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ALKALOIDS OF *Papaver orientale*

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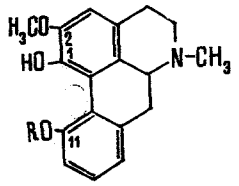
Papaver orientale L. (oriental poppy) is a perennial herbaceous plant, a representative of the section Oxytona Bernh. of the genus *Papaver* L. [1-3]. We have investigated the epigeal part of this plant collected in the Nakhichevan ASSR in the period of full flowering. Methanolic extraction yielded 0.49% 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=CH3

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EXPERIMENTAL

For thin-layer chromatography (TLC) we used KSK silica gel and the benzene–methanol (4:1) solvent system; the revealing agent was that of Draggendorff.

The mass spectra were taken on an MKh-1303 mass spectrometer, and the UV spectra on a Hitachi spectrometer.

Isolation and Separation of the Combined Alkaloids. The air-dry comminuted epigeal part of *P. orientale* (3.5 kg) was charged into a percolator and was covered with methanol. After a day the extract was run off and the raw material was covered with a fresh portion of methanol. This was repeated a total of eight times. Then the solvent was distilled off in vacuum. The residue was treated with 3% acetic acid. The acetic acid solution was washed with ether and was made faintly alkaline with Na_2CO_3, and the alkaloids were extracted with ether (fraction A, 7.5 g) and chloroform (fraction B, 4.1 g). After this, the alkaline solution was saturated with NH_4Cl and the alkaloids of phenolic nature were extracted with ether (fraction C, 4.4 g) and chloroform (fraction D, 1.2 g).

Fraction A was treated with ethanol, yielding 3.1 g of isothebaine and 1.5 g of thebaine. The fractional crystallization from ethanol of the material from the mother liquor gave an additional 0.55 g of isothebaine and 0.21 g of mecambridine. Fraction B after treatment with ethanol yielded 2.2 g of oripavine. Fractional crystallization from ethanol of the material from the mother liquor yielded 0.3 g of isothebaine and 0.11 g of mecambridine. After the isolation of these alkaloids, fractions A and B were combined (3.63 g) and chromatographed on a column of silica gel (100 g) using benzene–methanol mixtures (99:1; 98:2; 97:3; 96:4; 95:5; 9:1) and methanol.

The benzene–methanol (99:1) eluate yielded alpinigenine (0.16 g) and elution with a (98:2) mixture gave orientalidine (0.23 g) and mecambridine (0.11 g). The (97:3) eluate yielded isothebaine (0.24 g). On elution with the (95:5) mixture, thebaine (1.6 g) and oripavine (0.95 g) were isolated. The (9:1) fraction yielded protopine (0.08 g).

Fraction C was treated with ethanol, and 1.1 g of oripavine was separated off, while the mother liquor yielded 1.85 g of isothebaine. The mother liquors of fractions C and D were combined and chromatographed on a column of silica gel. Elution with benzene–methanol mixtures (99:1; 98:2; 97:3; 96:4; 95:5; 9:1) yielded isothebaine (0.81 g), oripavine (1.05 g), bracteoline (0.6 g), oripavidine (0.028 g), and isothebaidine (0.005 g).

Oripavidine, $[\alpha]_D$ −90° (c 0.27; methanol).

Isothebaidine, mp 236-237°C (decomp.), $[\alpha]_D$ +321° (c 0.05; methanol).

SUMMARY

From the combined alkaloids of *Papaver orientale* we have isolated isothebaine, oripavine, thebaine, mecambridine, orientalidine, alpinigenine, protopine, bracteoline, oripavidine, and the new alkaloid isothebaidine, the structure of which has been established.

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