Chemical Composition of the Wing Gland and Abdominal Hair Pencil Secretions of the Male African Sugarcane Borer, *Eldana saccharina* (Lepidoptera: Pyralidae)

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In addition to the previously identified wing gland lactone, eldanolide, and the tail brush components, vanillin and *p*-hydroxybenzaldehyde, several further terpenoid compounds, saturated and unsaturated alcohols and acids, a thioalcohol, as well as two saturated macrocyclic lactones, were identified in the wing gland and tail brush secretions of the male African sugarcane borer *Eldana saccharina* (Walker).

The stalk borer *Eldana saccharina* Walker is found in a large number of natural host plants in Africa [1]. Since 1970 it has become an increasingly serious pest in South African sugarcane fields [2] and it is also a recognized pest of maize and other cereal crops in West and East African countries [3]. Male moths of this insect, in common with other gallerines, have a gland at the base of each fore wing with a duct opening towards the wing tip, as well as a pair of prominent hair pencils on the eighth segment [4, 5]. These disseminating structures are assumed to be involved in pheromone communication in *E. saccharina*. The possible use of the synthetic pheromones for monitoring and/or controlling the insect has led to considerable interest in the identification and synthesis of the pheromone secreted by the male moth. The γ-lactone, *trans*-3,7-dimethyl-6-octen-4-olide (eldanolide) was identified as a component of the wing gland secretion [6, 7] and several independent syntheses have been elaborated for the natural (3S, 4R) isomer [8–11]. It has been suggested [7, 12] that eldanolide acts as a long-range attractant of the female. Vanillin and *p*-hydroxybenzaldehyde have been found in the abdominal hair pencil or tail brush secretion and were reported to act as an aphrodisiac [13]. In these studies extensive use was made of laboratory methods for the evaluation of the biological activity of the compounds identified in the exocrine secretions of the male moth. In our hands, however, neither the synthetic compounds, nor extracts of the glands showed any activity in field tests. In these field tests, live males in control traps normally attracted many more males than females and in EAG experiments the antennae of live males and females were found to be approximately equally responsive towards the wing gland and the tail brush secretions [14].

In this communication we report the identification of an additional 14 compounds in extracts of the exocrine glands of *E. saccharina*.

Material was collected for analytical work from freshly emerged virgin males. The moths were anaesthetized with chloroform vapour, whereafter the wing glands were removed and extracted with dichloromethane (E. Merck, Residue Analysis Grade). By exerting slight pressure on the abdomen, the hairs of the hair pencils were extruded, removed with a pair of small scissors before the brushes were fully everted, and extracted with a small volume of dichloromethane. Gas chromatographic analysis (SE-30, glass capillary column, 40 m × 0.3 mm, film thickness 1.0 μm) of the resulting extracts of the wing gland and tail brush secretions produced gas chromatograms which revealed the presence of a considerable number of hitherto unidentified components. Low and high resolution mass spectrometric data obtained by EI and CI GC-MS analysis, ^{1}H and ^{13}C NMR of some of the preparatively isolated com-

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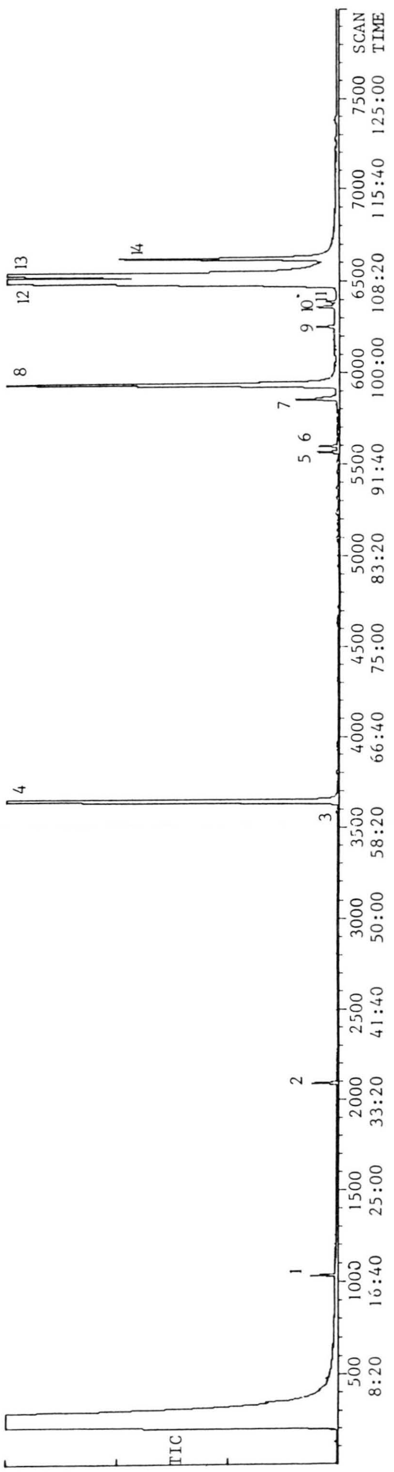


