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THE CHEMICAL IDENTIFICATION OF THE GRANARY WEEVIL AGGREGATION PHEROMONE

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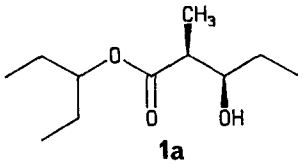
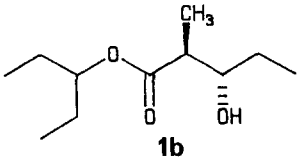
ABSTRACT: (R*,S*)-1-Ethylpropyl 2-methyl-3-hydroxypentanoate is identified as the major component of the aggregation pheromone of Sitophilus granarius (L.), the granary weevil.

The granary weevil [Sitophilus granarius (L.)] is a serious cosmopolitan pest of stored cereal grains, accounting for millions of dollars in losses annually. Controls relying on pesticides and fumigants are now threatened due to increasing insect resistance[1]. Thus an attractant to monitor this pest's presence in stored grain would be very useful.

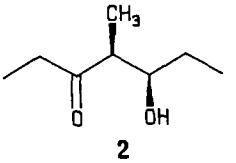
Faustini et al.[2] reported the existence of a granary weevil male-produced aggregation pheromone. We now report the isolation, purification, identification and synthesis of this pheromone for which we propose the name "sitophilate", 1a.



1a



1b



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To generate samples for GC-MS analysis, 250 1-dram vials each containing a single 2-day-old virgin male granary weevil, a single cracked wheat kernel, and a highly absorbent antibacterial assay disc were maintained under standard rearing conditions[3] for 2 weeks. Discs were then batch extracted with hexane. After concentration, the crude extract was purified by preparative GLC (3% SE-30 on Chromasorb W-HP®, 4.0m x 6.35mm ID column, temperature programmed at 5°C per min from 50°C to 240°C, the pheromone eluting at 158°C). Solutions containing about 1.5ug in 1 ml of hexane showed a single GC peak eluting at 145°C on a 25m OV-17 capillary column, (10°C/min). The CI (CH_4) mass spectrum showed an intense $(M+H)^+$ ion at m/z 203. The EI spectrum showed no molecular ion at m/z 202, but consideration of accurate masses of fragments[4] suggested $C_{11}H_{22}O_3$ as the formula, although $C_{10}H_{18}O_4$ remained a remote possibility. The presence of a hydroxyl was shown by loss of water from m/z 115, as well as formation of an acetate and a trimethylsilyl ether.

The EI base peak at m/z 74 suggested, erroneously, a methyl ester, while the TMS ether base peak at m/z 131 pointed to the CH_3CH_2CHOH- group. Placement of this group beta to the carbonyl was implied by the retro-aldol losses of CH_3CH_2CHO from m/z 202 and 173 along with corresponding losses in the acetate and TMS derivatives.

A 400 MH_z ^{1}H-NMR was obtained on a solution of approximately 10 ug of material (from 870 vials) in 0.4 ml of 99.96%D C_6D_6. The NMR spectrum ruled out a methyl ester, and the clear evidence for three ethyl groups is nicely accomodated by 1a/1b. The base peak in the EI spectrum is now explained by the combination of a McLafferty rearrangement (loss of C_5H_{10}) and retro-aldol loss of propionaldehyde, with formation of the propionic acid ion.

Synthesis of a 1:1 mixture of 1a and 1b was accomplished by reaction of the 3-pentanol ester of 2-bromopropionic acid (from 2-bromopropionyl chloride and an excess of 3-pentanol), propionaldehyde and zinc in toluene (83% yield crude, b.pt. 85-100°, 1mm). The expected two isomers (1:1) were preparatively separated on GC (10% SP-1000, 15 PSI, 160°) upon elution at 11.5 and 13.0 min (n-$C_{18}H_{38}$ elutes at 12.5 min). The ^{1}H NMR of the late eluting isomer was identical to that of the natural material. The natural pheromone was correlated to the erythro isomer 1a by both ^{1}H and ^{13}C-NMR spectroscopy[6]. Racemic 1a was comparable to the naturally produced pheromone in attracting male and female granary weevils, while synthetic racemic 1b was significantly less attractive. This substance bears an obvious relationship to the rice weevil pheromone, 2[7] and even has the same relative configuration of optical centers; we conjecture that the absolute configuration will be found to be likewise.

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4. (m/z, intensity): [173.116(1,$C_9H_{17}O_3$), 144.115 (4,$C_8H_{16}O_2$), 133(2), 132(1), 131(1), 115.075(42,$C_6H_{11}O_2$), 103.039(21,$C_4H_7O_3$), 97(6), 87.079(4,$C_5H_{11}O$), 85.027 ($C_4H_5O_2$), 74.035(100,$C_3H_6O_2$), 59(26), 57(27)].
5. 1a: 4.83ppm(9 lines, J=6Hz,CHOCO); 3.77(6 lines, 4.3Hz, CHOH); 2.38(q of d, 7.2, 4.0Hz,$\underline{CH}CH_3$); 2.28(bd, 4.6Hz,CHO$\underline{H}$); 1.2-1.5(complex mult., CH_2); 1.15(d, 7.2Hz,CH$\underline{CH_3}$); 0.88,0.77,0.75(t, 7.4Hz,3xCH_3). ^{13}C(50MHz,C_6D_6):76.55, 73.39, 44.87, 27.45, 26.89, 26.84, 11.33, 10.68, 9.85, 9.81. 1b: 4.74(9 lines, 6Hz), 3.40(p,6.4Hz); 2.45(d,6.9Hz); 2.30(q of d, 7.2,6.4Hz, $\underline{CH}CH_3$); 1.2-1.4 (complex mult.,CH_2's); 1.00(d,7.2Hz); 0.83,0.67,0.66(t,7.4Hz,3xCH_3). ^{13}C:76.58, 74.71, 45.60, 28.14, 26.94, 14.74, 10.29, 9.87, 9.84.
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