

Volatile Constituents of the Red Wood Ant *Formica rufa* L. (Hymenoptera: Formicidae)

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Dedicated to Prof. H.-J. Bestmann on the Occasion of His 60th Birthday

Formica rufa, Volatile Secretions, Mass Spectrometry

From workers of the red wood ant *Formica rufa* L. 68 compounds could be identified by combined gas chromatography–mass spectrometry. Abdomina contain a row of bishomologue saturated and unsaturated uneven numbered hydrocarbons with undecane as the major product. In addition, 13 formic acid esters could be identified among which hexadecyl formate is present in particularly large amounts. Main components of the head extracts are methyl 3-ethyl-4-methylpentanoate, 3-ethyl-4-methylpentanol and tricosane.

In continuation of our studies on the chemical communication systems of Formicine ants [1, 2] recent results on the identification of volatile constituents of the red wood ant *Formica rufa* L. (Hymenoptera: Formicidae) are presented. Several of these compounds appear to be closely related to biologically active substances known from other insect orders.

Heads, thoraces and abdomens of freshly caught *F. rufa* workers [1] were dissected and extracted with pentane. The concentrated extracts were analysed by GC/MS using a Varian 311 A mass spectrometer. Gaschromatograms of extracts of heads and abdomens are shown in Fig. 1; identified compounds are listed in Table 1.

Abdomen

As is known from other *Formica* spp. [3–7] the volatile constituents of the abdomen of *F. rufa* are qualitatively and quantitatively dominated by hydrocarbons, most of which are unbranched. The main component is undecane which acts as an alarm pheromone [8]. Most of the alkanes are accompanied by groups of alkenes; under the conditions used in this study the compound with the longest GC retention time proved to be the respective 1-alkene. In some unsaturated hydrocarbons double bond posi-

tion(s) remain unknown. Starting with (Z,Z,Z)-3,6,9-tridecatriene a row of four bishomologue homoconjugated trienes, compounds **18**, **23**, **36** and **49**, of the linolenic acid type could be identified. These compounds belong to a class of polyenes which have been recently described as sex pheromones of Arctiidae, Geometridae and a subfamily of Noctuidae [9, 10]. Compound (**49**), (Z,Z,Z)-3,6,9-nonadecatriene, has been identified as a component of the sex pheromone blend of the geometrids *Boarmia selenaria* [11], *Peribatodes rhomboidaria* [12] and *Alsophila pometaria* [13]. Biological significance of the ant trienes has to be established.

Among oxygen containing volatiles of the abdomen [3–7, 14] several straight chain saturated and unsaturated primary alcohols and acetates, like (Z)-5-tetradecenol (**55**) and its acetate (**54**), are structurally closely related to typical sex pheromones of Lepidoptera [15]. In addition, 13 formic acid esters could be identified for the first time from a *Formica* species. Hexadecyl formate (**56**) was found in particularly large amounts. Compounds **57**, **61** and **64** are derivatives of hexadecanol which in contrast to the C-14-compounds **51**, **54** and **55** very likely contain the double bond in position 7 (based on comparison of GC-retention times). Compounds **35**, **39** and **44** form a “triplet” which similar to many other volatiles known from Hymenoptera carries the functional group in the 2-position.

To ensure that the formic acid esters found were not artifacts formed from the respective alcohols and

