ALKALOIDS FROM *Papaver atlanticum* BALL AND *Papaver glaucum* BOISS. *et* HAUSKN*.

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In addition to the alkaloids previously found in the aerial part of *P. atlanticum* BALL, *viz.* protopine, rhoeadine (predominant constituents), rhoeagenine, stylopine, cryptopine, sanguinarine, magnoflorine and papaverrubines A, B, E and D, we have now isolated the tertiary bases isothebaine, scoulerine, corytuberine and a new quaternary alkaloid 13β-hydroxy-N-methylstylopinium hydroxide (*I*). The presence of papaverrubine B and muramine was also detected (TLC). The contents of the bases in the roots of *P. atlanticum* were found similar to those in the aerial part. Magnoflorine was isolated from the roots in a considerable yield. The dominant alkaloids isolated from *P. glaucum* BOISS. *et* HAUSKN. were glaudine and glaucamine; they were accompanied by protopine, papaverrubine B and traces of sanguinarine, coptisine and papaverrubine C. Magnoflorine and corytuberine have been isolated from this species for the first time and the presence of allocryptopine, cryptopine, corydine, isocorydine and papaverrubines D and H has been demonstrated.

The present paper deals with two *Papaver* species: *P. atlanticum* BALL from the section *Pilosa* PRANTL and *P. glaucum* BOISS. et HAUSKN. from the section *Mecones* BERNH. The aim of the study was to supplement the present-day knowledge of the occurrence of minor alkaloids and to verify the presence of quaternary alkaloids in these species.

P. atlanticum is a perennial herb, domestic in Morocco, little variable chemically and morphologically. Alkaloids of this species have been the subject of a number of studies[1-6]. The main representatives are protopine and rhoeadine, the minor ones being rhoeagenine, coptisine, sanguinarine, cryptopine, 13-oxoprotopine, 13-oxocryptopine, stylopine, oxysanguinarine and papaverrubines E and D. Also detected (chromatographically) were papaverrubines A and C. Our recent work[7] describes isolation of magnoflorine from the roots of *P. atlanticum* in a considerable yield. According to chemotaxonomic studies the alkaloid spectrum of *P. atlanticum* is

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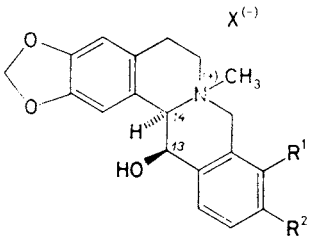
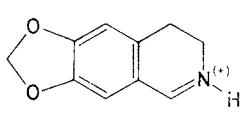
similar to that of the related species *P. rupifragum*[8,9]. A distinctive feature has been supposed to be the presence of papaverrubine B in *P. rupifragum*[8], but we have now demonstrated this alkaloid in *P. atlanticum*, too.

In the present study we worked up separately the aerial part and the roots of *P. atlanticum*. In accordance with the previous results, the main alkaloids isolated from the tertiary portion of the aerial part were protopine and rhoeadine. Further, by column chromatography of the non-phenolic portion of the bases on silica gel, we separated the previously demonstrated bases rhoeagenine and stylopine. Newly we have isolated the tertiary alkaloid isothebaine, found before only in the section *Macrantha*, and, in a negligible yield, another base, denoted *PA* 1; the latter, however, could be characterized only by its melting point and mass and UV spectra, but the amount of the material was too small for the determination of its structure. In the mother liquors of the non-phenolic portion we detected chromatographically cryptopine, sanguinarine, papaverrubines A, C, E and D, and newly also muramine and papaverrubine B. Scoulerine was isolated from the fraction of the phenolic tertiary bases from this species for the first time.

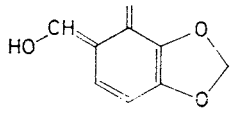
No significant differences in composition of the tertiary alkaloids were found between the roots and the aerial part. The main alkaloid components isolated from the roots were, likewise, protopine and rhoeadine. Chromatographically detected were rhoeagenine, cryptopine, isothebaine, muramine and papaverrubines A, B, C, D and E.



I, $R^1 + R^2 = -OCH_2O-$
II, $R^1 = R^2 = -OCH_3$



a



b

Magnoflorine was isolated from the portion of strongly polar alkaloids in either part of the plant. Its yield from the aerial part corresponded to a content of merely 0·02%, but in the roots its content was found to be exceptionally high (0·39%). A similar, high content of magnoflorine had been found by us in *P. oreophillum* from the same section[10]. Isolated, for the first time from both parts of this species, were the strongly polar tertiary alkaloid corytuberine (in the form of hydriodide) and a new laevorotary alkaloid, which we have identified as 13β-hydroxy-N-methylstylopinium iodide (*I*), have been isolated from both parts of this species for the first time.

