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# THERMAL ANALYSIS OF 1-DEOXY-1-GLYCINO-D-FRUCTOSE AND 1-β-ALANINO-1-DEOXY-D-FRUCTOSE

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ABSTRACT

Aspects of the pyrolysis of 1-deoxy-1-glycino-D-fructose and 1-β-alanino-1-deoxy-D-fructose are reported Thermal analysis and parallel chemical investigations demonstrate that formation of these Amadori compounds provides a low-energy route to the thermal degradation of their amino acid and sugar moieties Furthermore, the pathway leads to the production of increased quantities of various aroma compounds as compared with controls Pyrolysis of the 1-amino-1-deoxyketoses also produces the toxic compound protoanemonin, a degradation pathway leading to its formation is proposed

## INTRODUCTION

When an aldose and an amino acid are heated, the glycosylamine so formed may undergo the Amadori rearrangement to give a 1-amino-1-deoxyketose[1] Many investigators consider that 1-amino-1-deoxyketoses are important intermediates in non-enzymic browning reactions and have proposed degradation mechanisms to explain how these compounds produce volatiles that contribute to the organoleptic characteristics of thermally processed foods[2–7] In definitive work of Hodge *et al*, the thermolysis of 1-deoxy-1-piperidino-D-fructose[3] and 1-deoxy-1-L-prolino-D-fructose[6] is discussed. A recent publication of Shigematsu *et al* [7] reports degradation products from three further Amadori compounds

Sugars undergo caramelisation reactions at relatively high temperatures[8], but it has been suggested that, in the browning reaction, the formation of 1-amino-1-deoxyketoses leads to the production of aroma volatiles at lower temperatures and in higher yields[9] Despite the significance of Amadori compounds, there appears to be little information concerning this aspect of their thermolysis The present paper discusses the pyrolysis of 1-deoxy-1-glycino-D-fructose and 1-β-alanino-1-deoxy-D-fructose with reference to the question of a low-energy pathway to formation of aroma In addition, investigations of more-general aspects of the thermolysis of these Amadori compounds are reported

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RESULTS AND DISCUSSION

Differential scanning calorimetry (d s c ), thermogravimetric analysis (t g ), and gas chromatography–mass spectrometry were used to study the series of physical transformations and chemical reactions that occurred during pyrolysis As it was not possible to ensure that the pyrolysis conditions used in these techniques were identical, the results obtained from the different instruments may not be directly comparable[10], however, certain general trends are apparent

D s c and t g data for glucose, glycine, and 1-deoxy-1-glycino-D-fructose, are shown in Figs 1 and 2, respectively The traces for glucose and glycine are similar to those reported by other investigators[11–14] The sharp transition signalled in the initial region of the d s c endotherm for 1-deoxy-1-glycino-D-fructose (145°) corresponds to the onset of melting of the sample The wide, unsymmetrical appearance of the peak, together with the rapid fluctuations in the trace, indicates that the sample melts with decomposition The t g results for this compound also show that the decomposition of the sample commences in this region According to the t g trace, the initial degradation proceeds comparatively rapidly to leave a substantial quantity of residue, which then decomposes relatively slowly, thus there are two main stages of pyrolysis However, when a lower rate of heating is used, the first stage of the t g curve may be seen to arise from a number of consecutive and concurrent reactions, as

