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IDENTIFICATION OF PHEROMONES FROM THE MALE SWIFT MOTH HEPIALUS HECTA L.

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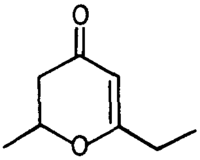
Main components of the pheromone blend of the male swift moth Hepialus hecta L. are identified as 6-ethyl-2-methyl-3,4-dihydro-2H-pyran, 1,8-dimethyl-3-ethyl-2,9-dioxabicyclo[3.3.1]non-7-ene and 1,8-dimethyl-3-ethyl-2,9-dioxabicyclo-[3.3.1]non-7-en-6-one.

Chemical structures of pheromones of male Lepidoptera show a great variety, just in contrast to those of female moths [1]. Hepialus hecta L. is a species of the primitive family of Hepialidae where the males attract females after sunset [2]. For this purpose males display big hindleg scale-brushes containing volatile compounds, the smell of which has been described as "wild strawberries" or "pineapple".

We report here on the identification of the major components and some minor constituents of the male tibial scenting organs of H. hecta. Males where caught in Upper Bavaria during their calling flights. After dissection from the tibia the scales were extracted with pentane. The fresh scale organ and the concentrated fruitlike smelling extract proved to be electrophysiologically active on male and female antennae.

A gas chromatogram on a 50 m fused silica column coated with SE 54 showed three major compounds and several trace compounds. The amount of the main products (A),(B),(C) per individuum was about 40 µg, 5 µg and 5 µg. Compounds (A),(B), (C) were isolated by preparative gas chromatography on a 6 ft x 1/8" packed column with 3 % SE 30 on Chromosorb W-AW DMCS, 80-100 mesh under temperature program 70-180°C - 2°C/min. Mass spectra (70 eV) were obtained with a Varian MAT 311A and a Finnigan computer system SS200. Plotted spectra of compounds (B) and (C) are shown in Fig. 1. ^{1}H-NMR und ^{13}C-NMR spectra were recorded on a Bruker WM400; spectral data are given in Tab. 1 and 2.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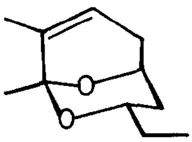
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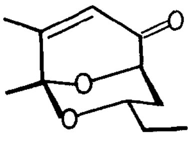
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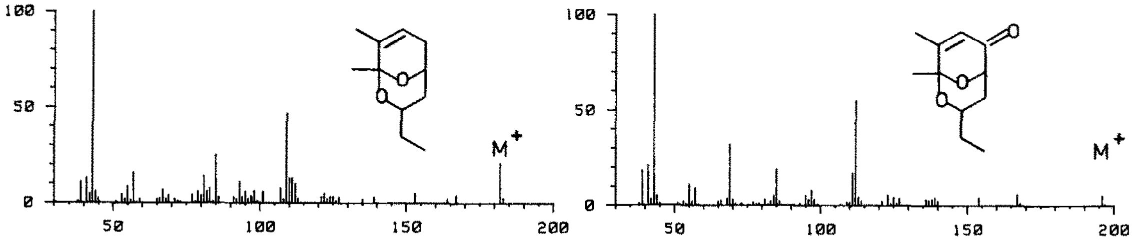
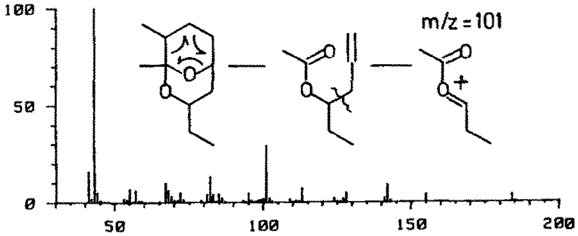


Figure 1: EI-mass spectra of compounds (B) and (C) (70 eV)



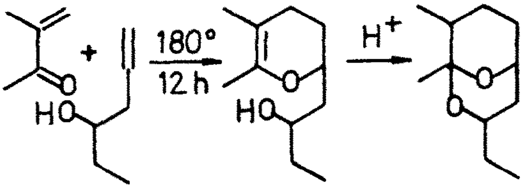


Figure 2: EI-mass spectrum of (B') Proposed formation of m/z 101

Figure 3: Synthesis of compound (B')

