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RESEARCH REPORT

Comparison of the volatile compounds of *Dermestes maculatus* and *Dermestes ater* pupae: application of headspace solid-phase microextraction-gas chromatography-mass spectrometry (HS-SPME-GC/MS)

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Abstract

The headspace solid phase microextraction gas chromatography-mass spectrometry (HS-SPME-GC/MS) method was used for the determination of the volatile compounds of *Dermestes maculatus* and *D. ater* pupae. These beetles are of economic importance and they are a common pest of stored products and also serve as an intermediate host of the parasitic tapeworm, therefore an understanding of their biology is very important. Analyses of the volatile compounds of *D. maculatus* and *D. ater* pupae revealed differences between the insect species in their chemical composition. Sixteen volatile compounds of *D. ater* pupae, including 6 hydrocarbons, 5 fatty acids, 3 esters, and 2 aldehydes were identified. The major volatile compound in *D. ater* pupae was pentacosane. Ten compounds were present in < 10 % concentrations. A further five were present in < 1 % concentrations. A total of 39 compounds were identified in the *D. maculatus* pupae, including 28 esters of fatty acid, 4 fatty acids, 6 hydrocarbons and 1 aldehyde. Two volatile compounds were detected as major compounds: octadecadienoic acid methyl ester and octadecenoic acid methyl ester. A further eight were identified in smaller quantities (from 1.12 to 8.30 %) and the remaining volatile compounds were present in < 1 % concentrations.

Key Words: *Dermestes maculatus; Dermestes ater*; headspace solid-phase microextraction; GC-MS

Introduction

Insects are of growing significance in agriculture, veterinary medicine, medicine and human healthcare. The black larder beetle, *D. ater* and the hide beetle, *Dermestes maculatus,* belong to the Dermestidae (Coleoptera) family. They are a common pests of stored products. *D. ater* feeds on various plant and animal products such as raw skin and hide, stored meat, cheese, tobacco, dried fish, copra, silk, wool, milk and dried museum specimens (Bujang and Kaufman, 2010; Siddaiah and Kujur, 2016). These beetles also serve as an intermediate host of *Raillietina laticanalis* and *Choanotaenia infundibulum* in poultry (Bujang and Kaufman, 2010). The hide beetle, *D. maculatus* is a pest of the silk industry and it can damage stored animal products such as dried fish, cheese, hide, fur, bacon, and dog treats (Rajendran and Hajira Parveen, 2005; Shaver and Kaufman, 2009; Fontenot *et al.,* 2015). *D. maculatus* damages the wood and insulation of poultry houses (Cloud and Collison, 1985), but they are commonly used to clean carcasses as a part of the skeletonization process (Museumpest.net, 2012) and the adult beetles are used to estimate the post mortem interval (Shaver and Kaufman, 2009; De Souza and Linhares, 1997).

The volatile compounds of insects can be analyzed using many analytical techniques. For example, aggregation pheromones of the black larder beetle *Dermestes haemorrhoidalis* Kuster were analyzed by headspace gas chromatography-mass spectrometry (HS-GC/MS) and gas-chromatography with electroantennographic detection (GC-EAD) (Korada and Griepink, 2009).

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Organic compounds of the egg surface of queen diploid and haploid eggs and worker haploid eggs of the honeybee were extracted in dichloromethane and analyzed by gas chromatography-mass spectrometry (Katzav-Gozansky *et al.,* 2003). The main components of the external lipids of adult *Aleyrodes singularis* were extracted in chloroform and analyzed by gas chromatography-mass spectrometry (Soroker *et al.,* 2003). Cuticular hydrocarbons in the ant *Cardiocondyla wroughtonii* were analyzed by solid injection and GC-MS (Turillazzi *et al.,* 2002). The cuticular and internal n-alkane composition of *Lucilia sericata* larvae, pupae, male and female were separated by high-performance liquid chromatography with laser light scattering detector (HPLC-LLSD) and analyzed by gas chromatography-mass spectrometry with selected-ion monitoring (GC/MS-SIM) (Gołębiowski *et al.,* 2012a).

