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SPECIALIA

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Linalool from the cotton stainer *Dysdercus superstitiosus* (F.) (Heteroptera: Pyrrhocoridae)

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Summary. The isoprenoid linalool, together with several straight carbon-chain aliphatic materials, has been found in the scent glands of the cotton stainer *Dysdercus superstitiosus* (F.)

Within the Hemiptera – Heteroptera (land and water bugs), nearly 30 species in 10 families are known to produce glandular secretions consisting predominantly of hydrocarbons and carbonyl compounds[2,3]. These secretions are believed to serve in defence since they are produced when the insects are disturbed or irritated and are often directed towards the source of irritation[4]. Of over 80 species of Heteroptera whose metathoracic gland secretions have been analyzed, only a few species have been reported to produce monoterpenes[5–7]. The few reports of isoprenoid constituents in the scent oils are thus of great interest and deserving of further attention. Here we would like to report our findings that the isoprenoid linalool together with several straight carbon-chain aliphatic materials (hexanal,

Composition of the scent volatiles from adult metathoracic gland and larva posterior abdominal gland (5th instar) of *D. superstitiosus*

Scent gland						Identification	Mass-spectrum (m/z)
Metathoracic gland			Abdominal gland				
Peak No.	R.T.	% R.A.	Peak No.	R.T.	% R.A.		
-	-	-	**1**	0.8	2	Hexanal	EI 100(M^+), 82, 72, 56, 44 Cl 101(M+1), 82
1	1.6	44.6	**2**	1.7	6.5	Hex-2-enal	EI 98(M^+), 83, 69, 55, 41 Cl, 99(M+1), 85
-	-	-	**3**	4.6	16	Tridecane	EI 184(M+1), 101, 99, 85, 71, 57, 43 CI, 183(M-1), 141, 112, 85
2	2.7	3.3	-	-	-	Hexanol	EI 84(M-18), 73, 69, 55, 43 CI, 101(M-1), 84
(a)	6.6	1.5	-	-	-	Linalool	EI 154(M^+), 136, 121, 93, 80, 71, 69, 55, 41
3							CI 153(M-1), 137
(b)	6.8	47.9	**4**	6.7	16.6	Oct-2-2nal	EI 126(M^+), 108, 83, 70, 55, 41 CI 127(M+1), 109, 85
4	9.6	3.5	**5**	9.5	38	4-oxo-hex-2-enal	EI 112(M^+), 83, 55, 41 CI 113(M+1), 85
5	40.2	0.7	**6**	39.9	20.4	4-oxo-oct-2-enal	EI 140(M^+), 125, 111, 98, 83, 85 CI 141(M+1), 95, 80

Abbreviation: R.T., retention time; % R.A., percent relative amount; EI, electron impact; CI, chemical ionization; m/z, mass/charge.

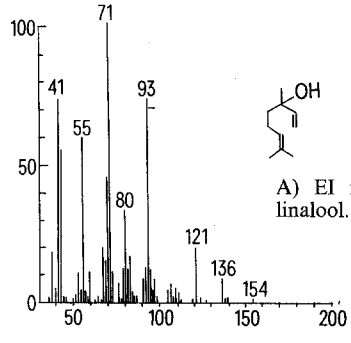
hex-2-enal, tridecane, hexanol, oct-2-enal, 4-oxo-hex-2-enal and 4-oxo-oct-2-enal) occurs in the scent gland of the cotton stainer *Dysdercus superstitiosus* (F.)

Method. A small collection of live *D. superstitiosus* from Nigeria was transported by air to Cardiff and there successfully maintained under laboratory conditions. Initially, a 1-gland test sample gas-chromatographic (GC) analysis of the scent materials was made from 1. the adult metathoracic gland, and 2. the larval (5th instar) posterior abdominal gland of *D. superstitious* for comparison with those of *Dysdercus intermedius* Distant and *Oncupeltus fasciatus* Dallas. The gas chromatograph used was a varian model 1400 gas chromatograph equipped with a flame ionization detector. The 180 cm glass column (i.d. 2 mm) was packed with OV 225 on 60–80 mesh gas chrom Q and was preceded by a 12 cm long glass precolumn (i.d. 4 mm). In each case the entire gland, still suspended in a droplet of saline to prevent collapse, was introduced into the precolumn by the wire coil spoon technique[8]. The chromatograph oven temperature was programmed at 10 °C/min from 80 to 200 °C with nitrogen flow rate at 30 ml/min. Chromatograms were numbered consecutively for purposes of identification and record storage. Comparison of retention times (R_t) of the various species and with reference compounds were made by co-injection under the same GC conditions.

