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THE ISOLATION, IDENTIFICATION AND SYNTHESIS OF 3,6-DIMETHYLHEPTAN-2,4-DIONE, A PHEROMONE OF THE MUSHROOM FLY, *MEGASELIA HALTERATA* (DIPTERA:PHORIDAE)

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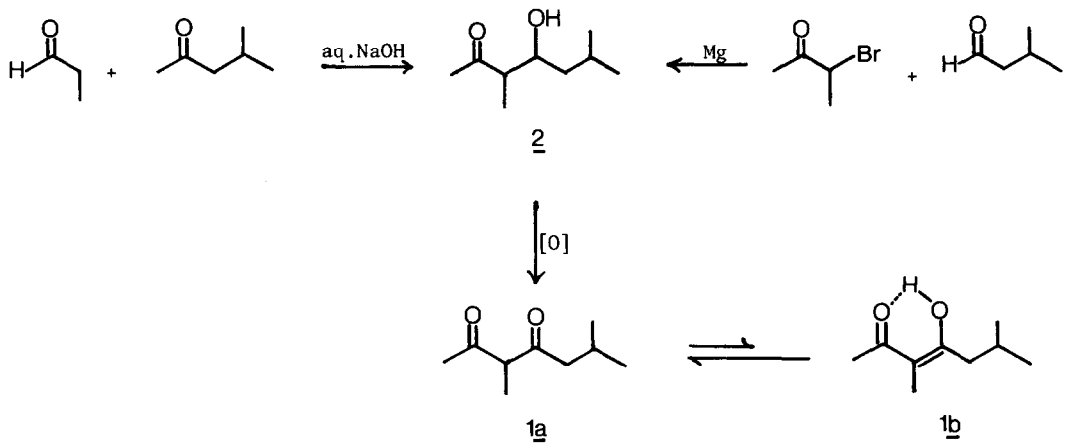
A pheromone of the female mushroom fly, *Megaselia halterata*, has been identified as 3,6-dimethylheptan-2,4-dione which exists as a mixture of keto and enol forms.

Megaselia halterata (Wood) is a familar mushroom pest in Great Britain and the United States. Adult flies enter mushroom houses and lay their eggs in compost. These hatch within two days and the three larval instars, completed in 9-10 days, are the most damaging to the mushrooms. The larvae feed and destroy the actively growing mycelium. The adults are a major nuisance to mushroom growers; they may cause allergies and bronchial asthma and may be vectors of mushroom diseases, e.g. *Verticillium malthousei*.[1] We report here the isolation, identification and synthesis of a female specific pheromone of the mushroom fly, 3,6-dimethylheptan-2,4-dione, a novel 1,3-diketone.

Bioassay studies showed that female mushroom flies attract males before mating indicating that a pheromone is secreted by the females. About 200 female flies were then extracted with dichloromethane (2ml) for 24 hours at 4°C and the extract concentrated to 10µl. G.l.c. studies of this solution revealed the presence of a major component which could not be seen in a similar extract of male flies.

About 4,000 female flies were, subsequently, extracted with dichloromethane (10ml) and the extract was concentrated to 100µl. Preparative g.l.c. (10% FFAP, 6'x⅜", 70 to 250°C, 8°C/min) yielded 30µg of a single component, which was active in attracting male mushroom flies. The high resolution mass spectrum of this compound indicated the molecular formula $C_9H_{16}O_2$ with the following fragments: m/z 156.1239 (M^+,3.2%,$C_9H_{16}O_2$), 141 (2.3,$C_8H_{13}O_2$), 114 (1.6,$C_7H_{14}O$ and $C_6H_{10}O_2$), 99 (20,$C_5H_7O_2$), 85 (62,C_5H_9O), 72 (22,C_4H_8O), 57 (100,C_4H_9) and 43 (91,C_2H_3O). The ions at m/z 43 and 72 indicate the presence of butan-2-one substituted at the 3-position. Similarly, ions at m/z 99, 85 and 57 confirmed that the substituent at C-3 is a C_4H_9CO- group. Based on this fragmentation pattern and H^1-nmr spectral data, the structure of the pheromone was assigned as 3,6-dimethylheptan-2,4-dione (1)[2] as a combination of the keto (1a) and enol (1b) tautomers in a 3:1 ratio. H^1-nmr (100MHz in CCl_4)[3]: (1a), δ0.90 (d,6H,J=6Hz,2xCH_3), 1.26 (d,3H,J=6.5Hz,CH_3), 2.09 (s,3H,CH_3CO), 2.15-2.4 (m,3H,CH_2-CH) and 3.5 (q,1H,J=6.5Hz, COCHCO); (1b), δ0.96 (d,6H,J=6Hz,2xCH_3), 1.82(s,3H,CH_3), 2.09 (s,3H,CH_3CO), 2.15-2.4 (m,3H, CH_2-CH) and 16.4 (s,1H,enolic OH). The two doublets at δ0.90 and 0.96 appear as a distorted



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1a 1b

triplet centred at δ0.93 and are due to the gem dimethyl groups of the ketone (1a) and enol (1b) tautomers. The signals at δ1.26(d) and δ1.82(s) are due to the C-3 methyl group of the keto and enol tautomers, respectively. The methylene and methine protons at C-5 and C-6 resonate at δ2.15-2.4(m) which is consistent with the spectra of carbonyl compounds with an isobutyl group such as isovaleraldehyde and 4-methylpentan-2-one. Decoupling studies also support the structure (1); irradiation of the peak at δ2.15-2.4(m) caused the apparent triplet at δ0.93 to collapse into two singlets.

The pheromone has been synthesised by two simple routes. Aldol condensation of isovaleraldehyde (0.05mole) with butan-2-one (0.1mole) in the presence of 15% aq. NaOH (3.5ml) in ether (10ml) for 24 hours at room temperature yielded 3,6-dimethyl-4-hydroxyheptan-2-one (2) as a colourless oil (64%, bp 48°C/0.04mm Hg). The hydroxy ketone (2) was also obtained (50%) by the reaction of 3-bromobutan-2-one with isovaleraldehyde in the presence of magnesium in an ether-benzene mixture.[4] 3,6-Dimethylheptan-2,4-dione (1) was obtained by Jones oxidation of (2) in acetone at 0°C (85%, bp 84-85°C/10mm Hg). Spectral and g.l.c. data of the synthetic material (1) were found to be identical to that of the natural product. Biological results on the activity of the pheromone will be reported elsewhere.

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References and Notes

1. E.S. Binns, B. Gurney, I.J. Wyatt, P.F. White, *Ann. appl. Biol.*, 1979, 92, 159.
2. ν_{max} (CCl_4); 2954cm^{-1}(m), 1702(s), 1616(s), 1451(m), 1248(m) and 1158(m). The absorption due to the enolic hydroxyl group was not observed in the spectrum of the natural product due to the low concentration employed. The i.r. spectrum of the synthetic pheromone showed this absorption at 3500cm^{-1}(br,w).
3. The H^1 n.m.r. spectra of keto (1a) and enol (1b) forms of (1) were assigned from the spectrum of the natural product and the integration normalised for the keto and enol forms.
4. J. Cologne and J. Grenet, *Bull. Soc. Chim. Fr.*, 1954, 1304.

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