Characterisation of “caramel-type” thermal decomposition products of selected monosaccharides including fructose, mannose, galactose, arabinose and ribose by advanced electrospray ionization mass spectrometry methods†

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The chemical analysis of caramel, formed upon heating of carbohydrates, remains a significant challenge due to the complexity of the resulting product mixture. Identification of the products formed upon heating of monosaccharides including fructose, mannose, galactose, arabinose and ribose is essential to understand the composition and properties of carbohydrate-rich processed foods. In this work, we report on the use of combined mass spectrometry techniques, including high performance liquid chromatography and electrospray ionization multi-stage tandem mass spectrometry (ESI-MSn). The composition of the obtained caramel was examined by high resolution mass spectrometry along with van Krevelen and Kendrick analysis. We found that caramel is composed of oligomers with up to six carbohydrate units formed through unselective glycosidic bond formation, their dehydrated products by losing up to eight water molecules, hydrated products and disproportionation products. An accurate mass measurement and subsequent fragment ion studies of all caramel samples (around 40 compounds) can thus be identified. Glycosidic bond and ring cleavages of sugar moieties were the major observable fragmentation pathways during this experiment. The innovative analytical strategies for the complex mixture analysis used provide a comprehensive account of the chemical composition of caramel, one of the most popular dietary materials over the world.

Introduction

Current estimations reveal that around 60% of all foods consumed by humans are thermally processed prior to ingestion. Recent archaeological evidence shows that the human ancestor Homo erectus used fire to cook food as early as 1 million years ago. Around 10 000 years ago humans started to prepare thermally processed food such as bread from carbohydrate rich plant materials. Although thermal processing of food has accompanied mankind’s history and development for millennia our scientific understanding of the composition of thermally processed food is still very limited, mainly due to limitations in analytical science. In a typical thermally processed food depending on processing conditions up to 50% of its original raw material chemical composition is transformed into a myriad of novel chemical structures. The name Louis Camille Maillard is in particular associated with the thermal processing of food due to his first realisation in his seminal 1912 publication that carbohydrates and amino acids react readily under typical food processing conditions. The resulting material is extraordinarily complex in terms of the number of novel chemical entities formed and results typically in unresolved chromatographic humps. Such unresolved humps have withstood for decades any analytical characterisation due to the lack of resolution provided by separation science. We have recently overcome this problem by using a combination of high resolution mass spectrometry and targeted LC-tandem mass spectrometry, allowing the formulation of a global picture of processed food composition.

In this contribution we apply our analytical methods and strategies to a selection of the dietary most relevant thermally processed monosaccharides. The resulting caramel type materials are of particular interest to the food industry because of their taste, aroma, colour and sweetness. They play a significant role in nonenzymatic browning reactions, including caramelisation, that control food quality and create caramel when heated. Caramel has widely been used for colouring and flavouring of foods and beverages, for instance beer, soft drinks, soups and candies.

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Caramel is, in particular, a complex mixture of volatile and non-volatile fractions of low- and high-molecular-weight compounds. The volatile fractions represented by furans such as hydroxymethylfurfural (HMF) and hydroxyacetylfuran (HAF), furanones such as hydroxymethylfurfuranone (HDF) and dihydroxydimethylfuranone (DDF), and the pyranones have been thoroughly studied. The non-volatile products form into two classes of products, products obtained from monosaccharides and polymeric materials. The latter has been divided into three classes of Caramelans (C_{24}H_{34}O_{14}), Carmelens (C_{16}H_{18}O_{23}) and Caramelins (C_{12}H_{18}O_{36}) as early as 1858 by Gelis and later by Kitaoka and Suzuki. The former has been shown to contain deoxy-glucosones after catalytic involvement of an amino acid amine functionality and further dehydration products of monosaccharides that lead ultimately to aromatic furanes or methylglyoxal.

Despite its importance, the majority of the chemical composition of thermally treated carbohydrates remains unresolved if not mysterious. Some examples of products of heating of carbohydrates have been described and include for example the dehydration products of fructose, difructose di-anhydrides (DFAs).

The process of examination has been continued using graphical interpretation tools such as the van Krevelen and Kendrick mass spectral interpretation strategies to characterise the chemical composition of caramel. We have combined herein high resolution and tandem mass spectrometry techniques in the investigation of saccharide thermal decomposition products. Different non-MS techniques have been applied in the characterisation of thermally treated food materials, such as NMR or GC.

