Tetrahedron Letters No.40, pp. 3893-3896, 1967. Pergamon Press Ltd. Printed in Great Britain.

ON THE COMPONENTS OF SECRETION OF MANDIBULAR GLANDS OF THE ANT LASIUS (DENDROLASIUS) FULIGINOSUS.

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(Received in UK 5 July 1967)

From the total extract of the ant Lasius (Dendrolasius) fuliginosus Latr., Pavan[1] separated a liquid substance (named dendrolasin) produced by mandibular glands. To this new substance Quilico[2,3] assigned the structure of β-(4,8-dimethyl-nona-3,7-dienyl)-furan (I).

Pavan[1] hypothesized that dendrolasin is not the only product of the mandibular glands of the ant. By GLC we could now demonstrate that small quantities of 4 other terpenic substances are in fact contained.

In order to identify these substances, owing to the difficulty of getting sufficient quantities of glands secretion, we examined the steam-volatile fraction of the ethereal total extract of the ants ▽. This fraction contains, besides the components of the gland secretion, other substances coming from the whole body ‡. As expected, the steam-volatile fraction of the abdomen extract contains larger quantities of said substances ≡ †.

The steam-volatile substances were fractionated under reduced pressure (3 fractions). Many substances were separated by preparative GLC and identified by IR and MS. For some other

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▽ The ants were collected in the Pavia country side.

‡ The extracts have been examined as soon as prepared. After a few days under room temperature the methyl-heptenone peak increases and some new peaks appear.

≡ The variation in the ratio of the percentage of hydrocarbons and methyl-ketones may be attributed to the fact that the total extract comes from insects collected in autumn while the abdomen extract comes from insects collected in springtime.
The steam-volatile fraction of the extract of the isolated heads shows a composition very similar to the secretion of mandibular glands.

† The presence of a small quantity of dendrolasin in abdomen extract, in our opinion, is to be attributed to the inevitable pollution of the ants with their very secretion, during the collection and beheading.

substances (peaks N. 2, 7, 10, 13, 14,) the MS was recorded directly on the effluent from GLC (columns A, 100-180 °C; ΔT=2 °C/min). In any case the identity was confirmed by GLC comparative analysis with authentic specimens (columns A, B and C, several temp. between 100 and 180 °C).

TABLE I

Peak N°	Total extract: Preparative GLC (column type and temp. °C)	Total extract: Assignment	% composition by GLC (column A; 100-180 °C; ΔT=2 °C/min): Total extract	Mandibular glands secretion %	Abdomen extract %
1	From fract, 1(D, 170)	n-undecane	9,7	—	18,9
2		6-methyl-hept-5-en-2-one	0,6	lowest traces	——
3		perillen	0,3	0,4	——
4	From fract, 1(D, 170)	n-tridecane	0,5	—	12,8
5		X_1	traces	0,3	——
6	From fract, 2(D, 170)	cis-citral	0,7	0,7	traces
7		n-pentadecane	traces	—	3,8
8	From fract, 2(D, 170)	trans-citral	3,2	4,5	traces
9		X_2	0,4	0,7	——
10		tridecan-2-one	—	—	traces
11	From fract, 2(E, 160)	dendrolasin	82,3	86,4	17,0 †
12	From fract, 2(E, 160)	pentadecan-2-one	1,1	—	35,0
13		farnesal	1,2	7,0	——
14		heptadecan-2-one	traces	—	12,4

Notes to the table

Apparatus:
Analytical GLC and GLC combined to MS: Perkin-Elmer 880 flame ionization detector, carrier He.
Preparative GLC: Aerograph A-705 flame ionization detector, carrier gas N_2.

