

CONSTITUENTS OF *CORYDALIS STEWARTII*\*

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**Key Word Index**—*Corydalis stewartii*; Papaveraceae; ginnol; protopine; tetrahydrocoptisine; domesticine; isoboldine; coptisine.

**Plant.** *Corydalis stewartii* Fedde. **Source.** West Pakistan. The plant was collected and identified by Prof. Qazilbash, Peshawar University where a voucher specimen is deposited. **Uses.** The juice of the plant is used in the treatment of eye diseases.<sup>1</sup> **Previous works.** Protopine,<sup>2</sup> and several alkaloids of unknown structure.<sup>1</sup>

**Present work.** Ginnol (0.5% yield, m.p., m.m.p.) was isolated from the MeOH extract of the air-dried whole herb (620 g). Alkaloids were purified by means of preparative chromatography (Column and TLC) from the mother liquors of ginnol as described earlier.<sup>3</sup> Protopine (0.126%, m.p., m.m.p.). *d*-Tetrahydrocoptisine (0.032%, m.p., m.m.p.). Domesticine (0.035%, m.p., IR,<sup>4</sup> UV,<sup>4</sup> MS, NMR), *O*-methylation with CH<sub>2</sub>N<sub>2</sub> gave nantenine (m.p., MS,<sup>5</sup> NMR). Isoboldine (0.040%, m.p., UV,<sup>6</sup> MS,<sup>7</sup> NMR<sup>7</sup>), *O*-methylation with CH<sub>2</sub>N<sub>2</sub> afforded *d*-glaucine (m.p., m.m.p.). Coptisine, isolated as iodide (m.p., m.m.p.), reduction with NaBH<sub>4</sub>-MeOH gave *dl*-tetrahydrocoptisine (m.p., m.m.p.). This is the first record of the occurrence of domesticine and isoboldine in the genus *Corydalis*.

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\* Part X in the series "Constituents of *Corydalis* Species". For Part IX see S. NARUTO, K. NAMBA and H. KANEKO, *Phytochem.* **11**, 2642 (1972).

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SANGUINARINE DERIVATIVES FROM *ROMNEYA COULTERI*\*

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**Key Word Index**—*Romneya coulteri*; Papaveraceae; sanguinarine; dihydrosanguinarine.

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We have previously reported<sup>1,2</sup> on the main alkaloids of *Romneya coulteri* var. *trichocalyx* (Eastwood) Jepson and now wish to report that this plant also contains sanguinarine (isolated as the 14-methoxydihydrosanguinarine derivative) and dihydrosanguinarine. Experimental details of isolation and identification are given below.

### EXPERIMENTAL

Dried, powdered root (200 g) of *Romneya coulteri* var. *trichocalyx* (Eastwood) Jepson<sup>1</sup> was macerated with 100 ml of 10% Na<sub>2</sub>CO<sub>3</sub> solution, and 300 ml of 1:1 *n*-BuOH–benzene was added, and the mixture allowed to stand overnight. It was filtered and the filtrate was extracted 3 × with 100 ml of 1M H<sub>2</sub>SO<sub>4</sub>. The acidic layers were combined, made basic to pH 9, and extracted with 3 vol. CHCl<sub>3</sub>. The CHCl<sub>3</sub> solutions were combined, dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated to yield 1.3 g of crude gummy alkaloids. This residue was dissolved in CHCl<sub>3</sub> and chromatographed through a column of Florisil (55 g, 60–100 mesh, Fisher Scientific Co.) prepared in CHCl<sub>3</sub>. Elution with CHCl<sub>3</sub> yielded first, after evaporation, 120 mg of crude syrup which contained mainly two alkaloids by TLC (*R<sub>f</sub>* = 0.52 and 0.65 silica gel with EtOAc). Visualization was with Dragendorff's reagent and UV light. The previously isolated alkaloids (coulteropine, romneine, protopine, and reticuline) were eluted in later fractions.

The 120 mg of crude alkaloids was separated by preparative TLC into two bands which were removed from the silica gel with MeOH and CHCl<sub>3</sub>. The *R<sub>f</sub>* = 0.65 band material (35 mg) was recrystallized from benzene–EtOH to yield dihydrosanguinarine, m.p. 188–190°, identical with a sample prepared by reduction of authentic sanguinarine. The *R<sub>f</sub>* = 0.52 band (62 mg) was recrystallized from CHCl<sub>3</sub>–MeOH to yield light tan crystals, m.p. 216–219°, assigned the 14-methoxydihydrosanguinarine structure by comparison with an authentic sample prepared as follows. Commercial 'sanguinarine nitrate' (Aldrich Chemical Co.; a mixture of sanguinarine, chelerythrine, protopine, and other alkaloids) was purified by a chromatographic scheme like that described above for the isolation work to yield pure sanguinarine nitrate. This was dissolved in basic solution, extracted with CHCl<sub>3</sub>, and the residue crystallized from CHCl<sub>3</sub>–MeOH to yield light tan crystals of m.p. 216–219°, identical with the isolated compound. *Anal.*: Calc. for C<sub>21</sub>H<sub>18</sub>NO<sub>5</sub>: C, 69.22; H, 4.97; N, 3.84. Found: C, 69.29; H, 4.65; N, 3.54. MS: *m/e* 364 (M<sup>+</sup>); 332 (base peak = M<sup>+</sup> – OCH<sub>3</sub>).

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<sup>2</sup> F. R. STERMITZ and L. C. TENG, *Tetrahedron Letters* 1601 (1967).

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## PIPERACEAE

### CONSTITUENTS FROM *PIPER BANKSII*

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**Key Word Index**—*Piper banksii*; Piperaceae; elemicin; dillapiole; *N*-isobutyl-*trans*-2, *trans* 4-octadienamide.

*Plant*. *Piper banksii* Miq.—Piperaceae. *Source*. Clump Point, near Tully, N. Queensland. Herbarium No. SN 8276. *Previous work*. Related species, *P. novae-hollandiae*.<sup>1</sup>

*Leaf and stem*. Constituents extracted and separated as before.<sup>1</sup> Steam volatile oil contained elemicin and dillapiole. The only amide detected was *N*-isobutyl-*trans*-2, *trans*-4-octadienamide, but the small plant sample precluded examination of minor components.

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