New Colored Compounds from the Maillard Reaction between Xylose and Lysine

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An aqueous xylose−lysine model system was heated for 1 h under reflux, and the colored ethyl acetate-extractable compounds were separated. The structural elucidation of the first three-ring colored compound ever isolated from this Maillard model system and the partial characterization of a second one are described. Structure elucidation was based mostly on heteronuclear two-dimensional NMR.

Keywords: *Maillard reaction; nonenzymic browning; colored compounds; lysine; xylose; heteronuclear two-dimensional NMR*

INTRODUCTION

Color formation is one of the most important effects of the Maillard reaction. Most of the colored compounds formed are melanoidins, i.e., high molecular weight polymers. Owing to their disordered structures, they are particularly difficult to study and little information is available regarding them (Ames and Nursten, 1989; Ledl and Schleicher, 1990). More work has been done on the characterization of low molecular weight colored compounds that could represent some of the substructures incorporated into melanoidins. They were isolated only from model systems, often from simple amine/sugar mixtures. Among amino acids, only glycine and lysine have been investigated. Few of the isolated compounds could be completely characterized: in general they have two (Severin and Kronig, 1972; Ledl et al., 1983; Nursten and O'Reilly, 1983; Banks et al., 1988) or three rings (Ledl and Severin, 1978; Nursten and O'Reilly, 1986). These rings often contain oxygen or nitrogen and are frequently linked by a −CH═ group. Many other compounds have been isolated, but they were insufficiently pure or in such a small amount that complete structural elucidation was not possible (Nursten and O'Reilly, 1983, 1986).

In the present paper, we describe the purification and characterization of a new compound from the reaction between xylose and lysine and give further structural information on a compound already isolated by us (Ames et al., 1993).

MATERIALS AND METHODS

Materials. D-(+)-Xylose, L-lysine monohydrochloride, ethyl acetate, ethanol, chloroform, and methyl acetate were of analytical grade and were used without any purification. Methanol for HPLC was purchased from Baker, and water for HPLC was produced with a Milli-Q Water purification System (Millipore). Preparative TLC was performed on silica gel 60 F254 plates (Merck, 20 × 20 cm^2, thickness 2 mm, with concentration zone 4 × 20 cm^2). Samples for HPLC were filtered through disposable Nylon 66 filters (0.45 μm, Alltech).

HPLC Analyses. They were conducted on a HP-1050 quaternary pump fitted with a Rheodyne injector (20 μL loop) and equipped with a HP-1050 diode array detector (DAD). The system was controlled by an HP ChemStation (DOS Series, Hewlett-Packard). Spectral data were recorded from 220 to 550 nm for peaks of interest (peak width, 0.05 min; threshold, 1.00 mAU). Semipreparative HPLC was performed using a similar pump equipped with a Rheodyne injector (200 μL loop), an UV−visible detector Waters Lambda Max model 481, or a HP-1050 variable wavelength detector.

The analytical column was a Lichrosorb RP-18 (5 μm, 250 × 4 mm^2, Merck, Germany), and the flow rate was 1 mL/min. The semipreparative column was a Supelcosil SPLC-18 (5 μm, 250 × 10 mm^2, Supelco, U.S.), used with a flow rate of 2 mL/min. The samples were dissolved in methanol:water (60:40).

Gradients used were (ratios refer to the percentage of methanol and water, M/W) as follows: (A) from 0/100 M/W to 100/0 M/W over 60 min; (B) from 30/70 M/W to 55/45 M/W over 30 min, then to 100/0 over 5 min; (C) from 30/70 M/W to 100/0 M/W over 35 min; (D) from 30/70 M/W to 85/15 M/W over 10 min, to 91/9 M/W over 17 min, then to 100/0 M/W over 3 min.

Mass Spectrometry (MS). Direct introductions were performed on a Finnigan-MAT TSQ70 with an ICIS Data System. Chemical ionizations (CI-MS) were obtained using isobutane as the reagent gas. FAB spectra (FAB-MS) were produced using a standard FAB source and a Xenon Ion Tech Gun. Thioglycerol, glycerol, and nitroglycerol were used as matrices. Liquid chromatography/mass spectrometry (TS-MS) was performed on a Finnigan-MAT TSQ700 interfaced through a Thermospray TSP-2 to a liquid chromatographer Waters 600-MS fitted with a UV−vis Waters 486 detector and a Rheodyne injector 7125 (20 μL loop). Eluents tested were CH_3OH:H_2O (35:65), $AcONH_4$ (0.05 M):CH_3OH (35:65), $AcONH_4$ (0.05 M) (100%), and CF_3COOH (1%). The data were acquired by a computer DEC station J120 (Digital Equipment Co.) equipped with an ICIS data system. UV and mass profiles were acquired simultaneously.

