ALKALOIDS FROM *Corydalis solida* (L.) SW. MASS SPECTROMETRY OF QUATERNARY BENZYLISOQUINOLINE ALKALOIDS*

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From the strongly polar fraction from the tubers of *Corydalis solida* (L.) SW., a new quaternary alkaloid, (+)-N-methyllaudanidinium iodide, was isolated after conversion to iodides. Mass spectrometric behaviour of this type of quaternary alkaloids is described. In the tubers (0·37% of alkaloids) the main alkaloid component is (+)- and (±)-tetrahydropalmatine; other dominant alkaloids include protopine, (+)-corydaline, allocryptopine, dehydrocorydaline and jatrorrhizine. (±)-Corybulbine, (+)-corypalmine, (−)-isocorypalmine, (−)-scoulerine, (−)-stylopine, corysamine, palmatine, (+)-N-methyllaudanidinium hydroxide, (−)-*cis*-N-methylcanadinium hydroxide and *cis*-N-methylstylopinium hydroxide represent minor alkaloids. The last three mentioned were isolated in the form of iodides. Bulbocapnine, coptisine, berberine and columbamine were detected in trace amounts. The main alkaloid of the aerial parts of the plant (0·35% of alkaloids) is berberine, accompanied by coptisine, (−)- and (±)-canadine, (−)-stylopine, isoboldine, protopine, columbamine and (−)-*cis*-N-methylcanadinium hydroxide (isolated in the form of iodide) as significant components. Among minor alkaloids allocryptopine, (−)-isocorypalmine, (+)-corypalmine, (±)- and (−)-tetrahydropalmatine, corysamine, dehydrothalictricavine, palmatine and *cis*-N-methylstylopinium hydroxide (as iodide) were isolated and trace amounts of jatrorrhizine and bulbocapnine were detected.

Corydalis solida (L.) SW. (syn. *C. digitata* PERS., *C. bulbosa* (L.) DC.) from the section *Pes-gallinaceus* IRM. is together with *C. cava* (L.) SCHW. et KOERTE (section *Radix-cava* IRM.) the most widespread species of the *Corydalis* genus in Czechoslovakia. This is a perennial herb with a solid tuber, substantially smaller than the tubers of *C. cava*. The literature data on the alkaloids from the species *C. solida* are very contradictory, especially as regards the main alkaloid. While some authors[1-4] isolated bulbocapnine from the aerial part as the main alkaloid, others could not detect it either at all[5-7] or in trace amounts[8]. In the tubers, to which little attention has been devoted so far, it was not found[4-6]. From the aerial part[1-4,6-8] or from the tubers[4-6] predominantly tetrahydroprotoberberine alkaloids were isolated or detected, *i.e.* (+)-corydaline, (+)- or (−)-stylopine, (±)-, (+)- or (−)-tetrahydropal-

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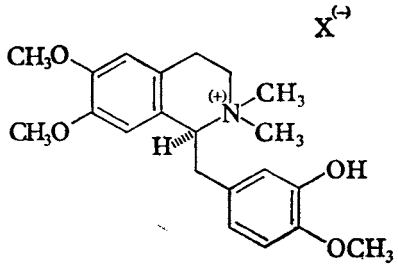
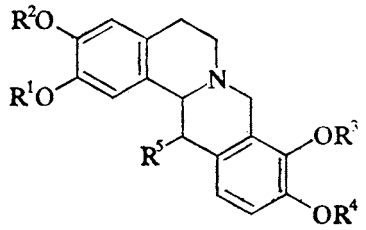
matine, (−)-canadine, (±)-sinactine and (±)-tetrahydrocorysamine, protopine alkaloids protopine and allocryptopine and among aporphines in addition to the mentioned bulbocapnine also isoboldine (aurotensine), (+)-corydine, (+)-isocorydine, domesticine, nantenine and predicentrine[8]. Ochotensine and solidaline[7], isolated in negligible amounts, represent other structural types. Of quaternary alkaloids only berberine[8] was identified; the other papers mentioned have not studied the question of the presence of quaternary alkaloids.

