Volatile secretions of *Zonocerus variegatus* (L) (Orthoptera : Pyrgomorphidae)

A. WADA, A.E. ODE AND T. O. OLAGBEMIRO*

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

(Received 26th July 1981)

Introduction

The grasshoppers *Zonocerus variegatus* belong to the order orthoptera (Family - Pyrgomorphidae), and can be recognized not only from their variegated colours of yellow and black but also from the characteristic acrid smell which is their sole defence against predators.[1] They are distributed all over tropical and South Africa and causes considerable damage to a veriety of crops. In Nigeria it is an economically important insect as it feeds on various crops including cotton, cassava, maize, yam, millet, guinea corn, cow-pea, sugarcane, cocoa, kola, banana, citrus, oil-palm, castor oil plant and leafy vegetables.[1]

Like several other orthopteran species, *Z. variegatus* exhibits aggregation behaviour and it is often seen in groups or large numbers like locust. This aggregation is probably mediated by phermones as has been observed in the cockroach, cricket, locust and bees.[1,3,4] However, unlike other insect orders, very few orthopteran pheromones have been chemically identified. A variety of aromatic compound as well as an allenic ketone has been identified from the grasshopper Romalea.[5] To date, no phermone has definitely been identified for this variegated grasshopper.

Consequently, we have utilized the technique of combined gas-chromatography - mass spectometry to study the volatile extracts of the adult male and female *Z. variegatus* which are pests to agricultural produce in tropical Africa to elucidate the chemical composition of its secretion, in order to give a clue as to their pheromonal roles.

Experimental

The grasshopper used in this investigation, about 5,000 females and 10,000 males were caught in June, on an agricultural farm at Kadawa, a village sixty (60) kilometers south of Kano, Kano State, Nigeria. They were caught alive using net trappings and were stored immediately in methylene chloride (dichloromethane), then kept in a freezer prior to analysis:

Both male (10,000) and female adults (5,000) were extracted separately and in batches using chromatoquality methylenechloride. The separate solvent extracts were dried over sodium sulphate and a small sample of each sex of insect was examined first on the Varian 1400 gas chromatography equipped with a flame ionizaiton detector and a glass column packed with 3% OV 225 on 60-80 mesh Gas Chrom Q. Analysis were carried out under two different conditions 1) oven temperature 80°C with Nitrogen flow rate at 30lb/in^2. and 2) oven temperature 80°C with Nitrogen flow rate at 20lb/in^2. A final analysis of the volatiles was performed on a Finnigan 4000 quadrupole mass spectrometer equipped with a 9610 microprocessor gas chromatogram, INCOS real time data system (32K core) and printonix data plotter. The gas chromatograph oven temperature was programmed between 80-320°C using an OV 225 packed column. Chemical ionization (CI) with methane as the reagent gas, source temperature 300°C and electron impact (EI) with source temperature, 280°C, modes were employed in the analyses of the scent materials.

Results and Discussion

Abbreviation: R.T., Retention time; R.A., Relative amount (%); M.W., Molecular weight; CI, Chemical ionization, EI, Electron impact; m/s (%), mass/charge

(% relative peak intensity).

From the mass spectral analysis of the extracts of the scent volatiles of *Z. variegatus* we obtain the following mass spectral data:

MALE ZONOCERUS

PEAK 1. (R.T., 44.3; R.A., 89.3). M.W., 312 m/s CH_4 CI 313 (M+1, 100), 97(27), 83(37).
m/s EI 312 (M+, 15), 281(9), 253(10), 239(30), 125(45), 111(18), 97(80), 85(60), 73(100).
Proposed identity - Methyl nonadecanoate.

PEAK 2. (R.T., 46.25; R.A., 3.5). M.W., 326
m/s CH_4 CI 327(M+1, 100), 281(10), 87(11).
m/s EI 326(M^+, 11) 281(8), 139(4), 125(13), 111(35), 97(10), 87(100), 85(45), 83(10).
Proposed identity - Ethyl nonadecanoate.

PEAK 3. (R.T., 48.7; R.A., 2.4). M.W., 172.
m/s CH_4 CI 173(M+1, 100), 127(20), 85(35).
m/s EI 172(M^+, 8), 128(20), 125(18), 113(6), 111(21), 99(8), 97(26), 85(100).
Proposed identity - Decanoic acid.

