

Flavor Components Generated from Inulin

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Inulin is a linear oligmer of 2→1-linked β -D-fructose ending in an α -D-glucose unit, as a nonreducing sugar. The objective of this study was to investigate the reactions between inulin and asparagine as well as those between inulin and diammonium hydrogen phosphate (an ammonia precursor) using model systems at 200 °C in water. The flavor components formed from these reactions were found to be similar to those obtained from the corresponding reactions with fructose. It is implied that inulin may chemically function as fructose under these conditions. Further experiments showed that inulin started to be depolymerized into fructose in aqueous solution at 150 °C. As a result, this study demonstrates that although inulin cannot directly react with nitrogen-containing compounds to participate in Maillard reactions, it can do so indirectly after it is depolymerized into fructose. These findings suggest that inulin may be used as a fructose precursor in wet food systems.

Keywords: *Inulin; fructose; asparagine; diammonium hydrogen phosphate; GC/MS*

INTRODUCTION

Inulin, a natural product, is an oligmer of 2→1-linked β -D-fructose ending in an α -D-glucose unit, as a nonreducing sugar. The preparation of inulin from dahlia was described in 1981 (Mitchell et al., 1981). Recently, several patents issued described the usage of inulin in foods including its use for chocolate preparation (Frip-piat et al., 1993), as a low-fat or fatfree food ingredient (Buliga et al., 1995; Hartigan et al., 1997), and as a soft drink material (Schweren and Heck, 1996). Also, it was claimed that inulin can be used to improve and to preserve the flavor of seasonings (Harada et al., 1992). However, in the literature, the flavor compounds thermally generated from inulin are not reported. The objective of this study was to investigate the role inulin plays in the reactions with amino acids as well as with ammonia. Specifically, asparagine was chosen as a representative amino acid, and diammonium hydrogen phosphate was chosen as an ammonia precursor. The results obtained from the reactions of inulin are compared with those from the corresponding reactions with fructose.

EXPERIMENTAL PROCEDURES

Material. Inulin, asparagine, fructose, and diammonium hydrogen phosphate (DAP) were purchased from Sigma Chemical Co. (St. Louis, MO).

Preparation of the Reaction Mixtures from Asparagine and Inulin or from Asparagine and Fructose. In an enclosed reaction vessel (Parr Instrument Co., Moline, IL), 13.2 g of asparagine (0.1 mol), 0.9 g of inulin or fructose (0.005 mol), and 100 mL of water were heated at 200 °C for 30 min; each reaction mixture obtained was cooled to room temperature and extracted with methylene chloride (40 mL \times 3). The extract was concentrated by a rotary evaporator and a stream of nitrogen to ~10 mL.

Preparation of the Reaction Mixtures from Inulin and Ammonia or from Fructose and Ammonia. DAP was used as an ammonia precursor to supply ammonia during the

reactions. Under the same conditions as described above, DAP (1.32 g, 0.01 mol) was used instead of asparagine to react with inulin or fructose.

GC/MS Analysis. The concentrated extracts were analyzed by GC/MS on a DB-Wax fused silica column (30 m \times 0.32 mm, 0.15 μ m film thickness) with a mass selective detector (EI; 70 eV). The oven temperature was programmed from 50 to 190 °C at 6 °C/min. The components identified were reported in area percentage.

Depolymerization of Inulin. One gram of inulin and 50 mL of water were heated in an enclosed vessel to specified temperatures (100, 150, and 200 °C) for 15 min. The reaction mixture obtained was analyzed according to a published HPLC method (Thean and Funderburk, 1977) for fructose content.

RESULTS AND DISCUSSION

Since carbohydrates are usually more readily decomposed than amino acids, the amount of asparagine used for the reactions was considerably higher than the amount of fructose or inulin used. The ratio of asparagine to fructose was established by the previous work, from which asparagine and fructose were individually treated under the same reaction conditions and the yields of the volatile components generated were estimated. As a result, the ratio of asparagine to fructose was determined to be 0.1 mol to 0.005 mol. Because inulin is a polymer, the amount of inulin was determined by weight to be the same amount of fructose, 0.9 g. The GC profiles obtained from the reactions of inulin/asparagine and of fructose/asparagine are very similar. The components identified from these reactions along with the percentage data are compiled in Table 1. These results show that both reactions generated very similar compounds including various pyrazines, pyrroles, maleimides, and pyrazinones. Of those compounds identified, the two 2(1*H*)-pyrazinones have already been reported as asparagine-specific Maillard products (Shu and Lawrence, 1995) and the formation of the two maleimides appears to originate from asparagine alone (Wilken and Baltes, 1990).

