causes changes of different magnitudes in the CSs of the $4'-OCH_3$, $5'-OCH_3$, and $N-CH_3$ protons in the erythro and threo series. Furthermore, it has been found that TFA causes specific changes in the CSs and SSCCs of the H_1 and H_9 protons in the bases of these series. The possibility has been shown of using the results of the influence of different solvents to solve structural and stereochemical problems in the study of the alkaloids phthalide-isoquinoline series.

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ALKALOIDS OF *Thalictrum isopyroides*

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Thalisopine, thalisopidine, cryptopine, thalicmine, thalicminine, dehydrothalicmine, and magnoflorine have been isolated previously from *Thalictrum isopyroides* [1]. The present paper gives the results of a study of the roots of *Th. isopyroides* C.A.M. collected on the Ustyurt plateau in the period of fruit-bearing on May 25, 1973. From the nonphenolic fraction of the ether-extractable total, by chromatography on a column of alumina we isolated a crystalline base (I) with mp 104-105°C (ether).

The UV spectrum of (I) [λ_{max}, nm, 249, 268 (sh.), 271, 283, 294, 324, 330 infl.] is characteristic for 1,2-dihydroisoquinolin-1-ones [2]. IR spectrum: 1658 cm^{-1} (conjugated $C=O$ group). Mass spectrum: m/e 219 (M^+), 204, 190, 176, 109.5 (M^{++}).

The NMR spectrum of (I) ($CDCl_3$, ppm) contains a singlet at 3.67 (3 H, NCH_3), a singlet at 3.93 (6 H, 2 × OCH_3), two one-proton singlets at 6.88 and 7.65 (H-5 and H-8, respectively), and two one-proton doublets at 7.06 and 6.68 (J = 7 Hz, H-3 and H-4). A comparison of the results obtained and those given in the literature enabled (I) to be identified as 6,7-dimethoxy-2-methyl-1,2-dihydroisoquinolin-1-one, which has been isolated previously only from *Hernandia ovigere* [3].

From the phenolic fraction of the combined alkaloids we obtained in the form of an oil an optically active base (II) with $[\alpha]_D$ +45° (c 0.13; CH_3OH). The UV spectrum (II) showed three maxima: at 282 nm, 305 nm, and 316 nm, infl., which are characteristic for 1,2,9,10-tetrasubstituted aporphine alkaloids [4]. The PMR spectrum of (II) showed signals at (ppm) 2.49 (3 H, NCH_3), 3.65 (3 H, OCH_3 at C-1), 3.82 (3 H, OCH_3), 3.85 (3 H, OCH_3), and 3.90 (3 H, OCH_3), and in the region of aromatic protons two one-proton singlets were observed at 6.73 and 7.85 (H-8 and H-11, respectively). The mass spectrum of (II) contained the peaks of ions with m/e 371 (M^+), 370 (M − 1), 356 (M − 15), 340 (M − 31), and 328 (M − 43).

The methylation of (II) with diazomethane gave thalicsimidine [5]. Consequently, the base (II) is a new one and we have called it thalisopynine. Since the base (II) possesses distinct phenolic properties (it dissolves in alkali and is readily methylated and acetyl-

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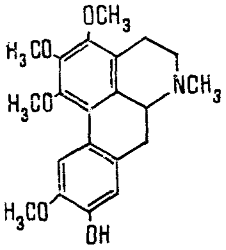
ated), the hydroxy group must be present at C-9 or C-10, as is also confirmed by the NMR spectrum of the O-acetyl derivative (III) of (II).

The NMR spectrum of (III) shows a paramagnetic shift of the signals of the H-8 and H-11 aromatic protons by 0.13 and 0.17 ppm, respectively [6].

The question of the mutual positions of the hydroxy and methoxy groups in ring D was answered with the aid of a measurement of the intramolecular nuclear Overhauser effect (NOE) between the OCH_3 and H-11 protons.

On irradiation with an additional radiofrequency field having a frequency ν_2 = 382 Hz, corresponding to the resonance transitions of the protons of the OCH_3 group, the intensity of the signal of the H-11 aromatic proton at 7.85 ppm rose by 30%, while the intensity of the H-9 signal did not change. The detection of a NOE between the OCH_3 and H-11 protons unambiguously shows the mutual arrangement of the OCH_3 and OH groups in thalisopynine at C-10 and C-9 respectively, and the structure of thalisopynine as 9-hydroxy-1,2,3,10-tetramethoxyaporphine (II):



II

It must be mentioned that 9-hydroxy-1,2,3,10-tetramethoxyaporphine has been synthesized previously [7], but this is the first time that it has been isolated from plant raw material.