UV−Visible Spectroscopy. UV−visible spectra were obtained over the range 200−600 nm using a Jasco mod. 7800 instrument controlled by the SCAN JAS 7800 program.

Nuclear Magnetic Resonance Spectroscopy (NMR). ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX-600 spectrometer at 600 and 150.9 MHz, respectively. CH_3-OH-d_4 and DMSO-d_6 were used as solvents, and tetramethylsilane was used as the internal standard. Chemical shifts were expressed in parts per million (δ). Heteronuclear two-dimensional $^1H-^{13}C$ correlations (one-bond), heteronuclear multiple quantum correlations (HMQC; Bax and Morris, 1981), and multiple-bond correlations (HMBC; Bax and Summers,

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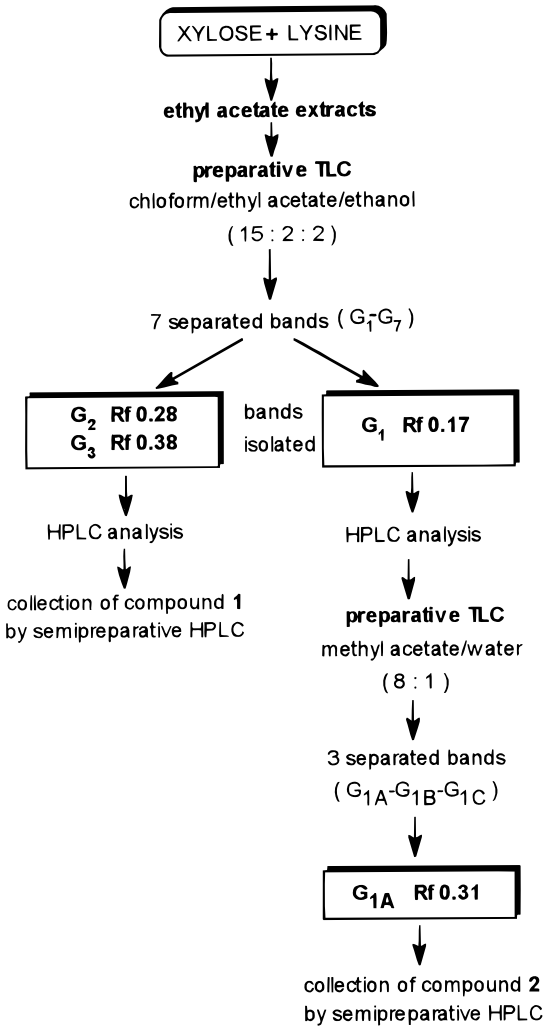


Figure 1. Sequence adopted for the purification of compounds **1** and **2**.

1986) were carried out in the ^{1}H-detected mode with broadband decoupling in the ^{13}C domain.

Preparation of the Model System. Lysine monohydrochloride (91.33 g, 0.5 mol) and xylose (75.06 g, 0.5 mol) were dissolved in distilled water (0.5 L, previously boiled). The solution was heated for 1 h at 100 °C under reflux. During this time, the pH value dropped from 5.22 to 2.66. The resulting brown mixture was extracted with ethyl acetate (6 × 200 mL). The combined extracts were dried with sodium sulfate, and the solvent was evaporated under vacuum at 40 °C. The residue (0.52 g) was dissolved in methanol, analyzed by HPLC-DAD with gradient A, and separated into different fractions by TLC. Colored compounds were purified by semipreparative HPLC.

Compound Separation. The sequence adopted for the purification of compounds **1** and **2** is illustrated in Figure 1. TLC separations were conducted on silica gel using as eluent a mixture of chloroform/ethyl acetate/ethanol (15:2:2). Seven bands (G1-G7) were detected in daylight and under ultraviolet radiation at 366 nm. They were scraped from the TLC plate and extracted with methanol. The solvent was filtered and concentrated, and the residue was analyzed by HPLC-DAD.

