ALKALOIDS OF THE *Papaveraceae*. LI.*
ADDITIONAL ALKALOIDS FROM *Argemone albiflora* HORNEM.

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In addition to berberine, allocryptopine, protopine, sanguinarine and chelerythrine other alkaloids have been isolated from *Argemone albiflora* HORNEM., *i.e.* norchelerythrine, norsanguinarine, (−)-scoulerine, (−)-β-scoulerine methohydroxide, and three additional bases, alkaloid AA 1, AA 2, and AA 3. Simultaneously the identity of the alkaloid HF 1 from *Hunnemannia fumariaefolia* SWEET and (−)-scoulerine has been established.

From *Argemone albiflora* HORNEM. (synonym *A. alba* LESTIB.) only berberine[1,2] and further[2] allocryptopine, protopine, sanguinarine, chelerythrine have been isolated so far. Traces of coptisine were also demonstrated. In addition to this a relatively appreciable amount of phenolic type bases[2] were found in the above-ground parts of the plant, but their nature has not yet been elucidated. In this paper our attention was devoted to the study of minor alkaloids and mainly to the question of the presence of quaternary alkaloids which we have recently detected in *A. ochroleuca* SWEET[3] and *A. platyceras* LINK et OTTO[4]. For this study we used plant material from two collections and worked up the above-ground parts and the roots of one sample separately on the one hand, and the whole plant of another sample on the other. Applying the usual procedure we separated first the alkaloids which were found in this plant earlier[2], *i.e.* allocryptopine and berberine as main alkaloids and protopine, sanguinarine and chelerythrine as minor alkaloids. From the non-phenolic fraction we isolated small amounts of another two alkaloids of very weak basicity which were found to be identical with norchelerythrine (*Ia*) and norsanguinarine (*Ib*). None of these two alkaloids has been found in *Argemone* species so far. Norchelerythrine was prepared for the first time synthetically as an intermediate during the total synthesis of chelerythrine and also by demethylation of the natural chelerythrine[5]. It was isolated so far as a natural component only from *Toddalia aculeata* PERS. (*Rutaceae*)[6].

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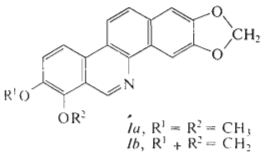
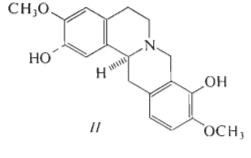
In the mass spectrum of the alkaloid isolated from *A. albiflora* the molecular ion formed the base peak and according to high-resolution measurement it had the composition $C_{20}H_{15}NO_4$ (M^+ 333·1000, calculated: 333·1001). The only more prominent fragmentation processes were the gradual splitting off of methyl radicals, carbon monoxide, and of formaldehyde from the methoxy groups and the methylenedioxy grouping[7]. On the basis of the mass spectral data the substance was formulated as a benzophenanthridine alkaloid, *Ia*, or its positional isomer. The IR and UV spectra corresponded to the literature data for norchelerythrine[5,6]. The identity of the substance with norchelerythrine (*Ia*) was further corroborated by mixed melting point, IR and UV spectra, and R_F values, by direct comparison with an authentic specimen[6] and a sample which we prepared by N-demethylation of chelerythrine chloride.

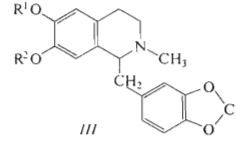
Norsanguinarine was prepared for the first time by N-demethylation of the chloride or iodide of sanguinarine[8,9] and later on as an intermediate of the total synthesis of sanguinarine[10,11]. Recently it was found for the first time as a natural component in the callus tissue of *Papaver somniferum* L.[12]. The alkaloid which we isolated from *A. albiflora* contained in its high-resolution mass spectrum molecular ion of mass 317·0697 (for $C_{19}H_{11}NO_4$ calculated: 317·0688). The spectrum with fragment



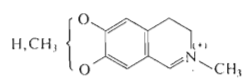
Ia, $R^1 = R^2 = CH_3$
Ib, $R^1 + R^2 = CH_2$



