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RESEARCH ARTICLE

Comparison of Volatile Maillard Reaction Products from Tagatose and Other Reducing Sugars with Amino Acids

In Hee Cho, Sarah Lee, Hae-Roung Jun, Hoe-Jin Roh, and Young-Suk Kim

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Abstract In this study, in order to investigate the effects of tagatose on the Maillard reaction, volatile Maillard reaction products (V-MRPs) produced from aqueous model systems containing various reducing sugars (glucose, galactose, fructose, and tagatose) and amino acids (glycine, valine, leucine, asparagine, and cysteine) were analyzed and then compared. Furans, furan derivatives, pyrazines, and some sulfur-containing heterocyclic compounds, such as thiazoles, thiophenes, and thiols, were mainly identified. The amounts of furans and furan derivatives were higher in the model systems of ketoses (fructose or tagatose) with amino acids than those of aldoses (glucose or galactose) with amino acids. In particular, 2-acetylfuran was detected 2-20 times more in the V-MRPs of tagatose as compared to those produced from the other reducing sugars. Also, 2-acetylpyrrole, one of nitrogen-containing heterocyclic compounds, was more abundant from the thermal reactions of tagatose-glycine and tagatose-valine compared to those of other reducing sugars-amino acids. More 2-acetylthiazole and thiophenes were found in tagatose-cysteine model system than in those of glucose with cysteine.

Keywords: D-tagatose, Maillard reaction, volatile Maillard reaction product (V-MRP), reducing sugar, amino acid

Introduction

D-Tagatose is a ketohexose, an epimer of D-fructose isomerized at C-4 position. It was identified in gum exudates of cacao tree (*Sterculia setigera*) (1) and also found as a component of an oligosaccharide in lichens of *Rocella* species (2). In addition, in the bacterial metabolism of lactose, it may be formed by enzymatic isomerization catalyzed by L-arabinose isomerase under alkaline conditions in the presence of calcium (3). This monosaccharide, which is a virtually odorless, white or almost white, and non-hygroscopic crystal, has almost the same sweetness as sucrose but less than half the calorie of sucrose (4). Since it is relatively stable in foods, to which it is added, during processing and storage, it can be used as various food additives such as sweetener, texturizer, stabilizer, and humectant. It is also useful in formulating dietetic foods with a low glycemic index (5,6).

Maillard reaction, also called as a non-enzymatic browning reaction, includes the reactions of amino acids, amines, peptides, and proteins with aldehydes, ketones, and reducing sugars (7). Since most foods have sugars and amino acids as well as other precursors, Maillard-type reaction can easily occur during processing and storage of foods (8). Maillard reaction in foods has been associated with development of taste and odor attributes as well as dark brown colors. Some changes that take place by the Maillard reaction can improve palatability and consumer acceptance as in roasting of coffee or meat and baking of bread (9).

Maillard reaction is influenced by many factors, such as temperature, pH, water activity, and reactants types and concentrations (10,11). In particular, sugar type is well known as a major factor regulating the reaction rates and pathways in Maillard reaction (12-19). Fructose showed a higher reactivity for the formation of 5-hydroxymethyl-2-furaldehyde compared to glucose and sucrose (16,17). On the other hand, in the case of 2-acetylfuran generation, the reactivity of sugars decreased in the order ribose, fructose,

In Hee Cho, Sarah Lee, Hae-Roung Jun, Young-Suk Kim (✉)
Department of Food Science and Technology, Ewha Womans University, Seoul 120-750, Korea
Tel: + 82-2-3277-3091; Fax: + 82-2-3277-4213
E-mail: yskim10@ewha.ac.kr

Hoe-Jin Roh
R&D Center, Orion Confectionery, Seoul 140-715, Korea

glucose, rhamnose, and sucrose (18,19). In general, the activity of Maillard reaction is influenced by sugar types as follows: pentoses (xylose or arabinose)>hexoses (glucose or fructose)>disaccharides (lactose or maltose)>trisaccharide >corn syrup solid>maltodextrin>starch (20). Yaylayan (21) suggested that either Amadori or Heyns products could be formed from initial condensation reaction between amino acid and reducing sugar, depending on whether the reducing sugar is aldose or ketose. They also explained that the α-hydroxy carbonyl group of Amadori compounds was more reactive than the aldehyde group of Heyns products. Also, the key odorants and sensory profiles according to reducing sugars and amino acids have been studied in the model systems of thermal reactions (22-24). Roasted and popcorn-like odor notes were more intense in the model system of hexose with amino acid model system, whereas pentose from the reaction of amino acid showed more seasoning-like and caramel-like odor notes (24).

