Identification of Cyclic Enolethers from Insects: Alkyldihydropyranes from Bees and Alkyldihydro-4H-pyran-4-ones from a Male Moth*

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Mass spectrometric fragmentation patterns of alkyl-3,4-dihydro-2H-pyranes and alkyl-2,3-dihydro-4H-pyran-4-ones are described. Through GC/MS analyses, respective compounds showing unbranched carbon skeletons are identified for the first time as volatile signals of social and solitary bees and of the male moth *Hepialus hecta* L.

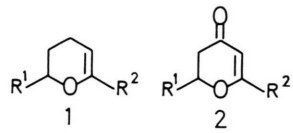
We studied mass spectrometric fragmentation patterns of cyclic enolethers to facilitate their identification from natural material [1]. Mass spectra of alkyl-3,4-dihydro-2H-pyranes (**1**) are characterized by fragments which correspond to:

A) α-cleavage at 2-C;
B) *retro* cleavage ("Retro-Diels-Alder-Reaction");
C) *retro* cleavage with hydrogen transfer to the oxygen containing fragment;
D) an acylium fragment which contains 6-C and the respective substituent.

Signals caused by fragmentations C and D are particularly intense when the substituent at 6-C is a methyl- or an ethyl-group, while A and B are of low intensities when 6-C carries a longer chain.

We now found, that an alkyl chain of at least *n*-propyl, attached to the sp^2-carbon atom which carries the oxygen, in dihydropyranes as well as in dihydrofuranes and tetrahydrooxepines may furnish intense signals corresponding to:

E) Mc-Lafferty rearrangement at the side chain;
F) a "formal" γ-cleavage at the side chain;
G) Mc-Lafferty rearrangement of the oxygen containing fragment produced by *retro* cleavage B.



Mass spectra of alkyl-2,3-dihydro-4H-pyran-4-ones (**2**) resemble those of alkyl-3,4-dihydro-2H-pyranes because they also show fragmentations A-G. However, due to the presence of the carbonyl group dihydropyrones may give some additional signals.

On the basis of these results we identified for the first time several alkyldihydropyranes and alkyldihydro-4H-pyran-4-ones both from social and solitary bees and from a male moth (see Table I).

During our investigations on odour communication in bees we studied the cephalic secretions of solitary bees, of social stingless bees and of honey bees. Among the complex multicomponent mixtures we identified small amounts of several new cyclic enolethers. In the abdomina of workers of *Apis mellifica* L. we found 2,6-dimethyl-3,4-dihydro-2H-pyrane (**1a**). This compound is also present in head extracts of the stingless bee *Scaptotrigona bipunctata* (Lepeletier) which additionally contain two bishomologues, 2-methyl-6-propyl-3,4-dihydro-2H-pyrane (**1b**) and 2-methyl-6-pentyl-3,4-dihydro-2H-pyrane (**1c**). The latter compound was also found in *Nannotrigona testaceicornis* (Lepeletier), *Plebeia droryana* Friese, *Tetragona clavipes* (F.) and in some Taeniandrena species. Fig. 1 shows a plotted mass spectrum of **1c** which we now identified as one of the main components of the cephalic scent mark secretion of the solitary bee *Andrena wilkella* K. [2]. Besides 6-butyl-3,4-dihydro-2H-pyrane (**1f**), head extracts of *Partamona cupira* (Smith) contain 6-heptyl-2-methyl-3,4-dihydro-2H-pyrane (**1d**) and 2-methyl-6-nonyl-3,4-dihydro-2H-pyrane (**1e**).

Compounds **1a–1e** form a new row of unbranched bishomologue cryptic 2-hydroxyalkan-6-ones which seem to originate from the acetate pool and which

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Table I. Cyclic enolethers identified from insects; mass spectra; ^{1}H-NMR-spectra.

