OCCURRENCE OF MAGNOFLORINE AND CORYTUBERINE IN SOME WILD OR CULTIVATED PLANTS OF CZECHOSLOVAKIA

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Magnoflorine was isolated for the first time from *Adonis vernalis* L., *Clematis recta* L. and *Epimedium versicolor* MORR., further also from *Aquilegia* sp., *Caltha palustris* L., *Isopyrum thalictroides* L., and *Aristolochia clematitis* L. It was detected in *Adonis aestivalis* L., *Clematis vitalba* L., *Consolida regalis* GRAY, and *Helleborus viridis* L. Corytuberine was isolated for the first time from *Caltha palustris* L. and detected in small amounts in *Adonis vernalis, A. aestivalis, Aquilegia* sp., *Consolida regalis, Clematis recta, Eranthis hiemalis* L., *Helleborus foetidus* L., *H. niger* L., *H. viridis, Isopyrum thalictroides*, and *Aristolochia clematitis*. From *Consolida regalis* a quaternary alkaloid (iodide $C_{22}H_{34}NO_2I$) was isolated as the main component, probably of diterpenoid type. A small amount of coptisine was isolated from *Isopyrum thalictroides* and *Aquilegia* sp.

Magnoflorine (*I*), a quaternary aporphine alkaloid, is one of the most widespread isoquinoline alkaloids occuring in many families, especially of the order *Ranales* (*Polycarpicae*), and to a lesser extent in some families of other orders (*cf.*[1-3]) which are all derived phylogenetically from *Ranales* or *Magnoliales*[4,5]. Chemotaxonomically it is considered such a characteristic feature[6,7] so that Hegnauer labelled it "Leitalkaloid" for the *Polycarpicae* order. It is also widespread in the *Papaveraceae* familly of the *Papaverales* (*Rhoedales*) order, as we have found in the past two decades (for a review see, for example, ref.[8]). In allmost all taxa from *Papaveraceae*, magnoflorine (*I*) is accompanied by a larger or smaller amount of its tertiary N-demethyl derivative, corytuberine (II). Knowledge on the occurence of these highly polar alkaloids was facilitated by a simple and efficient isolation technique (*cf.*[8-10]). In contrast to magnoflorine the occurence of corytuberine in families other than *Papaveraceae* and *Fumariacesae* had not been known until recently; only in recent years two findings in the families *Lauraceae* and *Menispermaceae*[11,12] have been published*.

We were interested in the distribution of magnoflorine and especially corytuberine in wild or cultivated plants growing in Czechoslovakia on which no information has been available so far in literature. Using qualitative tests for alkaloids we carried out screening of 30 species of the *Ranunculaceae*, *Berberidaceae*, and *Aristolochiaceae* and we selected 17 species for preliminary investigation, the result of which is pre-

* Corytuberine was also isolated from *Annona cherimolia* MILL. (*Annonaceae*)[33], recently.

sented in this communication. In all the three families mentioned the presence of magnoflorine was known (*cf.*[1-3]), but not that of corytuberine. We found corytuberine in almost all the species investigated, but in small amounts. In extremely high yield (hydriodide up to 0·84%) we isolated corytuberine as the main alkaloid from the leaves of the *Mahonia aquifolium* (PURSH.) NUTT. (*Berberidaceae*)[13], where its presence has not been detected as yet.

The occurence of magnoflorine in *Ranunculaceae* was tested chromatographically[14,15]; recently it was isolated mainly from many species of *Thalictrum* (*cf.*[1-3]). Among *Ranunculaceae* we investigated preliminarily fifteen species. We isolated magnoflorine in an unusually high yield from the roots of *Adonis vernalis* L. (iodide 0·65%) in which it was detected only chromatographically so far[14]. This plant is one of the richest sources of magnoflorine altogether. It has not been detected in the aerial parts. On the other hand, in the related species *A. aestivalis* L., which in contrast to the perennial *A. vernalis* is an annual, only traces of magnoflorine were detected and an orange, so far unidentified, alkaloid was isolated which in its spectral properties resembles quaternary protoberberines. In both species of *Adonis* genus negligible amounts of corytuberine were detected.

