NMR spectrum taken in CDCl<sub>3</sub> showed the signals from three OH groups in the 3.84 ppm (6H, s) and 3.65 ppm (3H, s) regions, of a N-CH<sub>3</sub> group at 3.41 ppm (3H, s) and from aromatic protons at 6.80 ppm (1H, s), 6.75 ppm (1H, d), and 6.77 ppm (1H, d).

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The mass spectrum of (V) showed the peaks of ions with m/e 341, 340, 326, 298, and 267; M<sup>+</sup> was absent.

From the spectral characteristics it may be assumed that the base is the N-oxide of corydine or of isocorydine. The reduction of (V) with Zn/HCl gave isocorydine [2], which was identified by comparison with an authentic sample.

This is the first time that isocorydine N-oxide has been isolated from plant raw material and it is therefore a new alkaloid.

This is the first time that isoboldine, thalicmidine N-oxide, and reticuline have been isolated from plants of the genus *Berberis*.

#### LITERATURE CITED

1. A. Karimov, M. B. Telezhenetskaya, K. L. Lutfullin, and S. Yu. Yunusov, *Khim. Prirodn. Soedin.*, 558 (1976).
2. H. Guinaudeau, M. Leboeuf, and A. Cave, *Lloydia*, 38, 4, 275 (1975).
3. V. G. Khodzhaev, S. Kh. Maekh. and S. Yu. Yunusov, *Khim. Prirodn. Soedin.*, 631 (1972).
4. K. W. Gopinath, T. R. Govindachari, B. R. Pai, N. Viswanthan, *Ber.*, 92, 776 (1959).
5. R. H. F. Manske, *The Alkaloids*, Vol. IX, Academic Press, New York (1967), p. 94.

#### GALANTHAMINE FROM SOME SPECIES OF THE FAMILY AMARYLLIDACEAE

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Continuing a search for new possible sources of galanthamine among plants of the family Amaryllidaceae, we have investigated *Eucharis subedentata* Benth., *Vallota speciosa* Th. Dur. et Schinz (introduced species obtained from the V. L. Komorov Botanical Institute of the Academy of Sciences of the USSR), and *Galanthus nivalis* L., subsp. *angustifolius* (G. Koss) Artjushenko, which we collected in the Kabardino-Balkarsk ASSR. There is no information in the literature on the presence of galanthamine in these species [1-7].

The comminuted air-dry leaves and bulbs were moistened with a 15% solution of ammonia and extracted with a mixture of chloroform and ethanol. The extraction was carried out by treatment on a shaking machine for 2 h or by steeping for 18 h. The filtrate was evaporated to dryness. The combined alkaloids extracted from the raw material were dissolved in ethanol and chromatographed on a fixed alkaline layer of KSK silica gel in the chloroform-ethyl acetate-ethanol (2:2:1) system. After treatment with iodine, the bands corresponding to galanthamine were separated off and galanthamine was eluted with a mixture of chloroform and methanol. The operation was repeated several times. After evaporation, samples of substances were obtained which were identified by comparing their NMR spectra with those of an authentic sample of galanthamine. The constants of the galanthamine corresponded to those given in the literature [1].

The quantitative contents of galanthamine determined by a chromatocolorimetric method were: in *Eucharis subedentata*, leaves 0.10%, bulbs 0.05%; *Vallota speciosa*, leaves 0.05%, bulbs 0.05%; *Galanthus nivalis* L. subsp. *angustifolius*, leaves 0.05%, bulbs 0.73%, calculated on the absolutely dry weight of the raw material. This is the first time that galanthamine has been isolated from the species mentioned.

#### LITERATURE CITED

1. S. Yu. Yunusov, *Alkaloids* [in Russian], Tashkent (1974).
2. R. H. F. Manske, *The Alkaloids, Chemistry and Physiology*, Vol. VI, Academic Press, New York (1960), p. 322.
3. R. H. F. Manske, *The Alkaloids*, Vol. XI, Academic Press, New York (1968), p. 307.
4. R. H. F. Manske, *The Alkaloids*, Vol. XV, Academic Press, New York (1975), p. 111.

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