Formation of Pyrroles and Tetrahydroindolizin-6-ones as Hydroxyproline-Specific Maillard Products from Erythrose and Arabinose

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By means of mass, IR, and ^1H NMR spectroscopies 12 pyrroles (among them 1-(1-pyrrolyl)-2-butanone, 1-(1-pyrrolyl)-3-buten-2-one, 4-hydroxy-1-(1-pyrrolyl)-2-butanone, 1-furfurylpyrrole, 2-(1-pyrrolyl)-cyclopentanone, 2-(1-pyrrolyl)-2-cyclopenten-1-one, 5-(1-pyrrolyl)-2-cyclopenten-1-one) and 5,6,7,8-tetrahydroindolizin-6-one as well as 8-(hydroxymethyl)-5,6,7,8-tetrahydroindolizin-6-one were characterized in hydroxyproline/arabinose (erythrose) model experiments.

INTRODUCTION

Collagens from skin, tendon, and bone contain large amounts of L-hydroxyproline. Iozefowicz et al. (1977) determined 10% in collagen and 1–2% by weight L-hydroxyproline in meats and processed meats by ^{13}C NMR spectroscopy. Hydroxyproline glycosides have been isolated from tomato and tobacco cell walls. Akiyama et al. (1980) identified hydroxyproline arabinosides in suspension-cultured tobacco cells. So far, little is known about the formation of Maillard products from L-hydroxyproline.

During Maillard reaction proline is transformed into more than 120 proline-specific compounds (among them pyrrolidines, piperidines, tetrahydropyridines, 2,3-dihydro-1*H*-pyrrolizines, 5,6-dihydroindolizines, di- and tetrahydroazepines, and 1,3-oxazines) (Tressl, et al, 1981, 1985).

The closely related hydroxyproline forms a much smaller spectrum of specific Maillard products. In 1965 Kobayasi and Fujimaki reported the formation of 1-acetonylpyrrole and pyrrole during roasting of hydroxyproline with glucose. 1-Acetonylpyrrole was perceived with a mushroomlike odor quality. In 1981 we characterized 5,6,7,8-tetrahydroindolizin-6-one, 1-furfurylpyrroles, and 2-(1-pyrrolyl)-cyclopentenones as well as 2-[(1-pyrrolyl)methyl]cyclopentenones as specific compounds derived from hydroxyproline. In this paper we report the identification of 15 hydroxyproline-specific compounds in hydroxyproline/arabinose (erythrose) model experiments and their formation by Strecker degradation and aldol type reactions.

EXPERIMENTAL SECTION

Sample Preparation. Equimolar amounts of hydroxyproline and monosaccharide (17 mmol of erythrose, 58 mmol of arabinose) dissolved in water were refluxed for 2 h as well as autoclaved for 1.5 h at 150 °C. After the mixtures were cooled to room temperature, the compounds were extracted three times with freshly distilled ether. The combined extracts were dried over anhydrous sodium sulfate and concentrated to 5 mL on a Vigreux column.

Reaction of Hydroxyproline with α-Dicarbonyls ⇌ Enolones. Equimolar amounts of hydroxyproline and 2-hydroxy-2-cyclopenten-1-one (0.01 mol) were dissolved in water and autoclaved for 1.5 h at 150–160 °C in a stainless-steel laboratory autoclave equipped with a 100-mL duran glass tube. After the mixture was cooled to room temperature, the compounds were extracted with ether. 2-(1-Pyrrolyl)cyclopentanone, 2-ethoxy-2-cyclopenten-1-one, 2-hydroxycyclopentanone, 2-hydroxy-2-cyclopenten-1-one, and pyrrole were formed in a ratio of 82:14:0.1:3:0.1. The extract was separated by liquid adsorption chromatography on silica gel (activity II–III) into five fractions with pentane–methylene chloride (9:1) (F1), pentane–methylene chloride (3:1) (F2), pentane–ether (9:1) (F3), pentane–ether (1:1) (F4), and ether (F5) in 40-mL portions. The eluates were concentrated to 1 mL and analyzed by GC.

