PMR spectrum (CDCl₃, ppm, δ scale, HMDS = 0): 3.89 (s, 3 H, OCH₃); 2.97 (s, 9 H, 3×OCH₃). One proton singlets at 6.96, 7.82, and 8.54 were due to protons at C-3, C-8, and C-11, respectively. The protons of the pyridine ring appeared in the form of two one-proton doublets at 7.57 (J = 5.5 Hz) and 8.67 (J = 5.5 Hz). The mass spectrum of (I) had strong peaks of ions with m/z 351 (M⁺) and 336 (M - 15)⁺.

The reduction of (I) with zinc in sulfuric acid followed by Hess methylation yielded (\pm) -glaucine. Consequently, base (I) was oxoglaucine.

Base (II) (eluent benzene-ether (5:1)) crystallized from chloroform-methanol (1:1), mp 252°C. UV

spectrum: $\lambda_{\max}^{C_2H_5OH}$ 243, 303, 327, 339 nm (log ε 4.71, 4.33, 3.78, 3.74). PMR spectrum (CF₃COOH), ppm: 2.64 (s, 3 H, C-CH₃); 3.61 (s, CH, OCH₃); 6.76 (m, 2 H) and 7.70 (m, 3 H) (5×ArH).

The mass spectrum showed intense peaks of ions with m/z 212 (M⁺, 100%), 197, and 169. The facts given above, and also the absence of a depression of the melting point of a mixture with an authentic sample enabled (II) to be identified as harmine [4].

Eleven bases have been isolated from <u>Th.</u> <u>foetidum</u>. Harmine and oxoglaucine have been detected in a plant of the genus Thalictrum for the first time.

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COMPONENTS OF Haplophyllum perforatum

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The plant <u>Haplophyllum performatum</u> (family Rutaceae), which is widely distributed in Central Asia and South Kazakhstan, is interesting in view of the fact that its chemical composition depends greatly on the conditions of growth. This plant has yielded 25 alkaloids, many of which are produced only from a definite growth site [2], and therefore <u>H. perforatum</u> from new collection points is frequently an independent object of chemical study.

We have investigated the alkaloids of the epigeal part collected in the budding and incipient flowering period in the Baisun region of Surkhandar'ya province (I) and in Chimgan (II).

Methanolic extracts obtained from I (3.93 kg) and II (1.83 kg) were evaporated to dryness and the residues were dissolved in chloroform. The alkaloids were extracted from the chloroform solution (A) with 10% sulfuric acid. From the acid solutions 26 g and 0.71 g of mixtures of bases, respectively, were obtained.

From the total alkaloids of the epigeal parts of I and II we isolated skimmianine (1.57 g), evoxine (1 g), a mixture of crystals (B) and skimmianine (0.02 g), and 7-isopentenyloxy- γ -fagarine (0.01 g), respectively. Chromatography on alumina of the residues obtained by distilling the chloroform solutions (A) gave in the case of I the lignan eudesmine (10.2 g) and the alkaloids perfamine (3.5 g), flindersine (0.65 g), and haplamine (4.56 g), and in the case of (II) eudesmine (2.67 g), flindersine (2.80 g), and haplamine (8.2 g). The substances were identified by direct comparison with authentic samples. The mixture of crystals (B) was rechromatographed on a column of silica gel. Ethyl acetate eluates gave a substance with mp 125-136°C, the spectral characteristics of which [PMR spectrum (δ , ppm, CDCl₃): 3.72 (singlet, 3 H, OCH₃); 6.78 and 7.28 (two doublets, 2 H each, two pairs of ortho-aromatic protons); and 6.15 and 7.52 (two doublets, 1 H each, J = 16 Hz,

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 395-396, May-June, 1983. Original article submitted December 17, 1982. trans-olefinic protons); mass spectrum, m/z (%): 178 (M^+ , 100%), 147 (90), 119 (30)]; permitted it to be regarded as methyl p-coumarate, as was confirmed by the results of a comparison with an authentic sample obtained previously from <u>H</u>. latifolium [3].

This is the first time that methyl p-coumarate has been detected in the plant H. perforatum.

The results of a comparative investigation of the components of <u>H</u>. <u>perforatum</u> collected in the Baisun region (I) and in Chimgan (II) are given below:

Compound	Amounts of substances (on the mass of the dry epigeal part)		mp. °C
	í í	Н	
Skimmianine	0.04	0,001	175-176
Evoxine 7-Isopentenyloxy-y-	0,025		155-156
fagarine		0,0005	104-105
Perfamine	0.089		164-165
Flindersine	0.016	0,113	190-191
Haplamine	0,116	0.448	200-20
Eudesmine	0,254	0,145	106-107
Methyl p-coumarate	0,0006	*****	135 —136

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SYNTHETIC ANALOGS OF Peganum ALKALOIDS.

II. SYNTHESIS OF 5-METHOXY- AND 5-HYDROXY-

SUBSTITUTED DEOXYVASICINONES AND DEOXYPEGANINES

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UDC 547.944/945+547.856.1

Continuing work on the synthesis of analogs of alkaloids of the peganine series [1], we have obtained 5methoxy- and 5-hydroxy-substituted deoxyvasicinones (DOVs) and deoxypeganines (DOPs). The necessary 6methoxyanthranilic acid (IV) was obtained from m-dinitrobenzene (I), which was converted into 6-methoxy-2nitrobenzonitrile (II) as described in [2]. The latter was reduced by the usual method [3] to the amino derivative (III), which was hydrolyzed with 20% NaOH [4] to (IV) (scheme). By the condensation of (IV) with α pyrrolidone under conditions given previously [1] we synthesized 5-methoxy-DOV (V), mp 140-141°C, hydrochloride 222-225°C (decomp.). NMR (CDCl₃), ppm: 3.00 (2 H, t, C-9); 2.13 (2 H, m, C-10); 4.00 (2 H, m, C-11); 3.80 (3 H, s, OCH₃); 7.42 (1 H, t, J = 7.5 Hz, C-7); 6.73 and 7.00 (1 H each, d, J = 7.5 Hz, C-6, C-8). The mass spectrum of (V) showed a difference from the spectra of the 6-, 7-, and 8-methoxy isomers [5] mainly in the relative intensity of M⁺ and the fragmentary ions. A certain analogy in the fragmentation of 8-methoxy-DOV consists in the formation of the (M - 1)⁺ and (M - 3)⁺ ions. The ejection of HCO, observed in 8-methoxy-DOV has become the main process in the case of (V) (see scheme). The directions of fragmentation were conformed by measurements of the elementary compositions of the fragmentary ions. Thus, analysis of mass spectra permits a determination of the positions of a methoxy group in the aromatic ring of a quinazolone system.

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 396-397, May-June, 1983. Original article submitted January 11, 1983.