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Primary reactions of sucrose thermal degradation

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Abstract

Thermal degradation of sucrose at 185 °C in a closed glassware and presence of air was studied with the help of GC/MS after acetylation of reaction products. Also model compounds were used to support the mechanism of thermolysis. Goal was to identify all the primary reactions of the process. It was observed that already after 5 min of treatment, two glucopyranose isomers were formed as products of sucrose glycosidic bond splitting. The furanose structure is probably transformed to anhydrofructoses, as 2,6-anhydrofructose was identified among the degradation products in much smaller amount than D-glucose. At longer thermolysis times some diastereoisomers of sucrose present in the reaction mixture, but some new products with longer retention times (RT) occurred. Also isomers of levoglucosan were observed after 1 h of treatment. This indicates that splitting of glycosidic bond is the most prominent primary reaction. The dehydration towards anhydrosucroses seams to be a minor primary reaction and might proceed via configuration changes on the pyranose ring. © 2003 Elsevier Science B.V. All rights reserved.

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1. Introduction

Sucrose is the most common sweetener with increasing world production [1]. Caramelization of this compound takes place during food processing applications.

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In this way syrupy mixture could be produced in concentrated water solutions and in presence of additives like citric acid [2]. As far as our knowledge there is no information available about the first step of thermal degradation of crystalline sucrose in absence of solvent or catalyst. Our goal was to find out if the dehydration proceeds before splitting of glycosidic bond. We, therefore, heated sucrose at temperature slightly above its melting point. It is known that at this temperature the oxidation reactions are not taking place [3]. Anhydrosucroses were synthesized as reviewed [4], but none of them were produced by thermal treatment. We prepared a mixture of acetylated anhydrosucroses to find out about their GC/MS characteristics. The acetylation methodology was chosen instead of silylation or methylation because anhydrosucroses were characterized by MS only as per-*O*-acetylated derivatives [5,6]. Also MS fragmentation of octa-*O*-acetyl-sucrose is known [7]. *mano*-and *altro*-Sucroses as potential products of sucrose thermal transformation were also prepared synthetically [8].

2. Experimental

2.1. Chemicals

Sucrose octaacetate, D-glucose, 1,6-anhydro- β -D-glucose, D-fructose and all other chemicals were commercial grade and were not further purified prior to use.

2.2. Thermolysis of sucrose

Sucrose (0.05-0.5 g) in 10 ml glass tube with Teflon cup was tempered in a heating block at 185 °C [9]. After desired heating time sample was acetylated as ascribed below.

2.3. Preparation of model compounds

Sucrose (5 g; 14.6 mmol) was dissolved in pyridine (75 ml) and *p*-toluensulfonylchloride (2.9 g; 15 mmol) in pyridine (10 ml) was added and the mixture was stirred at 5 °C for 120 h. The sample was evaporated under reduced pressure and dissolved in methanol solution of sodium methanolate (100 ml; 2.38 M) and tempered for 24 h at 70 °C. After vacuum evaporation and dissolving in water the sample was neutralized to pH 7 with 0.1 M HCl, decolorized with active carbon (2 g), filtered-off and evaporated. The product was dissolved in minimal amount of ethanol and the formed crystals, which according to NMR originated from tosylating agent, were repeatedly separated. The remaining solution contained 1',4'-anhydrosucrose in mixture with other compounds as determined by NMR [10], was lyophilized (0.7188 g). Part of the sample (0.05 g) was acetylated in pyridine (0.81 ml) in presence of catalytic amount of dimethylaminopyridine and acetic anhydride (0.94 ml) for 24 h at room temperature. After evaporation and extraction with water-CHCl₃ mixture, the chloroform fraction was subsequently extracted with 2 M HCl, water, saturated NaHCO₃ solution, water and dried with Na₂SO₄ and concentrated. In this way prepared mixture of anhydrosucroses was analyzed by GC/MS. 1,6-Anhydro- β -D-glucopyranose, D-glucose and D-fructose were acetylated in a same way as above.

2.4. Analysis

The GC/MS analysis were run on Hewlett–Packard 5890A/5790B instruments in a scan mode, equipped with PTE 5 (30 m × 0.25 mm ID; 0.25 μ m film) GC column; using helium as carrier gas at 0.97 ml min⁻¹ rate; 50 kPa pressure; 275 °C injection and detector temperature. The following temperature program was used: 150 °C (3 min), heating at 10 K min⁻¹ to 280 °C and maintaining the reached temperature for 9 min. The MS conditions: 70 eV; mass range: 43–700 amu; EMV: 2400 V; threshold: 1000. Obtained mass spectra were interpreted with the help of WILEY and NIST mass spectra library databases. NMR spectra were recorded at 300 MHz on Bruker spectrometer in D₂O.