We have combined herein high resolution and tandem mass spectrometry together with recently reported novel data interpretation strategies to characterise the chemical composition of caramel, formed when fructose, galactose, mannose, ribose and arabinose, common monosaccharides in food and pharmaceutical industries, are heated. We aim to understand the complexity of thousands of the reaction products formed that can physically neither be separated nor compared to authentic reference materials. High resolution mass spectrometry with liquid chromatography/tandem mass spectrometry (LC/MS/MS) was employed for the determination of molecular formula lists. The process of examination has been continued using graphical interpretation tools such as the van Krevelen and Kendrick diagrams to provide a rough picture about structural trends, likely reaction mechanisms. Targeted tandem LC-MS and direct infusion tandem MS experiments have been conducted to confirm selected structures and provide global and comprehensive information on the chemical composition of caramel.

Materials and methods

Chemicals

Solvents (analytical grade), D(–)-galactose, D(–)-fructose, D(+)mannose, D(–)-ribose and D(–)-arabinose were purchased from Sigma-Aldrich (Bremen, Germany).

Sample preparation

All sugar samples (1 g) were heated in an oven for 2 h at 140 °C (fructose), at 180 °C (galactose and mannose) and at 160 °C (ribose and arabinose). The caramelised samples were stored at room temperature. Caramelised carbohydrates (1 mg) were dissolved in methanol–water (1 : 1, v/v, 1 mL) and directly used for microTOF and direct infusion ION TRAP experiments. When required, they were dissolved in water and used for LC-MS.

High resolution MS

High-resolution mass spectra were recorded using a Bruker Daltonics microTOF instrument employing both negative and positive electrospray ionization modes. A microTOF Focus mass spectrometer (Bruker Daltonics) was fitted with an ESI source and internal calibration was achieved with 10 mL of 0.1 M sodium formate solution. Calibration was carried out using the enhanced quadratic calibration mode. All MS measurements were performed in both negative and positive ion modes. It should be noted that the intensities of the measured peaks in a TOF calibration influenced the magnitude of the mass error with high-intensity peaks resulting in detector saturation displaying larger mass errors. Usually this problem can be overcome by using spectra averaging on the side flanks of a chromatographic peak or by taking more diluted samples.

Data analysis

Molecular formulae were calculated using Bruker software Data Analysis 4.0. Data were subsequently exported to Excel to carry out mathematical operations such as determination of H/C and O/C ratios or Kendrick analysis. All graphs were created using Origin 7.5.

LC-MS

The LC equipment (Agilent 1100 series, Bremen, Germany) comprised a binary pump, an auto sampler with a 100 µL loop, and a DAD detector with a light-pipe flow cell (recording at 220 and 254 nm and scanning from 200 to 600 nm). This was interfaced with an ion-trap mass spectrometer fitted with an ESI source (Bruker Daltonics HCT Ultra, Bremen, Germany) operating in an Auto MS mode to obtain fragment ion m/z. MS², MS³, and MS⁴ fragment-targeted experiments were performed to focus only on compounds producing a parent ion at m/z 143, 149, 161, 179, 197, 263, 287, 305, 323, 341, 359, 395, 413, 449, 431, 467, 485, 503, 521, 527, 545, 611, 629, 647, 659, 665, 677, 683, 773, 791, 809, 827 and 845. Tandem mass spectra were acquired in an Auto-MS mode (smart fragmentation) using a ramping of the collision energy. The maximum fragmentation amplitude was set to 1 volt, starting at 30% and ending at 200%.
MS operating conditions (negative mode) have been optimised using glucose with a capillary temperature of 365 °C, a dry gas flow rate of 10 L min⁻¹ and a nebulizer pressure of 12 psi.

**HPLC**

Separation was achieved on a 250 × 4.6 mm i.d. column containing diphenyl 5 µm and 5 × 4.6 mm i.d. guard column of the same material (Varian, Darmstadt, Germany). Solvent (water-formic acid 1000 : 0.05 v/v) was delivered at a total flow rate of 850 µL min⁻¹ by 25 min isocratic.

**Thermogravimetric analysis (TGA)**

Thermogravimetric analyses (TGA) were performed using a TA Instruments SDT Q600 instrument. The temperature was ramped from 25 to 140 °C for fructose, to 180 °C for galactose and mannose and to 160 °C for ribose and arabinose at a rate of 5 °C min⁻¹ and kept at the final temperature for 2 h using a nitrogen atmosphere.

