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Note

Influence of the amine moiety on the thermal degradation of *N*-substituted 1-amino-1-deoxyfructoses

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Amadori compounds (1-amino-1-deoxyketoses) are intermediates in the sequence of reactions between aldoses and amines that leads to the formation of brown pigments[1]. Studies on the pyrolysis of Amadori compounds indicate that they are also precursors of many organoleptically important volatiles formed when such biological materials as food and tobacco are heated[2–5]. Evidence suggests that degradation through 1,2-enolisation is the main pathway to brown colour, whereas 2,3-enolisation is more important in flavour production[6,7].

It has been proposed that the basicity of the amino moiety influences the pathway by which Amadori compounds undergo degradation. For example, according to this hypothesis, the relative amounts of 1,2 and 2,3-enolisation[8] occurring during pyrolysis depend on the basicity of the amino substituent. Furthermore, 1-deoxy-1-piperidino-D-fructose, an Amadori compound having a strongly basic amino moiety, may undergo degradation via a modified 2,3-enolisation pathway. This leads to the formation of aminated reductone fragmentation-products[7]. In the present study, a range of Amadori compounds was pyrolysed to investigate further the influence of the amino substituent on Maillard degradation. The quantities of pyrolysate fractions were measured and the volatile organic products subjected to gas chromatography and combined gas chromatography–mass spectrometry.

Table I summarises the mass-balance data for the pyrolysis of the Amadori compounds. These data, together with those for 1-deoxy-1-glycino-D-fructose and 1-β-alanino-1-deoxy-D-fructose[5], do not show an overall relationship between the basicity of the amine moiety and the quantities of pyrolysate fractions. The amount of carbon dioxide released from the pyrolysis of 1-deoxy-1-prolino-D-fructose confirms that decarboxylation of the α-amino acid moiety is an important decomposition-reaction[3].

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TABLE II

VOLATILE ORGANIC PYROLYSIS-PRODUCTS FROM THE 1-AMINO-1-DEOXYFRUCTOSES

Compounds[a]	*1-Deoxy-1-morpholino-* D-*fructose*	*1-Deoxy-1-(*N*-methyl-anilino)-* D-*fructose*	*1-Deoxy-1-* p*-toluidino-* D-*fructose*	*1-Deoxy-1-dibenzyl-amino-* D-*fructose*	*1-Deoxy-1-prolino-* D-*fructose*	*Hexose C atoms*	*Mass spectrum* (m/z)	*M.s. ref.*
Methanol	+	+	+	+	+	1	31, *32*, 29	9
Acetaldehyde	+	+	+	+	+	2	29, *44*, 43	9
Ethanol	++	++	+	+	++	2	31, 45, 27, 29, *46*	9
Furan					+	4	39, *68*	9
Acetone	++	+		+	+	3	43, *58*, 15	9
Acetic acid	+++	++	++	++	+++	2	43, 45, *60*	9
2-Methylfuran	+	+			+	5	*82*, 53, 81	9
2,3-Butanedione	+	+	+	+		4	43, 15, *86*	9
Propanoic acid	+	+	+	+	+	3	28, 29, *74*, 27, 45	9
Benzene	+					6	*78*, 52, 77, 51, 50	9
Acrylic acid	++					3	27, *72*, 55, 26	9
Pyrrolidine		+			++		*71*, 70, 43	9
Acetol		+				4	43, 31, *74*	9
2,5-Dimethylfuran	+	+				6	43, *96*, 95, 53, 81	9
2,3-Pentanedione	+	+		+	+	5	43, 29, 57, 27, *100*	9
Toluene			+	+			91, *92*, 61, 51, 50	9
Acetoin		+				4	45, 43, *88*	9
Morpholine	++++						57, 29, *87*, 86, 56	9
2,5-Hexanedione		+				6	43, 71, 99, *114*	9
2-Furaldehyde		+	+			5	*96*, 95, 39, 29	9
2-Furfuryl alcohol		++	+	+		5	*98*, 41, 39, 81, 53, 97	9
Acetol acetate		+		+		6	43, 15, 42, 86, *116*	9
Protoanemonin			+	+		5	42, *96*, 26, 68, 54	5
2-Furyl methyl ketone	+		+	+	+	5	95, *110*, 39, 42	9
Benzaldehyde				+++			77, *106*, 105, 51, 50	9
Dimethylpyrrole			+			6	94, *95*, 80	9
N-Methylaniline		++++					106, *107*, 78	9
2-Hexadienoic acid			+			6	97, *112*, 67, 41, 39	9

