Generation of aroma compounds from glucose by extrusion cooking
First insight on formation pathways using the CAMOLA approach
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INTRODUCTION
Extrusion cooking is gaining increasing importance in food industry as a cost efficient way of manufacturing numerous food items including cereal products. It permits in one processing step to perform several operations such as mixing, transporting, cooking and texturing. However, desirable flavour characteristics associated with conventionally cooked cereals do not develop to the same extent during extrusion cooking. Consequently, the extruded cereals are generally inferior in flavour as compared to those obtained by conventional cooking. Currently, no information is available concerning reaction mechanisms leading to odour active molecules under extrusion conditions. However, this knowledge is essential to develop flavouring strategies for extruded products.

Objective
The aim of our study was to get a first insight into the reaction mechanisms leading to selected odorants generated from glucose during extrusion cooking.

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

SPME – GC × GC-TOFMS
- Sample preparation: ground sample (1g) + Na2SO4 (4g) + water (6g)
- Extraction: SPME 30 min at 70°C
- Column setup: DB-1701 (30 m × 0.25mm × 0.25 μm) and DB-FFAP (2m × 0.1mm × 0.1 μm)
- Modulation time: 6 s
- Detection: LECO Pegasus® IV Time-Of-Flight MS
  - Acquisition rate: 200 scans/s
  - Detector voltage: 1750 V

RESULTS & CONCLUSIONS

Current knowledge based on model systems
α-Dicarbonyls & α-hydroxycarbons

Figure 1: Formation of 2,3-butanedione from glucose and proline under roasting condition according to Schieberle et al [1].

Figure 2: Formation of 2,3-butanedione from intact glucose skeleton [3].

Figure 3: Formation of 2,3-butanedione from glucose and glycine under pyrolysis according to Yaylayan [2].

Figure 4: Formation of 2,3-pentanedione from glucose and alanine under pyrolysis [2].

Figure 5: Hypothetical pathway to 2,3-pentanediol from 2,3-butanedione and formaldehyde [3].

Cyclic enolones

Figure 6: Contribution of different formation pathways to 2,3-butanedione as calculated from the isotopic distribution.

Figure 7: Isotopic patterns in 2,3-pentanedione and 3-hydroxy-2-butanone

Figure 8: Major formation pathways of 2,3-butanedione in rice extrudate enriched with glucose and glycine

Figure 9: Formation of 4-hydroxy-2,5-dimethyl-3(2H)-furane (HDMF) in glucose proline system under roasting and in aqueous solutions [1,4]

Figure 10: Formation of cyclotene from 1-deoxy-2,3-hexodiulose [5].

Formation during extrusion cooking

- Under extrusion cooking, 2,3-butanedione is mainly formed by recombination of C3 + C1 fragments (72%).

- C3-fragment originates from carbohydrate whereas C2 fragment originates primarily from glucose and moderately from carbohydrate.

- Minor part of 2,3-butanedione is formed from intact glucose skeleton (15%) and by recombination of C2 + C3 glucose fragments (6%).

- 2,3-Pentanediol is formed almost exclusively from intact sugar skeleton.

- 3-Hydroxy-2-butanone is most probably formed by reduction of 2,3-butanedione as it shows similar isotopic distribution.

- Under extrusion cooking, HDMF, dihydromaltol and cyclotene are almost exclusively formed from intact glucose skeleton.

- Isotopic pattern of all these compounds is similar to that of 2,3-dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one indicating 1-deoxy-2,3-hexodiulose as intermediate.

Conclusions
✓ For the first time, CAMOLA experiments with [U-13C6]-glucose were applied to extrusion cooking in a real food system based on rice flour.
✓ Formation pathways of several odour active compounds during extrusion cooking were substantiated: 2,3-butanedione is mainly formed by recombination of C3 + C1 fragments; 2,3-pentanediol as well as HDMF, dihydromaltol and cyclotene are almost exclusively formed from the intact sugar skeleton.