The alkaloids from the plants growing on the territory of Czechoslovakia have not yet been studied. The results of the research of alkaloids from domestic plants are presented in this paper. Since our aim was to use for our studies homogeneous population from one locality so far as possible, we had at our disposal relatively small amounts of plant material which were insufficient for the study of trace alkaloids. From this material we isolated a total of 22 individual alkaloids of which 14 were discovered in *C. solida* for the first time. One of them, isolated in the form of its iodide, represents a new so far undescribed natural alkaloid for which we derived the structure of (+)-N-methyllaudanidinium iodide (*I*, X = I).



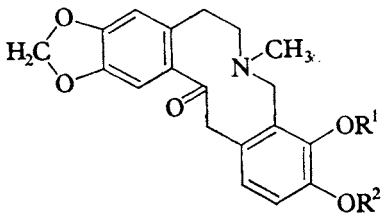
I



IIa, $R^1 = R^2 = R^3 = R^4 = CH_3$, $R^5 = H$
IIb, $R^1 = R^2 = R^3 = R^4 = R^5 = CH_3$
IIc, $R^1 = R^3 = R^4 = R^5 = CH_3$, $R^2 = H$
IId, $R^1 = R^3 = R^4 = CH_3$, $R^2 = R^5 = H$
IIe, $R^1 = R^5 = H$, $R^2 = R^3 = R^4 = CH_3$
IIf, $R^1 = R^3 = R^5 = H$, $R^2 = R^4 = CH_3$
IIg, $R^1 + R^2 = R^3 + R^4 = CH_2$, $R^5 = H$
IIh, $R^1 + R^2 = CH_2$, $R^3 = R^4 = CH_3$, $R^5 = H$

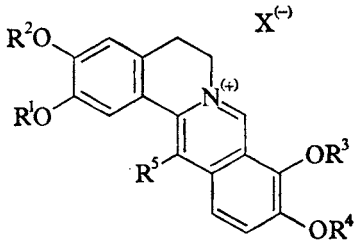
As already observed in *C. cava*[9] the composition of alkaloidal fractions from the tubers and the aerial parts of *C. solida* also differed considerably. The content of the sum of the alkaloids in the tubers of *C. solida* (0·37%) was more than ten times lower than that in *C. cava*. (+)-Tetrahydropalmatine (*IIa*) was obtained as the main alkaloid, and together with it a smaller amount of (±)-tetrahydropalmatine which was accompanied by a significant amount of protopine (*IIIa*), (+)-corydaline (*IIb*) and allocryptopine (*IIIb*). Among the minor tertiary alkaloids small amounts of (±)-

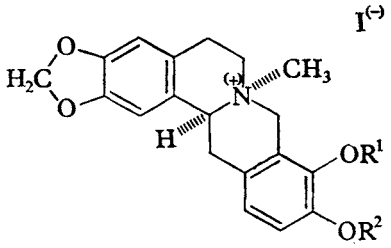
-corybulbine (*IIc*), (+)-corypalmine (*IId*), (−)-isocorypalmine (*IIe*) and (−)-scoulerine (*IIf*) were isolated. All the last mentioned four alkaloids were isolated from *C. solida* for the first time. (−)-Stylopine (*IIg*) and an unidentified alkaloid CS 1, m.p. 158°C, were isolated in very small amounts, while traces of bulbocapnine were detected chromatographically.



IIIa, $R^1 + R^2 = CH_2$
IIIb, $R^1 = R^2 = CH_3$

From the fraction of quaternary non-phenolic protoberberines, which were converted to chlorides, dehydrocorydaline chloride (*IVa*, X = Cl) was isolated which also belonged among the dominant alkaloids of the tubers. Corysamine chloride (*IVb*, X = Cl) and palmatine chloride (*IVc*, X = Cl) were isolated in smaller amount, and traces of coptisine and berberine could be also detected. From the fraction of the iodides of quaternary alkaloids, obtained from the aqueous phase after addition of potassium iodide by extraction with chloroform[10], jatrorrhizine iodide (*IVd*, X = I), (−)-*cis*-N-methylcanadinium iodide (*Va*), and *cis*-N-methylstylopinium iodide (probably the (−)-form, *Vb*) were isolated and traces of columbamine de-