No.	R_1	R_2	Insect species	MS (EI, 70 eV) *m/z* (%), [Fragmentation]	^{1}H-NMR 270 MHz
1a	CH_3	CH_3	*A. mellifica*[a] *S. bipunctata*	112 (20), 97 (10) [A], 83 (3), 71 (40) [C], 69 (12), 67 (6), 58 (8), 55 (31), 43 (100) [D]	C_6D_6: 1.14 (d, 3H), 1.41 (m, 2H), 1.75 (s, 3H), 1.85 (m, 2H), 3.75 (m, 1H), 4.43 (m, 1H)
1b	CH_3	C_3H_7	*S. bipunctata*	140 (20), 125 (7) [A], [F], 112 (41) [E], 99 (18) [C], 97 (29), 83 (20), 71 (46) [D], 70 (22) [G], 55 (100), 43 (67)	C_6D_6: 0.91 (t, 3H), 1.16 (d, 3H), 1.26–1.52 (m, 2H), 1.62 (m, 2H), 1.77–2.04 (m, 2H), 2.09 (t, 2H), 3.78 (m, 1H), 4.48 (m, 1H)
1c	CH_3	C_5H_9	*S. bipunctata* *N. testaceicornis* *P. droryana* *T. clavipes* *Taeniandrena spp.*	168 (18), 126 (14) [B], 125 (41) [F], 112 (100) [E], 97 (36), 84 (29), 83 (46), 70 (35) [G], 55 (86), 43 (56)	C_6D_6: 0.88 (t, 3H), 1.17 (d, 3H), 1.23–1.67 (m, 8H), 1.79–2.07 (m, 2H), 2.13 (t, 2H), 3.89 (m, 1H), 4.15 (m, 1H)
1d	CH_3	C_7H_{15}	*P. cupira*	196 (10), 125 (53) [F], 112 (100) [E], 97 (22), 84 (21), 83 (32), 70 (20) [G], 58 (18), 55 (60), 43 (37)	C_6D_6: 0.88 (t, 3H), 1.18 (d, 3H), 1.20–1.34 (m, 10H), 1.55–1.71 (m, 2H), 1.78–2.10 (m, 2H), 2.16 (t, 2H), 3.81 (m, 1H), 4.53 (m, 1H)
1e	CH_3	C_9H_{17}	*P. cupira*	224 (6), 125 (46) [F], 112 (100) [E], 97 (15), 84 (13), 83 (20), 70 (13) [G], 58 (13), 55 (38), 43 (27)	C_6D_6: 0.91 (t, 3H), 1.18 (d, 3H), 1.20–1.53 (m, 16H), 1.78–2.06 (m, 2H), 2.16 (t, 2H), 3.79 (m, 1H), 4.52 (m, 1H)
1f	H	C_4H_9	*P. cupira*	140 (17), 111 (9) [F], 98 (100) [E], 85 (11) [D], 83 (27), 70 (20) [G], 57 (15), 56 (15), 55 (61), 43 (48)	C_6D_6: 0.88 (t, 3H), 1.23–1.48 (m, 4H), 1.78 (m, 2H), 1.96 (m, 4H), 3.96 (m, 2H), 4.44 (t, 1H)
2a	CH_3	C_2H_5	*H. hecta*	140 (55), 125 (2) [A], 111 (3), 99 (92) [C], 98 (14) [B], 69 (100), 57 (62) [D], 55 (7), 43 (25)	$CDCl_3$: 1.08 (t, 3H), 1.41 (d, 3H), 2.22 (q, 2H), 2.34 (m, 2H), 4.44 (m, 1H), 5.25 (m, 1H)
2b	C_2H_5	C_2H_5	*H. hecta*	154 (16), 126 (3), 125 (4) [A], 99 (100) [C], 98 (5) [B], 69 (51), 57 (51) [D], 56 (17), 43 (38)	$CDCl_3$: 0.99 (t, 3H), 1.10 (t, 3H), 1.62–1.89 (m, 2H), 2.25 (q, 2H), 2.37 (m, 2H), 4.26 (m, 1H), 5.28 (m, 1H)
2c	C_2H_5	CH_3		140 (35), 125 (3), 112 (3), 111 (3) [A], 97 (2), 85 (100) [C], 84 (4) [B], 69 (23), 56 (13), 43 (77) [D]	$CDCl_3$: 0.92 (t, 3H), 1.55–1.83 (m, 2H), 1.91 (s, 3H), 2.28 (m, 2H), 4.19 (m, 1H), 5.18 (m, 1H)
2d	CH_3	C_5H_9		182 (27), 167 (1) [A], 141 (58) [C], 140 (16) [B], 139 (17) [F], 126 (60) [E], 99 (11) [D], 98 (21), 97 (22), 84 (100) [G], 69 (72), 55 (25), 43 (31)	$CDCl_3$: 0.92 (t, 3H), 1.34 (m, 4H), 1.46 (d, 3H), 1.58 (m, 2H), 2.24 (t, 2H), 2.42 (m, 2H), 4.50 (m, 1H), 5.31 (m, 1H)

[a] Found in abdomina: has been erroneously reported as a constituent of the cephalic secretion [1].