Purification of Compound 1. The two yellow bands G2 and G3, with R_f values of 0.28 and 0.38, respectively, both showed an interesting compound with an absorbance maximum in the visible region when analyzed by HPLC/DAD with gradient A. Purification was carried out by repeated injections of 200 μL of the sample on the semipreparative RP-18 column using gradient B, which had been optimized for this purpose. Using these conditions, the retention time (t_R) was 22 min. During this procedure, the UV−visible detector was set at 400 nm. After evaporation of the solvents, the purity of the yellow compound **1** (solid, 1.4 mg) was checked by HPLC-DAD.

Purification of Compound 2. Band G1, with an R_f value of 0.17, was analyzed by HPLC-DAD, with gradient A. It was further separated by TLC on silica gel using methyl acetate/water (8:1) as the mobile phase. The most polar band G1A was isolated and analyzed by HPLC-DAD with gradient C, and a colored compound with t_R = 18 min was isolated by semipreparative HPLC, using gradient D and monitoring at 410 nm. After the evaporation of the solvent, compound **2** was obtained as a yellow solid (0.8 mg). Its purity was checked by HPLC-DAD.

RESULTS

Heating an equimolar mixture of lysine and xylose produces a very large number of different reaction products. The color of the reaction mixture is dark brown owing mainly to the presence of melanoidins but also partly to the low molecular weight colored compounds. Two compounds of the latter class were isolated from the ethyl acetate soluble fraction. Starting from 0.5 mol of each reagent and refluxing without pH control, 0.52 g of a dark brown residue was obtained. The first separation was achieved by preparative TLC (see Figure 1) and permitted the recovery of seven bands which were analyzed by HPLC using a diode array detector. Bands G2 and G3 with R_f values of 0.28 and 0.38, respectively, were chosen for further purification because both showed the presence of the same colored product whose spectrum was different from those of all the compounds isolated previously from the same model systems. Band G1 contained a compound already isolated by us but whose structure had not been completely elucidated (Ames et al., 1993).

Further purification of the two colored compounds was achieved by semipreparative HPLC.

Compound 1. After HPLC purification of bands G2 and G3 using gradient B, HPLC-DAD analysis with gradient A showed that the purity of the compound was satisfactory (98% at 400 nm). The electronic absorption spectrum had maxima at 400, 260, and 310 nm, indicating extended delocalization. CI-MS gave an intense ion at 289 *m/z* (55%), which indicated that the molecular weight of the compound was 288 amu. A relatively high degree of fragmentation resulted: the ion at 258 *m/z* (18%) corresponded to a loss of CH_2O, at 242 *m/z* (5%) to a loss of 46, at 211 *m/z* (15%) to a loss of 46 + 31, and at 113 *m/z* (14%). The base peak was at 97 *m/z*. The molecular weight was confirmed by FAB-MS.

The even molecular weight suggested that no or an even number of nitrogens was present in the molecule. Starting from the hypothesis of no nitrogens, some of the most reasonable empirical formulas could be $C_{17}H_{20}O_4$, $C_{16}H_{16}O_5$, or $C_{15}H_{12}O_6$.

The structural elucidation was based mostly on NMR experiments in methanol-d_4 and in DMSO-d_6. Table 1 shows the chemical shifts of the 12 hydrogens present in the molecule, supporting the hypothesis that the molecular formula is $C_{15}H_{12}O_6$. Decoupling (Table 2) and D_2O exchange experiments permitted the sequences of correlated hydrogens to be established: $H_A-H_D-H_C$ (reasonably a monosubstituted furan ring), H_K-H_B, H_G-H_M, H_L-H_K, and H_F-H_I (CH_2OH).

Despite the small amount of compound available, the use of heteronuclear two-dimensional spectra, using an inverse detection method, allowed us to obtain complete information on the ^{13}C chemical shifts and one-bond (Figure 2) or multiple-bond (Figure 3) correlations (Tables and 3). Six quaternary carbons were detected: C_9 at 131.3 ppm, C_3 at 141.5 ppm, C_{12} at 152.0 ppm, C_1 at 172.7 ppm, and C_8-C_{11} at 189.3 ppm.