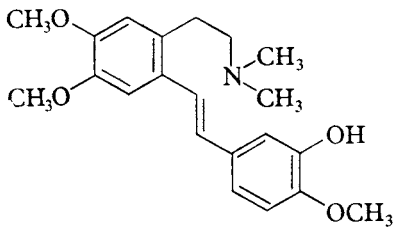
IVa, $R^1 = R^2 = R^3 = R^4 = R^5 = CH_3$
IVb, $R^1 + R^2 = R^3 + R^4 = CH_2$, $R^5 = CH_3$
IVc, $R^1 = R^2 = R^3 = R^4 = CH_3$, $R^5 = H$
IVd, $R^1 = R^3 = R^4 = CH_3$, $R^2 = R^5 = H$
IVe, $R^1 + R^2 = CH_2$, $R^3 = R^4 = CH_3$, $R^5 = H$
IVf, $R^1 + R^2 = R^3 + R^4 = CH_2$, $R^5 = H$
IVg, $R^1 + R^2 = CH_2$, $R^3 = R^4 = R^5 = CH_3$
IVh, $R^1 = R^5 = H$, $R^2 = R^3 = R^4 = CH_4$

Va, $R^1 = R^2 = CH_3$
Vb, $R^1 + R^2 = CH_2$

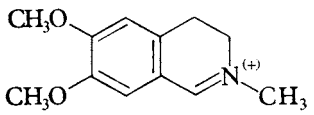
tected. With the exception of berberine the presence of none of the mentioned quaternary alkaloids has been described in *C. solida* so far. In the mother liquor after crystallization of iodides a further alkaloid was detected on a thin layer which was obtained in pure state by column chromatography on silica gel.

A direct comparison of the mass, IR and UV spectra and the chromatographic properties proved the structural identity of this alkaloid with (±)-N-methyllaudanidinium iodide which was prepared by methylation of an authentic specimen of (±)-laudanidine (called laudanine) with methyl iodide. However, since the natural alkaloid isolated from *C. solida* is dextrorotatory, the structure and configuration of (*S*)-(+)-N-methyllaudanidinium hydroxide (*I*, X = OH) follows for it, *i.e.*, it corresponds configurationally to the levorotatory tetrahydroprotoberberines.

The mass spectrometric behaviour of this type of compounds has not been described so far. The non-volatile iodide of the mentioned alkaloid (*I*, X = I) was pyrolysed during the measurement of its mass spectrum in the ion source and it gave two components. On elimination of hydrogen iodide a methine of the stilbene type (*VI*)



VI

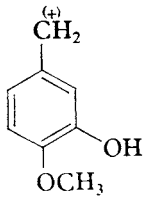


VII

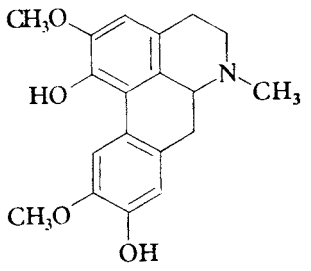
was formed which manifested itself by the molecular peak at mass 357·1946, corresponding to the composition $C_{21}H_{27}NO_4$ (calculated: 357·1940). Splitting off of methyl iodide gave a tertiary benzyltetrahydroisoquinoline base the molecular peak of which was practically not present in the spectrum.* The peaks of iodine (*m/z* 127) and methyl iodide (*m/z* 142) confirm the methiodide character of the alkaloid studied. Methine contributes to the spectrum by negligible fragments $M-CH_3$, $M-OCH_3$, $M-NH(CH_3)_2$ and an intensive peak at *m/z* 58 units ($CH_2 = N^+(CH_3)_2$) which confirms the presence of two methyl groups on the nitrogen atom. The structure of the alkaloid is revealed mainly by the tertiary base fragments:

* Methiodides of phenethylisoquinoline alkaloids have a considerably similar mass spectral fragmentation pattern. However, the molecular peak of the pyrolytically formed tertiary base is clearly distinguishable in the spectrum, having usually an approximately equal intensity to the molecular peak of the simultaneously formed methine. The higher stability of the molecular peak of the tertiary base can be explained by the fact that the main fragment, the dihydroisoquinolinium ion of the type *VII*, is not formed by the cleavage of the benzyl bond in this case.