EXPERIMENTAL

The UV spectra were taken on a Hitachi spectrometer (in ethanol), the mass spectra on an MKh-1303 spectrometer, and the NMR spectra on a JNM-4H-100/100 MHz instrument (with hexamethyldisiloxane as internal standard; δ scale).

The total material (6.2 g) was dissolved in benzene and the solution was washed with 4% KOH. The alkaline extract was washed with benzene (2 × 50 ml), acidified with 20% hydrochloric acid, and then made alkaline again and the base was extracted with ether. This gave 4.20 g of the total phenolic material (fraction A).

The benzene solution yielded 1.84 g of total nonphenolic material (fraction B).

6,7-Dimethoxy-2-methyl-1,2-dihydroisoquinolin-1-one (I). Fraction B was chromatographed on a column of alumina using ether as the eluent. This gave 0.032 g of base (I) with mp 104-105°C (ether).

Thalisopynine (II) was obtained by chromatographing fraction A on a column of alumina. The base was eluted with ether and then with chloroform. The chloroform eluate yielded 0.13 g of thalisopynine.

O-Methylthalisopynine (Thalicsimidine). An ethereal solution was added to a solution of 0.04 g of thalisopynine in absolute ethanol. After 2 days (monitoring by TLC) the thalisopynine had been converted completely into thalicsimidine.

O-Acetylthalisopynine (III). A mixture of 0.05 g of thalisopynine, 1 ml of acetic anhydride, and 0.5 ml of pyridine was left at room temperature (25°C) for 5 days. Then the reaction mixture was poured into ice water, made alkaline with 20% KOH, and extracted with ether, and the ethereal extract was distilled to give 0.052 g of (III).

SUMMARY

6,7-Dimethoxy-2-methyl-1,2-dihydroisoquinolin-1-one and the new aporphine base 9-hydroxy-1,2,3,10-tetramethoxyaporphine, which has been called thalisopynine, have been isolated from *Thalictrum* for the first time.

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ALKALOIDS OF *Papaver orientale*

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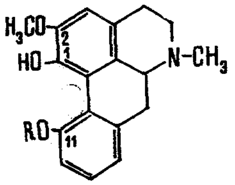
UDC 547.943

Papaver orientale L. (oriental poppy) is a perennial herbaceous plant, a representative of the section Oxytona Bernh. of the genus *Papaver* L. [1-3]. We have investigated the epigeal part of this plant collected in the Nakhichevan ASSR in the period of full flowering. Methanolic extraction yielded 0.49% of combined alkaloids, which were separated into phenolic and nonphenolic fractions. From the combined nonphenolic alkaloids we isolated isothebaine, oripavine, thebaine, mecambridine, orientalidine, alpinigenine, and protopine, and from the phenolic fraction isothebaine, oripavine, bracteoline, oripavidine [4] and a new base which we have called isothebaidine (I). All the alkaloids mentioned above were shown to be identical with authentic samples. The UV spectrum of (I) is similar to that of isothebaine. The mass spectrum of (I) had the peaks of ions with m/e 297 (M^+), 296 (M − 1), 282 (M − 15), 280 (M − 17), 266 (M − 31), 254 (M − 43), 236.

The facts given above enable isothebaidine to be assigned to the aporphine alkaloids [5] and permit the assumption that (I) is O-demethylisothebaine. To confirm this, (I) was methylated with diazomethane. The course of the reaction was followed chromatographically. It was found that initially two products were formed, one of which was identical with isothebaine (II). On further methylation, an O,O-dimethyl ether was formed which was identical with the O-methyl ether of isothebaine according to TLC and mass spectrometry. The formation of an intermediate product identical with isothebaine shows that one of the hydroxy groups is present at C_1. The presence in the mass spectrum of (I) of an intense ion M − 17 (50%) and the low intensity of the M − 31 ion (7%) shows that the methoxy group in (I) can be located only at C_2 [6]. Consequently, isothebaidine has the structure (I):



I R=H
II R=CH_3

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