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-pyrans 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 hexta

We studied mass spectrometric fragmentation  
patterns of cyclic enolethers to facilitate their iden­  
tification from natural material [1]. Mass spectra of  
alkyl-3,4-dihydro-2H-pyrans (1) are characterized  
by fragments which correspond to:  
A) a-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  
aryl- 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 sp2-carbon atom which  
carries the oxygen, in dihydropyranes as well as in  
dihydropuranes and tetrahydrooxepines may furnish  
intense signals corresponding to:  
E) Mc-Lafferty rearrangement at the side chain;  
F) a "formal" y-cleavage at the side chain;  
G) Mc-Lafferty rearrangement of the oxygen con­  
taining 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-pyrans  
because they also show fragmentations A-G. However,  
due to the presence of the carbonyl group  
dihydropyranes may give some additional signals.

On the basis of these results we identified for the  
first time several alkyldihydropyranes and alkyl-  
dihydro-4H-pyran-4-ones both from social and  
solitary bees and from a male moth (see Table 1).

During our investigations on odour communic­  
tion in bees we studied the cephalic secretions of  
social stingless bees and of honey  
bees. Among the complex multicomponent mixtures  
we identified small amounts of several new cyclic  
enolethers. In the abdomen of workers of Apis mellifera  
L. we found 2,6-dimethyl-3,4-dihydro-2H-pyran (1a). This compound is also present in head  
extracts of the stingless bee Scaptotrigona bipunctata  
(Lepetrier) which additionally contain two bisho­  
mologues, 2-methyl-6-propyl-3,4-dihydro-2H-pyran  
(1b) and 2-methyl-6-pentyl-3,4-dihydro-2H-pyran  
(1c). The latter compound was also found in  
Nanno­  
trigona testaceicornis (Lepetlier), Plebeia droryana  
Friese, Teqragona clavipes (F.) and in some Taenian­  
drena 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-pyran (1f), head extracts of  
Partamona cupra (Smith) contain 6-heptyl-2-  
methyl-3,4-dihydro-2H-pyran (1d) and 2-methyl-6-  
nonyl-3,4-dihydro-2H-pyran (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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casion of her 85th birthday.  
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<table>
<thead>
<tr>
<th>No.</th>
<th>R₁</th>
<th>R₂</th>
<th>Insect species</th>
<th>MS (EI, 70 eV) m/z (%), [Fragmentation]</th>
<th>¹H-NMR 270 MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>CH₃</td>
<td>CH₃</td>
<td><strong>A. mellifica</strong>&lt;sup&gt;a&lt;/sup&gt;</td>
<td>112 (20), 97 (10) [A], 83 (3), 71 (40) [C], 69 (12), 67 (6), 58 (8), 55 (31), 43 (100) [D]</td>
<td>C₆D₆: 1.14 (d, 3H), 1.41 (m, 2H), 1.75 (s, 3H), 1.85 (m, 2H), 3.75 (m, 1H), 4.43 (m, 1H)</td>
</tr>
<tr>
<td>¹b</td>
<td>CH₃</td>
<td>C₃H₇</td>
<td><strong>S. bipunctata</strong></td>
<td>140 (20), 125 (7) [A], 112 (41) [E], 99 (18) [C], 97 (29), 83 (20), 71 (46) [D], 70 (22) [G], 55 (100), 43 (67)</td>
<td>C₆D₆: 0.91 (t, 3H), 1.16 (d, 3H), 1.26 to 1.52 (m, 2H), 1.62 (m, 2H), 1.77 to 2.04 (m, 2H), 2.09 (t, 2H), 3.78 (m, 1H), 4.48 (m, 1H)</td>
