Presumed Sex Pheromone from Androconial Glands of Male Cotton Harlequin Bug *Tectocoris diophthalmus* (Heteroptera; Scutelleridae) Identified as 3,5-Dihydroxy-4-pyrone

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3,5-dihydroxy-4-pyrone (Rubiginol) has been identified as a presumed sex pheromone from the cotton harlequin bug *Tectocoris diophthalmus* (Thunberg). It accumulates as a temporary crystalline deposit in the male adult on the external surface of the androconial glands which occur in three pairs on abdominal sternites IV to VI.

Introduction

The chemistry and biology of sex pheromones in heteropteran insects is a largely unexplored field although recent progress in the manipulation of populations of a predaceous bug [*Podisus maculiventris* (Say)] and its parasitoids by an attractant formulation based on the composition of a male produced pheromone has been reported [1]. The numerous secretory units in the abdominal sternites in the males in many pentatomoid bugs supply a probable source of sex pheromonal materials [2]. Clearly delimited glandular patches are to be seen on the ventral surface of the abdomen in some scutellerid bugs [3]. The patches contain numerous secretory units each one comprising a secretory cell and an epicuticular bristle-like structure set in a socket [3]. They will be called here androconial glands after Carayon [3] who likened them to the scent scales (androconia) to be found on the wings of the males in certain lepidopterans. In the cotton harlequin bug *Tectocoris diophthalmus* (Thunberg) three pairs of androconial glands are present on the abdominal venter on sternites IV to VI (Fig. 1). The white deposit at times to be seen coating the external surfaces of these glands [3, 4] is apparently extruded through

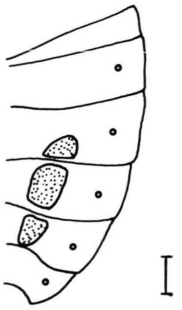

Fig. 1. Left-hand side of abdomen of male *T. diophthalmus* adult showing the position of the androconial glands (stippled) on sternites IV, V and VI. Scale line = 1 mm.

openings created by basal rupture of the individual androconial elements [3]. It can be removed when a new deposit may be formed [4]. We have been able to collect samples of this extruded material from *T. diophthalmus* from Queensland in Australia and are now able to report that it consists of a rarely recorded metabolite, 3,5-dihydroxy-4-pyrone, or Rubiginol [5].

Material and Methods

T. diophthalmus adults were collected from their host plants within Malvaceae (*Hibiscus* spp., *Lagunaria patersonii*) in the grounds of the Mt. Cootha botanical gardens and elsewhere (Redcliffe) in

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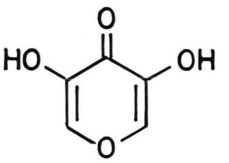
the area of Brisbane, Australia. In the laboratory they were maintained for a while on cuttings obtained from suitable host plants. The crystalline androconial deposit was removed from male bugs using a stainless steel needle. In one individual a renewal of deposit occurred overnight. Curiously, a uniform deposit of secretion on all three pairs of androconial glands was never seen.

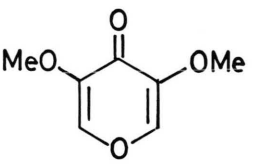
The melting point data was obtained with a Kofler hot-stage melting point apparatus. Electron impact (EI) mass spectra were recorded using an A.E.I. MS 902 mass spectrometer at 70 eV. For positive ion chemical ionization (CI) mass spectrometry, methane was used as reagent gas. The ^{1}H-NMR spectrum was recorded at 250 MHz in deuteriochloroform using a WM-250 Bruker instrument. A KBr disc was used to obtain the infrared (IR) absorption spectrum of the material. The ultraviolet (UV) absorption spectrum was recorded in ethanol.

Results

Examination of the androconial secretion under the microscope on the hot stage of the melting point apparatus revealed that it consisted of fine colourless needles. Upon heating, the sample eventually sublimed leaving no discernible residue. On the open hot stage sublimation occurred at 127–128 °C; under a coverslip the sublimation temperature of the deposit was raised to 135–139 °C. Within a sealed tube the melting point was found to be 198–199 °C, when some yellowing of the sample occurred. The high resolution EI mass spectrum indicated a probable molecular ion at *m/z* 128.01098 (base peak, 100%), corresponding to a molecular formula of $C_5H_4O_4$ (M required, 128.01098). The correctness of the molecular formula was confirmed by the CI mass spectrum which showed only *m/z* 129, corresponding to $C_5H_5O_4^+$ (i.e. M +1). The high resolution EI mass spectrum also showed prominent fragment ions at *m/z* 100.01806 (10%; $C_4H_4O_3$, M–CO), 71.01297 (26%; $C_3H_3O_2$), 54.01115 (32%; C_3H_2O), 53.00375 (27%; C_3HO) and 42.01042 (15%; C_2H_2O). The fragmentation pattern indicates that three of the oxygen atoms in the molecule could be contributing to the carbonyl groups of a trione or ketoaldehyde rather than to carboxylic acid, lactone or anhydride functions. The ^{1}H-NMR spectrum showed only two resonances, a sharp singlet at δ 7.92 and a broad singlet at δ 6.18 in a 1:1 ratio.

The structural possibilities for a molecular formula of $C_5H_4O_4$ are limited. Only one, 3,5-dihydroxy-4-pyrone (Rubiginol), seemed consistent with the foregoing data (I).





Rubiginol was recorded in Nature first as a product of the oxidative degradation of glucose by the bacterium *Gluconobacter liquefaciens* [5]. It has been found since in other bacterial systems [6]. Elsewhere it has been recorded as an oxidation product from cellulose [7] and among other combustion products in Tobacco smoke [8]. The trivial name, Rubiginol, describes the reddish colour seen in the first sample to have been isolated from a natural source [5], but the pure material is evidently a whitish colour.

Further confirmation of identity of Rubiginol from *Tectocoris* was supplied by melting point (198–199 °C), UV absorption spectrum (λ max 253 and 293 nm), and IR absorption spectrum (strong absorptions at 3320, 1594, 1572, 1198, 1085 and 872 cm^{-1}) in comparison with published data (6,7). A melting point of 133–134 °C for the diethyl ether (II) (M^+ 156.04132 corresponding to $C_7H_8O_4$) prepared by treatment of the *Tectocoris* Rubiginol with ethereal diazomethane was close to the published value (135 °C) for this derivative [7].

Discussion

A sexual function for the secretion from the androconial glands of the males of *Tectocoris* has been proposed [3]. It is possible that during courtship, release and transference of secretion occurs when the androconial glands of the male brush against the body of the female [3]. Rubiginol or perhaps some other as yet undetected component of the androconial secretion presumably exerts a physiological action on the female as an aphrodisiac. Perhaps a visible deposit of Rubiginol is to be found as a rule only on those males that have been unable to locate a female. We hope that this work will lead to an even-

tual solution to the problem of the biological significance of androconial glands in Scutelleridae.

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