3. Results and discussion

Isothermal heating of 0.05 g of sucrose at 185 °C was chosen as optimal after preliminary experiments at higher temperatures and bigger amounts of sample. Since it is problematical to exclude the presence of oxygen in the sample and also it is known that at temperatures slightly above melting point [3], oxidation reactions are not affecting the process, we have run all experiments in cupped tubes [9] and presence of air. After 5 min of treatment the sample was already homogeneously melted and first degradation products could be detected. In Fig. 1a there is a GC chromatogram of acetylated sample after 10 min of treatment showing three signals with retention times (RT) 21.45, 21.56 and 36.31 min as listed in Table 1. The first two signals are considered as α - and β -anomers of D-glucose with identical mass spectra (MS, Fig. 1b and c) and listed in Table 1 and Fig. 1a as peak # 1. All the mass spectra are plotted without original base peak m/z 43, to show the less abundant ions. In this way the second most abundant ion is a base peak in all the spectra. Usually the ions with bigger values are more important for carbohydrate structure interpretation. As could be proved also by ion analysis the first two peaks contain ions m/z 200 and 242, which are characteristic for pyranose structures. The ions m/z 101 and 187 typical for furanose ring are present only in sucrose spectrum (peak # 2, RT 36.31 min). The presence of D-glucose shows that the primary reaction is the splitting of glycosidic linkage of sucrose.

After 15 min of treatment (Fig. 2a) many new small peaks were observed. Peak # 3 (RT 17.87 min, Table 1) was assigned by the database to 1,3,4-tri-*O*-acetyl-2,6-anhydrofructose (Fig. 2b). It is also in agreement with MS data of this compound prepared synthetically [10]. This product was also observed previously as caramelization product of sucrose under acidic conditions [2]. This indicates that the furanose part of sucrose forms after splitting of glycosidic bond an anhydrostruc-



Fig. 1

Peak#	RT (min)	Assigned compound ^a	m/z ion
1	21.45	D-glucopyranose	200, 242
	21.56	D-glucopyranose	200, 242
2	36.31	Sucrose	331
3	17.87	2,6-anhydrofructose	170
4	33.25	Sucrose isomer	347
5	37.00	Sucrose isomer	605
6	18.28	1,6-anhydro-β-D-hexopyranose	229, 186
7	18.91	1,6-anhydro-β-D-hexopyranose	186
8	18.41	1,6-anhydro-β-D-glucopyranose	229, 186
9	27.75	Anhydrosucrose	169
10	30.12	Anhydrosucrose	229
11	33.35	Anhydrosucrose	211

Assignments of individua	l peaks of GC/MS of	lata of sucrose thermolysis

^a As per-O-acetate derivative.

Table 1

ture. As this compound was present only in traces in Fig. 1a, we assume that the furanose structure is less stabile. The presence of new peaks close to sucrose seams to be more important. The peak at RT 33.25 min gave MS (Fig. 2c) with ions at m/z: 347, 331, 281, 227, 211 and 207. Also new compounds with RT values bigger than for sucrose gave MS data with ions, m/z: 331 and 211 (Fig. 2d). We assume that these products are isomers of sucrose differing only in hydroxyl configuration. *mano*- and *altro*-Sucrose octaacetates were prepared and their MS contained ions, m/z: 331 and 347, which were also present in our spectra obtained with different MS technique [8]. As these ions are formed from both pyranose and furanose parts of sucrose and *manno*- and *altro*- isomers could not be assigned by MS, the running of authentic samples by GC/MS would be the optimal prove of the presence of the above compounds. On Fig. 2d there was present also ion, m/z 605, which could be also formed by fragmentation of furanose as well as pyranose part of sucrose molecule. This was the biggest fragment observed.

When sucrose was tempered at 185 °C for 30 min the analyzed reaction mixture did not contain sucrose (Fig. 3a) and after 1 h (Fig. 3b) two additional peaks at RT 18.28 and 18.91 min could be observed. Their MS were similar (Fig. 3c and d) and both spectra contained ion, m/z 186.

To support these findings, we have prepared 2,3,4-tri-O-acetyl-1,6-anhydro- β -D-glucopyranose, which gave GC profile with single peak at RT 18.41 min (Fig. 4a) with ions, m/z: 229, 186, 157, 144, 140, 127 and 155 (Fig. 4b), which were all present in the spectra on Fig. 3c and D. Since the RT values were slightly different, we assume that the new compounds are isomers of prepared model. The RT of authentic

Fig. 1. GC/MS data (see Section 2 and Table 1) of sucrose thermolyzed for 10 min: (a) GC analysis; (b) MS analysis of the component at RT 21.45 min; (c) MS analysis of the component at RT 21.56 min; (d) MS analysis of the peak at 36.31 min.



