ON ALKALOIDS OF THREE *Papaver* SPECIES FROM THE SECTION *Scapiflora* REICHB.*

František VĚŽNÍK[a], Irgash A. ISRAILOV[b], Eva TÁBORSKÁ[a] and Jiří SLAVÍK[a]

[a] *Department of Medical Chemistry and Biochemistry, Purkyně University, 662 43 Brno, Czechoslovakia and*
[b] *Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbekh Soviet Socialist Republic, Tashkent, USSR*

Received July 3rd, 1984

The main alkaloid of the aerial part of *P. croceum* LEDEB. was nudaurine (*I*), isolated for the first time. In addition to amurine, known to be present in this species, oxysanguinarine (*II*) and corydine (*IIIa*) were also newly isolated and the presence of papaverrubine D demonstrated. In the fraction of tertiary bases from *P.kerneri* HAYEK allocryptopine and epialpinine (*IV*) were isolated as further alkaloids in addition to the already known alkaloids amurensine (the main alkaloid), amurensinine, amurine, alpinigenine, muramine, protopine, mecambridine, nudaurine, cryptopine and papaverrubines B, D, and G. In the fraction of quaternary bases the presence of traces of coptisine was detected, and in addition to alborine (alkaloid PO-5) *cis*-N-methyltetrahydropalmatinium hydroxide (*V*) was isolated for the first time in the form of iodide from *P. kerneri*. In *P. tatricum* (NYÁR.) EHREND. allocryptopine, epialpinine, and amurensinine were identified as the dominant alkaloids, while among the minor components protopine, amurensine, muramine, palmatine, coptisine, corytuberine (*IIIb*), N-methyltetrahydropalmatinium hydroxide, and N-methylamurensinium hydroxide could be demonstrated. Corydine (*IIIa*) and corytuberine (*IIIb*) represent the first two aporphine alkaloids found in the *Scapiflora* section.

The section *Scapiflora* REICHB. of the *Papaver* L. genus (*Papaveraceae* family) includes botanically distinct species from European mountains (the *Alpina* group) and the northern polar regions of the Northern Hemisphere (the *Nudicaulia* group). The taxonomy of this section is not easy to survey. Fedde[1] mentions only 5 species, with numerous subspecies and varieties. Newly, many of them are considered independent species. Recently Novák[2] studied the taxonomic evaluation of the *Scapiflora* section. This section is characterized by a relatively low content of alkaloids (about 0·1%). The presence of isopavinane, protopine and rhoeadine alkaloids and the absence of an aporphine type of alkaloids is considered a characteristic chemotaxonomical character of the alkaloidal composition of the species of the *Scapiflora* section. In this paper we concentrate on the study of the alkaloids from three species of this section.

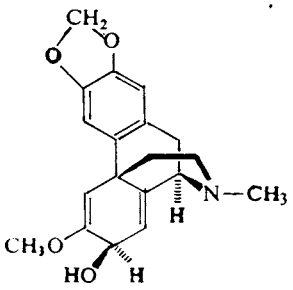
* Part LXXX in the series Alkaloids of the *Papaveraceae*; Part LXXIX: This Journal *50*, 1216 (1985).

Papaver croceum LEDEB. (syn. *P. alpinum* var. *croceum* LEDEB., *P. nudicaule* var. *croceum* LEDEB.) is a perennial species from the series of *Nudicauliatae*[2], with a Mongolian-Siberian distribution area, reaching to Central Asia. So far very little has been known about alkaloids of this species. From the cultivated *P. nudicaule* var. *croceum* the morphinane-dienone alkaloid amurine was isolated which is very widespread in the species of the *Scapiflora* section. Further the protopine alkaloids muramine, 12-oxomuramine and protopine[3,4] were found in it. In this study we investigated the aerial part of *P. croceum* from a natural locality in Kirghizia (USSR). According to our expectation we could detect in the population investigated a very low content of alkaloids, 0·11%. By chromatographic separation on a silica gel column we obtained 4 individual alkaloids. We identified as the main one the morphinane-dienone alkaloid nudaurine (*I*) which was isolated from *P. croceum* for the first time, and we also found the formerly described amurine. Among the minor alkaloids, the benzophenanthridine alkaloid oxysanguinarine (*II*) and the aporphine alkaloid corydine (*IIIa*) could be demonstrated, and chromatographically also traces of the rhoeadane alkaloid papaverrubine D were detected. Their presence in *P. croceum* has not been described so far either. The demonstration of corydine (*IIIa*) represents the first finding in the species of the *Scapiflora* section. The presence of the protopine alkaloids muramine, 13-oxomuramine and protopine, found earlier, could not be demonstrated by us in the population investigated. In the fraction of quaternary alkaloids we detected chromatographically the presence of two as yet unidentified components.