Compound **11** was transferred into fraction F5, and after removal of the ether the residue was dissolved in $CDCl_3$ and **11** was characterized by IR and ^1H NMR spectroscopy. In similar experiments pyruvaldehyde, 2,3-butanedione, and furfuraldehyde were autoclaved with hydroxyproline, and the pyrroles were separated from other compounds by adsorption chromatography.

6 was isolated from the hydroxyproline/erythrose extract by liquid adsorption chromatography as described for **11**. **6** could be isolated from fraction F5 without further purification. By the same procedure **14** was isolated from the hydroxyproline/arabinose experiment.

Gas Chromatography (GC)–Mass Spectrometry (MS). Capillary GC–mass spectrometry was carried out by using a 25-m glass capillary (0.32-mm i.d.) coated with CP Wax Chrompack (column A) and a 50-m glass capillary (0.32-mm i.d.) coated with CP sil 5CB (column B) coupled with a double-focusing mass spectrometer CH 5-DF (Varian MAT). Conditions were as follows: column A, temperature program 70–230 °C at 6 °C/min, Carlo Erba fractovap 2101, ionization voltage 70 eV, resolution 2000 (10% valley); column B, temperature program 100–260 °C at 4 °C/min.

Preparative Gas Chromatography. Investigations were carried out with a Varian Aerograph. Column C: 3-m (2-mm i.d.) glass 15% Carobwax 20 M on 80–90 mesh Chromosorb WAW/DMCS, temperature program 60–230 °C, 4 °C/min.

^1H NMR and IR Spectroscopies. ^1H NMR spectra were recorded at 270 MHz on a Bruker WH 270 NMR spectrometer in $CDCl_3$ solution. Chemical shifts are with reference to tetramethylsilane (Me_4Si) as internal standard; coupling constants J in Hertz. Infrared spectra were obtained from $CDCl_3$ or CCl_4 solutions with a Perkin-Elmer Model 275 instrument.

RESULTS AND DISCUSSION

Equimolar amounts of hydroxyproline and monosaccharides were heated in water at 100 °C as well as 150 °C for 2 and 1.5 h, respectively. The volatiles were extracted with freshly distilled diethyl ether and investigated by capillary GC–MS. Individual components were isolated by preparative GC and identified by MS, IR, and ^1H NMR spectroscopies. Tables I and II present the results of this study. Compounds **1–5** were identified by mass spec-

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Table I. Mass and ^1H NMR Spectra of Pyrroles, Characterized in Hydroxyproline Model Experiments[a]

pyrrole (1): MS 67 (100), 41 (57), 40 (50), 39 (57)

1-acetonylpyrrole (2): MS 123 (34), 81 (10), 80 (100), 78 (18), 53 (54), 51 (8), 43 (27), 41 (4), 39 (8)

3-(1-pyrrolyl)-2-butanone (3): MS 137 (22), 94 (100), 78 (19), 67 (21), 53 (15), 51 (15), 43 (58), 41 (36), 39 (43)

1-(1-pyrrolyl)-2-butanone (4): MS 137 (29), 81 (10), 80 (100), 78 (12), 57 (16), 53 (27)

1-(1-pyrrolyl)-3-butene-2-one (5): MS 135 (44), 107 (20), 106 (9), 93 (1), 81 (10), 80 (100), 78 (15), 68 (1), 53 (37), 51 (8), 39 (6)

4-hydroxy-1-(1-pyrrolyl)-2-butanone (6): MS 153 (17), 135 (4), 107 (3), 95 (2), 80 (100), 73 (8), 68 (13), 53 (27), 43 (8); ^1H NMR δ 2.26 (br s, 1 H, OH), 2.56 (t, 2 H, J = 7 Hz, CH_2CH_2OH), 3.86 (t, 2 H, J = 7 Hz, CH_2CH_2OH), 4.66 (s, 2 H, > NCH_2CO), 6.25 and 6.64 (each mc, 2 H, α'-CH and β'-CH) IR 3420 (s), 3120 (w), 2960 (m), 2840 (m), 1715 (s), 1250 (s), 1060 (s) cm^{-1}