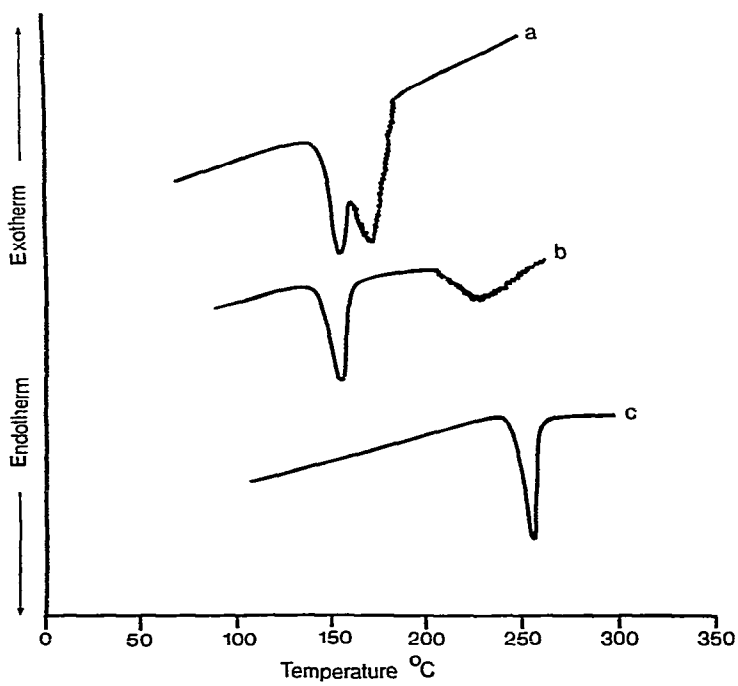



Fig. 1. Differential-scanning calorimetric curves for (*a*) 1-deoxy-1-glycino-D-fructose, (*b*) glucose, and (*c*) glycine

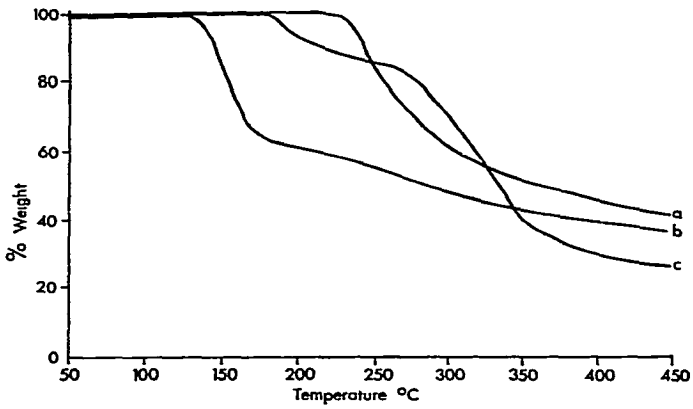



Fig 2 Thermogravimetric analysis curves for (*a*) glycine, (*b*) 1-deoxy-1-glycino-D-fructose, and (*c*) glucose, heating rate 4°/min

