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FORMATION OF THE MAIN DEGRADATION COMPOUNDS FROM ARABINOSE, XYLOSE, MANNOSE AND ARABINITOL DURING PYROLYSIS

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Abstract

The thermochemical behaviour of sugars (*D*- and *DL*-arabinose, *D*- and *DL*-xylose and *D*-mannose) and sugar alcohol (*D*- and *DL*-arabinitol) was investigated by TG and pyrolysis-gas chromatography with mass-selective detection (Py-GC/MSD). The temperature of pyrolysis was 500 and 550°C. The TG-curves were measured both in air and nitrogen atmospheres, from 25 to 700°C with the heating rate of 2°C min^{-1}. In each case, the main pyrolysis products were classified into the following compound groups: (*i*) furanes, (*ii*) pyranes, (*iii*) cyclopentanes, (*iv*) cyclohexanes, (*v*) anhydroglucopyranoses, (*vi*) dianhydroglucopyranoses and (*vii*) saturated fatty acids.

For example, the main peaks of the chromatograms of pentoses (arabinose, xylose), hexose (mannose) and sugar alcohols (arabinitols) were different. The greatest peak of pentoses in gas-chromatogram was 2-furancarboxaldehyde and that of hexose was (2H)-furan-3-one. The greatest peak of arabinitols at pyrolysis temperature of 500°C was furan methanol and at 550°C α-angeligalactone. 5-hydroxymethyl-2-furan carboxaldehyde was found only in the pyrolysis of *D*-mannose (hexose). The former study showed that it was not found in pyrolysis of pentoses. The amount of CO_2 and H_2O was not determined.

Keywords: arabinitol, arabinose, hexose, mannose, pentose, pyrolysis, sugar alcohol, thermal decomposition, xylose

Introduction

In the solid-state arabinoses and xyloses are pentopyranose structures and mannose is a hexapyranose structure. Arabinitol is an acyclic polyalcohol. Hassel and Ottar suggested that the pyranose ring can exist in two possible conformations, $^4C_1$ and $^1C_4$ [1]. The conformation placing both the $–CH_2OH$ group and the –OH group in axial orientations on the same side of the ring is energetically unfavourable. Reeves proposed six boat forms as possible ring conformations for the pyranose ring [2]. In addition the pyranose sugars appear as α- and β-anomer. The energetically favoured conformations proposed for the sugars are α-*D*-arabinose, $^1C_4$, β-*D*-xylose, $^4C_1$, and β-*D*-mannose, $^1C_4$ [3]. *DL*-form is an equimolar racemic mixture of the enanthioforms or cocrystal. Often *DL*-form is energetically more stabile than *D*- or *L*-form. The knowl-

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edge of crystal structure and ring conformation is important in order to understand chemical and physical properties of carbohydrates.

The pyrolysis means controlled splitting of the sample into small molecules with heat in oxygen free circumstances [4]. The quantities of compounds during pyrolysis depend on the temperature program used. The temperatures used in general are between 400–900°C. Formed compounds are separated and analysed by the arrangement of GC/MS [5].

There are three stages in pyrolysis: initiation, propagation and termination. The fast raising of the temperature of the sample into pyrolytic temperature and the fast removing of the products with inert gas (helium) from the heated part of the equipment are important as to avoid secondary reactions and to obtain optimal degradation. The TG-curve helps to find the right temperature of pyrolysis.

Sugars and sugar alcohols are industrially produced for both food and pharmaceutical applications, and also for the synthesis of fine chemicals such as ascorbic acid and surface-active agents [6]. The reason for using different sugars and sugar alcohols as sweetening agents in various foods could be both technological and physiological. Some of these compounds have good thermal stability, some of them are consumable by diabetics, some have lower cariogenic effect, and some are low in calories. Sugars and sugar alcohols are bulk sweeteners, which form an essential part of the food product and so they strongly influence its appearance and texture.

In our previous investigation of pyrolysis of some solid fuels, betaine and lactitol have been studied [7–9]. Often sugars and sugar alcohols are heated either on purpose or accidentally. Therefore it is good to know their thermal behaviour. In this paper we investigate the pyrolysis of arabinose, xylose, mannose and arabitol.

Experimental

Samples

Each sample consisted of a small amount of either a commercial or a synthesised reagent. The reagents are described in detail in Table 1. *DL*-arabinitol was prepared from an ethanol-water (3:2) mixture of *D*-arabinitol and *L*-arabinitol by slow evapo-

Table 1 The samples used, producer and purity

Reagents	Producer	Purity
D-arabinose	Sigma	99
DL-arabinose	Sigma	98
D-arabinitol	Aldrich	99
DL-arabinitol	this work	99
D-mannose	Merck Fluka	bacteriologie >99
D-xylose	Xyrofin	100
DL-xylose	Sigma	99

ration. Purity of the reagents was determined by HPLC. The powder diffraction pattern was measured from all reagents to ensure their right structural form.