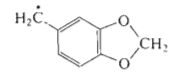
II



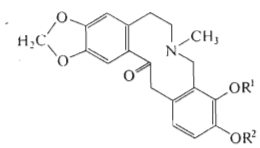
III



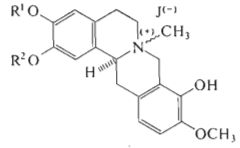
"*a*"



"*b*"



IVa, $R^1 = H$, $R^2 = CH_3$
IVb, $R^1 = CH_3$, $R^2 = H$



Va, $R^1 = CH_3$, $R^2 = H$
Vb, $R^1 = H$, $R^2 = CH_3$

ions at m/e 259 ($M-CH_2O-CO$), 201 ($M-2\,CH_2O-2\,CO$) and 174 ($201-HCN$) corresponded to that of norsanguinarine[11]. The identity with norsanguinarine was later confirmed by mixed melting point determination and the comparison of the IR and UV spectra, and R_F value with those of a preparation obtained on N-demethylation of sanguinarine chloride. All values found agreed with those in the literature[11,12].

As the main component of the phenolic fraction of bases we isolated (−)-scoulerine (*II*) which also has not been found in other species of *Argemone* genus so far. It occurs only in the above-ground part of the plant, while in roots it could not be detected even in traces. The mass, PMR, IR and UV spectra of this alkaloid corresponded to the literature data[13–15] and coincided with the spectra of a synthetic specimen of (±)-scoulerine[15]. On this occasion we again studied the problem of the structure of the alkaloid HF 1 isolated some time ago[16] from *Hunnemannia fumariaefolia* SWEET the identity of which with (−)-scoulerine could not be solved unambiguously in consequence of minor discrepancies observed during the comparison with an authentic specimen available at that time. The identity of the alkaloid HF 1 with (−)-scoulerine was now confirmed unequivocally so that the name "alkaloid HF 1" may be eliminated from the literature.

Two additional bases were isolated from the phenolic fraction in minute amounts. They were provisionally named as alkaloid AA 1, and AA 2, but could be investigated only superficially due to the lack of material. Alkaloid AA 1 was amorphous and according to its mass spectrum its composition was $C_{19}H_{21}NO_4$. In its IR spectrum the following bands were observed: 805 cm^{-1} (1,2,4-trisubstituted benzene ring), 870 cm^{-1} (1,2,4,5-tetrasubstituted benzene ring), bands in the 925–1245 cm^{-1} (O_2CH_2), 2850 and 2920 cm^{-1} (OCH_3). The UV spectrum indicated that the base is of a benzylisoquinoline alkaloid type. Its mass spectrum also had the basic characteristic of benzylisoquinoline type alkaloids[17]: negligible molecular ion (m/e 327) and $M-1$ ion, and an unusually intense fragment of mass 192 ($C_{11}H_{14}NO_2$, $M-135$). This fragment is formulated by structure "a" and its complementary radical of mass 135 by structure "*b*". According to the metastable transition $m^x = 163{\cdot}2$ the fragment "*a*" splits off the methyl substituent and is transformed to an ion of m/e 177. From the facts mentioned the structure *III* ($R^1 + R^2 = H + CH_3$) may be inferred for alkaloid AA 1.

Alkaloid AA 2 was also amorphous but formed a well crystallising perchlorate which was used for its purification. According to mass spectrometry the base has the composition $C_{20}H_{21}NO_5$. Mass spectrometry indicates the same fragments as hunnemanine[18] (*IVa*) with which it has a practically identical UV spectrum. However, their IR spectra and some other properties differ. In contrast to this it is corresponding in all respects with the alkaloid which we isolated from the root of *Eschscholtzia douglasii* (HOOK. et ARN.) WALP. and *E. californica* CHAM. Preliminarily

it may be judged that it could be a positional isomer of hunnemanine of probable structure *IVb*.