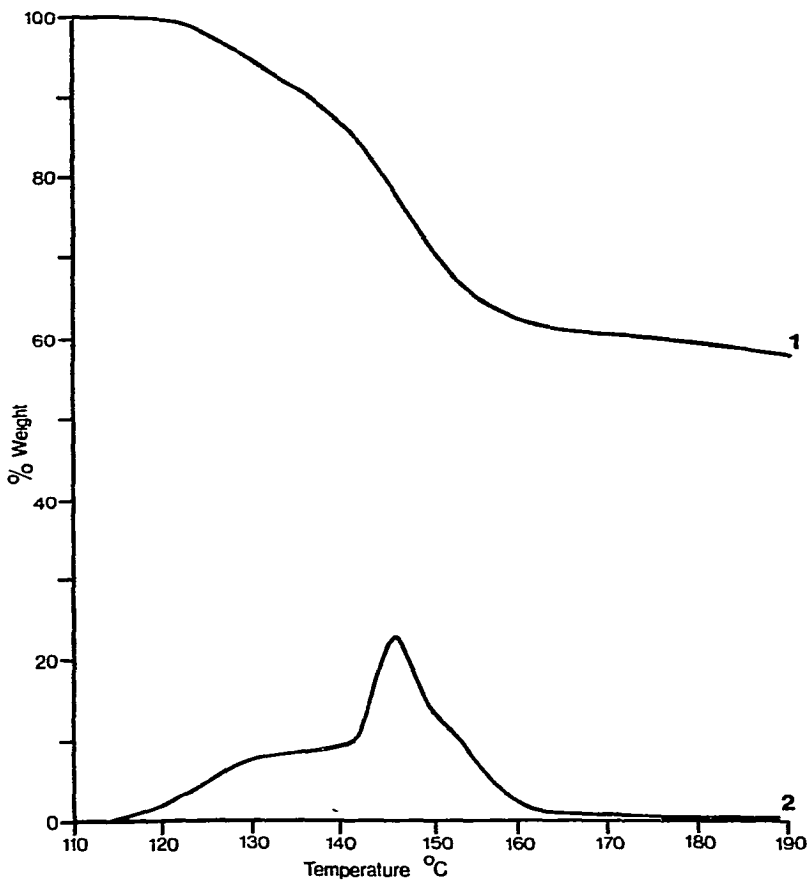



Fig 3 Thermogravimetric analysis (*1*) and derivative thermogravimetry (*2*) curves for 1-deoxy-1-glycino-D-fructose, heating rate 0 5°/min

TABLE I

PYROLYSIS PRODUCTS FROM AMADORI COMPOUNDS AND CONTROLS

| *Pyrolysis product* | *Yield (%)* | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | *15 min at 195°* | | | | | *1 h at 400°* | | | | |
| | *Glucose* | *Glycine* | *1-Deoxy-1-glycino-D-fructose* | *β-Alanine* | *1-β-Alanino-1-deoxy-D-fructose* | *Glucose* | *Glycine* | *1-Deoxy-1-glycino-D-fructose* | *β-Alanine* | *1-β-Alanino-1-deoxy-D-fructose* |
| Char | 96 4[a] | 97 1[a] | 58 2 | 77 8[a] | 60 7 | 23 3 | 36 4 | 39 4 | 24 0 | 38 0 |
| Tar | | | 1 5 | | 2 3 | 10 1 | 12 8 | 1 0 | 10 3 | 2 3 |
| Carbon dioxide | 0 1 | 0 5 | 16 1 | 1 0 | 2 5 | 4 5 | 5 3 | 17 8 | 3 7 | 9 6 |
| Carbon monoxide | 0 | 0 | Tr | 0 1 | 0 | 1 3 | 2 1 | 4 2 | 1 5 | 3 7 |
| Water | 2 5 | 2 2 | 20 2 | 20 6 | 29 7 | 42 7 | 33 0 | 25 3 | 41 5 | 36 3 |
| Organic volatiles[b] | 0 2 | 0 | 1 0 | 0 1 | 2 0 | 14 5 | 8 5 | 9,0 | 12 0 | 7 0 |
| Unaccounted[c] | 0 8 | 0 2 | 3 0 | 0 4 | 2 8 | 3 5 | 1 9 | 3,3 | 7 0 | 3 1 |

[a]Distinct separation of residue into tar and char had not occurred [b]Recovered from the volatile-traps (see Experimental) [c]This fraction contained any untrapped nitrogenous gases

