ALKALOIDS OF PAPAVER LACERUM

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There are no previous reports on the chemical constituents of Papaver lacerum Popov. (syn. P. laevigatum auct. non Bieb.), a species which is native to Turkey and Soviet Armenia (1). This communication reports the presence of four alkaloids extracted from the stems and capsules of a Turkish sample of P. lacerum collected in Anatolia. The major alkaloid was the aporphine, roemerine (1), while another aporphine, N-methyl asimilobine (2), and the proaporphines mecambrine (3) and pronuciferine (4)

were obtained as minor alkaloids. The alkaloids were identified by their ultra-violet, mass and proton magnetic resonance spectra and by chromatographic comparison with reference compounds. The proton magnetic resonance spectrum of the isolated N-methyl asimilobine (2) clearly differentiated it from the corresponding 1-hydroxy-, 2-methoxy-analogue, lirinidine (2). The alkaloids, roemerine, mecambrine and pronuci-

ferine, have been isolated from a number of *Papaver* species (2-5); *N*-methyl asimilobine does not appear to be a common alkaloid, although it has been reported recently to be the major alkaloid of an Egyptian sample of *P. rhoeas* (6).

P. lacerum is in the section Papaver (≡Orthorhoeades Fedde) which includes P. rhoeas, P. commutatum, P. postii, P. dubium, P. arenarium, P. stylatum and P. clavatum. Morphologically, P. lacerum is similar to P. dubium L. (syn. P. laevigatum

$$\frac{3}{4}$$
 R₁-R₂= OCH₂O
 $\frac{1}{4}$ R₁ = R₂= OMe

Bieb.), which is a widespread, variable species found in Europe and in Asia. Mecambrine and roemerine have been reported from *P. dubium*, together with the rhoeadine-type alkaloids, rhoeadine, isorhoeadine, rhoeagenine, several papaverrubines, berberine, coptisine, protopine and sanguinarine (7–11). In view of the variable alkaloid constituents reported from several species of the section Papaver, the possibility of chemical races of

P. lacerum cannot be ignored. Hence it would be of interest to investigate further samples of P. lacerum from other parts of Turkey and Soviet Armenia for the presence of alkaloids.

EXPERIMENTAL

PLANT MATERIAL.—The plant material was collected at Kayser, Turkey, by G. Sariyar and A. Baytop, June 21, 1977. Identification as P. lacerum Popov. was determined by Professor A. Baytop, and a reference sample is retained in the herbarium of the Faculty of Pharmacy, University of Istanbul.

Isolation of alkaloids.—Dried capsules and stems (130 g) were macerated (3 x) with methanol, and the combined filtered extracts were concentrated to dryness under reduced pressure. The residue was extracted with 3% acetic acid (5 x 25 ml); the combined acid extracts were washed with light petroleum, made alkaline with 25%ammonium hydroxide solution, and extracted with diethylether (3 x 40 ml). The tracted with diethylether (3 x 40 ml). The combined ethereal extracts, when washed, dried and concentrated to dryness under reduced pressure, yielded 207 mg of total crude alkaloid (0.16%). Preparative tlc with absorbent Silica gel G (Merck) and the solvent system, benzene-acetone-ammonium hydroxide (90:10:1), yielded amorphous roemerine (105 mg) and a pale brown phous roemerine (105 mg) and a pale brown solid (46 mg). After further preparative tle with alumina G (Merck) and the solvent system benzene-acetone-methanol (7:2:1), the solid yielded the amorphous alkaloids mecambrine (19 mg), pronuciferine (5 mg), and N-methyl asimilobine (1 mg).

IDENTIFICATION OF ALKALOIDS.—Roemerine (1) exhibited uv, ms (12), and 1H nmr spectra (13) identical with those reported in the literature and R_f values on the identical with those of the reference alkaloid. Mecambrine (3) exhibited uv (14) and ms (15) spectra identical with those reported in the literature. ¹H nmr, 60 MHz (CDCl₂) δ 6.92 (2H, m, $J_{8,12}$ 2Hz, $J_{8,9}$ 8 Hz; C-8H, C-12H), 6.32 (2H, m, $J_{9,11}$ 1 Hz, $J_{8,9}$ 8 Hz; C-9H, C-11H), 6.53 (1H, s; C-3H), 5.83 (2H, q; ar OCH₂O), 2.37 (3H, s; NMe); the R₂ values identical with those of the tle Rf values identical with those of the reference sample.

Pronuciferine (4) exhibited uv (14), ms (16) and ¹H nmr spectra identical with those reported in the literature and tlc Rf values identical with those of the reference sample.

N-methylasimilobine (2) exhibited uv, ms, and 'H nmr spectra identical with the literature values (6) and tle R_t values identical with those of the reference sample.

ACKNOWLEDGMENTS

We are grateful to Professor F. Šantavý (roemerine, pronuciferine, mecambrine) and Professor A. Cavé (N-methylasimilobine) for gifts of reference compounds and to Professor A. Baytop for identification of the plant material. We thank Mr. D. Carter and Mr. W. Baldeo for determination of ms and ¹H nmr spectra.

Received 16 September 1980

LITERATURE CITED

- 1. J. Cullen in P. H. Davis (ed.), Flora of Turkey and the Aegean Islands, Vol. 1, 1965, Edinburgh University Press, pp. 219-236.
- H. Guinaudeau, M. Leboeuf and A.

- H. Guinaudeau, M. Leboeuf and A. Cavé, Lloydia, 38, 275 (1975).
 H. Guinaudeau, M. Leboeuf and A. Cavé, J. Nat. Prod., 42, 325 (1979).
 F. Šantavý in R. H. F. Manske (ed.), The Alkaloids—Chemistry and Physiology, Vol. 12, 1970, Academic Press, London and New York, pp. 333-454.
 F. Šantavý in R. H. F. Manske and R. Rodrigo (eds.), The Alkaloids—Chemistry and Physiology, Vol. 17, 1979, Academic Press, London and New York, pp. 385-544.
 S. El Masry, M. G. El Ghazooly, A. A. Omar, S. M. Khafagy and J. D. Phillipson, Planta Med., 41, 61 (1981).
- son, Planta Med., 41, 61 (1981).
- H. G. Boit and H. Flentje, Naturwissenschaften, 47, 180 (1960).
- 8. A. Němečková and F. Šantavý, Coll. Czech. Chem. Commun., 27, 1210 (1962).
- A. Němečcková, F. Šantavý and D. Walterová, Coll. Czech. Chem. Commun., 35, 1733 (1970).
- J. Slavik, Coll. Czech. Chem. Commun., 10.
- 28, 1738 (1963).
 S. Pfeifer and S. K. Banerjee, Die Pharmazie, 19, 286 (1964).
 S. Pfeifer and L. Kuhn, Die Pharmazie, 11.
- **23**, 199_(1968).
- S. R. Johns, J. A. Lamberton and A. A. Sioumis, Austr. J. Chem. 22, 1311
- (1969). 14. K. L. Stuart and M. P. Cava, Chem. Rev., 68, 321 (1968).
- L. Dolejš, Coll. Czech. Chem. Commun., 39, 571 (1974).
 M. Tomita, A. Kato, T. Ibuka, H. Furakawa and M. Kozuka, Tetrahedron Letts. 2825 (1965).