From the fraction of highly polar bases a quaternary alkaloid was isolated in the form of iodide of m.p. 258°C as the main component and it was found identical with (−)-β-scoulerine methiodide (*Va*). During mass spectral measurements this alkaloid split off pyrolytically methyl iodide (*m/e* 142) under formation of a tertiary base of mass 327 (M^+). The resulting spectrum with characteristic peaks at masses 326, 178 (base peak), 176, 150 and 135 was identical with the spectrum of scoulerine[13].

The same structure (*Va*) was also assigned to the alkaloid cyclanoline[19] (iodide m.p. 185°C) which was isolated for the first time from *Cyclea insularis* (MAKINO) DIELS[20] and later from several additional plants. As cyclanoline iodide gave on methylation an O,O'-dimethyl derivative identical with (−)-α-tetrahydropalmatine methiodide it was inferred that it is the α-form of (−)-scoulerine methiodide[19,21]. The diastereoisomeric β-form has not yet been described in the literature. For comparison we prepared (−)-scoulerine methiodide by methylation of (−)-scoulerine with methyl iodide. In analogy to other tetrahydroprotoberberines the higher melting β-form was formed as the main reaction product, which according to its melting point (258°C), mixed melting point, specific rotation, IR and UV spectra was identical with the natural alkaloid from *A. albiflora*. From the mother liquors we then isolated in a smaller yield a better soluble, lower melting α-form which was identical with an authentic sample of (−)-cyclanoline iodide. As a control the natural alkaloid from *A. albiflora* was also compared with an authentic specimen of steponine[22] (*Vb*) which is a positional isomer of cyclanoline[23]. However, the identity of both substances could be excluded on the basis of physical constants and UV and IR spectra.

(−)-β-Scoulerine methohydroxide occurs only in the above-ground part but not in the root of the plant. As the main component of the quaternary bases from the root a different alkaloid was isolated in the form of crystalline perchlorate, provisionally indicated as alkaloid AA 3 which could not be investigated in greater detail due to its negligible supply.

EXPERIMENTAL

The melting points were determined both on a Kofler block and in a capillary and they were not corrected. The mass spectra were measured on a mass spectrometer AEI–MS 902 with the energy of ionising electrons of 70 eV, the PMR spectra on a Varian T-60 using tetramethylsilane as internal standard, the UV spectra on a Unicam SP 500 or SP 700 apparatus, IR spectra on Infrascan of Hilger and Watts. For thin-layer chromatography silica gel with gypsum (5 : 1) and the following systems were used: cyclohexane–chloroform–diethylamine of the following ratios: 7 : 2 : 1 (S_1), 4 : 5 : 1 (S_2) and 3 : 6 : 1 (S_3), benzene–ethanol–25% ammonia 100 : 20 : 1 (S_4), benzene–ethyl acetate–diethylamine 5 : 4 : 1 (S_5), ethanol–water–25% ammonia 15 : 9 : 1 (S_6), and 1-propanol–formic acid–water 12 : 1 : 7 (S_7). Detection was carried out under UV light,

or with Dragendorff reagent or potassium iodoplatinate. Paper chromatography was carried out on Whatman paper No 1 (descending technique) with 1-butanol–acetic acid–water 10 : 1 : 3 (S_8). The spots were detected on the basis of their fluorescence in UV light or by spraying with the Dragendorff reagent. The alkaloids isolated from this plant earlier[2] were identified on the basis of their melting point and mixed melting point, or also UV and IR spectra, R_F values and colour reactions.

Isolation of Alkaloids

The plants were cultivated in the Experimental Botanical Garden of the Medical Faculty in Brno from the seeds of the same origin as in paper[2] and they were gathered at the stage of unripe fruits on September 18th, 1968 (sample 1) and September 11th, 1969 (sample 2). The material was dried at room temperature. For extraction, 3870 g of the dry above-ground parts and 513 g of the dry root of sample 1 and 5280 g of the dry whole plant of sample 2 were utilised. In the subsequent text unless stated otherwise the isolation of alkaloids is described for sample 2.