The amount of DAP needed for these reactions was also determined from the previous work. It was found

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Table 1. Components Identified from the Reaction of Inulin/Asparagine (Inu/Asn) and the Reaction of Fructose/Asparagine (Fru/Asn)

component identified	from Inu/Asn, area %	from Fru/Asn, area %
pyrazine	0.52	0.60
methylpyrazine	8.90	9.02
2,5-dimethylpyrazine	13.27	13.73
2,6-dimethylpyrazine	17.00	17.72
cyclopentenone	0.53	0.54
6-methyl-2-ethylpyrazine	2.34	2.05
5-methyl-2-ethylpyrazine	1.70	1.59
trimethylpyrazine	4.11	3.66
2-methyl-5-ethylpyridine	1.35	1.09
3,6-dimethyl-2-ethylpyrazine	7.56	6.03
3,5-dimethyl-2-ethylpyrazine	1.00	0.76
2-methyl-6-vinylpyrazine	0.37	0.36
5-methyl-2,3-diethylpyrazine	0.87	0.66
pyrrole	0.32	0.29
6-methyl-2,3-diethylpyrazine	0.72	0.71
5-methyl-2-formylpyrrole	1.22	1.96
2-acetyl-5-methylpyrrole	0.52	0.59
2-(2-hydroxyethyl)-6-methylpyrazine	0.55	0.65
2,3-dimethylmaleimide	15.58	18.20
2-methyl-3-ethylmaleimide	0.54	0.42
3,6-dimethyl-5-ethyl-2(1 <i>H</i>)-pyrazinone	15.34	14.28
3-methyl-5,6-diethyl-2(1 <i>H</i>)-pyrazinone	3.23	3.30

Table 2. Components Identified from the Reaction of Inulin/DAP and the Reaction of Fructose/DAP

component identified	from Inu/DAP, area %	from Fru/DAP, area %
pyrazine	5.98	8.17
methylpyrazine	41.44	56.05
acetoin	0.61	0.50
acetol	8.16	5.91
2,5-dimethylpyrazine	10.12	3.71
2,6-dimethylpyrazine	13.53	9.46
2-ethylpyrazine	1.47	2.08
2,3-dimethylpyrazine	1.43	1.15
6-methyl-2-ethylpyrazine	0.69	0.68
5-methyl-2-ethylpyrazine	0.25	0.50
trimethylpyrazine	1.81	0.87
vinylpyrazine	trace	0.54
3,6-dimethyl-2-ethylpyrazine	0.25	trace
2-methyl-6-vinylpyrazine	trace	trace
pyrrole	0.69	0.44
acetylpyrrole	0.42	0.54
furfuryl alcohol	0.94	1.13
2-formylpyrrole	0.36	trace
Furaneol	0.46	0.55
2-(hydroxymethyl)-5-methylpyrazine	0.83	3.01
5-methyl-2-formylpyrrole	0.43	0.96
2-(2-hydroxyethyl)-6-methylpyrazine	0.28	0.58
2-acetyl-4-methylimidazole	2.68	0.58

that DAP supplied a substantially higher amount of ammonia than asparagine, so that DAP chosen was 0.01 mol and asparagine chosen was 0.1 mol. The GC profiles obtained from the reactions of inulin/DAP and fructose/DAP are also similar. The components identified from these reactions are compiled in Table 2. These results show that both reactions generated similar compounds. It is interesting to note that Furaneol, a valuable flavor compound, was found in both reactions.

Table 3. Fructose Contents after Inulin Was Heated in Water at Different Temperatures

temp, °C	% of original wt	temp, °C	% of original wt
20	0	150	40
100	0	200	41

It should be noted that the similarity between the two sets of data in Table 1 as well as in Table 2 was more qualitative than quantitative.

Consideration of the above data implies that in water medium under relatively high temperature inulin functions chemically as fructose. As a result, inulin is expected to follow the well-known Maillard and Strecker pathways to generate flavor compounds. To confirm this proposal, depolymerization of inulin was investigated by heating inulin in water at different temperatures, and the contents of fructose formed were measured by HPLC as shown in Table 3. From these data, it was found that inulin started to be depolymerized at 150 °C into fructose at 40% of the original weight of inulin.

This study clearly demonstrated that although inulin cannot directly react with nitrogen compounds to participate in Maillard reactions, it can do so indirectly after it is depolymerized into fructose. Also, this study suggests that inulin can be used as a fructose precursor in wet food systems.

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