5,6,7,8-tetrahydroindolizin-6-one (7): MS 135 (95), 107 (13), 106 (89), 94 (10), 93 (100), 92 (22), 80 (18), 79 (36), 78 (22), 77 (19), 67 (17), 66 (35), 65 (24), 52 (32); ^1H NMR δ 2.72 and 3.09 (each m, 2 H, AA'BB' spectrum of H-7 and H-8), 4.54 (s, 2 H, H-5), 6.01 (mc, 1 H, H-1), 6.17 (t, 1 H, J = 2.8 Hz, H-2) 6.57 (dd, 1 H, J = 2.8, 1.6 Hz, H-3); decoupling experiments: irradiation at δ 6.01–6.57 (d, J = 2.8 Hz), 6.17 (d, J = 2.8 Hz), 3.09 (sharpened, symmetrical with respect to 2.72); IR 3115 (w), 2965 (m), 2850 (m), 1725 (s), 1490 (m), 1420 (m), 1330 (s), 1310 (s), 1075 (s) cm^{-1}

3-methyl-2,3-dihydro-1*H*-pyrrolizin-2-one[b] (8): MS 135 (97), 118 (19), 107 (32), 106 (100), 80 (23), 79 (41), 78 (48), 77 (27), 67 (35), 53 (79), 51 (28), 39 (35)

1-hydroxy-3-(1-pyrrolyl)-2-butanone[b] (9): MS 153 (18), 122 (4), 94 (100), 78 (11), 67 (16), 53 (15), 51 (10), 41 (32), 39 (18), 31 (8)

1-furfurylpyrrole (10): MS 147 (25), 117 (3), 81 (100), 73.5 (8), 53 (37)8 51 (18), 39 (16); ^{H} NMR δ 5.00 (s, 2 H, CH_2), 6.16 (m, 2 H, H-3, H-4), 6.24 (dd, J = 3.4, 0.8 Hz, 1 H, H-3'), 6.32 (dd, J = 3.4, 1.8 Hz, 1 H, H-4'), 6.75 (m, 2 H, H-1, H-5), 7.36 (dd, J = 1.8, 0.8 Hz, 1 H, H-5')

2-(1-pyrrolyl)cyclopentanone (11): MS 149 (57), 120 (11), 106 (8), 94 (15), 93 (100), 92 (10), 67 (20), 66 (28), 65 (9), 55 (9), 53 (10), 51 (13), 43 (23), 41 (18), 39 (31); ^1H NMR δ 1.97 (mc, 1 H, H-4), 22 (mc, 2 H, H-3, H-4'), 2.38 (mc, 1 H, H-5), 2.48 (mc, 1 H, H-5'), 2.64 (mc, 1H, H-3'), 4.43 (dd, 1 H, J = 11.5, 8 Hz, H-2), 6.22 and 6.99 (each mc, 2 H, α'-CH and β'-CH); IR 3120 (w), 2920 (m), 2860 (m), 1740 (s), 1450 (m), 1360 (m), 1250 (m) cm^{-1}

2-(1-pyrrolyl)-2-cyclopenten-1-one (12): MS 147 (66), 119 (14), 118 (100), 117 (13), 104 (12), 91 (38), 64 (18), 58.5 (10), 51 (24), 39 (28); ^1H NMR δ 2.61 (mc, 2 H, H-5), 2.69 (mc, 2 H, H-4), 6.22 (mc, 2 H, β'-CH), 7.24 (t, 1 H, J = 3.1 Hz, H-3), 7.25 (mc, 2 H, α'-CH); decoupling experiments irradiation at δ 7.25 6.22 (s), 2.69 (sharpened, symmetrical with respect to 2.61), 2.61/2.69–7.24 (s), 6.22–7.25 (s)

