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Thermal decomposition of ascorbic acid [1]

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Abstract

Thermal degradation of L-ascorbic acid at 300 °C in the absence of a solvent yielded mostly furan derivatives and α,β-unsaturated cyclic ketones with a five-membered ring. Some of the furan derivatives are the same as those obtained in the Maillard reaction, with the reductones undergoing retroaldol reaction, decarboxylation, oxidation, and hydrolysis. In propylene glycol, under milder conditions (180 °C), the carbonyl and dicarbonyl derivatives resulting from the decomposition react with the solvent and give cyclic acetals and ketals (1,3-dioxolanes). The products were identified by GC–MS using the SPECMA data bank.

Keywords: Ascorbic acid; Thermal degradation; GC-MS analysis; Furan derivatives

1. Introduction

L-Ascorbic acid (**1**, further referred to as ascorbic acid) is a well-known natural antioxidant and vitamin (vitamin C) which is widely distributed in nature, especially in green plants. It is also synthesized in the liver of most vertebrates (such as rats). However, humans, monkeys, and guinea pigs do not possess the enzymes necessary for its biosynthesis and hence they have to supplement their diets with ascorbic acid.

Ascorbic acid, the first vitamin to be discovered, exhibits antiscorbutic properties (prevention of scurvy). It is used as a food additive, a flour improver in bakeries, an animal food additive, an antioxidant, and for the prevention of the common cold, certain types of cancer, and other diseases. It acts as an efficient radical inhibitor.

Structurally, ascorbic acid (**1**) is a sugar acid, a γ-lactone, and an enediol. It is unstable and is easily oxidized to dehydro-L-ascorbic acid (**2**). Its function in the various biochemical reactions is thought to be related to its activity as a biological oxidation–reduc-

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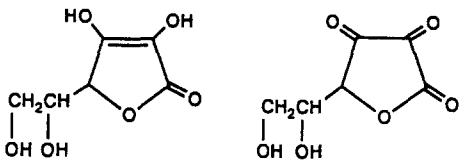
tion agent, hydrogen carrier, and free-radical trap. The anion of ascorbic acid is resonance-stabilized.



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The most important sources of ascorbic acid in the human diet are various fruits (especially citrus fruits), vegetables, herbs (parsley), grasses and, to a lesser extent, meats (liver) [1–3].

Upon heating of these foods, ascorbic acid behaves in the same fashion as reducing sugars in the Maillard reaction [4–9]. Its degradation products react with amino acids, peptides, and lipids (or their degradation products) and give rise to a large number of aromatic and polymeric products (melanoidins) via nonenzymatic browning reactions.

Kurata and Sakurai showed that degradation of ascorbic acid in an acidic medium leads to decarboxylation, formation of an intermediate 3-deoxy-L-pentosulose, and subsequent cyclization to furfural [10]. Later, they reported on the oxidative degradation of ascorbic acid, identifying furfural, L-*threo*-pentos-2-ulose, 3-deoxy-*glycero*-pentos-2-ulose-1,4-lactone, and ethylglyoxal as the major products [11].

The Maillard reaction between ascorbic acid and twenty amino acids was studied at 44 and 72 °C by Yu et al. [12]. Thermal degradation of ascorbic acid and dehydroascorbic acid results in the formation of ten substituted furans [13]. Spectroscopic studies (^{1}H-, ^{13}C-NMR, and ESR) were used to elucidate the structure of dehydroascorbic acid and to investigate its reactions from the physiological point of view [14].

During concentration of citrus juices on an evaporator, the initial higher temperature leads to oxidation of ascorbic acid while concentration under diminished pressure preserves ascorbic acid better [15]. Related studies have dealt with the effect of ascorbic acid and oxygen on the nonenzymatic browning reactions in orange juice [16,17], and on the oxidation and degradation of ascorbic acid [18]. Shin and Feather examined the stability of ascorbic acid under physiological conditions alone, in the presence of α-*N*-formyl-L-lysine at pH 7.0 in a phosphate buffer, and in the presence of oxygen [19]. Degradation of the intermediate L-*threo*-hex-2,3-diulosonic acid yielded threonic, oxalic, glyceric, and glyoxylic acid.