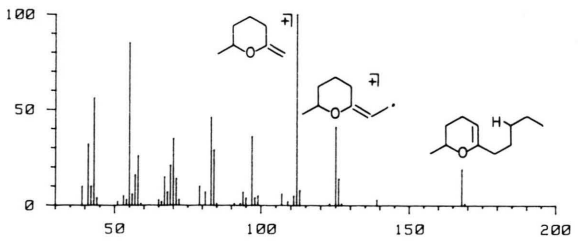

Fig. 1. 70 eV Mass spectrum of 2-methyl-6-pentyl-3,4-dihydro-2 H-pyrane and fragmentation.

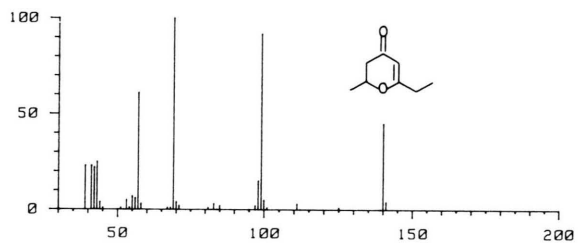

Fig. 2. 70 eV Mass spectrum of 6-ethyl-2-methyl-2,3-dihydro-4 H-pyran-4-one.

may be biogenetically closely related to spiroacetals like 2,8-dimethyl-6,8-dioxaspiro [5.5]undecane which we also found in several of the insect species mentioned above [2, 3].

2,3-Dihydro-4H-pyranes are very rare in insects: 2,5-diethyl-2-formyl-2,3-dihydro-4H-pyrane, the Diels-Alder-dimer of 2-methylenebutanal, has been described from Blattidae [4].

As part of our studies on pheromones of male lepidoptera we analyzed the fruitlike smelling volatiles of the odoriferous organs of the male swift moth *Hepialus hecta* L. The gaschromatogram showed a major component and two minor ones, while several additional substances could be detected in trace amounts. The main compound (mol. weight $140 = C_8H_{12}O_2$ as determined by high resolution mass spectrometry) was identified as 6-ethyl-2-methyl-2,3-dihydro-4 H-pyran-4-one (**2a**). Fig. 2 shows a plotted mass spectrum of this compound, which to our knowledge is the first compound identified from Hepialidae. Additionally, a homologue of (**2a**), 2,6-diethyl-2,3-dihydro-4 H-pyran-4-one (**2b**), proved to be present in trace amounts. The two minor components and some of the trace components mentioned above, are derivatives of the 2,9-dioxabicyclo [3.3.1]non-7-ene system [5].

While the new 2,3-dihydro-4 H-pyran-4-ones show unbranched carbon skeletons, tetrasubstituted compounds which are probably derived from propionate units have been identified from *Stegobium paniceum* L. and *Lasioderma serricorne* F. (Col. Anobiidae) [6, 7].

GC analyses and GC/MS investigations were carried out on 50 m glas capillary columns with WG 11 as a stationary phase and on 50 m fused silica capillaries coated with SE 54. Mass spectra were obtained with a Varian MAT 311A. Chemical structures of natural products were confirmed by comparison of GC/MS data with those of authentic reference samples. Mass spectral data and ^{1}H-NMR data of the compounds are compiled in Table I.

Alkyl-3,4-dihydro-2 H-pyranes were prepared by Grignard reaction of lactones with alkylmagnesiumhalides followed by elimination of water from the obtained cyclic hemiacetals [8]. Optically active dihydropyranes may be produced from respective optically active lactones. Alkyl-2,3-dihydro-4 H-pyran-4-ones were prepared by acylation of β-ketoesters with $\alpha\beta$-unsaturated acylhalogenides followed by cyclization, saponification and decarboxylation [9]. Bioassays with synthetic compounds will be described elsewhere.

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