OCCURRENCE OF MORPHINE AS A MINOR ALKALOID IN *Papaver decaisnei* HOCHST.*

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From the mature capsules of the species *Papaver decaisnei* HOCHST. papaverine was isolated as the main alkaloid and morphine, rhoeadine and coptisine as the minor components. The presence of a small amount of narcotine, thebaine, codeine, protopine, corytuberine, and traces of papaverrubines A, C, D and E and thebaine methohydroxide was also proved.

In spite of the fact that already about 63 species or lower taxonomic units of the genus *Papaver* were investigated, the presence of morphine was detected so far in two species from the section *Mecones* only, *i.e.* in *P. somniferum* L. and *P. setigerum* DC., which are often called "true opium poppies". While the morphinane alkaloid thebaine was found in a larger number of species from the sections *Orthorhoeades*, *Mecones*, *Miltantha*, and *Macrantha*, the existence of the enzymatic system capable of O-demethylation of thebaine to codeine, and further up to morphine, was known merely in *P. somniferum* and *P. setigerum*. In addition to the two mentioned species Fedde[1] classifies further three species into the section *Mecones* BERNH. They are *P. glaucum* BOISS. et HAUSKN. and *P. gracile* AUCH. which differ, however, in their alkaloids and some morphological characters from *P. somniferum* and *P. setigerum* to such an extent that doubts have arisen regarding their accurate classification in the section *Mecones*[2,3] and suggestions have been put forward to reclassify them into the section *Orthorhoeades.* More recently this problem is treated in ref.[4]. In *P. glaucum* and *P. gracile* alkaloids of the rhoeadane type occur as dominant alkaloids. In *P. gracile* only rhoeadine and oxysanguinarine[5] were detected, and *P. glaucum* contains glaudine[6] (glaupavine[7]) as the main alkaloid. As for the alkaloids of the fifth species of this section, *P. decaisnei* HOCHST., nothing was known so far. From the chemotaxonomic point of view the investigation of the alkaloids of this species seemed very desirable.

We had only small amounts of dry ripe capsules of the species *P. decaisnei* of Turkish origin at our disposal, which permitted a preliminary investigation of alkaloids

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* Part LXXII in the series Alkaloids of the *Papaveraceae*; Part LXXI: This Journal *45*, 1301 (1980).

only. From this material we isolated the sum of the bases in 0·22% yield, and from them we separated papaverine (0·12%) as the main alkaloid. From the mother liquors after papaverine we isolated rhoeadine (0·014%) which has never been found in "opium poppies", and we also detected by thin-layer chromatography the presence of small amounts of narcotine, thebaine, codeine, protopine, traces of papaverrubines A, C, D and E, and several other unidentified alkaloids. In the fraction of quaternary protoberberines coptisine was detected. From the fraction of bases extractable with chloroform–ethanol from the aqueous phase under weakly alkaline reaction an alkaloid was isolated which according to its melting point, mixture melting point, UV spectrum and TLC data in several systems was identical with morphine (yield 0·023%). In the fraction of quaternary alkaloids extractable in the form of iodides with chloroform we detected by TLC as the main component an alkaloid, which according to its R_F value was very probably identical with thebaine methiodide.* Further we detected corytuberine and two additional non-identified, probably quaternary, alkaloids.

P. decaisnei is thus the third species from the genus *Papaver* in which the presence of morphine and several additional characteristic opium alkaloids has been proved. On the basis of these alkaloids *P. decaisnei* can undoubtedly be classified among the biochemical relations of *P. somniferum* and *P. setigerum*, even though the presence of papaverine as the main alkaloid in it makes it related to the species *P. commutatum* FISCH. et MEY. from the section *Orthorhoeades* (*cf.*[10–12]) with which it also has a content of rhoeadine in common.

EXPERIMENTAL

The melting points were determined on a Mettler FP 51 apparatus and they were not corrected. The UV spectra were measured on a Unicam SP 1800 instrument, in methanol. Chromatographies were carried out both on thin layers of silica gel G (Merck) in the solvent systems cyclohexane–diethylamine 9 : 1 (S_1), cyclohexane–chloroform–diethylamine 7 : 2 : 1 (S_2) and 5 : 4 : 1 (S_3), methanol–25% ammonia 200 : 1 (S_4), benzene–dioxane–ethanol-25% ammonia 10 : 8 : 1 : 1 (S_5)[13], ethyl acetate–methanol–25% ammonia 17 : 2 : 1 (S_6)[13], benzene–methanol 4 : 1 (S_7), benzene–diethylamine 19 : 1 (S_8), chloroform–ethanol–diethylamine 8 : 1 : 1 (S_9), ethanol–water–25% ammonia 15 : 9 : 1 (S_{10}). methanol–water–25% ammonia 15 : 3 : 1 (S_{11}) and 1-propanol–water–85% formic acid (S_{12}), and on Silufol UV 254 sheets (Kavalier) in the systems methanol–diethylamine 4 : 1 (S_{13}) and 1 : 1 (S_{14}). Fluorescent alkaloids were detected in the UV light, papaverrubines by 20 min exposure to concentrated hydrochloric acid fumes (formation of purple spots) and spots of other alkaloids with potassium iodoplatinate.

