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Formation of the reduced form of furaneol® (2,5-dimethyl-4-hydroxy-tetrahydrofuran-3-one) during the Maillard reaction through catalysis of amino acid metal salts

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ABSTRACT

Under pyrolytic conditions the acidity/basicity of Maillard reaction mixtures can be controlled through the use of hydrochloride or sodium salts of amino acids to generate a diversity of products. When the degradation of glucose was studied under pyrolytic conditions using excess sodium glycinate the reaction was found to generate a major unknown peak having a molecular ion at m/z 130. Subsequent in-depth isotope labelling studies indicated that acetol was an important precursor of this compound under pyrolytic and aqueous heating conditions. The dimerisation and cyclisation of acetol into 2,5-dimethyl-4-hydroxy-tetrahydrofuran-3-one was found to be catalysed by amino acid metal salts. Also, ESI/qTOF/MS studies indicated that the unknown peak has expected molecular formula of $C_6H_{10}O_3$. Finally, a peak having the same retention time and mass spectrum was also generated pyrolytically when furaneol® was reduced with $NaBH_4$ confirming the initial hypothesis regarding the unknown peak to be the reduced form of furaneol®.

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1. Introduction

Thermally generated 3(2*H*)-furanone derivatives such as 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone (furaneol)®, 2-ethyl-4-hydroxy-5-methyl-3(2*H*)-furanone (homofuraneol), and 4-hydroxy-5-methyl-3(2*H*)-furanone (norfuraneol®) are considered to be important flavour compounds because of their low odour threshold values and diverse flavour profiles. Although naturally biosynthesised in fruits, plants and microorganisms through multistep enzymatic reactions (Blank & Fay, 1996; Schwab, 2013; Slaughter, 1999), these furanones have also been reported to form in varying concentrations in a number of thermally processed foods and in Maillard model systems. Under relatively mild pH conditions, 3(2*H*)-furanones are known to originate either directly from intact sugars or in the presence of amino acids and 1,2-dicarbonyl intermediates generated during the Maillard reaction (Blank, Devaud, & Fay, 1996; Blank & Fay, 1996). Additionally, similar to other Maillard reaction products, the amount and type of the thermally generated furanones have been found to be dependent on the nature of the reactants (sugars and amino acids) and reaction conditions (temperature, time and duration) (Slaughter, 1999). Interestingly, in a recent investigation (Wang, 2014) of thermal degradation of glucose in the presence of amino acid salts, a major and unique product was observed when glucose was pyrolysed in the presence of sodium glycinate. This unknown product exhibited a molecular ion at m/z 130 and based on the initial data obtained it was hypothesised to be the reduced form of furaneol® (2,5-dimethyl-4-hydroxy-tetrahydrofuran-3-one). This hypothetical structure, however, was not reported in the literature except in the patent document of Ross Karl-Heinz et al. (1981) titled "Preparation of 2,5-Dimethyl-4-hydroxy-2,3-dihydrofuran-3-one" (U.S. Patent No 4,290,960, 1981). In their efforts to chemically synthesise furaneol®, Ross Karl-Heinz et al. (1981) generated the "novel" 2,5-dimethyl-4-hydroxy-tetrahydrofuran-3-one in a three-step reaction starting with the epoxidation of hex-3-ene-2,5-diol into 3,4-epoxy-hexane-2,5-diol, followed by the cyclisation of the latter into 2,5-dimethyl-3,4-dihydroxytetrahydrofuran, which after oxidation over a silver catalyst generated the 2,5-dimethyl-4-hydroxytetrahydrofuran-3-one (IUPAC name 4-hydroxy-2,5-dimethyloxolan-3-one also known as 2,5-anhydro-1,6-dideoxy-3-hexulose). Ross Karl-Heinz et al. (1981) also reported that the "novel" 2,5-dimethyl-4-hydroxytetrahydrofuran-3-one had a boiling point of 61–65 °C at 1 mbar. In the final step of the furaneol® synthesis, the 2,5-dimethyl-4-hydroxytetrahydrofuran-3-one was oxidised to directly generate furaneol® in 75–80% recovery yield. Unfortunately, no information about the sensory properties of the reduced furaneol® (2,5-dimethyl-4-hydroxy-tetrahydrofuran-3-one) was reported. However, furanone derivatives are known to possess common flavour characteristics related to their

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chemical structure. In fact, their caramel-like aroma note is attributed to their molecular structure and ability to form a hydrogen bond between the 4-hydroxy group and the adjacent keto group in a planar configuration (Hodge, 1967; Schwab, 2013); hence, the reduced furaneol can be expected to have flavour notes similar to that of furaneol®.

Considering the knowledge gap in this particular 3(2*H*)-furanone derivative, the present study aimed at using sugar and amino acid model systems in addition to isotope labelling techniques to investigate the origin and the mechanism of its formation from Maillard reaction precursors under pyrolytic and aqueous heating conditions.

2. Materials and methods

2.1. Reagents and chemicals

Glucose, acetol (90%), DL-lactaldehyde solution ($\geqslant$95%), glycine (98%), alanine (99%), glycine sodium salt hydrate (98%), calcium chloride, copper (II) chloride (99.9%), zinc chloride ($\geqslant$98%), potassium hydroxide, 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone (98%), and sodium borohydride (99%) were purchased from Sigma–Aldrich Chemical Co. (Oakville, ON, Canada). Labelled [^{13}C-1] glucose (99%), [^{13}C-2]glucose (99%), [^{13}C-3]glucose (99%), [^{13}C-4] glucose (99%), [^{13}C-5]glucose (99%), [^{13}C-6]glucose (99%), [U6-^{13}C]glucose (99%), [^{13}C-1]glycine (98%), [^{13}C-2]glycine (99%), and [^{15}N]glycine (98%) were purchased from Cambridge Isotope Laboratories (Andover, MI).

