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Intact Carbohydrate Structures as Part of the Melanoidin Skeleton

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Model melanoidins from monomeric, oligomeric, and polymeric carbohydrates, and amino acids formed under aqueous as well as water-free reaction conditions, were submitted to acidic catalyzed hydrolysis. Their degradation products were detected qualitatively and quantitatively by HPTLC and HPLC−DAD. A considerable amount of monomer carbohydrates from hydrolysis of model melanoidins formed under water-free reaction conditions was detected. It can be seen clearly that the amount of carbohydrates released increased with increasing degree of polymerization of the carbohydrates used as starting material. In comparison, the hydrolysis of melanoidins formed in aqueous condition resulted in only a small glucose release. It seems that in the Maillard reaction under water-free conditions, a significant amount of di- and oligomer carbohydrates were incorporated into the melanoidin skeleton as complete oligomer with intact glycosidic bond, forming side chains at the melanoidin skeleton. Additional side chains could be formed by transglycosylation reactions. With increasing water content, hydrothermolytic as well as retro-aldol reactions of the starting carbonyl components became significant, and therefore the possibility of forming side chains decreased. The results are consistent with the postulated melanoidin structure being built up mainly from sugar degradation products, probably branched via amino compounds.

KEYWORDS: Melanoidins; oligosaccharides; structural discussion; hydrolysis

INTRODUCTION

There are currently three main proposals for the structure of melanoidins: (a) Heyns and Hauber (*1*), and later Tressl et al. (*2*), postulated a polymer consisting of repeating units of furans and/or pyrroles, formed during the advanced stages of a Maillard reaction, and linked by polycondensation reactions; (b) Hofmann (*3*) detected low-molecular-weight colored substances, which were able to cross-link proteins via ϵ-amino groups of lysine or arginine to produce high-molecular-weight colored melanoidins; and (c) in a third structural proposal, the melanoidin skeleton is mainly built up of sugar degradation products, formed in the early stages of a Maillard reaction, polymerized through aldol-type condensation, and possibly linked by amino compounds (*4*−*6*).

Starting materials, as well as reaction conditions, have a strong influence on elemental composition and structure of melanoidins (*5*, *7*). It can therefore be assumed that, in real food systems, the above-mentioned structural proposals each partially supplement each other, or that different structures coexist.

As well as instrumental methods for structural elucidation of melanoidins (*8*), thermolytic and chemical degradation reactions have also been described in the literature. Identification of degradation products should assist in drawing conclusions on the initial melanoidin structure. For instance, oxidation and reduction reactions led to bleaching of melanoidin color, generally accompanied by a decrease in molecular weight (*4*, *9*−*11*). Concrete information about melanoidin structures was, however, not obtained by these methods.

Water solubility of melanoidins can be increased by altering the pH of the solution (*12*, *13*), additionally, the melanoidin color intensity changed. In general, at high pH values the brown color intensified, and at low pH values, melanoidin bleaching could be observed (*14*).

Benzing-Purdie and Ripmester (*15*, *16*) detected no changes in spectroscopic properties (IR, NMR), nor in microanalysis data, of a xylose/glycine melanoidin model after alkaline-catalyzed hydrolysis. In contrast, acid hydrolysis led to a 20% decrease in weight of the model melanoidins, which was explained by loss of volatiles such as CO_2, H_2O, and NH_3. Other degradation products were not determined.

On acid treatment of roasted coffee samples to improve separation of melanoidin fractions, Packert (*17*) detected small amounts of monosaccharides, which were also present as polysaccharide constituents (arabinogalactomannans) of green coffee beans.

Within the scope of our investigations on the structure and properties of melanoidins, we compared melanoidins formed

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from oligomeric carbohydrates and amino acids, as well as melanoidins from mono- and disaccharides. To determine structural differences in their composition, we investigated their degradation products after acid hydrolysis. Differences in the reaction mechanisms of melanoidin formation for monomer and oligomer carbonyl compounds can additionally be substantiated by such means.

In earlier work, we postulated a basic structure for monosaccharide/glycine melanoidins (*5*) being formed by aldol condensations of α-dicarbonyl compounds as main intermediates of the early stage of the Maillard reaction, partially branched by amino compounds. Hydrolytic investigations are now to be used to also confirm this structure for melanoidins formed from oligosaccharides and amino acids.

