

by carrying out TLC and GLC using synthetic triacontyl hexadecanoate as a reference compound. Ethanolysis of the wax esters was also carried out and the mixture of the ethyl esters was analysed by GLC. The major constituent of the wax ester was thus found to be hexacosyl eicosanoate. The acids and alcohols composing the esters are given in Table 2. The free *n*-aliphatic acids were analysed by GLC as methyl esters and the principal component was shown to be octacosanoic acid (Table 1). Sitosterol was identified by m.p., m.m.p., IR and analyses of the sterol and its acetate.

#### EXPERIMENTAL

Dried shade leaves (7.6 kg) were powdered and extracted with hexane. The extract deposited a granular solid (35.6 g) on concentration which was filtered. The filtrate was completely dried to give a semi-solid waxy mass (184 g).

**Wax esters.** A portion of the waxy mass (15 g) was chromatographed on alumina (E. Merck). Elution with hexane gave esters, m.p. 71–72°,  $\nu_{\max}$  1740, 730, 720  $\text{cm}^{-1}$ . The composition of the chain lengths was found: C<sub>42</sub>, 7.1%; C<sub>44</sub>, 30.2%; C<sub>46</sub>, 47.2%; C<sub>48</sub>, 13.5%; C<sub>50</sub>, 2.0% on GLC analysis (Hewlett-Packard 402 gas chromatograph with flame ionization detector; Column 91.5 × 0.32 cm stainless steel tube packed with 80–100 mesh silanised acid washed chromosorb W coated with 2% Silicone SE30).

**Sitosterol.** Elution of the column with hexane–benzene (1:1) gave sitosterol identified by m.p., m.m.p., IR, analyses of the sterol, and its acetate.

**Wax acids.** Further, elution with ethyl acetate yielded a solid (13 mg), m.p. 83–85°,  $\nu_{\max}$  1705, 730, 720  $\text{cm}^{-1}$ .

**Wax alcohols.** The greenish yellow granular solid was recrystallised alternately from hexane and acetone to yield a colourless residue, m.p. 77–78°,  $\nu_{\max}$  3400, 2950, 1470, 728, 720  $\text{cm}^{-1}$ . Found: C, 82.48; H, 13.70. C<sub>30</sub>H<sub>62</sub>O requires: C, 82.11; H, 14.24.

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### PAPAVERACEAE

#### ALKALOIDS OF *ARGEMONE SUBFUSIFORMIS*\*

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**Key Word Index**—*Argemone subfusiformis* subsp. *subfusiformis*; Papaveraceae; protopine; allocryptopine; berberine; sanguinarine; chelerythrine.

**Plant.** *Argemone subfusiformis* Ownb. subsp. *subfusiformis*.<sup>1</sup> **Source.** Collected in Córdoba Province, Argentina (local name 'cardo santo', 'cardo amarillo'). A voucher specimen is deposited in the university herbarium (Museo de Botánica, Universidad

\* Part III in the series "Alkaloids of Argentine Medicinal Plants". For Part II see M. N. GRAZIANO, G. E. FERRARO and J. D. COUSSIO, *Lloydia* 34, 453 (1971).

† From which KNO<sub>3</sub> crystallized, 1% of the dried plant weight.

<sup>1</sup> G. B. OWNBAY, *Brittonia* 13, 91 (1961).

Nacional de Córdoba, Córdoba, Argentina). *Uses. Medicinal.*<sup>2</sup> *Previous work.* Phytochemical screening.<sup>3</sup> Sister species.<sup>4,5</sup>

*Present work.* The air-dried above ground plant (without capsules) was extracted exhaustively with 95% EtOH. The extract was concentrated to a syrup *in vacuo*†, dissolved in CH<sub>2</sub>Cl<sub>2</sub>, extracted with 5% HCl, alkalized with NH<sub>4</sub>OH and extracted with CH<sub>2</sub>Cl<sub>2</sub>, which upon concentration yielded berberine crystallized as the chloride. After most of the berberine was removed, the alkaloid mixture was then separated by conventional procedures, including fractional crystallization from EtOH (protopine and allocryptopine), and preparative TLC on silica gel P F<sub>254</sub> using xylene-MeCOEt-MeOH-Et<sub>2</sub>NH (20:20:3:1). Bands at *R<sub>f</sub>* 0.75 and 0.82 were extracted with CHCl<sub>3</sub>-EtOH (3:1) and yielded chelerythrine and sanguinarine respectively. In addition TLC analysis also revealed the presence of traces of at least three other unidentified bases. Yield of crude mixed alkaloids: 0.40% of the dried plant weight. The approximate alkaloid composition (% of alkaloid from the total mixture) was as follows: protopine 41%; allocryptopine 28%; berberine 9%; sanguinarine 5%; chelerythrine 4%.

All the alkaloids were identified by comparing the UV, IR and NMR spectra with those of authentic samples and by m.p., m.m.p., co-chromatography (TLC 3 solvents) and GC.

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<sup>2</sup> A. L. CABRERA, *Flora de la Provincia de Buenos Aires*, Vol. IV, Part III, p. 266, Colección Científica del I.N.T.A., Buenos Aires (1967).

<sup>3</sup> R. V. D. RONDINA, M. E. MENDIONDO and J. D. COUSSIO, *Rev. Invest. Agropec.* Serie 2, **VII**, 271 (1970).

<sup>4</sup> F. R. STERMITZ, S. M. WORKMAN and W. M. KLEIN, *Phytochem.* **10**, 675 (1971).

<sup>5</sup> M. H. BENN and R. E. MITCHELL, *Phytochem.* **11**, 461 (1972).

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## SOLANACEAE

### SOLASODINE GLYCOSIDES AND DIOSGENIN FROM *SOLANUM PINNATUM*

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**Key Word Index**—*Solanum pinnatum*; Solanaceae; solasonine; solamargine.

A sample of a plant growing near Longotoma, Aconcagua, identified as *Solanum pinnatum* Cav. (Voucher specimen No. BC10 deposited in the herbarium of the Museo Nacional de Historia Natural, Santiago), was examined for glycoalkaloids and sapogenins. The crude basic glycoside mixture isolated from stems and leaves afforded solasonine, solamargine, and a glucose- and rhamnose-containing glycoside of solasodine, probably identical