Table 1. ^{1}H Chemical Shifts and ^{1}H−^{13}C Correlations of Compound 1 in Methanol-d_4

^{1}H	chemical shift (ppm)	integral	multiplicity	^{13}C one-bond correlation	^{13}C multiple-bond correlation
A	7.88	1	d	C_{15}	$C_{12}-C_{13}-C_{14}$
B	7.47	1	d	C_{10}	$C_7-C_9-C_{12}-C_{11/8}$
C	7.07	1	d	C_{13}	$C_{12}-C_{14}-C_{15}$
D	6.67	1	dd	C_{14}	$C_{12}-C_{13}-C_{15}$
E	6.58	1	s	C_2	$C_1-C_3-C_4$
F	5.90[a]	1 OH	t		
G	4.11	1	t	C_4	
I	4.54	2	s	C_5	C_1-C_2
K	4.36	1	dt	C_7	C_3-C_9
L	4.29	1	ddd	C_6	C_3-C_9
M	4.17	1	ddd	C_6	C_3-C_9

[a] Chemical shift obtained in DMSO-d_6.

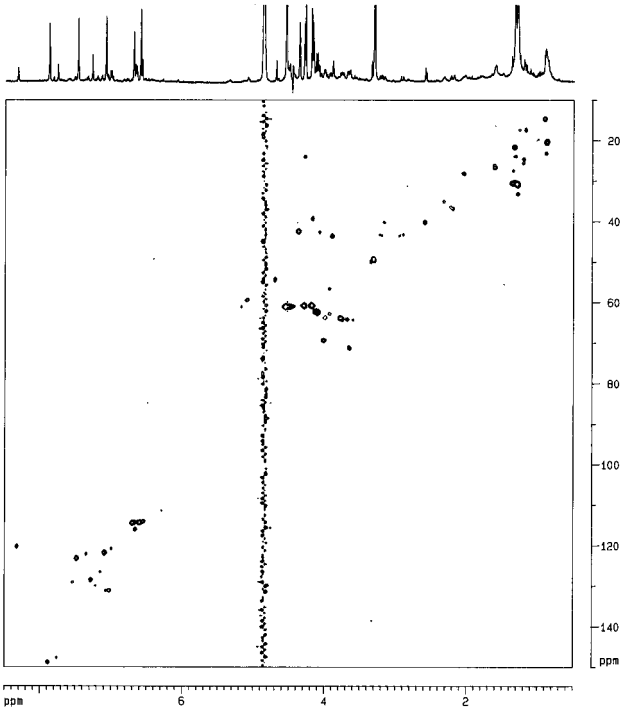


Figure 2. Inverse heteronuclear correlation spectrum ^{1}H−^{13}C (one-bond) of compound 1 in methanol-d_4.

Table 2. Hydrogen Coupling Constants *J* (Hz) of Compound 1 in Methanol-d_4

	A	B	C	D	E	I	K	L	M
A				1.8					
B							1.6		
C				3.5					
D	1.8		3.5						
E						1.1			
I					1.1				
K		1.6						2.4	3.4
L							2.4		11.0
M							3.4	11.0	

These results confirmed the presence of a monosubstituted furan ring (structure **3**); sequence H_F-H_I corresponds to structure **4**, while sequence $H_G-H_{L,M}-H_K$ has an aliphatic character (structure **5**). H_B is attached to a carbon of a double bond at 123.1 ppm and has a

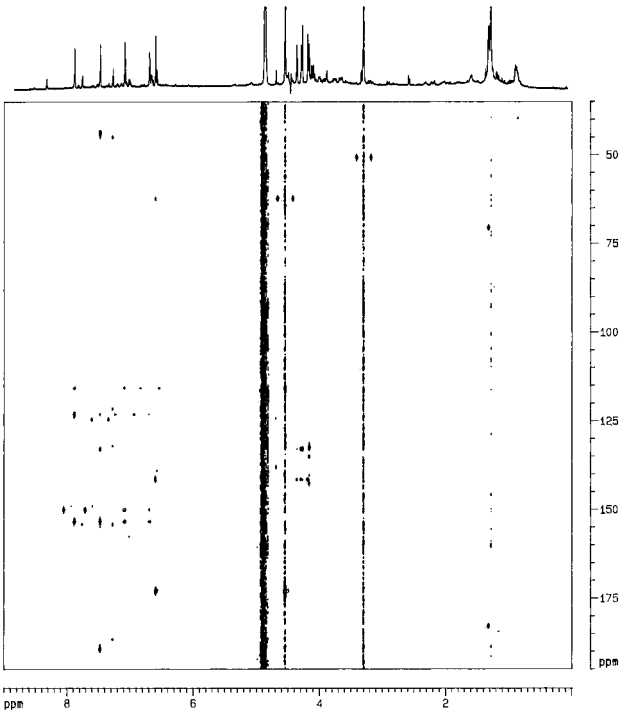


Figure 3. Inverse heteronuclear correlation spectrum ^{1}H−^{13}C (multiple-bond) of compound **1** in methanol-d_4.

