

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°, ν_{\max} 1740, 730, 720 cm^{-1} . The composition of the chain lengths was found: C₄₂, 7.1%; C₄₄, 30.2%; C₄₆, 47.2%; C₄₈, 13.5%; C₅₀, 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°, ν_{\max} 1705, 730, 720 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°, ν_{\max} 3400, 2950, 1470, 728, 720 cm^{-1} . Found: C, 82.48; H, 13.70. C₃₀H₆₂O 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*.¹ *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 KNO₃ crystallized, 1% of the dried plant weight.

¹ G. B. OWNBEY, *Brittonia* 13, 91 (1961).

Nacional de Córdoba, Córdoba, Argentina). *Uses.* Medicinal.² *Previous work.* Phytochemical screening.³ *Sister species.*^{4,5}

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 CH₂Cl₂, extracted with 5% HCl, alkalized with NH₄OH and extracted with CH₂Cl₂, 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 F₂₅₄ using xylene-MeCOEt-MeOH-Et₂NH (20:20:3:1). Bands at R_f 0.75 and 0.82 were extracted with CHCl₃-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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⁵ 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

with a previously described product obtained by partial hydrolysis of solamargine.¹ Hydrolysis of the remaining glycosides furnished two neutral compounds: diosgenin and (25R)-spirosta-3,5-diene.²

EXPERIMENTAL

M.ps of the glycoalkaloids are uncorrected. TLC of the glycosides and aglycones was carried out on Merck silica gel G using *n*-BuOH-(H₂O-satd)-Et₂NH-MeOH (85:10:2) (System I), or C₆H₆-CHCl₃ (9:1) (System II) respectively, spraying with 20% SbCl₃ in CHCl₃. The sugars were examined by TLC on Merck Kieselguhr G prepared with 0.02 M NaOAc, using AcOEt-*i*-PrOH-H₂O (65:23:12) (System III), spraying with anisaldehyde-H₂SO₄.³

Isolation of the alkaloids. Dried, powdered leaves and stems of *S. pinnatum* collected in December 1970 (1.2 kg) were extracted with 5% AcOH, and the basic glycosides were precipitated with NH₄OH. The dried, ground precipitate was extracted with EtOH (Soxhlet), yielding 40 g crude alkaloids (3%). 8 g of the alkaloid mixture were chromatographed on Al₂O₃, eluting with H₂O-satd *n*-BuOH.

SP-1. 0.85 g, *R_f* 0.7 (System I), m.p. 235-240°, [α]_D²³ -90 ± 3° (*c* 0.62, EtOH). Hydrolysis with 0.1 N HCl yielded solasodine hydrochloride, m.p. 295-300°, *R_f* (System II) and IR spectrum identical with those of an authentic sample. The acid solution contained glucose and rhamnose, identified by co-chromatography (System III). (Found: C, 63.44; H, 8.89; N, 1.92. C₃₉H₆₃NO₁₁·H₂O requires: C, 63.30; H, 8.85; N, 1.89%.)

Solamargine. 1.1 g, *R_f* 0.44 (System I), m.p. 274-276°, [α]_D²³ -111 ± 3° (*c* 0.48, MeOH). Identical with a reference sample (m.m.p., TLC, IR, hydrolysis products).

Solasonine. 1.46 g, *R_f* 0.3 (System I), m.p. 266-268°, [α]_D²³ -90 ± 4° (*c* 0.55, pyridine). Identical with a reference sample (m.m.p., TLC, IR, hydrolysis products, picrate).

Isolation of the sapogenins. The basic mother liquors of the crude alkaloid precipitate were acidified to 2.5 N with HCl and refluxed (10 hr) to yield a mixture of crude aglycones. These, dried and ground, were extracted with C₆H₆ (Soxhlet), and the soluble material was fractionated on Al₂O₃, eluting with C₆H₆ and C₆H₆-CHCl₃ mixtures.

(25R)-spirosta-3,5-diene. 214 mg, *R_f* 0.72 (System II), m.p. 142-150°, [α]_D²³ -164 ± 5° (*c* 1.4, CHCl₃), λ_{\max} 228, 233, 242 nm (log ϵ 4.15, 4.18, 4.00). Identical with a reference sample (TLC, IR).

Diosgenin. 550 mg, *R_f* 0.44 (System II), m.p. 206.5-210°, [α]_D²³ -119 ± 3° (*c* 1.1, CHCl₃). Identical with an authentic sample (m.m.p., TLC, IR, acetate).

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