The dry ground plant (5280 g) was extracted seven times with cold methanol, total 170 l. The extract was worked up in the same manner as in paper[2] and alkaloid fractions *A*, *B*, *E* and *I* (see[24,25]) were isolated from the extract. Total yield of alkaloids was 0·048%. The crude bases of fraction *A* were separated[24] to fraction *AC* and *AD*. From the ethereal solution of the bases of fraction *AC* 12 mg of norchelerythrine (*i.e.* 0·00023%) crystallised out and from the mother liquor a smaller amount of allocryptopine was obtained. The remaining bases afforded on crystallisation from methanol 4·1 mg of norsanguinarine (0·0001%). Fraction *AD* was separated[24] to non-phenolic (AD_1) and phenolic (AD_2) bases. From fraction AD_1 allocryptopine was separated by crystallisation from ether (total yield 1·07 g, 0·020%) and protopine by crystallisation from chloroform–ethanol (0·15 g, 0·003%). From the mother liquor quaternary benzophenanthridines were separated in the form of non-basic *ps*-cyanides which after conversion to bases were separated on a column of acid alumina[26]. In this manner 14·6 mg of chelerythrine (0·0003%) and 4·2 mg of sanguinarine (0·0001%) were obtained. In the amorphous residue of non-phenolic bases *AC* and AD_1 (total 80 mg) only residues of the above mentioned alkaloids were demonstrated by thin-layer chromatography. From the bases of fraction AD_2 (−)-scoulerine (191 mg, 0·004%) was separated in the form of weakly soluble hydrochloride. The amorphous residue of the bases obtained from the mother liquor after scoulerine hydrochloride was dissolved in a minimum amount of chloroform and diluted with an excess of ether. Alkaloid *AA* 1 (14 mg, 0·0003%) separated. The filtrate after the precipitate of alkaloid *AA* 1 was evaporated and the residue dissolved in a small amount of methanol, and crude alkaloid *AA* 2 (9·1 mg, 0·0002%) was precipitated by addition of an excess of ether. The alkaloid was purified by crystallisation of its perchlorate from methanol. In the amorphous residue (27 mg) only traces of allocryptopine and scoulerine could be demonstrated by thin-layer chromatography. From fraction *B* the main part of berberine was separated in the form of its chloride (1·26 g) and the rest was obtained as base on alkalisation of the mother liquors with sodium hydroxide and extraction with ether (total yield calculated as base 0·018%). The salt of (−)-β-scoulerine methohydroxide passed into fraction *E* which contained mainly non-alkaloid substances. This alkaloid was separated from fraction *E* in the form of its iodide by extraction with chloroform after previous addition of a solution of potassium iodide. From the concentrated chloroform solution 16·4 mg of (−)-β-scoulerine methiodide (0·0003%) crystallised out. In the mother liquor thin-layer chromatography in S_6 could demonstrate in addition to the residues of this alkaloid (R_F 0·61) also the presence of a small amount of four additional alkaloids of R_F 0·28, 0·45, 0·65, and 0·76. Fraction *I* contained almost exclusively non-alkaloidal components.

From the dry root of sample 1 (513 g) total alkaloids (0·35%) were isolated in the same manner. From them 6·3 mg of norchelerythrine (0·0012%) and a negligible amount of norsanguinarine, allocryptopine (558 mg, 0·11%), protopine (7·8 mg, 0·0015%), chelerythrine and sanguinarine (total 4·4 mg, 0·001%) and berberine (948 mg calculated as base, 0·185%) were separated. Fraction AD_2 (22·5 mg) was amorphous and according to thin-layer chromatography it did not contain a distinct amount of scoulerine. Fraction *E* (38 mg) was also amorphous. Conversion to perchlorates and their crystallisation from methanol gave 17·3 mg of perchlorate of alkaloid *AA* 2 (13·5 mg of base, 0·003% of root). Fraction *I* (0·24 g) contained predominantly non-alkaloidal substances. The quaternary bases present were separated in the form of perchlorates (25 mg) which on crystallisation from methanol afforded 2·1 mg of crystalline perchlorate of alkaloid *AA* 3, m.p. 240—250°C (decomp.), R_F value in S_6 0·65, the presence of which was also demonstrated in sample 2. In the remaining amorphous perchlorates two other alkaloids of R_F in S_6 0·55 and 0·76 were found. The presence of scoulerine metho-salt (R_F 0·61) could not be proved even in traces.