Table 3. ^{13}C Chemical Shifts of Compound 1 in Methanol-d_4

name	chemical shift (ppm)	feature
C_1	172.7	quat.
C_2	115.1	CH
C_3	141.5	quat.
C_4	63.6	CH
C_5	62.5	CH_2
C_6	62.2	CH_2
C_7	43.7	CH
C_8	189.3	quat.
C_9	131.3	quat.
C_{10}	124.4	CH
C_{11}	189.3	quat.
C_{12}	152	quat.
C_{13}	123.1	CH
C_{14}	115.5	CH
C_{15}	150.3	CH

long-range coupling with one of the two carbonyls at 189.3 ppm (structure **6**). The long-range correlation of the same hydrogen with the carbon at 43.7 ppm permits the connection of fragments **5** and **6** to give **7**. H_E, a singlet at 6.58 ppm, is attached to the carbon at 115.1 ppm, and its correlations suggest fragment **8**. The same hydrogen has a long-range coupling with the carbon at 43.7 ppm which permits the connection of fragments **4** and **8** (structure **9**). Connecting together all the fragments, the proposed structure is **1**, which is also supported by the fragment at *m*/*z* 113 in the mass spectrum (Chart 2).

Compound 2. Band G1 was submitted to a second TLC separation on silica gel, using methyl acetate/water as the mobile phase, and three bands were separated. Band G1A was removed and further purified by semi-preparative HPLC with gradient D. Its purity was checked by HPLC-DAD with gradient C (92% at 410 nm), and the compound had a t_R of 18 min. The UV−visible spectrum had maxima at 410, 330, and 245 nm.

As conventional mass spectrometry (DIS-EI, DIS-CI, and FAB) gave unclear results, TS-MS was used. All the solvents examined gave the same results (see Materials and Methods). The spectra were clear with

Chart 1

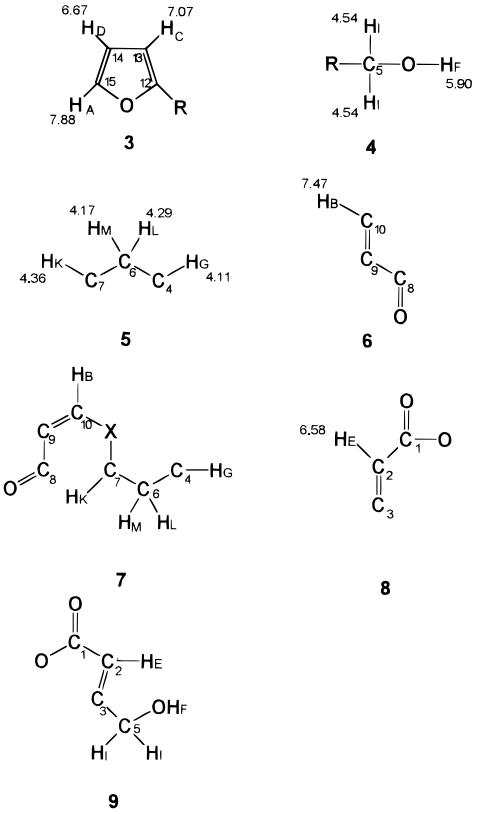
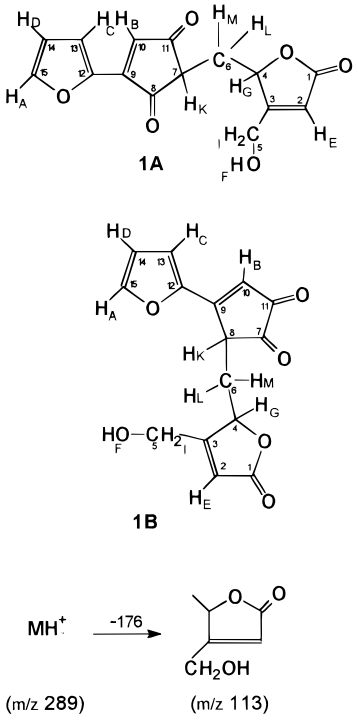


Chart 2



an intense molecular ion and a limited number of fragments. The molecular ion is a duplet at 483−485 *m/z* (50−58%), which suggests the presence of two compounds, with molecular weights of 482 and 484 amu, possibly differing for the presence of a double bond. The most relevant fragments are singlets at 308 *m/z* (10%, M − 174), 264 *m/z* (13%, M − 218), 234 *m/z* (12%, M − 248), 212 *m/z* (base peak, M − 270), 182 *m/z* (65%, M − 300), and 168 *m/z* (%).