Measuring systems and measurements

The TG-measurements were done with Perkin Elmer TGA-7. The sample pans used were open Pt-pans and the amount of sample was 5–12 mg. Measurements were done in dynamic air and nitrogen atmospheres with a flow rate of 50 mL min^{-1}. The heating rate was 2°C min^{-1} and the temperature range was 25-700°C.

About 0.1–0.3 mg of each sample was pyrolyzed in a quartz tube (0.3 cm×1.0 mm i.d.) using a CDS Analytical Inc. Pyroprobe 1000 heated filament pyrolyzer coupled to a HP 5890 II Plus gas chromatograph. The GC was interfaced to a HP 5972 series mass selective detector [10]. The samples were heated three times to 80°C for 1 s before measurements. Temperature of the pyrolysis interface was 250°C. The scanning rate to pyrolysis temperature (500 and 550°C) was 20°C ms^{-1} and the time of pyrolysation was 10 s. The inert gas used was helium, which was also used as a carrier gas in GC and MS analyses. The temperature of the gas chromatograph was kept at 45°C for 4 min after which the heating continued to 240°C with the heating rate of 4°C min^{-1} and furthermore to 280°C with the heating rate of 39°C min^{-1}. The mass range of the mass spectrometry was 45–300 and the scanning rate was 2.7 scans min^{-1}.

Results and discussion

TG

The TG- and DTG-curves of *D*-arabinose and *D*-arabinitol in the air atmosphere are presented in Fig. 1. *DL*-arabinitol decomposed similar to *D*-arabinitol and the other sugars measured in this study decomposed similar to *D*-arabinose. The sugars decomposed in four stages. The sugar alcohols *D*-arabinitol and *DL*-arabinitol degraded in just one stage between 160–295 and 170–300°C, respectively. The residue, a carbon rich char, was 4.1% for *D*-arabinitol and 2.9% for *DL*-arabinitol. In the air atmosphere the residues burned to CO_2 when heated to 500°C and in the nitrogen atmosphere the residues evapo-

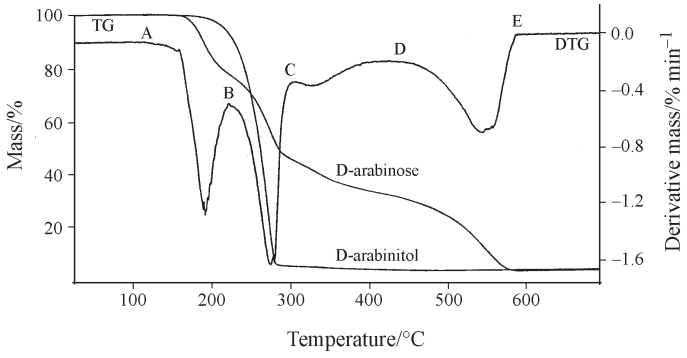

Fig. 1 The TG and DTG curves of *D*-arabinose and *D*-arabinitol measured in nitrogen

rated when heated to 580°C. The degradation information of the sugars investigated in this study is seen in Table 2. The information contains the temperatures and percentage mass losses of each stage, according to the measured DTG-curves.

Table 2 Mass losses and temperatures from TG and DTG curves (Fig. 1)

	D-arabinose	*DL*-arabinose	*D*-xylose	*DL*-xylose	*D*-mannose
			Air		
A/°C	118	147	148	138	117
B/°C	229	235	228	230	211
C/°C	303	307	297	297	296
D/°C	388	382	390	390	365
E/°C	518	548	531	539	519
			Mass loss/%		
AB	23.4	21.6	17.0	17.4	12.6
BC	31.1	36.3	34.2	27.8	35.8
CD	13.1	11.7	13.3	22.6	20.0
DE	32.3	30.5	35.5	32.3	31.6
			Nitrogen		
A/°C	116	142	144	137	117
B/°C	225	233	229	233	207
C/°C	307	313	306	308	308
D/°C	409	389	430	408	400
E/°C	594	585	638	599	581
			Mass loss/%		
AB	22.9	20.0	14.3	18.0	10.8
BC	33.4	39.0	30.5	31.6	45.6
CD	12.8	10.7	23.5	20.9	20.3
DE	30.9	30.3	31.8	29.5	23.3
			Fusion temperature [11]		
t onset/°C	150		143		120
t peak/°C	160		157		134

When comparing our values of T_i (degradation starting) with the melting values of T_o (onset) and T_p (peak) in literature, it is obvious that in the case of the sugars degradation begins before melting and it corresponds to water loss and fusion [11–13]. Ramos-Sanchez *et al.* have proposed that the first decomposition peak is a polymerization marker through glycosidic linkages [14]. When the water release of glycosidic condensation reaction is at its maximum, it is for pentopyranes 6% and for hexopyranes 5%. As seen in Table 2, the water release here is much greater than just

the condensation water. It is the great difference between the initial temperatures of the degradation and the extrapolated onset temperatures. The latter correspond to values in the literature.