Alkaloids from *Isopyrum thalictroides* L. have already been investigated several times[15-18]. From the rhizomes of this plant we isolated magnoflorine (iodide 0·16%) and detected a small amount of corytuberine. The content of tertiary alkaloids was high (up to 1·95%). From one sample we isolated a negligible amount of coptisine. The aerial part contained only a small amount of tertiary bases (0·016%) and only traces of magnoflorine and corytuberine. The presence of pseudocoptisine and other quaternary pseudoprotoberberines isolated by Moulis *et al.*[17] could not be detected in our material.

The occurence of magnoflorine in *Caltha palustris* L. has been known[14,19]. From two collections of roots of our population we isolated magnoflorine in 0·008% and 0·014% yields (as iodides) and detected a small amount of corytuberine. From the aerial part we isolated corytuberine (hydriodide 0·001%) as the dominant alkaloid. This evidently represents the first isolation of corytuberine from *Ranunculaceae*. The root and the aerial part contain negligible amounts of further tertiary alkaloids of which we identified chromatographically protopine and probably allocryptopine. Protopine was isolated from this plant earlier[20].

The genus *Clematis* is mentioned in literature as being free of alkaloids[14,15]. In contrast to these data our domestic population of the species *C. recta* L. gave distinctly positive tests for alkaloids. We isolated from its roots and aerial parts magnoflorine (iodide 0·003% and 0·001%) as the main alkaloid. In both parts of the plant negligible amounts of tertiary bases and traces of corytuberine were detected. This is the first case of the isolation of magnoflorine from the *Clematis* genus. On the other hand, we detected only traces of magnoflorine in the aerial part and the root of *C. vitalba* L.

In *Consolida regalis* GRAY (syn. *C. arvensis* OPIZ, *C. segetum* (LAM.) SCHUR, *Delphinium consolida* L.) tertiary diterpenoid alkaloids (delcosine, delsoline, anthranoyllycoctonine *etc.*, *cf.*[21]) are known; magnoflorine was detected chromatografically[14,15]. From the plant material collected in our country we isolated after separation of a mixture of tertiary alkaloids (0·05%) a new alkaloid as the main component of the strongly polar fraction, in the form of iodide, preliminarily labelled CR 1, m.p. 288°C, probable composition $C_{22}H_{34}INO_2$, which is evidently the main alkaloid of the plant (yield 0·04%). It is dextrorotatory and from its IR spectrum the presence of a carbonyl group and an alcoholic hydroxyl group can be deduced, and it probably does not contain the N-ethyl group (according to the mass spectrum). With great probability it is a quaternary C_{20}- diterpenoid alkaloid, and it is evidently the first finding of a quaternary alkaloid of this type in nature. In the mother liquors magnoflorine and traces of corytuberine were detected.

Magnoflorine[14,15,22,23] was detected in all the species of garden varieties and cultivars of the *Aquilegia* genus tested so far, and in some instances it was accompanied by berberine or other alkaloids of undetermined structure[22,23]. For a preliminary study we used one of the cultivars of *Aquilegia* sp., which is cultivated in our country as a decorative plant. From the root and the aerial part we isolated magnoflorine (iodide 0·025% or 0·004%) as the main alkaloid, and a small amount of coptisine which was discovered in the *Aquilegia* genus for the first time. Both parts of the plant contained a negligible amount of tertiary bases and traces of berberine and corytuberine.

In the tubers and the aerial part of *Eranthis hiemalis* L. we detected only trace amounts of corytuberine. The *Helleborus* genus too is considered practically free of alkaloids. The occurence of the alkaloids celliamine, sprintilline, sprintillamine, and alkaloid *V*, which were isolated in 1927 by Keller and Schöbel[24,25] allegedly from the roots of *H. viridis* L., has not been confirmed since and the presence of alkaloids has not been found at all[14,15].* Nevertheless, using the procedure used in this study and a sensitive detection technique, trace amounts of corytuberine could be detected reliably both in the roots and the aerial parts of *H. viridis* L., *H. niger* L., and *H. foetidus* L. In *H. viridis* corytuberine is accompanied by a small amount of magnoflorine.

