

## THE CONSTITUENTS OF SOME *HELICHRYSUM* SPECIES (FAMILY COMPOSITAE)\*

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*Helichrysum diosmifolium* (Vent.) Sweet is a much branched shrub up to 5 m high. It is common in the Sydney area, being usually associated with shale outcrops. Solvent extraction of the leaves yielded a mixture of crystalline acids which could be separated into ursolic acid (2.6%), morolic acid (3-hydroxyolean-18-en-18-oic acid) (0.025%), and 16 $\alpha$ ,17-dihydroxy-16 $\beta$ -(—)-kauran-19-oic acid (0.005%).

Ursolic acid is a very common naturally occurring triterpene. Morolic acid has been previously isolated from a saponin found in the heartwood of *Moru excelsa* Benth.,<sup>1</sup> from *Agauria salicifolia* Hook.,<sup>2,3</sup> from the bark of *Eucalyptus papuana* F. Muell.,<sup>4</sup> and from a saponin present in the stems of *Adina pilulifera* (Lour.) Franch.<sup>5</sup> 16 $\alpha$ ,17-Dihydroxy-16 $\beta$ -(—)-kauran-19-oic acid has been isolated from a *Beyeria* species<sup>6</sup> and from *Ricinocarpus stylosus* Diels.<sup>7</sup> It is of interest that similar tetracyclic diterpenes have recently been isolated from *Helichrysum dendroideum* N. H. Wakefield,<sup>8</sup> a small tree growing in south-eastern New South Wales and eastern Victoria.

*Helichrysum ramosissimum* Hook. yielded on diethyl ether extraction a dark gum from which the  $\gamma$ -pyrone, maltol (3-hydroxy-2-methyl-4H-pyran-4-one), could be sublimed out in 0.35% yield. No other pure compounds were isolated from the extract. The nuclear magnetic resonance spectrum of maltol in deuterochloroform exhibited a three-proton singlet at  $\delta$  2.38 (C-methyl); a pair of one-proton doublets at  $\delta$  6.43 ( $J$  5.5 c/s) and  $\delta$  7.72 ( $J$  5.5 c/s) was ascribed to the two olefinic hydrogens. A low, diffuse signal at  $\delta$  7.20 (1H) was ascribed to the hydrogen bonded hydroxyl. This compared well with published values.<sup>9,10</sup>

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Maltol has been reported to occur in the twigs of the larch (*Pinus larix* L.),<sup>11</sup> in *Corydalis ochotensis*,<sup>12</sup> in *Tsuga diversifolia*,<sup>13</sup> in several species of *Abies*,<sup>13</sup> and in *Evodiopanax innovans* Nakai.<sup>14</sup> It has also been found in roasted malt,<sup>15</sup> in coffee extract,<sup>16</sup> in dried skim milk,<sup>17</sup> in wood tar,<sup>18</sup> and amongst the products of the alkaline degradation of streptomycin.<sup>19</sup>

### Experimental

All melting points are uncorrected. Light petroleum had b.p. 40–60°. Infrared spectra were measured in Nujol mulls on a Perkin–Elmer Infracord 137 spectrophotometer. N.m.r. spectra were recorded on a Varian A60 spectrometer with tetramethylsilane as internal reference.

#### Extraction of the Leaves of *Helichrysum diosmifolium*

The whole leaves (635 g), collected from plants growing at Berowra, N.S.W., were de-waxed by dipping into warm, light petroleum. Evaporation of the solvent yielded some pale yellow wax (1 g). The de-waxed leaves were ground and extracted successively with light petroleum and chloroform in a Soxhlet apparatus. The light petroleum extract (2 l.) deposited a crystalline solid on cooling (3.4 g). Concentration of the filtrate to a smaller volume (c. 700 ml) resulted in the precipitation of an additional amount of solid (2 g). The filtrate yielded some oily material (13 g) on evaporation of the solvent. The combined solids were recrystallized (charcoal) from ethanol. The first crop of crystals consisted of crude morolic acid (0.16 g). Evaporation of the mother liquor to dryness yielded crude ursolic acid (4.8 g). Evaporation of the chloroform extract to dryness yielded a green solid (12 g). This was dissolved in diethyl ether and extracted successively with a saturated NaHCO<sub>3</sub> solution and a 5% NaOH solution. The NaHCO<sub>3</sub> extract yielded on acidification crude (I) (30 mg). The NaOH extract yielded more ursolic acid (11.5 g).

#### Characterization of the Compounds Isolated

**Morolic acid.**—Several recrystallizations of the crude acid from methanol yielded colourless needles of morolic acid, m.p. 175–176° (dec.),  $[\alpha]_D^{20} + 34^\circ$  (c. 1.0 in MeOH) (lit.<sup>20</sup> m.p. 273° (dec.),  $[\alpha]_D^{20} + 33^\circ$ ). It formed methyl morolate, m.p. 233–234° (lit.<sup>20</sup> 228–229°), acetyl morolic acid, m.p. 258–260° (dec.) (lit.<sup>20</sup> 256–257° (dec.)), and methyl morolate acetate, m.p. 263–264° (lit.<sup>20</sup> 263–264°). The identity of methyl morolate and of methyl morolate acetate was established by a mixed m.p. determination and by a comparison of the i.r. spectrum with that of the relevant authentic specimen.

**Ursolic acid.**—The crude acid could not be purified by repeated recrystallizations from methanol. However, it yielded methyl ursolate, m.p. 170° (lit.<sup>21</sup> 171°), acetyl ursolic acid, m.p. 287–289° (lit.<sup>21,22</sup> 285°, 296–297°), and methyl ursolate acetate, m.p. 248–249° (lit.<sup>21</sup> 248–248.5°). All three derivatives were found to be identical with authentic specimens (mixed m.p. and i.r. spectra).

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*16,17-Dihydroxy-16 $\beta$ -(—)-kauran-19-oic acid.*—Recrystallization from methanol yielded needles, m.p. 258–259° (lit.<sup>6,7</sup> m.p. 260–262°), mol. wt. 336 (mass spec.). A pyridine solution of the acid was laevorotatory, though the concentration was too low to allow an exact measurement (lit.<sup>6</sup>  $[\alpha]_D -88^\circ$  in pyridine). Its identity was established by a mixed m.p. determination and comparison of its i.r. spectrum with that of an authentic specimen.

*Extraction of Helichrysum ramosissimum*

The dried and ground plant (350 g), collected on the Nerang Highway, south Queensland (1st batch IC 2445, 2nd batch SN 7677), was extracted at room temperature with diethyl ether (10 l.). On removal of the solvent a dark, malodorous gum was obtained (21.4 g). On prolonged heating on the water-bath, maltol (II) (1.2 g) sublimed out. Recrystallization from diethyl ether yielded colourless, slender blades, m.p. 164–165° (lit.<sup>11</sup> 162–164°);  $\lambda_{\max}$  (EtOH) 277 m $\mu$ ,  $\log \epsilon$  3.92 (lit.<sup>19</sup>  $\lambda_{\max}$  274 m $\mu$ ,  $\log \epsilon$  3.92). The compound gave a deep purple colour with aqueous FeCl<sub>3</sub> solution. The benzoate of (II) crystallized in colourless needles from ethanol, m.p. 113.5° (lit.<sup>19</sup> 113°).

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