ON ALKALOIDS FROM THE AERIAL PARTS OF THREE *Eschscholtzia* SPECIES*

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In the aerial parts of *Eschscholtzia californica* Cham., *E. douglasii* (Hook. *et* Arn.) Walp. and *E. glauca* Greene the main alkaloidal component is the quaternary base californidine. Eschscholtzine, allocryptopine, and protopine belong among the dominant tertiary alkaloids, which are accompanied by a small amount of N-methyllaurotetanine and the quaternary benzophenanthridines (sanguinarine, chelerythrine, chelirubine, chelilutine, and macarpine). The pavinane alkaloids isonorargemonine, caryachine, norargemonine, and bisnorargemonine and the aporphine alkaloids corydine and isocorydine were isolated from the aerial part of the *E. douglasii* species for the first time. These alkaloids were also detected in *E. californica* and *E. glauca*. Corytuberine was also isolated from all three species. From the fraction of quaternary alkaloids after conversion to iodides, in addition to californidine, escholamidine iodide was isolated from *E. californica* and *E. douglasii* species. From *E. douglasii* N-methylcaryachininium iodide and from *E. glauca* magnoflorine iodide were also isolated. The presence of a small amount of the mentioned quaternary alkaloids, as well as traces of escholamine were also detectable in all three species.

The genus *Eschscholtzia* Cham. from the *Papaveraceae* comprises a large number of taxons of an unclear systematic value. Fedde[1] mentions 123 species of which, however, the predominant part is nowadays considered as microspecies, lower systematic units or as synonyms. Duke[2] mentions 13 valid species. Taxonomically the *Eschscholtzia* genus is an extraordinarily difficult group, because the species represent a very plastic and polytypical group with a large number of ecotypes and cytotypes (differing in their chromosome number) (*cf.*[3]). They are annual to perennial plants native predominantly to California and adjacent regions of North America. We have referred on alkaloids from the roots of *E. californica* Cham., *E. douglasii* (Hook. et Arn.) Walp. and *E. glauca* Greene in the preceding communications of this series[4-6]. All these closely related taxons are classified by Fedde[1] on the level of species into the section *Eurycraspedontae* Fedde. More lately they are regarded as microspecies or as synonyms and they are classified into the *E. californica* Cham. species *sensu lato*. Nonetheless, these three investigated taxons display certain chemical differences when mutually compared, especially distinct with respect to the

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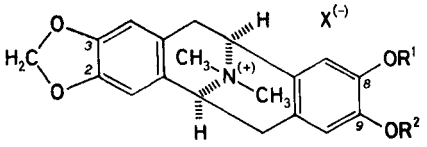
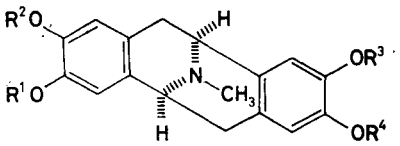
quaternary alkaloids[4], which can be considered a characteristic feature of each of the taxons mentioned.

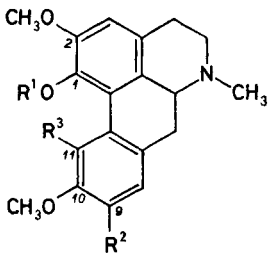
In this paper we investigate the alkaloids from the aerial parts of the three mentioned species. The plant material used was from the same harvest as the roots, investigated earlier[4,5]. The main alkaloid of all three species is the quaternary base californidine (N-methyleschscholtzinium hydroxide[7]; *Ia*, X = OH), which we already isolated from these plants several years ago[4,6,7]. Its content in the aerial parts of the three investigated taxons did not differ considerably (from 0·19% to 0·23% of the dry plant material). The content of the tertiary alkaloids was also almost identical (0·14–0·16%). The dominant components of the tertiary non-phenolic bases are eschscholtzine (*IIa*), allocryptopine and protopine (present in approximately the same amounts, *i.e.* each about 0·02–0·03%). Eschscholtzine (*IIa*) is a typical component of the aerial parts and it does not occur in the roots (*cf.*[5,7]). A mixture of quaternary benzophenanthridines was isolated in low yield, consisting of sanguinarine and chelerythrine, accompanied by chelirubine, chelilutine, and macarpine. All these alkaloids were already isolated earlier by us from the mentioned species[7–9]. The main components of the phenolic tertiary bases of all three species was (+)-N-methyllaurotetanine (also called lauroscholtzine[10], *IIIa*), which was detected in *E. californica*[10,11]; its occurrence in *E. douglasii* and *E. glauca* has not so far