Fig. 1. Gas chromatogram (total ion current detection) of the wing gland secretion of the male African sugarcane borer, *Eldana saccharina*. Glass capillary column coated with SE-30 (40 m × 0.3 mm, film thickness 1.0 µm); 40–240 °C at 2 °C/min.

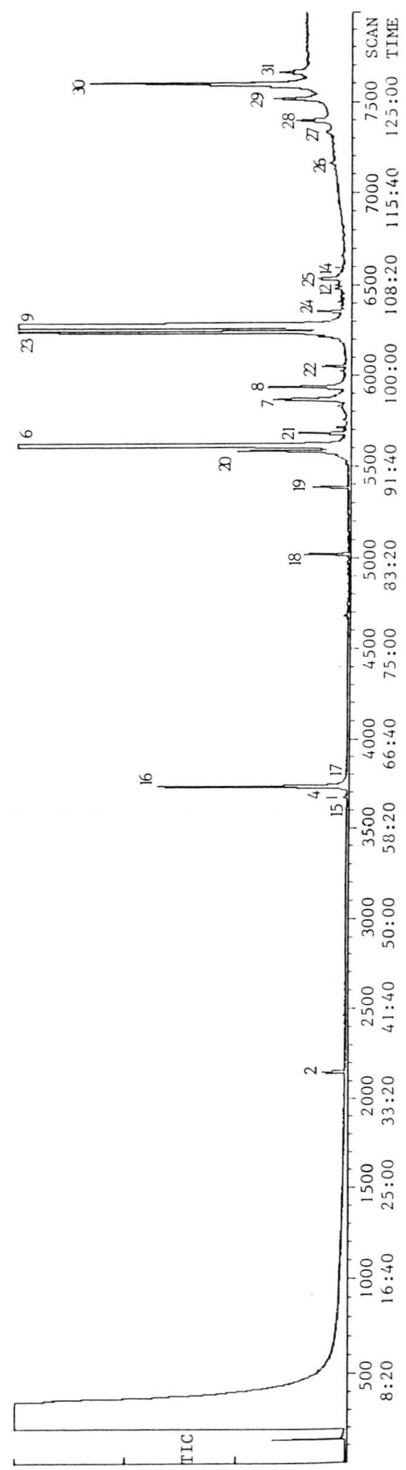
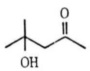
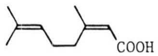
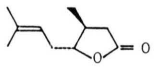
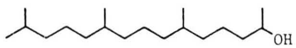
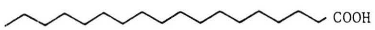


Fig. 2. Gas chromatogram (total ion current detection) of the abdominal hair pencil secretion of the male African sugarcane borer, *Eldana saccharina*. GC parameters as in Fig. 1.

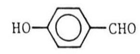
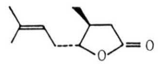
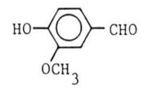
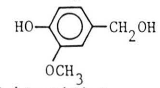
ponents, and comparison with authentic synthetic material, were employed to identify components in the exocrine secretions of male *E. saccharina* moths. Gas chromatograms (total ion current detection) of the wing gland and tail brush secretions are given in Figs. 1 and 2 respectively. The identified compounds are listed in Table I. Since considerable variations were observed in the quantitative composition of dif-

Table I. Compounds identified in the wing gland and abdominal hair pencil secretion of the male African sugarcane borer, *Eldana saccharina*. (a) Numbering as in Fig. 1; (b) numbering as in Fig. 2; (c) low resolution EI/MS; (d) high resolution EI/MS; (e) low resolution CI/MS; (f) ^{1}H NMR; (g) ^{13}C NMR; (h) retention time comparison with synthetic material.