NMR spectra were registered in CH_3OH-d_4, DMSO-d_6, and $CDCl_3$ at 300 or 600 MHz. The best results were

Table 4. ^{1}H Chemical Shifts and ^{1}H−^{13}C Correlations of Compound 2 in DMSO-d_6

^{1}H	chemical shift (ppm)	integral	multiplicity	^{13}C one-bond correlation	^{13}C multiple-bond correlation
A	8.04	1	d	147.8	113.0−119.3−149.8
B	7.96	1	s	129.0	125.3−142.5
C	7.58	1	d	141.8	106.9−110.2−151.6
D	7.43	1	s	120.0	27.4−125.3−170.6
E	7.33	1	d	117.4	67.5−120.0−126.7−149.8−179.2
F	7.18	1	d	119.3	147.8−149.8
G	6.76	1	dd	113.0	147.8−149.8
I	6.42	1	dd	110.2	141.8−151.6
K	6.24	1	d	106.9	141.8−151.6
L	5.88	1	m	67.5	117.4−126.3
M	5.45	1 OH	all		
N	5.32	1 OH	all		
O	4.23	1	d	60.4	126.3
P	4.05	1	d	60.4	126.3
Q	3.90	2	s	27.4	142.5−151.6

Table 5. Hydrogen Coupling Constants *J* (Hz) of Compound 2 in DMSO-d_6

	A	C	E	F	G	I	K	L	O	P
A					1.6					
C						2.2				
E								1.8		
F					3.5					
G	1.6			3.5						
I		2.2					3.2			
K						3.2				
L			1.8							
O										12.0
P									12.0	

obtained in DMSO-d_6 at 600 MHz. The ^{1}H NMR showed 16 hydrogens (Table 4). Two of them are due to hydroxyl groups (H_M and H_N) because they disappear by addition of D_2O. Couplings between hydrogens are shown in Table 5. The following sequences could be recognized: H_A−H_G−H_F, H_C−H_H−H_I, H_E−H_L, and H_O−H_P, while H_{Q2}, H_D, and H_B are singlets. It was also possible to obtain a satisfactory natural abundance direct ^{13}C NMR spectrum, while inverse heteronuclear correlation gave ^{1}H−^{13}C one-bond (Figure 4) and multiple-bond correlations (Figure 5). Ten quaternary carbons were detected, and only three of them did not show long-range correlations. H_A−H_G−H_F and H_C−H_H−H_I have ^{1}H and ^{13}C chemical shifts and coupling constants typical of a furan ring (fragments **10** and **11**). H_E at 7.33 ppm connected to a carbon at 117.4 ppm indicates the presence of a double bond. It has a 1.8 Hz coupling with H_L at 5.88 ppm. This low coupling constant is consistent with an allylic coupling. H_E also has a long-range coupling with the carbonyl at 179.2 ppm and a carbon in position 2 of furan **10**. It is therefore possible to assemble fragment **12**. The quaternary carbon at 126.3 ppm has a long-range coupling with the geminal spin system (4.05 and 4.23 ppm, J = 12 Hz). These chemical shifts are typical of a CH_2OR group. This group can be connected to fragment **12** at position R_2 or R_3, but position R_2 can be eliminated due to the lack of coupling with the vinylic hydrogen H_E (structure **13**). Similar observations permitted to complete structure **11**. The peak at 3.9 ppm integrates for