Other studies have examined the effect of ascorbic acid and fructose on the nonenzymatic browning of peeled and crushed tomatoes [20], on the reducing properties of ascorbic acid in the presence of complex-forming metal ions [21], the kinetics of sulfite inhibition of browning of ascorbic acid [22], and the kinetics of formation of threose from ascorbic acid, dehydroascorbic acid, and L-*threo*-hex-2,3-diulosonic acid, in the presence and in the absence of oxygen, at pH 7.0 and 37 °C [23].

Cysteine hydrochloride exerts a protective effect upon preservation of ascorbic acid in processed pineapples and guavas [24]. Related studies have investigated the variations of ascorbic acid content and its effect on the quality and stability of pulp obtained from a single type of fruit or their combinations (guava–citrus, guava–mango, citrus–mango) [25].

Feather [9] has described the active role of ascorbic acid in the Maillard reaction, as a follow-up on several earlier articles [26,27]. At pH 7.90 and 37 °C, ascorbic acid is unstable in the presence of oxygen, even in the absence of compounds with amino groups. It decomposes with the formation of carbonyl compounds which subsequently react with amines in the Maillard reaction giving threose, glyceraldehyde, L-*threo*-pentosulose, and 3-deoxy-L-*glycero*-pentosulose [19].

The foregoing survey of the literature demonstrates an interest in studies of ascorbic acid as a reducing sugar in the Maillard reaction. These studies were carried out in an aqueous medium under different conditions, with the variables including, but not limited to, pH, temperature, various additives (amino acids, peptides) and inhibitors (metal ions, sulfites), and the presence or absence of oxygen and various oxidizing agents (thermal degradation).

Here, we have investigated the dry thermal degradation of ascorbic acid (without a solvent) at 300 ± 10 °C and its thermal degradation in propylene glycol (a food solvent) at 180 °C.

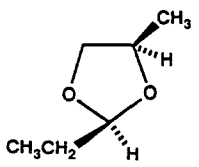
2. Experimental

General methods.—Dry degradation of ascorbic acid. Ascorbic acid (**1**, 1.0 g, 5.68 mmol) was heated at 300 ± 10 °C in a pyrolyzer, with dynamic entraining under N_2. The carrier gas (N_2) carried the volatile components of pyrolysis into three traps where they

were absorbed in Et_2O at a temperature below −20 °C. The ether solution was filtered through a silica gel column, the ether was evaporated, and the volatile degradation products were analyzed by GC–MS (for conditions, see *GC–MS analyses*).

Degradation of ascorbic acid in propylene glycol at 180 °C. Ascorbic acid (**1**, 3.6 g, 0.0204 mol) was added to anhydrous propylene glycol (20 mL, 20.7 g, 0.27 mol). The mixture was heated on an oil bath to 180 °C and stirred for 6 h. No ascorbic acid was detectable by thin-layer chromatography (TLC) after 6 h. The mixture was extracted with 7:3, v/v petroleum ether–CH_2Cl_2, the extract was dried (Na_2SO_4) and quickly filtered through a silica gel column under diminished pressure. The solvents were removed on a rotary evaporator and the residue was analyzed by GC and GC–MS.

Synthesis of the acetals.—Synthesis of (Z)- *and* (E)-*2-ethyl-4-methyl-1,3-dioxolanes.* Propylene glycol (20 mL, 20.7 g, 0.27 mol) and propanal (19.6 mL, 15.8 g, 0.27 mol) were placed in a 100-mL flask and *p*-toluenesulfonic acid (0.5 g) and anhydrous Na_2SO_4 (10 g) were added to remove water formed during the reaction. The mixture was refluxed for 6 h at 77 °C. After 6 h, no propanal could be detected in the mixture by GC. The mixture was neutralized with 2 M NaOH, the organic layer was separated, washed with water, dried (Na_2SO_4), and filtered. The acetals were distilled at atmospheric pressure between 113–115 °C [28], while the higher-boiling products were distilled under diminished pressure (20 mm Hg). The residue was analyzed by TLC and by GC–MS. The GC–MS analysis indicated the presence of three products: the two isomeric 2-ethyl-4-methyl-1,3-dioxolanes (**3** and **4**, *Z* and *E*, respectively, total 70%) in a ratio $Z:E = 2:1$, and 2-methyl-2-pentenal (**5**, 30%) resulting from the aldol reaction of propanal. This α,β-unsaturated aldehyde is clearly more stable than the corresponding unsaturated acetals which were not detected.



