Tetrahedron Letters No. 30, pp 2617 - 2618, 1977. Pergamon Press. Printed in Great Britain.

TRAIL PHEROMONE OF THE PHARAOH'S ANT, MONOMORIUM PHARAONIS: ISOLATION AND IDENTIFICATION OF FARANAL, A TERPENOID RELATED TO JUVENILE HORMONE II

F.J. Ritter*, I.E.M. Brüggemann-Rotgans, P.E.J. Verwiel, C.J. Persoons and E. Talman
Centraal Laboratorium TNO, Delft, The Netherlands

(Received in UK 18 April 1977; accepted for publication 9 June 1977)

The poison gland of the Pharaoh's ant contains two attractive alcaloidal pheromones, which are components of its odour trail[1-3]. The Dufour's gland, however, produces trace amounts of a much more active compound, the true trail pheromone. We now wish to describe its identification.

The pheromone was isolated from about 10^5 worker ants by benzene extraction, liquid and gaschromatography, using trail-following tests[3] for monitoring the isolation procedure. In total 70 µg were obtained of a compound which was called faranal.

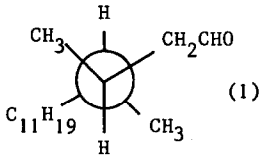
The structure was elucidated using micro-ozonolysis, GC/MS, IR and NMR (300 MHz, solvent C_6D_6). IR bands at 1727, 2710, and 2820 cm^{-1}, an NMR signal (1 proton) at δ 9,42 (dd. 2.5 Hz and 1.5 Hz) showed that faranal contains a non-conjugated aldehyde group. From the mass spectrum (highest mass m/e 250) and the NMR spectrum (30 protons), the molecular formula $C_{17}H_{30}O$ was derived. The presence of two non-conjugated trisubstituted C=C bonds (protons at δ 5.19 and 5.16, both broadened t. 7 Hz; the two overlapping triplets were observed as separate signals when CS_2 was used as a solvent) proves faranal to be a branched acyclic dienal.

Ozonolysis yielded butanone, levulinic aldehyde and 3,4-dimethylhexane-dial-1,6 which were identified by their mass spectra. Reduction of faranal to the alcohol with $NaBH_4$ in ethanol and subsequent ozonolysis yielded levulinic aldehyde and 3,4-dimethyl-6-hydroxy-hexanal-1. These data establish that faranal is a 3,4,7,11-tetramethyl-6,10-tridecadienal-1.

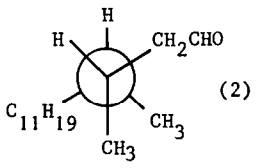
The chemical shifts of the broadened singlets due to the methyl groups attached to C=C allow assignment of the configuration of the corresponding double bonds: δ 1.56 is assigned to $\underline{CH_3}\diagdown\!\!\diagup C{=}C\diagdown\!\!\diagup H$ with E configuration and δ 1.70 to $\underline{CH_3}\diagdown\!\!\diagup C{=}C\diagdown\!\!\diagup H$ with Z configuration. Double resonance identified the corresponding olefinic proton signals: δ 5.16 coupled to 1.56 (E) and δ 5.19 to 1.70 (Z). Saturation of the C_9 methylene group (broadened quartet, δ 2.18) caused the triplet at 5.19 to collapse into a singlet. This means that the double bond at position 10 is (Z) and consequently the double bond at position 6 must be (E).

The remaining problem concerned the relative configuration at C_3 and C_4. The Newman projections of the preferred conformations, with least steric hindrance for the larger groups, are presented in (1) for the 3R,4S configuration and in (2) for the 3S,4S configuration.

The experimental value of about 4 Hz for $J_{3,4}$ is in good agreement with a conformation with gauche hydrogen atoms, as in (2), whereas for $J_{3,4}$ in a conformation with anti opposed hydrogen atoms, as in (1), a value of about 10 Hz would be expected.

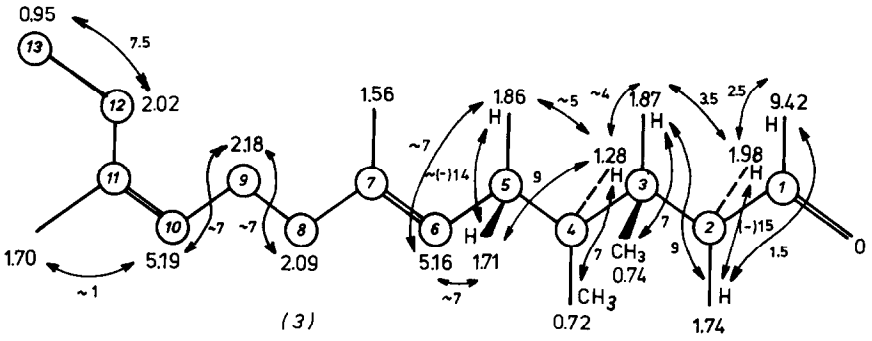


(1)



(2)

In conclusion, the structure of faranal appears to be (6E,10Z)-3,4,7,11-tetramethyl-6,10-tridecadienal-1, with 3S,4S configuration at the chiral centers (3), or its optical antipode (3R,4R).



(3)

Structure of faranal, (6E,10Z)-3,4,7,11-tetramethyl-6,10-tridecadienal-1. Proton chemical shifts (values with two decimals) and coupling constants in C_6D_6. (Drawn: (3S,4S) configuration). In circles: numbers of carbon atoms 1-13.

It is interesting to note that the larger part of the molecule, from C_5 to C_{13}, including the methyl branches and the stereochemical configuration, is the same as that of juvenile hormone II, a well-known compound in insect biochemistry[4], apart from the fact that the hormone has a (Z)-epoxyde group and faranal a (Z) double bond at the 10 position.

When extracts of Dufour's glands were subjected to capillary gaschromatography (SE 30) it appeared that the most active fraction in the trail-following assay had the same Kovâts retention index (1780) as the isolated faranal. In the dual choice test[1] 1 ng showed optimal activity, but even 1 pg gave significantly positive results.

In the trail-following test, workers as well as queens and males followed a circular trail down to concentrations of < 1 pg/cm, which is about 10^4 times lower than the lower limit for the alkaloidal pheromones from the poison gland, monomorine I and III[3]. More details about the biological experiments will be published elsewhere[5].

References

1. F.J. Ritter, I.E.M. Rotgans, E. Talman, P.E.J. Verwiel and F. Stein, Experientia, 29, 530 (1973).
2. E. Talman, F.J. Ritter and P.E.J. Verwiel, Mass Spectrometry in Biochem. and Med., (A. Frigerio and N. Castagnoli, eds.), Raven Press, New York 1974, p. 197.
3. F.J. Ritter and C.J. Persoons, Drug Design (ed. E.J. Ariens), Vol VII, Academic Press, New York, 1976, p. 59.
4. A.S. Meyer, A.A. Schneiderman, E. Hanzmann and J.H. Ko, Proc. Nat. Acad. Sci. US, 60, 853 (1968).
5. F.J. Ritter, I.E.M. Brüggemann-Rotgans, P.E.J. Verwiel, E. Talman, F. Stein, J. LaBrijn and C.J. Persoons, Proceed. VIIIth Intern. Congr. I.U.S.S.I., Pudoc, Wageningen 1977.