Compounds 38617, 38650, and 38694 were ineffective even at the 0.5% level. A phytotoxic response was noted at the 0.5% level in only 2 of the materials, 20702-c and 36313.

Although little can be said concerning structure-activity relationships among these compounds, the results suggest that the presence of a methoxy group ortho to the THP group considerably increases the activity of the THP ether of unsubstituted phenol (36235). Even greater improvement is obtained by the presence of a dioxymethylene group on the phenol molecule. Suprisingly, though the THP ether of 3,4-methylenedioxybenzyl alcohol (20702-c) is not derived from a phenol, it proved to be one of the most effective compounds in this series. It was noted that, though the THP ethers of 2-hydroxybenzaldehyde and of 2-hydroxy-5-methoxybenzaldehyde are not effective at either concentration, the THP ether of 2-hydroxy-4-methoxybenzaldehyde is highly effective even at the 0.1% level.

These data add to the numbers of materials which are promising as feeding deterrents for striped cucumber beetle[5]. As the beetle is a significant problem on cucurbits due to both its feeding and transmission of disease, an effective antifeedant would be an attractive alternative to present control tactics.

1 Mention of a proprietary product in this paper does not constitute an endorsement of this product by the USDA.
2 Acknowledgments: We thank C. Harding for assistance with the synthesis and N. Tromley for assistance with the bioassays.
3 Schoonhoven, L.M., Ent. exp. appl. *31* (1982) 57.
4 Weidhaas, D.E., unpublished results.
5 Reed, D.K., Jacobson, M., Warthen, Jr, J.D., Uebel, E.C., Tromley, N.J., Jurd, L., and Freedman, B., USDA-SEA Tech. Bull. No. 1641 (1981).
6 Karrer, W., Konstitution und Vorkommen der Organischen Pflanzenstoffe, vol. I, p. 72. Birkhäuser Verlag, Basel 1958.
7 Karrer, W., Konstitution und Vorkommen der Organischen Pflanzenstoffe, vol. I, p. 88. Birkhäuser Verlag, Basel 1958.
8 Hofmann, A.W., Chem. Ber. *11* (1878) 329.
9 Kiliani, H., Arch. Pharm. *234* (1896) 438.
10 Beroza, M., J. Am. Oil Chem. Soc. *31* (1954) 302.
11 Karrer, W., Konstitution und Vorkommen der Organischen Pflanzenstoffe, vol. I, p. 157. Birkhäuser Verlag, Basel 1958.
12 Karrer, W., Konstitution und Vorkommen der Organischen Pflanzenstoffe, vol. I, p. 159. Birkhäuser Verlag, Basel 1958.
13 Ribereau-Gayon, P., Plant Phenolics, p. 199. Hafner Press, New York 1972.

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3-Methyl-2-hexanone from the triatomine bug *Dipetalogaster maximus* (Uhler) (Heteroptera; Reduviidae)

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Summary. The occurrence of 3-methyl-2-hexanone as a major component of the secretion and possible alarm substance from the metasternal scent glands in the triatomine bug *Dipetalogaster maximus* is reported.

Dipetalogaster maximus (Uhler) is a very large 33-42 mm long blood sucking (triatomine) bug. It occurs naturally in Mexico at the extreme southern tip of semi-arid California Baja (Sur)[2]. *Trypanosoma cruzi*, which causes Chagas' disease in humans, is transmitted by triatomine bugs. Although *D. maximus* is not, because of its restricted distribution, important as a carrier of *T. cruzi*[2] the early larval stages are proving useful in xenodiagnosis, as a natural means of detecting *T. cruzi* in patients suspected of having Chagas' disease[3].

In the efforts which continue to be made to secure improvements in the techniques used to detect and control the noxious triatomines searches have been made for behavior modifying chemicals which the insects themselves produce[4]. Here we should like to report evidence indicating that 3-methyl-2-hexanone is a major component of the secretion and a possible alarm substance from the metasternal (= metathoracic) scent glands of *D. maximus*.

