ON ALKALOIDS FROM *Argemone polyanthemos* (FEDDE) OWNB.*

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From *Argemone polyanthemos* (FEDDE) OWNB. allocryptopine and berberine were isolated as main alkaloids in addition to a smaller amount of (−)-scoulerine, norchelerythrine, coptisine, protopine, sanguinarine and chelerythrine.

Several years ago Stermitz and coworkers[1] investigated alkaloids from *Argemone polyanthemos* (FEDDE) OWNB.[2] (classified in the older botanical literature under the name *A. intermedia* SWEET, *cf.*[3]) and found in the above-ground part of the plant berberine as the main alkaloid in addition to a smaller amount of allocryptopine and traces of protopine and sanguinarine. From plant material cultivated in Czechoslovakia a sum of alkaloids was obtained in 0·04% yield (per dry plant) and from it allocryptopine and a smaller amount of berberine were isolated. In agreement with the authors mentioned we also proved the presence of a small amount of protopine and sanguinarine as well as four additional alkaloids which were found to be identical with (−)-scoulerine, norchelerythrine, coptisine and chelerythrine.

While both last named alkaloids are rather widely distributed among *Argemone* species we found recently (−)-scoulerine and norchelerythrine in *A. albiflora* HORNEM.[4] as the first case of the occurrence of these alkaloids in *Argemone* genus. The findings mentioned confirm the close biochemical relation of the species *A. polyanthemos* and *A. albiflora* which were classified by Stermitz[1] into the alliance IVa. It is remarkable that in contrast to three other *Argemone* species which we investigated recently[4-6] *A. polyanthemos* contains only trace amounts of an unidentified quaternary alkaloid.

EXPERIMENTAL

The melting points were determined on a Kofler block and were not corrected. The UV spectra were measured in methanol on a Unicam SP 500 apparatus and the IR spectra (KBr technique) on an Infrascan (Hilger and Watts) spectrophotometer. For thin-layer chromatography silica gel with gypsum (5 : 1) was used in combination with the following solvent systems: cyclohexane–chloroform–diethylamine in the ratios 7 : 2 : 1 (S_1), 4 : 5 : 1 (S_2), and 3 : 6 : 1 (S_3),

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benzene–ethyl acetate–diethylamine 5 : 4 : 1 (S_4), ethanol–water–25% ammonia 15 : 9 : 1 (S_5), methanol–water–25% ammonia 8 : 1 : 1 (S_6) and cyclohexane–methanol 1 : 1 (S_7). Paper chromatography was carried out on Whatman paper No 1, descending technique, with 1-butanol–acetic acid–water 10 : 1 : 3 (S_8). Detection of spots was carried out under the UV light or with Dragendorff reagent. Allocryptopine and protopine were identified by their melting points, mixed melting point with an authentic sample, and R_F values in four solvent systems.

Isolation of Alkaloids

The plants were cultivated in the Experimental Botanical Garden of the Medical Faculty in Brno from the seeds obtained from the Botanical gardens in Gatersleben and Poznań. The plants were gathered at the stage of unripe fruits on September 6th, 1972, and dried at room temperature.

The dry ground plant (5790 g) was extracted seven times with cold methanol (total 140 l). The extract was worked up in the same manner as described in paper[4] and fractions *A*, *B*, *E* and *I* were isolated from the extract. The crude bases of fraction *A* were separated to fractions *AC*, AD_1 and AD_2. From a solution of the bases of fraction *AC* in methanol norchelerythrine (44 mg; 0·0008%) crystallised out, m.p. 213–214°C (chloroform–methanol), undepressed on admixture of authentic alkaloid (see[4]). The identity was confirmed by UV and IR spectra, R_F values in S_1 and S_2, and colour reactions. From the mother liquor a smaller fraction of allocryptopine was isolated by crystallisation from ethanol. In the amorphous residue of bases (25 mg) traces of another alkaloid of R_F 0·29 (S_1), 0·52 (S_2), and 0·65 (S_4) were proved in addition to allocryptopine. From the non-phenolic fraction AD_1 allocryptopine was isolated by crystallisation from ether (total yield 0·99 g; 0·017%), m.p. 160–161°C (ethanol). Crystallisation of the rest of the bases from chloroform–ethanol gave protopine (23 mg; 0·0004%), m.p. 206–207°C (chloroform–ethanol). From the mother liquor quaternary benzophenanthridine bases were separated in the form of non-basic pseudo-cyanides which were converted to bases in the conventional manner (6·7 mg; 0·0001%) and identified as sanguinarine (R_F 0·86 in S_7, 0·46 in S_8; orange fluorescence) and chelerythrine (trace amounts; R_F 0·71 in S_7, 0·55 in S_8; yellow fluorescence). In the amorphous residue of bases (35 mg) the presence of allocryptopine and protopine only was demonstrated by thin-layer chromatography.

From the phenolic fraction AD_2 (–)-scoulerine was separated (86·2 mg; 0·0015%) in the form of a poorly soluble hydrochloride. The base had m.p. 201–202°C (methanol), undepressed on admixture of an authentic specimen (see[4]), $[\alpha]_D^{19}$ –326° ± 15° (*c* 0·1, methanol). The identity was confirmed by UV and IR spectra and R_F values in S_1, S_2 and S_3. Hydrochloride had m.p. 245–246°C (methanol), undepressed on admixture with an authentic specimen. The bases were set free from the mother liquor after the scoulerine hydrochloride and a small amount of allocryptopine was obtained on crystallisation from ethanol. The remaining amorphous bases (15 mg) contained, according to thin-layer chromatography, the remainders of allocryptopine and scoulerine only.

Berberine chloride was obtained from the fraction *B* on crystallisation from dilute hydrochloric acid (total yield of berberine, calculated as base, was 0·69 g, *i.e.* 0·012%), R_F value 0·56 (S_8; yellow-green fluorescence), tetrahydro derivative m.p. 163–165°C (ether), undepressed in admixture with an authentic sample. From the mother liquors after berberine chloride alkalisation with sodium hydroxide and extraction with ether gave the remaining bases (42·8 mg; 0·0007%) which were composed almost exclusively of coptisine: R_F value 0·44 (S_8; yellow fluorescence), tetrahydro derivative m.p. 218°C (chloroform–ethanol), undepressed with an authentic sample.

Fraction *E* was non-alkaloidal. By crystallisation of fraction *I* the residue of berberine iodide was separated (14 mg; m.p. 259–262°C, undepressed in admixture with an authentic specimen;

the identity was confirmed also by its R_F values in S_5 and S_8). The residue was predominantly non-alkaloidal. Chromatography on a thin-layer demonstrated only trace amounts of an alkaloid of R_F 0·10 (S_5) or 0·08 (S_6).

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REFERENCES

1. Stermitz F. R., Nicodem D. E., Wei C. C., McMurtrey K. D.: Phytochemistry *8*, 615 (1969).
2. Ownbey G. B.: *Monograph of the Genus* Argemone *for North America and the West Indies.* Memoirs of the Torrey Botanical Club, Vol. 21, No 1. The Seeman Printery, Durham, N.C. 1958.
3. Fedde F. in the book: *Das Pflanzenreich — Regni vegetabilis conspectus.* (A. Engler, Ed.) Part IV, Vol. 104. Leipzig 1909.
4. Haisová K., Slavík J., Dolejš L.: This Journal *38*, 3312 (1973).
5. Haisová K., Slavík J.: This Journal *38*, 2307 (1973).
6. Slavík J., Slavíková L., Haisová K.: This Journal *38*, 2513 (1973).

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