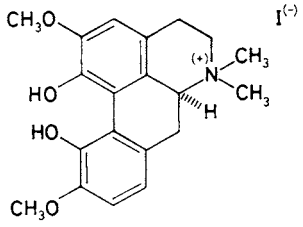
Anemone nemorosa L., *A. ranunculoides* L., *A. silvestris* L., *Ficaria verna* HUDS., and *Ranunculus auricomus* L. displayed trace amounts of alkaloids in qualitative tests. Investigation of the rhizome of *A. nemorosa* showed, however, that this species

* These discrepancies still remain unclear. Since the mentioned alkaloids are very like some alkaloids from the species of *Veratrum* (*Liliaceae*) both in their elemental composition[25] and biological effects[26] it may be supposed that a confusion or a massive contamination with the roots of some species of *Veratrum* took place, because earlier they were also called in pharmacy *Radix Hellebori*.

contains only traces of non-quaternary bases, while the presence of magnoflorine or corytuberine could not be detected.

Magnoflorine was isolated from the roots and the rhizomes of all four species of the *Epimedium* genus of *Berberidaceae* (*cf.*[27,28]) investigated so far while in *E. pubigerum* MORR. *et* DEC. an additional alkaloid was detected, resembling corytuberine[28]. Allegedly the aerial parts are free of alkaloids. We also isolated magnoflorine (iodide 0·14%) from the underground parts of *E. versicolor* MORR. which is cultivated in our country as a decorative plant. In the aerial parts it was detected in negligible amounts only, while the presence of corytuberine could not be detected in any part of the plant. Magnoflorine was found in this species for the first time.

The only member of the *Aristolochia* genus from the *Aristolochiaceae* family, growing wild in our country, is the species *A. clematitis* L. The *Aristolochia* genus is characterized by the presence of yellow or red nitrophenanthrene carboxylic



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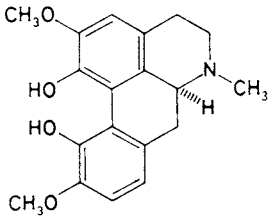

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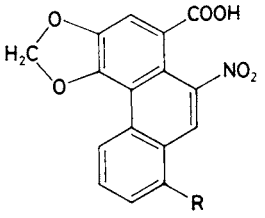

IIIa, R = OCH_3
IIIb, R = H

acids which are biogenetically derived from aporphine alkaloids (*cf.*, for example[27,29]). They are usually accompanied by magnoflorine (*cf.*[1-3,27]). From the roots of our population of *A. clematitis* we also could isolate magnoflorine (0·14%) as the main alkaloidal component which was already known to occur in this species[30]. We could not detect it in the aerial part, but we found in both parts of the plant small amounts of corytuberine. From the root we isolated the sum of aristolochic acids

in high yield (0·84%), from which we isolated as the main component (0·48% of the root) aristolochic acid-I (*IIIa*) and in lower yield aristolochic acid-II (*IIIb*). A substantially lower amount of aristolochic acids was obtained from the aerial parts (0·12%) from which aristolochic acid-I (0·04%) was isolated accompanied by aristolochic acid-II. In both plant parts small amounts of four further aristolochic acids could be detected. The content of non-quaternary alkaloids was negligible.

From these findings the conclusion can be drawn that in the species investigated (of the *Ranunculaceae*, *Berberidaceae*, and *Aristolochiaceae* families) corytuberine is almost a regular companion of magnoflorine, even though its content is usually low (with the exception of the leaves of *Mahonia aquifolium*). It seems a regular phenomenon that the largest amounts of magnoflorine are accumulated by the underground parts of perennial species, while in the aerial parts and in annual species magnoflorine is present usually in trace amounts only, or is absent altogether. In the case of corytuberine these relationships seem to be to a great extent reversed. The results of this study represent a further support for the views on the direct phylogenetic relationships of the *Papaveraceae* and *Fumariaceae* families with the order *Ranales* (*Ranunculales*)[4–7], but not with the other families of the *Rhoeadales sensu* WETTSTEIN (*Brassicaceae*, *Capparidaceae*, *Resedaceae*, *Moringaceae*, and *Tovariaceae*) which are characterized mainly by the presence of glucosinolates and which have either botanically[4,5], or biochemically[6,7] nothing in common with *Papaveraceae* and *Fumariaceae*[6,7].