5-(1-pyrrolyl)-2-cyclopenten-1-one (13): MS 147 (66), 121 (28), 119 (10), 118 (100), 117 (10), 93 (63), 67 (22), 66 (22)8 65 (23), 58.5 (10), 51 (27), 39 (30)

8-hydroxy-5,6,7,8-tetrahydroindolizin-6-one[b] (14): MS 165 (42), 134 (100), 106 (56), 79 (16), 45 (24), 44 (20), 43 (27), 31 (11); ^1H NMR signals at δ 6–7 (pyrrole-H), 4.5–5 (>NCH_2CO), 4.7–5.1 (CH_2OH, sharpened by addition of D_2O), 2–3 ($COCH_2$) superimposed strongly by signals of not identified components; IR 3420 (s), 3130 (w), 2960 (m), 2860 (m), 1720 (s), 1470 (m), 1370 (s)8 1260 (m), 1060 (m), 1010 (w) cm^{-1}

isomer of 6[c] (15): MS 153 (27), 135 (15), 124 (4), 107 (15), 106 (40), 94 (22), 81 (10), 80 (100), 79 (10), 78 (10), 68 (15), 67 (10), 53 (28), 41 (11), 39 (10)

2,3-dihydroxy-5-(1-pyrrolyl)-2-cyclopenten-1-one[b] (16): MS 179 (29), 177 (15), 151 (12), 120 (6), 118 (6), 117 (45), 94 (32), 93 (100), 92 (63), 80 (5), 68 (5), 67 (13), 65 (5), 51 (5)8 41 (11)

7-methyl-2,3,4,5,6,7-hexahydrocyclopent[*b*]azepin-8(1*H*)-one (17): MS 165 (100), 164 (32), 150 (20), 137 (33), 136 (43), 122 (83), 109 (51), 108 (62), 95 (70), 94 (46), 81 (29), 80 (28), 67 (59), 55 (24), 54 (24), 53 (34)

7-methyl-2,3,6,7-tetrahydrocyclopent[*b*]azepin-8(1*H*)-one (18): MS 163 (78), 162 (100), 148 (16), 134 (10), 121 (3), 120 (18), 106 (16), 93 (15), 91 (15), 80 (10), 79 (17), 77 (18), 66 (11), 65 (17), 53 (11), 52 (12), 51 (11)

[a] Abbreviations: s = singlet, t = triplet, m = multiplet, mc = center of a multiplet, br s = broad singlet, dd = doublet of doublets. [b] Tentatively assigned. [c] Structure unknown, presumably 3-hydroxy-4-(1-pyrrolyl)butanal.

trometry; **2** and **3** were also formed on heating hydroxyproline with pyruvaldehyde and 2,3-butandione, respectively. **5** was transformed into **4** by catalytic hydrogenation. **6** was generated in the hydroxyproline/erythrose model experiment and purified by adsorption chromatography. The mass spectrum suggested a hydroxy derivative of **4**. Both components possess a base peak at m/e 80 (corresponding to a azafulven cation or pyridinium cation) that is further degraded by loss of HCN into a fragment of m/e 53 ($C_4H_5^+$) (Porter and Baldas, 1971). The fragment m/e 135 (M – 18) shows a hydroxy group in **6**. The ^1H NMR spectrum exhibited the typical pattern of a 1-pyrrolyl system (δ 6.25, 6.64 (each mc, 2 H)) and an A_2X_2 system due to the methylene protons of the hydroxyethyl group. The singlet at δ 4.66 (2 H) is consistent with the >NCH_2CO group. The IR spectrum confirmed a carbonyl (1710 cm^{-1}) and a hydroxy group (3400 cm^{-1}). Therefore, all spectroscopic data are in agreement with the proposed structure. The mass spectrum of **7** did not permit a structural assignment. **7** was isolated and enriched from the hydroxyproline/erythrose model system by preparative GC. The IR spectrum exhibited a carbonyl band (1725 cm^{-1}). The ^1H NMR spectrum showed three heteroaromatic protons and three methylene groups.

