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STRUCTURE AND SYNTHESIS OF THE WING GLAND PHEROMONE OF THE MALE AFRICAN SUGAR-CANE BORER : ELDANA SACCHARINA (WLK.) (LEPIDOPTERA,PYRALIDAE)

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Summary : The structure of the sex attractant isolated from the wing glands of E.saccharina has been determined by chemical and physical methods as trans-3-methyl-4-dimethylallyl-γ-lactone 1. The synthesis of racemic 1 is described.

The African sugar-cane borer : Eldana saccharina (Wlk.)is an endemic species of Lepidoptera which has shown remarkable adaptation to recently introduced field crops like sugar-cane and maize, causing increasing damages in several countries (1). Laboratory studies of its sexual behaviour revealed the existence of two male pheromones secreted by wing glands and abdominal hair pencils respectively. In separate communications we described the sexual behaviour (2) and the chemical composition of the aphrodisiac secretion produced by the hair pencils (3).

Herein we wish to report the structure determination and synthesis of the wing gland pheromone which acts as a long range attractant to females (2).

GC/MS analysis (SE-52 coupled to a Riber R10-10 mass spectrometer) of a crude methylene chloride extract of wing glands showed one major volatile component with a molecular ion peak at m/e = 168. Purification of this extract by preparative GC(5% SE-52 on GCQ) gave a sample which could be further analysed by GC/MS at high resolution.(SE-30 coupled to a AEI-MS9 mass spectrometer). The molecular formula could be established as $C_{10}H_{16}O_2$(calc : 168.1150 , found : 168.1165) while the base peak at m/e 99 (calc : 99.0446 , found : 99.0445) corresponds to $C_5H_7O_2$ due to a loss of C_5H_9. Further fragmentation through loss of CO leads to a small peak at m/e 71.

Microozonolysis at the µg level (O_3,-70° in CH_2Cl_2,$(C_6H_5)_3P$)(4) followed by a GC/MS analysis gave C_3H_6O and $C_7H_{10}O_3$ as the only products establishing the existence of only one double bond.

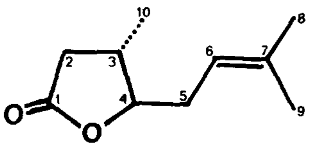
Consequently jasminlactone 2 (5) became an attractive candidate. Although the mass spectra of 1 and an authentic sample of 2 showed great similarity, the pheromone 1 had a significantly shorter retention time on GC which in turn suggested the presence of a side chain. A monoterpenoid structure had to be taken into consideration and biogenetic arguments favored a structure derived from geraniol. Nevertheless the great variety of carbon skeletons encountered among monoterpenes combined with the fact that 1 is a metabolite of the animal kingdom made it necessary to obtain NMR data.

The extraction of 268 wing glands followed by preparative GC led to the isolation of approximately 10 µg of 1 (GC estimation).

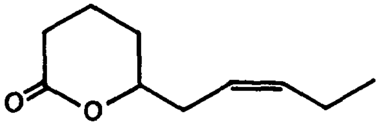
The NMR spectrum of this sample was recorded at 250 MHz in a micro cell system. It shows a broad triplet of an olefinic proton at 5,15δ(1H),a quadruplet like multiplet at 4,07 δ (J=5-7Hz) which can be assigned to a lactone proton, a multiplet at 2,7 δ (1 H, dd ,J = 15,7 Hz) corresponding to one of the geminal protons in α position to the carbonyl group of the lactone and some not well resolved signals between 2,5 and 2,0δ(4-6H). Two singlets of three protons each at 1,75δand 1,64δare attributed to two methyl groups on a double bond and a doublet at 1,12δto the methyl group attached to a methine carbon.

Decoupling at 2,30δtransforms the methyl resonance at 1,12δinto a singlet and modifies the signals at 4,07δ and 2,7 δ .

The above data are in agreement with structure 1 for the wing gland pheromone.

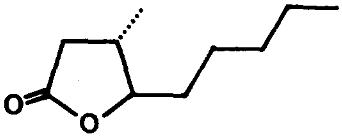


1



2

Comparison of the NMR spectrum of 1 with those of two readily available reference samples 3 and 4(6) strongly favored a trans stereochemistry of the two substituents in spite of the small difference between J_{trans}(7Hz) and J_{cis}(8,5Hz) and a slightly different coupling pattern of H-4 in 1 and in the trans reference sample. This problem and the need of products for behavioural studies prompted synthetic studies along two different routes which will be described below.