dihydroisoquinolinium ion *VII* (*m/z* 206, $C_{12}H_{16}NO_2$) and a complementary benzyl fragment *VIII* of *m/z* 137. According to the metastable transition at 177·0 the fragment *VII* eliminates a molecule of methane and is converted to an ion of mass 190 ($C_{11}H_{12}NO_2$). In the spectrum of the sample labelled in the ion source with [O—^{2}H]ethanol the molecular peak of the methine and the ion *VIII* were shifted by one mass unit, while the fragments at *m/z* 206 (*VII*), 190 and 58 did not change in agreement with the presence of the phenolic hydroxyl in the benzylic part of the molecule. A further quaternary benzyltetrahydroisoquinoline alkaloid, called pseudorine[10], which we newly isolated from *Papaver pseudo-orientale* (FEDDE) MEDW., behaved analogously during the mass spectral measurement.



VIII



IX

In the aerial part (0·35% of alkaloids) the main alkaloidal component was berberine (*IVe*) the presence of which in this plant was described recently[8]. A further quaternary protoberberine alkaloid, coptisine (*IVf*) also belonged to the dominant components. In the fraction of tertiary bases (−)- and (±)-canadine (*IIh*) predominated, which was not detected in tubers, and it was accompanied by significant amounts of (−)--stylopine (*IIg*), isoboldine (*IX*), protopine and allocryptopine. Unlike in tubers tetrahydropalmatine, isolated as a mixture of (−)- and (±)-form, is present in the aerial part only in small amounts while corydaline is missing completely. Additional minor tertiary alkaloids are represented by (−)-isocorypalmine and (+)-corypalmine, while bulbocapnine was found in trace amounts. From the fraction of quaternary protoberberines and after conversion to chlorides corysamine chloride, palmatine chloride and dehydrothalictricavine chloride (*IVg*, X = Cl) were isolated in addition to the mentioned berberine and coptisine. From the highly polar fraction obtained in the form of iodides columbamine iodide (*IVh*, X = I), (−)-*cis*-N-methylcanadinium iodide (both belong among the dominant alkaloids of the aerial part) and a small amount of *cis*-N-methylstylopinium iodide were isolated. Jatrorrhizine was detected in trace amounts. The presence of magnoflorine or corytuberine was detected neither in the aerial part nor in the tubers.

It is rather unusual that some tetrahydroprotoberberines occur in the population of *C. solida* studied in both enantiomeric forms, the mutual ratios of which differ considerably for individual alkaloids (for example in tetrahydropalmatine the (+)-form predominates, while in the case of canadine it is the (−)-form), while others occur as pure optical isomers, but of opposite configuration, as for example in the case of (*R*)-(+)-corydaline and (*S*)-(−)-stylopine, (*R*)-(+)-corypalmine and (*S*)-(−)-isocorypalmine and others. A similar phenomenon, but to a far smaller extent, was also observed in the case of alkaloids from *C. cava*[9]. From this it may be judged that the biosynthesis and maybe also further biotransformations of alkaloids in *C. solida* are not always strictly stereospecifically controlled.

In conclusion it may be said that the main qualitative difference between the alkaloids of closely related domestic species of *C. cava*[9] and the studied population of *C. solida* consists in that in all parts of *C. cava* the apoporphine base bulbocapnine is the main alkaloid, while in *C. solida* protoberberine and protopine alkaloids strongly predominate, and aporphines are represented only by a small amount of isoboldine. As is evident, the results of our study are substantially very close to the findings of Manske[6] and Kiryakov and coworkers[8], but they differ considerably from the findings of other authors[1-4]. If in the case of studies mentioning bulbocapnine[1-4] as the main alkaloid from *C. solida* any possible confusion or contamination with *C. cava* can be excluded (both species often grow together), the existence of at least two chemotypes of different geographic occurrence must be assumed. One of them contains bulbocapnine as the main alkaloid, the other tetrahydroprotoberberines and protopines, while bulbocapnine is present only in trace amounts. The population from the territory of Czechoslovakia studied here belongs to this second chemotype.

