

# Acetals in food flavourings

JÁN PET'KA<sup>1</sup>, Johann Leitner<sup>1</sup>, Jose Maria Bueno<sup>2</sup> and Peter Szolcsányi<sup>3</sup>

<sup>1</sup> Austria Juice GmbH, Kröllendorf 45, 3365 Allhartsberg, Austria

<sup>2</sup> Hausmann S.A., Carrer Indústria, 34, Sant Andreu de la Barca, 08740 Barcelona, Spain

<sup>3</sup> Slovak University of Technology, Department of Organic Chemistry, Radlinského 9, 812 37 Bratislava Slovakia

## Abstract

Matching of competitor flavours is one of the most common tasks for the majority of flavour chemists working for a flavour house. It is obvious to find various artefacts in those flavourings, where carbonyl compounds, alcohols and acids are together part of the recipe. Unfortunately, mass spectra of many of these compounds are not available in the commercial mass spectra databases. We decided to systematically investigate the reaction products of carbonyl compounds with the most common solvents used in the flavour industry – ethanol and propylene glycol, by means of gas chromatography– mass spectrometry. In a second study, we investigated the formation of acetals of selected alcohols and aldehydes, naturally occurring in concentrated apple condensates. Mass spectra of unpublished acetals are presented, together with results of a complementary storage study at different pH levels of the base.

## Introduction

Aldehydes are essential constituents of the flavour of various foods, such as citrus fruits or apples [1]. Aldehydes are quite reactive because of the electronegativity of oxygen on the carbonyl group, what in the presence of alcohols leads to the formation of labile hemiacetals. This process can be both acid and base catalysed. In the acid catalysed reaction, protonation of carbonyl group occurs and a carbocation intermediate is produced. Acidic conditions and excess of alcohol cause transformation of the carbocation to acetal and water [2]. Diols and triols are capable of reacting intramolecularly to form cyclic acetals. These reactions generally proceed rapidly due to their low activation energies. Acetals are stable at neutral pH, because the equilibrium reaction needs the protons, which are at pH 7 not available. Up to four isomers can be formed in the case of propylene glycol due to its chirality and diastereomerism [3].

In current business world, the matching of competitor's flavours is one of the main tasks for the creators of food flavours – the flavourists. Acetal formation makes this task much more complicated, because mass spectra of acetals of many aldehydes are still not available in the commercial mass spectra databases, such as NIST [4] or Wiley [5].

The aim of this study was to systematically synthesize acetals of all aldehydes we had on our shelf with the most common solvents used in flavour industry: ethanol and propylene glycol. In this work, we present the mass spectra of acetals not found in literature. We additionally synthesized the acetals of the most common aldehydes and alcohols as found in apple condensate (FTNF), because we hypothesized that some of them could be among the unknown peaks we found in the FTNFs concentrated to high degree with the Spinning Cone Column (Flavourtech, Griffith, AU) technique. We performed a storage study as well in following media: soft drink base, mineral water, water and yoghurt to prove the stability of some acetals.

## Experimental

### Materials

All compounds used in this study were of food grade, purchased from Sigma-Aldrich (Munich, D).

### Aldehydes to be reacted with ethanol and propylene glycol (PG):

2-methyl-propanal, 2-phenyl-2-butenal, 5-methylfurfural, acetaldehyde,  $\alpha$ -amylcinnamaldehyde, anisaldehyde, benzaldehyde,  $\beta$ -homocyclocitral, butyraldehyde, cinnamaldehyde, citral, citronellal, decanal, dodecanal, ethylvanillin, furfural, heptanal, hexanal, isovaleraldehyde, melonal, nonanal, octanal, perillaldehyde, phenylacetaldehyde, piperonal, p-tolualdehyde, trans-2-decenal, trans-2-hexenal, trans-2-methyl-2-butenal, undecanal, valeraldehyde, vanillin.

### Flavouring compounds for the FTNF study:

acetaldehyde, benzaldehyde, hexanal; propanol, 1-butanol, 2-methylbutanol, isobutanol, isopropanol, 3-methylbutanol, n-hexanol, n-pentanol.

### Preparation of acetals:

100  $\mu$ L of carbonyl compound, 890  $\mu$ L of solvent, 10  $\mu$ L of acetic or formic acid, 2 days at 37°C.

