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Elucidating the Secrets of the Maillard Reaction Cascade – The Role of Amadori Compounds

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The reaction of reducing sugars with amino acids and proteins, referred to as the Maillard reaction or non-enzymatic browning, is the major source of color, taste and aroma that is characteristic for many heated foods, such as meat, bakery, and cocoa. For example the almost odorless green coffee beans are transformed into dark brown roasted coffee with delicious taste and aroma. Amadori compounds, 1-amino-1-deoxyketoses, play a pivotal role in the Maillard reaction cascade. It is also assumed that they participate in the formation of advanced glycated end products (AGEs) under physiological conditions. Pentose-based Amadori compounds are very unstable compared to their hexose-based analogues and have rarely been reported in the literature.

It is rather challenging to obtain reliable data on the nature, amounts, and fate of Amadori compounds due to (i) the high complexity of Maillard systems and (ii) the high diversity in polarity of Amadori compounds. Modern analytical methods combine chromatographic separation efficiency and mass discrimination by tandem mass spectrometry (MS/MS). Separation by high-performance cation-exchange chromatography (HPCEC) followed by electrochemical detection (ECD) or tandem MS in the positive electrospray ionization (ECI^+) mode turned out to be the most suitable approach. Alternatively, capillary electrophoresis coupled to MS/MS can be used.

We have succeeded for the first time to monitor pentose-based Amadori compounds, such as N-(1-deoxy-D-xylulos-1-yl)glycine (Xyl-Gly). Reaction of D-xylose and glycine at 90 °C (pH 6) for 2 h showed rapid formation of Xyl-Gly (~12 mol %, 15 min) followed by slow decrease over time. Analysis of pentose-derived Amadori compounds represents a major breakthrough in studying occurrence, formation, and decomposition of these labile Maillard intermediates.

Several hexose-based Amadori compounds could be identified and quantified in an aqueous extract of dried vegetables and fruits. Sample preparation consisted of maceration of dried tomatoes in water, homogenization, and filtration. N-(1-deoxy-D-fructos-1-yl)-L-glutamic acid (Fru-Glu) was found as the major Amadori compound in dried tomatoes. About 1.5 g/100 g of Fru-Glu was determined, known for its umami taste properties that are also characteristic for dried tomatoes. Such data are now readily accessible to reveal taste-active constituents of natural products. Several other Amadori compounds could also be detected, *i.e.* Fru-Ala, Fru-Leu and Fru-Phe, indicating that no further clean-up was required.

Simultaneous analysis of non-volatile Maillard reaction products such as Amadori compounds combined with a minimum of sample clean-up opens new avenues to study reaction mechanisms of the Maillard reaction cascade and elucidate new constituents in thermally processed foods and natural products with interesting sensory and other bio-active properties.

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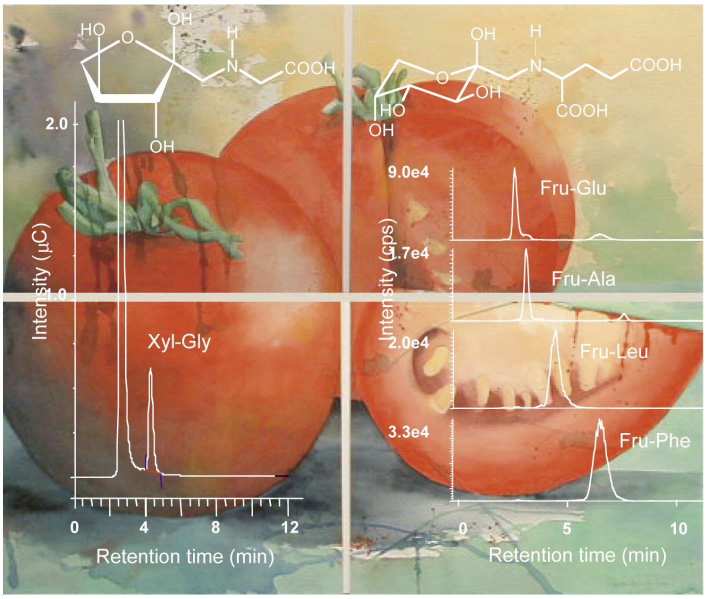

Rapid HPCEC-ECD analysis of the pentose-based Amadori compound N-(1-deoxy-D-xylulos-1-yl)glycine (Xyl-Gly), shown in the major β-anomeric form. HPCEC-MS/MS analysis of hexose-based Amadori compounds found in dry tomato, *e.g.* N-(1-deoxy-D-fructos-1-yl)-L-glutamic acid (Fru-Glu) shown in the major β-pyranoid form ($^2C_5$ conformation). The picture is taken from *http://www.arton5th.com/hennig/tomaten.html* and was painted in watercolors by Claudia Hennig.

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