

The IR spectra of the substances isolated were identical with those of coronopilin in the region of skeletal vibrations. It is possible that their structures have a common basic skeleton.

On the basis of the results given above it may be assumed that the substances isolated are sesquiterpene lactones which have evidently not been studied previously.

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26 September 1967

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UDC 634.986.22

#### THE NEUTRAL SUBSTANCES OF THE OLEORESIN OF PINUS PALLASIANA

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Khimiya Prirodnykh Soedinenii, Vol. 4, No. 3, pp. 193-194, 1968

We have separated the oleoresin collected in the middle of May in the Yalta Leshkoz [forestry farm] into an acidic and a neutral fraction. The latter (after removal of the monoterpene fraction by distillation) was saponified with an ethanolic solution of caustic potash and the unsaponifiable part, amounting to 6% of the initial oleoresin, was chromatographed on neutral alumina (activity III). Petroleum ether extracted a hydrocarbon fraction (23%) and a mixture of petroleum ether and benzene (95:5) an aldehyde fraction (30%). Benzene eluted a mixture of saturated aliphatic alcohols the main component of which was tetracosanol with mp 74-75° C (from acetone). A mixture of benzene and ether (95:5) eluted  $\beta$ -sitosterol (23%).

The aldehyde fraction was chromatographed on a column of silica gel impregnated with silver nitrate [1]. The process of separation was followed by thin-layer chromatography in the same adsorbent [2].

A mixture of petroleum ether and benzene (93:7) eluted a small fraction (0.15%) consisting of a mixture of dehydroabietinal and abietinal (identified by chromatographic comparison with authentic samples) and then pimarinal (72%), with mp 62.5-63.5° C (from methanol);  $[\alpha]_D^{20} +103^\circ$  (c 2.5; chloroform). Semicarbazone, mp 214.5-216° C (decomp, from ethanol); 2,4-DNPH, mp 198-199° C (from ethanol). The latter gave no depression of the melting point with an authentic sample of pimarinal 2,4-DNPH. A 92:8 mixture of the same solvents eluted liquid isopimarinal (25%)  $[\alpha]_D^{21} -12^\circ$  (c 5; chloroform). Semicarbazone, mp 223-224.5° C (decomp, from ethanol), 2,4-DNPH, mp 181.5-185.5° C (from ethanol). A mixture of the latter with an authentic sample of isopimarinal 2,4-DNPH melted without depression.

No diterpene alcohols corresponding to the resin acids were found.

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22 January 1968

Institute of Chemistry AS Moldavian SSR

UDC 547.943

#### ALKALOIDS OF FUMARIA

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Khimiya Prirodnykh Soedinenii, Vol. 4, No. 3, pp. 194-195, 1968

From Fumaria parviflora Lam. [1], collected on the 12th April 1966 in the vegetation period in the region of Shargun, Surkan-Dar'inskaya Oblast, by chloroform extraction we have obtained 0.49% of combined alkaloids. By

separating the alkaloids according to their solubility in organic solvents and also on a column of alumina, we have isolated protoprine, cryptopine, d-bicuculine,  $\gamma$ -adlumine, a base with mp 158–159° C, fumaridine, and fumaramine [2].

The authenticity of the  $\gamma$ -adlumine was shown by its oxidation with potassium permanganate to a 3,4-methylenedioxy dicarboxylic acid and m-hemipinic acid and the identity of its physical properties with literature data [3].

The base with mp 158–159° C,  $[\alpha]_D^{25} + 127.7^\circ$  (c 1.1; chloroform) had  $R_f$  0.79 on chromatography in a thin layer of silica gel [chloroform–methanol (8:2)] and  $R_f$  0.73 on a paper chromatogram [1-butanol–acetic acid–water (100:5:100)].

The IR spectrum of the base had absorption bands at 940  $\text{cm}^{-1}$ , 1035 ( $\text{CH}_2\text{O}_2$ ), 1505, 1610 (aromatic ring), and 1760  $\text{cm}^{-1}$  ( $=\text{CO}$ ), and the UV spectrum had  $\lambda_{\text{max}}$  296  $\text{m}\mu$  ( $\log \epsilon$  3.90). The NMR spectrum had a singlet at  $\tau = 7.55$  (N–CH<sub>3</sub>), two singlets at  $\tau = 6.10$ , 6.23 (2 OCH<sub>3</sub>), and a quadruplet at  $\tau = 4.30$  ( $\text{CH}_2\text{O}_2$ ), two one-proton doublets at  $\tau = 2.92$ , 2.68 (ortho aromatic protons), and two singlets at  $\tau = 3.43$ , 3.70 (para aromatic protons). Oxidation of the base with dilute nitric acid gave hydrastinine and hemipinic acid. All this permits the conclusion that our base is d- $\alpha$ -hydrastine [4], which we have found in this plant for the first time. From *Fumaria vaillantii* Loisl, collected in the Tashkent Oblast on 3–5 May 1965 in the period of vegetation and incipient fruit-bearing, we obtained 0.54% of total alkaloids by chloroform extraction. Separation of the mixture of alkaloids yielded protopine, d- $\alpha$ -hydrastine, fumaridine, and fumaramine.

The NMR spectra were taken by M. R. Yagudaev on a JNM-4H-100/100 MHz instrument in deuterochloroform with HMDS as internal standard.

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23 November 1967

Institute of the Chemistry of Plant Substances AS UzSSR

UDC 547.944/945

#### THE ALKALOIDS OF PEDICULARIS

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Khimiya Prirodnikh Soedinenii, Vol. 4, No. 3, p. 195, 1968

We have studied the alkaloids of the epigeal part of four species of Pedicularis. The results can be seen from the following table.

Species	Place and time of collection (year, date)	Vegetation period	Total alkaloids, % by weight of the raw material
<i>P. dolichorhiza</i> Schrenk.	Basin of the R. Talas, KirgSSR, 24 June 1966	Flowering	0.29
<i>P. olgae</i> Rgl.	Chimgan, Tashkent Oblast, 27 March 1967	Incipient bud formation	0.70
<i>P. macrochila</i> Vved.	Kungei Ala-Tau, KazSSR, 15 June 1967	End of flowering	0.31
<i>P. olgae</i> Rgl.	Sarydasht, TadzhSSR, 20 June 1967	Flowering	0.80

We investigated the alkaloids of *P. dolichorhiza* in more detail. By chloroform extraction, *P. dolichorhiza* yielded 0.18% of combined ethereal bases and 0.11% of combined chloroform bases. From the ethereal fraction by treatment with acetone, we isolated a base with mp 218–220° C (acetone),  $[\alpha]_D^{25} + 38^\circ$  (c 0.315; methanol) identical with the plantagonine from *P. olgae* [1].

The mother liquor was separated with respect to basicity into five fractions. The 3-rd and 4-th fractions yielded