The components of the scent glands were identified by combined gas chromatography-mass spectrometry (GC-MS). This was achieved by injecting a 10-gland sample in a minimum of saline into the spectrometer using the solventless wire coil technique as above. The Finnigan 4000 quadrupole mass spectrometer was equipped with a 9610 microprocessor gas chromatograph, INCOS real time data system (32K core) and Printronix data plotter. The GC oven temperature was programmed at 4 °C/min from 80 to 200 °C. Chemical ionization (CI) with methane as the reagent gas, source temperature 240 °C, and electron impact (EI) with source temperature 260 °C, were employed in the analysis of the scent materials.

Results. Figure 1 shows the GC traces obtained from the metathoracic and abdominal glands of *D. superstitiosus.* Comparison of the GC retention times with authentic samples indicated peak identities as follows: Figure 1A, metathoracic gland, (**1**) hex-2-enal; (**2**) hexanol; (**3**) a mixture of linalool (3,7-dimethyl-1, 6-octadien-3-ol, **3a**) and oct-2-enal, (**3b**); (**4**) 4-oxo-hex-2-enal; (**5**) 4-oxo-oct-2-enal; figure 1B, abdominal gland, (**1**) hexanal; (**2**) hex-2-enal; (**3**) tridecane; (**4**) oct-2-enal; (**5**) 4-oxo-hex-2-enal; (**6**) 4-oxo-oct-2-enal. The GC-MS studies carried out on both glandular volatiles under EI and methane CI conditions confirmed the assignments made by GC as shown in the table.

The identity of linalool in the metathoracic gland of *D. superstitiosus* was proposed chiefly from mass-spectral evidence. The EI-spectra obtained from peak **3** of the metathoracic gland indicated that it was a mixture of linalool and oct-2-enal. Peak area measurements indicated that these 2 compounds together accounted for about 50% of the volatile materials in the metathoracic scent gland of *D. superstitiosus.* Although the 2 compounds were difficult to resolve under our GC conditions, they were successfully resolved by mass-chromatography. This technique displayed the ions m/z methane CI, 153(M-1, 10%), 137(M-17, 100%) for linalool (fig. 2) and 127(M+1,72%), 109(100%), 85(35%) for oct-2-enal. Methane CI was used because linalool gives a very simple spectrum under these (CI)



A) EI mass-spectrum of authentic linalool. (Aldrich Chemical Co. Ltd.).

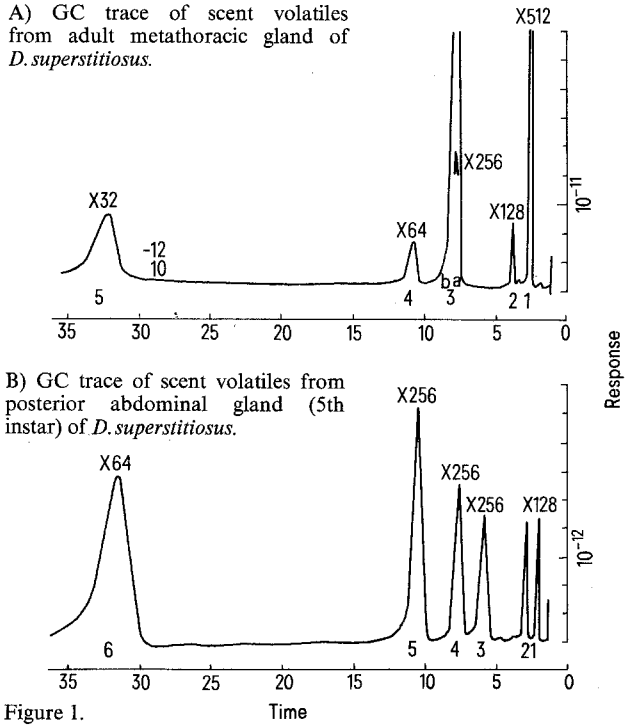
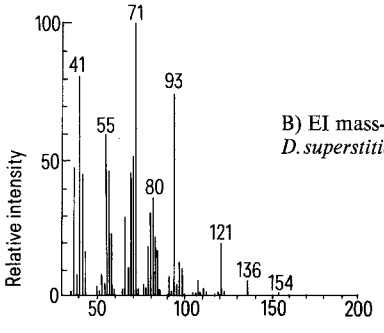
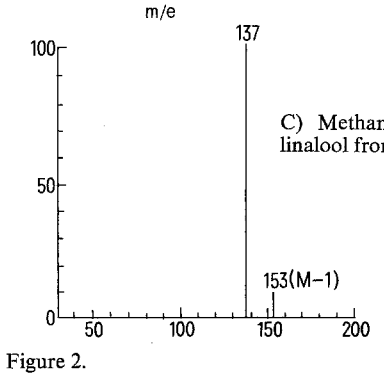


Figure 1.