**Infrared (IR) analysis**

Infrared (ATR-IR) spectra were recorded using neat material on a Bruker Vector 33 spectrometer. IR absorptions are given in wavenumbers (cm⁻¹).

**¹H NMR**

¹H NMR spectra were acquired on a JEOL ECX-400 spectrometer operating at 400 MHz, at room temperature in D₂O, using a 5 mm probe. The chemical shifts (δ) are reported in parts per million (ppm).

**Results and discussion**

An investigation of the thermogravimetric data along with the mass spectra of caramelised samples at different temperatures enabled the optimisation of heating conditions. Thermogravimetric curves were recorded and heating conditions were chosen for further analysis that exhibited around 10–12% weight loss (ESI†). This weight loss corresponds to the loss of one water molecule on average per monosaccharide unit and thus a quantitative reaction yield. In fact, 2 h reaction time at 180 °C for galactose and mannose, at 140 °C for fructose, whereas for ribose and arabinose at 160 °C revealed to be the best heating parameters. It should be noted that the heating times exceed typical food processing times by a factor of two. However, products formed after prolonged heating are largely identical when compared to those formed at shorter heating times only with reduced product yields. Mass spectra were acquired in both positive and negative ion modes from five heated monosaccharides. Spectra of caramelised: (a) fructose (1), (b) galactose (2), (c) mannose (3), (d) ribose (4) and (e) arabinose (5) in the negative ion mode are shown in Fig. 1. The positive ion mass spectra were dominated by sodiated molecular ions. Table 1 illustrates the mass/charge ratio (m/z) of the product ions, elemental composition, and average mass error for heated mannose as the representative monosaccharide.

![Fig. 1](image-url) Mass spectra of caramelised: (a) fructose, (b) galactose, (c) mannose, (d) ribose and (e) arabinose in the negative ion mode using a direct infusion into an ESI-TOF-MS instrument.
Chemometric data interpretation

While mass spectrometric data are really complex, the novel data interpretation strategies (van Krevelen and Kendrick analysis) initially applied for petrol products by Marshall and colleagues can easily be employed. The van Krevelen as well as the Kendrick analyses have been utilized only a few times for dietary materials, such as wine, black tea thearubigins and caramel. The van Krevelen diagrams were generated from high-resolution mass data, where the elemental H/C and O/C ratios were calculated from the molecular formulae obtained from the experimental high resolution MS data and both of them were plotted in a two-dimensional graph against each other. Fig. 2 represents the van Krevelen diagrams consisting of a plot of H/C vs. O/C atomic ratios for caramelised 1, 2, 3, 4 and 5. Certain classes of compounds have a set of elemental ratios, e.g. in carbohydrate H/C is ~2 and O/C is ~1. A significant number of points are found in the area of the van Krevelen plots of caramelised monosaccharides (I). The group of points is present on the top left corner with high H/C and low O/C ratios, which represents compounds after reduction (III). The next group of points on the bottom corner with low H/C and O/C ratios suggests formation of aromatic compounds (IV).

Many points appear in the middle range of the graph similar to the ones on the line with a negative slope, which arise from the successive dehydration process (II). A series of peaks, products from various chemical reactions, could be visually identified here.

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The Kendrick plots with the H$_2$O increment were prepared from the theoretical and experimental high-resolution masses derived from TOF-MS experiments for heated monosaccharides. Fig. 3 presents a two-dimensional display of the Kendrick mass defect versus nominal Kendrick mass, for all peaks higher than 20 of baseline noise, including ions of even and odd mass for mannose.

The investigation of diagrams shows the presence of some homologous series of compounds. The coloured points represent the starting materials of different masses losing several molecules of water (up to eight). The same class and type of compounds with different number of H$_2$O units thus fall on a single horizontal line, with peaks separated by 18 Da in nominal Kendrick mass, but zero difference in the Kendrick mass defect. Many elemental compositions in a single caramel negative ion mass spectrum could be identified rapidly from these groupings.

The diagrams confirmed the formation of oligomers of starting materials with up to eight water molecules. The dehydration and hydration products of monosaccharides and their oligomers are indeed formed and easily visualized. These novel techniques help us understand the whole range of products and the reactions carrying out when carbohydrates are heated. The next step was to characterise thus formed compounds in detail by tandem mass spectrometry and focus on the further investigation of oligomers of hexoses, particularly dehydration and hydration products.