Pyrolysis

The pyrolysis was done both at 500 and at 550°C in order to get more reliable information on degradation. The decomposition products of the pyrolysis of *D*-arabinose, *D*-mannose and *D*-arabinitol are listed in Table 3 and the total ion current (TIC) pyrograms of these same three compounds when pyrolyzed to 500°C are in Fig. 2. Most peaks of the chromatograms were managed to identify by comparing the mass spectra of the degradation products to the spectra of literature. The retention time and mass spectrum of 2-furancarboxaldehyde, furanmethanol, phenol and 3-methyl-1,2-cyclopentane-dione were confirmed by injecting the compounds directly to GC/MSD without pyrolysis. Re-

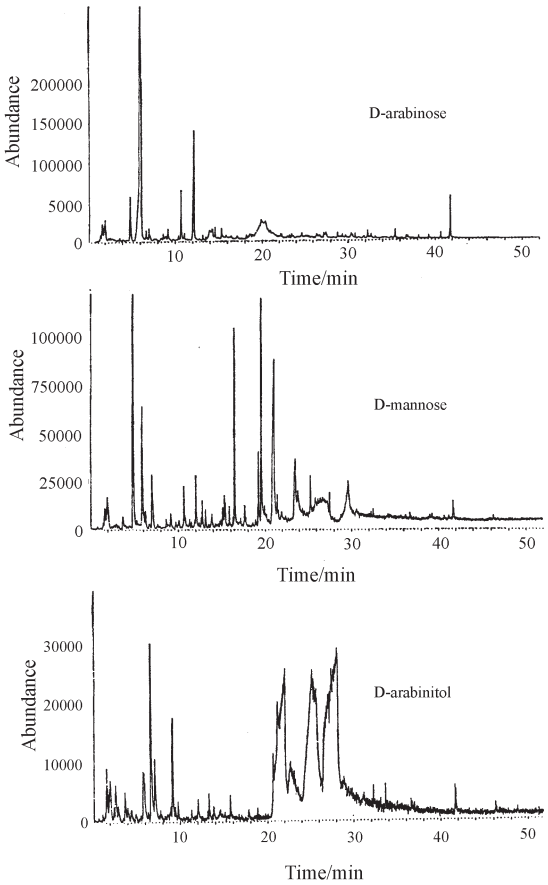

Fig. 2 The total ion current (TIC) pyrogram of a – *D*-arabinose, b – *D*-mannose and c – *D*-arabinitol pyrolyzed at 500°C

Table 3 Retention time and the main decomposition products of *D*-arabinose, *D*-mannose and *D*-arabinitole in pyrolysis from TIC by Py-GC/MSD at 500°C

Sample	Time/min	Molecular ion /me^{-1}	Decomposition product
D-arabinose	4.8	84	(2H)-furan-3-one
	5.9	96	2-furancarboxaldehyde
	6.6	98	furanmethanol
	8.6	110	1-(2-furanyl)-ethanone
	9.1	98	α-angelicalactone
	12.1	114	3-hydroxy-2-penteno-1,5-lactone
	13.1	112	3-methyl-1,2-cyclopentanedione
	15.3	126	methyl ester of furoic acid
	28.8	162	tricyclo[6.2.0.0(3,6)]dec-1(8)-en-2,7-dione
	41.7	256	hexadecanoic acid
D-mannose	4.8	84	(2H)-furan-3-one
	5.8	96	2-furancarboxaldehyde
	6.7	98	furanmethanol
	8.6	110	1-(2-furanyl)-ethanone
	9.2	98	α-angelicalactone (5-methyl-furan-2-one)
	10.6	110	5-methyl-2-furaldehyde
	11.5	94	phenol
	12.0	114	3-hydroxy-2-penteno-1,5-lactone
	13.1	112	3-methyl-1,2-cyclopentanedione
	15.3	126	methyl ester of 2-furoic acid
	16.5	126	3-hydroxy-2-methyl pyran-4-one
	19.2	142	3,5 dihydroxy-2-methyl (4H) pyran-4-one
	19.5	144	1,4:3,6-dianhydro-α-*D*-glucopyranose
	20.9	126	5-hydroxymethyl-2-furaldehyde
	23.5	144	1,4-dideoxy-*D*-glycero-hex-1-enopyranos-3-ulose
	29.5	162	1,6-anhydro-β-*D*-glucopyranose
	41.7	256	hexadecanoic acid
D-arabinitol	4.9	84	(2H)-furan-3-one
	5.9	96	2-furancarboxaldehyde
	6.7	98	furanmethanol
	9.1	98	α-angelicalacton
	12.0	114	3-hydroxy-2-penteno-1,5-lactone
	13.1	112	3-methyl-1,2-cyclopentanedione
	22.8	162	1,6-anhydro-β-*D*-glucopyranose
	41.7	256	hexadecanoic acid