Table 1. ^{1}H-NMR spectra 400 MHz ($CDCl_3$)

	B	C	C'	C"
CH_3-	0.88(t)	0.88(t)	0.90(t)	0.89(t)
	1.41(s)	1.53(s)	1.40(s)	0.94(d)
	1.64(m)	1.95(d)	1.65(t)	1.41(s)
CH_2-	1.30-1.90(m,5H)	1.33-1.98(m,4H)	1.20-1.93(m,4H)	1.28(m)*
	2.64(m,1H)			1.43-1.53(m, 2H)
				1.59(dt, 1H)
				1.70-1.80(m, 2H)
CH-	3.77(m)	3.64(m)	3.70(m)	1.68(m)
	4.13(bt)	4.32(bd)	4.17(bt)	3.82(m)
	5.75(bs)	6.15(bs)	4.62(m)	3.86(m)
			5.69(bs)	3.95(m)

*) together with impurities

Table 2. ^{13}C-NMR spectra ($CDCl_3$)

Compound B:

1-C	3-C	4-C	5-C	6-C	7-C	8-C	1-CH_3	8-CH_3	3-CH_2-CH_3
95.4	68.0	30.4	66.6	36.4	123.4	133.0	24.7	9.4	29.4/18.5
	(66.6)	(29.4)	(68.0)						(30.4)

Compound C:

1-C	3-C	4-C	5-C	6-C	7-C	8-C	1-CH_3	8-CH_3	3-CH_2-CH_3
96.1	69.3	32.2	75.1	**	126.9	**	24.8	9.0	29.1/19.3
		(29.1)							(32.2)

**) carbon atoms 6-C and 7-C remained invisible in the noise

Compound (A) has been previously identified as 6-ethyl-2-methyl-2,3-dihydro-4H-pyran-4-one [3].

Identification of compound (B) - isolated amount ca. 200 µg: High resolution ms showed its molecular weight to be 182,1307 corresponding to $C_{11}H_{18}O_2$. The compound did not react with $LiAlH_4$, but could be catalytically hydrogenated to a pair of diastereomers (B'), $C_{11}H_{20}O_2$, the mass spectrum of which is shown in Fig. 2. The fragmentation pattern of (B') resembled that of alkyl-6,8-dioxabicyclo[3.2.1]octanes [4]. However, a fragment at m/z 101 ($C_5H_9O_2$ by high res. ms) strongly pointed to the 2,9-dioxabicyclo[3.3.1]nonane system. According to our experiences gained through the identification of 1,3-dimethyl-2,9-dioxabicyclo[3.3.1]nonane from Norway spruce [5], we tentatively classified (B') as 3-ethyl-1-methyl-2,9-dioxabicyclo[3.3.1]nonane containing an additional methyl group.

A detailed analysis of the hydrogen resonances of compound (B) - see Tab. 1 - was obtained from a 2-D H,H-COSY spectrum [6]. Starting from the methyltriplet at 0.88 ppm the anisochronic protons of the respective methylene group are found at 1.39 and 1.53 ppm. Both couple with the proton at 3.77 ppm which is attached to 3-C. Through cross peaks 3-H is linked to 4-H at 1.80 ppm and 4'-H at 1.35 ppm, which in turn couple with 5-H at 4.31 ppm. Identification of 5-H leads to the discovery of 6-H at 2.64 ppm and 6'-H at 1.86 ppm. A broad singlet is found at 5.75 ppm which gives a cross peak with 6'-H and a methyl group at 1.65 ppm. This methyl group and the proton at 5.75 ppm must be bond to sp^2-carbons 7-C and 8-C respectively. The partial structure is completed by ^{13}C-NMR data - see Tab. 2: the ^{13}C-signal at 95.37 ppm has to be attributed to an acetalic carbon atom which inevitably carries the methyl group at 24.71 ppm (corresponding to the singulett at 1.41 ppm in the ^1H-NMR spectrum). The coupling constants $J_{3,4}$ = 3.0 Hz and $J_{3,4'}$ = 12.4 Hz clarify the stereochemistry at 3-C. Because of the trans-diaxial coupling of 12,6 Hz the ethyl group is in the equatorial position.

