

Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

THERMAL DEGRADATION OF 1-AMINO-1-DEOXYKETOSSES AND THEIR  
ROLE IN FLAVOUR DEVELOPMENT

A Thesis

presented in partial fulfilment of the  
requirements for the degree of  
Doctor of Philosophy in Food  
Technology at Massey University.

by

Edward John Birch

March, 1981.

## ABSTRACT

Sugars undergo caramelisation reactions at relatively high temperatures but when amino compounds are present, Maillard browning reactions are possible and these occur under less severe conditions. The reaction conditions and the basic character of the amino compounds determine the range of flavour compounds formed. The first step during Maillard browning is the condensation of a reducing sugar with an amine to form a glycosylamine and this compound may then undergo the Amadori rearrangement to form a 1-amino-1-deoxyketose.

The pyrolysis of two 1-amino-1-deoxyketoses (1-deoxy-1-glycino-D-fructose and 1- $\beta$ -alanino-1-deoxy-D-fructose) was studied in this investigation to examine their participation in a low energy route to aroma formation. Thermal analysis and parallel chemical investigations showed that the formation of these Amadori compounds facilitates the thermal degradation of their sugar and amino acid moieties. In addition increased quantities of various aroma compounds are produced, compared with the controls. In particular, the toxic compound protoanemonin is formed and a degradation pathway leading to its production is proposed.

Most of the work involving the elucidation of degradation pathways during Maillard browning have involved studies in aqueous systems. Browning reactions between glucose and amino acids were also observed during heating in the dry-state in this study. These reactions are very vigorous once initiated and this precluded the study of a glucose plus amino acid control by the techniques used to study the pyrolysis of the 1-amino-1-deoxyketoses. Such reactions occur

at temperatures below those required for the thermal degradation of the corresponding Amadori rearrangement compound thus questioning the involvement of these compounds in the lowest energy thermolysis pathway in the absence of moisture. The results of experiments designed to investigate the role of Amadori compounds during the browning of sugar-amino acid systems in the dry-state demonstrated however that the reactions reported to occur in aqueous systems can also account for the dry-state processes at temperatures up until the spontaneous decomposition of the 1-amino-1-deoxyketose can occur. That the 1-amino-1-deoxyketose does not brown by itself or in the presence of glucose as readily as a glucose plus amino acid system is presumably a basicity effect. The stronger base (the amino acid) may promote a solid-state enolisation of the glucose and hence initiate browning at a somewhat lower temperature. The results of these experiments also demonstrate the stability of the 1-amino-1-deoxyketoses and show that their formation is not a rate-limiting step during browning.

In the third section of this thesis the effect of changing the amine moiety on the degradation pattern of 1-amino-1-deoxyketoses is assessed. Previous research has indicated that glucose by itself and Amadori compounds formed from weak primary bases degrade via an initial 1,2 enolisation step to form mainly 2-furaldehydes and pyrrole derivatives while 1-amino-1-deoxyketoses containing a strong basic moiety (usually formed from a secondary base) degrade via a 2,3 enol intermediate and give rise to fragrant caramel aroma compounds. Several 1-amino-1-deoxyketoses were prepared using primary and secondary bases covering a range of pK<sub>b</sub> values. These compounds were pyrolysed and their decomposition characteristics monitored by thermal analysis methods. Parallel

analysis of the volatiles produced and a comparison of the results from previous investigations generally endorsed the reported hypotheses on the degradation of Amadori compounds. It was found that the structure of the base and functional groups present influenced the degradation phenomena as well as the basicity. The thermal decomposition of amino acid - derived Amadori compounds for instance, did not fit into the pattern of that observed for 1-amino-1-deoxyketoses derived from other bases. The amino acid influences the degradation traits by promoting 1,2 enolisation and charring rather than aiding 2,3 enolisation similar to bases of comparable pkb.

## ACKNOWLEDGMENTS

The author thanks his supervisors, Professor E.L. Richards and Dr J. Lelievre (Department of Food Technology, Massey University) and Dr G.B. Russell (Applied Biochemistry Division, DSIR) for their suggestions and interest throughout this study and help in formulating and constructive critique of the manuscript.

The author expresses his appreciation to the following persons for their assistance and counsel:

Prof R. Hodges (Chemistry Department, Massey University) for discussions on mass spectrometry.

Dr R. Norris (Dairy Research Institute) for help and advice on aspects of differential scanning calorimetry.

Mr D.E. Rogers and Dr N. Milestone (Chemistry Division, DSIR) for running thermogravimetry and derivative thermogravimetry samples.

Prof A. Campbell and staff (Chemistry Department, Otago University) for elemental analyses.

Dr G. Midwinter (Chemistry Department, Massey University) for amino acid analyses.