Thanks to the use of a number of analytical techniques, it is possible to identify many of the volatile compounds in insects (Cerkowniak *et al.,* 2013). For example, hydrocarbons were identified in *Heliothis virescens* pupae, *Helicoverpa zea* pupae (Buckner *et al*., 1996), *Aleyrodes singularis* adult and exuviae (Nelson *et al.,* 1998), *Lucilia sericata* larvae, pupae, male and female (Gołębiowski *et al.,* 2012a), *Chrysomya rufifacies* larvae (Zhu *et al.,* 2006), *Calliphora vomitoria*, *Calliphora vicina* and *Protophormia terraenovae* (Roux *et al*., 2008), *Musca domestica* (Butler *et al*., 2009), and *Sitophilus granaries* (Nawrot *et al.,* 2010). Fatty acids were present in *Heliothis virescens* pupae, *Helicoverpa zea* pupae (Buckner *et al.,* 1996), *Eurosta solidaginis* larvae (Nelson and Lee*,* 2004), *Melanoplus sanguinipes* adult, *Melanoplus packardii* adult (Soliday *et al.,* 1974) and diapause and non-diapause larvae of *Cydia pomonella* (Khani *et al.,* 2007). Aldehydes and alcohols were found in *Heliothis virescens* pupae, *Helicoverpa zea* pupae (Buckner *et al.,* 1996), *Aleyrodes singularis* adult and exuviae (Nelson *et al.,* 1998), *Chorthippus brunneus* males and females (Gołębiowski *et al*., 2016), *Musca domestica* larvae, pupae, male and female (Gołębiowski *et al.,* 2012b), *Scaptotrigona postica* workers (Poiani *et al*., 2015) and the nymphs and exuviae of *Bemisia argentifolii* (Buckner *et al.,* 1999). Esters were identified in *Calliphora vomitoria* larvae, pupae, male and female (Gołębiowski *et al.,* 2013) and *Acanthoscelides obtectus* (Gołębiowski *et al*., 2008). Organic compounds in the cuticular lipids serve various functions in insects. They are the primary energy source, and a structural component of membranes. They are often involved in chemical communication such as pheromones, and in defense as components of defensive secretions, and as antimicrobial agents (Cakmak *et al.,* 2007; Khani *et al*., 2007; Martins and Ramalho-Ortigão, 2012; Mann *et al.,* 2013; Ottaviani, 2014; Cerkowniak *et al*., 2015; Kühbandner and Ruther, 2015; Nguyen *et al*., 2015). However, volatile compounds mainly serve as pheromones.

Kairomones play a very important role in insect life. Kairomones are often used for host location, recognition and acceptance over shorter distances (Vet and Dicke, 1992; Vinson, 1998). These compounds are usually identified in host eggs, larvae, pupal cuticle, frass, silk, cocoons and glandular secretions (Afsheen *et al*., 2008). The role of host-related kairomones was investigated for example in the case of *Hyphantria cunea* (Drury), a host of the parasitoid *Chouioia cunea* Yang (Zhu, 2016). The study demonstrated that *C. cunea* is attracted to volatile kairomones from *H. Cunea*. Moreover, it has been shown a significant positive response of mated female *C. cunea* to 1-dodecene.

Furthermore, the volatile compounds secreted by insects can be used to detect insects in stored grains. The VOCs were identified e.g. in *Tribolium castaneum* (red flour beetle) and *Cryptolestes ferrugineus* (rusty grain beetle) by headspace analysis (Senthilkumar *et al.,* 2012). It was found that the amount of volatiles produced by *T. castaneum* adults increased with an increase in insect density in stored wheat.

In our study, HS-SPME-GC/MS was used for the determination of the volatile compounds of *D. maculatus* and *D. ater.*

Materials and Methods

Rearing of D. ater *and* D. maculatus

Both *Dermestes* species were kept at 25 ^{o}C with cyclic changes of light (L:D 12:12) in separate glass aquaria with a layer of wood shavings spread on the bottom and covered with mesh cloth to prevent insects escape. The beetles and larvae were fed beef meat *ad libitum*. Fully grown final instar larvae which ceased feeding were regularly isolated from the basic colonies and kept in glass jars until pupation in order to avoid slaughtering of larvae immobilized before pupation and naked pupae by younger larvae.

Headspace solid-phase microextraction

Polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber was used for the analysis of the volatile compounds extracted from *D. maculatus* and *D. ater* pupae - insects belonging to the Dermestidae family. For experiments,1-day-old pupae were used. Five insects of each species of Dermestidae (0.19 g *D. maculatus* and 0.17 g *D. ater*) were used for the analysis. The insects were placed in 4 ml glass vials prior to extraction. Next was added 4.8 μl of the undecane as standard and the capsule was capped. The samples were heated in a heating block. The best conditions for the HS-SPME-GC/MS were taken from literature (Cerkowniak *et al.,* 2017). The extraction time was 50 min, the extraction temperature -105 °C, desorption time 10 min at 230 °C. Analyzes were repeated 3 times.