### Gas Chromatography-Mass spectrometry:

Gas chromatograph Agilent 7890B equipped with autosampler Gerstel Robotic and mass detector Agilent 5977B, operated at 70 eV (all Gerstel, Mühlheim a.d. Ruhr, Germany), S/SL injector, injection volume 0.5  $\mu$ L, split ratio 200:1, injector temperature: 230°C, column: Restek Vms 20 m x 0.8 mm x 1  $\mu$ m (Restek GmbH, Bad Homburg, Germany), carrier gas: helium, constant flow = 1 mL/min, acquisition mode: Scan, 26-250 amu, oven program: 50°C (3min), 10°C/min, 250°C (6min), retention indices: C<sub>7</sub>-C<sub>20</sub>.

### Headspace analysis:

Alpha M.O.S. Heracles II (Toulouse, France), PAL autosampler, S/SL injector, injection volume: 2mL from 1g/L solution of the corresponding acetals, splitless mode, injector temperature: 200°C, columns: Restek MXT-5 and MXT-1701, both 10 m x 0,18 mm x 0,4  $\mu$ m, carrier gas: hydrogen, oven program: 40°C (5s), 0.6°C/s, 250°C (60s), detector: 2x flame ionization detector.

## Results and discussion

Acetals of aldehydes with propylene glycol and / or ethanol were subject of various studies [3, 6-8]. In table 1 we show the spectra of those acetals, which have not been published in any mass spectra database yet [9].

We were not able to find the following acetals at our reaction conditions:

- With ethanol were not reacting: 2-phenyl-2-butenal, 5-methylfuraldehyde,  $\alpha$ -amylcinnamaldehyde, anisaldehyde, citral, ethylvanillin, perillaldehyde, piperonal, trans-2-decenal, trans-2-hexenal, trans-2-methyl-2-butenal and vanillin
- With isopropanol were not reacting benzaldehyde and trans-2-hexenal
- With propylene glycol we observed only sluggish reaction of: 2-phenyl-2-butenal, 5-methylfurfural and perillaaldehyde

**Table 1:** The first 10 most abundant mass fragments of acetals, which have not been published yet

| Aldehyde                 | Alcohol  | RI   | <i>m/z</i> (Abundance)  |
|--------------------------|----------|------|---|
| β-Homo-cyclocitral       | PG       | 1575 | 87(1000), 59(235), 41(72), 88(45), 91(36), 79(32), 95(30), 107(30), 31(29), 77(24)                      |
| 5-Methylfurfural         | PG       | 1311 | 168(1000), 108(984), 95(977), 94(704), 153(673), 167(480), 79(472), 82(471), 81(168), 111(149)          |
| α-Amylcinnamaldehyde     | PG       | 1971 | 189(1000), 131(308), 190(139), 117(121), 115(105), 91(83), 87(74), 129(67), 59(58), 128(53)             |
| Citronellal              | PG       | 1479 | 87(1000), 127(915), 121(750), 59(474), 41(368), 69(349), 95(284), 136(218), 81(169), 109(142)           |
| p-Tolualdehyde           | PG       | 1496 | 177(1000), 119(967), 163(514), 91(420), 92(368), 178(312), 105(225), 104(132), 133(130), 103(118)       |
| trans-2-Decenal          | PG       | 1578 | 113(1000), 127(444), 69(273), 55(262), 169(251), 41(189), 211(115), 83(107), 114(107), 59(79)           |
| trans-2-Methyl-2-butenal | PG       | 1075 | 127(1000), 69(420), 83(301), 87(243), 59(211), 41(159), 55(151), 97(126), 67(92), 39(72)                |
| β-Homo-cyclocitral       | Ethanol  | 954  | 103(1000), 75(462), 47(200), 195(75), 149(74), 107(66), 104(57), 93(48), 81(47), 91(45), 123(45)        |
| Melonal                  | Ethanol  | 1343 | 103(1000), 86(883), 75(558), 82(385), 47(349), 123(241), 69(226), 41(207), 125(171), 81(161)            |
| p-Tolualdehyde           | Ethanol  | 1394 | 149(1000), 121(511), 93(248), 91(211), 119(144), 150(120), 77(80), 65(46), 122(45), 29(31)              |
| Undecanal                | Ethanol  | 1602 | 103(1000), 199(264), 75(182), 47(107), 97(87), 83(72), 57(69), 104(56), 69(56), 55(55), 85(54), 200(38) |
| Benzaldehyde             | Propanol | 1457 | 149(1000), 107(949), 79(230), 77(135), 105(127), 150(113), 43(86), 108(76), 41(50), 27(29)              |
| Hexanal                  | Propanol | 1281 | 131(1000), 143(981), 89(806), 43(757), 83(647), 101(364), 55(255), 41(228), 144(96), 57(95)             |
| Benzaldehyde             | Butanol  | 1639 | 163(1000), 107(962), 79(169), 164(124), 105(106), 77(93), 108(78), 41(67), 29(50), 51(16)               |
| Hexanal                  | Butanol  | 1454 | 57(1000), 157(798), 159(630), 83(508), 83(647), 103(402), 101(351), 41(244), 55(191), 29(144)           |