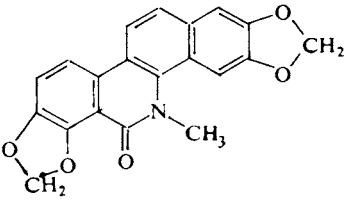
Papaver kerneri HAYEK (syn. *P. alpinum* ssp. *kerneri* (HAYEK) FEDDE) is a perennial species from the southern and eastern Alps (Austria, Italy), classified by Novák into the series *Rhaeticatae*[2]. The alkaloids of this species were investigated by Maturová and coworkers[5,6] and Pfeifer and coworkers[7,8]. They could detect the presence of amurensine, alpinigenine[5,6,8], nudaurine[5,8], amurensinine, sanguinarine[6,8], oxysanguinarine, amuronine[5], 13-oxomuramine (alpinone), coptisine, O-methylalpinigenine (epialpinine) or alpinine[6], amurine, alpinine, protopine, cryptopine, muramine, mecambridine (oreophiline), alborine (alkaloid PO-5)[8], and papaverrubines B, E[7], D[7,8] and G[8]. The plant material investigated in this study was cultivated in Brno. In *P. kerneri* we also found a low content of alkaloids (0·13%). In agreement with the results of earlier studies we isolated from the tertiary fraction the isopavinane base amurensine as the main alkaloid which is accompanied by amurensinine, amurine, alpinigenine, muramine, protopine, mecambridine, and nudaurine. Chromatographically we also proved the presence of papaverrubines B, D, G, cryptopine, and coptisine. Moreover we also isolated a small amount of allocryptopine from this species for the first time. In contrast to German authors[8] who mentioned the presence of alpinine (*IVa*), we found epialpinine (O-methylalpinigenine) (*IVb*), identified by direct comparison with an authentic specimen[9]. However, the possibility cannot be exluded that the more stable epialpinine (14*R*) (*IVb*) was formed as an artifact during the

isolation procedure, by epimerization at $C_{(14)}$ of the originally present alpinine (14*S*, *cf.*[9]) (*IVa*). From the quaternary fraction we isolated the already described alborine (alkaloid PO-5) in the form of iodide, and also a further alkaloid in trace amount which was identified on the basis of its mass spectrum and chromatographic data as *cis*-N-methyltetrahydropalmatinium iodide[10] (*V*). This alkaloid, which is a biogenetic precursor of alpinine, alpinigenine, and muramine, has not been found so far in the *Scapiflora* section. We also isolated the strongly polar alkaloid PK1 of the composition $C_{21}H_{21}NO_5$ (according to its mass spectrum) which we were unable to identify owing to the scarcity of the material.

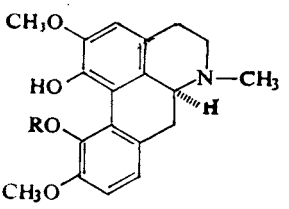
Papaver tatricum (NYÁR.) EHREND. (syn. *P. alpinum* subsp. *tatricum* NYÁR.)