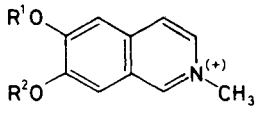
Ia, $R^1 + R^2 = CH_2$
Ib, $R^1 = H$; $R^2 = CH_3$



IIa, $R^1 + R^2 = R^3 + R^4 = CH_2$
IIb, $R^1 = H$; $R^2 = R^3 = R^4 = CH_3$
IIc, $R^1 = R^4 = H$; $R^2 = R^3 = CH_3$
IId, $R^1 + R^2 = CH_2$; $R^3 = H$; $R^4 = CH_3$
IIe, $R^1 + R^2 = CH_2$; $R^3 = CH_3$; $R^4 = H$
IIf, $R^1 + R^2 + R^3 = CH_3$; $R^4 = H$



IIIa, $R^1 = CH_3$; $R^2 = OH$; $R^3 = H$
IIIb, $R^1 = R^2 = H$; $R^3 = OCH_3$
IIIc, $R^1 = CH_3$; $R^2 = H$; $R^3 = OH$
IIId, $R^1 = R^2 = H$; $R^3 = OH$



IV

been known. The remaining amorphous phenolic alkaloids represented a very complex and difficultly separable mixture of a large number of alkaloids which, according to TLC, had a qualitatively identical composition in all three species. For chromatographic separation on alumina we used amorphous mixtures of bases, obtained from *E. douglasii*. Of the known alkaloids we isolated norargemonine (*IIb*) and bisnorargemonine (*IIc*) which are present in the aerial parts in small amounts only, while in the roots they form the main component of the phenolic fraction[5].

The pavinane structure could be assigned to the further two alkaloids on the basis of the mass spectrometric fragmentation and characteristic UV spectra. In the mass spectrum of the first of them characteristic ions at *m/z* 325·1314 (M^+, $C_{19}H_{19}NO_4$), 324 (M − 1), 190 ($C_{11}H_{12}NO_2$; *IV*, $R^1 + R^2 = CH_3 + H$) and 188 ($C_{11}H_{10}NO_2$; *IV*, $R^1 + R^2 = CH_2$). From this the structure could be derived, corresponding either to caryachine (*IId*) or isocaryachine (*IIe*). Other physical properties (m.p., optical rotation, UV spectrum) indicated the identity with (−)-caryachine (*IId*)*. This alkaloid was isolated so far from *Cryptocarya chinensis* HEMSL. (*Lauraceae*)[12-14] only, while isocaryachine, prepared synthetically[15], is not yet known as a natural substance. The second of the two newly found pavinane alkaloids was identified on the basis of the melting point, optical rotation, and spectral data and direct comparison with an authentic sample as isonorargemonine (*IIf*), which has been described in two species of Argemone genus (*Papaveraceae*)[16,17] and in *Thalictrum revolutum* DC. (*Ranunculaceae*)[18].

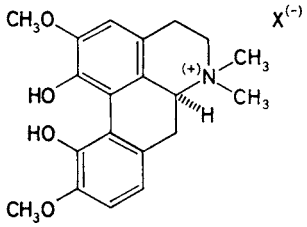
Two aporphine alkaloids were further isolated in minute quantities, *i.e.* corydine (*IIIb*) and isocorydine (*IIIc*). While isocorydine was found recently in *E. californica*[11], corydine was isolated from the *Eschscholtzia* genus for the first time. All the four last mentioned alkaloids were also detected in *E. californica* and *E. glauca*.

In the fraction of quaternary protoberberines the presence of a negligible amount of coptisine, berberine and traces of corysamine were also demonstrated.

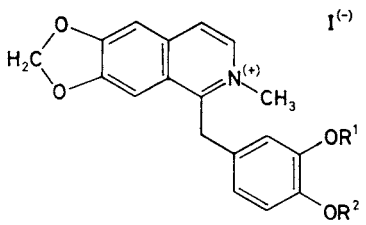
The strongly polar alkaloids were obtained in the usual manner (*cf.*[19]) after addition of potassium iodide and extraction with chloroform. The main component of this fraction was californidine in all three species. It was separated after conversion of iodides to a well crystallizable perchlorate (*Ia*, X = ClO_4). From the mother liquors after californidine perchlorate from *E. glauca* magnoflorine perchlorate (esholine[6]; *V*) was isolated as minor alkaloid. This is the first detection in *E. glauca*, interesting in the fact that its presence could not be detected[4] in the roots of this plant, although in the roots of *E. californica* and *E. douglasii* magnoflorine is one of the dominant alkaloids of the quaternary fraction. In contrast to this magnoflorine occurs in the aerial parts of *E. californica* and *E. douglasii* in traces only. After conversion of the amorphous residue of the perchlorates to iodides corytuberine was isolated in the form of hydriodide (*IIId*) from all three species.