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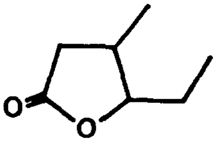
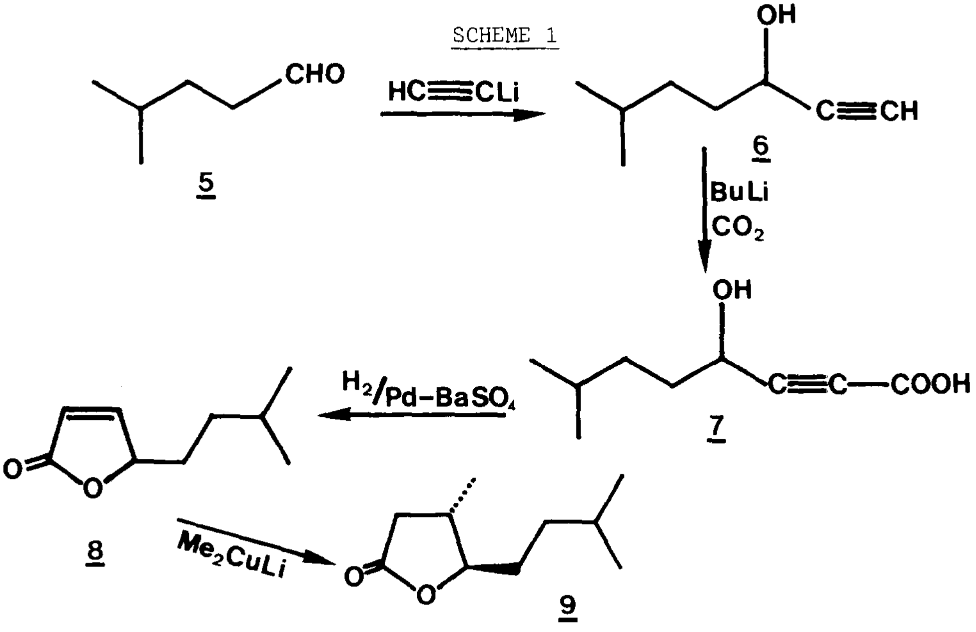


4

At first the synthesis of the dihydroderivative (synthesis of pure 4-methylpentene-3-al presented difficulties in our hands) of 1 was undertaken in order to prove unambiguously the structure and relative stereochemistry of the pheromone. Scheme 1 outlines the reactions which led to the synthesis of the trans-dihydrolactone 9.(The high stereospecificity of the addition of Me$_2$CuLi to butenolides has been demonstrated previously(6). Since analogues of intermediate 7 have been successfully used for the preparation of optically active γ-lactones(7),this route will later be useful for future preparations of optically active 1).

SCHEME 1

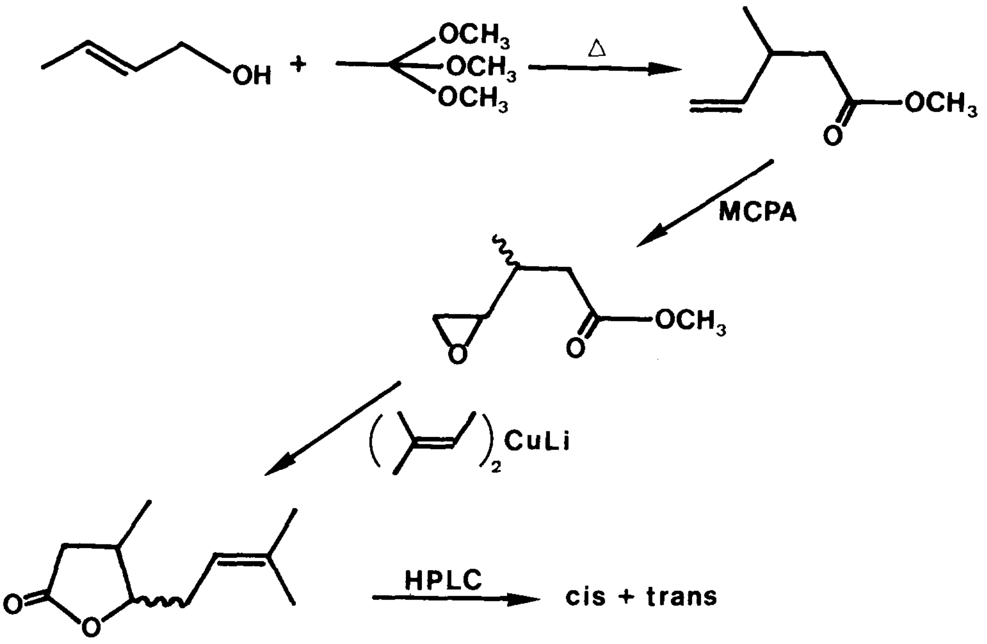


Cochromatography of 9 with a hydrogenated sample of wing gland pheromone on glass capillary columns coated with Carbowax 20M and SE-52 gave identical retention times for these compounds demonstrating the trans stereochemistry for 1.

Surprisingly,small but significant differences were observed in the coupling pattern of the proton on C-4 indicating the influence of the double bond on the conformation of the molecule.

In order to resolve this problem we undertook the synthesis of $(\pm)$ 1 along scheme 2.

SCHEME 2



Although this method gives only a mixture of stereoisomers, preparative HPLC provided two pure compounds whose stereochemistry was determined by NMR decoupling experiments. The NMR spectra of the trans isomer and the pheromone 1 were superimposable establishing thus definitely the structure and relative stereochemistry of the wing gland pheromone as 1.

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