B) EI mass-spectrum of linalool from *D. superstitiosus.*



C) Methane CI mass-spectrum of linalool from *D. superstitiosus.*

Figure 2.

conditions, consisting of $(M-1)^+$ m/z 153 as well as m/z 137 which is the base peak in the spectrum[9]. Neither of these 2 ions (m/z 153, 137) are present in the methane CI spectrum of oct-2-enal. Similar mass-chromatography carried out under EI conditions gave supportive evidence for the presence of linalool in *D. superstitiosus* as the EI-spectrum of the sample from the cotton stainer (fig. 2B) is virtually superimposable on that of authentic linalool (fig. 2A).

Linalool was not detected in the dorsal abdominal scent glands of the larvae of *D. superstitiosus*. It was absent from any other parts of the larvae and adult insect when examined under our GC-MS conditions; its production is evidently confined exclusively to the adult metathoracic scent gland. It was not found in either the metathoracic or the 3rd abdominal scent gland of *Pyrrhocoris apterus* L., which indicates that it is not universally present in the species of Pyrrhocoridae. The larval glands of *D. superstitiosus* were found to contain 4-oxo-oct-2-enal, 4-oxo-hex-2-enal, oct-2-enal, tridecane, hex-2-enal, hexanal but no linalool.

Discussion. Although it is produced by the cotton plant[10], it is considered unlikely that linalool from a dietary source is taken up preformed and accumulated in the metathoracic scent gland of cotton stainers. It is most probably produced by a conventional isoprenoid pathway in the tissue of the insect. We suggest that linalool has some unique role to play in the ecology of cotton stainers of the genus *Dysdercus*.

Possible roles for the scent volatiles of *Dysdercus* (defence, alarm, cannibal, aggregating and sex attractant behaviours) have been suggested[6,11].

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The composition of Taft E_s^o constants: An application of biased alternatives to least squares

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Summary. A systematic analysis of the composition of E_s^o like rate constants clearly revealed that Taft E_s^o-values depend upon the size of the substituents. Further evidence in favor of this view is adduced even in a case where OLS led to the conclusion that E_s^o should be completely independent of the size of the substituents, since biased estimators (PCRA, LRRA) showed that this statement is not correct. Furthermore, it seems that the magnitude of the steric effect represented by E_s^o is a function of the thickness of the substituent along 2 directions perpendicular on its main axis and is not influenced by its length.

An essential prerequisite of every quantitative approach to biological structure-activity (QSAR) or chemical structure-reactivity (LFER) relationships is the development of reliable substituent constants. According to Verloop, Hoogenstraaten and Tipker[3], the development of steric substituent constants is still in its early stages. The steric substituent constants E_s^o have been defined by Taft[4] on the basis of the acidic hydrolysis and esterification of ortho substituted benzoates and benzoic acids, respectively. In 1969, Charton[5] reexamined E_s-values for aliphatic and aromatic systems and concluded that the aliphatic E_s-values are linear functions of the corresponding van der Waals radii r_v, whereas E_s^o should not in any way depend upon the substituent's size. However, it has been demonstrated recently that the interpretation of Taft E_s^o constants in terms of predominating inductive, mesomeric, and steric contributions depends at least partly upon the sample structure, although in nearly all cases about 80% of the variation of E_s^o could have been accounted for by the van der Waals radius[6]. Furthermore, the independent variables used in such correlations are often multicollinearly related, a fact from which a lot of problems may arise if an interpretation is intended. In order to reduce the uncertainty associated with the magnitudes and even the signs of the regression coefficients if multicollinearity is present in the data, the application of biased estimators[7-11] may be preferable. Our work was directed towards further clarifying the meaning of E_s^o in terms of inductive, mesomeric, and steric influences. In order to keep the problems of interpretation to a minimum, solvent effects onf E_s^o have been disregarded and, furthermore, instead of E_s^o the rate constants of the basic reactions: a) esterification of benzoic acids by methanol/HCl at 25 °C and 40 °C[12,13] and b) esterification of

Table 1. Some measures of the steric substituent effect[a]

Group	z_1	E_s(corr.)	E_s^o
H	0.2223	0.79	–
F	0.3300	0.42	0.49
I	−0.5054	−0.74	−0.20
OMe	0.9819	0.34	0.99
OEt	0.9146	0.29	0.90
Me	−0.3459	0.00	0.00
NO_2	−1.2447	−0.87	−0.75
Br	−0.2716	−0.42	0.00
Cl	−0.0811	−0.17	0.18

[a]For notations and references see text.