* Unfortunately we could not obtain an authentic sample of caryachine for comparison.

From *E. californica* and *E. douglasii* a further quaternary phenolic alkaloid was isolated, *i.e.* escholamidine iodide (*VIa*), which we found earlier in *E. cf. oregana* GREENE[20] from the section *Stenocraspedontae* FEDDE. In *E. glauca* it was detected only in trace amounts. From *E. douglasii* we isolated additionally a further quaternary alkaloid which according to its melting point, optical rotation and spectral analyses was identical with N-methylcaryachinium iodide (*Ib*, X = I). This alkaloid was found so far only in *Cryptocarya chinensis* HEMSL. (*Lauraceae*)[21]. In all three species a negligible amount of escholamine (*VIb*) was detected, which is the main alkaloid of the species *E. cf. oregana* GREENE[22].



V



VIa, $R^1 = CH_3$; $R^2 = H$
VIb, $R^1 + R^2 = CH_2$

Although a relatively small number of species or lower taxa of the *Eschscholtzia* genus has been investigated so far, it is already possible to differentiate at least three biochemical groups characterized by their alkaloids. The three closely related species from the section *Eurycraspedontae*, *i.e. E. californica*, *E. douglasii*, and *E. glauca*, belong to the first group which contain the tertiary and the quaternary alkaloids of the pavinane type as the dominant type. *E. cf. oregana* GREENE from the section *Stenocraspedontae*, which shows a high content of quaternary benzylisoquinoline alkaloid escholamine (*VIb*) may be classified in the second group. The species *E. lobbii* GREENE represents a third biochemical group, characterized by protopine, scoulerine, and corytuberine, and in contrast to the two preceding groups it practically does not contain quaternary alkaloids or alkaloids of the pavinane type either[23].

EXPERIMENTAL

The melting points were determined on a Mettler FP 51 instrument and they were not corrected. The mass spectra were measured on an AEI 902 spectrometer, the IR spectra in Nujol on a Specord 75 IR (Jena) spectrophotometer and the UV spectra in methanol on a Unicam SP 1800 instrument. For thin-layer chromatography (TLC) silica gel G Merck was used with the systems cyclohexane–diethylamine 9 : 1 (S_1), cyclohexane–chloroform–diethylamine 7 : 2 : 1 (S_2), 5 : 4 : 1 (S_3), and 3 : 6 : 1 (S_4), chloroform–diethylamine 9 : 1 (S_5), chloroform–ethanol–diethylamine 8 : 1 : 1 (S_6), methanol–25% ammonia 200 : 1 (S_7), methanol–water–25% ammonia 5 : 1 : 1

(S_8), methanol–water–diethylamine 15 : 3 : 1 (S_9), ethanol–water–25% ammonia 15 : 9 : 1 (S_{10}), acetone–diethylamine 3 : 2 (S_{11}), and 1-propanol–water–85% formic acid 12 : 7 : 1 (S_{12}). Detection was carried out with potassium iodoplatinate. For the detection of quaternary benzophenanthridines silufol UV 254 foils (Kavalier) were used in the system cyclohexane saturated with methanol (S_{13}) and paper chromatography (PC) on Whatman No 1 paper, descending mode, in 1-butanol–water–acetic acid 10 : 3 : 1 (S_{14}) and ethanol–water 3 : 2 (S_{15}). Detection was carried out in UV light.

Extraction and Isolation of the Alkaloids

All three species were cultivated in The Centre for the Cultivation of Medicinal Herbs, Medical Faculty, Brno, and they were harvested at the stage of flowers and fruits (*E. californica* on 19 Aug 1969, *E. douglasii* on 29 Aug 1969, and *E. glauca* on 4 and 12 Oct 1966). The aerial parts were separated from the roots (for their examination see[4-6]), dried at room temperature and extracted shortly after.