Although D-tagatose, which has reducing group in its structure, can be a carbon source for the Maillard reaction, limited studies has been conducted on the interaction between D-tagatose and protein/or amino acids, mainly focused on the kinetics of browning (25,26). The aim of present study was to compare volatile Maillard reaction products (V-MRPs) from the thermal interactions between various reducing sugars (glucose, galactose, fructose, and tagatose) and amino acids (glycine, valine, leucine, asparagine, and cysteine) in order to compare the effects of tagatose in Maillard reaction with other reducing sugars.

Materials and Methods

Chemicals D-Tagatose was supplied by Arial Foods Ingredients Amba (Skanderborgvej, Denmark) Other sugars (D-glucose, D-galatose, and D-fructose), amino acids (glycine, L-valine, L-leucine, L-asparagine, and L-cysteine), and an internal standard compound (satonin) were all purchased from Sigma-Aldrich (St. Louis, MO, USA).

Thermal reaction Each 0.0625 mol of sugar (D-glucose, D-galatose, D-fructose, or D-tagatose) and 0.0125 mol of amino acid (glycine, L-valine, L-leucine, L-asparagine, or L-cysteine) were dissolved in 100 mL of distilled water, respectively, and transferred to a stainless cylinder, before reacted at 180°C in a drying oven (Eyela NDO-600SD,

Table 1. Volatile Maillard reaction products formed from thermal interactions of glycine with glucose, galactose, fructose, and tagatose

RI[1)]	Possible compound	Relative peak area (%)				ID[2)]
		Glu-Gly	Gal-Gly	Fru-Gly	Tag-Gly	
	Furans &Furan derivatives					
804	2-Methyl-tetrahydro-furan-3-one	ND	ND	0.03±0.00	0.04±0.02	MS/RI
831	Furfural	0.24±0.03[3)]	0.28±0.11	0.66±0.12	1.40±0.53	MS/RI
854	2-Furanmethanol	ND	0.01±0.00	0.01±0.01	0.03±0.02	MS/RI
908	2-Acetylfuran	0.01±0.00	0.05±0.01	0.30±0.06	0.90±0.40	MS/RI
960	5-Methylfurfural	0.02±0.01	0.02±0.00	0.03±0.00	0.09±0.01	MS/RI
1,027	2-Hydroxy-3-methyl-2-cyclopenten-1-one	trace	0.02±0.01	0.02±0.00	0.04±0.01	MS/RI
1,248	5-(Hydroxymethyl)-2-furancarboxaldehyde	0.63±0.33	0.46±0.16	1.82±1.70	8.80±3.80	MS/RI
1,312	5-Acetyl-2-furanmethanol	0.02±0.01	ND	0.01±0.01	0.02±0.01	MS/RI
	Other *O*-containing heterocyclic compounds					
1,110	3-Hydroxy-2-methyl-4H-pyran-4-one	0.01±0.00	0.01±0.00	ND	0.02±0.01	MS/RI
1,147	2,3-Dihydro-3,5-dihydoxy-6-methyl-4H-pyran-4-one	ND	ND	0.02±0.00	0.04±0.00	MS/RI
	Pyrazines					
725	Pyrazine	0.01±0.01	0.02±0.01	ND	ND	MS/RI
820	2-Methylpyrazine	0.01±0.00	0.02±0.00	0.02±0.00	0.02±0.01	MS/RI
915	2,3-Dimethylpyrazine	ND	ND	0.01±0.00	0.01±0.01	MS/RI
1,000	Trimethylpyrazine	ND	ND	0.10±0.01	0.02±0.00	MS/RI
	Other *N*-containing heterocyclic compounds					
1,028	2-Acetylpyridine	0.01±0.00	ND	0.01±0.01	0.05±0.01	MS/RI
1,067	2-Acetylpyrrole	0.01±0.00	0.01±0.01	0.03±0.01	0.05±0.02	MS/RI
1,165	2-Acetyl-1-methylpyrrole	ND	ND	0.01±0.01	0.03±0.01	MS/RI