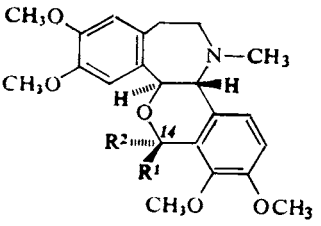
I



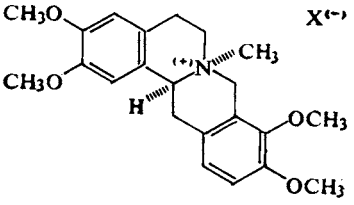
II



IIIa, R = CH_3
IIIb, R = H



IVa, $R^1 = OCH_3$, $R^2 = H$
IVb, $R^1 = H$, $R^2 = OCH_3$



V

grows in the Alps and Carpathians. In this species of undefined origin the presence of amurensine, alpinigenine, alpinine, sanguinarine, coptisine, and undefined papaverrubines has been described[6]. Now we made a preliminary study of the alkaloids from the herbarium material of the plant collected at an exactly defined site in the Great Fatra Moutains in Slovakia. The results differ considerably from the findings of the authors mentioned[6]. The dominant alkaloid was allocryptopine, accompanied by epialpinine and amurensinine. Of the minor components protopine, amurensine, muramine, palmatine, coptisine, corytuberine (*IIIb*), N-methyltetrahydropalmatinium iodide, and N-methylamurensininium iodide were identified. The proved presence of corytuberine represents the first finding of this alkaloid in the *Scapiflora* section.

EXPERIMENTAL

The melting points and the mixed melting points were determined in open capillary or on a Kofler block and they are not corrected. The UV spectra were measured in ethanol on a Hitachi spectrophotometer (Japan) or in methanol on a Unicam 1800 spectrophotometer (Great Britain). The IR spectra were recorded in KBr pellets on a UR-10 (Zeiss Jena, GDR) instrument or in nujol on an IR-75 Specord (Zeiss Jena, GDR) instrument. The mass spectra were recorded on a MCH-1303 (USSR) or an AEI-MS 902 instrument. The ^{1}H NMR spectra were measured on a Jeol (Japan) instrument in C^2HCl_3, using hexamethyldisilane as internal reference. Thin-layer chromatography (TLC) was carried out on layers of silica gel KSK (USSR) or LS 5–40 μm (Lachema) with gypsum as binder, using the following systems: cyclohexane–diethylamine 9 : 1 (S_1), cyclohexane–chloroform–diethylamine 7 : 2 : 1 (S_2), benzene–diethylamine 19 : 1 (S_3), benzene–acetone–methanol 7 : 2 : 1 (S_4), benzene–methanol 9 : 1 (S_5), chloroform–ethanol–diethylamine 8 : 1 : 1 (S_6), methanol–25% ammonia 200 : 1 (S_7), methanol–water–25% ammonia 15 : 3 : 1 (S_8), ethanol–water–25% ammonia 15 : 9 : 1 (S_9), 1-propanol–water–85% formic acid 12 : 7 : 1 (S_{10}), methanol–water–36% hydrochloric acid 15 : 3 : 1 (S_{11}). For commercial Silufol plates (Kavalier) the system methanol–diethylamine 4 : 1 (S_{12}) was used. Descending paper chromatography (PC) was carried out on paper Whatman No 1 in 1-butanol–acetic 98% acid–water 10 : 1 : 3 (S_{13}) and ethanol–water 3 : 2 (S_{14}). The spots of fluorescing alkaloids were detected in UV light at 235 and 336 nm, while for the detection of papaverrubines hydrochloric acid fumes were used. Other alkaloids were detected by spraying with potassium iodoplatinate or in iodine vapours and spraying with Dragendorff's reagent. Column chromatography was carried out on silica gel L 80–160 μm (Lachema).

Extraction and Isolation of Alkaloids

The ground plant material was extracted with cold methanol. After evaporation of the solvent, the crude sum of the alkaloids was dissolved in acetic acid (0·5 mol l^{-1}). After alkalization with a saturated sodium carbonate solution, fraction A was extracted with ether. This fraction was further fractionated by a modified procedure[11] to phenolic and nonphenolic components. After adjustment of the pH of the aqueous phase above 13 by addition of sodium hydroxide (10 mol l^{-1}), fraction B was extracted with ether. After bringing the pH value of the aqueous phase to about 8, fraction E was extracted with chloroform. The aqueous phase was then acidified with sulfuric acid to about pH 6·0 to 6·5, potassium iodide was added and the solution extracted with chloroform or a mixture of chloroform–ethanol (4 : 1), obtaining thus quaternary alkaloids in the form of iodides (fraction I).

Papaver croceum LEDEB.