Decoupling experiments established the structure of **7** as 5,6,7,8-tetrahydroindolizin-6-one. Upon irradiation of the multiplet a 6.01 ppm the two methine signals at 6.17 and 6.57 ppm were simplified to doublets, showing the expected coupling constant of 2.8 Hz. Simultaneously, the methylene signal at 3.09 ppm was sharpened, building up a symmetrical AA'XX' pattern together with the multiplet

Table II. Pyrroles Characterized in Hydroxyproline/Monosaccharide Model Experiments: a, 2 h, 100 °C; b, 1.5 h, 150 °C (Figures Represent Concentrations in ppm)

		ERY		ARA				ERY		ARA	
		a	b	a	b			a	b	a	b
1		10	90	30	70	10		-	10	75	3600
2		280	2000	320	660	11		-	-	8	20
3		+	10	-	5	12		-	-	130	90
4		15	80	-	10	13		-	-	50	15
5		5	200	-	-	14		-	-	7	150
6		770	7900	-	-	15		15	150	-	-
7		5	150	-	-	16			340 c		
8		5	50	-	-	17		-	70	-	-
9		5	45	-	-	18		-	5	-	-

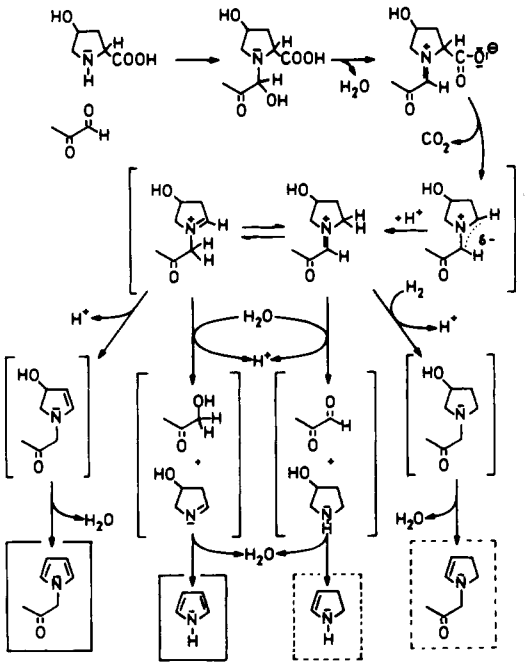

Figure 1. Formation of 1-acetonylpyrrole and pyrrole.

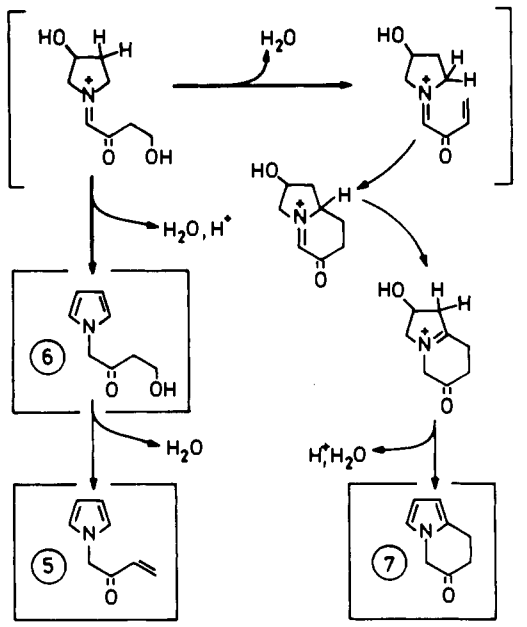

Figure 2. Formation of 4-hydroxy-1-(1-pyrrolyl)-2-butanone, 1-(1-pyrrolyl)-3-buten-2-one, and 5,6,7,8-tetrahydroindolizin-6-one in hydroxyproline/erythrose model experiments.