TABLE II

VOLATILE, ORGANIC, PYROLYSIS PRODUCTS FROM 1-DEOXY-1-GLYCINO-D-FRUCTOSE AND 1-β-ALANINO-1-DEOXY-D-FRUCTOSE

| *Compounds*[a] | *1-Deoxy-1-glycino-D-fructose* | | *1-β-Alanino-1-deoxy-D-fructose* | | *Mass spectrum* m/e | *M.s. ref* |
|---|---|---|---|---|---|---|
| | *195°/15 min* | *400°/1 h* | *195°/15 min* | *400°/1 h* | | |
| Propene | | ++ | | + | 41, *42*, 39, 27 | 17 |
| Methanol | +++ | ++ | | + | 31, *32*, 29 | 17 |
| Acetaldehyde | ++++ | +++ | ++++ | +++ | 29, *44*, 43 | 17 |
| Butene | | ++ | | + | 41, *56*, 39 | 17 |
| 1,3-Butadiene | | + | | + | 41, *56*, 55 | 17 |
| Ethanol | ++ | + | ++ | + | 31, 45, 27, 29, *46* | 17 |
| Acetonitrile | | ++ | | + | *41*, 40, 39 | 17 |
| Furan | + | + | + | + | 39, *68*, 38 | 17 |
| Acetone | +++ | ++ | ++ | + | 43, *58*, 15 | 17 |
| Acrylonitrile | | + | | | 26, *53*, 52, 51 | 17 |
| Acetic acid | | ++++ | + | ++++ | 43, 45, *60* | 17 |
| Propionitrile | | + | | + | 28, 54, *55*, 26 | 17 |
| 2-Methylfuran | ++ | ++ | ++ | + | *82*, 53, 81 | 17 |
| Butanedione | ++ | + | ++ | | 43, 15, *86* | 17 |
| Propanoic acid | | ++ | | | 28, 29, *74*, 27, 45 | 17 |
| Methyl propanoate | | + | | | 29, 57, 27, 59, *88* | 17 |
| Acrylic acid | | + | | +++ | 27, *72*, 55, 26 | 17 |
| Acetol | | ++ | | ++ | 43, 31, 15, *74* | 17 |
| Benzene | + | + | | + | *78*, 52, 77, 51, 50 | 17 |
| 2,5-Dimethylfuran | + | +++ | | + | 43, *96*, 95, 53, 81 | 17 |
| 2,3-Pentanedione | + | + | ++ | + | 43, 29, 57, 27, *100* | 17 |
| Phenol | + | + | | | 94, 39, 65, 66 | 17 |
| Pyrrole | | + | ++ | + | *67*, 39, 41, 40 | 17 |
| 1-Methylpyrrole | + | ++ | | | *81*, 80, 39, 42 | 17 |
| Pyridine | + | | | + | *79*, 52, 51, 50 | 17 |
| Toluene | | + | | | 91, *92*, 39, 65 | 17 |
| *N*-Methylformamide | | + | | | *59*, 30, 29, 58 | 18 |
| 2-Methylpyrazine | | + | | | *94*, 67, 39, 53, 40 | 17 |
| 2-Methylpyrrole | | + | | | 80, *81*, 53, 27 | 17 |
| *N*-Methylacetamide | | + | | | *73*, 43, 40, 58 | 18 |
| 2-Furaldehyde | ++ | | ++ | + | *96*, 95, 39, 29 | 17 |
| 2-Furfuryl alcohol | | + | | | *98*, 41, 39, 42, 53 | 17 |
| 2,4(5)-Dimethylpyrrole | | + | | | 94, *95*, 80 | 17 |
| Protoanemonin | +++ | + | ++++ | +++ | 42, *96*, 26, 68, 54 | 19 |
| 2,6(6)-Dimethylpyrazine | | ++ | | + | *108*, 42, 40, 39, 81 | 20 |
| 2,3-Dimethylpyrazine | | ++ | | + | *108*, 67, 42, 40 | 20 |
| 2-Furylmethylketone | +++ | + | ++ | ++ | *95*, 110, 39, 42 | 17 |
| 5-Methyl-2-furaldehyde | ++ | + | ++ | + | *110*, 109, 53 | 17 |
| Trimethylpyrazine | | ++++ | | | 42, *122*, 39, 81 | 21 |
| Tetramethylpyrazine | | ++ | + | | 54, *136*, 42, 53 | 21 |
| 2-Acetylpyrrole | | | | ++ | 94, *109*, 66, 43 | 17 |

[a] ++++ = Major product, +++ = >10% pyrolysate, ++ = 1–10% of pyrolysate, + =<1% of pyrolysate

demonstrated by the derivative thermogravimetry (d t g ) curve in Fig 3 A similar pattern of d s c and t g results was obtained for 1-β-alanino-1-deoxy-D-fructose and controls

Compounds arising during the two main stages of the pyrolysis of 1-amino-1-deoxyketoses were then investigated The conditions used to sample the first stage were derived by obtaining kinetic information from the t g curves Thermolysis was treated as a two-stage reaction[15] and the data were analysed according to the method of David and Zelenyánski[16] The results indicated that, with a temperature of 195° for 15 min, ~90% of the initial phase of decomposition is complete at a point when the second stage has barely commenced In order to check that these conditions were appropriate for sampling the first stage of thermolysis, the weight of residue remaining after treatment for 15 min at 195° was shown to agree with that at the corresponding point in the t g curve A temperature of 400° for 1 h was used to study the overall decomposition