Gas chromatography/mass spectrometry

The volatile compounds of *D. maculatus* and *D. ater* pupae were analyzed on a GC/MS QP-2010 SE (Shimadzu) equipped with a fused silica Rtx-5 capillary column, 30 m x 0.25 mm i.d., and with a 0.25 μm thick film. The oven temperature of 80 °C was increased to 190 °C at a rate of 4 °C/min, isotherm at 190 °C for 10 min, then the temperature was increased from 190 °C to 300 °C at a rate of 6 °C/min. Helium was used as the carrier gas at a

column head pressure of 60 kPa and electron impact was applied to the ionization (70 eV). The transfer line and injector temperatures were maintained at 300 and 230 °C, respectively. The ion source was kept at 200 °C. The analysis of volatile compounds was carried out by GC/MS in the total ion current (TIC) mode.

Results

Seventeen and thirty-nine volatile compounds were identified in the pupae of *D. ater* and *D. maculatus,* respectively. Figs 1 - 6 give examples of the mass spectra of esters of fatty acid, fatty acids, aldehydes and hydrocarbons.

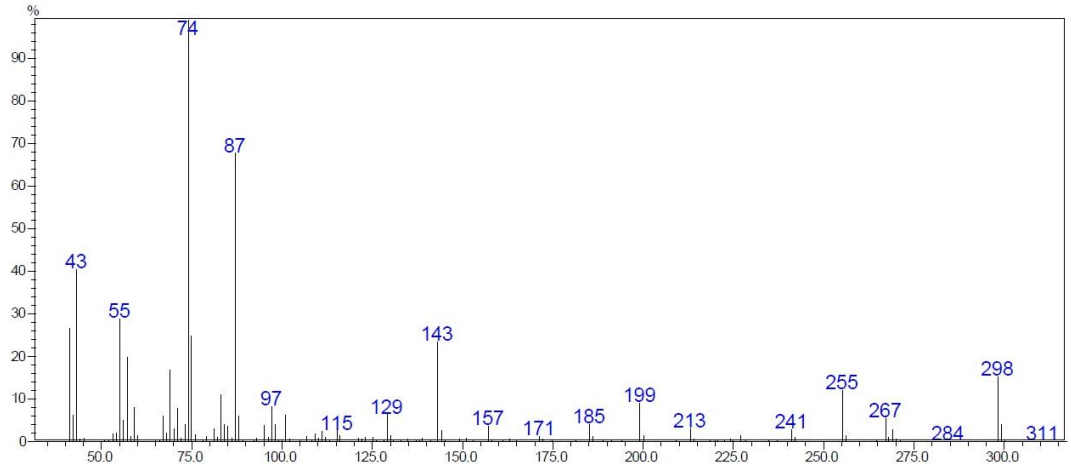

Fig. 1 Mass spectrum of octadecanoic acid, methyl ester.

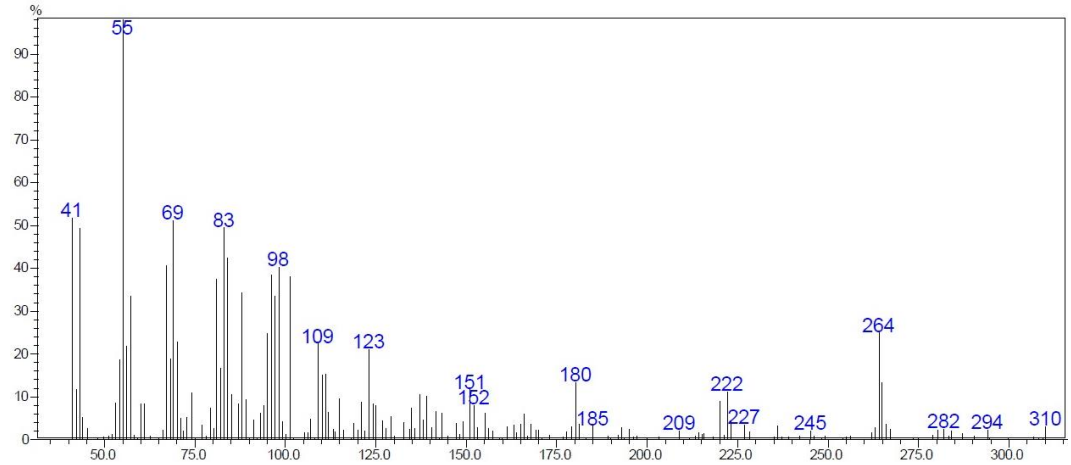

Fig. 2 Mass spectrum of octadecenoic acid, ethyl ester.