The peaks in the mass spectra of this alkaloid corresponding to masses 142 (CH_3I), 128 (HI) and 127 (I) testify to a quaternary methiodide. The absence of the peak of m/z 58 ($CH_2{=}N^+(CH_3)_2$) suggests that the compound contains only one N-methyl group, as is so, *e.g.*, in quaternary tetrahydroprotoberberines. The ion $C_{10}H_{10}NO_2$ (m/z 176) can accordingly be regarded as a product of retrograde Diels–Alder condensation (*a*)[11]. The fully aromatic form of hydroxy-methoxy-N-methylisoquinolinium is ruled out by the presence of a satellite dehydrogenated ion (*a* − 2 H). The ions forming a cluster corresponding to masses 164–162 may represent complementary fragments, produced by the retro-Diels–Alder condensation. If the ion of m/z 164 is assigned structure *b*, the isolated alkaloid can then be formulated as *I*.

Methiodides of common tetrahydroprotoberberines, without a hydroxy substituent at the 13-position, decompose pyrolytically in measuring the mass spectra to methine (release of HI) and a tertiary base (release of CH_3I). The molecular peaks of the two products are usually accompanied by M − 1 fragments only, the peak of the tertiary base being always much higher than that of methine. However, the upper part of the mass spectrum of the alkaloid isolated exhibits a cluster of small peaks on masses 353–346 and more intensive clusters on masses 339–332 and 323–318. The molecular peaks of methine (m/z 353) and the tertiary base (m/z 339) make up only a small part of the cluster. The composition of some higher satellite peaks was determined by measurement with a high resolution power: m/z 337: $C_{20}H_{19}NO_4$ ($M_{methine} - O$); m/z 335: doublet 4 : 3 : $C_{20}H_{17}NO_4$ ($M_{methine} - H_2O$) + $C_{19}H_{13}NO_5$ ($M_{tert.base}$ − − 4 H); m/z 321 : $C_{19}H_{15}NO_4$ ($M_{tert.base} - H_2O$). Similar clusters of peaks in the highest region of the spectrum were observed even with ophiocarpine-N-oxide[12]. The mass spectrum of non-substituted ophiocarpine contains essentially just a well-defined molecular peak (M 355) and a peak M − 1 (ratio of intensities 2 : 1). To make the comparison more reliable we prepared ophiocarpine methiodide (*II*) by N-methylation of ophiocarpine. Its mass spectrum contained clusters of peaks similar to those in the spectrum of the isolated alkaloid, but shifted higher by 16 mass units (m/z 369–362, 355–348, 339–334).

The propounded structure has been verified by direct comparison with a preparation obtained by N-methylation of authentic 13β-hydroxystylopine (*cis* position of hydrogen atoms on $C_{(13)}$ and $C_{(14)}$). The methylation gave rise to both the quaternary isomers of 13β-hydroxy-N-methyl-stylopine, with the position of the rings B and C *cis* or *trans*. Crystallization from methanol gave a product melting at 272–273°C, which probably was, judging by paper chromatography, the *trans* form (lower R_F, *cf.* ref.[13]); the mother liquor contained a mixture of both the *cis* and the *trans* forms. The mass spectrum of the isolated alkaloid was quite identical with that of synthetized, crystalline methiodide; the former, however, appeared to be the *cis* form (a higher R_F value).

The data stated above identify the isolated alkaloid as 13β-hydroxy-N-methylstylopinium iodide (*I*), probably with the B/C *cis* junction. As a natural alkaloid

it has not been described before. Its tertiary analogue, 13β-hydroxystylopine, was found only in several species of the *Fumariaceae* family, where the occurrence of 13-substituted tetrahydroprotoberberines is more frequent than in the family *Papaveraceae*.

P. glaucum BOISS. et HAUSKN., wide-spread east of the Mediterranean, is an annual species from the section *Mecones* BERNH., classed by Preininger et Novák[14] to the new section *Glauca*. In earlier papers[5,15-18] the main bases isolated from this taxone were rhoeadine alkaloids, *viz.* glaudine (also isolated independently at about the same time and given the name glaupavine[5]) and glaucamine. Another sample was found[5] to contain an additional rhoeadine alkaloid, epiglaudine, probably formed by epimerization of glaudine (glaupavine)[5]. Isolated minor components were coptisine, oxysanguinarine and papaverrubine B. Chromatographically detected were chelerythrine, sanguinarine, protopine and papaverrubines A, C, and D.