The processing of all three samples was carried out practically in the same manner. The ground plant material (*E. californica* 2 290 g, *E. douglasii* 2 555 g, *E. glauca* 2 180 g) was extracted with ethanol in a Soxhlet extractor, ethanol was distilled off and the residue dissolved in 1% sulfuric acid and filtered. Using the conventional procedure (*cf.*[9,19]) the alkaloidal fractions A, B, E, and I were obtained from the filtrate. The yields of the alkaloids obtained from the samples are indicated in the further text in the order *E. californica*, *E. douglasii*, and *E. glauca*. The sum of the bases of fraction A was 3·33 g (0·15%), 4·08 g (0·16%), and 3·02 g (0·14%), resp. The bases of the fraction A were separated (*cf.*[9,19]) to the non-phenolic fractions AC_1 and AD_1 and the phenolic fractions AC_2 and AD_2. The bases of the fraction AC_1 were dissolved in chloroform and neutralized with a hydrogen chloride solution in methanol. The eschscholtzine hydrochloride which crystallized out (including the fractions obtained by systematic crystallizations from the mother liquors) was converted to the base *IIa* which was crystallized from ether (total yield of base 0·68 g, 0·54 g, and 0·54 g). From the mother liquors after the separation of eschscholtzine hydrochloride, which were converted to bases and crystallized from methanol, a small amount of allocryptopine and protopine was obtained. In the remaining amorphous residue (0·10 g, 0·02 g, and 0·12 g) a negligible amount of corydine, isocorydine and four unidentified bases were detected. From fraction AD_1 quaternary benzophenanthridines were isolated first by the conventional method in the form of pseudo-cyanides (see for example ref.[19]); after conversion to bases (0·06 g, 0·08 g, and 0·20 g; 0·003%, 0·003%, and 0·009%) sanguinarine and chelerythrine were detected in them, in addition to a small amount of chelirubine, chelilutine, and macarpine (according to TLC in S_{13} and PC in S_{14} and S_{15}). The bases obtained from the filtrate after the precipitation of pseudo-cyanides afforded by systematic crystallizations from chloroform–ethanol and ethanol protopine (0·34 g, 0·74 g, and 0·43 g) and allocryptopine (0·60 g, 0·77 g, and 0·47 g). The amorphous residue (0·09 g, 0·07 g, and 0·16 g) contained according to TLC additional two to three unidentified alkaloids. The phenolic bases from the fraction AC_2 (0·22 g, 0·19 g, and 0·15 g) and AD_2 (0·68 g, 1·41 g, and 0·68 g), which according to TLC had practically the same composition, were combined, dissolved in ethanol and converted to tartrates by addition of an equivalent amount of (−)-tartaric acid (*cf.*[10]). The N-methyllaurotetanine tartrate which crystallized out was filtered off under suction (including the fractions obtained from the mother liquors). The yields of the base *IIIa*: 0·19 g, 0·20 g, and 0·025 g. The amorphous bases obtained from the mother liquors represented according to TLC a very complex mixture of a large number of alkaloids.

In fraction B (21 mg, 17 mg, and 12 mg) a small amount of coptisine, berberine and traces of corysamine were detected in addition to non-alkaloidal compounds by TLC and PC. The

brown-red fraction E (0·84 g, 0·74 g, and 0·78 g) was amorphous and according to TLC it also represented a complex mixture of alkaloids, qualitatively very similar to fractions AC_2 and AD_2.

The amorphous residues of the phenolic bases AC_2, AD_2 and the fraction E from *E. douglasii* were combined and purified (1·40 g) and then separated on a column of alumina (115 g) (Reanal) activity approximately II. Fractions of 50 ml volume were collected and the following solvents used: benzene–ether 1 : 1 (fractions 1, 2) and 2 : 3 (fractions 3, 4), ether (fractions 5—12), ether–chloroform 1 : 1 (fractions 13—18), chloroform (fractions 19—29), chloroform–methanol 9 : 1 (fractions 30—60), 7 : 3 (fractions 61—64), and 1 : 1 (fractions 65—80), and methanol (fractions 80—92). Fractions 1—11 were non-alkaloidal. Isocorydine (1·1 mg) was obtained from fraction 12 by crystallization from methanol. The bases from fractions 13—15 were converted to hydrochlorides which were crystallized from dilute hydrochloric acid to afford corydine hydrochloride (base 1·3 mg, amorphous). Fraction 19—20 (90·6 mg, a mixture of about 5 alkaloids according to TLC) was dissolved in dilute sulfuric acid, the solution was alkalized with ammonia and extracted with ether. From the concentrated ethereal solution 30·1 mg of caryachine (*IId*) crystallized out. Fraction 21—24 (126·0 mg) was worked up in the same manner. Crystallization from ether gave 55·8 mg of isonorargemonine (*IIf*) (with a small admixture of caryachine), which was purified by crystallization from a mixture of methanol and water 1 : 1. Fraction 25—29 (74·8 mg, a mixture of about 4 alkaloids according to TLC) was crystallized from methanol to afford norargemonine (*IIb*; 8·9 mg); in the mother liquor the presence of the remains of N-methyllauroteta-nine (*IIIa*) could be detected by TLC. From fraction 30—36 (453·8 mg, a mixture of about 6 alkaloids according to TLC) bisnorargemonine (*IIg*; 3·1 mg) was obtained by crystallization from methanol. Fraction 37—92 remained amorphous and according to TLC they contained a large number of unidentified alkaloids.

