C_{24}-, C_{22}-, C_{20}- and C_{18}-Macrocyclic Lactones in Halictide Bees

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Macrocyclic lactones of extra large ring size were found to make up the major part of the Dufour gland secretion in females of two species of *Halictus* bees (Hymenoptera, Apidae). We have earlier described the identification of 16-hexadecanolide and 18-octadecanolide in two species of *Halictus* and 16-hexadecanolide, 18-octadecanolide and 20-eicosanolide in one species of *Colletes*.[1,2] Octadecanolide, eicosanolide and docosanolide have recently been identified in American *Halictus* bees by Hefetz *et al.*[3] In the present work the Dufour gland secretion of *Halictus rubicundus* (Christ.) from Kansas, USA and *Halictus leucaheneus arenosus* (Ebmer) from Öland, Sweden were analyzed. The main components in *H. rubicundus* were identified as 20-eicosanolide, 22-docosanolide and 24-tetracosanolide in the approximate proportions 2:3:1. *H. leucaheneus arenosus* was found to contain 18-octadecanolide, 20-eicosanolide, 22-docosanolide and 24-tetracosanolide in the approximate proportions 8:4:2:1.

Exaltolide and ambrettolide have long been known to occur in plants. The macrocyclic ketones muscone and civetone are known from the musk deer and the civet cat, respectively. The occurrence of these macrocyclic compounds, which are also used in the perfumery industry, were reviewed by Lederer.[4] To our knowledge the lactones described here represent the largest macrocyclic rings known from insects and the largest simple macrocyclic lactones so far identified from natural sources. The synthesis of macrocyclic lactones has been reviewed by Back.[5]

Several studies [6–9] suggest that the Dufour gland secretion may function in forming the hydrophobic cell lining in the nests of the bees. We believe [9] that its function could be a dual one. ω-Hydroxy acids present in the gland could both form hydrophobic polymers and also cyclize to form monomeric compounds suitable as marking pheromones. The smell of the abdominal secretions of the bees, when compared to the smell of reference compounds, indicates that the macrocyclic lactones are indeed present in it. Earlier [2] we have conducted direct inlet mass spectrometry on fresh Dufour gland secretion. Both the macrocyclic lactones and their corresponding ω-hydroxy acids were found in large amounts (1 mg quantity) in the secretion.

Experimental. Dufour glands were dissected, removed, and immediately placed in 200 μl of hexane for extraction. The chemical analyses were made with the help of GC–MS (LKB 2091) using a precolumn inlet system without split and capillary columns, 25 m long, coated with Silicone OV-101. The chemical identifications are based on mass spectra and capillary gas chromatographic retention values. 16-Hexadecanolide and 18-octadecanolide were available for comparison. The retention values for the (even numbered) macrocyclic lactones C_{16} to C_{24} on an OV-101 Silicone capillary column are $[(N+2)\times 100+94]\pm 2$ where N is the number of carbon atoms in the lactone. The retention value of docosanolide is thus 2494. The mass spectra show a fragmentation pattern typical for a long straight chain compound with $m/e=55$ as the largest peak. In the low mass region, small but significant fragments are present at $m/e=60$, 61 and 73 (10 to 20 % relatively intensity). Characteristic fragments in the region of high mass is M, M−18, M−46, (M−18−28) and M−60 (5 to 25 % relative intensity).

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