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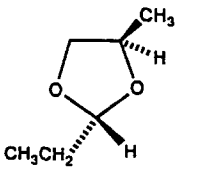

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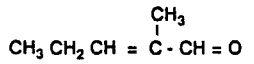

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The mass spectra of the synthesized 1,3-dioxolanes were identical with their spectra reported in the literature [29] and the spectra obtained after the reaction of ascorbic acid with propylene glycol.

Other acetals and ketals. Other acetals and ketals can be obtained from the corresponding aldehydes and ketones in the same fashion as described above but at different temperatures and with different reaction times. They can be distilled under diminished pressure.

Analyses.—Thin-layer chromatography (TLC). Ready-made silica gel chromatographic plates were used to follow the course of the various reactions just described. The following eluting solvents were used: (a) For the degradation of ascorbic acid: 1:1, v/v AcOEE–EtOH; (b) for the synthesis of acetals: petroleum ether or *n*-hexane for alkyl-1,3-dioxolanes (low polarity), 9:1, v/v benzene–EtOH for more polar compounds. The spots were detected in ultraviolet light at 254 nm.

Gas chromatography (GC). Analytical GC separations were performed on an Intersmat IGC 120 FL gas chromatograph fitted with a capillary nonpolar OV-1 column (50 m × 0.25 mm i.d.) and a flame-ionization detector. The temperature was programmed from 70 to 220 °C at 2 °C/min (injected sample 0.06 μL; sensitivity S4 or S16). Integrations were carried out with an Intersmat ICR-1B integrator and were not corrected for varying detector responses.

GC–MS analyses. Mass spectra were recorded on a Ribermag R-10.10 mass spectrometer (quadrupole) at an ionizing potential of 70 eV. The instrument was coupled to a Delsi 700 gas chromatograph with a nonpolar DB1 column (50 m × 0.35 mm i.d). The temperature was kept for 5 min at 80 °C and then programmed from 80 to 180 °C (or 200 °C) at 3 °C/min and from 200 to 300 °C at 8 °C/min. In the case of the dry degradation at 300 ± 10 °C, the analyses were performed on a GC–MSP Hewlett–Packard instrument at an ionizing potential of 70 eV. The conditions were: helium as the carrier gas (34 mL/s), MSD-HP 5971A detector, nonpolar capillary OV-1 column (25 m × 0.2 mm × 0.33 μm), injected

sample volume 3 μL, temperature 40 °C for 5 min, then programmed from 40 to 240 °C at 6 °C/min and from 240 to 280 °C at 10 °C/min, detector temperature 180 °C, interface temperature 280 °C.

Identification. Using our program, the gas-chromatographic data (Kováts indices) and the mass spectra were compared with the information in our GC–MS SPECMA data bank. In most cases, this com-