The crude iodides of fraction *I* were dissolved in hot water, the solution was filtered and the filtrate additioned with a 20% aqueous sodium perchlorate solution. The crystalline precipitate of the perchlorates formed was filtered off under suction. By crystallization from water or methanol the main fraction of californidine perchlorate was obtained (*Ia*; 4·38 g, 5·61 g, and 4·61 g). The perchlorates obtained from the mother liquors afforded a mixture of perchlorates of californidine and escholamidine (0·17 g, 0·10 g, —) when crystallized from methanol. This mixture could not be separated by further crystallizations. Therefore it was converted to iodides and then separated[24] to a phenolic and a non-phenolic fraction. From the phenolic fraction escholamidine iodide could be isolated (46·6 mg, 11·6 mg, traces) by crystallization from methanol.

The amorphous residue of the perchlorates from all three species was also separated to a non-phenolic (I_1) and a phenolic (I_2)[14] fraction. From fraction I_1 a further part of californidine perchlorate (0·01 g, 0·15 g, and 0·14 g) was obtained after conversion to perchlorates and crystallization from methanol. From the mother liquors which were converted to iodides N-methylcaryachinium iodide was obtained (*Ib*; traces, 58·9 mg, traces) after crystallization from water. The phenolic fraction I_2 was crystallized from water to afford magnoflorine perchlorate (traces, traces, 60·0 mg); after conversion of the remains of the alkaloids to iodides and crystallization from methanol corytuberine hydriodide (13·6 mg, 35·0 mg, 30·1 mg) was obtained. In the mother liquor after fraction I_1 from all three species trace amounts of escholamine could be detected by TLC (R_F 0·41 in S_8, 0·36 in S_{10}, 0·32 in S_{11}, 0·82 in S_{12}).

Characterization of the Isolated Alkaloids

The isolated alkaloids were characterized by their melting points, mixed melting points, optical rotation values, UV, IR or also mass spectra and TLC. The yields of individual alkaloids in % of dry material are given in parenthesis in the order: *E. californica*, *E. douglasii*, and *E. glauca*. The presence, if proved by TLC only, is indicated by +.

Californidine (Ia) (perchlorate 0·19; 0·23; 0·22): perchlorate from water, needles, m.p. 331—332°C (Kofler block); R_F: S_8 0·27, S_9 0·16, S_{10} 0·29, S_{11} 0·00, S_{12} 0·78.

Eschscholtzine (IIa) (0·030; 0·022; 0·025): from ether, long needles, m.p. 130—131°C; hydrochloride m.p. 225—226°C (chloroform); R_F: S_1 0·45, S_2 0·80.

Allocryptopine (0·026; 0·030; 0·022): from ethanol, prisms, m.p. 160—161°C; R_F: S_1 0·29, S_2 0·55.

Protopine (0·015; 0·029; 0·022): from chloroform–ethanol, prisms, m.p. 207—208°C; R_F: S_1 0·39, S_2 0·64.