Materials and methods. Larvae and adults of *D. maximus* were obtained from Cambridge, England[1] (the larvae were reared to adulthood in our laboratory, in Cardiff). The metasternal scent glands were isolated by dissection under 200 mM NaCl. They are present only in the adult insect. The electron impact gas chromatographic-mass spectrometric (GC-MS) analyses[1] were carried out using a 7070H VG mass spectrometer at 70 eV with the ion source temperature 190 °C, separator 180 °C and 200 μA ionizing current. Separations were achieved with a 2 m × 2 mm i.d. glass column packed with 3% OV 225 on 100-120 mesh Gas Grom Q; basic programme, 10 ml helium/min, column 70 °C isothermal for 7 min and then temperature programmed at 10 °C/min to 200 °C. The glandular samples were introduced by a simple solventless open column procedure[5]. Standard samples were injected in the usual way in solution in acetone or ethanol. Chemical reductions were carried out with excess sodium borohydride in ethanol (2 μl ethanol for 1 gland). Acidification of the reaction mixture was effected with 2 N hydrochloric acid prior to

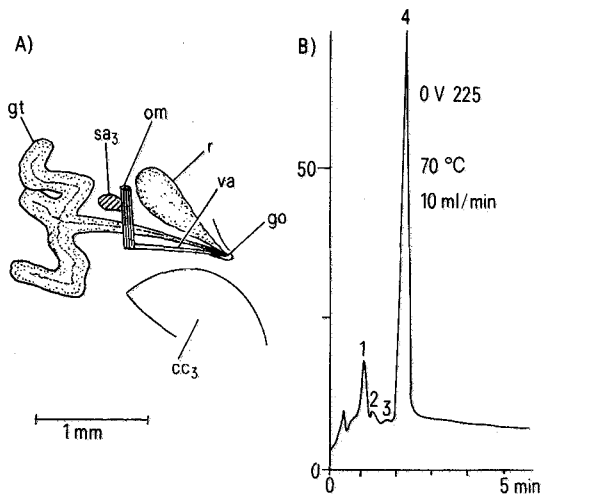

Figure 1. *A* Metasternal scent gland, right-hand side of metathorax; cc_3, 3rd coxal articular cavity; go, position of gland opening; gt, gland secretory tubule; om, opener muscle; r, reservoir; sa_3 metasternal apophysis; va, valve opener arm. *B* Total ion current monitor trace from GC-MS analysis of a single entire gland. 4 peaks were recorded within 3 min after start at 70 °C.

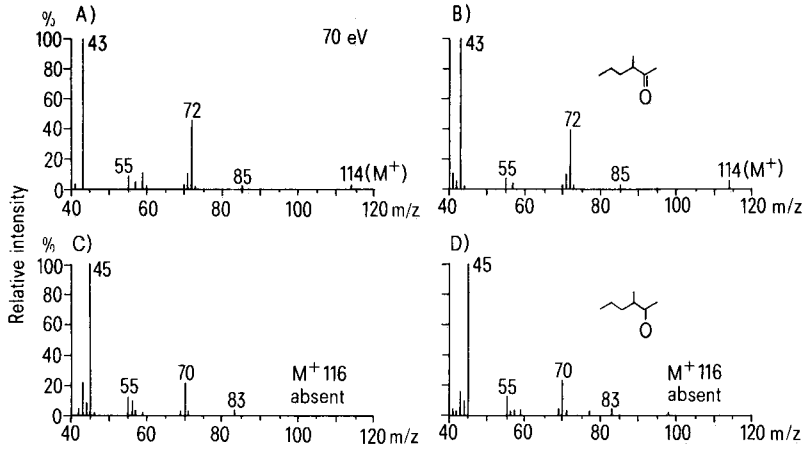

Figure 2. Mass spectra of *A* 3-methyl-2-hexanone from *Dipetalogaster*, *B* authentic 3-methyl-2-hexanone (Aldrich Chemical Co. Ltd), *C* 3-methyl-2-hexanol obtained by reduction from *Dipetalogaster* scent gland, *D* 3-methyl-2-hexanol obtained by reduction from authentic 3-methyl-2-hexanone. Reducing agent, sodium borohydride in ethanol.

GC-MS. Chemical ionization (CI) GC-MS was performed with ammonia as the reagent gas. The estimate of secretion volume was obtained by a gas chromatographic technique (GC) in which dodecane was the external standard.

Results. The metasternal scent gland from either side consists of a pigmentless branched secretory tubule and a pale amber colored pear-shaped reservoir (fig. 1A). It opens by a small pore located near the anterior margin of the 3rd coxal articular cavity. The opening is equipped with a simple valve, valve opener muscle and prominent, heavily sclerotized, valve opener arm. The reservoir contains an apparently colorless liquid sometimes together with a brownish deposit of a particulate material.