Norchelerythrine: needles m.p. 213—214°C (chloroform–methanol), undepressed on admixture of an authentic sample[6] and the sample prepared from chelerythrine chloride (see below), insoluble in water and in dilute aqueous acid solutions, almost insoluble in cold methanol and poorly soluble in chloroform. Mass spectrum: M^+ 333 (100), 319 (6), 318 (28), 317 (13), 291 (10), 290 (49), 275 (19), 274 (6), 232 (8), 217 (5), 189 (6), 188 (7), 116·5 (8), 164 (7), 144·5 (11), 136 (3), 94·5 (4), 87 (4), 81 (3), 57 (3), 43 (4). UV spectrum (ethanol), λ_{max} (log ε): 211 nm (4·30), 243 nm (4·57), 256 nm (4·54), 276 nm (4·67), 287 nm shoulder (4·51), 324 nm (4·18), 338 nm sh. (4·00), 363 nm sh. (3·56), 385 nm (3·49), λ_{min} 226 nm (4·26), 251 nm (4·42), 260 nm (4·53), 314 nm (4·16), 376 nm (3·46), and IR spectrum (in KBr) were identical with those of a sample prepared from chelerythrine chloride and agreed with the literature data[5,6]. The R_F values 0·52 (S_1) and 0·93 (S_2) were also equal as the values of both reference preparations (in UV grey-blue fluorescence, after detection with Dragendorff reagent a brown-violet spot). With conc. sulfuric acid it gave a yellow colour, with conc. nitric acid an orange one.

Preparation of norchelerythrine from chelerythrine chloride: Chelerythrine chloride (49·0 mg; containing one molecule of crystal water) was heated on a paraffin bath at the temperature of melting point (200—205°C) for one minute. Crystallisation of the melt from chloroform–methanol gave 36·0 mg (89%) of a product which after crystallisation from the same mixture had m.p. 213—214°C, undepressed on admixture of an authentic sample[6]. The hydrochloride prepared from the base in chloroform–methanol solution on addition of conc. hydrochloric acid crystallised in strong yellow needles which were decolorized on heating (splitting off hydrogen chloride), m.p. 205—208°C. The UV spectrum (a solution of base in 1M-HCl in ethanol), λ_{max} (log ε): 213 nm (4·38), 245 nm shoulder (4·44), 266 nm (4·68), 278 nm sh. (4·55), 301 nm sh. (3·28), 313 nm (4·46), 338 nm (4·26), 390 nm (3·81), 433 nm (3·76); λ_{min} 228 nm (4·29), 293 nm (4·16), 331 nm (4·21), 358 nm (3·62), 417 nm (3·75) is practically identical with the spectrum of chelerythrine chloride[27]).

Norsanguinarine: needles of m.p. 285—287°C (chloroform–methanol), undepressed with a sample prepared from sanguinarine chloride, insoluble in water and dilute aqueous acid solutions, almost insoluble in methanol, poorly soluble in chloroform. Mass spectrum: M^+ 317 (100), 316 (7), 289 (6), 288 (6), 287 (4), 286 (3), 261 (12), 260 (11), 259 (16), 258 (4), 233(8), 232 (8), 231 (9), 230 (9), 229 (8), 204 (11), 203 (20), 202 (24), 201 (43), 200 (11), 176 (14), 175 (20), 174 (27), 158·5 (11), 158 (12), 157·5 (12), 150 (10), 101 (12). The UV spectrum (ethanol), λ_{max} (log ε): 212 nm (4·33), 243 nm (4·67), 251 nm shoulder (4·50), 275 nm sh. (4·50), 281 nm (4·55), 293 nm sh. (4·41), 328 nm (4·22), 341 nm sh. (4·00), 382 nm (3·60), 399 nm (3·65), λ_{min} 222 nm (4·24),