EXPERIMENTAL PROCEDURES

Preparation of Melanoidins. Melanoidins were prepared according to Cämmerer and Kroh (*5*). The carbonyl compounds glucose (D-GLC) (Merck water-free), maltose (mal) (Merck, monohydrate), lactose (lac) (Merck, monohydrate), maltotriose (MT) (Fluka, > 93% HPLC), maltooligosaccharide mixture DP 3-10 (MO) (Merck), or maltodextrin 10 (Dex) (from maize starch, Fluka) were used, along with the amino acids glycine (gly) (Serva) or D,L-alanine (D,L-ala) (Fluka).

For preparation of MO and Dex melanoidins, 50 g of carbohydrate and 5 g of gly were mixed thoroughly in solid state, and aliquots of 5 g were heated at 170 °C for 25 h.

Separation of High-Molecular-Weight Melanoidin Fractions (HMW). *By Dialysis.* Dialysis was performed with 5 g of melanoidin in 50 mL of distilled water (water-free melanoidins) or 50 mL of reaction solution (aqueous melanoidins) per tube in 1 L of distilled water using cellulose dialysis tubing (Spectra Por, Carl Roth, Germany; molecular weight cutoff 12,000−14,000 Da, pore size 1.5−3.0 μm). Water was changed every 10−12 h. Total dialysis time depended on the carbohydrate used, and ranged from 150 to 300 h. After dialysis, samples were freeze-dried and checked for absence of nonreacted starting materials by HPTLC (*18*) or HPGPC (*5*).

By Gel Chromatography. A Pharmacia (Uppsala, Sweden) chromatography system was used with applicator, glass column XK 26 (1000 × 26 mm i.d.), recorder (Rec. 102), and detector (Uvicord SD, 195 and 405 nm). Chromatography was performed with 2 g of melanoidin, which had been finely ground and dissolved in 25 mL of distilled water, shortly boiled, and filtered. A 5-mL portion of the deep brown solution was put on a Sephadex column (G 25 fine; Pharmacia) and eluted with distilled water at a flow rate of 100 mL/h. The high-molecular-weight melanoidins eluted at about 150 mL. The fractions were collected and freeze-dried and checked for absence of nonreacted starting materials by HPTLC (*18*) and HPAEC (*19*).

HPTLC. *Carbohydrates.* Quantitative and qualitative detection of carbohydrates with HPTLC was performed according to Kroh et al. (*18*).

Amino Acids. For quantitative analysis of amino acids, conditions the same as those for carbohydrates were used (*18*). However, the plates were developed with a solution of 0.5% ninhydrin in ethanol, and heated for 10 min at 110 °C, and the spots were scanned at 385 nm. Quantification by external calibration was performed in duplicate.

HPAEC/PAD. For quantitative determination of carbohydrates with HPAEC/PAD the method described by Hollnagel and Kroh (*19*) was used.

Hydrolytic Degradation. *Aqueous/Acid.* For hydrolytic investigations, 20 mg of melanoidin was dissolved in 1 mL of distilled water or acid and heated in a sealed tube up to 6 h at 105 or 120 °C. Several combinations of concentration, reaction time, and temperature were used: (a) HCl: 0.5, 2, and 6 N/room temperature and 105 °C/1, 2, 4, and 6 h (b) trifluoroacetic acid: 1 and 2 M/100 °C and 120 °C/1 h; (c) H_2SO_4: 4%/120 °C/1 h; (d) H_2O: 105 °C/1 and 2 h.

After cooling, the mixtures were dissolved in 1 mL of distilled water, and the solutions were subjected to HPTLC analysis.

Optimal Hydrolytic Conditions used for Quantitative Determinations. Aliquots (20 mg) of melanoidin were dissolved in 1 mL of 1 N HCl and heated for 1 h at 105 °C in sealed tubes. After rapid cooling, 1 mL of distilled water was added, and the mixture was filtered, and diluted if necessary.