The present paper deals with alkaloids isolated from a greater quantity of the plant material. The alkaloids were extracted into methanol after wetting the drug with a dilute solution of sodium carbonate. The main base of the tertiary portion proved to be crystalline glaudine (0·13% of the dry weight). The yield of glaudine was dependent on the method of extraction. In an experiment in which a sample of the plant material was worked up without the previous alkalization, the portion of glaudine, among the other alkaloids, was much smaller, the predominant constituent of the tertiary portion being its more stable epimer, epiglaudine. The finding of epiglaudine in this species may be an artifact, due to epimerization of glaudine in the isolation. Another significant constituent of the tertiary portion was glaucamine. Apart from the previously demonstrated papaverrubines B, C and coptisine, we have succeeded in detecting, for the first time, other minor bases, *viz.* allocryptopine, cryptopine, corydine, isocorydine and papaverrubines D and H.

From the portion of the strongly polar bases were isolated, for the first time from this taxone, corytuberine hydriodide and its quaternary derivative magnoflorine, widely spread in the family *Papaveraceae*.

EXPERIMENTAL

The melting points, measured on the Kofler stage, are not corrected. The mass spectra were recorded with a spectrometer AEI MS 902, the UV spectra with a spectrophotometer Pye Unicam SP 1800 in methanol, the IR spectra with an apparatus IR 75 Zeiss Specord (Jena) in chloroform or Nujol.

TLC on silica gel LS 5/40 (Lachema) with plaster as binder ran in systems cyclohexane–diethylamine 9 : 1 (S_1), cyclohexane–chloroform–diethylamine 7 : 2 : 1 (S_2), benzene–acetone–methanol 7 : 2 : 1 (S_3), benzene–diethylamine 19 : 1 (S_4), methanol–water–ammonium hydroxide 15 : 3 : 1 (S_5), ethanol–water–ammonium hydroxide 15 : 9 : 1 (S_6), propanol–water–formic acid 12 : 7 : 1 (S_7). TLC on Silufol plates (Kavalier) ran in systems methanol–diethylamine 4 : 1 (S_8) and cyclohexane–methanol 3 : 1 (S_9). Paper chromatography (PC) on Whatman No 1 ran in

systems butanol–water–glacial acetic acid 10 : 3 : 1 (S_{10}) and ethanol–water 3 : 2 (S_{11}). The spots of fluorescent alkaloids were detected under UV light (at 235 and 336 nm), papaverrubines were detected with vapour of conc. hydrochloric acid (purple colouration). The spots of the other alkaloids were developed with a spray of potassium hexaiodoplatinate (TLC) or the Dragendorff reagent (PC). Column chromatography was carried out on aluminium oxide for that purpose (Reachim, U.S.S.R.) and on silica gel L 100/250 (Lachema).

Extraction and Isolation of the Alkaloids

The plant material was grown in the Centre for Cultivation of Medicinal plants, Medical Faculty in Brno, from seeds obtained from various botanical gardens. The materials were harvested at the stage of flowering and unripe fruits. The material was dried at room temperature, ground and extracted with cold methanol in a percolator. The crude sum of the alkaloids, left after the methanol had been distilled off, was dissolved in acetic acid (0·5 mol l^{-1}) and fractionated in the usual manner[19] into portions A, B, and I.