EXPERIMENTAL

The melting points were determined on a Mettler FP 51 instrument and they were not corrected. The mass spectra were measured on a AEI MS 902 spectrometer, the IR spectra in nujol (unless stated otherwise) on a Specord 75 IR instrument (Zeiss, Jena), and the UV spectra in methanol on a Unicam SP 1800 spectrophotometer. For thin layer chromatography (TLC) both silica gel G Merck was used, for tertiary alkaloids the systems cyclohexane–diethylamine 9 : 1 (S_1), cyclohexane–chloroform–diethylamine 7 : 2 : 1 and 5 : 4 : 1 (S_2), for quaternary alkaloids the systems methanol–water–25% ammonia 15 : 3 : 1, ethanol–water–25% ammonia 15 : 9 : 1 (S_3) and 1-propanol–water–85% formic acid 12 : 7 : 1 (S_4), and also Silufol UV 254 (Kavalier) with the systems methanol–diethylamine 4 : 1 and 1 : 1 (for quaternary protoberberines). Paper chromatography (PC) was carried out on paper Whatman No 1, descending mode, in systems 1-butanol–water–acetic acid 10 : 3 : 1 and ethanol–water 2 : 1. Fluorescing alkaloids were observed in UV light, while the spots of other alkaloids were detected with potassium iodoplatinate (TLC) or Dragendorff's reagent (PC). For column chromatographies Silica gel L 100/160 (Lachema, Czechoslovakia) was used.

Extraction and Isolation of Alkaloids

The plants were collected in a natural locality in the vicinity of Brno on May 5th, 1977, at the stage of unripe fruits. The tubers and the aerial parts were separated, dried at room temperature and extracted immediately so that oxidation of native alkaloids with aerial oxygen should be avoided. The weight of the tubers was 62% and of the aerial parts 38% of the whole plants. The herbarium specimen of the plant investigated is deposited in our department.

Dry ground tubers (248 g) and dry ground aerial parts (149 g) were extracted separately in a Soxhlet extractor with ethanol. Ethanol was distilled off and the residue treated with 1% sulfuric acid and filtered. The insoluble material was washed repeatedly with water and the filtrates were combined. From the acid aqueous filtrate alkaloidal fractions *A*, *B*, *I* and *E* were obtained in the conventional manner (see for example ref.[11]).

Tubers

The crude bases of the fraction *A* (0·96 g) were separated (ref.[12]) to a non-phenolic (A_1) and a phenolic (A_2) fraction. From the bases of fraction A_1 (0·80 g) protopine (107·0 mg) and allocryptopine (15·6 mg) were isolated by crystallization from methanol. The bases from the mother liquor were dissolved in 3·5% hydrochloric acid and extracted with chloroform, affording a fraction of hydrochlorides extractable with chloroform (A_1C) and a fraction which cannot be extracted with chloroform (A_1D). After conversion to bases fraction A_1C was crystallized from ether and methanol, giving corydaline (130·9 mg) and tetrahydropalmatine (213·3 mg, a mixture of (+)- and (±)-form), and from the mother liquors further purification and crystallization gave stylopine (1·8 mg), allocryptopine (13·3 mg), (±)-tetrahydropalmatine (21·4 mg) and a negligible (less than 1 mg) of a non-identified alkaloid CS 1, m.p. 155–158°C, R_F 0·45 in S_1. The remaining amorphous material (64·1 mg) according to TLC contained in addition to the remains of the mentioned alkaloids also three non-identified bases. Fraction A_1D was crystallized from chloroform–methanol and methanol to give protopine (138·0 mg) and allocryptopine (90·7 mg). The remaining amorphous bases (12·2 mg) contained according to TLC only the remains of the two mentioned alkaloids. From fraction A_2 (0·10 g) corybulbine (9·6 mg), corypalmine (6·8 mg) and isocorypalmine (2·6 mg) were obtained by crystallization from methanol. The amorphous residue of the bases was converted to hydrochlorides and crystallized from dilute hydrochloric acid to give scoulerine hydrochloride (3·1 mg). From the mother liquor 25·0 mg of amorphous bases were regenerated which contained according to TLC in addition to the mentioned three alkaloids also negligible amounts of bulbocapnine and a non-identified alkaloid.