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) instrument, and the UV spectra in methanol on a Unicam SP 1 800 spectrophotometer. For thin-layer chromatography (TLC) silica gel G Merck was used with the systems cyclohexane–diethylamine 9 : 1 (S_1), cyclohexane–chloroform–diethylamine 8 : 1 : 1 (S_2), 7 : 2 : 1 (S_3), and 6 : 3 : 1 (S_4), methanol–25% ammonia 200 : 1 (S_5), chloroform–ethanol–diethylamine 8 : 1 : 1 (S_6), methanol–water–25% ammonia 15 : 3 : 1 (S_7), ethanol–water–25% ammonia 15 : 9 : 1 (S_8), and also Silufol UV 254 sheets (Kavalier) with the systems methanol–diethylamine 4 : 1 (S_{10}) and 1 : 1 (S_{11}), and cyclohexane–ethyl acetate 3 : 2 (S_{12}). The fluorescing spots were detected in UV light and then sprayed with potassium iodoplatinate.

Methods

The wild growing plants were collected at the stage of flowers and unripe fruits in natural localities of South Moravia, with the exception of *Adonis vernalis* (a protected plant in Czechoslovakia) which was cultivated in the Centre for the Cultivation of Medicinal Plants, Medical Faculty, Brno. Other plants cultivated in Czechoslovakia as decorative plants were also from this centre (*Aquilegia* sp., *Epimedium versicolor*, *Eranthis hiemalis* and the *Helleborus* species). The plants were dried at room temperature. In the following text, the data of the harvest and the weight of dry plant material are given in brackets.

The dry plant material was extracted with methanol in a Soxhlet extractor, methanol was distilled off and the residue dissolved in 1% sulfuric acid and filtered. Unless stated otherwise, the method common in our studies was used for the isolation of alkaloids[8-10]: from the acid filtrate non-basic substances of lipidic nature were first extracted with ether (fraction L), then the aqueous layer was extracted with ether after alkalization with sodium carbonate (fraction A) and sodium hydroxide to pH > 13 (fraction B; only in the case of *Aquilegia* sp. and *Isopyrum thalictroides*). The reaction of the aqueous phase was then adjusted with 20% sulfuric acid to pH 6—7, an excess of potassium iodide dissolved in a small volume of water was added and the mixture extracted several times with chloroform or chloroform containing 20% of ethanol (fraction I). The crude fractions obtained after evaporation of the solvents were then purified in the conventional manner. Magnoflorine iodide and corytuberine hydriodide were obtained from fraction I by crystallizations from methanol and the preparations from individual plant samples were identified by their melting point, mixed melting point, UV, and IR spectra, or also mass spectrum and optical rotation values, as well as by chromatographic comparison with the authentic samples.

Characterizations of Alkaloids

Magnoflorine (I): iodide prisms from methanol, m.p. 265—266°C, $[\alpha]_D^{21}$ +193° ± 3° (*c* 0·2, methanol). The mass spectrum was identical with that of an authentic specimen (*cf.*[31]), the same as the UV spectrum, λ_{max} nm (log ε) 225 (4·65), 274 (4·07), 312 (3·97), λ_{min} 264 (4·02), 292 (3·84), and the IR spectrum, ν(OH) 3 170 cm^{-1}. R_F values: 0·44 (S_7), 0·63 (S_8), 0·61 (S_9), blue fluorescence in UV light, a violet-brown spot after detection.

Corytuberine (II): hydriodide, lustrous leaflets from methanol, m.p. 212—213°C, undepressed on admixture of a reference sample, $[\alpha]_D^{22}$ +180° ± 3° (methanol, *c* 0·1); UV spectrum, λ_{max} nm (log ε) 223 (4·63), 270 (4·07), 308 (3·84), λ_{min} 256 (3·99), 292 (3·76), IR spectrum, ν(OH) 3 490, 3 520, and (3·99), 292 3 590 cm^{-1}, and R_F values 0·56 (S_6), 0·78 (S_7), 0·88 (S_8), and 0·84 (S_9) and blue-violet fluorescence and a brown-grey spot after detection, are all identical with the values of an authentic sample.

Analysis of Plants

Adonis aestivalis (July 10th, 1984; whole plant, 445 g): fractions A and I contained only negligible amounts of alkaloids; from fraction I 3·2 mg of an alkaloid (0·0007%, probably iodide) were obtained by crystallization from methanol, as orange platelets, not melting up to 295°C and carbonizing. UV spectrum, λ_{max} (log ε, calculated for mol. weight 450), 206 (4·46), 227 (4·64), 279 (4·45), 352 (4·40), λ_{min} 209 (4·44), 251 (4·32), 312 (4·01), reminding the spectra of quaternary protoberberines. R_F value: 0·69 (S_7). In the mother liquors small amounts of alkaloids with R_F 0·07 and 0·23 (in S_7) were detected by TLC, as well as traces of magnoflorine and corytuberine.