at 2.72. These observations established the allylic position of the methylene group at 3.09 ppm (relative to the methine proton at 6.01 ppm) and the direct connection to a second methylene group, the chemical shift of which (2.72 ppm) is in agreement with a neighboring carbonyl group. Finally, the singlet at 4.54 ppm (2 H) is consistent with an $>NCH_2CO$ arrangement. The mass spectrum of **7** showed a major fragment at m/e 106 (M - 29) and a base peak at m/e 93 (M - 42). As shown in Figure 2 compounds **6** and **7** may be formed via 3-deoxytetrosone in the erythrose/hydroxyproline model experiment. **8** and **9** were generated as minor constituents in the erythrose/hydroxyproline model experiment. Their concentrations were too low for NMR spectroscopic investigations. The mass spectrum of **8** suggested an isomer of **7** and was similar to that of 5,6,7,8-tetrahydroindolizin-8-one (Shigematsu et al., 1975). This compound was formed in a glucose/proline model experiment. But the isolated 5,6,7,8-tetrahydroindolizin-8-one was not consistent with compound **8**. The mass spectrum of **8** possessed a parent peak at m/e 135. **8** was reduced with $NaBH_4$ to a compound with parent peak at m/e 137 and transformed into an oxime with methoxyhydroxylamine. The mass spectrum of **8** showed a fragment at m/e 118 (M - 17) that was also detected in the spectrum of 5,6,7,8-tetrahydroindolizin-8-one and may be formed from the enol derivative. The base peak of **8** at m/e 106 (M - 29) indicates a carbonyl group in **8**. According to mass spectrometric fragmentation **8** was tentatively identified as 3-methyl-2,3-dihydro-1*H*-pyrrolizin-2-one. The mass spectrum of **9** suggested an isomer of **6**. Both compounds possessed parent peaks at m/e 153 and were reduced with $NaBH_4$ to compounds with parent peaks at m/e 155. The base peak at m/e 94 (M - 59) is consistent with 1-hydroxy-3-(1-pyrrolyl)-2-butanone. This compound was also formed as a minor constituent by the reaction of hydroxyproline with 1-hydroxy-2,3-butanedione generated by hydrolysis of the corresponding 1-bromo derivative (Doerner, 1958).

Components **8** and **9** may be formed from 1-deoxytetrosone in a similar reaction sequence as outlined for compounds **6** and **7** from 3-deoxytetrosone. Compound **10** was formed as main compound in the hydroxyproline/arabinose model experiment. The MS and ^1H NMR spectra of **10** are consistent with 1-furfurylpyrrole formed on heating hydroxyproline with furfuraldehyde. Compounds **11–14** were generated in the hydroxyproline/arabinose model experiments. Compounds **11** and **12** showed similar mass spectrometric fragmentations (M - 29, M - 43, M - 56), and **12** was transformed into **11** by catalytic hydrogenation. **11** was formed on heating 1,2-cyclopentanedione with hydroxyproline and identified as 2-(1-pyrrolyl)cyclopentanone. The IR spectrum exhibited a carbonyl band at 1740 cm^{-1} typical of five-membered ring systems. The ^1H NMR spectroscopic data are consistent with the proposed structure, showing the typical pattern of a pyrrolyl group (δ 6.22, 6.69 (each mc, 2 H)) and a more complex spectrum of the cyclopentane protons. The chemical shift of the double doublet due to the methine proton (δ 4.43 (J = 12, 8 Hz)) clearly demonstrates the 2-position of the pyrrole group in **11**. The mass spectrum of **12** suggested a pyrrolylcyclopentenone. By catalytic hydrogenation **12** was transformed into **11**. **12** was isolated from the hydroxyproline/arabinose experiment by preparative GC and investigated by ^1H NMR spectroscopy. The spectroscopic data showed a pyrrolyl group with increased chemical shift difference (6.22 and 7.25 ppm, respectively) as observed in *N*-(3-oxo-1-propen-2-yl)pyrrole units. In addition there are two strongly coupled methylene groups at 2.61 and 2.69 ppm that form a symmetrical AA'BB' pattern upon decoupling of the olefinic proton signal and the α'-H signals (both at 7.25 ppm). Thus, the structure was clearly established as 2-(1-pyrrolyl)-2-cyclopenten-1-one (**12**).