2.2. Synthesis of metal–amino acid salts

Copper glycinate, zinc glycinate, calcium glycinate and copper alaninate were prepared according to a previously published procedure (Nashalian & Yaylayan, 2015) by dissolving glycine (0.75 g) or alanine (0.89 g) in methanol (10 mL) in the presence of KOH (0.05 g), followed by the addition of half a mole of $CuCl_2$ (0.67 g) or $ZnCl_2$ (0.68 g) or $CaCl_2$ (0.56 g). The precipitates were washed with methanol, filtered and dried. The metal–amino acid complexes were confirmed by obtaining their elemental composition from their accurate masses determined by ESI/qTOF/MS.

2.3. Preparation of the model systems for pyrolysis

Homogenised mixtures (0.5 mg) containing 2:1 ratio of glycine to sugar, 2:1 glycine sodium salt hydrate to sugar, or 1:2 ratio of sugar to KOH were packed inside a quartz tube (0.3 mm thickness), plugged with quartz wool, and inserted inside a coil probe and pyrolysed at 200 °C for 20 s under helium atmosphere. Isotopically labelled precursors were analysed similarly except model systems containing labelled glycine where pyrolysis was performed in the presence of KOH (Supplementary Table S1). All samples were analysed in duplicate.

2.4. Preparation of aqueous model systems for ESI/qTOF/MS analysis

Acetol and sodium glycinate hydrate (in a 1:2 relative molar ratio) were dissolved in water (2 mL) and heated on a sand bath in an open vial (5 mL capacity) at 150 °C for 1 h until dry. The reaction mixture was then analysed by ESI/qTOF/MS. All samples were analysed in duplicate.

2.5. Pyrolysis–gas chromatography–mass spectrometry (Py–GC–MS)

Samples were analysed according to previously published procedures (Guerra & Yaylayan, 2010; Nashalian & Yaylayan, 2015); in summary a Varian CP-3800 GC coupled to a Varian Saturn 2000 mass spectrometry detector (Varian, Walnut Creek, CA) was used for the analysis of the model systems. The pyrolysis unit included a valved interface (CDS 1500), which was installed onto the GC injection port and connected to a CDS Pyroprobe 2000 unit (CDS Analytical, Oxford, PA). The samples were analysed on a DB-5MS column (5% diphenyl, 95% dimethylpolysiloxane) with column dimensions of 50 m length × 0.2 mm internal diameter × 33 μm film thickness (J & W Scientific, Folsom, CA) using helium as the carrier gas. The GC column flow rate was regulated by an electronic flow controller (EFC) and set at a delayed (30 s) pressure pulse of 70 psi for the first 4 min and maintained with a constant flow of 1.5 mL/min for the rest of the run. The GC oven temperature was set at -5 °C for the first 5 min using CO_2 as the cryogenic cooling source and then increased to 50 °C at a rate of 50 °C/min. Then, the oven temperature was again increased to 270 °C at a rate of 8 °C/min and kept at 270 °C for 5 min. The MS transfer line temperature was set at 250 °C, the manifold temperature was set at 50 °C, and the ion trap temperature was set at 175 °C. An ionisation voltage of 70 eV was used, and EMV was set at 1850 V.

2.6. Electrospray ionisation/quadrupole time of flight/mass spectrometry (ESI/qTOF/MS) analysis

Samples were analysed according to a previously published procedure (Nashalian & Yaylayan, 2015); in summary, the dry reaction mixtures were dissolved in LC-grade water to a concentration of 1 mg/mL. The samples were then diluted 10-fold in 10% methanol prior to analysis by ESI/qTOF/MS. The ESI/qTOF/MS system was comprised of a Bruker Maxis Impact quadrupole-time of flight mass spectrometer (Bruker Daltonics, Bremen, Germany) operated in positive ion mode. Samples (1 μl) were injected directly into the ESI/qTOF/MS. Instrument calibration was performed using sodium formate clusters. The electrospray interface settings were the following: nebuliser pressure 0.6 bar, drying gas 4 L/min, 180 °C, capillary voltage 4500 V. Scan range was from *m/z* 100 to 1000. The data was analysed using Bruker Compass Data Analysis software version 4.1.

2.7. Structural identification of the 2,5-dimethyl-4-hydroxytetrahydrofuran-3-one (reduced furaneol®)

The proposed structure of the reduced furaneol® (2,5-dimethyl-4-hydroxy-tetrahydrofuran-3-one) was confirmed based on the *in situ* formation from commercial standards, mass spectral fragmentation (presented in Fig. 1), elemental composition obtained from high resolution ESI/MS data, and isotope labelling. The isotope labelling experiments were carried out using individually labelled [^{13}C-1] to [^{13}C-6]glucose, individually labelled [^{13}C-1], [^{13}C-2], [^{15}N]glycine, and [U_6-^{13}C]glucose precursors. The reported percent label incorporation values (corrected for natural abundance and for percent enrichment) are the average of duplicate analyses and are rounded off to the nearest multiple of 5%.

3. Results and discussion

The Maillard reaction can be considered as a natural manifestation of combinatorial chemistry of sugars, amino acids and their degradation products, generating a variety of chemical structures. The series of subsequent reactions such as dehydrations, eliminations, aldolisation, retro-aldolisation and cyclisations that follow the initial carbonyl–amine reaction can generate a myriad of products depending on different reaction conditions, such as reactant type, concentration, and pH of the system (Van Boekel, 2006).

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