A. vernalis (July 9th, 1984). Root (136 g): fraction A consisted of 6·8 mg of bases (0·005%), the main alkaloid had R_F 0·12, another R_F 0·06 (in S_1); from fraction I 0·86 g of magnoflorine iodide was obtained, and TLC of the mother liquor showed the presence of a small amount of an alkaloid with R_F 0·09 (in S_7) and traces of corytuberine. Aerial part (146 g): base of fraction A 3·0 mg (0·002%); fraction I contained only traces of an alkaloid, R_F 0·33 (S_7), the presence of magnoflorine or corytuberine could not be detected.

Anemone nemorosa (April 24th, 1981). Root (27 g): a negligible amount of bases of fraction A, in fraction I the presence of alkaloids could not be detected.

Aquilegia sp. (July 3rd, 1984). Root (69 g): in fraction A (0·8 mg; 0·001%) TLC (in S_1 and S_3)

demonstrated the presence of at least three alkaloids; fraction B consisted of a small amount of coptisine with a trace of berberine (R_F 0·57 and 0·27 in S_{10} and 0·83 and 0·72 in S_{11}); from fraction I magnoflorine iodide (17·4 mg) was obtained and a small amount of corytuberine was found in the mother liquors. Aerial part (68 g): in fraction A (1·0 mg; 0·001%) at least 10 alkaloids could be detected by TLC in S_1 and S_3, while in fraction B alkaloids could not be detected; from fraction I 2·6 mg of magnoflorine iodide were isolated and traces of corytuberine detected by TLC.

Caltha palustris (May 19th, 1984). Root (556 g): in fraction A (12·9 mg; 0·002%) TLC (in S_1, S_2, S_3, and S_5) demonstrated a small amount of protopine (R_F 0·39, 0·60, 0·83, and 0·66), probably allocryptopine (R_F 0·29, 0·51, 0·70, and 0·44), and four unidentified alkaloids; from fraction I 43·2 mg of magnoflorine iodide (0·008%) were obtained; from another locality (April 25th, 1981) the yield of magnoflorine was 0·014%. In the mother liquors a small amount of corytuberine was detected. Aerial part (850 g): in fraction A (17·1 mg; 0·002%) practically the same alkaloids could be demonstrated by TLC as in the root, from fraction I 5·5 mg of corytuberine hydriodide were isolated and a small amount of magnoflorine detected.

Clematis recta (July 14th, 1984). Root (49 g) and aerial part (303 g): the bases of fraction A were present only in traces; from fraction I 1·3 mg or 2·8 mg, respectively, of magnoflorine-iodide were isolated and traces of corytuberine detected.

C. vitalba (July 14th, 1984). Root (54 g) and aerial part (170 g); traces of alkaloids were found in fraction A, while in fraction I only traces of magnoflorine were detected by TLC.

Consolida regalis (July 14th, 1984; whole plant 270 g): according to TLC the amorphous fraction A (131·6 mg) was a mixture of at least ten alkaloids (in S_1 and S_3). When crystallized from methanol, fraction I afforded 105·2 mg of the iodide of alkaloid CR 1, m.p. 288°C, $[\alpha]_D^{24}$ $+29° \pm 1°$ (*c* 0·2, methanol). Mass spectrum: 343 (M — HI, $C_{22}H_{33}NO_2$), 342 (base peak), 328, 326, 325, 315, 314, 312, 300, 260, 257, 252, 241 ($C_{14}H_{27}NO_2$), 239, 186, 159, 142 (CH_3I), 128 (HI), and 127 (I). UV spectrum: λ_{max} 221 nm (log ε 4·32). IR spectrum: ν 1 760 cm^{-1} (C=O), 3 320 cm^{-1} (OH). R_F value 0·13 in S_8. In the mother liquors magnoflorine was detected by TLC as the main component, and a small amount of corytuberine.

Eranthis hiemalis (May 8th, 1984): The presence of the bases of fraction A could not be demonstrated in the tubers (16·4 g) or in the aerial parts (7·8 g) either. In fraction I of both parts a small amount of corytuberine was detected.