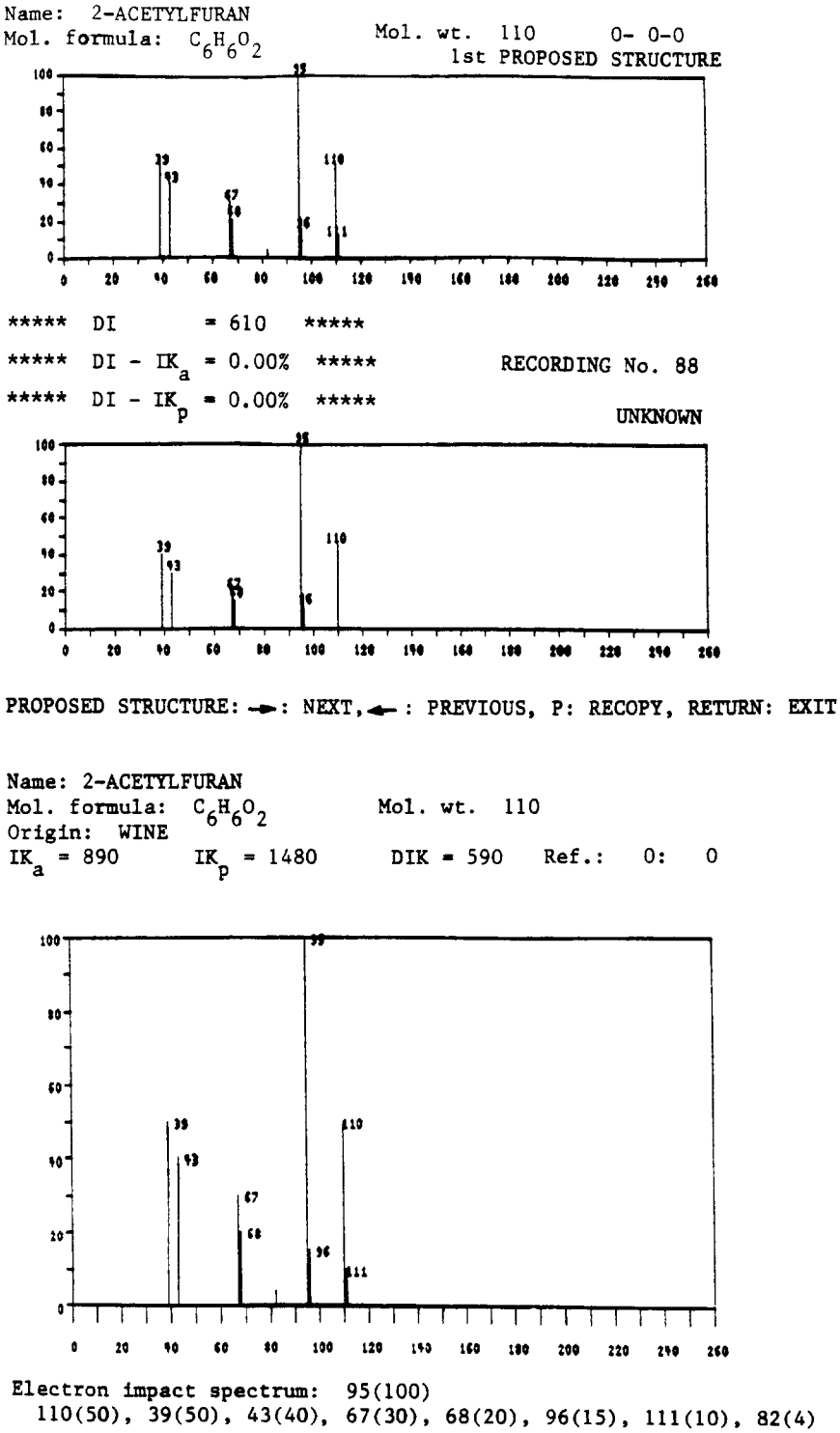
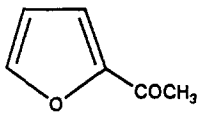


Fig. 1. GC–MS SPECMA data bank identification of 2-acetylfuran (**6**). Top spectrum: Reference spectrum of 2-acetylfuran in the SPECMA data bank, with its molecular weight, molecular formula, and registry number. Middle spectrum: The unknown. Bottom spectrum: The top spectrum reproduced in detail. Dissimilarity index, DI = 6–10.

puter-executed comparison resulted in a positive identification of the respective compounds. An example of the identification procedure is shown in Fig. 1. The dissimilarity index, DI, indicates the degree of agreement between the respective spectra. When DI = 00, the spectra are identical. The higher the value of DI, the more different the spectra. When DI > 25-50, the spectrum is filed as an 'unknown'.