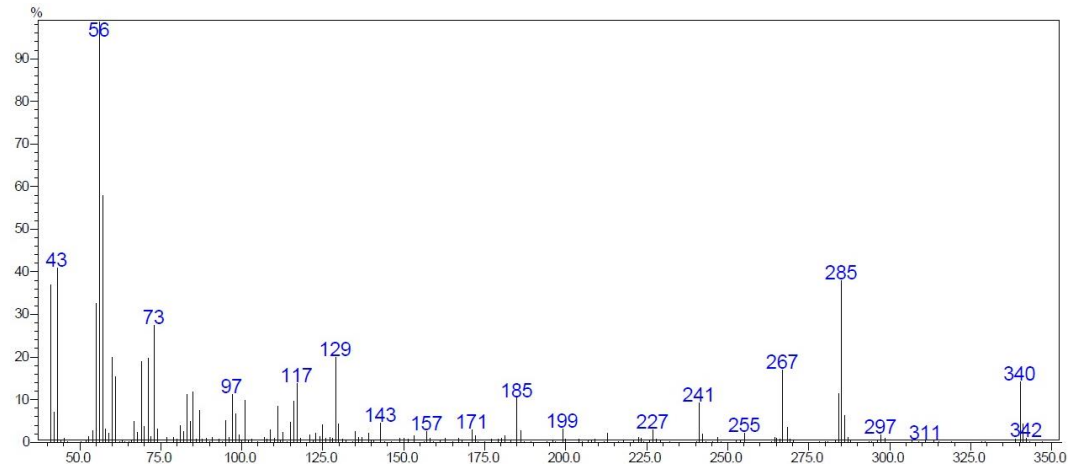

Fig. 3 Mass spectrum of octadecanoic acid, butyl ester.

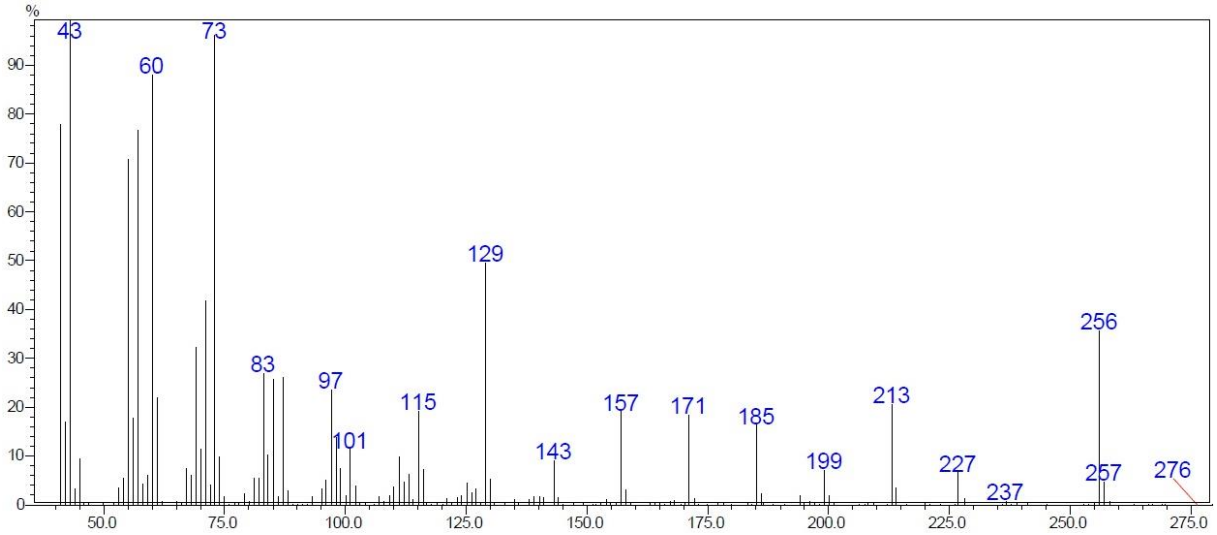

Fig. 4 Mass spectrum of hexadecanoic acid.