[1)]Retention indices were determined using *n*-paraffins C_7-C_{22} as external references.
[2)]Tentative identification was performed as follows: MS/RI, mass spectrum was identical with that of Wiley mass spectral database (1995, Hewlett Packard Co.), and retention index was consistent with that of the literatures (15-17); MS, mass spectrum was consistent with that of Wiley mass spectrum database.
[3)]Mean±SD (*n*=3); ND, not detected

Rikakikai Co., Ltd., Tokyo, Japan) for 100 min.

Extraction of V-MRPs produced from thermal reaction A 500 mL of the reacted sample was directly extracted with 50 mL of dichloromethane, stirring at 400 rpm for 20 min, after adding 0.4 mL of 1,000 ppm satonin (w/v in dichloromethane) as an internal standard. The obtained solvent layer was filtered through anhydrous sodium sulfate to remove any residual water and then concentrated to a final volume of 0.1 mL using a gentle stream of nitrogen gas. All sample preparations were performed in triplicate.

Gas chromatography (GC) analysis GC analysis was conducted on a DB-5 column (30 m length×0.25 mm i.d.× 0.25 μm film thickness, J&W Scientific, Folsom, CA, USA) using a Varian CP-3800 GC (Varian, Walnut Creek, CA, USA) equipped with flame ionization detector (FID). The carrier gas was helium at a constant flow rate of 0.8 mL/min. One μL of the extract was injected into the capillary column with a split ratio of 1:20. The oven temperature was held at 40°C for 1 min, raised to 150°C at 5°C/min and to 250°C at 13°C/min, and then held at 250°C for 15 min. The injector and detector temperatures were 230 and 250°C, respectively.

GC-mass spectrometry (MS) analysis GC-MS analysis was performed using an HP 6890A series GC-5972 mass selective detector (MSD) (Hewlett-Packard, Palo Alto, CA, USA) equipped with a DB-5MS column (30 m length× 0.25 mm i.d.×0.25 μm film thickness, J&W Scientific). The carrier gas was helium at a constant flow rate of 0.8 mL/min. One μL of the extract was injected with a split ratio of 1:10. The oven temperature was held at 40°C for 4 min, raised to 250°C at 5°C/min, and then held at 250°C for 5 min. The injector and detector temperatures were 250 and 280°C, respectively. The mass detector was operated in the electron impact mode with an ionization energy of 70

Table 2. Volatile Maillard reaction products formed from thermal interactions of valine with glucose, galactose, fructose, and tagatose