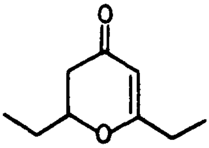
Unambiguous attribution of the methyl group at 1.65 ppm to either 7-C or 8-C was impossible by NMR. Therefore 1,7-dimethyl-3-ethyl-2,9-dioxabicyclo[3.3.1]-nonane and 1,8-dimethyl-3-ethyl-2,9-dioxabicyclo[3.3.1]nonane were prepared by Diels-Alder reaction of 5-hexen-3-ol with 3-penten-2-one or 3-methyl-3-buten-2-one followed by intramolecular cyclization of the initially formed dihydropyran - see Fig. 3. The mass spectrum of 1,8-dimethyl-3-ethyl-2,9-dioxabicyclo[3.3.1]nonane was in accord with that of compound (B').

Compound (B) therefore is (1R,3S,5S)-1,8-dimethyl-3-ethyl-2,9-dioxabicyclo-[3.3.1]non-7-ene or its antipode.

Identification of compound (C) - isolated amount ca. 200 µg: High resolution mass spectrometry showed its molecular weight to be 196.1149 corresponding to $C_{11}H_{16}O_3$. Reduction with $LiAlH_4$ yielded an alcohol (C') = $C_{11}H_{18}O_3$, which suggested (C) to be an aldehyde or ketone. Catalytic hydrogenation furnished a carbonyl compound $C_{11}H_{18}O_3$. The ^{13}C-NMR spectrum of (C) resembled that of (B).

Since its ^{1}H-NMR spectrum, which also resembled that of (B) - showing two methylene protons less than that of (B) -, ketone (C) was regarded as an oxidation product of compound (B). At 4.32 ppm 5-H appeared as a broad doublett, coupling only with 4H and 4'-H which suggested that 6-C carries the additional oxygen. This was supported by the fact, that the ^{1}H-NMR spectrum of the allylic alcohol (C') revealed a new proton at 4.62 ppm, which coupled with 5-H as well as with a proton and a methyl group attached to sp^2 carbons 7-C or 8-C respectively. To clarify this, (C') was hydrogenated (5 % Pd/C) to the saturated 6-hydroxyacetal (C"), the ^{1}H-NMR spectrum of which showed a coupling of 6-H with a methylene group at 7-C. Compound (C) therefore is (1R,3S,5R)-1,8-dimethyl-3-ethyl-2,9-dioxabicyclo[3.3.1]non-7-en-6-one or its antipode.

GC/MS analyses of the crude scale extract led to the identification of trace components which are closely related to (A), (B) and (C): 2,6-diethyl-2,3-dihydro-4H-pyran-4-one (D), 1,3,8-trimethyl-2,9-dioxabicyclo[3.3.1]non-7-ene (E) and 1,3-diethyl-8-methyl-2,9-dioxabicyclo[3.3.1]non-7-ene (F) as well as 1,3,8-trimethyl-2,9-dioxabicyclo[3.3.1]non-7-en-6-one (G) and 1,3-diethyl-8-methyl-2,9-dioxabicyclo[3.3.1]non-7-en-6-one (H). Compound (G) has been previously synthesized 7) as a model for the structurally related talaromycin.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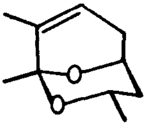
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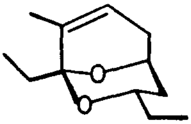
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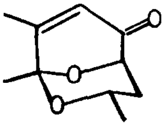
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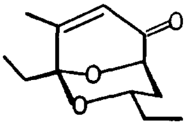
H

Syntheses of the compounds, bioassays and fine structure studies of the scent organ, odor receptors on the antennae of both sexes and the behaviour will be published elsewhere.

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