For extraction 530 g of the dry aerial part of the plant were used which were collected in July 1979 during the flowering period in Terskoi Alatai, Kirghiz SSR. Fractionation of the crude sum of the alkaloids gave a fraction of non-phenolic bases A_1 (360 mg) and a phenolic fraction A_2 (147 mg), further trace amounts of fraction B, fraction E (60 mg) and fraction I (30 mg).

Chromatographic separation of the bases of the fraction A_1 on a silica gel column, using benzene–methanol (99 : 1) for elution, gave 5·2 mg of oxysanguinarine (0·001% of dry residue). With benzene–methanol (98 : 2) 6·8 mg of corydine (0·001%) were eluted, with benzene–methanol (95 : 5) 24·2 mg of amurine were obtained, and with benzene–methanol (90 : 10) 58·1 mg of nudaurine (0·011%) were isolated. In the mother liquors of fraction A_1 the presence of trace amounts of papaverrubine D and 5 further unidentified bases were detected by TLC in S_1 to S_4. The separation of fraction A_2 on a silica gel column gave only a trace amount of amurine and mixed fractions containing amurine, nudaurine and corydine. From fraction E column chromarography on silica gel gave 2·0 mg of amurine (total of 26·1 mg; 0·005%). Other fractions were mixtures. In fraction B the presence of alkaloids could not be demonstrated. Fraction I remained amorphous even after repeated purifications. Using TLC the presence of two unidentified alkaloids of R_F values 0·13 and 0·25 (S_8) or 0·15 and 0·42 (S_{11}), respectively, could be ascertained.

Papaver kerneri HAYEK

The plant material was cultivated in the Centre for Cultivation of Medicinal Plants of the Medical Faculty, Purkyně University, Brno, from the seeds obtained from various European botanical gardens. They were harvested at the stage of flowering on August 4th, 1967. For the study 1835 g of whole plants were used. Fractionation of the crude total alkaloids gave fraction A (2·210 g), trace amounts of fraction B, fraction E (0·195 g) and fraction I (0·196 g). Fraction A was further separated to a fraction of bases the hydrochlorides of which can be extracted with chloroform at acid reaction (AC), and fraction of bases the hydrochlorides of which are insoluble in chloroform (AD). Crystallization of the fraction AC from methanol gave 120·0 mg of amurensine. The residual material and the fraction AD were separated to non-phenolic fractions AC_1 (109·1 mg), AD_1 (153·7 mg) and phenolic ones AC_2 (61·8 mg), AD_2 (31·8 mg). Fraction AC_1 was separated on a silica gel column with benzene. The elution gave fractions of mixed character from which 3·0 mg of a base were isolated by preparative TLC in S_2, identical with epialpinine (0·00017%). In the mother liquors the presence of trace amounts of papaverrubines B, D, and G was detected by TLC in systems S_1 to S_4. Further elution with benzene–chloroform (99·9 : 0·1) gave fractions from which 1·2 mg of alpinigenine (0·00006%) and 1·1 mg of an unidentified amorphous base of (R_F 0·32 in S_2) were isolated by preparative TLC in S_2. Using benzene–chloroform mixtures (99 : 1 to 95 : 5) fractions of mixed character were eluted in which the presence of trace amounts of epialpinine, alpinigenine, protopine, cryptopine, and mecambridine were detected by TLC. Elution with chloroform and chloroform–methanol (99 : 1) afforded fractions from which preparative TLC in S_2 gave 3·1 mg of protopine (0·00017%), 0·9 mg of allocryptopine, 1·8 mg of amurine (0·00010%), 1·1 mg of mecambridine (0·00006%), 0·8 mg of nudaurine (0·00004%), 0·6 mg of amurensinine (0·00003%); the presence of cryptopine and muramine was also detected chromatographically. Methanol eluted fractions from which crystallization from methanol gave 1·9 mg of allocryptopine (a total of 3·8 mg, 0·00021%) and 0·9 mg of muramine (0·00005%). Crystallization of fraction AC_2 from methanol gave 47·9 mg of amurensine (a total of 167·9 mg, 0·0091%). The remaining bases from the mother liquors were amorphous and they contained traces of the above-mentioned alkaloids. Fraction AD_1 was amorphous and traces of amurine, protopine and allocryptopine could be detected in it by TLC. Fraction AD_2 contained predominantly non-alkaloidal components. In fraction B the presence of trace