263 nm (4·36), 320 nm (4·20), 366 nm (3·50), 385 nm (3·58), as well as the IR spectrum (in KBr) were identical with the spectra of a sample prepared from sanguinarine chloride and agree with the literature data[11,12]. The R_F values, 0·63 in S_1 and 0·94 in S_2, were identical with those of a reference sample (in UV yellow-white fluorescence, with Dragendorff reagent a pink spot). With conc. sulfuric or nitric acid it assumes an orange colour.

Preparation of norsanguinarine from sanguinarine chloride: Sanguinarine chloride (53·0 mg; with 3 molecules of crystal water) was heated on a paraffin bath at 205°C for 5 minutes. Crystallisation from chloroform–methanol afforded 35·9 mg of a product (90%) which after recrystallisation melted at 285—287°C. The hydrochloride, prepared in a chloroform–methanol solution on addition of conc. hydrochloric acid, crystallised in the form of orange needles which lost their colour on heating (splitting off hydrogen chloride), and melted at 277—281°C. The UV spectrum (a solution of base in 1M-HCl in ethanol), λ_{max} (log ε): 215 nm (4·37), 244 nm (4·52), 273 nm (4·54), 278 nm shoulder (4·49), 309 nm sh. (4·24), 323 nm (4·42), 340 nm sh. (4·20), 397 nm (3·69), 467 nm (3·69), λ_{min} 224 nm (4·32), 259 (4·47), 294 nm (4·11), 365 nm (3·56), 427 nm (3·50), is practically identical with the spectrum of sanguinarine chloride[27].

(—)-*Scoulerine*: prisms of m.p. 201—202°C (methanol), in air assumes a red colour, $[\alpha]_D^{21}$ —355° ± ± 5° (*c* 0·20, methanol). Mass spectrum with the the main peaks at *m/e* 327 (M^+), 326, 192 and 150 is identical with the spectrum of an authentic sample and it coincides with the literature data[12]. PMR spectrum (in dimethyl sulfoxide), τ 6·10 to 6·24 (OCH_3), 4·3 (OH), 3·17 to 3·40, (aromatic protons) agrees with the data from the literature[14]. The UV spectrum (methanol), λ_{max} (log ε) 285 nm (3·97), λ_{min} 251 nm (2·92), and the IR spectrum (in KBr and in nujol), ν(OH) 3440 and 3530 cm^{-1} are identical with those of an authentic specimen[15]. So are the R_F values, 0·12 in S_1, 0·52 in S_2, 0·64 in S_3 and 0·62 in S_4. The hydrochloride (from methanol) had m.p. 266—268°C (capillary), or 245—247°C (Kofler block), undepressed on admixture of an autentic sample[14].

Alkaloid AA 1: the base was amorphous (m.p. unsharp at 155—158°C), composition according to mass spectrometry is $C_{19}H_{21}NO_4$ (found: 327·1454, calculated: 327·1470). UV spectrum methanol), λ_{max} (log ε): 232 nm shoulder (3·96), 284 nm (3·65), λ_{min} 263 nm (3·36). R_F value 0·08 in S_1, 0·21 in S_2, 0·34 in S_3, 0·22 in S_4, 0·26 in S_5, and 0·82 in S_6. With conc. sulfuric acid it gave a violet colour, with Erdmann reagent a yellow one, with Marquis reagent grey-green and with conc. nitric acid a yellow colour.