RI[1)]	Possible compound	Relative peak area (%)				ID[2)]
		Glu-Val	Gal-Val	Fru-Val	Tag-Val	
	Furans &Furan derivatives					
804	2-Methyl-tetrahydro-furan-3-one	ND	ND	0.09±0.03	0.07±0.01	MS/RI
834	Furfural	0.50±0.08[3)]	0.58±0.33	1.02±0.19	1.65±0.10	MS/RI
860	2-Furanmethanol	0.06±0.01	0.02±0.01	0.04±0.01	0.04±0.02	MS/RI
910	2-Acetylfuran	ND	0.21±0.06	ND	0.13±0.26	MS/RI
961	5-Methylfurfural	0.08±0.01	0.08±0.02	0.10±0.04	0.14±0.04	MS/RI
1,244	5-(Hydroxymethyl)-2-furancarboxaldehyde	0.98±0.31	1.23±0.30	2.72±1.40	3.25±1.77	MS/RI
1,312	5-Acetyl-2-furanmethanol	0.02±0.00	0.04±0.02	ND	0.09±0.01	MS/RI
	Other *O*-containing heterocyclic compounds					
1,030	2-Hydroxy-3-methyl-2-cyclopenten-1-one	0.11±0.04	0.12±0.03	0.10±0.04	0.09±0.04	MS/RI
1,149	2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	ND	ND	ND	0.03±0.01	MS/RI
	Pyrazines					
725	Pyrazine	0.05±0.01	0.18±0.10	ND	ND	MS/RI
820	2-Methylpyrazine	0.21±0.07	0.12±0.07	0.26±0.07	0.13±0.02	MS/RI
910	2,5-Dimethylpyrazine	0.19±0.07	ND	2.43±0.57	ND	MS/RI
912	Ethylpyrazine	0.05±0.01	0.13±0.10	ND	ND	MS/RI
917	2,3-Dimethylpyrazine	0.04±0.01	ND	ND	0.03±0.01	MS/RI
925	2-Vinylpyrazine	0.03±0.01	0.04±0.01	ND	ND	MS/RI
997	2-Ethyl-5-methylpyrazine	0.02±0.01	0.04±0.01	0.17±0.01	ND	MS/RI
1,000	Trimethylpyrazine	0.06±0.02	ND	0.17±0.02	0.04±0.02	MS/RI
1,062	2-Methylpropylpyrazine	ND	0.04±0.01	ND	ND	MS/RI
1,309	2-(2-Methylpropyl)-2,6-dimethylpyrazine	ND	ND	0.02±0.01	ND	MS/RI
	Other *N*-containing heterocyclic compounds					
1,069	2-Acetylpyrrole	ND	0.04±0.01	0.02±0.01	0.06±0.02	MS/RI
1,175	2-Acetyl-1-methylpyrrole	ND	ND	0.01±0.00	ND	MS/RI

[1)]Retention indices were determined using *n*-paraffins C_7-C_{22} as external references.
[2)]Tentative identification was performed as follows: MS/RI, mass spectrum was identical with that of Wiley mass spectral database (1995, Hewlett Packard Co.), and retention index was consistent with that of the literatures (15-17); MS, mass spectrum was consistent with that of Wiley mass spectrum database.
[3)]Mean±SD (*n*=3); ND, not detected

eV and a scanning range of 33-550 a.m.u.

Identification and quantification of V-MRPs Identification of volatile compounds was tentatively made on the comparison of their mass spectra with those of on-computer library (Wiley 275I, 1995; Hewlett-Packard) or manual interpretation. In addition, linear retention indices (RI) of each compounds, determined using *n*-paraffins C_7-C_{22} as external references (27), were compared with those in the published literatures (28-30). The quantification of volatile compounds was obtained by comparing the peak area of each volatile compound with that of an internal standard (satonin) in GC-MS total ion chromatogram.

Results and Discussion

To investigate the effects of tagatose in the Maillard reaction, V-MRPs formed from the thermal interactions of various reducing sugars (glucose, galactose, fructose, and tagatose) and amino acids (glycine, valine, leucine, asparagine, and cysteine) were determined and compared. Table 1-5 list the V-MRPs identified in various model systems with their relative peak areas and RIs on the DB-5MS column, respectively. The most abundant volatile compounds formed via the Maillard reaction were mainly aliphatic aldehydes, ketones, diketones, and shorter organic acids. However, it is well known that heterocyclic compounds containing oxygen, nitrogen, sulfur, or combinations of these atoms can contribute much more significantly to the odor characteristics of thermally processed foods (31). In this study, furans, furan derivatives, pyrazines, and some sulfur-containing heterocyclic compounds were identified as V-MRPs. In particular, furfural, 2-acetyl furan, 5-methyl furfural, pyrazine, 2-methylpyrazine, 2,3-dimethylpyrazine, and trimethylpyrazine were found in all model systems studied.