N-Methyllaurotetanine (IIIa) (0·008; 0·008; 0·001): base amorphous, $[\alpha]_D^{20}$ +105° ± 3° (*c* 0·7, methanol). UV spectrum: λ_{max}, nm (log ε) 220 (4·46), 283 (4·08), 305 (4·03), shoulder 316 (3·96), λ_{min} 256 (3·65), 293 (3·94), in agreement with the literature data[25]; IR spectrum: 805 and 830 cm^{-1} (1,2,3,4-tetrasubstituted benzene ring), 870 and 880 cm^{-1} (1,2,4,5-tetrasubstituted benzene ring), 1 450, 1 510, and 1 580 cm^{-1} (aromatic system), broad absorption band at about 3 400 cm^{-1} (OH). Hydrobromide from methanol–ether, long needles, m.p. 221—222°C, (−)-tartrate from methanol, m.p. 231—232°C. R_F: S_2 0·19, S_3 0·25, S_4 0·42, S_5 0·81, S_6 0·94. The identity was confirmed by direct comparison with an authentic sample.

Escholamidine (VIg) (iodide 0·002; 0·0005; +): iodide from methanol, m.p. 232—233°C, undepressed on admixture with an authentic sample from *E. cf. oregana* crystallized from methanol (from water, m.p. 118—122°C, about 180°C conversion to needles, m.p. 212—214°C; see[20]), $[\alpha]_D^{24}$ 0° ± 3° (*c* 0·2, methanol). Mass spectrum: *m/z* 323·1151 (for $C_{29}H_{17}NO_4$ 323·1157), 309 (M − CH_3I), 308·0902 (for $C_{18}H_{14}NO_4$ 308·0923), 142 (CH_3I), 137 and 127 (I). On labelling with [O—^{2}H]ethanol all the mentioned ions (except 142 and 127) were shifted. UV spectrum: λ_{max}, nm (log ε) 206 (4·57), 223 (4·49), 254 (4·73), 285 (3·79), 314 (3·93), shoulder 350(3·92), λ_{min} 214 (4·43), 276 (3·75), 297 (3·75); after addition of 1M-NaOH λ_{max} 214 (4·63), 253 (4·70), 306 (3·99), shoulder 350 (3·66), λ_{min} 228 (4·44), 276 (3·68). IR spectrum: ν(OH) 3 140 and 3 250 cm^{-1}. All the spectra were identical with the spectra of escholamidine iodide[20]. Perchlorate from methanol, m.p. 225°C (sharp), undepressed on admixture with an authentic sample. R_F: S_8 0·54, S_9 0·53, S_{10} 0·24, S_{11} 0·23, S_{12} 0·70.

Magnoflorine (V): (traces; traces; perchlorate 0·003): perchlorate from methanol, m.p. 281—283°C, undepressed with an authentic sample. The identity was confirmed by UV and IR spectra and R_F values: S_8 0·61, S_9 0·46, S_{10} 0·71, S_{11} 0·00, S_{12} 0·72.

Corytuberine (IIId) (hydriodide 0·0006; 0·0014; 0·0014): hydriodide from methanol, m.p. 213—214°C, undepressed with an authentic sample. UV spectrum: λ_{max}, nm (log ε) 224 (4·65), 270 (4·07), 311 (3·83), λ_{min} 258 (4·00), 292 (3·69) and IR spectrum: ν(OH) 3 400 cm^{-1}, 3 490 and 3 600 cm^{-1} were identical with the spectra of a reference sample, the same as the R_F values: S_5 0·25, S_6 0·53, S_9 0·84, S_{10} 0·91, S_{11} 0·14, S_{12} 0·85.

(−)-*N-Methylcaryachinium iodide* (Ib) (+; 0·0023; +): needles (from water), m.p. 177—178°C $[\alpha]_D^{22}$ −226° ± 3° (*c* 0·3, methanol); ref.[21] gives m.p. 174—175°C and $[\alpha]_D^{24}$ −160° (methanol). Mass spectrum: *m/z* 339, 338, 324—322, 308, 204, 188 (base peak), 142 and 127. IR spectrum: ν(OH) 3 400 cm^{-1}. UV spectrum: λ_{max}, nm (log ε) 209 (4·66), 290 (3·84), shoulder 224 (4·66), λ_{min} 257 (3·07). R_F values: S_{10} 0·40, S_{11} 0·03, S_{12} 0·76.