## Table of Contents

	Page
Abstract	ii
Acknowledgments	v
List of Tables	ix
List of Figures	x
INTRODUCTION	
I.1 The involvement of Amadori compounds in non-enzymic browning - a review	1
I.1.1 The nature of non-enzymic browning	1
I.1.2 The chemistry of non-enzymic browning	1
I.1.2.1 Caramelisation	1
I.1.2.2 Maillard browning	2
I.1.3 Evidence for the involvement of Amadori compounds in Maillard browning	4
I.2 Scope of this investigation	7
I.3 Experimental approach for studying the thermal degradation of carbohydrates	9
PART A	
A.1 Summary	11
A.2 Introduction	12
A.3 Thermal analysis by d.s.c., t.g. and d.t.g.	13
A.3.1 Experimental	13
A.3.1.1 Amadori compounds	13
A.3.1.2 Thermal analysis	13
A.3.2 Results and discussion	14
A.4 Analysis of decomposition products from the 1-amino-1-deoxyketoses and controls	22
A.4.1 Pyrolysis conditions	22
A.4.2 Experimental	22
A.4.2.1 Pyrolysis	22
A.4.2.2 Gas chromatography	22
A.4.2.3 Gas chromatography - mass spectrometry	23
A.4.3 Results and discussion	23

	Page
A.5 The formation of protoanemonin	29
A.5.1 Introduction	29
A.5.2 Experimental	29
A.5.2.1 Protoanemonin	29
A.5.2.2 3-deoxy-D-erythro-hexosulose	31
A.5.2.3 Radioactive 1- $\beta$ -alanino-1-deoxy-D-fructoses	31
A.5.2.4 Pyrolysis, g.c., g.c.-m.s.	31
A.5.2.5 Measurement of radioactive protoanemonin	31
A.5.3 Results and discussion	32
PART B	
B.1 Summary	37
B.2 Introduction	38
B.3 Evidence for the formation of Amadori compounds in sugar-amino acid systems on heating in the dry-state	40
B.3.1 Experimental	40
B.3.2 Results and discussion	40
B.4 Observations on the rate of browning of model systems in the dry-state in hot oil, where one component is molten	42
B.4.1 Introduction	42
B.4.2 Experimental	42
B.4.3 Results and discussion	42
B.5 Study of the involvement of 1- $\beta$ -alanino-1-deoxy-D-fructose in the lowest energy route to product formation during the browning of a glucose- $\beta$ -alanine mixture in the dry-state	46
B.5.1 Introduction	46
B.5.2 Experimental	46
B.5.2.1 Browning reactions	46
B.5.2.2 Glucose analysis	47
B.5.2.3 Analysis of $\beta$ -alanine and 1- $\beta$ -alanino-1-deoxy-D-fructose	47
B.5.3 Results and discussion	48



	Page
PART C	
C.1 Summary	63
C.2 Introduction	64
C.3 Thermal analysis by d.s.c., t.g. and d.t.g.	69
C.3.1 Experimental	69
C.3.1.1 Amadori compounds	69
C.3.1.2 Thermal analysis	70
C.3.2 Results and discussion	70
C.4 Analysis of pyrolysis products from the 1-amino-1-deoxyfructoses	80
C.4.1 Experimental	80
C.4.2 Results and discussion	80
APPENDICES	
A1 Pyrolysis procedures	96
A1.1 Pyrolysis unit design	96
A1.2 Operation of the pyrolysis unit and definition of mass balance fractions	97
A2 Preparation of Amadori compounds	99
A2.1 Synthetic procedures	99
A2.2 Infrared spectra	103
A3 Colourimetric analysis of Browning reaction mixtures	107
REFERENCES	111

## List of Tables

Table		Page
A.1	Pyrolysis products from Amadori compounds and controls	24
A.2	Volatile organic pyrolysis products from 1-deoxy-1-glycino-D-fructose and 1- $\beta$ -alanino-1-deoxy-D-fructose	27,28
A.3	Pyrolysis products from 3-deoxy-D-erythro-hexosulose at 195 <sup>o</sup> /15 min	33
A.4	Incorporation of radioactivity into pyrolysis products of 1- $\beta$ -alanino-1-deoxy-D-fructoses derived from glucose labelled at various positions	35
B.1	Formation of 1-deoxy-1-glycino-D-fructose from glucose plus glycine mixtures heated in the dry-state	41
B.2	Rate of browning of various systems in paraffin	43
C.1	Physical data for amines under study	78
C.2	Pyrolysis products from the 1-amino-1-deoxyfructoses at 250 <sup>o</sup> /15 min	81
C.3	Pyrolysis products from 1-deoxy-1-prolino-D-fructose under various thermal treatments (15 min duration)	84
C.4	Volatile organic pyrolysis products from 1-deoxy-1-morpholino-D-fructose	86
C.5	Volatile organic pyrolysis products from 1-deoxy-1-p-toluidino-D-fructose	87
C.6	Volatile organic pyrolysis products from 1-deoxy-1-dibenzylamino-D-fructose	88
C.7	Volatile organic pyrolysis products from 1-deoxy-1-prolino-D-fructose and 1-deoxy-1-N-methylanilino-D-fructose at 250 <sup>o</sup> /15 min	89
C.8	General relationship between the basic moiety of 1-amino-1-deoxyfructoses and the observed pyrolysis products	95