PEAK 4. (R.T., 51.3; R.A., 4.7). M.W., 424
m/s CH_4 CI 425(M+1, 25), 324(80), 312(40).
m/s EI 311(M-114,6) 298(7), 285(16), 222(15), 212(18), 193(16), 149(22), 135(30), 131(35), 117(40), 103(45).
Proposed identity - Unknown.

FEMALE ZONOCERUS

PEAK 1. (R.T., 37.0; R.A., 88.9). M.W., 270.
m/s CH_4Cl 271(M+1, 100), 243(6), 225(12), 101(5), 88(13).
m/s El 270(M^+,5), 241(3), 227(6), 157(10), 143(4), 115(8), 101(51), 88(100), 74(8), 60(50), 45(60).
Proposed identity - Ethyl pentadecanoate.

PEAK 2. (R.T., 39.4; R.A., 8.9) M.W., 284.
m/s CH_4Cl 285(M+1, 100) 239(14), 145(19), 85(50).
m/s El 284(M^+, 6), 215(12), 238(15), 157(5), 101(50), 88(100), 83(40), 60(35), 45(80).
Proposed identity - Ethyl hexadecanoate.

PEAK 3. (R.T., 49.5; R.A., 2.8). M.W., 438.
m/s CH_4Cl 439(M+1, 80), 356(10), 175(40)
m/s El 438(M^+, 5), 326(4), 312(6), 298(10), 286(11), 216(5), 212(11).
Proposed identity - Unkown.

Each compound identified above matched spectra on file in the computerized mass spectral search system, and were varified further by column chromatographic separation and comparison with authentic samples. Attempts to provide structures for the compounds responsible for m/s 424 and m/s 438 in both the male and female zonocerus respectively were unsuccessful, although the spectral patterns indicate both compounds may be high molecular weight alkanes.

Although pyrrolizidine alkaloids have been reported in *Zonocerus variegatus*,[6] the compounds methyl nonadecanoate, ethyl nonadecandate, decanoic acid, ethyl pentadecanoate and ethyl hexadecanoate have not been previously reported in this insect order. The use of esters as pheromones is not uncommon in many insect orders, and since *Z. variegatus* are well noted for their aggregation behaviour, the possible utility of these esters for this pheromonal role cannot be overlooked. Whether it is the male or female secretion or a combination from both sexes is utilized for this purpose is uncertain. This study is currently under investigation.

Acknowledgement

We are grateful to the Bayero University Research and Higher Degrees Committee for financial support; Dr. Oba Oyidi, Institute of Agriculture, Ahmadu Bello University, Zaria, Nigeria for helpful suggestion; and to the Department of Chemistry, University College, Cardiff, Wales, U.K. for allowing us time on their gc-ms.

References

1. O. Oyidi, The variegated grasshopper, *Zonocerus variegatus* (ORTHOPTERA: Pyrgomorphidae). Samaru Agric. Newsletter **16, N0. 3**, 86 (1974).

2. W.W. Page, J.R.W. Harris, A. Youdeowei, Defoilation and consequent crop loss in cassava caused by the grasshopper *Zonocerus variegatus* (ORTHOPTERA: Pyrgomorphidae) in southern Nigeria. **Bull Ent. Res., 70,** 151 (1980).
3. J.G. MacConnell, R.M. Silverstein, Recent results in pheromone chemistry; *Angew. Chem. Internat. Ed.,* **12,** 644 (1973).
4. T. Kauffmann, Observation on aggregation, migration and feeding habits of *Zonocerus variegatus* in Ghana (ORTHOPTERA: Acridoidae). *Ann. Ent. Soc. Amer.,* **58,** 426 (1965).
5. J. W. Wheeler, Insects and Mammalian pheromones *Lloydia,* **39,** 1 (1976).
6. E. Bernays, J. A. Edgar, M. Rothschild, Pyrrolizidine alkaloids seqestered and stored by aposmatic grasshopper *Zonocerus variegatus.* J. Zool. Lond., **182,** 85 (1977).