amount of coptisine was detected by TLC on Silufol in S_{12} and PC in S_{13} and S_{14}. Fraction E was predominantly of non-alkaloidal character. Crystallization of the purified fraction I from methanol gave 0·7 mg of alborine iodide (0·00004%). The bases from the mother liquors were further separated on a silica gel column in chloroform. On elution with chloroform–methanol mixtures (99 : 1 to 95 : 5) mixed fractions were obtained from which 0·7 mg of an amorphous alkaloid (0·00004%) were isolated by preparative TLC in S_8, the mass spectrum of which was identical with that of N-methyltetrahydropalmatinium iodide[10]. Paper chromatography in S_{13} and S_{14} showed that it was identical with the *cis*-form. Further, 0·8 mg of alkaloid PK1 (0·00004%) were isolated from fraction I.

Papaver tatricum (NYÁR.) EHREND.

The plants were collected at the flowering period on July 6th, 1980 (Tlstá, Velká Fatra)*. Two whole dry plants were available of the weight 1·04 g. In the alkaloidal fraction A (10·3 mg; 1·0%) allocryptopine, epialpinine, amurensinine, protopine, amurensine, and muramine were identified by TLC in systems S_1, S_2, and S_7 (cochromatography with authentic samples), in fraction B (traces) palmatine and coptisine were identified in systems S_{12}, S_{13}, and S_{14}, and in fraction I (3·1 mg) corytuberine, N-methylamurensinium iodide, and N-methyltetrahydropalmatinium iodide were detected in systems S_6, S_8, S_9, and S_{10}.

Characterization of the Alkaloids Isolated

The absolute configuration has not been determined.

Nudaurine (I): from acetone, m.p. 199–200°C, $[\alpha]_D^{25} = -41°$ (*c* 0·45, methanol). Mass spectrum, *m/z*: 327 (M^+, 100%), 326, 312, 310, 309, 294. IR spectrum (KBr): 3 100–3 500 (OH), 1 665 to 1 630 (double bond), 1 515, 1 495 (aromatic system), 1 030, 935 cm^{-1} (OCH_2O). UV spectrum (ethanol): λ_{max} nm (log ε): 244 (4·00), 292 (3·78), λ_{min} 271 (3·61). ^1H NMR spectrum: 2·25 ppm (s, 3 H), 3·60 (s, 3 H), 5·80 (s, 2 H), 4·53 (d, 1 H, $J = 4$ Hz), 5·13 (s, 1 H), 5·62 (d, 1 H, $J = 4$ Hz), 6·46 (s, 1 H), 6·71 (s, 1 H), 1·30–3·45 (7 H). The data are in agreement with the literature[11,12]. Oxidation of nudaurine with manganese dioxide afforded a product which was identical with amurine[12] according to its m.p., mass spectrum, IR, and ^1H NMR spectra.

Amurine: from acetone, m.p. 212–213°C, $[\alpha]_D^{25} = +9°$ (0·43, methanol). Mass spectrum, *m/z*: 325 (M^+), 324, 310, 297, 282, 162·5 (M^{++}). IR spectrum (KBr): 1 680 cm^{-1}, 1 660, 1 623 (cyclohexadienone system), 1 570, 1 490 (aromatic system), 1 040, 935 (OCH_2O). UV spectrum (ethanol): λ_{max} nm (log ε) 238 (3·67), 290 (3·70), λ_{min} 258 (2·95). ^1H NMR spectrum: 2·25 ppm (s, 3 H), 3·60 (s, 3 H), 5·80 (s, 2 H), 6·27 (s, 2 H), 6·57 (s, 1 H), 6·79 (s, 1 H), 1·65–3·65 (7 H). The mentioned data agree with those from literature[12]. Reduction with sodium borohydride gave two products of which one was identical with nudaurine (*I*), while the second is probably epinudaurine.

Oxysanguinarine (II): from methanol, m.p. 362–364°C. Mass spectrum, *m/z*: 347 (M^+), 346, 318, 289, 173·5 (M^{++}). UV spectrum (ethanol): λ_{max} nm (log ε) 241 (4·72), 287 (4·69), 327 (4·22), 344 (4·22), 369 (4·09), λ_{min} 260 (4·33), 309 (4·16), 336 (4·20), 361 (4·09). The spectral data were in agreement with the literature[13]. The identity was also confirmed by comparison with a preparation synthetized from sanguinarine by oxidation with potassium ferricyanide.