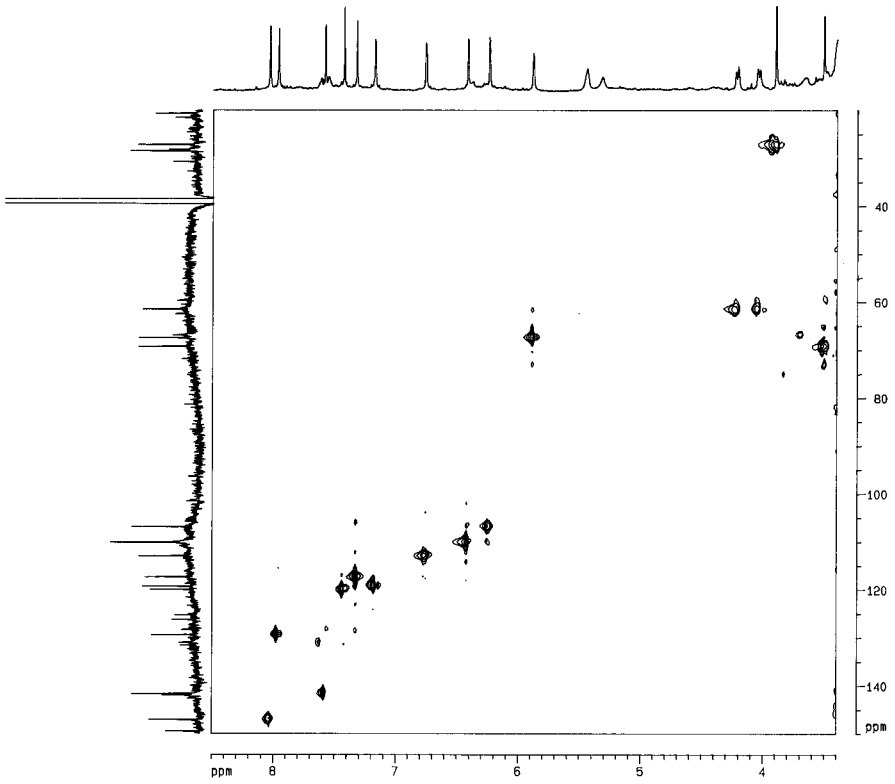


Figure 4. Inverse heteronuclear correlation spectrum $^{1}H-^{13}C$ (one-bond) of compound **2** in DMSO-d_6.

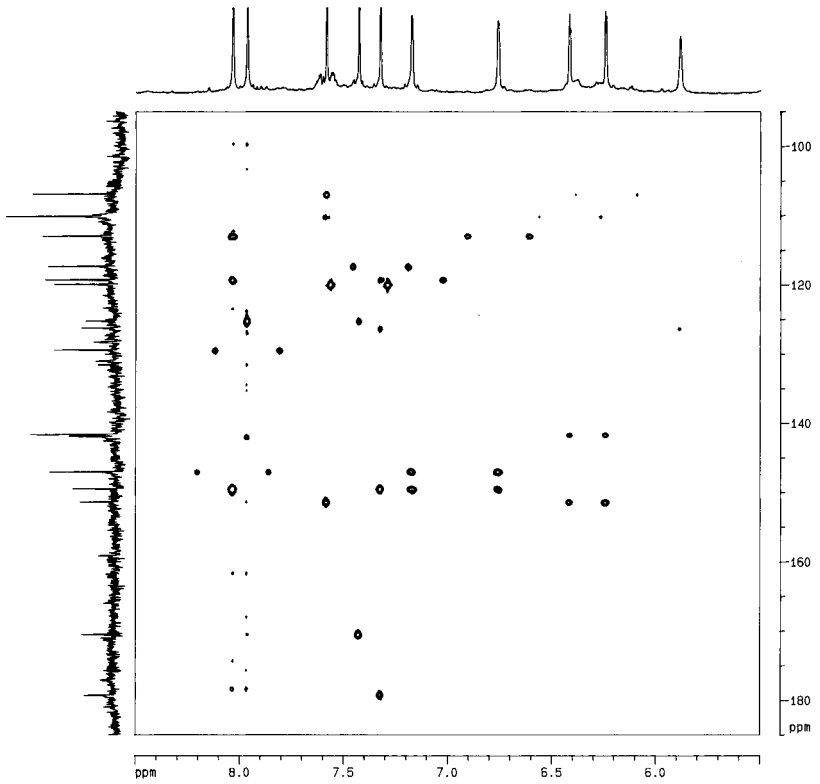
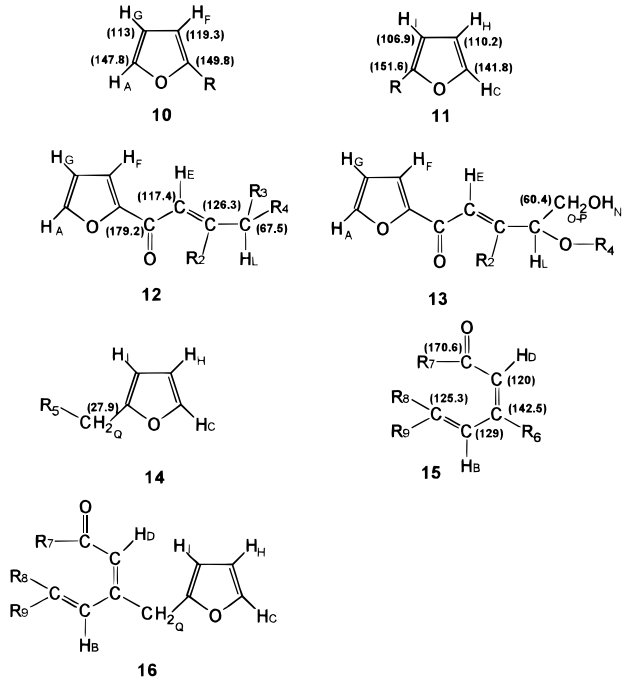