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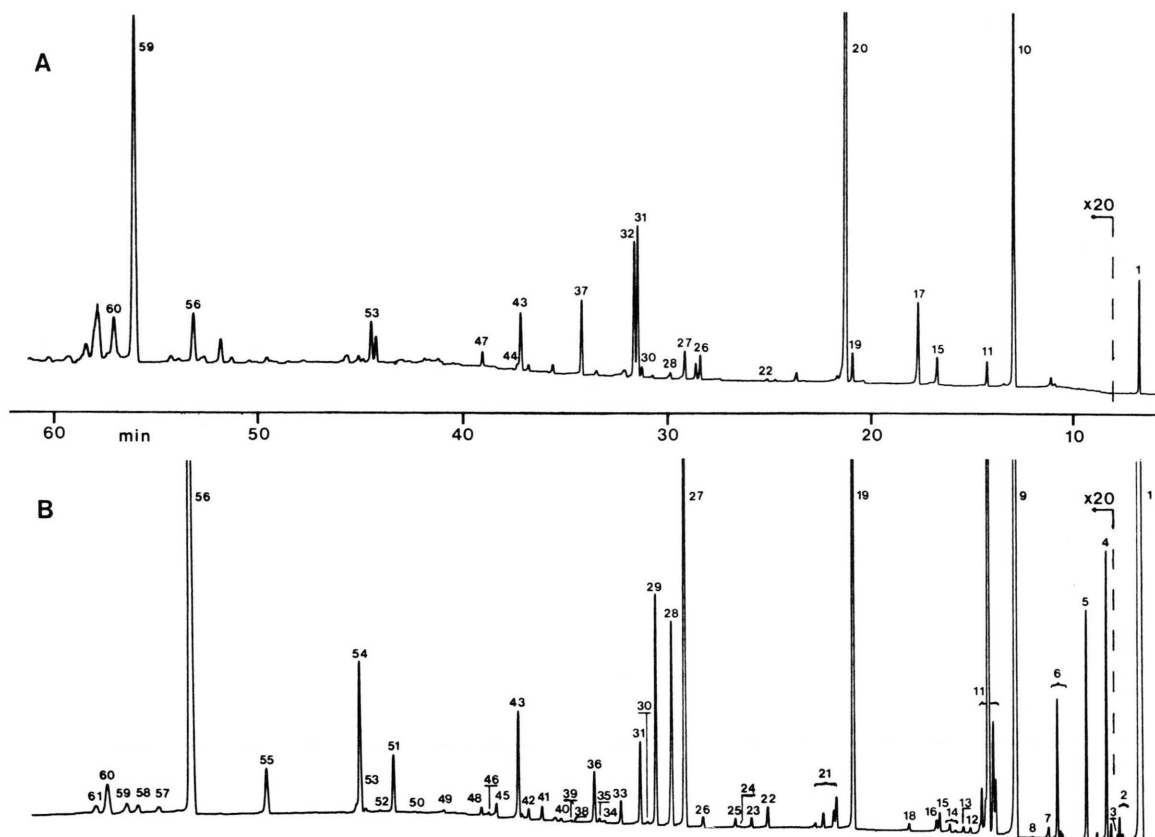


Fig. 1. Gaschromatograms of volatile constituents of *Formica rufa* workers: A = heads, B = abdomens. 50 m glass capillary, WG 11 as stationary phase, 50–180 °C, rate 3°/min.

formic acid, freshly collected workers were crushed at -70°C over solid sodiumbicarbonate which was immediately extracted with pentane: the esters were still found in unchanged concentrations. In view of the relatively large amounts of formic acid present in the abdomina, the occurrence of formates is not surprising, however, it has to be clarified whether they play a role as intraspecific or interspecific chemical signals.

Formic acid esters have been seldomly found in insects. While neryl formate is an alarm pheromone of *Tyrophagus putrescentiae* [16], 1,3,5,7-tetramethyldecyl formate is the aggregation pheromone of another acarid mite, *Lardoglyphus konoi* [17]. Nonylformate was found in the defensive secretion of the Carabid beetle, *Helluo costatus*, where it acts as a potential wetting agent to facilitate the penetration of the major defensive component, formic acid

[18]. A similar function has been discussed for undecane and tridecane from Dufour's glands of *F. sanguinea* [19]. It is interesting to note that formates of long chain alcohols have been described as synthetic substances mediating male behaviour of several Lepidopteran species [15]. E.g., in *Heliothis virescens* (Z)-11-hexadecenyl formate [20] turned out to disrupt male orientation towards the female sex pheromone, (Z)-hexadecenal [21]. Formic acid esters have also been found in mammals: among other formates hexadecyl formate was found in the pre-orbital gland of the small neotragine antelope *Raplicerus melanotis* [22].

Formates are not easily identified by GC/MS because their EI-spectra strongly resemble those of the corresponding alcohols. However, a fragment of low intensity (0.5–5%) at m/z 47, representing the protonated acid, and their relatively short retention times

Table I. Volatile constituents of *Formica rufa* workers.