Papaver atlanticum

Extraction from the aerial part. A dry material (4·55 kg) was used. Crystallization of the crude portion A from methanol separated rhoeadine (1·89 g) and protopine (1·13 g). The bases from the mother liquors of the portion A were resolved into fraction of non-phenolic bases A_1 (1·30 g) and a fraction of phenolic bases A_2 (0·71 g). Crystallization of A_1 from methanol afforded protopine (77·0 mg), rhoeadine (49·0 mg) and rhoeagenine (94·2 mg). The bases remaining in the mother liquors of A_1 were separated chromatographically on a column of silica gel. Elution with a mixture benzene–ether 3 : 1 afforded stylopine (2·2 mg); a mixture benzene–ether 2 : 1 eluted fractions containing (according to TLC) rhoeadine, rhoeagenine, papaverrubine B, traces of sanguinarine and two unknown bases. The yield of crystallized rhoeadine was 50·0 mg. Elution with ether–chloroform, 10 : 1 to 4 : 1, gave further fractions (mixtures), from which 3·3 mg of crystalline base PA 1 was obtained. The fractions eluted with chloroform–methanol (49 : 1) contained isothebaine as the main alkaloid and traces of protopine and cryptopine; their crystallization afforded isothebaine (0·8 mg). By increasing the content of methanol in chloroform–methanol mixtures (19 : 1 to 4 : 1) the fractions also contained protopine, cryptopine, muramine and traces of allocryptopine. Repeated crystallization of these fractions gave protopine (60·2 mg). The amorphous portion of A_2 (0·56 g) was fractionated chromatographically on a column of silica gel. The fraction eluted with benzene–ether (2 : 1) was a mixture of two non-identified alkaloids, of R_F values 0·42 and 0·61 (S_2). Ether–chloroform (5 : 1) eluted scoulerine (3·2 mg). Another fraction, eluted with chloroform–ether (1 : 4) gave, after purification, the base PA 1 (2·0 mg). Chloroform with increasing contents of methanol eluted a number of fractions, which were found (chromatographically) to contain isothebaine, PA 1, protopine, cryptopine and other two, non-identified bases. Coptisine chloride (58·7 mg) was isolated from portion B, and palmatine was detected in the mother liquors. Portion I was crystallized from methanol, giving magnoflorine iodide (97·7 mg), corytuberine hydriodide (123·0 mg) and 13β-hydroxy-N-methylstylopinium iodide (135·7 mg). The amorphous portion from the mother liquor contained some non-alkaloid substances and bases that we did not succeed in separating.

Extraction from the roots. 1·00 kg of the roots was worked up in the same way as the aerial part. Fractionation of a crude portion A (1·53 g) gave 1·05 g of fraction A_1 and 0·35 g of A_2. The former was crystallized from methanol, yielding protopine (0·34 g) and rhoeadine (0·23 g). The amorphous part of the mother liquor was found to contain, in addition to the above-said alkaloids, cryptopine, isothebaine, muramine, rhoeagenine, papaverrubines A, B, C, E, and three unknown

bases. The fraction A_2 remained amorphous and, according to TLC, contained two bases that we did not identify. Portion B afforded coptisine chloride (5·0 mg), portion I was crystallized from methanol, giving magnoflorine iodide (5·85 g), 13β-hydroxy-N-methylstylopinium iodide (54·8 mg) and corytuberine hydriodide (254·0 mg).

Papaver glaucum

In a preliminary extraction of a small sample of the plant material with methanol in the Soxhlet apparatus the extract turned deep red, as a result of decomposition of the papaverrubines. Analysis by TLC showed that the main alkaloid of the tertiary portion of the bases was epiglaudine. Another sample of the same material was wetted with aqueous sodium carbonate and extracted with cold methanol; the main alkaloid in the extract was glaudine. On the basis of this finding, 6·40 kg of the material (the whole plant) was alkalinized with 250 ml of aqueous sodium carbonate (200 g/l) and extracted with cold methanol.

Portion A (16·14 g) was first crystallized, separating glaucamine (1·67 g) and papaverrubine B (0·20 g). Then it was resolved into a fraction of non-phenolic bases, A_1 (9·13 g) and phenolic bases, A_2 (0·47 g). Crystallization of A_1 from methanol gave another crop of glaucamine (0·21 g), crystallization from ether gave glaudine (4·50 g). The amorphous residue of A_1 was chromatographed on a column of aluminium oxide. Using benzene as eluant we obtained fractions containing predominantly glaudine, and small quantities of epiglaudine and papaverrubine B. By crystallization from ether we isolated glaudine (3·83 g) and papaverrubine B (0·10 g), and also demonstrated papaverrubine H in the mother liquor. Elution with benzene–chloroform (99 : 1) gave fractions, from which glaucamine (13·4 mg) and protopine (12·0 mg) were separated by crystallization. Chromatographically detected in the mother liquors were cryptopine, isocorydine, corydine, sanguinarine, papaverrubines C and D and other four, non-identified bases. The fraction A_2 remained amorphous even after purification and contained (TLC) small amounts of glaudine, epiglaudine, papaverrubines C and D and two unknown bases. Portion B afforded coptisine chloride (1·2 mg). Portion I (0·86 g) was crystallized from methanol, giving magnoflorine iodide (36·0 mg) and corytuberine hydriodide (98·3 mg); two more, unknown bases were demonstrated chromatographically.