tention times corresponded well with the retention times in pyrolysis. The degradation products were mainly got in the order of their molecular ion. The strongly polar compounds moved in a column slower than the nonpolar ones. A great peak of arabinoses and xyloses with retention time of 10.5 min was not managed to identify. The degradation compound of mannose in the same retention time was 5-hydroxy-2-furancarboxyaldehyde. However, the mass spectrum of this was different from the spectra of the unidentified degradation compounds of arabinoses and xyloses. CO_2 and H_2O were not determined because the mass range of MS was 45–300.

The decomposition products from the two temperatures of pyrolysis did not differ greatly. The main components of pyrolysis were the same in both temperatures but the intensity ratios of the peaks in the chromatograms were somewhat different. On the basis of the chromatograms the samples were divided into three groups: (*i*) *D*- and *DL*-arabinose and *D*- and *DL*-xylose (pentose), (*ii*) *D*-mannose (hexose) and (*iii*) *D*- and *DL*-arabinitol (sugar alcohol). The main peaks of pentoses, hexose and sugar alcohols in their chromatograms differed from each other. 2-furancarboxyaldehyde was the greatest peak of pentoses and (2H)-furan-3-one of mannose. The greatest peak of arabinitols changed when the temperature of pyrolysis was raised. Furanmethanol was the greatest peak at 500°C and α-angeligalacton at 550°C. The number of degradation compounds was greater in the case of mannose than others studied. The amount of lighter decomposition products of pentoses was greater than of mannose or arabitols. There were only a few pyrolysis products of the secondary reaction, which molecular mass were higher than the starting materials (hexadecanoic acid).

In each case, the main pyrolysis products were classified into the following compound groups: (*i*) furanes [(2H)-furan-3-one, 2-furancarboxaldehyde, furanmethanol, 1-(2-furanyl)-ethanone, α-angeligalactone, 5-hydroxymethyl-2-furaldehyde, methyl ester of 2-furoic acid and 5-hydroxymethyl-2-furaldehyde], (*ii*) pyranes [3-hydroxy-2-penteno-1,5-lactone, 3-hydroxy-2-methyl pyran-4-one, 3,5-dihydroxy-2-methyl (4H)pyran-4-one, 1,4-dideoxy-*D*-glycero-hex-1-enopyranos-3-ulose], (*iii*) cyclopentanes[3-methyl-1,2-cyclopentanedione,3-hydroxy-2-methyl-2-cyclopenten-1-one], (*iv*) cyclohexanes [phenol, tricyclo[6.2.0.0(3,6)]dec-1(8)-en-2,7-dione], (*v*) anhydroglucopyranoses [1,6-anhydro-β-*D*-glucopyranose (levoglucosan)], (*vi*) dianhydroglucopyranoses [1,4:3,6-dianhydro-α-*D*-glucopyranose] and (*vii*) saturated fatty acids [hexadecanoic acid].

5-hydroxymethyl-2-furaldehyde was found only in the pyrolysis products of d-mannose (hexose). According to Kaburaki *et al.* 5-hydroxymethyl-2-furaldehyde is not found in the pyrolysis of pentoses [15]. Ohnishi *et al.* did not found 3-hydroxy-2-penteno-1,5-lactone in the pyrolysis of *D*-xylose [16]. Their measurement was done in lower temperature than this study.

Conclusions

On the basis of TG, arabinoses, xyloses and mannose decomposed mainly similarly. However, their decomposition differed from the decomposition of arabinitol. For

arabinitol the residue in nitrogen atmosphere was carbon-rich char, which decomposed or volatilized up to a temperature 580°C.

The pyrolysis gave many same decomposition products for all of the samples. The pyrolysis of *D*- and *DL*-form of a compound differed only slightly. The pyrolysis chromatograms of arabinoses and xyloses were similar, only the peak intensities in chromatograms differed slightly from each other. Mannose gave a greater number of the decomposition products than the others. 5-hydroxymethyl-2-furancarboxaldehyde was found only in the pyrolysis of *D*-mannose (hexose). The intensity ratio of the decomposition peaks in the pyrolysis chromatograms changed from sample to sample, and arabinoses and xyloses gave lighter decomposition products than mannose and arabinitols.

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