* For the donation of the herbarium specimen we thank Dr K. Kubát of the District National Science Museum in Litoměřice.

Corydine (IIIa): from methanol, m.p. 147—149°C. Mass spectrum, *m/z*: 341 (M^+), 340, 326, 324, 310, 298, 170·5 (M^{++}). UV spectrum (ethanol): λ_{max} nm (log ε) 211 (4·85), 266 (4·19), 304 (3·87), λ_{min} 247 (3·72), 288 (3·78). The identity was confirmed by comparison with an authentic sample.

Amurensine: from methanol, m.p. 214—215°C. Mass spectrum, *m/z*: 325 (M^+), 324, 309, 282, 267, 188 b.p. On labelling 1 atom of deuterium enters the molecule. The spectrum was in agreement with the literature data[14]. UV spectrum (methanol): λ_{max} nm (log ε) 230 (4·06), 250 sh (3·67), 296 (3·94), λ_{min} 262 (2·96). IR spectrum (nujol): the characteristic peaks of the OH group absorption were not visible. TLC data were in agreement with those of an authentic specimen, and the spectral data corresponded to those from literature[15].

Epialpinine (IVb): from methanol, m.p. 121—123°C, undepressed on admixture with an authentic sample[9]. UV spectrum (methanol): λ_{max} nm (log ε) 209 (4·66), 230 sh (4·21), 284 (3·85), λ_{min} 262 (3·56). IR spectrum (chloroform): 1 610 cm^{-1}, 1 725. On boiling with hydrochloric acid ($4 . 10^{-3}$ mol l^{-1}) a product identical with alpinigenine was formed.

Alpinigenine: amorphous. UV spectrum (methanol): λ_{max} nm (log ε) 230 (4·18), 285 (3·77), λ_{min} 262 (3·28). It was identified by comparison with an authentic sample (TLC data).

Protopine: from chloroform–ethanol, m.p. 204—206°C, undepressed with an authentic preparation. UV spectrum (methanol): λ_{max} nm (log ε) 230 (2·94), 290 (3·84), λ_{min} 263 (3·61). IR spectrum (nujol): 1 660 cm^{-1} (C=O). The TLC data were in agreement with those of an authentic sample.

Allocryptopine: from methanol, m.p. 161—163°C, undepressed on admixture of an authentic preparation. UV spectrum (methanol): λ_{max} nm (log ε) 232 (3·89), 285 (3·77), λ_{min} 256 (3·57). IR spectrum (nujol): 1 665 cm^{-1} (C=O). The TLC data were in agreement with those of an authentic sample.

Mecambridine: from methanol, m.p. 182—183°C, undepressed on admixture of an authentic sample. UV spectrum (methanol): λ_{max} nm (log ε) 229 (4·16), 288 (3·73), λ_{min} 257 (2·81). The TLC data were in agreement with those of an authentic preparation.

Amurensinine: from methanol, m.p. 142—143°C. UV spectrum (methanol): λ_{max} nm 230, 251 sh, 295, λ_{min} 260. TLC in agreement with an authentic sample.

Muramine: from methanol, m.p. 173—175°C, undepressed on admixture of an authentic preparation. UV spectrum (methanol): λ_{max} nm (log ε) 208 (4·72), 222 sh (4·41), 254 (3·91), 284 (3·90), λ_{min} 248 (3·90), 268 (3·88). TLC in agreement with an authentic preparation.

Alborine iodide (alkaloid PO-5): from methanol, yellow needles which did not melt up to 360°C. UV spectrum (methanol): λ_{max} nm (log ε) 245 (4·33), 263 (4·31), 292 (4·50), 336 (420), λ_{min} 243 (4·30), 254 (4·28), 272 (4·25), 318 (4·19). TLC in agreement with an authentic sample.

cis-N-*Methyltetrahydropalmatinium iodide* (V): amorphous. Mass spectrum, *m/z*: 355 (M^+), 354, 324, 192, 190, 164, 149, 142, 127. UV spectrum (methanol): λ_{max} nm (log ε) 222 (4·29), 235 sh (4·26), 288 (3·75), λ_{min} 263 (2·80). TLC and PC data were in agreement with those of the sample isolated from *Argemone ochroleuca*[10].