Comparison of oxygen-containing heterocyclic compounds in various model systems Oxygen-containing heterocyclic compounds, including furans and furan derivatives, could be formed via degradation and cyclization of Amadori compounds and Heyns products in the Maillard reaction (20). Amadori compounds and Heyn's products could be produced by various reactions, such as enolization, migration of carbonyl group, oxidation of the carbonyl group, and

Table 3. Volatile Maillard reaction products formed from thermal interactions of leucine with glucose, galactose, fructose, and tagatose

RI[1)]	Possible compound	Relative peak area (%)				ID[2)]
		Glu-Leu	Gal-Leu	Fru-Leu	Tag-Leu	
	Furans &Furan derivatives					
806	2-Methyl-tetrahydro-furan-3-one	ND	ND	0.06±0.02	0.03±0.04	MS/RI
832	Furfural	0.17±0.03[3)]	0.19±0.06	0.64±0.15	1.18±0.60	MS/RI
863	2-Furanmethanol	0.07±0.01	0.08±0.01	0.05±0.02	0.12±0..05	MS/RI
910	2-Acetylfuran	ND	0.10±0.03	ND	1.90±1.40	MS/RI
960	5-Methylfurfural	0.05±0.01	0.11±0.03	0.08±0.06	0.12±0.04	MS/RI
	Other *O*-containing heterocyclic compounds					
740	3-Methyl-pentan-2-one	ND	ND	ND	0.05±0.03	MS/RI
1,035	2-Hydroxy-3-methyl-2-cyclopenten-1-one	trace	ND	0.09±0.04	0.06±0.07	MS/RI
	Pyrazines					
725	Pyrazine	0.12±0.03	0.24±0.08	0.02±0.01	ND	MS/RI
821	2-Methylpyrazine	0.18±0.08	0.12±0.06	0.34±0.07	0.22±0.10	MS/RI
908	2,5-Dimethylpyrazine	0.19±0.10	ND	3.17±0.84	ND	MS/RI
913	Ethylpyrazine	0.04±0.01	0.06±0.02	ND	ND	MS/RI
920	2,3-Dimethylpyrazine	0.01±0.01	0.03±0.01	ND	ND	MS/RI
927	2-Vinylpyrazine	0.03±0.01	0.02±0.01	ND	ND	MS/RI
1,005	Trimethylpyrazine	0.06±0.04	ND	0.01±0.01	0.03±0.01	MS/RI
1,319	2-(2-Methylpropyl)-2,6-dimethylpyrazine	0.08±0.01	ND	0.32±0.17	ND	MS/RI
1,070	2-Acetylpyrrole	0.02±0.01	trace	0.05±0.01	ND	MS/RI
1,087	2-Acetylpyridine	ND	ND	0.43±0.12	ND	MS/RI
1,177	2-Acetyl-1-methylpyrrole	ND	ND	0.02±0.01	ND	MS/RI

[1)]Retention indices were determined using *n* -paraffins C_7-C_{22} as external references.
[2)]Tentative identification was performed as follows: MS/RI, mass spectrum was identical with that of Wiley mass spectral database (1995, Hewlett Packard Co.), and retention index was consistent with that of the literatures (15-17); MS, mass spectrum was consistent with that of Wiley mass spectrum database.
[3)]Mean (*n*=3)±SD; ND, not detected

Table 4. Volatile Maillard reaction products formed from thermal interactions of asparagine with glucose, galactose, fructose, and tagatose