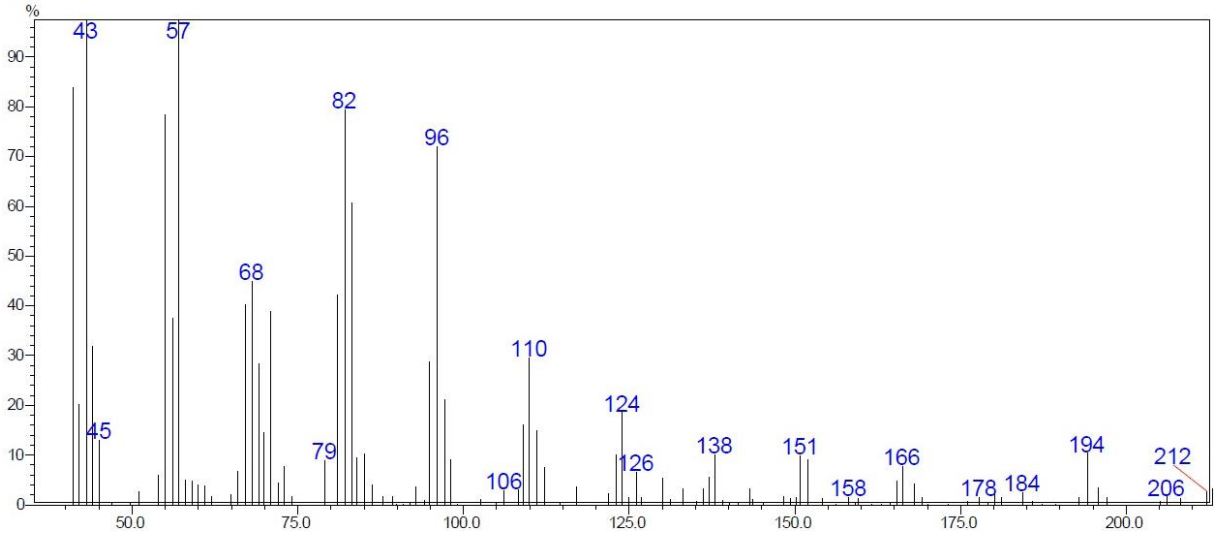

Fig. 5 Mass spectrum of hexadecanal.

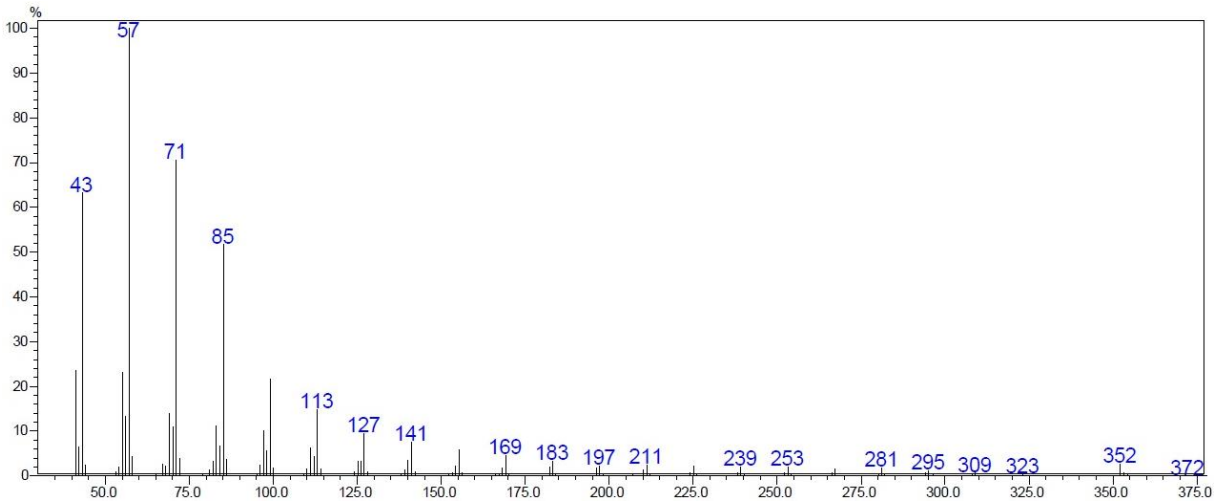

Fig. 6 Mass spectrum of pentacosane.

Table 1 Chemical composition of the volatile compounds found in pupae of *D. ater*

D. ater		
No	**Relative content [%]**	**Compounds**
1.	0.50	Decanoic acid
2.	3.58	Dodecanoic acid
3.	3.72	Tetradecanoic acid
4.	2.24	Hexadecanal
5.	0.94	Tetradecanoic acid, 1-methylethyl ester
6.	8.45	Hexadecanoic acid
7.	0.66	Octadecanal
8.	0.62	Octadecenoic acid
9.	0.41	Hexadecanoic acid, butyl ester
10.	9.93	Tricosane
11.	1.71	Octadecanoic acid, butyl ester
12.	3.17	Tetracosane
13.	1.34	Pentacosene
14.	54.28	Pentacosane
15.	1.50	Hexacosane
16.	6.95	Heptacosane