Alkaloid PK1: amorphous. Mass spectrum, *m/z*: 367 (M^+, $C_{21}H_{21}NO_5$), 352 ($M^+ - CH_3$). UV spectrum (methanol): λ_{max} nm 214, 229 sh, 386, λ_{min} 256.

R_F values

In S_1, S_2, and S_5: nudaurine 0·08, 0·32, 0·33, amurine 0·07, 0·23, 0·68, corydine 0·16, 0·52, 0·59, oxysanguinarine 0·91, 0·86, 0·99; in S_1 and S_2: protopine 0·42, 0·65, allocryptopine 0·22, 0·61,

cryptopine 0·25, 0·63, muramine 0·14, 0·52, epialpinine 0·51, 0·82, amurensinine 0·34, 0·55, mecambridine 0·10, 0·34, alpinigenine 0·24, 0·50, amurensine 0·04, 0·09; in S_1, S_2 S_3, and S_4: papaverrubine B 0·15, 0·48, 0·32, 0·60, papaverrubine D 0·04, 0·16, 0·20, 046, papaverrubine G 0·09, 0·26, 0·24, 0·52. In S_7, S_8, and S_{11}: alborine 0·01, 0·10, 0·60, PK1 0·50, 0·71, —; in S_6, S_8, S_9, and S_{10}: corytuberine 0·74, 0·82, 0·90, 0·76, N-methylamurensinium iodide 0·02, 0·15, 0·42, 0·65, N-methyltetrahydropalmatinium iodide 0·35, 0·34, 0·69, 0·74; in S_{12}, S_{13}, and S_{14}: coptisine 0·55, 0·43, 0·07, palmatine 0·27, 0·55, 0·23; in S_7, S_8, S_{13}, and S_{14}: *cis*-N-methyltetrahydropalmatinium iodide 0·10, 0·18, 0·75, 0·35, *trans*-form 0·10, 0·18, 0·60, 0·19.

For the mass spectra measurements we thank Dr L. Dolejš of the Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, Prague and for the samples of muramine, amurensinine, and alpinigenine our thanks are due to Dr M. Maturová of the Medical Faculty, Palacký University, Olomouc. For technical assistance we thank Mrs A. Kuncová of our laboratory.

REFERENCES

1. Fedde F.: *Papaveraceae-Hypecoideae et Papaveraceae-Papaveroideae.* In the book by Engler A.: *Das Pflanzenreich — Regni vegetabilis conspectus.* Part IV, Vol. 104. Leipzig, 1909.
2. Novák J.: *Taxonomické hodnocení sekce* Scapiflora Reichb. *rodu* Papaver. l. Agricultural University, Prague 1978.
3. Boit H. G., Flentje H.: Naturwissenschaften *47*, 180 (1960).
4. Flentje H., Döpke W.: Pharmazie *21*, 321 (1966).
5. Maturová M., Moza B. K., Sitař J., Šantavý F.: Planta Med. *10*, 345 (1962).
6. Maturová M., Pavlásková D., Šantavý F.: Planta Med. *14*, 22 (1966).
7. Pfeifer S., Banerjee S. K.: Pharmazie *19*, 286 (1964).
8. Pfeifer S., Dohnert H.: Pharmazie *23*, 585 (1968).
9. Slavík J., Slavíková L.: This Journal, in press.
10. Haisová K., Slavík J.: This Journal *38*, 2307 (1973).
11. Slavíková L., Slavík J.: This Journal *31*, 3362 (1966).
12. Döpke W., Flentje H., Jeffs P. W.: Tetrahedron *24*, 4459 (1968).
13. Pandey V. B., Ray A. B., Dasgupta B.: Phytochemistry *38*, 275 (1975).
14. Dolejš L., Hanuš V.: This Journal *33*, 600 (1968).
15. Gözler B., Lantz M. S., Shamma M.: J. Nat. Prod. *46*, 293 (1983).

Translated by Ž. Procházka.