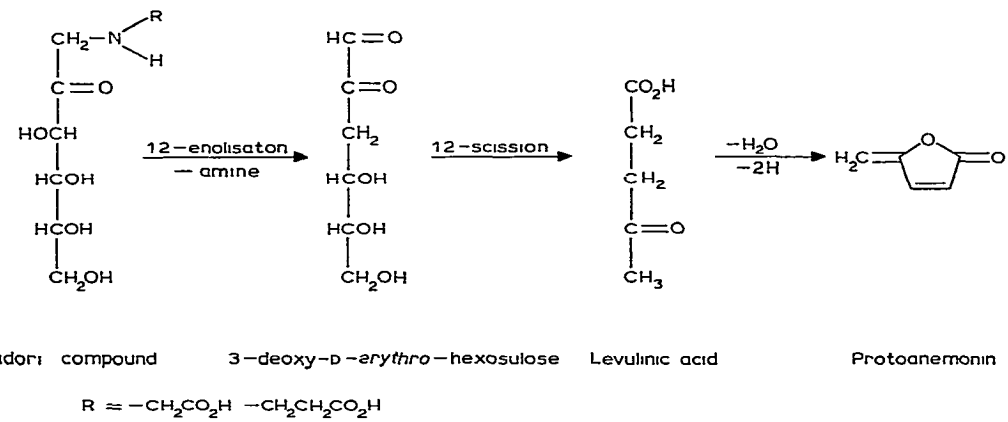
The results in Table I show that the Amadori compounds yield mainly char, water, and carbon dioxide during the first stage of their pyrolysis, with increased percentages of organic volatiles and carbon monoxide resulting on degradation at 400° for 1 h Table II shows that the organic volatiles are largely reduction compounds that would be expected as end-products in the pyrolysis of glucose[8], and some nitrogen-containing heterocycles are also present Although the organic volatiles are produced in small quantities, they are of interest, as many are aroma compounds The nitrogen heterocycles are particularly important in this context[4], much lower yields of these compounds were formed when the corresponding amino acids were pyrolysed under either set of conditions Comparison of the aforementioned thermal-analysis and pyrolysate data for the 1-amino-1-deoxyketoses with those for controls therefore demonstrates quantitatively that the Amadori compounds constitute part of a low-energy thermolysis pathway in which both the sugar and amino acid moieties are rendered more susceptible to degradation The products of this pathway include aroma volatiles, some of which are formed in increased quantities

A prominent feature of the results listed in Table I is that 1-deoxy-1-glycino-D-fructose produces a much higher yield of carbon dioxide than 1-β-alanino-1-deoxy-D-fructose or the controls Carbon dioxide is formed by the decarboxylation of amino acids during pyrolysis[22,23], and this reaction is known to be the preponderant initial decomposition-step in α- but not in β-amino acids In Amadori compounds, where the amino acid moiety is attached to a saccharide, 1,2-enolisation facilitates this reaction[6] These factors may therefore explain the relative proportions of carbon dioxide produced from the 1-amino-1-deoxyketoses Other degradation products in Table I may be understood in terms of well-established thermolysis pathways involving the sugar[3 6] and/or amino acid[22 23] components of the 1-amino-1-deoxyketoses

While the occurrence of most of the compounds in Table II conforms to expectation, this is not the case with the toxic vesicant protoanemonin[24]. This compound makes a relatively large contribution to the volatile organic fraction Traces of protoanemonin were also detected in the present study by subjecting glucose to a

temperature of 400° for 1 h A survey of the literature suggests that in only one instance has protoanemonin been recorded among the pyrolysates of amino-carbonyl systems, this was in a study of a sugar–protein mixture[19] in which yields were not reported Protoanemonin has not been found previously in pyrolysates from glucose Identification was confirmed by comparing its mass spectrum and retention times on two g l c columns with those of the authentic compound