Chemical composition of the volatile compounds found in the pupae of D. ater

Table 1 lists the volatile compounds identified in *D. ater* pupae. Among sixteen volatile compounds of *D. ater* pupae, 6 hydrocarbons, 5 fatty acids, 3 esters, and 2 aldehydes were present. The volatile compounds of *D. ater* pupae contained only 2 unsaturated compounds, among which were acid and hydrocarbon. The remaining compounds were saturated. The major volatile compound in *D. ater* pupae was pentacosane (54.28 %). The compounds occurring in smaller quantities (from 1.34 to 9.93 %) were: dodecanoic acid (3.58 %), tetradecanoic acid (3.72 %), hexadecanal (2.24 %), hexadecanoic acid (8.45%), tricosane (9.93%), octadecanoic acid butyl ester (1.71 %), tetracosane (3.17 %), pentacosanol (1.34 %), hexacosane (1.50 %) and heptacosane (6.95%). A further six were present in concentrations of <1%: decanoic acid, tetradecanoic acid 1-methylethyl ester, octadecanal, octadecenoic acid, hexadecanoic acid butyl ester and octadecenoic acid.

Chemical composition of the volatile compounds found in the pupae of D. maculatus

Table 2 lists the volatile compounds identified in *D. maculatus* pupae. Thirty-nine volatile compounds were identified in *D. maculatus* pupae. Among them, 28 esters, 4 fatty acids, 6 hydrocarbons and 1 aldehyde were present. The volatile compounds of *D. maculatus* pupae contained 14 unsaturated compounds, among which were 13 acids and only one hydrocarbon. Among the esters, 25 methyl, 2 ethyl, and 1 butyl ester were present. Two volatile compounds were detected as major compounds: octadecadienoic acid methyl ester (35.32 %), and octadecenoic acid methyl ester (26.74 %). A further eight were identified in smaller quantities (from 1.12 to 8.30 %): tetradecanoic acid methyl ester (2.80 %), tetradecanoic acid (1.12 %), hexadecenoic acid methyl ester (8.30 %), hexadecanoic acid methyl ester (7.67 %), hexadecanoic acid (2.26 %), octadecatrienoic acid methyl ester (5.80 %), eicosatetraenoic acid methyl ester (1.48 %) and pentacosane (2.55 %). The remaining volatile compounds were present in <1% concentrations.

Comparison of the volatile compounds found in the pupae of D. ater *and* D. maculatus

Analyses of the volatile constituents of *D. maculatus* and *D. ater* pupae revealed differences between the insect species in chemical composition. The following compounds present in *D. ater* larvae lipids were absent in *D. maculatus* larvae: decanoic acid, tetradecanoic acid 1-methylethyl ester, octadecanal, octadecenoic acid and hexadecanoic acid butyl ester. On the other hand, twenty eight compounds that were present in *D. maculatus* were absent in the lipids of the larvae of *D. ater* (Tables 1 and 2). Only eleven compounds were present in both insect species: dodecanoic acid, tetradecanoic acid, hexadecanal, hexadecanoic acid, tricosane, octadecanoic acid butyl ester, tetracosane, pentacosene, pentacosane, hexacosane, and heptacosane (Tables 1 and 2). Twenty five methyl esters were identified in the *D. maculatus* pupae, while only one ester was found in the *D. ater* pupae. The lipids of *D. maculatus* contained also four fatty acids, six hydrocarbons, two ethyl esters, one butyl ester and one aldehyde, while the lipids of *D. ater* contained also five fatty acids, six hydrocarbons, two butyl esters, two aldehydes and one ethyl ester. The major compounds in *D. ater* pupae were pentacosane (54.3 %), tricosane (9.9 %) and hexadecanoic acid (8.5 %), while the major compounds in *D. maculatus* pupae were octadecadienoic acid methyl ester (35.5 %), octadecenoic acid methyl ester (26.7 %), hexadecenoic acid methyl ester (8.3 %) and hexadecanoic acid methyl ester (7.8 %).