Alkaloid AA 2: the base was amorphous, easily soluble in chloroform, methanol and ethanol, insoluble in ether, turns brown in air. The mass spectrum with main peaks at *m/e* 355 (M^+), 206, 192, 163, 150 and 135, and the UV spectrum (methanol), λ_{max} (log ε) 230 nm shoulder (4·00), 288 nm (3·88), λ_{min} 256 nm (3·28), were practically identical with the spectra of hunnemanine and the alkaloid from *Eschscholtzia* species (alkaloid ED). The IR spectrum (in KBr) was identical with the spectrum of alkaloid ED but different from the spectrum of hunnemanine (in KBr). The perchlorate formed small prisms of m.p. 300—302°C (methanol) undepressed on admixture of the perchlorate of alkaloid ED, poorly soluble in boiling methanol, almost insoluble in cold methanol. The IR spectrum (in KBr) was identical with the spectrum of the perchlorate of alkaloid ED. Hydrochloride had m.p. 235—238°C (from water), differing from the hydrochloride of hunnemanine (from water m.p. 217—220°C). The R_F values also were different from the values for hunnemanine (given in brackets): 0·10 (0·04) in S_1, 0·12 (0·18) in S_2, 0·20 (0·30) in S_3, 0·18 (0·12) in S_4, 0·17 (0·25) in S_5, 0·70 (0·63) in S_6, 0·70 (0·64) in S_8. However, its R_F values were identical with those of alkaloid ED in all these solvent systems. With conc. sulfuric acid it turned violet, with Erdmann reagent it gave dark violet colour and with conc. nitric acid a yellow one (the same colour reactions were also given by alkaloid ED and hunnemanine).

(−)-β-*Scoulerine methohydroxide*: Its iodide crystallised from methanol in small prisms of m.p. 256−258°C (capillary) or 250−262°C (Kofler block), undepressed on admixture with a sample prepared by methylation of (−)-scoulerine with methyl iodide, $[\alpha]_D^{22}$ −119° ± 12° (*c* 0·06, methanol). IR spectrum (in KBr) was identical with the spectrum of a preparation obtained from (−)-scoulerine, but different from that of cyclanoline and steponine iodide. The UV spectrum (methanol), λ_{max} (log ε), 286 nm (3·75), λ_{min} 260 nm (2·92), was identical with the spectrum of a sample prepared from (−)-scoulerine and with the spectrum of cyclanoline. The same is true of the R_F values which were 0·53 in S_3, 0·61 in S_6, 0·78 in S_7 and 0·37 in S_8.

Preparation of (−)-*scoulerine methiodide from* (−)-*scoulerine*: (−)-Scoulerine (31 mg) was dissolved in methanol (2 ml) and methyl iodide (0·5 ml) was added to it. After several days standing the solvent was evaporated. Yield of methiodide was 46 mg (quantitative). Crystallisation from methanol gave the less soluble β-form (31·5 mg, 68%) and from the mother liquor a small amount of the α-form was obtained on crystallisation from methanol–ether. (−)-β-Scoulerine methiodide crystallised from methanol had m.p. 255−258°C (capillary) or 263−265°C (Kofler block), $[\alpha]_D^{22}$ −118° ± 10° (*c* 0·11, methanol). (−)-α-Scoulerine methiodide from methanol, m.p. 180°C (Kofler block), from methanol–ether, m.p. 160−165°C (evidently a solvate). For cyclanoline iodide the literature[19] gives m.p. 185°C; authentic sample[19] had m.p. 160−164°C, and in admixture with our preparation, crystallised from methanol–ether, it melted undepressed. The IR spectra (in KBr) of both specimens of the α-form were identical, but were not identical with the spectrum of the β-form.

Identification of alkaloid HF 1 with (−)-*scoulerine*. Alkaloid HF 1 (see[16]), m.p. 201−202°C (methanol), melted undepressed on admixture with (−)-scoulerine from *A. albiflora*; $[\alpha]_D^{23}$ −356° ± 3° (chloroform). Mass spectrum, IR and UV spectra were identical with those of the reference samples (see above), as also were R_F values. Hydrochloride, m.p. 266−268°C (methanol) melted undepressed on admixture of an authentic sample of (−)-scoulerine hydrochloride[14] or (−)-scoulerine hydrochloride from *A. albiflora*. Methiodide, m.p. 255−258°C (capillary), also melted undepressed with (−)-β-scoulerine methiodide. The R_F values of both preparations were identical.

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