**Comparison of datasets**

Nevertheless, mass spectra of studied monosaccharides exhibited differences in intensities of the main product ions. In the spectrum of galactose mainly dehydrated products such as a dimer, tetra- and pentamer are present. Among them a monomer and trimer were also observed with relatively high intensities. The MS spectrum of mannose exhibited oligomers as the predominant ions, followed by dehydrated ions. The most intensive ions in fructose's MS spectrum were its monomer.
along with formic acid adducts of a dimer and trimer, accordingly. Such adducts are present in the spectra of the rest of the monosaccharides although with low intensities. Formic acid being a product of degradation of monosaccharides is most probably formed in higher quantities in the case of fructose, which causes the formation of formic acid adducts.

Moreover, we prepared three radar plots for better visualization of differences between the aforementioned samples. The main axes show individual ions. The relative intensities are located from the centre of the plot to its axes and three studied monosaccharides are illustrated as coloured lines. The first chart shows differences in intensities of oligomers (Fig. 4a). The second plot describes dehydrated products, instead (Fig. 4b). Galactose forms dehydrated oligomers preferentially, followed by mannose and fructose. The third graph illustrates the ratios of different intensities of oligomers to dehydrated oligomers (Fig. 4c). It is visible that fructose varies from the rest of the monosaccharides in terms of the monomeric product with the highest ratio of 179/161, thus the lowest degree of dehydration.

Galactose shows higher degree of dehydration of oligomers followed by fructose and mannose. The fact that galactose preferentially formed dehydrated products might be explained by their stereochemistry. The axial C4–OH substituent of galactose causes intramolecular S$_2$2-like reaction producing most likely an oxygen-bridged molecule 6 (see Fig. 5).

When comparing thermally treated hexoses with pentoses major differences are apparent in the van Krevelen diagrams. Most interestingly the number of novel compounds formed during heating is significantly reduced when comparing pentose sugars with hexose sugars. Additionally there are considerably less data points in the polyaromatic heterocycle region of the van Krevelen plot if the pentose sugar heating products are compared to their hexose analogues. This finding comes as a surprise since one might expect that a C-5 moiety is structurally closer to a furanoid structure when compared to a C-6 moiety that requires a series of rearrangement steps to arrive at a furanoid product.

Characterisation of monomeric and oligomeric hexoses and pentoses
The MS$^n$ data of 1, 2 and 3 have thoroughly been studied. Monomers of monosaccharides appeared at m/z 179.0 in the negative ion mode. The generated oligomers of hexoses, which
are formed upon heating, emerged at m/z 341.0, 503.0, 665.2, 827.2 and 989.2 in the negative ion mode. All of these ions of characterised caramel samples were fragmented in the negative ion mode using a direct infusion into an ESI ion-trap mass spectrometer. Tandem MS data are summarized in the ESI.† Fragments of an ion at m/z 179.0 gave the base peaks at m/z 161.0 (2 and 3) and 90.0 (1) corresponding to an anion of monosaccharide after dehydration and anion of monosaccharide without three CH₂O molecules, arising from the cleavage of the glycoside ring, respectively.‡ In the next step, we performed ESI-LC-MS measurements using the optimised chromatographic conditions for caramel samples. The extracted ion chromatograms (EICs) were generated for monomeric monosaccharide and all oligomers of monosaccharides. EICs of the monomeric ion at m/z 179 exhibited for all samples one main peak, followed by three small chromatographic peaks. Fragmentation patterns for these ions are identical for all chromatographic peaks, nevertheless MS spectra differ between monosaccharides. The base peaks appeared at m/z 113 and 119 for galactose and mannose, respectively. The MS spectrum of fructose exhibited the main ion at m/z 89 with fragment ions at m/z 67 and 125.

The base peaks at m/z 179.0 are observed from dimers of 1 and 2 formed by the glycosidic bond cleavage between two monosaccharides and may occur at either the reducing or nonreducing end. Furthermore, 3 showed the base peak at m/z 323, which corresponds to a dimer without one water molecule. In particular, the dehydration process took place before the cleavage of the respective glycosidic bond. Fragment ions at m/z 221 [−4 × CH₂O] were quite intense and came from the cleavage of the glycoside ring. MS² spectra of the ion at m/z 503, a trimer of monosaccharides, for all caramel samples exhibited the base peak at m/z 341, belonging to a dimer of monosaccharides formed after the glycosidic bond cleavage at the nonreducing end. On the other hand, intensities of the fragment ions at m/z 179 were half higher than the fragments at m/z 161 which might deduce the glycosidic bond cleavage at the reducing end as well. This is probably not the reliable criterion for a good differentiation, because these ions can originate from the residual dimers. Fragmentations of the ions at m/z 665 corresponding to a tetramer of monosaccharides gave in the case of 2 and 3 the base peak at m/z 503, which indicate the glycosidic bond cleavage at the nonreducing end. In contrast to 2 and 3, the base peak of 1 appeared at m/z 485 derived from the glycosidic bond cleavage at the reducing end.