Characteristics of the Alkaloids Isolated

The isolated alkaloids were identified by their melting points, mixed melting points, UV and IR spectra, optical rotation and comparison of R_F values with those of authentic samples in TLC and PC. The yields of the individual alkaloids in % of dry weight of the aerial parts and the roots of *P. atlanticum* and *P. glaucum* are given in parentheses.

Rhoeadine (0·043%, 0·02%, —): needles crystallized from methanol, m.p. 250—252°C undepressed with an authentic sample, R_F: 0·51 (S_1), 0·75 (S_2).

Protopine (0·030%, 0·034%, 0·0002%): prisms of *m.p.* 208—209°C (methanol–chloroform) undepressed with an authentic preparation, R_F: 0·36 (S_1), 0·68 (S_2).

Rhoeagenine (0·002%, —, —): needles, m.p. 240—242°C (methanol); UV and IR spectra in accordance with reported data, R_F: 0·19 (S_1), 0·46 (S_2).

Stylopine (0·00004%, —, —): needles, m.p. 200—202°C (methanol), UV and IR spectra in accordance with reported data, R_F: 0·68 (S_1), 0·83 (S_2).

Isothebaine (0·0002%, —, —): prisms, m.p. 204—205°C (methanol) undepressed with an authentic preparation, UV and IR spectra identical with those of an authentic preparation, R_F: 0·14 (S_1), 0·50 (S_2).

Scoulerine (0·00007%, —, —): needles, m.p. 200—202°C (methanol) undepressed with an authentic preparation, UV and IR spectra identical with those of an authentic preparation, R_F: 0·05 (S_1), 0·16 (S_2).

Coptisine (0·0012%, 0·0005%, 0·00002%): chloride, orange needles not melting to 350°C, R_F: 0·55 (S_8), 0·43 (S_{10}), 0·07 (S_{11}). Reduction with Zn and HCl gave tetrahydro derivative, m.p. 218—219°C undepressed with an authentic preparation.

Alkaloid PA 1 (0·0001%, —, —): needles from methanol, m.p. 183—184°C; mass spectrum: *m/z* 281 (M^+, $C_{17}H_{15}NO_3$), 211; UV spectrum (methanol): λ_{max} nm (log ε) 240 (4·75), 269 3·72), 279 (3·63), 290 (3·60), 318 (3·51), 332 (3·60), λ_{min} nm (log ε) 263 (3·63), 275 (3·62), 286 (3·59), 304 (3·23), 322 (3·44); R_F: 0·02 (S_1), 0·17 (S_2).

Magnoflorine iodide (0·002%, 0·39%, 0·0005%): prisms from methanol, m.p. 262—263°C; UV and IR spectra in accordance with those of an authentic preparation, R_F: 0·35 (S_5), 0·49 (S_6), 0·56 (S_7).

Corytuberine hydriodide (0·003%, 0·024%, 0·0015%): needles from methanol, m.p. 210—211°C, UV and IR spectra in accordance with those of an authentic preparation, R_F: 0·80 (S_5), 0·83 (S_6), 0·76 (S_7).

Glaudine (*glaupavine*) (—, —, 0·13%): needles from ether, m.p. 101—103°C, hydrobromide of m.p. 252—254°C $[\alpha]_D^{20}$ +205 ± 5° (*c* 0·20, methanol); UV spectrum (methanol): λ_{max} nm (log ε): 214 (4·19), 238 (4·03), 289 (3·90), λ_{max} nm (log ε): 228 (3·98), 262 (3·41); R_F: 0·52 (S_1), 0·88 (S_2). Direct comparison of glaupavine and glaudine (spectra and TLC) showed their identity.

Glaucamine (—, —, 0·030%): prisms from methanol, m.p. 220—222°C, $[\alpha]_D^{20}$ 323 ± 5° (*c* 0·30, methanol); UV and IR spectra in agreement with the authentic preparation, R_F: 0·22 (S_1), 0·55 (S_2).

Papaverrubine B (—, —, 0·005%): needles from methanol, m.p. 201—203°C undepressed with with an authentic preparation; UV and IR spectra in agreement with authentic preparation, R_F: 0·21 (S_1), 0·50 (S_2).