According to mass spectrometric fragmentation **13** was identified as an isomer of **12**. **13** was transformed into **11** by catalytic hydrogenation. The mass spectrometric fragmentation of **13** [parent peak at m/e 147, a fragment at m/e 121 (M - 26), base peak at m/e 118 (M - 29), a major fragment at m/e 93 (M - 54)] is consistent with 5-(1-pyrrolyl)-2-cyclopenten-1-one.

The mass spectrum of **14** [parent peak at m/e 165, base peak at m/e 134 (M - 31), a major fragment at m/e 106 (M - 59)] suggested a hydroxymethyl derivative of **7**. **14** was reduced with $NaBH_4$ to a compound with a parent peak at m/e 167, base peak at m/e = 136 (M - 31), and a major fragment at m/e 118, comparable to the product

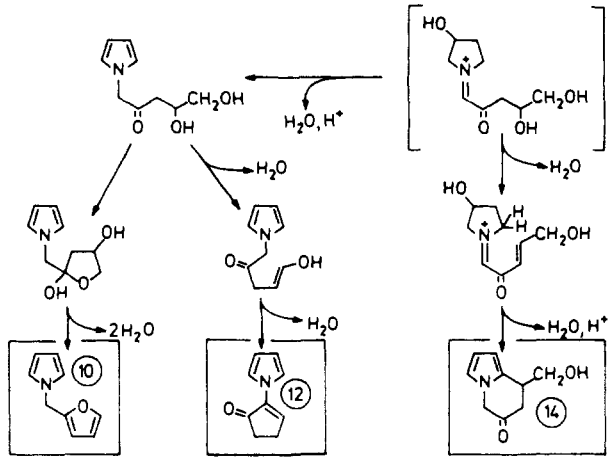

Figure 3. Formation of 1-furfurylpyrrole, 2-(1-pyrrolyl)-2-cyclopenten-1-one, and 8-(hydroxymethyl)-5,6,7,8-tetrahydroindolizin-6-one in hydroxyproline/arabinose model experiments.

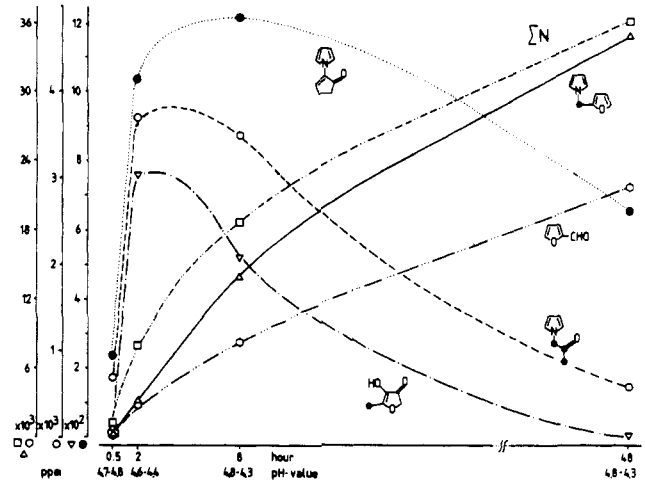

Figure 4. Concentration of some components in the hydroxyproline/arabinose model experiments as a function of reaction time (at 100 °C).