3. Results and discussion

Dry degradation of ascorbic acid at 300 ± 10 °C. — GC–MS analysis of the reaction mixture. The mixture resulting from the thermal degradation of ascorbic acid (2–3 min at 300 ± 10 °C) was analyzed by GC–MS. Out of the 32 separated products, ca. 20 compounds were identified, as shown in Table 1, with their respective structures presented in Scheme 1. The identification was accomplished using the SPECMA data bank. As an example, the procedure is illustrated for 2-acetylfuran (**6**) in Fig. 1. In this case, the dissimilarity index, DI, is 6–10. This indicates a very good agreement between the respective mass spectra.



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A comparison of the data in Table 1 with the

Table 1
GC–MS SPECMA data bank analysis of volatile products from thermal degradation of ascorbic acid at 300 °C

No.	Compound[a]	Scans[b]	Mol wt	*m/z*[c]
7	Butanedione	51	86	43, 86
8	A cyclic acetal	110	104?	45, 73, 43, 103
9	Unidentified	133	?	69, 39, 41, 40
10	Toluene (artifact)	214	92	91, 92, 65
11	$C_5H_6O_2$	436	98	40, 39, 41, 69, 98, 44
12	Furfural	490	96	96, 95, 39
13	$C_5H_6O_2$	634	98	40, 55, 98
14	2(or 3)-Methyl-2-cyclopenten-1-one	777	96	67, 96, 69
6	2-Acetylfuran	796	110	95, 110, 67
15	4,5-Dehydro-γ-butyrolactone	812	84	55, 84, 39
16	2-Hydroxy-2-cyclopenten-1-one	854	98	98, 55, 69
17	4-Methyl-2-cyclopenten-1-one	999	96	67, 96, 81, 95
18	2-Cyclohexen-1-one	1017	96	68, 96
19	2-Methyltetrahydrofuran-3-one	1070	100	67, 96, 81, 95
20	2-Hydroxy-2-cyclohexen-1-one	1105	112	43, 44, 55, 100
21	A methyl ketone	1135	114	43, 58, 69, 11
22	2-Hydroxy-3-methyl-2-cyclopenten-1-one (cyclotene)	1217	112	112, 55, 69, 83
23	$C_6H_{10}O_2$	1269	114	114, 55, 69, 85, 86
24	Unidentified	1317	?	70, 69, 55
25	Furoic acid	1415	112	95, 112
26	2-Hydroxy-3-ethyl-2-cyclopenten-1-one	1536	126	126, 56, 83
27	1-(2-Furyl)-2-hydroxy-1-propanone	1607	140	95, 140
28	A furoyl derivative	1651	122	109, 122, 95
29	A methyl ester, and a furan deriv.	1777	–	60, 73; 95, 110
30	A furoyl derivative	1906	?	95, 71
31	Unidentified	1966	–	97, 69, 95
32	2-Furoylfuran	2295	162	95, 162
33	Unidentified	2450	?	43, 69, 58
34	Isomer of No. **26**	2475	–	97, 95, 69
35	BHT (ether antioxidant)	2532	220	205, 220
36	Furil (*bis*-2,2-furoyl)	2675	190	95, 110
37	Unidentified	2824	?	95, 87, 69

[a] Principal reaction products are furfural (**12**, ≈ 70%), 2-hydroxy-2-cyclohexen-1-one (**20**, ≈ 10%), and furoic acid (**25**, ≈ 8%). The structures of the most important compounds are shown in Scheme 1.
[b] Nonpolar column (SE 30, 25 m × 0.35 mm id).
[c] Principal fragments are arranged in order of decreasing intensity.

