By column chromatography, the chloroform fraction of alkaloids yielded 45 mg of isocorydine and 32 mg of allocryptopine.

Dicentrine. mp 158-159°C, $[\alpha]_D$ +57° (c 0.56; chloroform). UV spectrum: λ_{max} 220, 282, 303 nm (log ε 4.53, 4.20, 4.21). Mass spectrum: m/z 339 (M^+), 338 (100%), 324, 307, 296, 281, 265.

PMR spectrum (ppm): 2.45 (s, $N-CH_3$), 3.79 (s, $2OCH_3$), 5.82 and 5.96 (d, J ∿ 2 Hz, CH_2O_2), 6.42, 6.70, 7.59 (s, 3 Ar—H), 2.25-3.25 (m, 7H).

Predicentrine. $[\alpha]_D$ +97° (c 0.28; ethanol). UV spectrum, λ_{max} 282, 303 nm (log ε 4.19, 4.20).

Mass spectrum: m/z 341 (M^+), 340 (100%), 326, 325, 310, 283, 266, 170.5 (M^{++}).

PMR spectrum, ppm,: 2.49 (s, $N-CH_3$), 3.48 (s, OCH_3), 3.79 (s, OCH_3), 3.82 (s, OCH_3), 6.52, 6.72, 7.86, (s, 3 Ar—H), 2.50-3.30 (m, 7H).

SUMMARY

Fifteen alkaloids have been obtained from two species of *Dicentra*. This is the first time that dihydrosanguinarine, scoulerine, isoboldine, predicentrine, reticuline, cheilanthifoline, and lederine have been isolated from plants of this genus.

LITERATURE CITED

1. F. Santavy, in: The Alkaloids, R. H. F. Manske and R. Rodrigo, eds., Academic Press, New York, Vol. XVII (1979), p. 385.
2. A. L. Takhtadzhyan, System and Phylogeny of Flowering Plants [in Russian], Moscow—Leningrad (1966), p. 106.
3. K. R. Stern, Brittonia, 13, 1 (1961).
4. Flora of the USSR [in Russian], Leningrad, Vol. VII (1937), p. 647.
5. R. H. F. Manske and W. R. Ashford, in: The Alkaloids, R. H. F. Manske and H. L. Holmes, eds., Academic Press, New York, Vol. IV (1954), p. 98.
6. S. U. Karimova, I. A. Israilov, M. S. Yunusov, and S. Yu. Yunusov, Khim. Prir. Soedin., 224 (1980).
7. I. A. Israilov, S. U. Karimova, M. S. Yunusov, and S. Yu. Yunusov, Khim. Prir. Soedin., 279 (1980).

ALKALOIDS OF *Papaver orientale*

I. A. Israilov, M. A. Manushakyan,
V. A. Mnatsakanyan, M. S. Yunusov,
and S. Yu. Yunusov

UDC 547.943

Continuing the separation of the total alkaloids of the plant *Papaver orientale* L., collected in the flowering phase in the region of Lake Sevan, orientalidine, mecambridine, isothebaine, and bracteoline have been isolated, together with new alkaloids — oreintine, O-methylisothebaine, and orientidine, the structures of which have been established.

Continuing a study of *Papaver orientale* L. from different growth sites [1-3], we have investigated the alkaloid composition of the epigeal part of the plant collected in the flowering phase in the region of Lake Sevan (Armenian SSR).

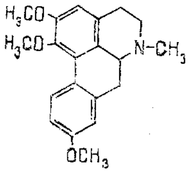
Methanolic extraction of the plant yielded 0.3% of total alkaloids, which were separated into nonphenolic and phenolic fractions. From the nonphenolic fraction we isolated orentalidine, isothebaine, mecambridine, and the new bases (I), (II), and (III), and from the phenolic

---

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 81-83, January-February, 1984. Original article submitted January 19, 1983.

fraction isothebaine and bracteoline. All the known alkaloids isolated were identified on the basis of their spectral characteristics and direct comparison with authentic samples [3].

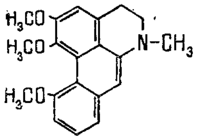
Base (I) was optically active, with the composition $C_{20}H_{23}O_3N$, and has been called orientine. Its UV spectrum had absorption bands at, λ_{max}, nm, 278 and 310 (inflection) (log ε 4.25, 3.21). The mass spectrum had the peaks of ions with m/z 325 (M^+), 324 (100%), 310, 294, 282, and 162.5 (M^{++}). The UV spectrum of the base and the nature of its mass-spectrometric fragmentation indicated that it belonged to the aporphine alkaloids [4]. The PMR spectrum showed the signals of a N-methyl group at 2.46 ppm and of three methoxy groups at 3.55, 3.74, and 3.77 ppm. In the region of aromatic protons there were one-proton singlets at 6.45 and 6.65 ppm and a one-proton doublet at 8.17 ppm (J = 9.5 Hz). The signal of the proton at C_{10} appeared in the form of a multiplet at 6.70 ppm and was superposed on the signal of the proton at C_8. The methylene and methine protons appeared at 2.50-3.70 ppm. The presence in the PMR spectrum of (I) of a weak-field signal in the form of a doublet at 8.17 pm, assigned to C_{11}–H, and also of strong-field singlets at 6.45 and 6.65 ppm from C_3–H and C_8–H, respectively, showed the presence of methoxy groups at C_1, C_2, and C_9. Thus, orientine has the structure



It must be mentioned that this structure was previously assigned to the alkaloid O-methylliridine [4] for which a different structure was later suggested [5].