The literature describing the pyrolysis of carbohydrates suggests a number of degradation pathways that could be adapted to account for the formation of protoanemonin 1,2-Enolisation is expected during the pyrolysis of the title Amadori compounds[6], if combined with amine elimination, this could yield 3-deoxy-D-*erythro*-hexosulose Further rearrangement and degradation of this intermediate could account for the presence of protoanemonin reported herein (see Scheme 1) Levulinic acid is a standard end-product of the pyrolysis of carbohydrates[8], and is formed from glucose *via* 1,2-scission[25] Protoanemonin is already known to be formed from levulinic acid under certain conditions[26,27]




Scheme 1 Pathway of protoanemonin formation

In an attempt to test Scheme 1, experiments were next performed under pyrolysis conditions of 280° for 30 min Such intermediate conditions were necessary as, at 195° for 15 min, the yield of protoanemonin was too low to make radioactive-tracer studies feasible, whereas at 400° for 1 h the estimation and separation of this compound is complicated by the presence of pyrazines Clearly different mechanisms may operate to different extents as thermal treatments change, and hence the conclusions reached about Scheme 1 may apply only to the selected time–temperature combination According to Scheme 1, 3-deoxy-D-*erythro*-hexosulose should yield protoanemonin when subjected to the conditions existing when the title compounds are pyrolysed by this thermal treatment In a study by Shafizadeh and Lai[28] of the degradation of 3-deoxy-D-*erythro*-hexosulose for 8 min at 550°, protoanemonin was not reported, however, in the present study with pyrolysis for 15 min at 280°, the

TABLE III

INCORPORATION OF RADIOACTIVITY INTO PROTOANEMONIN DERIVED FROM GLUCOSE LABELLED AT VARIOUS POSITIONS

| *Precursor* | *Specific activity ($10^3$ mCi mmol$^{-1}$)* |
|---|---|
| [1-$^{14}$C]Glucose | 4 26 |
| 1-$\beta$-alanino-1-deoxy-D-fructose | 3 93 |
| Protoanemonin | 0 39 |
| [2-$^{14}$C]Glucose | 4 42 |
| 1-$\beta$-alanino-1-deoxy-D-fructose | 4 19 |
| Protoanemonin | 4 06 |
| [6-$^{14}$C]Glucose | 4 49 |
| 1-$\beta$-alanino-1-deoxy-D-fructose | 4 37 |
| Protoanemonin | 2 94 |

compound was detected In a further experiment, it was confirmed that levulinic acid gives protoanemonin on pyrolysis for 15 min at 280° Thus both 3-deoxy-D-*erythro*-hexosulose and levulinic acid may be on a route whereby the Amadori compounds form protoanemonin

The carbon-skeleton cleavage shown in Scheme 1 was tested by using glucose $^{14}$C-labelled at positions 1, 2, or 6 The labelled sugars were used to synthesise 1-$\beta$-alanino-1-deoxy-D-fructoses, which were then pyrolysed The results are shown in Table III The specific activity of the protoanemonin from the 1-$\beta$-alanino-1-deoxy-D-fructose synthesised from [2-$^{14}$C]glucose shows virtually complete retention of the label, whereas the corresponding figures for the C-1 and C-6 label are 10 and 70%, respectively Hence scission between C-1 and C-2 is favoured, supporting the pathway outlined in Scheme 1, but a secondary mechanism that entails the loss of C-6 is also operative If these are the only mechanisms for formation of protoanemonin, all of the product should involve C-2–C-6 (70%) and C-1–C-5 (10%) This leads to a discrepancy of 20%, which can be explained by recombination of fragments, one and only one of which contains C-2 The labelling studies reported herein therefore stress that a single pathway for the formation of any given compound is unlikely under pyrolytic conditions[29].