From fraction *B* a golden yellow mixture of chlorides (0·14 g) was obtained by crystallization from dilute hydrochloric acid which was crystallized from water to give dehydrocorydaline chloride (89·0 mg), corysamine chloride (18·9 mg) and a mixed fraction (37·2 mg), from which chromatography on a silica gel column (50 g, elution with chloroform–methanol, 10 : 1, 5 : 1 and 5 : 2) gave in addition to both mentioned alkaloids also palmatine chloride (12·8 mg). The remaining impure residue of chlorides (16·2 mg) contained according to TLC and PC in addition to the mentioned alkaloids trace amounts of coptisine and berberine.

After separation of a smaller amount of dehydrocorydaline iodide fraction *I* was divided (ref.[13]) to a non-phenolic (I_1) and a phenolic (I_2) fraction. Crystallization of fraction I_1 from methanol gave N-methylcanadinium iodide (2·1 mg) and N-methylstylopinium iodide (1·4 mg). Fraction I_2 was crystallized from aqueous methanol to give jatrorrhizine iodide (29·4 mg). The residue of the mother liquor (40·1 mg) which according to TLC contained only one alkaloid (R_F 0·22 in S_3 and 0·61 in S_4, after detection with potassium iodoplatinate it was dark blue), was separated on a column of silica gel (20 g). Fractions of 10 ml were collected, using chloroform–methanol mixtures 10 : 1 (fractions 1–32), 5 : 1 (fractions 33–45) and 1 : 1 (fractions 46–51)

for elution. Fractions 1—14 were practically non-alkaloidal, from fractions 15—45 18·7 mg of N-methyllaudanidinium iodide were obtained and fractions 46—51 contained predominantly non-alkaloidal material. Fraction E was practically non-alkaloidal.

Aerial Part

The raw bases of fraction *A* were dissolved in 3·5% hydrochloric acid and separated by extraction with chloroform to hydrochlorides extractable with chloroform (*AC*) and those non-extractable (*AD*). Both fractions were separated in the conventional manner[1,2] to non-phenolic (AC_1 and AD_1) and phenolic (AC_2 and AD_2) fractions. Crystallization of the bases AC_1 from ether and methanol afforded stylopine (26·5 mg), canadine (24·7 mg) and tetrahydropalmatine (5·1 mg). From the amorphous residue canadine hydrochloride (22·4 mg) was obtained by crystallization from dilute hydrochloric acid, and from the mother liquor 26·5 mg of amorphous bases were regenerated which according to TLC contained the residues of the above-mentioned alkaloids and a negligible amount of three non-identified alkaloids. From fraction AC_2 isocorypalmine (9·3 mg) and corypalmine (2·0 mg) were obtained by crystallizations from methanol. The remaining amorphous residue (26·1 mg) contained according to TLC in addition to the mentioned two alkaloids an unidentified alkaloid (R_F 0·29 in S_2) as the main component, together with a small amount of two further alkaloids. A fraction AD_1 was crystallized from methanol, affording protopine (16·1 mg) and allocryptopine (12·6 mg). According to TLC the amorphous residue (16·1 mg) contained only the remains of the mentioned alkaloids. From fraction AD_2 isoboldine (17·7 mg), isocorypalmine (9·3 mg) and corypalmine (3·2 mg) were isolated by crystallizations from methanol. The amorphous residue (33·1 mg) contained according to TLC in addition to the three mentioned alkaloids the same unidentified alkaloid as the main component (R_F 0·29 in S_2) as in fraction AC_2, then a negligible amount of bulbocapnine and two further unidentified bases.

The alkaloids of fraction *B* were converted to chlorides and crystallized from water, giving berberine chloride (146·6 mg), coptisine chloride (44·6 mg), corysamine chloride (10·8 mg), dehydrothalictricavine chloride (7·4 mg) and palmatine chloride (6·1 mg), with coptisine and berberine chlorides as admixture. The remaining material (24·3 mg) consisted of an unseparated mixture of chlorides of the five mentioned alkaloids.

Crystallization of the iodides of fraction *I* from aqueous methanol gave columbamine iodide (16·1 mg) and crystallization of the residue from methanol (−)-*cis*-N-methylcanadinium iodide (18·6 mg). The amorphous residue was separated to a non-phenolic (I_1) and a phenolic fraction (I_2). From fraction I_1 *cis*-N-methylstylopinium iodide (3·0 mg), and a further fraction of (−)-*cis*-N-methylcanadinium iodide (5·9 mg) were separated by crystallization from methanol. In the amorphous residue only the residues of the mentioned alkaloids could be detected by TLC. Fraction I_2 (41·7 mg) contained predominantly non-alkaloidal substances. Only the presence of the residue of columbamine and a small amount of jatrorrhizine could be detected in it by TLC. Fraction *E* consisted on non-alkaloidal ballast substances.