Table 2 Chemical composition of the volatile compounds found in pupae of *D. maculatus*

D. maculatus		
No	**Relative content [%]**	**Compounds**
1.	0.02	Decanoic acid, methyl ester
2.	0.02	Nonanoic acid, 9-oxo-, methyl ester
3.	0.26	Dodecanoic acid, methyl ester
4.	0.08	Dodecanoic acid
5.	0.04	Tridecanoic acid, methyl ester
6.	0.02	Tridecanoic acid, 12-methyl-, methyl ester
7.	0.24	Tetradecenoic acid, methyl ester
8.	2.80	Tetradecanoic acid, methyl ester
9.	1.12	Tetradecanoic acid
10.	0.08	Pentadecanoic acid, methyl ester
11.	0.08	Tetradecanoic acid, 12-methyl-, methyl ester
12.	0.05	Hexadecanal
13.	0.22	Pentadecanoic acid, methyl ester
14.	0.75	Hexadecadienoic acid, methyl ester
15.	8.30	Hexadecenoic acid, methyl ester,
16.	7.67	Hexadecanoic acid, methyl ester
17.	0.23	Hexadecenoic acid
18.	2.26	Hexadecanoic acid
19.	0.24	Hexadecanoic acid, 14-methyl-, methyl ester
20.	0.57	Heptadecenoic acid, methyl ester
21.	0.07	Heptadecanoic acid, methyl ester
22.	5.80	Octadecatrienoic acid, methyl ester
23.	35.32	Octadecadienoic acid, methyl ester
24.	26.74	Octadecenoic acid, methyl ester
25.	0.72	Octadecanoic acid, methyl ester
26.	0.23	Octadecadienoic acid, ethyl ester
27.	0.17	Octadecenoic acid, ethyl ester
28.	1.48	Eicosatetraenoic acid, methyl ester
29.	0.70	Eicosatrienoic acid, methyl ester
30.	0.10	Eicosadienoic acid, methyl ester
31.	0.04	Tricosane
32.	0.11	Eicosenoic acid, methyl ester
33.	0.01	Eicosanoic acid, methyl ester
34.	0.17	Octadecanoic acid, butyl ester
35.	0.11	Tetracosane
36.	0.17	Pentacosene
37.	2.55	Pentacosane
38.	0.09	Hexacosane
39.	0.37	Heptacosane

Discussion

Chemical analyses of the volatile compounds of *D. maculatus* and *D. ater* pupae showed us that the esters of fatty acid are major compounds. The volatile compounds of *D. maculatus* and *D. ater* pupae contained 28 and 3 esters, respectively. Esters were identified in some other insect species. The cuticular lipids of *Calliphora vomitoria* larvae, pupae, males and females contained 6, 7, 5 and 7 fatty acid methyl esters (FAMEs) from C15:0 to C19:0, respectively (Gołębiowski *et al.,* 2013). The isopropyl esters, including isopropyl dodecanoate, isopropyl (Z)-9-tetradecenoate, isopropyl tetradecanoate, isopropyl (Z)-9-hexadecenoate and isopropyl hexadecanoate were detected in male abdominal extracts of the black larder beetle, *Dermestes haemorrhoidalis*, which belongs to the Dermestidae (Coleoptera) family (Korada and Griepink, 2009). The cuticular extract of female *Diaphorina citri* contained three esters: ethyl undecanoate, isopropyl tetradecanoate and 1-methylpropyl dodecanoate (Mann *et al.,* 2013).

Fatty acids are present in many insect species. For example, in the larvae of the wheat blossom midge, *Sitodiplosis mosellana,* 10 - 16 kinds of fatty acids, of which the predominant compounds were palmitic, oleic and linoleic acids, which were more than 95 % of the total fatty acids (Jun-Xiang *et al.,* 2001), can be observed. The cuticular extract of

female *Diaphorina citri* contained four acids: acetic acid, hexanoic acid, decanoic acid and pentadecanoic acid. The cuticular extract of male *D. citri* contained only two acids: dodecanoic acid and tetradecanoic acid (Mann *et al.,* 2013). In the surface lipids of pupae of *C. vomitoria* were 23 carboxylic acids from C8:0 to C24:0. The major compounds were: C18:1 (37.2 %), C16:1 (27.3 %) and C16:0 (23 %). Interestingly, pupae and larvae of this species showed complete resistance to *C. coronatus* infection (Gołębiowski *et al.*, 2013). In our work, we stated that the cuticular lipids of *D. ater* pupae contained five fatty acids from C10 to C18, and those of *D. maculatus* pupae contained four fatty acids from C12 to C16.