All MS² spectra of an ion 827 for 2 and 3 corresponding to pentamers of monosaccharides showed the base peak at m/z 665 (the anion of a tetramer). The cleavage of the glycosidic bond took place at the nonreducing end, as was observed for the aforementioned tetramers. Due to low abundance, the fragmentation process of the ion at m/z 827 for 1 did not occur at all. Whereas, fragmentations of the ion at m/z 989, a hexamer of monosaccharides, gave common fragments for all analyzed monosaccharides with the base peak appeared at m/z 827 excluding 1 with the base peak at m/z 647. The above-mentioned oligomers as well as the base peak at m/z 827 showed the particular cleavage of the external glycosidic bond, whereas for 1 the cleavage of the internal glycosidic bond (m/z 647). Fragmentation data of oligomers of hexoses for all caramel samples are consistent with exclusive cleavages of glycosidic bonds on the external part of the molecules at the nonreducing end. Only two exceptions in the case of a pentamer and hexamer of 1 gave the main fragmentation with internal glycosidic bonds.

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**Fig. 6** Extracted ion chromatogram and MS² spectra of the pseudomolecular ion at m/z 341.0 (C₁₂H₂₂O₁₁) for five selected chromatographic peaks of caramelised mannosse in the negative ion mode.
It was mentioned before that the extracted ion chromatograms (EICs) were generated for all oligomers of monosaccharides and as an example, the EIC of the ion at m/z 341 of dimannose gave a total of eight resolved chromatographic peaks, two of high, three of medium and three of low intensities (see Fig. 6).

The MS² spectra of particular compounds were recorded to afford an identical or different fragmentation pattern and proved that glycosidic bonds were not formed selectively. A full set of isomeric glucose derivatives with similar tandem MS data for 10 theoretically potential carbohydrates with similar tandem MS data proved that glycosidic bonds were not formed selectively. A full loss of 132 was observed, a water molecule, around 60%. For trimers of hexoses, 485 showed the base peak at m/z 161 and further ions of dehydrated oligomers using a direct infusion into an ESI ion-trap mass spectrometer. The mass spectra of the fragment ion at m/z 161 showed a loss of 60 as the main peak in the case of 3, which corresponds to two CH₂O molecules and a loss of 48 as the main peak of 1 and 2, which corresponds to one CH₂O and water molecule, both derived from the cross-ring cleavage. The fragmentation of the ion at m/z 323, corresponding to a dehydrated dimer of hexoses, exhibited the base peak at m/z 161 [C₆H₁₀O₅] for all caramelised monosaccharides after the glycosidic bond cleavage at the nonreducing end in the product ion, whilst the fragment ion at m/z 179 occurred with intensities around 10–20%. The water elimination from the monosaccharide at C1–C4 positions led to the formation of an enol that tautomerises to its carbonyl form. Additionally, IR and NMR data of caramel products confirmed the presence of such carbons. The formation of 1,6-anhydrohexoses at the reducing terminus must be considered. The fragmentation of dehydrated trimers at m/z 485.1 showed for all caramel samples the base peak at m/z 323, arising from dehydrated dimers. The MS spectra of the rest of the dehydrated ions 647 and 809 always contain the base peaks at m/z 485 and 647, respectively with a loss of 162 [C₆H₁₀O₅]. Further fragmentation of ions 485 gave the base peak at m/z 323 for all caramel samples. In the case of fructose, the MS² spectrum of 323 was obtained with the base peak at 233 and a neutral loss of 90 [3 × CH₂O] including the cleavage of the glycosidic ring.