p-Toluidine			++++				106, *107*	9
1-Acetonylmorpholine	+					3	128, *143*, 100, 70	[b]
Benzyl alcohol				+			79, *108*, 107, 77	9
Benzylamine				+			106, *107*, 30, 79	9
2,3-Dihydro-3,5-dihydroxy-6-methyl-4*H*-pyrane-4-one		++		++	+	6	43, 44, *144*, 101	9
N-Formylmorpholine	++					1	56, 57, *115*, 86, 100	[c]
N-Acetylmorpholine	++					2	57, 56, 86, 114, *129*	[c]
Morpholino-*C*-methyl-reductone	+					4	*171*, 128, 100, 154	[d]
Isomorpholino-*C*-methyl-reductone	+					4	*171*, 128, 100, 142	[d]
4-Hydroxy-2-morpholino-butanolacetone	+					4	112, 113, 127, *171*	[d]
N-Methyl-*N*-formylaniline		++				1	120, 106, 107, *135*	[c]
N-Methyl-*N*-acetylaniline		+				2	107, 106, 120, *149*	[c]
p-Methyl-*N*-phenylpyrrole			++			5	*157*, 156, 115	9
N-Formyl-*p*-toluidine			++			1	106, *135*, 107	[c]
N-Acetyl-*p*-toluidine			++			2	106, *149*, 107	[c]
N-(5-Methylfuryl)-*p*-toluidine			++			5	81, *157*, 156	[b]
Benzoic acid				+			105, 77, *122*	9
N-Benzylpyrrole				++		4	91, *157*, 65	9
N-Benzylacetamide				+		2	43, 30, 15, 106, *149*	9
N-Methyldibenzylamine				+++		1	91, 134, 120, *211*	[b]
N-Formyldibenzylamine				+		1	134, 91, 106, *225*	[c]
Dibenzylamine				++++			91, 106, 196, *197*	[c]
N-Formylpyrrolidine					++	1	*99*, 43, 70	3
N-Acetylpyrrolidine					++++	2	43, 70, *113*	3
N-Propanoyl-2-pyrrolidine					++	3	70, *127*, 43	3
N-5-Methyl-2-furfurylpyrrolidine					+	6	95, *165*, 164	3

[a] ++++ = major product; +++ = >10% of pyrolysate; ++ = 1–10% of pyrolysate; + = <1% of pyrolysate. [b] Tentative assignment deduced from mass-spectral breakdown pattern. [c] Identical with spectrum of authentic sample run on same instrument. [d] Tentative assignment, spectrum consistent with that of the piperidino analogue[2].

TABLE I

PYROLYSIS PRODUCTS FROM THE 1-AMINO-1-DEOXYFRUCTOSES AT 250°/15 MIN

Pyrolysis product	*Yield (%)*				
	*1-Deoxy-1-morpholino-*D-*fructose*	*1-Deoxy-1-(*N*-methylanilino)-*D-*fructose*	*1-Deoxy-1-*p*-toluidino-*D-*fructose*	*1-Deoxy-1-dibenzylamino-*D-*fructose*	*1-Deoxy-1-prolino-*D-*fructose*
Char	31.5	50.4	60.4	55.1	59.5
Tar	29.4	8.4	5.3	22.8	2.0
Carbon dioxide	3.8	3.7	3.1	4.3	13.1
Carbon monoxide	0.4	0.8	0.3	1.0	1.0
Water	28.2	23.8	21.6	12.7	17.0
Organic volatiles	7.0	10.2	9.2	2.2	6.8
Unaccounted	0	2.7	0.1	1.9	0.6

Compounds constituting the volatile organic fraction of Table I are listed in Table II. The organic volatiles obtained from the thermal degradation of 1-deoxy-1-prolino-D-fructose are consistent with those found by other workers[3,4], given the differences in pyrolysis conditions employed. Table II shows that a primary pyrolytic event in the decomposition of 1-deoxy-1-dibenzylamino-D-fructose, 1-deoxy-1-*N*-methylanilino-D-fructose, 1-deoxy-1-morpholino-D-fructose, and 1-deoxy-1-*p*-toluidino-D-fructose is scission of the carbon–nitrogen bond at C-1 of the hexose to release the free amine. The resultant fructosyl moiety may degrade via a 1,2- or a 2,3-enol intermediate[6]. The formation of 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyrane-4-one in these systems is evidence for the operation of the 2,3-enolisation pathway[3], whereas the isolation of 2-furaldehydes, *N*-substituted pyrrole derivatives, and protoanemonin indicates that 1,2-enolisation has occurred[5,6]. However, the relative importance of the two pathways is not clear because many of the other degradation-products listed in Table II could have arisen from either route.

Aminated reductone compounds were found in the volatile organic fraction obtained during the pyrolysis of 1-deoxy-1-morpholino-D-fructose. This observation demonstrates that the modified 2,3-enolisation pathway is operative, as shown for 1-deoxy-1-piperidino-D-fructose[7]. Morpholine is much less basic than piperidine; however structural similarities do exist between the two compounds. This result further shows that there is no simple relationship between base strength and the pathway by which Amadori compounds undergo degradation.

EXPERIMENTAL

Pyrolysis. — Amadori compounds were pyrolysed at 250° for 15 min and

mass-balance fractions collected as described previously[5]. Results for other thermal treatments are consistent with those described herein and have been reported elsewhere[10].

Gas chromatography and gas chromatography–mass spectrometry. — These procedures were performed as described in an earlier communication[5].

Amadori compounds. — Established methods were used to prepare the 1-amino-1-deoxyfructoses from D-glucose and the following bases (pKb values[11] at 25° are in parentheses): dibenzylamine[12] (8.52), *N*-methylaniline[13] (4.84), morpholine[12] (8.33), proline[3] (10.64), and *p*-toluidine[14] (5.08).

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