RESULTS

Melanoidins from monosaccharide (D-GLC), disaccharides (mal, lac), and oligosaccharides (maltotriose (MT), maltooligosaccharide (MO), and maltodextrin 10 (Dex 10)) were produced for hydrolytic studies. Glycine (gly) was chosen as amino compound and D,L-alanine (D,L-ala) was used for comparisons because gly has additional CH-acid reaction possibilities. Melanoidin formation reactions were performed under aqueous, as well as water-free, reaction conditions.

It was necessary to produce melanoidins free of both nonreacted starting materials and low-molecular-weight intermediates. Otherwise, the results of the hydrolytic measurements would have been inaccurate. Melanoidins formed from mono- and disaccharides were successfully purified by dialysis. However, separation of nonreacted starting materials in melanoidins formed from oligosaccharides was possible only by gel chromatography. In both cases, results were checked with chromatographic methods (HPTLC and HPAEC). A combination of the two methods offers the possibility of detecting mono- and disaccharides, as well as higher molecular weight carbohydrate moieties.

It was reported (*12*) that a small proportion of nonreacted starting material can be bound noncovalently to melanoidins and may be released simply by dissolution. Therefore, in parallel to acid-catalyzed hydrolysis, model melanoidins were also dissolved in distilled water alone and treated in sealed tubes for up to 2 h at 105 °C. The monosaccharides thus released were detected quantitatively and used as a blank. For all model melanoidins formed from D-GLC and gly, a release of maximum 0.3% gly and up to 1% D-GLC could be observed. This depends neither on melanoidin formation conditions nor on hydrolysis time. In maltose melanoidins, 0.1% gly and up to 0.8% D-GLC were found. These results indicate that only negligible amounts of nonreacted starting materials were bound in model melanoidins. Under the chosen conditions (water, pH 6.0), no glycosidic bonds in melanoidin skeleton should be cleaved.

Prior to quantitative measurement of acid-catalyzed hydrolysis, optimization of hydrolytic conditions was performed to obtain complete hydrolysis using three different acids at various concentrations under several hydrolytic conditions. Moreover, the possibility that a high content of inorganic ions could disturb HPTLC-based quantitative determination of hydrolysis products had to be taken into account. Because of these demands, the most satisfactory conditions for hydrolysis were 1 N HCl and 1 h at 105 °C in a closed system. Prolonged hydrolysis time (6 h) yielded only a marginal increase in product and could favor artifact formation.

Carbohydrate release from model melanoidins, observed under optimized hydrolytic conditions, is summarized in **Figure 1**.

With increasing degree of polymerization (DP) of carbohydrates used as starting material in the Maillard reaction, the release of monosaccharides increased from about 3% (D-GLC) via 20% (mal, lac) to 95% (Dex). Furthermore, lactose melanoidins indicated that the carbohydrates were preferentially released from the terminal end of saccharides incorporated in the melanoidin. D-Galactose (D-gal) is detected as the main hydrolytic product from a lactose melanoidin.

Subsequent hydrolytic investigations showed that the amount of intact monosaccharide released by hydrolysis was reaction-condition dependent.

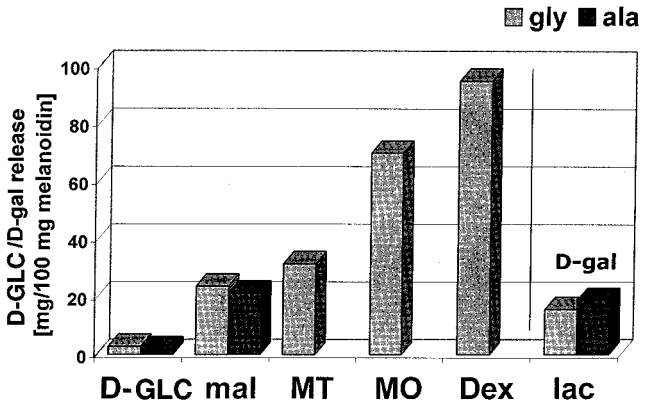

Figure 1. Release of monosaccharides by acid-catalyzed hydrolysis of melanoidins. MT, maltotriose; MO, maltooligosaccharide; Dex, maltodextrin 10; ala, D,L-alanine.

