Investigations into the Build-Up Mechanism of Phenylacetaldehyde in Honey and the Change of its Concentration Under Different Conditions

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Phenylacetaldehyde is a natural aromatic compound in honey[1] and can be generated from the amino acid phenylalanine, either with the help of enzymes (Fig. 1) or by Strecker degradation [2] (Fig. 2). But phenylacetaldehyde can also be used as a bee repellent for a simplified harvest of honey [3]. In this case the substance could be regarded as residue. The latter was the reason that *Stiftung Warentest* (Issue 4/2004) devaluated some honey samples due to the "increased" phenylacetaldehyde content (between 1.0 and 2.5 ppm) [4].

In this research project we wanted to prove that there exists a relationship between the content of phenylacetaldehyde and the content of phenylalanine. For the determination of phenylacetaldehyde in honey a Headspace-GC/MS method was suggested [3, 5]. Wildflower honey and a honey-like sugar syrup were analysed with this method. Afterwards the samples were spiked with phenylalanine, and it was found that the more phenylalanine the samples contained the higher was the amount of phenylacetaldehyde detected. The same happened regarding different incubation temperatures during Headspace analysis and the corresponding final concentrations of phenylacetaldehyde (Fig. 3).

These results showed that the content of phenylacetaldehyde in honey depends on its phenylalanine content and, furthermore, that the applied method cannot be used for honey. Therefore, another method was developed by extracting phenylacetaldehyde with tBME (tert-butyl methyl ether) at room temperature and analysing the extract by GC/MS (Fig. 4 and 5).

Using this method, an acacia honey with 26.6 ppm phenylalanine, a wildflower honey with 450 ppm phenylalanine, a pure honey-like sugar syrup and a syrup spiked with phenylalanine (250 ppm) were portioned off and stored in darkness (a) at room temperature (22°C) and (b) at 39°C as well as (c) under UV light at 22°C for up to 14 weeks. The concentration of phenylacetaldehyde in each sample was determined at intervals.
Under (a) the concentrations remained the same, under (b) and (c) the concentrations partially increased considerably, except those of the pure syrup (Fig. 6).

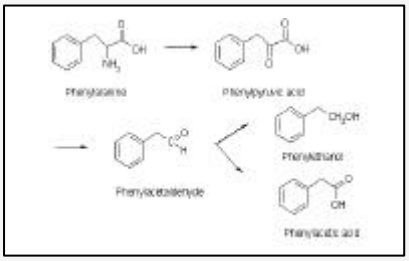

Fig. 1: Build-up mechanism of phenylacetaldehyde by enzymes

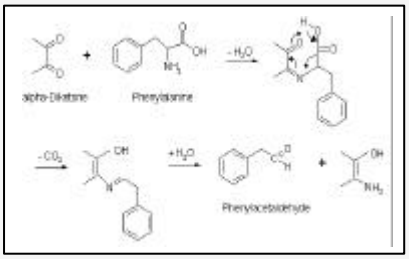

Fig. 2: Build-up mechanism of phenylacetaldehyde by Strecker degradation

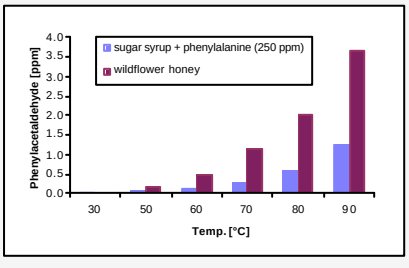

Fig. 3: Higher contents of phenylacetaldehyde with increased temperature during Headspace-GC/MS

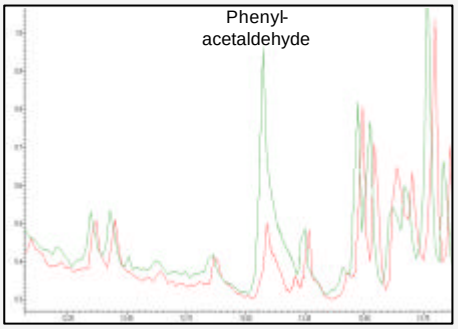

Fig. 4: TIC-Chromatograms on a DB 5 column Wildflower honey stored for 8 weeks at 22°C and at 39°C

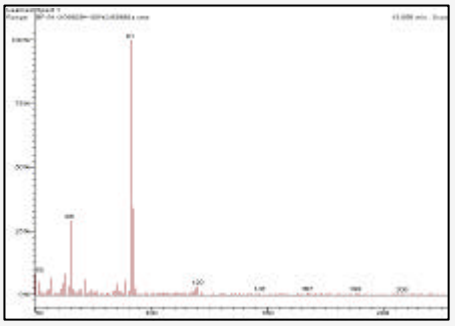

Fig. 5: Mass spectrum of phenylacetaldehyde. (Amounts were calculated at m/z 91 and m/z 65)

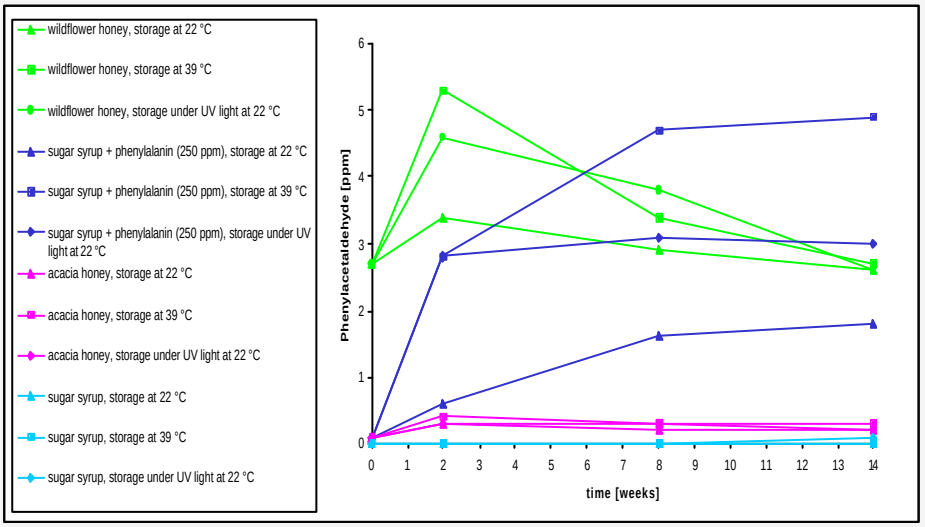

Fig. 6: Results of the storage tests: pure sugar syrup, acacia honey, sugar syrup spiked with phenylalanine and wildflower honey

References
[1] Lüllmann, C., Horn, H., "Das grosse Honigbuch", 2nd edition (2002), 109
[2] Report No. 26 of Kantonslabor Basel (25/09/2003), 1-2
[3] Deifel, A., "Die Chemie des Honigs", 23 (1) (1989), 25-33
[4] Stiftung Warentest 4 (2004), 20-26
[5] Bogdanov, S. et al, "Residues of para-dichlorobenzene in honey and beeswax", Journal of Apicultural Research 43 (1) (2004), 14-16

Conclusion
1. The content of phenylacetaldehyde depends on the phenylalanine content and on the storing conditions.
2. Levels of 1 – 2.5 mg/kg of phenylacetaldehyde cannot be regarded as residue, unless the phenylalanine content is taken into consideration