RI[1)]	Possible compound	Relative peak area (%)				ID[2)]
		Glu-Asp	Gal-Asp	Fru-Asp	Tag-Asp	
	Furans &Furan derivatives					
806	2-Methyl-tetrahydro-furan-3-one	ND	ND	0.07±0.16	0.10±0.04	MS/RI
834	Furfural	0.23±0.04[3)]	0.30±0.18	0.62±0.04	1.23±0.46	MS/RI
854	2-Furanmethanol	0.05±0.01	0.05±0.01	0.09±0.04	0.21±0.02	MS/RI
913	2-Acetylfuran	ND	ND	ND	0.94±0.26	MS/RI
938	5-Methyl-2(5*H*)-furanone	ND	ND	ND	0.03±0.02	MS/RI
962	5-Methylfurfural	ND	0.05±0.03	0.08±0.03	ND	MS/RI
1,243	5-(Hydroxymethyl)-2-furancarboxaldehyde	0.42±0.12	0.51±0.27	1.63±0.50	6.57±3.88	MS/RI
	Other *O*-containing heterocyclic compounds					
1,027	2-Hydroxy-3-methyl-2-cyclopenten-1-one	0.04±0.01	ND	ND	ND	MS/RI
	Pyrazines					
725	Pyrazine	0.50±0.08	1.17±0.31	0.03±0.02	0.05±0.01	MS/RI
820	2-Methylpyrazine	0.53±0.14	0.27±0.10	0.52±0.16	0.30±0.08	MS/RI
910	2,5-Dimethyl pyrazine	ND	ND	1.37±0.45	ND	MS/RI
912	Ethylpyrazine	0.13±0.05	0.13±0.03	ND	ND	MS/RI
917	2,3-Dimethylpyrazine	0.06±0.02	0.06±0.02	0.01±0.03	0.02±0.01	MS/RI
925	2-Vinylpyrazine	0.04±0.02	0.04±0.02	ND	0.05±0.05	MS/RI
993	2-Ethyl-3-methylpyrazine	ND	ND	ND	0.02±0.00	MS/RI
995	2-Ethyl-6-methylpyrazine	ND	ND	0.02±0.01	0.03±0.01	MS/RI
1,000	Trimethylpyrazine	ND	ND	0.08±0.02	0.02±0.00	MS/RI
	Other *N*-containing heterocyclic compounds					
1,032	2-Acetylpyridine	ND	ND	ND	0.12±0.05	MS/RI
1,064	2-Acetylpyrrole	ND	0.02±0.01	ND	ND	MS/RI
1,110	2-Acetyl-6-methylpyridine	ND	ND	0.05±0.02	ND	MS/RI

[1)]Retention indices were determined using *n*-paraffins C_7-C_{22} as external references.
[2)]Tentative identification was performed as follows: MS/RI, mass spectrum was identical with that of Wiley mass spectral database (1995, Hewlett Packard Co.), and retention index was consistent with that of the literatures (15-17); MS, mass spectrum was consistent with that of Wiley mass spectrum database.
[3)]Mean±SD (*n*=3); ND, Not detected

retro-aldol cleavage of C-C bonds (9). According to Yaylayan's study (21), the reaction rate for the formation of Amadori compounds and Heyns products depends on whether the reducing sugar is aldose or ketose. It was also demonstrated that reaction activity of aldose was higher than that of ketose. In our study, more furans and furan derivatives were formed from the thermal reactions of fructose and tagatose, ketoses, with amino acids compared to those in the case of glucose and galactose, aldoses, with amino acids. Those furan-type compounds usually have sweet, fruity, nutty, and caramel-like odor notes (20) and can be used in various food systems. In particular, 2-acetylfuran was detected 2-20 times more in the V-MRPs of tagatose as compared to those produced from other reducing sugars. It has strong sweet balsamic-cinnamic odor note and been found in processed foods (32-34). However, its formation mechanism has not been clearly shown, although it was determined to be one of major odor compounds in model system study such as serine/threonine/glutamine with ribose/glucose/fructose (15). According to Wang *et al.* (19), the reactivity of sugars in the formation of 2-acetylfuran decreased in order of ribose >fructose>glucose>rhamnose>sucrose.

Comparison of nitrogen-containing heterocyclic compounds in various model systems Various pyrazines, pyrroles, and pyridines were identified as nitrogen-containing V-MRPs in this study. More than 100 different pyrazines have been identified in various thermally processed foods (20). In general, pyrazines, which possess roasted, toasted, nutty, coffee-like, or cocoa-like odor notes, are the most abundant heterocyclic compounds among V-MRPs (35). The formation of pyrazines has been known to occur through the condensation of α-amino ketones, produced by the Strecker degradation of amino acids, with reducing sugars. Also, these compounds can be formed when sugar or sugar degradation products are heated with amino acids (9). In this study, the amounts of some pyrazines, such as pyrazine, 2,5-dimethylpyrazine, ethylpyrazine, 2-vinylpyrazine, 2-ethyl-5-methylpyrazine,

Table 5. Volatile Maillard reaction products formed from thermal interactions of cysteine with glucose, galactose, fructose, and tagatose

