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α-FARNESENE, DUFOUR'S GLAND SECRETION IN THE ANT APHAENOGASTER LONGICEPS (F.Sm.)

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The isolation and characterization of α-farnesene (III) from Dufour's (accessory venom) gland in the myrmicine ant, Aphaenogaster longiceps (F.Sm.) is reported.

Dissection of whole Dufour's glands from ten A. longiceps workers collected in the Royal National Park, near Sydney, yielded sufficient material for preliminary gas chromatographic and spectroscopic studies. Additional material for chemical studies was obtained by total extraction of A. longiceps workers with light petroleum, followed by a chromatographic separation of the Dufour's gland component on alumina. This material comprises 4% of the body weight of the live insect.

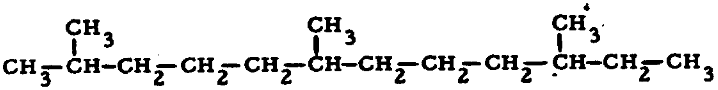
Gas chromatography (three columns)(1) showed the gland secretion to be homogeneous. Its infrared spectrum(2) showed bands characteristic of an unsaturated aliphatic hydrocarbon. A strong absorption at 1600 cm^{-1} suggested a conjugated diene whilst further absorptions at 3085, 985 and 890 cm^{-1} are characteristic of a mono-substituted ethylene. Also bands at 1635 and 835 cm^{-1} may be assigned to a trisubstituted double bond.(3)

Total extraction of A. longiceps provided sufficient material for NMR spectroscopy.(4) This material was not homogeneous; gas chromatography showed one major peak (90%) of the same retention time as that of the Dufour's gland secretion, and at least twelve minor peaks (10%) of longer retention times. The latter extractives are most likely hydrocarbons of the cuticle wax. Signals of the minor alkane constituents do not interfere with the NMR spectrum of the Dufour's gland hydrocarbon which integrates for 24 protons. It shows a multiplet (12H) centred at δ1.67 for the protons of four vinylic methyl groups. An unresolved doublet (4H) at δ2.00 is assigned to the protons of two allylic methylene groups, cf. geraniol.(5) A triplet (2H) at δ2.78 (J = 7.0 cps) is characteristic of a methylene group allylic to two double bonds, cf. methyl linoleate(5) and ocimene.(6) A complex structure (5H) between δ4.75 and δ5.6 is assigned to 5 vinylic protons. Finally a quartet (1H) centred at δ6.3 is characteristic of the lone proton in the system $R\text{-}CH \doteq CH_2$. The appearance of this proton at auch a low field indicates that the mono-substituted ethylene is part of a conjugated system.(7) The mass spectrum(8) of the pure gland secretion has a molecular ion peak at m/e 204. Thus the NMR and mass spectral data establish the molecular formula $C_{15}H_{24}$ for the Dufour's gland hydrocarbon of A. longiceps.

Hydrogenation(9) of the extracted material gave a saturated hydrocarbon which, on gas chromatography (three columns) had the same retention time as farnesane (I). The latter hydrocarbon was obtained by hydrogenation of a mixture of farnesenes derived from the pyrolysis of farnesyl acetate (II).(10) This reduction establishes the acyclic sesquiterpenoid skeleton, and from the evidence so far presented the structure of the Dufour's gland hydrocarbon could be either (III) or (IV).

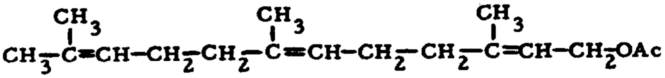
On reduction with sodium in ethanol(11) the Dufour's gland hydrocarbon gave a dihydro-derivative the NMR spectrum of which showed no signal at δ2.8 for the protons of a diallylic methylene group, but showed an unresolved doublet (8H) at δ2.0 which is assigned to the four allylic methylene groups in V. Moreover, this dihydro-derivative was identical (NMR and infrared spectra and retention time on three columns) with the dihydrofarnesene (V) obtained on reduction of the mixture of farnesenes from the pyrolysis of farnesyl acetate (II).(cf. 10) Thus the Dufour's gland hydrocarbon has structure III.