formed by reduction of **7**. Therefore, **14** was tentatively identified as a (hydroxymethyl)-5,6,7,8-tetrahydroindolizin-6-one. The IR spectrum confirmed a carbonyl (1720 cm^{-1}) and a hydroxy group (3400, 1060 cm^{-1}). Attempts to prepare a pure NMR sample of **14** by HPLC failed. The ^1H NMR spectrum of the isolated mixture of compounds indicated exchangeable proton signals as well as several signals in the pyrrole, OCH_2, and $COCH_2$ regions, but the very complex pattern did not permit an accurate assignment. The mass spectrum of compound **15** [base peak at *m/e* 80, parent peak at *m/e* 153, fragments at *m/e* 135 (M − 18) and *m/e* 106 (M − (18 + 29)] suggested an isomer of **6**. It was not possible to isolate **15** for NMR spectroscopic investigation. **16** is formed as main component on heating hydroxyproline with ascorbic acid. According to mass spectrometric fragmentation **16** was tentatively identified as 2,3-dihydroxy-5-(1-pyrrolyl)-2-cyclopenten-1-one. The mass spectra and retention times of **17** and **18** were consistent with 7-methyl-2,3,4,5,6,7-hexahydrocyclopent[*b*]azepin-8(1*H*)-one and 7-methyl-2,3,6,7-tetrahydrocyclopent[*b*]azepin-8(1*H*)-one, which were recently identified in proline/glucose model experiments (Tressl et al., 1985). The formation of pyrroles and 5,6,7,8-tetrahydroindolizin-6-ones in hydroxyproline/monosaccharide model experiments depends on the reducing sugars and the reaction conditions. As shown in Table II the concentrations of individual constituents increase 10–50-fold during pressure cooking at 150 °C compared to 100 °C. The formation of pyrroles may be explained by Strecker degradation of α-dicarbonyls as outlined in Figure 1. This reaction sequence is comparable to a sequence observed for the closely related proline (Tressl et al., 1985). The reactive iminium ion from hydroxyproline undergoes dehydration to pyrrole and 1-acetonylpyrrole. 3-Hydroxy-1-pyrroline and 3-hydroxypyrrolidine were not detected. In addition we did not observe the ring enlargement resulting in pyridine derivatives, which has been demonstrated for proline (Tressl et al., 1985). α-Dicarbonyls are transformed into the corresponding pyrroles and into pyrrole and α-hydroxy ketones. Compounds **4–9** were characterized in the erythrose experiment. Figure 2 presents a scheme that may explain the formation of the typical C_4 components via 3-deoxyosone route. 3-Deoxytetrosone is transformed into **6** as main product, which is further dehydrated to **5**. During this reaction **7** may be formed from the iminium intermediate by Michael addition. In an analogous reaction **8** and **9** may be formed via 1-deoxytetrosone. Arabinose (as well as xylose, ascorbic acid, and glucuronic acid) acts as precursor for **10–15**. The formation of **10**, **12**, and **14** may be explained via 3-deoxypentosone as outlined in Figure 3. **10** is formed on heating hydroxyproline with furfuraldehyde as main component. In an analogous reaction 1,2-cyclopentanedione is transformed into **11**. **16** was tentatively identified in the hydroxyproline/ascorbic acid experiment and may be formed via a reductinic acid type precursor. It is interesting that **17** and **18** (which were recently characterized as proline-specific compounds (Tressl et al., 1985)) are also formed in the hydroxyproline/erythrose experiment. Most of the hydroxyproline-specific components, presented in Table II, are methylene active and form colored products during heating. Figure 4 presents the changes of individual components in the hydroxyproline/arabinose experiment during heating at 100 °C. It can be seen that norfuraneol, **2**, and **12** exhibit maxima after 2–4 h, and their concentrations decrease after 8–48 h by aldol type reactions. On the other hand the amounts of **10** and furfuraldehyde increase continuously with the reaction time.

Registry No. 1, 109-97-7; **2**, 4805-24-7; **3**, 98612-18-1; **4**, 98612-19-2; **5**, 98612-20-5; **6**, 98612-21-6; **7**, 98612-22-7; **8**, 98612-23-8; **9**, 98612-24-9; **10**, 1438-94-4; **11**, 98612-25-0; **12**, 98612-26-1; **13**, 98612-27-2; **14**, 98612-28-3; **15**, 98612-29-4; **16**, 99573-49-6; **17**, 97826-66-9; **18**, 97826-67-0; 4-hydroxyproline, 51-35-4; erythrose, 1758-51-6; arabinose, 147-81-9; 2-hydroxy-2-cyclopenten-1-one, 10493-98-8; 2-ethoxy-2-cyclopenten-1-one, 40006-64-2.

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