Helleborus foetidus, H. niger (both on May 11th, 1984) and *H. viridis* (May 31st, 1984): the bases of fraction A were not present either in the roots (7 g, 3 g, and 63 g) or the aerial parts (57 g, 5 g, and 25 g); in fractions I a small amount of corytuberine could be detected by TLC (in *H. niger* traces only), in *H. viridis* also magnoflorine (more in the roots).

Isopyrum thalictroides (April 23rd, 1981). Rhizome (317 g): the yield of fraction A was 1·76 g (0·56%) of amorphous bases (from two samples from other localities it was 1·95% and 1·52%, collection in 1960); TLC demonstrated at least nine alkaloids of which the main component was an unidentified base with R_F 0·07 (S_1), 0·46 (S_3), and 0·54 (S_4). Fraction B was free of alkaloids (from one sample we isolated a small amount of coptisine in 1960). From fraction I magnoflorine iodide (0·51 g) was isolated and in the mother liquor a small amount of corytuberine was detected by TLC. Aerial part (79 g): the bases of fraction A (12·7 mg) consisted according to TLC of at least 16 alkaloids; fraction B was free of alkaloids. In fraction I TLC demonstrated a negligible amount of magnoflorine and traces of corytuberine. The presence of pseudocoptisine (*cf.*[17]), with R_F 0·21 (S_7), 0·07 (S_{10}), and 0·05 (S_{11}) or other related alkaloids could not be detected in any of the fractions.

Epimedium versicolor (May 10th, 1984). Rhizomes and roots (37 g): in fraction A only traces of alkaloids were found; from fraction I 51·2 mg of magnoflorine iodide were isolated. Aerial part (17 g): fraction A contained traces of alkaloids, in fraction I a small amount of magnoflorine was detected. The presence of corytuberine could not be demonstrated in any part of the plant.

Aristolochia clematitis. Root (July 20th, 1985; 68 g): after the evaporation of methanol from the extract 68 ml of 1% sulfuric acid was added to the residue and the mixture shaken. The yellow-orange precipitate (P) of crude aristolochic acids was filtered off under suction. From the filtrate fractions A and I were isolated in the conventional manner. In fraction A (2·8 mg) at least eight alkaloids could be detected by TLC in S_1 and S_3. From fraction I 97·3 mg of magnoflorine iodide were obtained and a small amount of corytuberine detected in the mother liquors. Isolation of aristolochic acids: the precipitate (P) was dissolved in 3% aqueous ammonia, the solution was filtered, acidified with 3·5% hydrochloric acid and green-yellow precipitate was extracted with chloroform containing 20% of ethanol. The chloroform layer was separated and extracted several times with a 5% sodium hydrogen carbonate solution. The alkaline aqueous layer was acidified with dilute hydrochloric acid, the precipitate of aristolochic acids was filtered off under suction and dried (yield 0·57 g). Aristolochic acid-I (325·7 mg) and aristolochic acid-II (105·9 mg) could be separated by crystallizations from methanol. In the residue of the mother liquor (124·1 mg) TLC showed in addition to the mentioned two acids also a small amount of four additional acids (R_F in S_{12} 0·16, 0·20, 0·57, and 0·62).

Aerial part (June 7th, 1981; 20 g): in fraction A (2·4 mg) at least nine alkaloids were detected of which some are identical with those from the root. In fraction I traces of corytuberine were detected; the presence of magnoflorine could not be proved. Isolation of aristolochic acids: the extract after distilling off of methanol was shaken with 20 ml of 1% sulfuric acid, then filtered and the insoluble material was extracted several times with chloroform and 3% aqueous ammonia. From the alkaline aqueous layer aristolochic acids were obtained similarly as from the root (yield 24·4 mg). Crystallization from methanol gave 8·1 mg of aristolochic acid-I and in the mother liquors aristolochic acid-II and four additional acids (the same as in the root) could be detected by TLC. Aristolochic acid-I (*IIIa*): from methanol golden-yellow needles, m.p. 280 to 281°C; UV spectrum, λ_{max} nm (log ε) 221 (4·44), 251 (4·57), 312 (4·12), 386 (3·72), λ_{min} 231 (4·39), 283 (4·02), 354 (3·60); IR spectrum: 805, 895, 945, 1 035, 1 145, 1 265, 1 515, 1 585, 1 690 cm^{-1}; R_F in S_{12} 0·35. Aristolochic acid-II (*IIIb*): from ethanol yellow-orange platelets, m.p. 270—271°C; UV spectrum, λ_{max} nm (log ε) 218 (4·34), 252 (4·50), 300 (4·13), plateau 356—376 (3·73), λ_{min} 227 (4·22), 283 (3·96), 344 (3·70); IR spectrum: 830, 870, 900, 935, 1 040, 1 055, 1 120, 1 130, 1 195, 1 230, 1 265, 1 505, 1 585, 1 615, 1 690 cm^{-1}; R_F in S_{12} 0·44. The mentioned data for both acids agree with the literature data[29,32].