Characterization of the Isolated Alkaloids

The isolated alkaloids were characterized by melting point and mixed melting point determinations (with authentic samples), optical rotation values, UV and IR and mass spectra, and chromatographical data (TLC, PC). The yields of individual alkaloids are given in brackets in % of dry tubers or aerial parts. The presence of the alkaloid, if proved by TLC and PC, is indicated +.

Tetrahydropalmatine (IIa) (0·095; 0·0034): the main fraction isolated from tubers, m.p. 128 to 129°C (methanol), was according to its $[\alpha]_D^{19}$ +198° ± 3° (*c* 0·50, methanol) a mixture of approximately 2/3 of the (+)-form and 1/3 of the racemate; the main part of the racemate was

separated by crystallization from methanol, while from the mother liquors a product melting at 142–143°C with $[\alpha]_D^{22}$ +256° ± 3° (*c* 0·27, methanol) was obtained which still contained about 10% of the racemate. (±)-Tetrahydropalmatine melted at 147–148°C (methanol), $[\alpha]_D^{19}$ 0 ± 3° (*c* 0·13, methanol). The preparation isolated from the aerial parts had m.p. (unsharp) 120–135°C, $[\alpha]_D^{23}$ −71° ± 10° (*c* 0·05, methanol) and it was a mixture of about 3/4 of the (±)--form and 1/4 of the (−)-form.

Protopine (IIIa), (0·056; 0·011); prisms, m.p. 207–208°C (chloroform–methanol); IR: ν(CO) 1 655 cm^{-1}.

(−)-*Corydaline* (IIb) (0·053; −): prisms, m.p. 135–136°C (methanol), $[\alpha]_D^{19}$ +312° ± 3° (*c* 0·28, methanol).

Allocryptopine (IIIb) (0·042; 0·008): prisms, m.p. 161–162°C (methanol); IR: ν(CO) 1 645 cm^{-1}.

(−)-*Stylopine* (IIg) (0·0007; 0·018): leaflets, m.p. 200–201°C (chloroform–methanol), $[\alpha]_D^{19}$ −307° ± 5° (*c* 0·11, chloroform).

Canadine (IIh) (−; 0·030): the isolated preparation, with m.p. very unsharp from 130–160°C (methanol) and $[\alpha]_D^{22}$ −233° ± 5° (*c* 0·10, methanol), was according to its optical rotation value a mixture of about 80% of the (−)-form and 20% racemate. Crystallization from methanol gave pure (±)-canadine, m.p. 165–166°C, $[\alpha]_D^{23}$ 0° ± 5° (*c* 0·10, methanol), and from the mother liquors the better soluble (−)-canadine was obtained with m.p. 131 to 133°C, $[\alpha]_D^{23}$ −280° ± 5° (*c* 0·10, methanol).

(±)-*Corybulbine* (IIc) (0·004; −): from chloroform–methanol m.p. 207–208°C, or 213 to 215°C, in dependence on the crystallization method, $[\alpha]_D^{23}$ 0° ± 5° (*c* 0·10, chloroform); identity was confirmed by direct comparison with a preparation obtained by reduction of dehydrocorybulbine iodide (m.p. 206–208°C)[9]. Literature[14,15] gives m.p. 206°C or 218–220°C, respectively.

(+)-*Corypalmine* (IId) (0·003; 0·001): m.p. 221–222°C (chloroform–methanol), $[\alpha]_D^{23}$ +304° ± ± 5° (*c* 0·03, chloroform).

(−)-*Isocorypalmine* (IIe) (0·001; 0·006): m.p. 226–227 C (chloroform–methanol), $[\alpha]_D^{23}$ −298° ± 5° (*c* 0·10, chloroform).

(−)-*Scoulerine* (IIf) (0·001; −): needles, from methanol, m.p. 195–197°C, rapidly turning red in air, $[\alpha]_D^{23}$ −345° ± 10° (*c* 0·02, methanol); hydrochloride from water m.p. 255–256°C.