## EXPERIMENTAL

*Thermal analysis* — T g and d t g data were obtained with a Mettler series No. 21 recording vacuum thermoanalyser with powdered samples (100 mg) in an open platinum crucible and a nitrogen atmosphere (gas flow-rate 100 mL/min) The temperature was raised at 4°/min and the range of 25–650° examined D s c traces were recorded on a Perkin–Elmer d s c 1B instrument Samples (10 mg) were placed in crimped aluminium pans having pierced lids and kept under nitrogen while the temperature was increased at 4°/min

*Pyrolysis* — The design of the pyrolysis unit was based on that of Simmonds *et al*[30] and consisted of a removable, stainless-steel tube that was sleeved by an insulated furnace containing a nichrome heater A platinum boat containing the sample (10 mg) was placed inside this tube One end of the pyrolysis unit contained a gas inlet and a swagelok port through which a thermometer was inserted to record the temperature above the sample boat The other end had swagelok fittings to which a trap comprising a 150 × 3 2 mm o d stainless-steel tube containing a porous polymer (Chromosorb 105, 80–100 mesh, Applied Science Labs, State College, Pa, 200 mg) could be attached The trap was adapted for direct insertion into a gas chromatograph[31] Temperatures were maintained at given levels for required times and the volatiles so formed carried by a stream of nitrogen (flow rate 8 mL/min) into the trap, which was cooled with Dry Ice Char was defined as the material remaining in the sample boat, and tar was that material coating the steel tube of the pyrolysis unit The carbon dioxide and carbon monoxide passing through the trap were determined as described by Shafizadeh and Lai[29]

*Gas chromatography–mass spectrometry* — Volatiles from the traps were separated on a 2 5 m × 3 2 mm outside dimension, stainless-steel column of Tenax–G C (Applied Science Labs) in a Hewlett–Packard 7620A gas chromatograph by using a temperature program of 30–210° at 2°/min The chromatograph was fitted with thermal-conductivity and flame-ionisation detectors When combined gas chromatography–mass spectrometry was employed, the column was placed in a Pye 104 gas chromatograph coupled to an AEI MS-30 double-beam instrument equipped with a silicone elastomer interface

*Amadori compounds* — 1-Deoxy-1-glycino-D-fructose and 1-β-alanino-1-deoxy-D-fructose were prepared according to published methods[32] For synthesis of the radioactive compounds, [1-$^{14}$C]glucose, [2-$^{14}$C]glucose, or [6-$^{14}$C]glucose (~50 μCi, Radiochemical Center, Amersham) was dissolved with D-glucose (2 g, B D H "Analar") in distilled water (5 mL) The solution was lyophilised and the residue dried at 60° *in vacuo* over phosphorus pentaoxide for 24 h

*Protoanemonin* — Protoanemonin was synthesised by acid-catalysed lactonisation of acetylacrylic acid[26], which was prepared from glyoxylic acid by the method of Scheffold and Dubs[33] The mass spectrum and g l c retention times for the product obtained by synthesis were compared with those of the compound obtained from the pyrolysates This check was carried out on two columns, namely Tenax–G C and 10% w/w E G A on 100–120 mesh Gas Chrom Q (Applied Science Labs)

*3-Deoxy*-D-erythro-*hexosulose* — This compound was prepared by the method of Kato[34]

*Radioactivity determinations* — Protoanemonin was collected from the g l c outlet by bubbling the effluent gas through distilled water (2 mL) in a cuvette The absorbance of the resulting solution was measured in a Unicam S P. 800 recording spectrophotometer and the concentration of protoanemonin determined[26] The entire u v spectrum of protoanemonin was recorded to confirm that conversion into anemonin had not occurred Activity of all samples was measured by transferring

an aliquot of an aqueous solution of known concentration to a vial containing toluene omnifluor–triton (2 1, 20 mL) and counting in an Isocap/300 Liquid Scintillation System (Searle Analytical) Counting efficiencies were determined by using a set of quenched standards and the counts adjusted accordingly