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per-O-acetyl-D-fructose was found to be at 21.18 min. As this peak was not present in Fig. 1a, we assume that after the splitting of glycosidic bond, the furanose component of sucrose might undergo to some more stabile anhydrofructose derivative like 2,6-anhydrofructose observed after 15 min at 185 °C (Fig. 2a).

We prepared also a mixture of anhydrosucroses by tosylation and subsequent dehydration of formed tosylates with sodium methanolate. The GC profile of acetylated mixture is on Fig. 5a. There are six distinguished peaks with RT 21.34, 25.65, 26.39, 27.75, 30.12 and 33.35 min. From these peaks the last one is very close to the one in Fig. 2a with RT 33.25 min. Its MS (Fig. 5b) has base peak with, m/z: 211 as well as ions at m/z: 331, 281, 229, 211 and 207. All these ions were also present in the spectrum on Fig. 2c except of ion, m/z: 229. This ion was observed on synthetically prepared per-O-acetyl-1', 4'-anhydro- and per-O-acetyl-3,6-anhydrosucrose [5,6], as well in the MS of levoglucosan on Fig. 4b. The two most prominent components of the model mixture (RT 27.75 and 30.12 min) which might be also present in the mixture on Fig. 2a gave similar MS data (compare Fig. 5c and d to B) differing only in the intensities of individual ions. In the most prominent peak the base ion was m/z: 229, which supports the anhydrosucrose structure [5,6]. The presence of 1', 4'-anhydro-sucrose in the model mixture was also supported by 1 H-NMR spectrum, which contained distinguished known H-1 signal at 5.48 ppm ascribed previously to this compound [11]. This indicates that also some anhydrosucroses could be formed as minor products. These are preliminary experiments and further research is needed towards preparation of individual anhydrosucroses and comparing their GC/MS data with components of thermolysis as well as employing other analytical techniques. At this stage the process could be ascribed by Scheme 1.

Additional problem is the evaluation of carbohydrates with the help of database libraries. The classical example is MS spectrum of 2,3,4-tri-*O*-acetyl-1,6-anhydro- β -D-glucopyranose, which according to previous results under undefined MS conditions gave spectrum with *m*/*z* ions: 288 (0.5%), 245 (1), 243 (2), 230 (20), 229 (18), 187 (41), 179(1), 141 (52), 128 (30), 127 (28), and 116 (100) [12]. Our MS data of the mentioned compound had *m*/*z* 116 only as a minor peak. As GC/MS technique generally does not provide molecular ions and for carbohydrates it is known that ions with higher values provide the most valuable structural information, a more sophisticated library for this class of compounds is needed. According to NIST library with the help of MASS FRONTIER 3.0 software a very similar spectrum in comparison to ours is assigned to 2,3,4-tri-*O*-acetyl-1,6-anhydro- β -D-talopyranose (ID #: 32019, C₁₂H₁₆O₈). Also MS data of 1,3,4-tri-*O*-acetyl-2,6-anhydro- β -D-fructofuranose (ID #: 6136, C₁₂H₁₆O₈) were in good agreement with our data.

Fig. 2. GC/MS data of sucrose thermolyzed for 15 min: (a) GC analysis, (b) MS analysis of component with RT of 17.87 min; (c) MS analysis of component with RT 33.25 min; (d) MS data of component with RT 37.00 min.



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Fig. 3



Fig. 4. GC/MS data of 2,3,4-tri-*O*-acetyl-β-D-glucopyranose: (a) GC analysis; (b) MS data of signal at RT 18.41 min.

4. Conclusions

The primary reaction of thermal degradation of sucrose is the splitting of glycosidic bond when it is treated at 185 °C. Except the products of subsequent reactions like 1,6-anhydro- β -D-hexoses also some sucrose derivatives are formed. They might be isomers of sucrose, with changed configuration on pyranose ring as well as anhydrosucroses. The presence of 1′, 4′-anhydro- and 3,6-anhydrosucroses is indicated according to GC/MS results of acetylated degradation products and supported by synthetically prepared models. It could be concluded that these primary reactions are taking place: splitting of glycosidic bond, dehydration and changes in configuration, resulting in formation of sucrose stereoisomers.

Fig. 3. GC/MS data of thermolyzed sucrose: (a) GC analysis of sample thermolyzed for 30 min; (b) GC analysis of sample treated for 1 h; (c) MS data of fraction with RT 18.28 min; (d) MS data of fraction with RT 18.91 min.





Fig. 5. GC/MS data of the mixture of per-*O*-acetylanhydrosucroses: (a) GC analysis; (b) MS data of fraction with RT 27.75 min; (c) MS data of component at RT 30.12 min; (d) MS data of peak at RT 33.35 min.

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