Isoboldine (IX) (−; 0·012): clusters from methanol, m.p. 125–126°C, $[\alpha]_D^{20}$ +40° ± 5° (*c* 0·13, chloroform).

Dehydrocorydaline chloride (IVa) (0·036; −): orange-yellow needles, m.p. 168–179°C (water); iodide (from methanol) had a very variable m.p., in dependence on the crystallization conditions (from 152–153°C to 230–231°C), the same as an authentic sample prepared by oxidation of corydaline[9].

Berberine chloride (IVe) (traces; 0·098): yellow needles, m.p. 205–206°C (water); iodide, yellow needles, m.p. 258–264°C (methanol) under decomposition.

Coptisine chloride (IVf) (+; 0·030): orange needles (water) which darkened above 220°C and did not melt up to 280°C (decomposition, carbonization); an authentic sample had the same behaviour.

Corysamine chloride (IVb) (0·008; 0·007): bronze coloured leaflets (water), darkening above 200°C but not melting till 280°C (decomposition, carbonization); an authentic sample behaved in the same manner.

Palmatine chloride (IVc) (0·005; 0·004): yellow needles, m.p. 197—199°C (water), undepressed in admixture with a reference sample.

Dehydrothalictricavine chloride (IVg) (—; 0·005): yellow needles, m.p. 184—196°C, iodide m.p. 215—218°C (methanol), undepressed on admixture with an authentic sample prepared by oxidation of thalictricavine[9].

Jatrorrhizine iodide (IVd) (0·012; +): orange clusters, m.p. 207—208°C (aqueous methanol); identical with a preparation from *Berberis vulgaris*.

Columbamine iodide (IVh, X = I) (traces; 0·011): orange-yellow clusters, m.p. 228—230°C (aqueous methanol); identical with a preparation from *Bocconia frutescens*[16].

(±)-N-*Methyllaudanidinium iodide* (I, X = I) (0·008; —): amorphous, $[\alpha]_D^{23}$ +72° ± 7° (*c* 0·04, methanol). Mass spectrum (*m/z*, intensity): 357 (1·5), 342 (0·2), 341 (0·3), 340 (0·2), 326 (0·3), 312 (0·3), 206 (100), 190 (11·3), 162 (2·9), 142 (16·7), 137 (1·7), 127 (4·9), 58 (11·3). UV spectrum: λ_{max} (log ε): 211 nm (4·50), 283 nm (3·65), shoulder 226 nm (4·25), λ_{min} 257 nm (3·06). IR spectrum (in KBr): 3 370, 3 010, 2 970, 2 940, 2 840, 1 615, 1 595, 1 520, 1 470, 1 440, 1 415, 1 355, 1 260, 1 160, 1 130, 1 115, 1 025, 1 005, 985, 910, 865, 815, 760, 740 cm^{-1}. R_F values 0·22 in S_3 and 0·61 in S_4 (a dark blue spot after detection). All the spectra and chromatographic properties were identical with those of a reference sample.

(—)-cis-N-*Methylcanadinium iodide* (Va) (0·0008; 0·016): leaflets from methanol, m.p. 165 to 166°C, about 180°C the melt solidifies and remelts at 215—222°C, it then solidifies again and melts finally at 249—251°C; an authentic sample and a mixture of both preparations behaved in the same manner; $[\alpha]_D^{23}$ —122° ± 3° (*c* 0·10, methanol).

cis-N-*Methylstylopinium iodide* (0·0006; 0·002): leaflets from methanol, m.p. 279—281°C, undepressed on admixture of an authentic preparation of the (—)-*cis*-form.

Preparation of (±)-N-Methyllaudanidinium Iodide (*I*)

(±)-Laudanidine (10·3 mg) was dissolved in 1·5 ml of hot methanol. After cooling 0·25 ml of methyl iodide were added and the mixture allowed to stand at room temperature for 24 h. After evaporation of the solvents the amorphous residue (14·6 mg) was submitted to analysis. The mass, UV and IR spectra were the same as in the case of a preparation isolated from *C. solida*; their R_F values in S_3 and S_4 systems were also equal.

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