ALKALOIDS OF THE *Papaveraceae*. XLV.*

PHENOLIC NON-QUATERNARY ALKALOIDS FROM THE ROOTS OF THREE *Eschscholtzia* SPECIES

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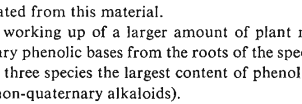
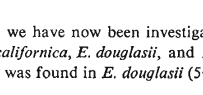
The main component of the non-quaternary alkaloid fraction from the roots of the species of the *Eschscholtzia* genus investigated up to now are non-phenolic bases allocryptopine and protopine in addition to a lesser amount of benzophenanthridine bases (see[1,2]). The presence of a small amount of unidentified phenolic bases was already detected earlier in the following species: *E. douglasii* (Hook. *et* Arn.) Walp. („*E. californica* Cham.", ref.[1]), *E. glauca* Greene, *E. lobbii* Greene and *E. sp.* (probably *E. oregana* Greene)[2]. From the species *E. californica* Cham. Manske and Kju Hi Shin[3] isolated a phenolic base in low yield, identified subsequently[4] as bisnorargemonine. However, in "a mixture of cultivated varieties" this substance was not found[3]; on the other hand another phenolic base, N-methyllaurotetanine (lauroscholtzine)[3], was isolated from this material.

After working up of a larger amount of plant material we have now been investigating non-quaternary phenolic bases from the roots of the species *E. californica*, *E. douglasii*, and *E. glauca* Of these three species the largest content of phenolic bases was found in *E. douglasii* (5·2% of the sum of non-quaternary alkaloids).

One of these phenolic bases is not easily extracted with ether and therefore it was obtained mainly from chloroform extracts. On the basis of its physical constants, UV, IR, and mass spectra (peaks at *m/e* 327 (M), 326 (M-1) and 190 (*IIa* or *IIb*)) it was identified as (−)-bisnorargemonine (*Ia*).



Ia, R = H
Ib, R = CH_3



IIa, $R^1 = CH_3$, $R^2 = H$
IIb, $R^1 = H$, $R^2 = CH_3$
IIc, $R^1 = R^2 = CH_3$

The second crystalline base obtained from ethereal extracts of the phenolic fraction was found identical with (−)-norargemonine (*Ib*). Its mass spectrum showing characteristic peaks at *m/e* 341 (M), 204 (*IIc*), and 190 (*IIa*) is also typical of the fragmentation of pavine alkaloids and identical with the spectrum of norargemonine[5,6]. This finding represents the first proved occurrence of norargemonine in the *Eschscholtzia* genus. Up till now it was found only in some *Ar-*

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gemone species (see for example[5,7,8]), and more recently, together with bisnorargemonine, in another family than *Papaveraceae*, *i.e.* in *Thalictrum dasycarpum* Fisch. et Lall (*Ranunculaceae*)[9]. The yields of both alkaloids are given in Table I. In the amorphous residue of the phenolic bases of all three species the presence of at least two additional, so far unidentified alkaloids, was observed.

TABLE I

The Content of Phenolic Alkaloids in the Roots of the *Eschscholtzia* Species
In % of dry material.

Alkaloid	*E. californica*	*E. douglasii*	*E. glauca*
(−)-Bisnorargemonine	0·008	0·071	0·006
(−)-Norargemonine	0·005	0·024	0·011
Amorphous bases	0·007	0·009	0·010

EXPERIMENTAL

The melting points were determined both in capillaries and on a Kofler block, and they were not corrected. The mass spectra were measured on a mass spectrograph MCh 1303, the IR spectra on Infrascan, Hilger and Watts, and the UV spectra (in methanol) on a Unicam SP 500 spectrophotometer. Thin layer chromatography was carried out on silica gel containing 20% of gypsum in cyclohexane-chloroform-diethylamine 2 : 7 : 1 (S_1) and in chloroform-diethylamine 9 : 1 (S_2). The spots were detected by spraying the plates with potassium iodoplatinate and Dragendorff reagent.

