CHAPTER 46

Generation of Roast-Smelling Compounds Upon Extrusion

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46.1 INTRODUCTION

Extrusion cooking offers several advantages, both from the manufacturing and from the product quality points of view. However, the desirable aroma characteristics associated with conventionally cooked cereals do not develop to the same extent during extrusion cooking. Consequently, extruded cereals are generally inferior in flavor compared to those obtained by conventional cooking, and thus there is a need to better understand generation of key odorants upon extrusion cooking. Currently, no information is available concerning reaction mechanisms leading to roast-smelling 1-pyrroline and tetrahydropyridine derivatives under extrusion conditions. In contrast, several pathways were proposed for the formation of these compounds in model systems both under roasting and under aqueous conditions [1–3].

The aim of our study was therefore to gain a deeper insight into the reaction mechanisms of roast-smelling compounds upon extrusion cooking. The approach consisted in CAMOLA experiments [4] with [U-13C6]-glucose applied to an extruded rice food system. The formation of several odorants including 2-AP, 2-PP, 2-ATHP, and 2-PTHP is discussed.

46.2 MATERIALS AND METHODS

46.2.1 Extrusion Trials

The extrusion trials were performed on the twin-screw extruder BC-21 (Clextral, France) using a model rice recipe. Rice flour was spiked with glucose (0.1 mol/kg), glycine (0.05 mol/kg), proline (0.01 mol/kg), and ornithine (0.01 mol/kg), and extruded under moderate conditions.
(135°C, 20% moisture, 400 rpm). The extruded products were dried in an Aerotherm oven (Wiesheu, Germany) at 120°C for 5 min. A similar trial was performed using a mixture of glucose and [U-13C6]-glucose (1:1) instead of glucose.

46.2.2 Analysis of Aroma Compounds

The samples were analyzed by solid phase micro-extraction in combination with 2D gas chromatography–time-of-flight mass spectrometry (SPME-GC × GC-TOFMS) as previously described [5].

46.3 RESULTS

The isotopic distributions obtained for 2-AP and 2-PP generated from CAMOLA experiments under extrusion conditions are shown in Figure 46.1.

The relative intensities of the ions m/z 111 (corresponding to unla- beled isotopomer) and m/z 113 (corresponding to an isotopomer incorporating two labeled carbon atoms in acetyl group as confirmed by the presence of ions m/z 84 and m/z 45; data not shown) indicate that 2-AP was mainly formed by acylation of the 1-pyrroline moiety (derived from proline or ornithine) via the C2-glucose fragment. Apart from this pathway, a small amount of 2-AP was also formed via incorporation of a C3-glucose fragment as indicated by the presence of ion m/z 114.

2-PP was mainly present as an unlabeled isotopomer (m/z 125) and as a triply labeled isotopomer (m/z 128). All three labeled carbon atoms were present in the propionyl group, as indicated by the presence of ions m/z 98/99 and m/z 60. Thus, under extrusion, 2-PP is mainly formed by

![Figure 46.1](image-url)
incorporation of a C₃-sugar fragment into 1-pyrroline derived from proline or ornithine.

The measured isotopic distribution of 2-ATHP and 2-PTHP is shown in Figure 46.2.

For both tautomers, an unlabeled isotopomer (m/z 125) and a triply labeled isotopomer (m/z 128) represented more than 90% of all the 2-ATHP isotopomers formed. Based on spectral data, the position of the labeled carbon atoms could be attributed: two labeled carbons were present in the acetyl group (ion m/z 45) and one in the piperidine ring (ion m/z 83/84). Therefore, incorporation of C₃-sugar fragments can be considered as a major pathway leading to 2-ATHP under extrusion.

Its higher analogue, 2-PTHP, was almost exclusively formed by incorporation of a C₄-sugar fragment, as indicated by high intensities of ions m/z 139 and ions m/z 143. The presence of the ions m/z 60 and ions m/z 83/84 indicated that three carbon atoms were located in the propionyl group, whereas the fourth labeled atom was integrated into the piperidine ring.

**46.4 DISCUSSION AND CONCLUSION**

Our data obtained for 2-AP are very comparable to those obtained by Hofmann and Schieberle [2]. Under dry heating conditions (160°C, 10 min, phosphate buffer pH 7) the authors observed formation of two main isotopomers of 2-AP in the model system containing [U-₁³C₆]-glucose and proline: the isotopomer of m/z 113, and the isotopomer of m/z 114. The ratio between the former and latter isotopomers was 4:1, which is similar to the ratio found in our extruded system (4.5:1). Based
on these results, the authors proposed two mechanisms for generation of 2-AP. Both mechanisms consider 2-oxopropanal as the reactive sugar fragment. One leads to 2-AP via interaction of the hydrated form of 2-oxopropanal with 1-pyroline, and includes elimination of the aldehyde group of 2-oxopropanal as carbon dioxide; the other suggests elimination of carbon-2 of the 1-pyrroline ring and thus incorporation of all the carbon atoms of 2-oxopropanal.

Similarly, our data concerning generation of 2-PP, 2-ATHP, and 2-PTHP are comparable to those published for model systems containing glucose and proline (either dry- or wet-heated) [1,2].

On the basis of the results, it can be concluded that the formation of the above-mentioned roast-smelling compounds upon extrusion follows similar pathways to those reported for dry- and wet-heated model systems containing glucose and proline. 2-AP is principally formed (i) by acylation of 1-pyroline via C_2-sugar fragments (major), and (ii) via ring opening of 1-pyroline incorporating C_3-sugar fragments (minor); 2-PP incorporates C_3-sugar fragments; 2-ATHP and 2-PTHP incorporate C_3- and C_4-sugar fragments, respectively.

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REFERENCES