RI[1)]	Possible compound	Relative peak area (%)				ID[2)]
		Glu-Cys	Gal-Cys	Fru-Cys	Tag-Cys	
	Furans &Furan derivatives					
832	Furfural	0.10±0.07[3)]	0.07±0.01	0.34±0.17	0.80±0.17	MS/RI
858	Furfurylalcohol	ND	0.02±0.02	ND	ND	MS/RI
862	2-Furamethanol	ND	ND	0.02±0.007	0.10±0.04	MS/RI
915	2-Acetylfuran	0.09±0.04	0.10±0.00	0.39±0.07	1.60±0.30	MS/RI
963	5-Methylfurfural	0.24±0.11	0.16±0.04	0.53±0.08	0.60±0.10	MS/RI
1,233	5-(Hydroxymethyl)-2-furancarboxaldehyde	0.60±0.23	ND	2.78±1.18	6.50±0.45	MS/RI
	Pyrazines					
820	2-Methylpyrazine	ND	ND	0.01±0.00	ND	MS/RI
	***S*-containing heterocyclic compounds**					
726	Thiazole	0.05±0.03	0.04±0.00	0.02±0.02	0.07±0.02	MS/RI
766	2-Methylthiophene	ND	0.01±0.00	0.02±0.02	0.03±0.01	MS/RI
805	2-Methylthiazole	ND	0.01±0.00	0.01±0.00	ND	MS/RI
810	4-Methylthiazole	ND	ND	0.01±0.01	ND	MS/RI
970	3-Thiophenethiol	0.08±0.02	0.11±0.04	0.06±0.03	ND	MS/RI
983	Dihydro-2-methyl-3(2H)-thiophene	ND	ND	0.03±0.01	0.05±0.01	MS/RI
998	2-Formylthiophene	0.10±0.04	ND	0.11±0.05	0.17±0.05	MS/RI
1,016	2-Acetylthiazole	0.14±0.10	0.14±0.06	0.28±0.03	0.06±0.02	MS/RI
1,030	2-Thiophenemethanol	0.03±0.01	0.02±0.01	ND	0.10±0.04	MS/RI
1,056	2-Methy-3-thiophenethiol	0.02±0.01	ND	0.02±0.01		MS/RI
1,117	2-Formyl-5-methylthiophene	0.02±0.00	0.08±0.01	0.07±0.01	0.05±0.01	MS/RI

[1)]Retention indices were determined using *n*-paraffins C_7-C_{22} as external references.
[2)]Tentative identification was performed as follows: MS/RI, mass spectrum was identical with that of Wiley mass spectral database (1995, Hewlett Packard Co.), and retention index was consistent with that of the literatures (15-17); MS, mass spectrum was consistent with that of Wiley mass spectrum database.
[3)]Mean±SD (*n*=3); ND, not detected

2-methylpropylpyrazine, and 2-(2-methylpropyl)-2,6-dimethylpyrazine, were smaller in the thermal interactions of tagatose and amino acids compared to those of other reducing sugars and amino acids. On the other hand, 2-acetylpyrrole, one of the most abundant and widely occurring pyrroles in foods (36), was found in our model systems. In particular, it was more abundant from the thermal reactions of tagatose-glycine and tagatose-valine compared to those of other reducing sugars-amino acids. The formation mechanism for 2-acetylpyrrole was proposed to be from proline and hydroxyproline via the Strecker degradation (37,38). Alternatively, sugars with more than 5 carbons could be precursors for 2-acetylpyrrole in the absence of proline and hydroxyproline (39).

Comparison of sulfur-containing heterocyclic compounds in various model systems Sulfur-containing V-MRPs, such as thiazoles, thiophenes, and thiols formed in the thermal reaction of cysteine with reducing sugars are shown in Table 5. In particular, the amount of 2-acethylthiazole was twice higher in the V-MRP of fructose with cysteine compared to glucose with cysteine, whereas being twice lower in the V-MRP of tagatose with cysteine than in that of galactose with cysteine. On the other hand, more thiophenes were found in the V-MRP of fructose and tagatose with cysteine than in those of glucose and galactose with cysteine. These sulfur-containing compounds could be formed via the reaction of sulfur-containing amino acids with intermediated of the Maillard reaction (40). In general, thiazoles have low odor thresholds and, therefore, is likely to contribute, to a large extent, to the overall nutty, roasted, coffee-like odor notes of processed foods. In particular, 2-acetylthiazole is well-known to have nutty, cereal, and popcorn odor, which is one of the most important sensory properties in the thermal reaction products (36).

