

## ANGIOSPERMAE

### ANACARDLACEAE

#### LIGNOCERIC ACID AND OTHER COMPOUNDS OF *SCHINUS MOLLE*\*

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*Plant. Schinus molle* L. 'pirul'.

Uses. The fruits, gum exudates and the leaves are used with medical purposes.<sup>7</sup>

*Previous work.* On the essential oil <sup>2-4</sup> and tannins<sup>4</sup> and sister *specie*.<sup>5</sup>

*Plant material.* Twigs and leaves collected in Monterrey, N.L. were extracted successively with petrol, Et<sub>2</sub>O and EtOH; chromatographed on silica gel.

*Light petroleum.* Lignoceric acid, C<sub>24</sub>H<sub>48</sub>O<sub>2</sub>, m.p. 81–82°, IR, NMR, mixed m.p. CO TLC. New compound: C<sub>29</sub>H<sub>46</sub>O<sub>2</sub>. (Found: C, 81.75; H, 11.07; O, 7.28; Calc. C, 81.63; H, 10.87 O, 7.50%). Mol. wt. M+ 426; m.p. 190–192°, [α]<sub>D</sub> IR + 29.6° (CHI). Important IR peaks: 3660, 3580 (m), 2900 (s), 2840 (m), 1620 (w), 1450 (m), 1435 (n), 1360, 1080, 870 cm<sup>-1</sup> LB color red, green, blue, to black, TNM test positive. UV λ<sub>max</sub><sup>EtOH</sup> 212 nm (c-1430). Acetate: m.p. 214–215°, [α]<sub>D</sub> + 44.0 (CHI). Important IR peaks: 3420 (m), 2900–2830 (s), 1740 (s), 1620 (w), 1455 (m), 1435 (m), 1370(m), 1360(m), 1225(s), 1045(m), 880 cm<sup>-1</sup>. β-Sitosterol: eluted by benzene–CHCl<sub>3</sub>; C<sub>29</sub>H<sub>50</sub>O (m.p., mixed m.p., 137–139°, [α]<sub>D</sub> -38° (CHI), coTLC and superimposable IR spectra of alcohol and acetate. EtOH–quercetrin (m.p., mixed m.p. ; IR, UV, coTLC). Reactions for alkaloids were negative.

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<sup>2</sup> A. CREMONI, *Ann. Chim. Appl.* **18**, 361 (1928).

<sup>3</sup> G. OTTOLINO, *Attie. Relaz. Pugl. Sci.* **6**, 49 (1948); C.A. **44**, 9807 d (1951).

<sup>4</sup> M. GONZALEZ, *Anales Fac. Quim. Farm.* **1**, 133 (1931).

<sup>5</sup> K. K. KAISTHA and L. B. KIER, *J. Pharm. Soc.* **51**, 1136 (1962).

### APOCYNACEAE

#### TRITERPENES FROM *MELODZNUS AUSTRALZS*

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A NUMBER of interesting indole alkaloids have been isolated from the root bark of the Southeast Asian woody shrub, *Melodinus australis* Maider and Bêche.<sup>1</sup> In our hands a

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<sup>1</sup> H. H. A. LINDE, *Helv. Chim. Acta* **48**, 1822 (1965).

specimen of the aerial parts yielded very little alkaloid (4.5 g of a crude mixture from 16.3 kg). Accordingly, we turned our attention to the more plentiful terpene fraction (143.6 g, 0.8%). Although a related species, *M. monogynous*, is reported<sup>2</sup> to contain the triterpenes lupeol and 3,20-lupanediol, no studies of a similar type have been carried out on *M. australis*. Accordingly, the ground leaves and stems were extracted with EtOH by percolation and the extractives were separated into broad chemical classes in the usual fashion (Experimental). The terpene-sterol fraction was chromatographed on silicic acid columns with fractions monitored by TLC and weight. Only two substances of consequence were present and these were identified as betulin and oleanolic acid after spectroscopic examination, preparation of suitable derivatives, and comparison with authentic specimens. Betulin and oleanolic acids are relatively common triterpenes but this is the first report of their occurrence in *Melodinus* sp. and is presented for its chemotaxonomic interest.<sup>3</sup>

#### EXPERIMENTAL

The plant parts consisted of the dry, powdered leaves and stems of *Melodinus australis*, Maider and Betche, and were purchased in 1965 from the Meer Corporation, New York, N.Y., as lot number 6-23835.

#### Isolation

The ground plant (16.3 kg) was percolated at room temp. with EtOH, 250 l. sufficing to exhaust the plant. The solvent was removed under reduced pressure at a temperature not in excess of 40° to give 1.15 kg (7 %) of a dark, gummy residue. This residue was partitioned between 2% citric acid and CHCl<sub>3</sub>. A considerable portion (300 g) was insoluble in either phase. The alkaloids were recovered from the citric acid solution by alkalization and extraction with CHCl<sub>3</sub>, etc., to yield 4.5 g (0.03 %) of a complex dark mixture. The CHCl<sub>3</sub> layer was evaporated and this residue (309 g) was further subfractionated by partition between hexane and MeOH containing 10% H<sub>2</sub>O. Evaporation of the MeOH layer produced 135 g (0.8 %) of crude terpenes-sterols. A portion of this (24 g) was chromatographed in the usual way over 400 g of SiO<sub>2</sub> (Mallinckrodt, 100 mesh). Compound A (subsequently identified as betulin) was present in fractions 22-35 (150 ml. each fraction). These weighed 8.67 g and crystallized from CHCl<sub>3</sub>-CH<sub>3</sub>OH, m.p. 244-247°. Ultimate purity was achieved by treating 328 mg of these crystals with C and rechromatographing on silica gel G using 8% CH<sub>3</sub>OH in CHCl<sub>3</sub> as eluant. In this way 305 mg of pure crystals, m.p. 254-255°, [ $\alpha$ ]<sub>D</sub> + 14° (CHCl<sub>3</sub>), [ $\alpha$ ]<sub>D</sub> + 18° (pyridine); diacetate, m.p. 220-222°, [ $\alpha$ ]<sub>D</sub> + 18° (CHCl<sub>3</sub>); dibenzoate, m.p. 178-180°, [ $\alpha$ ]<sub>D</sub> + 40° (CHCl<sub>3</sub>); dihydro derivative m.p. 274-6°, [ $\alpha$ ]<sub>D</sub> + 18° (pyridine) — 442.

% in CH <sub>3</sub> OH	ion of CHCl <sub>3</sub> in column with 2	
MeOH, which crystallized with great difficulty from		
SiO <sub>2</sub> -G material was chromatographed over	% CH <sub>3</sub> OH	CHCl <sub>3</sub> .
m.p. 298-303°;		262-264°,
[ $\alpha$ ] <sub>D</sub> + 65° (CHCl <sub>3</sub> );	219-224°, [ $\alpha$ ] <sub>D</sub> + 68° (CHCl <sub>3</sub> );	

<sup>2</sup> S. K. CHATTERJI, N. ANAND and M. L. DHAR, *J. Sci. Znd. Res. India* **18B**, 262 (1959); *J. Sci. Ind. Res. India* **13B**, 546 (1954).

<sup>3</sup> R. HEGENAUER, *Chemotaxonomie der Pflanzen*, Vol. III, p. 145, Birkhauser Verlag, Basel (1964).