Table 1. Comparison of Monosaccharide Release from Melanoidins Formed under Different Reaction Conditions

melanoidin	water-free conditions[a]	aqueous conditions[b]
	D-glucose release [mg/100 mg melanoidin]	
D-GLC/gly	2.9	0.3
D-GLC/D,L-ala	1.9	0.4
mal/gly	23.8	18.5
mal/D,L-ala	21.3	9.0
	D-galactose release [mg/100 mg melanoidin]	
lac/gly	15.7	5.5
lac/D,L-ala	19.0	4.3

[a] Water-free conditions: 20 min/170 °C. [b] Aqueous conditions: 10 h/100 °C.

Table 2. Comparison of Monosaccharide Release from Melanoidins Formed at Different Reaction Times

	aqueous conditions[a]		water-free conditions[b]	
melanoidin	reaction time	release [mg/100 mg melanoidin]	reaction time	release [mg/100 mg melanoidin]
		D-GLC		
mal/gly	10 h	18.5	20 min	23.8
	30 h	5.4	60 min	19.4
		D-gal		
lac/gly	10 h	5.5	20 min	15.7
	20 h	5.0	60 min	16.7
		D-GLC		
MO[c]/gly			1 h	28.5
			25 h	70.0

[a] Aqueous conditions: 100 °C. [b] Water-free conditions: 170 °C. [c] MO, maltooligosacharide.

In general, from aqueous-prepared melanoidins, the release was much lower than that from melanoidins prepared under water-free conditions (**Table 1**). In the monosaccharide model melanoidins (D-GLC/gly and D-GLC/D,L-ala), a change from water-free to aqueous reaction conditions reduced the amount of sugars released to 10% or lower. The effect is less pronounced for disaccharide models (mal, lac). It resulted in a decrease in released sugars to 25% (mal) and 60% (lac), of the amounts obtained for the respective water-free systems.

For disaccharide models, **Table 2** indicates the influence of reaction time used for melanoidin formation on the amount of acidic degradable sugar components. Prolongation seems to have an influence only on degradable D-GLC in maltose models,

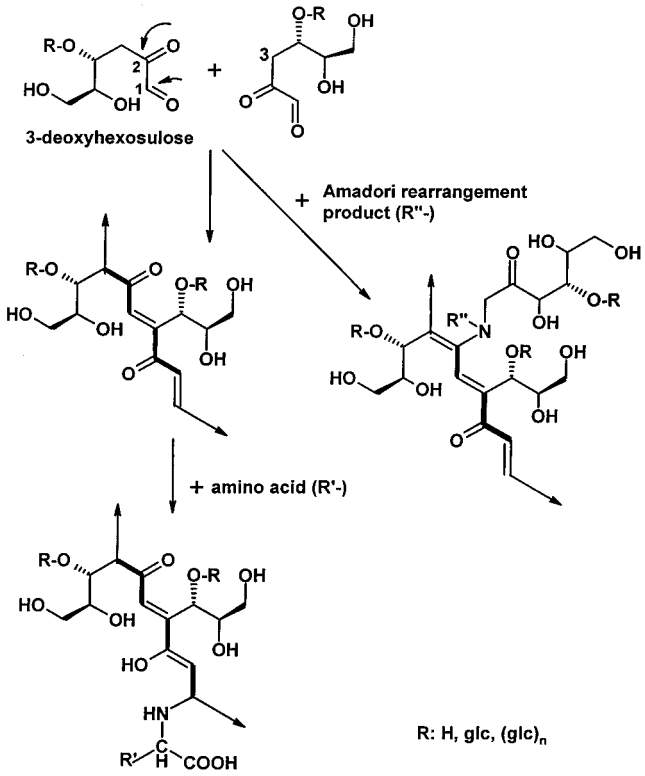

Figure 2. Part of possible melanoidin structure formed from 3-deoxyhexosulose involving amino compounds.

which is much stronger in the aqueous system than in the water-free system. In contrast, the amount of D-gal released by lactose models from both the aqueous or the water-free system could not be significantly influenced by reaction time.