Isonorargemonine (IIf) (+; 0·0022; +): clusters from ether or methanol–water (1 : 1), m.p. 205—206°C, undepressed on admixture with an authentic sample (m.p. 204—205°C), $[\alpha]_D^{22}$ −289° ± 3° (*c* 0·2, methanol); literature gives m.p. 219—220°C (methanol–water 1 : 1) and $[\alpha]_D^{25}$ −202° (chloroform)[16]. Mass spectrum: peaks at *m/z* 341·1619 (M^+; for $C_{20}H_{23}NO_4$ 341·1627), 340, 204 ($C_{12}H_{14}NO_2$) and 190. After labelling with [O—^{2}H]ethanol the peaks

were shifted by one mass unit at *m/z* 341, 340, and 190. IR spectrum: in the 3 000—4 000 cm^{-1} region (OH) the substance did not absorb (the same as norargemonine). UV spectrum: λ_{max}, nm (log ε) 209 (4·51), 287 (3·95), shoulder 226 (4·16), λ_{min} 249 (2·94); after addition of 1M-NaOH λ_{max} 215 (4·41), 293 (3·98), λ_{min} 263 (3·63). IR and UV spectrum and chromatographic behaviour (R_F: S_3 0·38, S_4 0·60, S_7 0·73) were identical with those of an authentic sample.

(−)-*Caryachine* (IId) (+; 0·0012; +): leaflets (from ether), m.p. 100—101°C, or prisms (from methanol), m.p. 169—170°C, $[\alpha]_D^{23}$ −254 ± 5° (0·1, methanol); literature gives m.p. 170°C and $[\alpha]_D^{20}$ −251° (ethanol)[26] or m.p. 174—175°C and $[\alpha]_D^{21}$ −269·6° (ethanol)[12]. Mass spectrum: *m/z* 325·1323 (M^+; for $C_{19}H_{19}NO_4$ 325·1314), 324, 190 ($C_{11}H_{12}NO_2$) and 188 ($C_{11}H_{10}NO_2$); after labelling with [O—^{2}H]ethanol deuterium entered the ions *m/z* 325, 324, and 190. UV spectrum: λ_{max}, nm (log ε) 210 (4·48), 292 (4·00), shoulder 225 (4·11), λ_{min} 253(3·34); after addition of 1M-NaOH λ_{max} 215 (4·55), 297 (4·02), shoulder 240 (4·00), λ_{min} 268 (3·34). IR spectrum: 705, 710, 760, 855, 905, 930, 995, 1 005, 1 020, 1 080, 1 105, 1 150, 1 210, 1 240, 1 260, 1 300, 1 330, 1 360, 1 450, 1 510, 1 600, 3 450, and 3 520 (OH) cm^{-1}. In the literature the IR spectrum is not published. The mass and the UV spectra are in agreement with the literature data. R_F values: S_3 0·41, S_4 0·63, S_7 0·77.

Norargemonine (IIb) (+; 0·00035; +): prisms from methanol, m.p. 250—251°C; UV spectrum: λ_{max}, nm (log ε), 209 (4·55), 288 (3·83), λ_{min} 252 (2·93), shoulder 226 (4·13), and IR spectrum were identical with those of an authentic sample, the same as the R_F values: S_2 0·22, S_3 0·32, S_4 0·52, S_5 0·86, S_6 0·97, S_7 0·74.

Bisnorargemonine (IIc) (+; 0·00012; +): prisms from chloroform–methanol, m.p. 252—253°C; UV spectrum: λ_{max}, nm (log ε), 209 (4·56), 288 (3·90), shoulder 226 (4·12), λ_{min} 252 (2·87), IR spectrum: ν(OH) 3 490 cm^{-1} and the R_F values were identical with those of a reference sample: S_2 0·03, S_3 0·04, S_4 0·10, S_5 0·36, S_6 0·61, S_7 0·72.

Corydine (IIIb) (+; 0·00005; +): the base was not crystallized; UV spectrum: λ_{max}, nm (log ε) 218 (4·74), 264 (4·21), 304 (3·98), λ_{min} 247 (4·04), 284 (3·92); it was in good agreement with the spectrum of a reference sample. Hydrochloride, from dilute hydrochloric acid, m.p. 262—265°C, undepressed on admixture with an authentic sample. R_F values: S_1 0·23, S_2 0·49, S_3 0·90.

Isocorydine (IIIc) (+; 0·00004; +): prisms from methanol, m.p. 184—185°C, undepressed on admixture of an authentic sample; UV spectrum: λ_{max}, nm (log ε) 221 (4·60), 266 (4·14), 302 (3·74), λ_{min} 247 (3·80), 290 (3·68), and R_F values (S_1 0·28, S_2 0·56, S_3 0·95) were identical with those of an authentic sample.

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Note added in proof: In formula *IIf* for $R^1 + R^2 + R^3$ should read $R^1 = R^2 = R^3$.