**Table 1:** continued

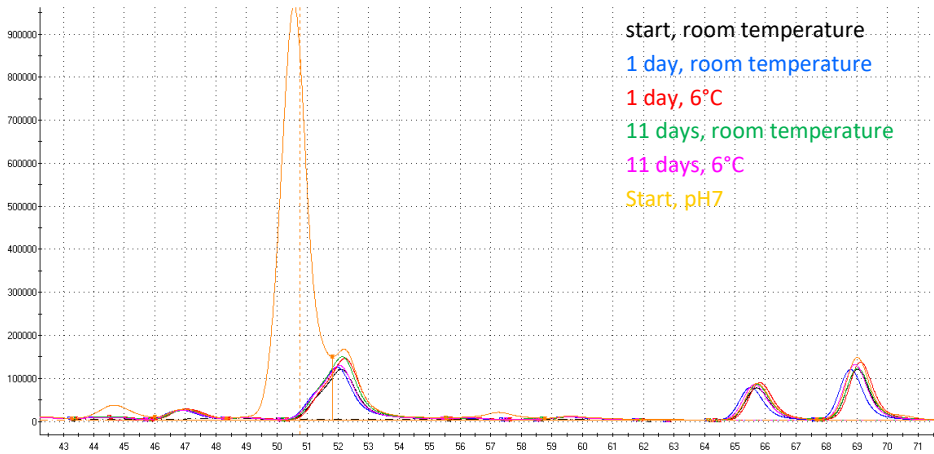
| Aldehyde     | Alcohol         | RI   | <i>m/z</i> (Abundance)   |
|--------------|-----------------|------|--|
| Benzaldehyde | Isobutanol      | 1535 | 107(1000), 163(798), 77(135), 105(127), 150(113), 43(86), 108(76), 41(50), 27(29)                |
| Hexanal      | Isobutanol      | 1281 | 57(1000), 157(462), 83(200), 159(197), 103(163), 101(162), 41(155), 55(91), 29(74), 43(50)       |
| Acetaldehyde | Pentanol        | 1307 | 115(1000), 71(961), 43(420), 187(229), 45(170), 41(118), 29(72), 55(61), 42(64), 97(56)          |
| Benzaldehyde | Pentanol        | 1826 | 177(1000), 107(926), 79(230), 77(135), 105(127), 150(113), 43(86), 108(76), 41(50), 27(29)       |
| Hexanal      | Pentanol        | 1634 | 71(1000), 171(766), 181(477), 43(473), 83(388), 101(360), 117(296), 55(161), 41(134), 42(65)     |
| Benzaldehyde | 2-Methylbutanol | 1740 | 107(1000), 177(821), 71(178), 43(131), 178(109), 79(99), 108(84), 105(61), 77(56), 41(50),       |
| Hexanal      | 2-Methylbutanol | 1545 | 71(1000), 171(385), 43(271), 101(167), 83(148), 187(109), 117(106), 77(56), 41(76), 29(48)       |
| Acetaldehyde | 3-Methylbutanol | 1232 | 71(1000), 115(723), 43(373), 41(90), 55(70), 72(67), 116(55), 45(40), 29(36), 39(26)             |
| Hexanal      | 3-Methylbutanol | 1556 | 71(1000), 171(384), 43(303), 187(248), 55(76), 41(70), 72(56), 117(48), 172(46), 29(31), 188(30) |
| Benzaldehyde | Hexanol         | 2014 | 191(1000), 192(145), 43(129), 79(89), 105(79), 108(72), 41(49), 85(48), 55(26), 29(22)           |
| Hexanal      | Hexanol         | 1815 | 85(1000), 185(634), 43(463), 215(335), 101(306), 83(277), 131(175), 57(138), 55(128), 41(121)    |

Due to the diminished electrophilicity of C=O group in conjugated aldehydes (via positive mesomeric effects), these carbonyl derivatives are less susceptible to AdN (nucleophilic addition) reactions of O-nucleophiles (e.g. alcohols in hemiacetalization) in comparison to more reactive aldehydes. This is due to the low reactivity of such compounds with ethanol, and thus, no formation of acyclic acetals occurs.