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REFERENCES

1. Guinaudeau H., Leboef M., Cavé A.: Lloydia *38*, 275 (1975).
2. Guinaudeau H., Leboef M., Cavé A.: J. Nat. Prod. Lloydia *42*, 325 (1979).
3. Guinaudeau H., Leboef M., Cavé A.: J. Nat. Prod. Lloydia *46*, 761 (1983).
4. Hutchinson J.: *Evolution and Phylogeny of Flowering Plants.* Academic Press, London and New York 1969.

5. Takhtajan A.: *Flowering Plants, Origin and Dispersal.* Oliver and Boyd, Edinburgh 1969.
6. Hegnauer R.: *Chemotaxonomie der Pflanzen*, Vol. 5. Birkhäuser Verlag, Basel and Stuttgart 1969.
7. Hegnauer R.: Planta Med. *9*, 37 (1961).
8. Slavík J.: Acta Univ. Palacki. Olomuc., Fac. Rerum Nat. *93*, 5 (1980).
9. Slavíková L., Slavík J.: This Journal *31*, 3362 (1966).
10. Slavík J., Slavíková L.: This Journal *49*, 704 (1984).
11. Chen Y., Kang Q., Song G., Hu Z., Huang J.: Zhongcaoyao *13*, 1, (1982); Chem. Abstr. *97*, 178723 (1982).
12. Silva R., Nagem T. J., Mesquita A. A. L., Gottlieb O. R.: Phytochemistry *22*, 772 (1983).
13. Slavík J., Bochořáková J., Košťálová D., Hrochová V.: Chem. Papers *39*, 537 (1985).
14. Nijland M. M., Uffelie O. F.: Pharm. Weekblad *100*, 49 (1965).
15. Frencel I.: Diss. Pharm. Pharmacol. *17*, 577 (1965).
16. Frencel I.: Diss. Pharm. Pharmacol. *20*, 303 (1968).
17. Moulis C., Gleye J., Stanislas E.: Phytochemistry *16*, 1283 (1977).
18. Moulis C.: J. Nat. Prod. Lloydia *44*, 101 (1981).
19. Nijland M. M.: Pharm. Weekblad *98*, 261 (1963).
20. Panov P., Panova L.: Dokl. Bolg. Akad. Nauk *29*, 399 (1976).
21. Pelletier S. W., Mody N. V. in the book: *The Alkaloids* (R. H. F. Manske and L. Rodrigo, Eds), Vol. XVII. Academic Press, New York—San Francisco—London 1979.
22. Winek Ch. L., Beal J. L., Cava M. P.: Lloydia *27*, 111 (1964).
23. Winek Ch. L., Beal J. L., Cava M. P.: J. Pharm. Sci. *53*, 734 (1964).
24. Keller O., Schöbel W.: Arch. Pharm. *265*, 238 (1927).
25. Keller O., Schöbel W.: Arch. Pharm. *266*, 545 (1928).
26. Franzen G.: Arch. Exp. Path. Pharm. *159*, 183 (1931).
27. Hegnauer R.: *Chemotaxonomie der Pflanzen*, Vol. 3. Birkhäuser Verlag, Basel und Stuttgart 1964.
28. Baytop T., Cubuken B.: Istanbul Univ. Eczacilik Fak. Mecm. *9*, 1 (1965); Chem. Abstr. *65*, 7626 (1966).
29. Mix D. B., Guinaudeau H., Shamma M.: J. Nat. Prod. Lloydia *45*, 657 (1982).
30. Pailer M., Pruckmayr G.: Monatsh. Chem. *90*, 145 (1959).
31. Dolejš L.: This Journal *49*, 2816 (1984).
32. Pailer M., Schleppnik A.: Monatsh. Chem. *88*, 367 (1957).
33. Villar A., Mares M., Rios J. L.: J. Nat. Prod. Lloydia *48*, 151 (1985).

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