A total ion current monitor trace produced during EI-GC-MS from a single entire gland (tubule and reservoir) is shown in figure 2B. Within 5 min after injection, 3 minor peaks and 1 major peak were recorded. No further peaks were observed during the subsequent temperature programme to 200 °C. Minor peaks 2 and 3 may not be true component peaks.

The major peak (peak 4) was identified (fig. 2A) as 3-methyl-2-hexanone. The mass spectrum of this component showed a base peak at m/z 43, a small but significant peak at m/z 114 (M^+), a prominent peak at m/z 72 and matched that of authentic 3-methyl-2-hexanone (fig. 2B). The CI mass spectrum contained a prominent quasimolecular ion (QM^+) at m/z 115 thereby indicating a molecular weight of 114; it also showed small but prominent peaks at m/z 113 (M-1), 99 (M-15) and 97 (M-17). Accurate mass measurement confirmed that the peak at m/z 114 (M^+) was attributable solely to ions of the formula $C_7H_{14}O$ (m/z expected, 114.1045; m/z found, 114.1042). Similarly, the peak at m/z 72 was found to be due solely to ions of the formula C_4H_8O (m/z expected, 72.0575; m/z found, 72.0586). Loss of peak 4 (retention time 2.3 min) and the appearance of a new peak (retention time 3 min) was observed on reduction of a glandular sample with sodium borohydride. The mass spectrum of the reduction product (fig. 2C) showed a base peak at m/z 45, a strong peak at m/z 70, but no molecular ion (M^+ expected, 116) and was virtually identical with the mass spectrum of 3-methyl-2-hexanol similarly formed by borohydride reduction from authentic 3-methyl-2-hexanone (fig. 2D). Mass spectra recorded both at the beginning and at the end indicated that peak 4 was homogeneous. Correspondence of retention times on the OV 225 column was observed between the *Dipetalogaster* and authentic 3-methyl-2-hexanone and between their reduction products.

The metasternal scent gland of *Dipetalogaster* is small relative to the size of the adult bug. By GC it was estimated that one of a pair of glands from a 333-mg male adult consisted of 85% 3-methyl-2-hexanone in only 0.0005 µl of secretion.

Adult resting bugs responded to the vapor from authentic 3-methyl-2-hexanone by movement away from the stimulus source. It is possible that the natural substance functions as an alarm pheromone. They responded similarly to the vapor from 2-heptanone.

The collection of further data was precluded by an acute shortage of material.

Discussion. 3-Methyl-2-hexanone is an addition to the list of aliphatic ketones recorded from insect exocrine secretions[6]. In fact, so far as we are aware, it has been recorded in nature only once previously, as a flavor component from canned beef[7]. Possible functions of this ketone for *D. maximus* include intraspecific or interspecific (e.g. in interactions with formicid predator) excitation of alarm behavior. Alarm substances have potential application in the control of the noxious species.

D. maximus is not obviously scented[8]. It lacks the Brindley's glands which in the adults of other triatomine bugs are a source of isobutyric acid[9,10]. The ecology of chemical defense in triatomine bugs is at present a little understood subject.

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2 Lent, H., and Wygodzinsky, P., Bull. Am. Mus. nat. Hist. *163* (1979) 123.
3 Marsden, P.D., Barreto, A.C., Cuba, C.C., Gama, M.B., and Ackers, J., Am. J. trop. Med. Hyg. *28* (1979) 649.
4 Schofield, C.J., and Patterson, J.W., J. Med. Ent. *13* (1977) 727.
5 Staddon, B.W., Everton, I.J., and Games, D.E., Comp. Biochem. Physiol. *62B* (1979) 259.
6 Blum, M.S., Chemical defenses of arthropods. Academic Press, New York 1981.
7 Peterson, R.J., Izzo, H.J., Jungermann, E., and Chang, S.S., J. Food Sci. *40* (1975) 948.
8 Mazzotti, L., Rev. Inst. med. trop. São Paulo *12* (1970) 320.
9 Pattenden, G., and Staddon, B.W., Ann. ent. Soc. Am. *65* (1972) 1240.
10 Games, D.E., Schofield, C.J., and Staddon, B.W., Ann. ent. Soc. Am. *67* (1974) 820.

0014-4754/83/040380-02$1.50 + 0.20/0