Extraction and Isolation of Alkaloids

The plants were cultivated in the Experimental Garden, Medical Faculty Brno, from seeds obtained from the Botanical Garden in Izmir (Turkey) and the correctness of their determin-

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* Recently[8] this alkaloid was isolated from *P. bracteatum* LINDL. in the form of chloride. Its occurrence in the thebaine chemical race of this species could also be confirmed[9].

ation was checked according to the description in ref.[1]. Vaucher specimens are deposited in the Department of Medical Chemistry and Biochemistry of the Faculty of Medicine, J. E. Purkyně University in Brno.

Dry ripe capsules, freed of seeds (harvest at the end of July 1979) and weighing 23 g were repeatedly extracted with methanol in the cold. Methanol was distilled off, the residue dissolved in cold 5% acetic acid and filtered. The filtrate was alkalized with sodium carbonate and extracted several times with ether (fraction *A*) and the aqueous layer was alkalized with sodium hydroxide and reextracted with ether (fraction *B*). The aqueous phase was then acidified with acetic acid, alkalized with ammonia and extracted with a mixture of chloroform and ethanol 4 : 1 (fraction *E*). The remaining aqueous phase was neutralized with 20% sulfuric acid, saturated potassium iodide solution was added, and the resulting solution was extracted with chloroform (fraction *I*).

Bases from fraction *A* were crystallized fractionally from methanol, affording 28·3 mg of papaverine (0·123%), which after recrystallization from methanol gave clusters of needles of m.p. 147—148°C. The melting point was undepressed in admixture with an authentic sample. The characteristic UV spectrum (λ_{max} ($\log \varepsilon$) 206 (4·50), 239 (4·91), 280 (3·94), 314 (3·64), 305 (3·42) and 320 (3·54) nm) was identical with that of an authentic sample and with the data in literature[14]. The identity was also confirmed by TLC. From the mother liquors after papaverine 3·2 mg of rhoeadine (0·014%) were obtained by crystallization from methanol, needles of m.p. 250—252°C (chloroform-methanol), undepressed with an authentic preparation. The R_F values on thin layers in several systems were also identical with those of the authentic sample. In the amorphous residue (15·6 mg) of the mother liquors the presence of narcotine, thebaine, codeine, protopine and at least three additional non-identified alkaloids was detected by TLC, in addition to negligible amounts of papaverrubines *D*, *C*, *A* and *E*.

In fraction *B* (1·6 mg) only coptisine could be demonstrated. From fraction *E* 5·3 mg of morphine (0·023%) were obtained by crystallization from methanol in the form of prisms with m.p. 254—255°C. The melting point remained undepressed on admixture of an authentic sample. The UV spectrum (λ_{max} ($\log \varepsilon$) 214 (4·34) and 286 (3·33) nm, λ_{min} 255 (3·03) nm) was identical with the spectrum of morphine published in ref.[14]. The R_F values in several systems also coincided with the values of the reference sample. In fraction *I* an alkaloid was detected as the main component, the spot of which was identical in three systems with the spot of thebaine methiodide, and two additional unidentified alkaloids (R_F in S_{10} 0·75, in S_{11} 0·68 and 0·86 and in S_{12} 0·61 and 0·68).

R_F values: In systems S_1, S_2, S_3, S_4, S_5 and S_6: Codeine 0·09, 0·23, 0·36, 0·39, 0·37, 0·48; morphine —, —, 0·07, 0·46, 0·18, 0·32; narcotine 0·27, 0·46, —, 0·80, 0·91, 0·94; papaverine 0·08, 0·39, —, 0·82, 0·80, 0·87; protopine 0·47, 0·64, —, 0·52, 0·88, 0·92; rhoeadine 0·55, 0·67, —, 0·76, 0·91, 0·92; thebaine 0·38, 0·52, 0·76, 0·52, 0·73, 0·80. In systems S_1, S_2, S_7 and S_8: papaverrubines A 0·40, 0·68, 0·81, 0·89; C 0·13, 0·40, 0·70, 0·49; D 0·06, 0·31, 0·58, 0·40; E 0·40, 0·68, 0·50, 0·74. In system S_9: corytuberine 0·62, morphine 0·68. In systems S_{10}, S_{11} and S_{12}: corytuberine 0·84, 0·84, 0·72; thebaine methiodide 0·19, 0·05, 0·46. In systems S_{13} and S_{14}; coptisine 0·49, 0·85.

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