Wing Gland Secretion

Constituent[a]	Compound		Amount (μg/male)
1		c,h	0.02
2	Unidentified		0.02
3		c,h	<0.01
4		c,d,f,g,h	1.2
5	Unidentified		0.02
6		c,h	0.01
7	$(CH_2)_{14}-C{=}O$ CH_2-O	c,h	0.1
8		c,h	1.1
9		c,h	0.01
10	Unidentified		0.03
11	Unidentified		0.04
12		c,h	2.0
13		c,h	1.0
14		c,h	0.3

Hair Pencil Secretion

Constituent[b]	Compound		Amount (μg/male)
2	Unidentified		0.02
15		c,h	<0.01
4		c,e,h	
16		c,d,e,f,g,h	0.8
17		c,e,h	<0.01
18	Unidentified		0.1
19	Unidentified		0.4
20	Unidentified		0.3
6		c,d,e,f,g,h	5.5
21		c,h	0.08
7	$(CH_2)_{14}-C{=}O$ CH_2-O	c,e,h	0.4
8		c,h	0.7
22	Unidentified		0.07
23		c,d,e,f,h	0.8
9		c,e,h	10.7
24		c,h	0.05
12		c,h	<0.01
25	$(CH_2)_{16}-C{=}O$ CH_2-O	c,h	0.3
14		c,h	<0.01
26	Unidentified		0.6
27	Unidentified M^{+}: 312	c,e	0.4
28	Unidentified M^{+}: 312	c,e	1.3
29	Unidentified M^{+}: 312	c,e	1.7
30	Unidentified M^{+}: 312	c,e	0.4
31	Unidentified M^{+}: 312	c,e	0.3

ferent batches of extracted material, the Figures in Table I are included only to give an approximate indication of the relative abundance of constituents in the wing gland and tail brush extracts.

Assignment of *Z* configuration to the double bonds in the unsaturated compounds was based on the comparison of the available spectroscopic and GC data with those of authentic synthetic compounds. Most of the compounds found in the secretions are commercially available or could be synthesized by simple one-step reactions from available starting materials. Silver oxide oxidation [15] of neral, for example, yielded (*Z*)-3,7-dimethylocta-2,6-dienoic acid (**3**) and catalytic hydrogenation of the aldehyde function of vanillin (**16**) with 5% Pt on carbon, using methanol as solvent, gave pure 3-methoxy-4-hydroxybenzyl alcohol (**17**). Perhydrogenation of farnesyl acetone (BASF, Ludwigshafen, G.F.R.) with the same catalyst and solvent gave 6,10,14-trimethyl-2-pentadecanol (**6**).

Eldanolide was synthesized from ethyl 3-methyl-4-pentenoate. By employing synthetic procedures elaborated by *i.a.* Uematsu *et al.* [9], this ester was converted to a mixture of diastereomeric *cis*- and *trans*-eldanolide isomers, from which pure *trans*-eldanolide (**4**) was isolated by preparative gas chromatography (10% SE-52 on Chromosorb WAW DMCS, 60–80 mesh, 14 m × 4 mm glass column). High concentrations of eldanolide were found in tail brush extracts of older males and it seems likely that this compound is transferred from the wing gland to the tail brush by the typical courtship behaviour of the male insect.

Component **2**, present in both the wing gland and tail brush extracts, has a mass spectrum practically identical to those of α-phellandrene and γ-terpinene, with a base peak and molecular ion at *m/e* 93 and 136 respectively. Gas chromatographic and mass spectral data clearly indicate that this component can only be a terpene, but it remained unidentified as no supporting evidence could be obtained by gas chromatographic comparison with a number of available terpenes with similar or slightly different mass spectra, such as the ocimene and allo-ocimene isomers. The tail brush secretion contains a group of five components (27 to 31 in Fig. 2) having the same molecular mass and similar mass spectra. It was found that component 30 could only be observed when using a capillary column that had not been subjected to more than about four injections of the tail brush extract. Further work to characterise these and the other still unidentified constituents of the exocrine secretions of this insect, and to determine the biological activity of the identified compounds, is being carried out.

Acknowledgements

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