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REFERENCES

1 R KUHN AND F WEYGAND, *Ber*, 70 (1937) 769–772
2 J E HODGE, *J Agric Food Chem*, 1 (1953) 928–943
3 F D MILLS, B G BAKER, AND J E HODGE, *J Agric Food Chem*, 17 (1969) 723–727
4 T M REYNOLDS, *Food Technol Aust*, 22 (1970) 610–619
5 J E HODGE, F D MILLS, AND B E FISHER, *Cereal Sci Today*, 17 (1972) 34–40
6 F D MILLS AND J E HODGE, *Carbohydr Res*, 51 (1976) 9–21
7 H SHIGEMATSU, S SHIBATA, T KURATA, H KATO, AND M FUJIMAKI, *Agric Biol Chem*, 41 (1977) 2377–2385
8 I S FAGERSON, *J Agric Food Chem*, 17 (1969) 747–750
9 J E HODGE, in H W SCHULTZ, E A DAY, AND L M LIBBEY (Eds), *Chemistry and Physiology of Flavours*, Avi Publishing Co, Westport, CT, 1967, chap 12
10 W W WENDLANDT, *Thermal Methods of Analysis*, Wiley–Interscience, New York, 1974, chap 2
11 T HATAKEYAMA, H YOSHIDA, C NAGASAKI, AND H HATAKEYAMA, *Polymer*, 17 (1976) 559–562
12 F SHAFIZADEH AND Y.-Z LAI, *Carbohydr Res*, 26 (1973) 83–89
13 B LORANT AND M BOROS, *Z Lebensm Unters Forsch*, 128 (1965) 22–28
14 A T PERKINS AND H L MITCHELL, *Trans Kans Acad Sci*, 60 (1957) 437–440
15 A VAN TETS, *Thermochimica Acta*, 15 (1976) 386–389
16 P K DAVID AND E ZELENYANSZKI, *J Thermal Anal*, 5 (1973) 337–340
17 A CORNU AND R MASOT (Eds), *Compilation of Mass Spectral Data*, Heyden and Son, London, 1966
18 E STENHAGEN, S ABRAHAMSSON, AND F W MCLAFFERTY (Eds), *Registry of Mass Spectral Data*, Vol 1, Wiley–Interscience, New York, 1974
19 A FERRETTI, V P FLANAGAN, AND J M RUTH, *J Agric Food Chem*, 18 (1970) 13–18
20 H A BUNDAROVICH, P FRIEDEL, V KRAMPL, J A RENNER, F W SHEPARD, AND M A GIANTURCO, *J Agric Food Chem*, 15 (1967) 1093–1099
21 P FRIEDEL, V KRAMPL, T RADFORD, J A RENNER, F W SHEPARD, AND M A GIANTURCO, *J Agric Food Chem*, 19 (1971) 530–532
22 P G SIMMONDS, E E MEDLEY, M A RATCLIFF, JR, AND G P SHULMAN, *Anal Chem*, 44 (1972) 2060–2066
23 M A RATCLIFF, JR, E E MEDLEY, AND P G SIMMONDS, *J Org Chem*, 39 (1974) 1481–1490
24 P G CALTRIDER, *Antibiotics*, 1 (1967) 671–673
25 J C SOWDEN, *J Am Chem Soc*, 71 (1949) 3568
26 E SHAW, *J Am Chem Soc*, 68 (1946) 2510–2513
27 C GRUNDMANN AND E KOBER, *J Am Chem Soc*, 77 (1955) 2332–2333
28 F SHAFIZADEH AND Y -Z LAI, *Carbohydr Res*, 40 (1975) 263–274
29 F SHAFIZADEH AND Y -Z LAI, *J Org Chem*, 37 (1972) 278–284
30 P G SIMMONDS, G P SHULMAN, AND C H STEMBRIDGE, *J Chromatogr Sci*, 7 (1969) 36–41
31 E WONG, L N NIXON, AND C B JOHNSON, *J Agric Food Chem*, 23 (1975) 495–498
32 E F L J ANET, *Aust J Chem*, 10 (1957) 192–197
33 P SCHEFFOLD AND P DUBS, *Helv Chim Acta*, 50 (1967) 798–807
34 H KATO, *Agric Biol Chem*, 26 (1962) 187–192