</tr>
<tr>
<td>¹c</td>
<td>CH₃</td>
<td>C₃H₅</td>
<td><strong>S. bipunctata</strong></td>
<td>168 (18), 126 (14) [B], 125 (41) [F], 112 (100) [E], 97 (36), 84 (29), 83 (46), 70 (35) [G], 55 (86), 43 (56)</td>
<td>C₆D₆: 0.88 (t, 3H), 1.17 (d, 3H), 1.23 to 1.67 (m, 8H), 1.79 to 2.07 (m, 2H), 2.13 (t, 2H), 3.89 (m, 1H), 4.15 (m, 1H)</td>
</tr>
<tr>
<td>¹d</td>
<td>CH₃</td>
<td>C₃H₁₅</td>
<td><strong>P. cupira</strong></td>
<td>196 (10), 125 (53) [F], 112 (100) [E], 97 (22), 84 (21), 83 (32), 70 (20) [G], 58 (18), 55 (60), 43 (37)</td>
<td>C₆D₆: 0.88 (t, 3H), 1.18 (d, 3H), 1.20 to 1.34 (m, 10H), 1.55 to 1.71 (m, 2H), 1.78 to 2.10 (m, 2H), 2.16 (t, 2H), 3.81 (m, 1H), 4.53 (m, 1H)</td>
</tr>
<tr>
<td>¹e</td>
<td>CH₃</td>
<td>C₃H₁₇</td>
<td><strong>P. cupira</strong></td>
<td>224 (6), 125 (46) [F], 112 (100) [E], 97 (15), 84 (13), 83 (20), 70 (13) [G], 58 (13), 55 (38), 43 (27)</td>
<td>C₆D₆: 0.91 (t, 3H), 1.18 (d, 3H), 1.20 to 1.53 (m, 16H), 1.78 to 2.06 (m, 2H), 2.16 (t, 2H), 3.79 (m, 1H), 4.52 (m, 1H)</td>
</tr>
<tr>
<td>¹f</td>
<td>H</td>
<td>C₄H₉</td>
<td><strong>P. cupira</strong></td>
<td>140 (17), 111 (9) [F], 98 (100) [E], 85 (11) [D], 83 (27), 70 (20) [G], 57 (15), 56 (15), 55 (61), 43 (48)</td>
<td>C₆D₆: 0.88 (t, 3H), 1.23 to 1.48 (m, 4H), 1.78 (m, 2H), 1.96 (m, 4H), 3.96 (m, 2H), 4.44 (t, 1H)</td>
</tr>
<tr>
<td>2a</td>
<td>CH₃</td>
<td>C₂H₅</td>
<td><strong>H. hecta</strong></td>
<td>140 (55), 125 (2) [A], 111 (3), 99 (92) [C], 98 (14) [B], 69 (100), 57 (62) [D], 55 (7), 43 (25)</td>
<td>CDC₃: 1.08 (t, 3H), 1.41 (d, 3H), 2.22 (q, 2H), 2.34 (m, 2H), 4.44 (m, 1H), 5.25 (m, 1H)</td>
</tr>
<tr>
<td>2b</td>
<td>C₃H₅</td>
<td>C₂H₅</td>
<td><strong>H. hecta</strong></td>
<td>154 (16), 126 (3), 125 (4) [A], 99 (100) [C], 98 (5) [B], 69 (51), 57 (51) [D], 56 (17), 43 (38)</td>
<td>CDC₃: 0.99 (t, 3H), 1.10 (t, 3H), 1.62 to 1.89 (m, 2H), 2.25 (q, 2H), 2.37 (m, 2H), 4.26 (m, 1H), 5.28 (m, 1H)</td>
</tr>
<tr>
<td>2c</td>
<td>C₂H₅</td>
<td>CH₃</td>
<td><strong>H. hecta</strong></td>
<td>140 (35), 125 (3), 112 (3), 111 (3) [A], 97 (2), 85 (100) [C], 84 (4) [B], 69 (23), 56 (13), 43 (77) [D]</td>
<td>CDC₃: 0.92 (t, 3H), 1.55 to 1.83 (m, 2H), 1.91 (s, 3H), 2.28 (m, 2H), 4.19 (m, 1H), 5.18 (m, 1H)</td>
</tr>
<tr>
<td>2d</td>
<td>CH₃</td>
<td>C₂H₅</td>
<td><strong>H. hecta</strong></td>
<td>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)</td>
<td>CDC₃: 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)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Found in abdomina: has been erroneously reported as a constituent of the cephalic secretion<sup>1</sup>.
Fig. 1. 70 eV Mass spectrum of 2-methyl-6-pentyl-3,4-dihydro-2H-pyran and fragmentation.

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

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-4H-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-4H-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 glass 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 1H-NMR data of the compounds are compiled in Table I.

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

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