DISCUSSION

Monosaccharides released by acid hydrolysis from melanoidins indicate that during Maillard reaction carbohydrates are not inevitably degraded to heterocycles such as furans or pyranes. Depending on Maillard reaction conditions it seems that a relevant part of di- and oligomeric carbohydrates react as complete molecules at the reducing end without glycosidic bond cleavage. Dicarbonyl groups in intermediate products can be assumed as reactive centers.

In a glucose/amino acid Maillard reaction system, the carbonyl compound reacts mainly via the Amadori product to form several deoxyosones which are able to react with each other in an aldol-type condensation to form a basic melanoidin skeleton of amino-branched sugar degradation products (*5*). For example, the nucleophilic attack of the carbanion in the C3 position of a 3-deoxyhexosulose can take place on the C1 of another molecule of deoxyhexosulose. **Figure 2** shows the possible structure of a melanoidin formed from 3-deoxyhexosuloses in this way. An attack on C2 of a 3-deoxyhexosulose is also possible, leading only to minor changes in the proposed structure. 1-Deoxyhexosuloses, 1-amino-1,4-didesoxyhexosuloses (*20*), in the case of oligosaccharides, 3-deoxypentosulose (*19*), and the initial Amadori rearrangement products themselves can react with a molecule of deoxyhexosulose to form the melanoidin backbone. Taking into account that retro-aldol products of carbohydrates with C2, C3, and C4 α-dicarbonyl structures formed during the early stage of Maillard reaction are also able to react in a comparable way, many variations of the melanoidin structure in **Figure 2** are conceivable. In addition, the proposed structure opens the

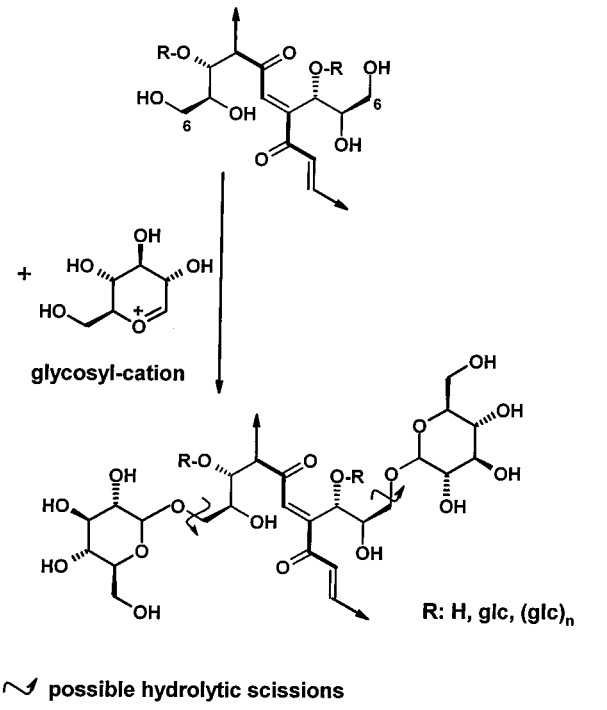

Figure 3. Schematic mechanism of 1,6-branched glucose side chain formation by transglycosylation.

possibility of incorporating amino acids by reaction with α-,β-unsaturated carbonyl structures.

The formation of structures in a water-free D-GLC/gly melanoidin model, which opens the possibility to release D-GLC, may be explained by transglycosylation reactions (**Figure 3**). A free D-GLC molecule might react with a carbohydrate structure via the formation of a glycosyl cation to form 1,6-branched saccharides (*18*). Thus, D-GLC can be incorporated as a side chain in the melanoidin skeleton and is easily split off by hydrolysis.

In contrast, enolizations and retro-aldol reactions play an important role in the reaction behavior of D-GLC in aqueous systems, resulting in the formation of highly reactive C2, C3, and C4 α-dicarbonyl compounds that are involved in the Maillard reaction instead of the D-GLC molecule (*21*). Transglycosylation reactions causing the formation of D-GLC side chains can take place only to a very small extent. Therefore, in aqueous melanoidin models the release of D-GLC was significantly lower than it was in the water-free model (**Table 1**).

