Secretion of the Metathoracic Glands of the Waterbug *Notonecta glauca* L. (Heteroptera; Notonectidae)

Odoriferous glands, so called because of the frequently odoriferous nature of the materials they produce, are of widespread occurrence in the Heteroptera. Where present the glands lie dorsally in the abdomen of the nymphs, ventrally in the metathorax of the adults; they are found in both terrestrial and aquatic representatives of the Heteroptera.

Analyses of the secretions from some aquatic representatives of this group have already been reported. The odoriferous secretion of the male belostomatid, *Belostoma indica* Vitalis, is a mixture containing *trans*-hex-2-enyl acetate and *trans*-hex-2-enyl butyrate, and is thought to function as a sex pheromone[1,2]. The secretion of the corixids *Sigara falleni* (Fieb.) and *Corixa dentipes* (Thoms.), on the other hand, is neither sex or species specific, and contains *trans*-4-oxohex-2-enal as major (> 95%) constituent[3,4]; this material has also been reported[5] as a minor (ca. 7%) constituent of the secretion of a terrestrial bug, the pentatomid *Nezara viridula* var. *Smaragdula* (F.). Quite unlike the adult secretion of Corixidae, that of the naucorid *Ilyocoris cimicoides* (L.), is a colourless and odourless liquid containing *p*-hydroxybenzaldehyde and methyl *p*-hydroxybenzoate as major constituents[6]. These same chemicals, it is interesting to note, have been reported[7] in the pygidial glands of several water beetles, belonging to the Dystiscidae. We now report that *p*-hydroxybenzaldehyde and methyl *p*-hydroxybenzoate are major constituents of the secretion from the metathoracic glands of the waterbug *Notonecta glauca* L., a representative of the Notonectidae.

The secretion from the metathoracic glands of *N. glauca* consists of brown liquid droplets suspended in a clear fluid. It is discharged to appear externally as a pair of irregular droplets each one lying on a slit-like opening between the mesothoracic epimeron and metathoracic episternum of each side; there is no visible difference between the male and female secretions. The secretion is discharged on anaesthetizing the insects with carbon dioxide, and can be collected conveniently with a fine capillary pipette.

The secretion has no perceptible odour, unless warmed when a distinct phenolic odour is detected. Gas liquid chromatographic (GLC) analysis (5% SE-30; 100°) of the secretion, in acetone solution, showed the presence of 2 components in the approximate ratio 7:3. Male and female secretions contained the same components in the same proportion. The retention time of the first eluted component was found to be indistinguishable from that of authentic *p*-hydroxybenzaldehyde, the retention time of the second eluted component to be indistinguishable from that of authentic methyl *p*-hydroxybenzoate. GLC also showed that the secretion of *N. glauca* was indistinguishable from that of *I. cimicoides*.

A mass spectrum of the secretion from *N. glauca* was identical to that of a composite spectrum of *p*-hydroxybenzaldehyde and methyl *p*-hydroxybenzoate. The spectrum showed 2 parent ions at m/e 152 and m/e 122 corresponding to the methyl ester ($C_8H_8O_3$ requires 152) and aldehyde ($C_7H_6O_2$ requires 122) respectively. A strong peak at m/e 121 corresponded to the hydroxybenzoyl cation ($HOC_6H_4\overset{+}{C}O$) by loss of H from the aldehyde, and $-OCH_3$ from the methyl ester. This ion further fragmented to the hydroxyphenyl cation m/e 93 (–CO; metastable peak 71.5), and then to ions corresponding to m/e 65 (–CO; metastable peak 45.4) and m/e 39 (–HC≡CH). The absence of a peak at m/e 120, corresponding to a P–CH_3OH fragment ('*ortho*-effect'; see ref. [8]) excluded the possibility of an *ortho* relationship in the methyl hydroxyester.

A proton nuclear magnetic resonance (NMR) spectrum of the secretion from 50 insects was obtained in deuteriochloroform; the spectrum was scanned repetitively with a computer of average transients, using TMS as trigger. This showed 2 singlets at τ 0.12 (–C*H*O) and τ 6.10 (–CO·OCH_3) and 2 groups (area 1:1) of 3 lines (separation 9 cycles) centred at τ 2.1 and τ 3.05. These are assigned to aromatic protons and each group of lines consists of a pair of overlapping doublets (J = 9 c/sec), the 6 lines making up 2 overlapping A_2B_2 systems. The separation (9 c/sec) within each double doublet is correct for *ortho*-coupling and the splitting pattern defines the substitution in the aromatic rings as *para*. An NMR-spectrum of an authentic mixture of *p*-hydroxybenzaldehyde and methyl *p*-hydroxybenzoate was completely superimposable (up to τ 7.0) on that of the secretion. *p*-Hydroxybenzaldehyde showed τ 0.12 (singlet, 1H), 2.19 (doublet, J = 9 c/sec, 2H), 3.05 (doublet, J = 9 c/sec, 2H), and methyl *p*-hydroxybenzoate showed τ 2.05 (doublet, J = 9 c/sec, 2H), 3.16 (doublet, J = 9 c/sec, 2H), 6.10 (singlet, 3H). The NMR-spectrum of the secretion showed an additional strong signal at τ 7.98 (–COCH_3?) and a broad peak at τ 8.25, suggesting that the secretion may also contain volatile ketonic derivatives; this is being investigated further.

The secretion showed an UV-absorption maximum (95% EtOH) at 270 nm (authentic *p*-hydroxybenzaldehyde showed a maximum at 268 nm and methyl *p*-hydroxybenzoate one at 259 nm) and principle IR-bands at 3240 (O–H, polymeric), 2810, 2740 (C–H, aldehyde), 1710 (C=O, aryl ester), 1685 (C=O, aryl aldehyde), 1606, 1590 (C=C, aromatic), and 850 cm^{-1} (*p*-substituted benzene). The IR-spectrum was similar to that of an authentic mixture of *p*-hydroxybenzaldehyde and methyl *p*-hydroxybenzoate.

To our knowledge the function of the secretions of these waterbugs has not been investigated. SCHILDKNECHT has suggested[7] that the function of the pygidial glands of Dystiscidae is to protect the insects against microorganisms, and a similar function could be ascribed to the metathoracic glands of waterbug imagines. The imagines of waterbugs should provide excellent material for testing this suggestion experimentally.

Zusammenfassung. Im Geruchssekret der Wasserwanze *Notonecta glauca* L. wurden *p*-Hydroxybenzaldehyd und *p*-Hydroxybenzoesäuremethylester eindeutig nachgewiesen. Daneben finden sich noch nicht identifizierte Stoffe ketonischer Natur.

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