In summary, as shown in Fig. 1, the total peak areas of furans and furan derivatives, nitrogen-containing heterocyclic compounds, and sulfur-containing heterocyclic compounds in model systems were studied. More furans and furan derivatives, exhibiting sweet, fruity, and caramel-like odor notes, were formed from the thermal reactions of tagatose with amino acids compared to other model systems. However, the amounts of nitrogen-containing heterocyclic compounds, such as pyrazine, 2,5-dimethylpyrazine, ethylpyrazine, 2-vinylpyrazine, 2-ethyl-5-methylpyrazine, 2-methylpropylpyrazine, and 2-(2-methylpropyl)-2,6-

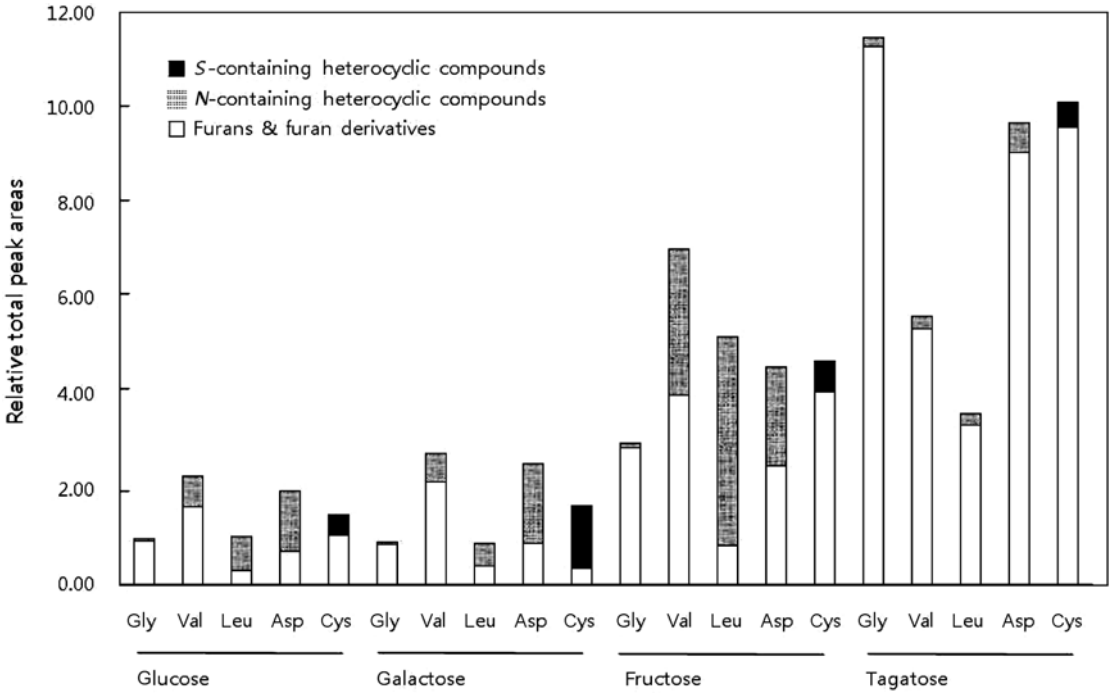

Fig. 1. Volatile Maillard reaction products identified in model systems.

dimethylpyrazine, were smaller in the thermal interactions of tagatose and amino acids. Also, although larger amounts of sulfur-containing heterocyclic compounds were found in the thermal reaction of galactose, an epimer of D-glucose, and cysteine than in that of glucose and cysteine, in the case of tagatose, an epimer of D-fructose, and cysteine, smaller amounts of sulfur-containing heterocyclic compounds were found compared to that of fructose and cysteine. On the base of results obtained above, it is expected that tagatose can affect diverse properties, including odor attribute, of foods via Maillard-type reaction, as differently as other reducing sugars such as glucose, galactose, and fructose, when used as food component.

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