Base (II) was optically active, with the composition $C_{20}H_{23}O_3N$. Its UV spectrum was similar to that of isothebaine. Mass spectrum: m/z 325 (M^+, 100%), 324, 310, 294, 282, 162.5 (M^{++}). The PMR spectrum showed the signals of protons on an N-methyl group at 2 46 ppm and of three methoxy groups, at 3.53 ppm (OCH_3) and 3.78 ppm (2 OCH_3). In the aromatic region there was a one-proton singlet at 6.57 ppm snd a multiplet at 6.68-7.32 ppm corresponding to three protons. Methylene and methylene protons appeared at 2.35-3.15 ppm. The UV, PMR, and mass spectra of the base permitted its assignment to the 1,2,11-trisubstituted aporphine alkaloids [4]. The spectral characteristics given above are close to those for racemic O-methylisothebaine obtained synthetically [4]. A comparison of base (II) with O-methylisothebaine obtained by the methylation of isothebaine with diazomethane showed their identity. Consequently, base (II) was (+)-O-methylisothebaine, and this is the first time that it has been isolated from a plant.

Base (III) was optically inactive, with the composition $C_{20}H_{21}O_3N$, and it has been called orientidine. Its IR spectrum had absorption bands at 1535, 1570, 1595, and 1640 cm^{-1}. Its UV spectrum contained absorption maxima at 215, 271, and 340 nm (log ε 4.45, 4.39, 3.38). In the mass spectrum of the base, the maximum peak was that of the molecular ion with m/z 323, with a fairly strong peak of an ion having m/z 308. The PMR spectrum revealed the spectrum of the protons of a N-methyl group at 2.94 ppm and of three methoxy groups at 3.44 ppm (OCH_3) and 3.85 (2 OCH_3). In the region of aromatic protons, a one-proton singlet appeared at 6.35 ppm and signals corresponding to four protons at 6.60-7.29 ppm. In the 3.05-3.25 ppm there was a multiplet corresponding to four protons. The facts given show that the base belongs to the group of dehydroaporphine alkaloids [4]. The Adams hydrogenation of base (III) gave O-methylisothebaine. Thus, orientidine has the structure



EXPERIMENTAL

For chromatography we used KSK silica gel with, for TLC, the following solvent systems: 1) benzene–ethanol (9:1) and 2) chloroform–ethanol (4:1). UV spectra were taken on a Hitachi spectrophotometer in ethanol, NMR spectra on a C-60-HL instrument in $CDCl_3$ with HMDS as standard (δ scale), mass spectra on a MKh-1303 mass spectrometer, and UV spectra on a UR-20 instrument (tablets with KBr).

Isolation and Separation of the Total Alkaloids. The air-dried comminuted plant *P. orientale* (6 kg) was treated with methanol until the alkaloids had been extracted completely. From the combined and concentrated ethanolic extract the total alkaloids were isolated by the usual method [3] and were separated into nonphenolic (ether-extracted, 7.6 g; chloroform-extracted, 2.1 g) and phenolic (ether-extracted, 11.7 g; chloroform-extracted, 1.1 g) fractions. From the ether-extracted nonphenolic material by treatment with ethanol, isothebaine (2.0 g) was isolated. The mother liquor was combined with the chloroform-extracted nonphenolic material and chromatographed on a column of silica gel with elution of the alkaloids by chloroform and chloroform–ethanol in various proportions. As a result, orientalidine (0.195 g), O-methylisothebaine (0.31 g), isothebaine (2.2 g), mecambridine (0.21), orientine (0.01 g), and orientidine (0.26 g) were isolated. Treatment of the ether-extracted phenolic material with ethanol yielded isothebaine (4.9 g). Chromatography of the mother liquor on a column of silica gel with elution by chloroform and chloroform–ethanol in various proportions yielded isothebaine (2.3 g) and bracteoline (0.4 g).

The chloroform-extracted phenolic material, on treatment with ethanol, yielded isothebaine (0.3 g).

Orientine, $[\alpha]_D$ +70° (c 0.16 methanol).

O-Methylisothebaine, $[\alpha]_D$ +26° (c 0.45; chloroform). UV spectrum: λ_{max} 273, 303 nm (log ε 4.26, 3.31).

Methylation of Isothebaine. An ethereal solution of diazomethane was added to 20 mg of isothebaine in 2 ml of absolute methanol. After a day, the solvent was evaporated off and a product was obtained which was identical with an authentic sample of O-methylthebaine.

Hydrogenation of Orientidine. The Adams hydrogenation of 30 mg of orientidine in 3 ml of acetic acid was carried out for 5 h. The acid solution after the separation of the catalyst was made alkaline with 25% ammonia, and the product was extracted with chloroform. After the solvent had been distilled off, the product obtained was identical with O-methylisothebaine according to TLC and IR spectroscopy.

SUMMARY

From the total alkaloids of *Papaver orientale* have been isolated orientalidine, mecambridine, isothebaine, and bracteoline, and the new alkaloids orientine, O-methylisothebaine, and orientidine, the structures of which have been determined.

LITERATURE CITED

1. R. A. Konovalova, S. Yu. Yunusov, and A. P. Orekhov, Zh. Org. Khim., 7, 1791 (1937).
2. I. A. Israilov, O. N. Denisenko, M. S. Yunusov, S. Yu. Yunusov, and D. A. Murav'eva, Khim. Prir. Soedin., 714 (1977).
3. I. A. Israilov, O. N. Denisenko, M. S. Yunusov, D. A. Murav'eva, and S. Yu. Yunusov, Khim. Prir. Soedin., 474 (1978).
4. H. Guinaudeau, M. Leboeuf, and A. Cave, Lloydia, 38, 275 (1975).
5. C. L. Chen and H. M. Chang, Phytochemistry, 17, 779 (1978).