Columns:
A) 7 ft x 0,125 in : 10% Carbowax 20M + Bentone 34 on silanized Chromosorb W 60-80 mesh
B) 5 ft x 0,125 in : 10% Apiezon L on silanized Chromosorb W 60-80 mesh
C) 150 ft x 0,02 in : open tubular, SE-30
D) 7 ft x 0,25 in : 20% Carbowax 20M on acid and alkali washed Chromosorb P 30-60 mesh
E) 10 ft x 0,25 in : 20% alkaline Carbowax on acid washed Chromosorb W 30-60 mesh

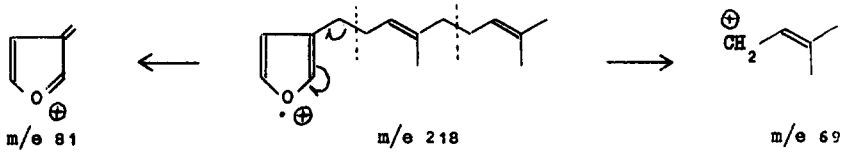
The substance of the peak N. 3 has been identified only through a careful study of its MS compared with the MS of dendrolasin. The MS of the unknown substance (see Table II) shows the molecular ion at m/e 150 ($C_{10}H_{14}O$), that, by methyl radical loss, produces a peak at m/e 135. The remaining peaks are present also in the MS of dendrolasin.

TABLE II

Mass Spectra [**] of dendrolasin and perillen

m/e	218	203	175	150	136	135	123	95	82	81	69	53	41	39
I% dendrolasin	4	10	15	-	12	-	10	14	24	48	100	36	80	17
I% unkn. subst. (peak 3) (perillen)				37	-	5	-	-	27	55	100	21	74	18

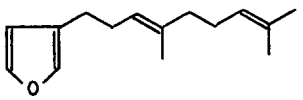
In the spectrum of dendrolasin the peaks at m/e 69 (base peak) and at m/e 81 may be easily explained as respectively deriving, the first by loss of the terminal isoprenic moiety by allylic cleavage[4], the second from the cleavage of bond β to the furan ring[5], as shown in the scheme:



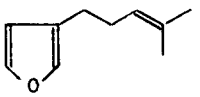
m/e 81 m/e 218 m/e 69

Peak m/e 41 ($CH_2=CH-\overset{\oplus}{C}H_2$) very likely derives from the fragmentation of the chain; peaks at m/e 39 and 53 (respectively cyclopropenyl cation and its higher homologous) must be originated from the fission of the furan ring[6].

The similarity between the MS of the unknown substance and of dendrolasin (I) regarding not only the presence but also the relative intensity of the meaningful peaks at m/e 82, 81, 69, 53 and 39, allowed us to give to this substance the structure of perillen (II).



I



II

The study of the unidentified substances X_1 and X_2 from mandibular gland secretion is

[**] Measured with Hitachi-Perkin Elmer RMU-6D instrument (single focus), ionizing current 60 μA, potential 70 eV. Samples were introduced in the ion source heated at 200 °C through the all glass heated inlet system.

in progress.

Recently Cavill[7] recognized farnesene as the only component of Dufour's gland of the ant Aphaenogaster longiceps. Farnesal is therefore the second acyclic sesquiterpenoid produced by ant glands.

Farnesal was found by Schmialek[8] in excrements of Tenebrio molitor, but it is uncer tain whether it represents a secretory product of the insect.©

The terpenic substances accompanying dendrolasin in the mandibular gland secretion are of particular interest also from the biogenetic point of view. Quilico[3] has already put in evidence the close relation existing between farnesal and dendrolasin and suggested the proba ble derivation of the furan ring from ring closure of isoprenic units. The presence of farnesal, besides dendrolasin, is in accordance with such a hypothesis; a further support to that comes from the finding of the structurally related citral and perillen. It is probable likely that the two furanoid substances derive from a single precursor by terpenic biosynthesis and uncom mon ring closure☒ . It is still dubious however whether perillen is a by-product or better an intermediate of dendrolasin biosynthesis. This could be ascertained by experiments of feeding with radioactive precursors.

© Schmialek acknowledged to farnesol a juvenile hormone activity. It might be that the light juvenile hormone activity of dendrolasin noted by Wigglesworth (9) is due to the small amount of farnesal contained in the sample of dendrolasin supplied by Pavan.

☒ A similar cyclisation was suggested to explain the biosynthesis of menthofuran via isopule gone (10).

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