Nr.	Compound	Abdomen	Head
1	undecane	M	M
2	undecenes	m	
3	5-methylundecane	s	
4	3-methylundecane	s	
5	dodecane	s	
6	dodecenes	s	
7	4-methyldodecane	t	
8	3,4-dimethylpentylformate	t	
9	tridecane	M	
10	methyl 3-ethyl-4-methylpentanoate		M
11	tridecenes	m	s
12	3-ethyl-4-methylpentylformate	t	
13	3-methyltridecane	t	
14	tridecadienes	t	
15	nonanal	t	s
16	tetradecane	t	
17	3,4-dimethylpentanol		m
18	(Z,Z,Z)-3,6,9-tridecatriene	t	
19	pentadecane	m	s
20	3-ethyl-4-methylpentanol		M
21	pentadecenes	t	
22	hexadecane	t	t
23	(Z,Z,Z)-3,6,9-pentadecatriene	t	
24	decylformate	t	
25	2-undecylformate	t	
26	decylacetate	t	s
27	heptadecane	m	s
28	Z-8?-heptadecene	s	t
29	undecylformate	s	
30	1-heptadecene	t	t
31	heptadecadiene	s	m
32	3-ethyl-4-methylpentyl 3,4-dimethylpentanoate		m
33	undecylacetate	t	
34	octadecane	t	
35	2-tridecanol	t	
36	(Z,Z,Z)-3,6,9-heptadecatriene	s	
37	3-ethyl-4-methylpentyl 3-ethyl-4-methylpentanoate		m
38	dodecylformate		t
39	2-tridecylformate		t
40	undecanol		t
41	dodecylacetate		t
42	nonadecane		t
43	Z-9?-nonadecene		s
44	2-tridecanol		t
45	tridecylformate		t
46	nonadecadiene		t
47	dodecanol		s
48	tridecenylformate		t
49	(Z,Z,Z)-3,6,9-nonadecatriene		t
50	tetradecylformate		t
51	Z-5-tetradecenylformate		s
52	tetradecylacetate		t
53	heneicosane		t
54	Z-5-tetradecenylacetate		s
55	Z-5-tetradecenol		s
56	hexadecylformate		M
57	Z-7?-hexadecenylformate		s
58	hexadecylacetate		s
59	tricosane		s
60	tricosene		s
61	Z-7?-hexadecenylacetate		s
62	* hexadecanol		m
63	* tetracosane		s
64	* Z-7?-hexadecenol		s
65	* pentacosane		m
66	* octadecylacetate		m
67	* pentacosene		s
68	* Z-9-octadecenylacetate		s

M, Main comp.; m, medium; s, small; t, trace.

* Not shown in Fig. 1 because of long retention time.

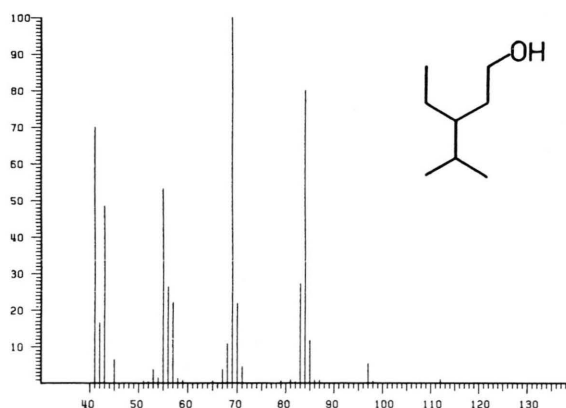
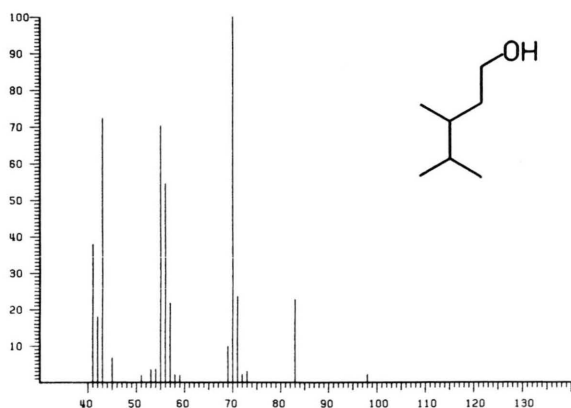


Fig. 2. 70 eV mass spectra of compounds 17 and 20.

on columns of medium polarity uncover a formate. Additional information may be obtained from CI-spectra [22].

Thorax

Besides large amounts of the typical row of saturated hydrocarbons with uneven numbers of carbon atoms, only nonanal was found in considerable concentrations.

Head

Although in other Formicidae past investigations have shown the presence of a number of oxygen containing compounds, especially from mandibular glands [23], little is known on the cephalic secretions of *Formica* spp. Among the volatile constituents found specifically in the heads of *F. rufa* workers, the chiral terpenoids **10**, **17**, **20**, **32** and **37** are particularly interesting. Compounds **10**, **20** and **37** were also found in the pentane extracts of freshly excised mandibular glands of *F. polyctena* queens. The biological significance of these odour components in the chemical communication systems of ants is presently under investigation. It is interesting to note that the trace compounds **8** and **12**, the formic acid esters of **17** and

20, are specifically found in the abdominal fraction. EI-mass spectra of the alcohols **17** and **20** are given in Fig. 2.

Conclusion

Results of our analyses clearly show that constituents of the abdomen of *F. rufa* fit well into the general concept of volatile signals derived from acetogenins [24] while major components of the cephalic secretions seem to originate from terpenes. Comparative studies on the odour bouquets of different *Formica* species are presently carried out. It appears that in contrast to the exclusive consideration of Dufour's glands compounds [4] the components of the cephalic secretions of *Formica* spp. may well be useful in chemosystematic classifications of closely related species. Results of these investigations will be published separately.

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