Figure 5. Inverse heteronuclear correlation spectrum $^{1}H-^{13}C$ (multiple-bond) of compound **2** in DMSO-d_6.

two hydrogens and is directly linked to a carbon at 27.4 ppm. This value indicates the presence of a methylene group without heteroatoms. These hydrogens are correlated with a quaternary carbon at 151.6 ppm on the furan ring (fragment **14**). It was also possible to build another short chain which contains protons H_B and H_D (fragment **15**). This new structure is consistent with the correlation between H_D and a carbonyl at 170.6 ppm, with a chemical shift typical of an ester. The quaternary carbon at 142.8 ppm presents several correlations with H_D and H_B and H_{Q2} of fragment **14**. Fragments **14** and **15** can therefore be assembled to give fragment **16**. Taking into account the presence of another OH (H_M), it is possible to arrive at the empirical formula $C_{19}H_{16}O_8$ for fragment 13 and 16 corresponding to a mass of 372 amu. A total of 110 amu is necessary to reach the molecular weight of 482 amu. At high field, both ^{1}H and ^{13}C NMR spectra contained some contamination which could hide some signals, and the proposed substructures could be connected through oxygens

Chart 3



which are not directly detectable by ^{1}H and ^{13}C NMR. TS-MS spectra, lacking abundant fragments at high mass, are not able to indicate how the fragments **13** and **16** are connected.

DISCUSSION

Two colored compounds were separated from a xylose−lysine model system by a complex procedure involving ethyl acetate extraction and TLC and HPLC separation.

Compound **2** was already separated by us some years ago (Ames et al., 1993). At that time it was possible to report only limited information regarding its structure. The isolation of a larger sample permitted the collection of MS spectra which gave a molecular weight of 482−484 amu. Previously, FAB-MS had been performed and had indicated a molecular weight of 445 amu. The difference is probably due to the different behavior of this compound when submitted to the two techniques.

Carefully planned 2D NMR experiments gave an almost complete picture of one-bond and multiple-bond $^{1}H-^{13}C$ couplings and ^{13}C chemical shifts and permitted the proposal of some substructures. Nevertheless, a complete structure elucidation was not possible. The purity of the compound was only 92%, and traces of impurities at high field, perhaps due to column bleeding, could hide some ^{1}H and ^{13}C signals. However, the compound certainly has two furan rings. Furan rings are present in most of the known colored Maillard compounds and can derive from the electrophilic condensation on a nucleophilic carbon of furfural, which is the main decomposition product of xylose. In structure **15** there is another five-carbon sequence, probably deriving from xylose. The other substructures derive probably from the recombination of fragments coming from retroaldol cleavage of the sugar (Ledl and Schleicher, 1990).

Although it was impossible to completely elucidate the structure, it must be underlined that this study reports data for the low molecular weight colored Maillard compound with the highest molecular weight ever recorded.

The lower molecular weight of compound **1** simplified its analysis, and structure **1A** is in very good agreement with both MS and NMR data. In this case it is also difficult to unravel the sequence of reactions which produced this compound, but recombination of fragments deriving from xylose by aldol condensation can be postulated. The carbon skeleton of xylose is easily identifiable in the sequence C9−C12−C13−C14−C15 and perhaps in C1−C2−C3−C4−C6.

Another possible structure of the same compound could be **1B**, in which the sequence C10−C11−C8−C7−C6 could derive directly from xylose. Taking into account the $^{1}H-^{13}C$ couplings this structure is acceptable, but it was excluded because the identical chemical shifts of C11 and C8 favor structure **1A**.

This compound is the first colored compound deriving from the reaction of xylose and lysine containing three rings whose structure has been completely elucidated. In the past, another three-ring compound was isolated by Nursten and O'Reilly (1986), from a xylose−glycine model system.

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