Mal, and to a lesser extent lac, were preferably submitted to hydrothermolytic degradation reactions under aqueous conditions which resulted in formation of the monosaccharides D-GLC and D-gal, respectively. Thus, with increasing reaction time the reaction behavior of these monosaccharides plays an increasing role for the formation of the melanoidin structure. But the significantly higher release of D-GLC from di- or oligosaccharide melanoidins cannot be explained by transglycosylation reactions alone. It was assumed that by incorporation of saccharides with intact glycosylic bonds, carbohydrate side chains were formed at the melanoidin skeleton (**Figures 2** and **3**; R: GLC or $(GLC)_n$). In addition to side chains formed by transglycosylation reactions, these side chains can also be degraded by acid hydrolysis to D-GLC molecules. Separation of disaccharides can be presumed as well, but they are not stable under acidic conditions and could be detected in only very small amounts.

Indications are that reaction time could also have an important influence on melanoidin formation because it influenced the stability of the glycosidic bond in di- and oligomeric carbohydrates.

Investigation of an aqueous mal/gly model formed during 10 h reaction time indicated that about 18% of mal was incorporated into the melanoidin without degradation of the glycosidic bond, forming D-GLC side chains which could be easily split off (**Table 2**). As well as hydrothermolytic degradation reactions of mal with longer reaction times, "peeling off" mechanisms at sugar side chains in the melanoidin also became more important (*19*). Therefore, after 30 h heating in an aqueous solution, a smaller amount of mal reacted in the classic way because of the increasing variety of possible reaction products. Under this conditions, 5% of mal could be detected as D-GLC and the mal melanoidin seemed to become more similar to D-GLC models. Lac was more stable against hydrothermolytic breakdown than mal was. With the lac melanoidin, doubling Maillard reaction time led to only a marginal decrease in degradable carbohydrate structures (**Table 2**).

It was remarkable that the amount of hydrolytic degradation products from MO melanoidins formed under water-free reaction conditions at shorter reaction times (60 min) was similar to that from MT or mal models (about 30% D-GLC), whereas the amount of degradable D-GLC increased with increasing reaction time (70% at 25 h; **Table 2**). It seemed that in the MO mixture lower molecular weight carbohydrates with higher reactivity were quickly involved in Maillard reaction. Only by prolonging reaction time were carbohydrates with higher DPs involved in Maillard reaction, forming melanoidins with much larger carbohydrate side chains. This was confirmed by a higher amount of D-GLC detectable after acid hydrolysis (**Table 2**).

It was expected that the type of amino acid should be relevant for the formation of specific increments in melanoidin structures. Release of intact amino acids by acid hydrolysis from model melanoidins was only marginal, and no differences between gly and D,L-ala models could be detected. This indicated that during Maillard reaction, amino acids (gly, D,L-ala) were almost completely used up in the formation of intermediates and the branching of sugar degradation products. Only very small amounts were incorporated in the melanoidin skeleton by, for instance, addition on carbonyl groups of deoxyosones or on α-,β-unsaturated endiol structures which could form degradable amino acid side chains (**Figure 2**).

Results of acid-catalyzed hydrolysis of melanoidins correlated very well with the results of earlier investigations with respect to microanalysis data of melanoidins formed under different reaction conditions (*5*). The amount of carbonyl compound per nitrogen atom incorporated into the melanoidin was elucidated (*7*). Using aqueous reaction conditions only about half of the carbonyl compound was incorporated into the D-GLC melanoidin in comparison with that incorporated under water-free reaction conditions. Hydrolytic investigations showed that D-GLC melanoidins produced under water-free reaction conditions were able to release double or more the amount of carbonyl compounds than aqueous melanoidins.

That intact glucose molecules released from melanoidins formed from di- or oligosaccharides indicated that during Maillard reaction of carbohydrate/amino acid model systems a significant proportion of di- or oligosaccharides is incorporated into the melanoidin without degradation of the glycosidic bonds. The increasing number of side chains in the melanoidin skeleton is consistent with increasing DP of carbohydrates used as starting material. It is evident that melanoidins formed from oligomer

or polymeric carbohydrates and amino acids undergo similar reaction mechanisms in Maillard reactions, and exhibit, therefore, under hydrolytic conditions behavior similar to that of melanoidins from mono- and disaccharides.

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