γ-Butyrolactone from the Black Stink Bug: *Aethus indicus* Westwood (Hemiptera: Pentatomidae)

T. O. Olagbemiro, M. N. Khan, and A. Mohammed

Department of Chemistry, Bayero University, P. M. B. 3011, Kano, Nigeria

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The volatile constituents of the black stink bug, *Aethus indicus* Westwood (Hemiptera: Pentatomidae) from Nigeria has been examined by combined gas chromatography-mass spectrometry. γ-Butyrolactone along with with several straight carbon-chain aliphatic materials have been identified in the scent gland complex.

In recent years, increasing interest in the role of chemicals in communication among insects has led to numerous studies of arthropod defensive secretions [1–4]. Particular interests have been shown in the pentatomid bugs which discharge a disagreeable scent that is believed to include unsaturated aldeyhdes as the characteristic component. Since ants were apparently repelled and paralyzed by it, this scent has been considered a "defensive substance" [5, 6]. The scent has also been described as an "alarm pheromone" because it was observed that dispersion of bug aggregates occurs following scent discharge of some of its own kind [7]. Studies of the chemical composition of the secretion of some stink bugs have shown the presence of alkanes, alkenyl acetates, alkenals and alcohols which are used as defensive substance [1, 2]. Our present paper reports on the chemical composition of the secretion from a previously unstudied pentatomid bug, *Aethus indicus*, *indegenous* to the Northern part of Nigeria.

Table I displays the result of the gas chromatography (GC) obtained from the metathoracic scent gland extracts of *Aethus indicus*. Comparison of the GC retention times with authentic samples indicate peak identities as follows: Hex-2-enal, dodecane, tridecane, oct-2-enyl-acetate, 4-oxo-oct-2-enal, γ-butyrolactone, and pentadecane. The table also exhibits the result of the GC-MS studies carried out on the metathoracic scent gland extracts of the stink bug. This result confirms the assignment made by the GC as shown in the table. Furthermore, a comparison of the GC retention times (R_f) as well as the mass spectral values (electron impact and chemical ionization) of a synthetic sample of γ-butyrolactone with that found in *Aethus indicus* was made. The R_f values as well as the mass spectral data of these separate samples were identical and superimposable.

All scent volatiles identified in Table I except γ-butyrolactone, have been previously reported in the glandular secretions of several pentatomids [1, 2, 8]. The amount of each component however varied between individual species of insects.

Although straight chain aliphatic esters have been reported among the members of this family, to our knowledge no cyclic ester (lactone) has been previously observed [3]. Lactones have in general been characterized as exocrine products of cockroaches, beetles, phasmids, ants and bees. Indeed, several of these lactones *i.e.* allomones such as γ-decalactone and δ-decalactone from *Trigona carbonaria* [9], δ-dodecalactone from pygidial glands of *Bledius mandibularis* [10], iridomyrmecin from the anal glands of workers of *Iridomyrmex humilis* [11], are unique compounds whose defensive roles in these insects have been successfully demonstrated. It is therefore suggested that γ-butyrolactone might play similar unique roles in the defensive and chemical ecology of *Aethus indicus*.

Materials and Methods

The insect, *Aethus indicus*, 8,500 of them, were collected on the campus of Bayero University, Kano, Northern Nigeria, using light traps, and were killed by immersion in chromatoquality methylene chloride. The metathorax was removed and extracted with a fresh portion of methylene chloride. A concentrated sample of the extract was examined first on a Varian 1400 gas chromatograph equipped with a flame ionization detector. The 180 cm glass column was packed with 3% OV 225 on 60–80 mesh gas chrome Q. The chromatograph oven temperature was programmed at 10 °C/min from 80 to 100 °C with nitrogen flow rate at 30 ml/min. Chromatograms were numbered consecutively for purposes of identification and record storage. Comparison of retention times of scent volatiles

Reprint requests to Dr. T. O. Olagbemiro.
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Table I. Composition of the scent volatiles from adult metathoracic gland of adult of *Aethus indicus*.

Peak No	R. T.	%R. A.	Identification	Mass-Spectrum *m/z*
1	1.9	8.4	hex-2-enal	EI 100(M^+), 82, 72, 56 CI 101(M + 1), 82, 55
2	3.8	15.3	dodecane	EI 170(M^+), 141, 127, 113, 71 CI 169(M − 1), 155, 85
3	5.2	30.5	tridecane	EI 184(M^+), 101, 99, 85, 71, 57 CI 183(M − 1), 141, 111, 85
4	6.3	0.6	pentadecane	EI 212(M^+), 99, 85, 71, 57 CI 211(M − 1), 155, 113
5	7.2	6.3	oct-2-enyl acetate	EI 198(M^+), 128, 85, 57, 43 CI 199(M + 1), 128, 71
6	9.11	18.5	4-oxo-oct-enal	EI 140(M^+), 125, 111, 98, 85, 57 CI 141(M + 1), 95, 93
7	9.5	8.1	γ-butyrolactone	EI 86(M^+), 56, 42 CI 87(M + 1)
8	11.2	5.2	pentadecane	EI 212(M^+), 99, 85, 71, 57 CI 211(M − 1), 155, 113
9	12.5	3.3	unknown?	EI 110(M^+), 95, 81, 54 CI 111(M + 1), 83

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

with reference compounds were made by co-injection under similar GC conditions.

The component of the scent glands and synthetic γ-butyrolactone were identified by combined gas chromatography-mass spectrometry (GC-MS). The analysis was performed on a Finnigan 4000 quadrupole mass spectrometer equipped with a 9610 microprocessor gas chromatography, INCOS real time data system (32 K core) and Printonix data plotter. The gas chromatograph oven temperature was programmed at 4 °C/min from 8 to 200 °C. Chemical ionization (CI) with methane as the reagent, source temperature 240 °C and electron impact (EI) with source temperature 260 °C, were employed in the analysis of the scent materials and synthetic products. γ-Butyrolactone was produced from succinnic anhydride by the method of Bailey and Johnson [12].

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