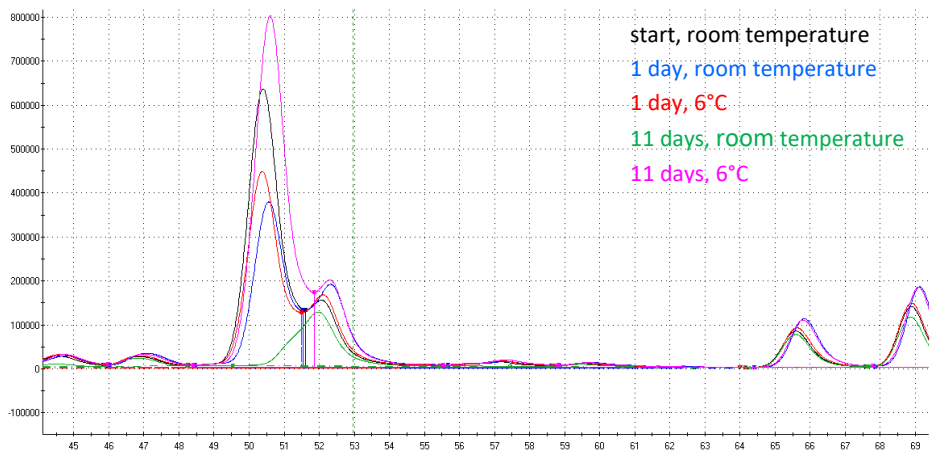
On the other hand, the use of propylene glycol as bis-O-nucleophile leads to the formation (though sluggish) of the corresponding cyclic acetals of the same carbonyls because the generation of 5-membered rings is thermodynamically favourable.

Unfortunately, we were not able to find any of the aldehydes we synthesized from apple alcohols and aldehydes in apple FTNF itself. The unknown peaks might possibly be rather combined acetals of aldehydes with two alcohols, such as acetals of acetaldehyde with ethanol and some other alcohol (ethyl-methyl, ethyl-butyl, etc.) This will be the subject of our further study.

In the storage study, we observed complete elimination of acetals in the low pH environment (soft drink base, yoghurt) within 2 hours after mixing (Figure 1). In media with higher pH, such as near-water drinks or mineral water, the decomposition of acetals was reduced considerably (Figure 2), which may raise the need for testing of these compounds by the food safety bodies, as many of acetals are still not in the Union list of flavourings and source materials [10].



**Figure 1:** Headspace chromatograms showing complete decomposition of acetaldehyde propylene glycol acetal at pH 3



**Figure 2:** Headspace chromatograms showing increased stability of acetaldehyde propylene glycol acetal stored at higher pH and at lower temperature

## References

1. Maarse, H. Volatile compounds in foods and beverages. (1991). New York: Marcel Dekker. 764 p.
2. Dewick, P.M. (2006) In: Essentials of organic chemistry : for students of pharmacy, medicinal chemistry and biological chemistry. J. Wiley: Chichester, West Sussex, England ; Hoboken, N.J. pp. 221-282.
3. Coleman, W.M. (2006) *J Chrom Sci*, 44(3): 167-173.
4. NIST Mass Spectral Database, (2014). National Institute of Standards and Technology.
5. Wiley Mass Spectral Database, (2017). John Wiley & Sons, Inc.
6. Woelfel, K., Hartman, T.G. (1998) In: Flavor analysis : developments in isolation and characterization, (Mussinan, C.J. and Morello, M.J., eds.). American Chemical Society: Washington, DC. pp. 193-210.
7. Heydanek, M.G., Min, D.B.S. (1976) *J Food Sci*, 41: 145-147.
8. Zhang, J., Reineccius, G.A. (2017) *Perf Flav*, 42(9): 32-49.
9. Search NIST 17 and Wiley MS Databases. (2017) [cited 2017 October]; Available from: <http://www.sisweb.com/software/ms/nistsearch.htm>.
10. Authorisation of Food Flavourings. (2017) [cited 2017; Available from: [https://webgate.ec.europa.eu/foods\\_system/main/?sector=FFL&auth=SANCAS](https://webgate.ec.europa.eu/foods_system/main/?sector=FFL&auth=SANCAS)].