## List of Figures

	Page
Introduction	
Fig I.1	Formation of Amadori compounds 3
Fig I.2	Suggested scheme for the production of melanoidins in an aldose-amino system 6
Part A	
Fig A.1	Differential scanning calorimetric curves for 1-deoxy-1-glycino-D-fructose and controls 15
Fig A.2	Thermogravimetric analysis curves for 1-deoxy-1-glycino-D-fructose and controls 16
Fig A.3	Thermogravimetric and derivative thermogravimetric curves for 1-deoxy-1-glycino-D-fructose, heating rate $0.5^{\circ}/\text{min}$ 18
Fig A.4	Kinetic transformation of the t.g. curve for 1-deoxy-1-glycino-D-fructose, heating rate $4^{\circ}/\text{min}$ 20
Fig A.5	Kinetic transformation of the t.g. curve for 1-deoxy-1-glycino-D-fructose, heating rate $0.5^{\circ}/\text{min}$ 21
Fig A.6	Pathway of protoanemonin formation 30
Part B	
Fig B.1	Browning route for sugars and primary amino acids 45
Fig B.2	Progress of the browning reaction between glucose and $\beta$ -alanine at $120^{\circ}$ in the solid state 49
Fig B.3	Progress of the browning reaction between glucose and $\beta$ -alanine in the presence of 1- $\beta$ -alanino-1-deoxy-D-fructose at $120^{\circ}$ in the solid state 50
Fig B.4	Progress of the browning reaction between glucose and $\beta$ -alanine at $150^{\circ}$ in the solid state 51
Fig B.5	Progress of the browning reaction between glucose and $\beta$ -alanine in the presence of 1- $\beta$ -alanino-1-deoxy-D-fructose at $150^{\circ}$ in the solid state 52

	Page	
Fig B.6	Disappearance of glucose during browning at 120° in the solid state	54
Fig B.7	Disappearance of glucose during browning at 150° in the solid state	54
Fig B.8	Change of absorbance during browning at 120°	56
Fig B.9	Change of absorbance during browning at 150°	57
Fig B.10	U.V. spectrum of browning products from glucose and $\beta$ -alanine at 120° in the solid state	58
Fig B.11	Weight losses during browning at 120° in the solid state	61
Fig B.12	Weight losses during browning at 150° in the solid state	61
Fig B.13	Relationship between the disappearance of glucose and $\beta$ -alanine during browning at 120° in the solid state	62
Fig B.14	First order plot for the disappearance of $\beta$ -alanine during browning of glucose + $\beta$ -alanine (1:1) at 120° in the solid state.	62
 Part C		
Fig C.1	Degradation of monoketoseamines via 1,2 enolisation	65
Fig C.2	Degradation of monoketoseamines via 2,3 enolisation	66
Fig C.3	Thermogram for the decomposition of 1-deoxy-1-prolino-D-fructose	71
Fig C.4	Thermogram for the decomposition of 1-deoxy-1-morpholino-D-fructose	72
Fig C.5	Thermogram for the decomposition of 1-deoxy-1-p-toluidino-D-fructose.	73
Fig C.6	Thermogram for the decomposition of 1-deoxy-1-N-methylanilino-D-fructose	74
Fig C.7	Thermogram for the decomposition of 1-deoxy-1-dibenzylamino-D-fructose	75
Fig C.8	T.g. and d.t.g. curves for the decomposition of piperidino-hexose-reductone	77

	Page	
Fig C.9	Relationship between basicity of amine substituent and residue remaining at 400° from the pyrolysis of 1-amino-1-deoxy-2-fructoses	79
Fig C.10	Relationship between basicity of amine substituent and decomposition temperature of 1-amino-1-deoxy-2-fructoses	79
Fig C.11	Proposed decomposition reactions of 1-deoxy-1-morpholino-D-fructose	92
 Appendices		
Fig A2.1	I.R. spectra of Amadori compounds	104
Fig A3.1	Change of absorbance with time for a 1-β-alanino-1-deoxy-D-fructose determination at 574 nm	109
Fig A3.2	Comparison between U.V. and T.M.S. methods for monitoring 1-β-alanino-1-deoxy-D-fructose levels during browning	110