Dehydrated oligomers of caramelised 1, 2, and 3 derived from a loss of two and three water molecules were observed at m/z 305.1, 467.1, 629.2 and at m/z 287.1, 449.1, 611.2, respectively. Fragmentation of an ion at m/z 305, a dimer without two water molecules, was possible only in the case of 3 and neutral losses of 16 and 66 [CH₂O + 2 × H₂O] were detected. Furthermore, ion 287 of a dimer after losing three water molecules gave in all caramel samples neutral losses of 48 [CH₂O + H₂O] and 126 [C₆H₁₀O₅]. The latter suggests the presence of hydroxymethylfurfural, supporting the elimination of all three water molecules at one saccharide moiety. Mass spectra of a trimer without two water molecules (467) showed neutral losses of 18 [H₂O], 180 [C₆H₁₀O₅] and 162 [C₆H₁₀O₅] predominantly. The base peak at 287 with a neutral loss of 162 for caramels was found for a trimer without three water molecules (m/z 449). The MS² spectra of 2 and 3 gave peaks with a neutral loss of 126 (Fig. 7). This is consistent with the behaviour of the aforementioned dehydrated dimers without three water molecules showing the presence of hydroxymethylfurfural and approves the elimination of all three water molecules from the same hexose moiety. Mass spectra of an ion at m/z 611, a tetramer...
without three water molecules, showed a neutral loss of 162 \([C_6H_{10}O_5]\) as the base peak for all caramel samples. The fragmentation of a tetramer without two water molecules \((m/z\ 629)\) was not possible due to low intensities of the precursor ion.

For all observed dehydration products the question remains open whether they are formed by dehydration of oligomeric hexoses or whether dehydration to form deoxyglucosones and related derivatives precedes formation of anomeric bonds and oligomerisation.

For heated ribose and arabinose, dehydrated monomers were found at \(m/z\ 131.0\) \([C_5H_{10}O_3]\) and monodehydrated oligomers up to hexamers at \(m/z\ 263.1\) \([C_{10}H_{16}O_8]\), \(395.2\) \([C_{15}H_{24}O_{12}]\), \(527.2\) \([C_{20}H_{32}O_{16}]\), \(659.2\) \([C_{25}H_{40}O_{20}]\) and \(791.3\) \([C_{30}H_{48}O_{24}]\). Next to monodehydrated dimers gave the main fragment at a neutral loss of 36 \([C_2H_2O]\) for trimers at \(m/z\ 359.2\) \([C_{15}H_{24}O_{12}]\) and didehydrated tetramers of arabinose neutral losses of 84 \([C_2H_2O]\).

Characterisation of hydration products

Hydration products have been detected at \(m/z\ 131.0\) \([C_5H_{10}O_5] \) and monodehydrated oligomers with neutral losses up to hexamers at \(m/z\ 263.1\ \([C_{10}H_{16}O_8]\), \(395.2\ \([C_{15}H_{24}O_{12}]\), \(527.2\ \([C_{20}H_{32}O_{16}]\), \(659.2\ \([C_{25}H_{40}O_{20}]\) and \(791.3\ \([C_{30}H_{48}O_{24}]\). Next to monodehydrated oligomers, dehydrated and trihydrate products were formed with relatively high intensities.

MS\(^2\) spectra of monodehydrated pentoses at \(m/z\ 131.0\) showed the base peaks with a neutral loss of 18. In the case of dehydrated pentoses the base peak ions at \(m/z\ 85.2\) were observed, originating from the ring-cleavages. MS\(^2\) spectra of monodehydrated dimers gave the main fragment at \(m/z\ 202\) for 4 after the cross-ring cleavage and at \(m/z\ 130.7\) for 5, after the glycoside bond cleavage. In the case of monodehydrated trimers at \(m/z\ 395.0\), the base peaks at \(m/z\ 288.8\) and \(m/z\ 262.8\) for 4 and 5, respectively, were observed. In the case of monodehydrated tetramer of arabinose neutral losses of 132 produced the main fragment ions. The same base peak for the monodehydrated hexamer with a neutral loss of 132 was observed for heated arabinose.

Conclusions

We demonstrated here an advanced mass spectrometric study on the composition of caramel, formed upon heating of five common monosaccharides. High-resolution mass spectrometry and fragmentation studies allowed us to assign formulae for around 40 compounds. We have described that caramel is...
composed of several thousands of compounds formed by a small number of unselective and chemoselective reactions. Such products derived from the caramelisation of fructose, galactose, mannose, ribose and arabinose including oligomers with up to six carbohydrate units formed through unselective glycosidic bonds, dehydration products of oligomers losing up to a maximum of eight water molecules, hydration products of sugar oligomers and disproportionation products. A similar MS fragmentation pattern of oligomers of monosaccharides, hydrated and dehydrated products for all caramel samples was observed. Furthermore, this work demonstrated the usefulness of the analytical strategies such as the van Krevelen and Kendrick analyses to study the composition of dietary compounds, such as caramel.

**Notes and references**