In our study, two saturated aldehydes: hexadecanal and octadecanal, were identified in *D. ater* and only one aldehyde (hexadecanal) was present in *D. maculatus*. Aldehydes were identified in some other insect species. For example, the unsaturated aldehydes: (*Z*)-7-tetradecenal and (*E*)-11-hexadecenal, are major sex pheromone components of *Prays oleae* (Lepidoptera: Yponomeutidae) and *Palpita unionalis* (Lepidoptera: Pyralidae) (Milonas *et al.,* 2009). The saturated aldehydes: hexadecanal, (*Z*)-9-hexadecenal and (*Z*)-11-hexadecenal, were found in the gland extracts of *Helicoverpa armigera* (Wu *et al.,* 1997). Aldehydes are also present in plants. For example, nonanal, decanal and (*E*)-2-hexenal are released from maize (*Zea mays*). GC-EAD analyses revealed a response from the Asian corn borer, *Ostrinia furnacalis* male and female to (*E*)-2-hexenal and nonanal (Huang *et al.,* 2009).

The following hydrocarbons from C23 to C27 were identified in *D. ater* and *D. maculatus*: tricosane, tetracosane, pentacosene, pentacosane, hexacosane and heptacosane, with the marked dominance of odd numbers of carbon atoms. Cuticular hydrocarbons are involved in various chemical communications in insects (Zhi-bin *et al.,* 2000). They are typically found in many insect species. For example, the following homologous series were identified in the cuticular lipids of the Western Flower Thrips, *Frankliniella occidentalis*: n-alkanes from C25 to C29, 3-methylalkanes with 26 and 28 carbon atoms, and branched monomethyl alkanes with 26, 28 and 30 carbon atoms (Gołębiowski *et al.,* 2007). Saturated hydrocarbons with a carbon chain length of 21 - 31 and six kinds of alkenes were identified in *Chrysomya rufif*acies larvae (Zhu *et al*., 2006). The extracts of elytra of the root weevil, *Diaprepes abbreviatus* contained four groups of homologous compounds: a group of normal hydrocarbons, a group of monomethyl-branched alkanes, a group of dimethyl-branched alkanes and alkenes (Lapointe *et al.,* 2004).

Composition of volatile organic compounds was investigated in larvae and pupae of blowfly (Frederickx, 2012). Using the SPME volatile collection and GC-MS analysis, approximately 90 compounds were identified in the three stages of larval development and the 10 stages of development of the pupae of *Calliphora vicina*. It helped to evaluate the age of flies, to establish a postmortem interval (PMI) in medical investigations. Especially because the composition of the volatile compounds of pupae and the compounds secreted by the larvae were significantly different The compounds secreted by larvae and the pupae were analyzed by an ascending hierarchical clustering (AHC). Pupae volatile profiles allow three groups to be distinguished: pupae of 1 - 3 days old; pupae of 4 - 7 days old and pupae of 8 - 10 days old. In the older pupae, from 1 to 3 days old, were identified: methyldisulphanylmethane and 4,7,7-trimethylbicyclo[3.1.1]hept-3-ene (alpha-pinene). The pupae from 4 to 7 days old were grouped in cluster because they emitted 3- methylbutanal, ethanol, methyldisulphanylmethane (dimethyldisulphide), methylsulphanyldisulphanylmethane (dimethyltrisulphide) and alpha-pinene. In VOCs of *C. vicina* pupae of 4 and 5 days old found 3-methylbutan-1-ol as characteristic compound. 6-day and 7-day-old pupae were grouped thanks acetic acid. In the last cluster were 8- to 10-day-old pupae. In this pupae as characteristic were identified: 2-methylpropan-1-ol, 1-methoxy-3-methylbutane, ethyl 3-methylbutanoate, 3-methylbutyl acetate and methyldisulphanylmethane (Frederickx, 2012).

The composition of hydrocarbons in insect species is also used as an indicator of the postmortem interval. For example, n-alkanes, methyl-branched alkanes, and dimethyl-branched alkanes in *Chrysomya megacephala* were identified (Zhu, 2007). For most of the hydrocarbons with molecular weight below n-C26 the abundance decreased significantly with the weathering time, what can be useful in determine the PMI.

Conclusions

The HS-SPME-GC/MS method is simple and successful for the determination of the volatile compounds of *D. maculatus* and *D. ater* pupae. This technique allows the positive identification and quantitation of fatty acids, hydrocarbons, esters of fatty acids, and aldehydes. Using HS-SPME-GC/MS, sixteen volatile compounds of *D. ater* pupae, including 6 hydrocarbons, 5 fatty acids, 3 esters, and 2 aldehydes were identified, while 39 compounds were identified in the pupae of *D. maculatus*, including 28 esters of fatty acid, 4 fatty acids, 6 hydrocarbons and 1 aldehyde.

The identified compounds can inhibit hyphal growth, prevent desiccation and can also often be involved in chemical communication. Therefore, more experiments need to be conducted to understand the physiological role of the identified compounds.

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