The complex pattern of the vinylic methyl protons (12H) in the range δ1.6-1.75 renders an assignment of configuration to the C_{6-7} double bond in α-farnesene (from Dufour's gland) hazardous, especially in the absence of data for each of the four α-farnesenes.(cf. 12) Now Ohloff et al.(6) showed that the proton at C_7 in the isomeric β-ocimenes has a signal centred at δ6.30 in trans-β-ocimene (VIa), and



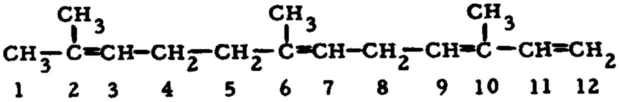
$$\mathrm{CH_3-\overset{CH_3}{\overset{|}{C}}H-CH_2-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}H-CH_2-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}H-CH_2-CH_3}$$

(I)



$$\mathrm{CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2OAc}$$

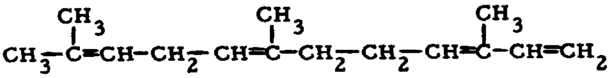
(II)



$$\mathrm{CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-CH=\overset{CH_3}{\overset{|}{C}}-CH=CH_2}$$

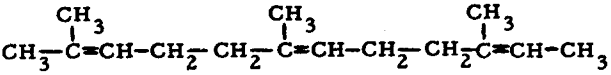
1 2 3 4 5 6 7 8 9 10 11 12

(III)



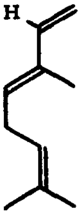
$$\mathrm{CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-CH=\overset{CH_3}{\overset{|}{C}}-CH_2-CH_2-CH=\overset{CH_3}{\overset{|}{C}}-CH=CH_2}$$

(IV)

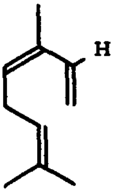


$$\mathrm{CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_3}$$

(V)



(VIa)



(VIb)

at $\delta 6.73$ in cis-β-ocimene (VIb). The equivalent proton in α-farnesene, from Dufour's gland, appears at $\delta 6.3$ thus suggesting that this conjugated diene is trans. Moreover, the ultraviolet absorption maximum at 232 mμ ($\varepsilon = 36,400$) for our α-farnesene(13) corresponds to that reported(6) for trans-β-ocimene (VIa), λ max 232 mμ ($\varepsilon = 27,600$) rather than for cis-β-ocimene (VIb), λ max 237 mμ ($\varepsilon = 21,000$).[x] Whilst a trans-configuration of the diene moiety in the Dufour's gland hydrocarbon is most likely, the assignment of configuration to this α-farnesene must await comparison of the natural and synthetic products. Stereospecific syntheses of the four α-farnesenes are in progress.

α-Farnesene has been reported, quite recently, as virtually the only sesquiterpene present in the natural coating of "Granny Smith" apples.(14) Gas chromatographic, together with infrared and NMR spectroscopic comparisons, show that the α-farnesene derived from apples is identical with that from the insect. The former report would appear to be the first in which α-farnesene has been isolated in a pure state, from a plant source. With the isolation and characterization of α-farnesene from Dufour's gland in the ant, A. longiceps, three sesquiterpenoids have now been detected in members of the Hymenoptera. Previously dendrolasin, that is β-(4, 8-dimethyl-3, 7-nonadienyl) furan, was isolated from the formicine ant, Lasius fuliginosus(Latr.)(15) in which it may function as adefensive secretion, and as an alarm substance.(16) Farnesol has been reported as a sex attractant of the male bumble bee, Bombus terrestris(L.)(17)

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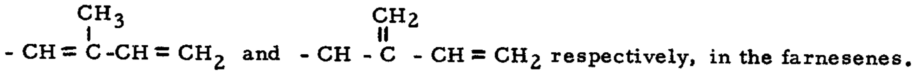
[x] The terms α- and β- refer to the terminal isopropenyl and isopropylidene groups in ocimene and other monoterpenes, but refer to the diene structures,



$-CH=\overset{CH_3}{\overset{|}{C}}-CH=CH_2$ and $-CH-\overset{CH_2}{\overset{\|}{C}}-CH=CH_2$ respectively, in the farnesenes.

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