Material

E. californica (gathered on 19. 8. 1969) and *E. douglasii* (gathered on 29. 8. 1969) were grown in the Experimental botanical garden of the Medical Faculty in Brno from the seeds of the same origin as in paper[10]. In the case of *E. glauca* nonquaternary bases isolated earlier from a material mentioned in the same paper[10] were made use of.

The Isolation of Alkaloids

The isolation of alkaloids was carried out with dry, ground roots (*E. douglasii* 3265 g, *E. californica* 1934 g, *E. glauca* 2480 g), in the conventional manner[2] and fractions A and E were used for the separation of the phenolic bases. In the subsequent text the isolation from the roots of *E. douglasii* is described (the yields obtained with the roots of *E. californica* and *E. glauca* are given in brackets).

From the fraction A, 63·1 g (37·4 g; 40·2 g) the main parts of protopine and allocryptopine were first separated by crystallisation from chloroform–ethanol and ethanol, and quaternary benzophenanthridine bases were isolated in the form of their non-basic pseudo-cyanides. The rest of the bases was dissolved in dilute sulfuric acid, alkalised with sodium hydroxide, and the nonphenolic bases (A_1) were extracted with ether. The aqueous layer was acidified with acetic acid, alkalised with ammonia and repeatedly extracted with ether (phenolic bases A_2). As the aqueous

layer still gave a strong positive reaction to alkaloids, it was extracted several times with chloroform (the obtained bases were combined with the fraction E).

The bases of the fraction A_2 contained according to thin layer chromatography norargemonine as the main component in addition to a lesser amount of bisnorargemonine. Fractional crystallisation from methanol, ethanol, and chloroform–ethanol gave 0·79 g (0·09 g; 0·27 g) of (—)-norargemonine, needles of m.p. 241—242°C (capillary), or 247—250°C (Kofler block), undepressed on admixture with an authentic preparation; $[\alpha]_D^{21} - 153° \pm 3°$ (*c* 0·30, chloroform). UV spectrum: λ_{max} 225 nm (log ε 4·10), λ_{max} 287 nm (log ε 3·88), λ_{min} 252 nm (log ε 2·65). IR spectrum (chloroform): ν(OH) 3 540 cm^{-1}. R_F values 0·65 in S_1 and 0·82 in S_2. The given constants correspond to those from the literature[5,7,8] and agree well with those of an authentic preparation. In the non-crystalline residue of the fraction A_2, weight 0·28 g (0·14 g; 0·25 g), thin layer chromatography demonstrated, in addition to the residues of norargemonine and bisnorargemonine, the presence of bases of R_F 0·57 and 0·74 (the main component) in S_2.

From the fraction E, 2·30 g (0·16 g; 0·15 g) of (—)-bisnorargemonine were obtained on crystallisation from methanol (including a small amount of material isolated from the fraction A_2), m.p. (from methanol) 254—255°C (capillary) or 261—262°C (Kofler block). The material (needles) melted undepressed on admixture with an authentic sample; $[\alpha]_D^{20} - 244° \pm 3°$ (*c* 0·32, methanol), $-244° \pm 3°$ (*c* 0·19, chloroform); it was very little soluble in boiling chloroform and little soluble in boiling methanol. Literature[8,11] gives m.p. 243—246°C, or[4] 254—256°C, $[\alpha]_D$ —265·8° (methanol)[11] or —222° (chloroform)[8]. UV spectrum, λ_{max} 288 nm (log ε 4·02), λ_{min} 252 nm (log ε 2·70), and IR spectrum (nujol), ν (OH), 3 490 cm^{-1}, were identical with those of authentic samples. R_F value in S_1 was 0·16 and in S_2 0·23. With concentrated sulfuric acid the substance is not coloured, with Fröhde reagent it gives a strong wine-red coloration (norargemonine gives the same coloration). Non-crystallising residue of the fraction E contained predominantly non-alkaloid substances.

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