13β-*Hydroxy*-N-*methylstylopinium iodide* (0·003%, 0·006%, —): m.p. 254—256°C (methanol), $[\alpha]_D^{20}$ −144 ± 5° (*c* 0·1, methanol); UV spectra (methanol): λ_{max} nm (log ε): 222 (4·24), 242—244 sh (4·00), 292 (3·97) λ_{max} nm (log ε) 262 (3·15): IR spectrum (Nujol): 3 220 cm^{-1} (OH); R_F: 0·21 (S_5), 0·32 (S_6), 0·66 (S_{10}), 0·75 (S_{11}). Mass spectrum, *m/z* (intensity): 353 (0·09), 352 (0·12), 351 (0·45), 350 (0·50), 349 (0·45), 348 (0·70), 347 (0·40), 346 (0·21), 339 (2·1), 338 (3·0), 337 (9·4), 336 (4·8), 335 (12·1), 334 (13·6), 333 (11·8), 332 (8·5), 323 (6·4), 322 (9·7), 321 (21·5), 320 (27·9), 319 (4·8), 318 (7·6), 176 (100), 174 (8·5), 164 (24·2), 163 (36·4), 162 (45·5), 161 (11·5), 148 (17·6), 142 (54·5), 128 (10·3), 127 (22·7).

Preparation of N-Methylophiocarpinium Iodide (*II*)

To 30 mg of ophiocarpine (m.p. 186—187°C) in 1·5 ml of methanol were added 1 ml of methyl iodide and 1 ml of ether. The mixture was boiled under a reflux condenser for 4 h on a water bath, then left standing overnight; yield 40 mg of *II* (m.p. 273—275°C). UV spectrum (methanol): λ_{max} nm (log ε) 202 (4·43), 210—212 sh (4·32), 274—276 (3·75) λ_{min} nm (log ε) 249 (3·11); IR spectrum (Nujol): 3220 cm^{-1} (OH); R_F 0·20 (S_5), 0·30 (S_6), 0·64 (S_{10}), 0·71 (S_{11}); Mass spectrum *m/z* (intensity): 369 (0·22), 368 (0·22), 367 (0·78), 366 (0·23), 365 (0·20), 364 (0·13), 363 (0·13), 362 (0·05), 355 (0·90), 354 (1·4), 353 (2·5), 352 (1·3), 351 (1·9), 350 (1·3), 349 (1·2), 348 (0·54), 339 (2·5), 338 (2·5), 337 (5·3), 336 (4·8), 335 (3·1), 334 (2·5), 180 (8·1), 179 (5·2), 178 (8·6), 177 (14·4), 176 (100), 174 (5·0), 142 (13·3), 128 (1·1), 127 (9·2).

Preparation of 13β-Hydroxy-N-methylstylopinium Iodide (*I*)

The starting (−)-13β-hydroxystylopine (m.p. 214°C) was very poorly soluble in the usual organic solvents. For this reason 10 mg of this alkaloid was dissolved in 2 ml of dilute sulphuric acid (0·1 mol l^{-1}), and the solution was alkalinized with ammonia and extracted with ether. The ethereal extract was concentrated to 1 ml, then 0·5 ml of methanol and 0·2 ml of methyl iodide were added and the mixture was refluxed for 4 h. After cooling *I* was separated (3·7 mg, m.p. 272–273°C). The mass and UV spectra were identical with those of the natural alkaloid. R_F: 0·52 (S_{10}), 0·32 (S_{11}). As found by PC, the mother liquor also contained the other isomer of the quaternary methiodide, of higher R_F values: 0·66 (S_{10}) and 0·75 (S_{11}). It was chromatographically identical with the natural alkaloid.

R_F Values of Chromatographically Demonstrated Alkaloids

In systems S_1, S_2, and S_3 respectively: allocryptopine 0·22, 0·63, 0·28; corydine 0·15, 0·48, 0·62; cryptopine 0·23, 0·65, 0·14; epiglaudine 0·37, 0·75, 0·78; isocorydine 0·15, 0·48, 0·62; muramine 0·14, 0·53, 0·30. In S_1 and S_2 sanguinarine 0·90, 0·77, In S_1, S_2, and S_4: papaverrubine A 0·32, 0·71, 0·85; papaverrubine B 0·21, 0·50, 0·77; papaverrubine C 0·11, 0·24, 0·46; papaverrubine D 0·06, 0·35, 0·25; papaverrubine E 0·27, 0·61, 0·75; papaverrubine H 0·17, 0·45, 0·63. In systems S_8, S_{10}, and S_{11}: palmatine 0·27, 0·55, 0·23.

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