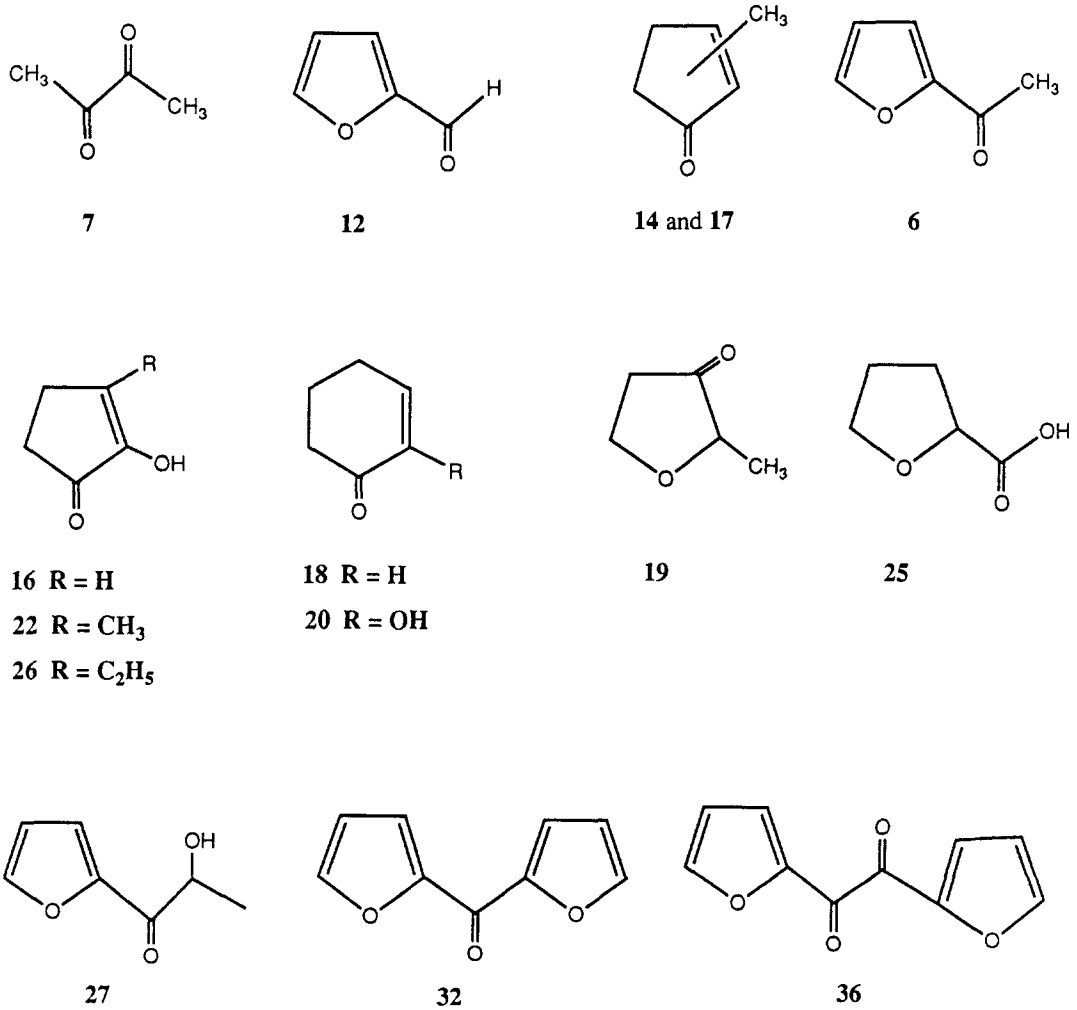
results obtained by Velíšek et al. [13] shows that some of the products identified in our study were the same, such as furfural (**12**), 2-acetylfuran (**6**), furoic acid (**25**), and furil (**36**). On the other hand, we were able to identify 2-cyclopenten-1-ones (**14**, **16**, **17**, **22**, **26**), 2-cyclohexen-1-one (**18**) and its 2-hydroxy derivative (**20**), 1-(2-furyl)-2-hydroxy-1-propanone (**27**), and 2-furoylfuran (**32**). Twelve compounds could not have been identified on the basis of their mass spectra because of the unavailability of the reference spectra and the absence of molecular ions.

The fragment with *m/z* 95 for the compound **29**, as well as the fragments with *m/z* 95 and 97 obtained in the mass spectra of **31** and **34** seem to suggest structures with the furoyl and dihydrofuroyl groups, respectively $[C_4H_4O \cdot C(O)-$ and $C_4H_4O \cdot CH(OH)-$, where C_4H_4O = furyl]. However, furoin, which is a combination of the foregoing two structures (mol wt 192) has not been found, perhaps because of its oxidation to furil (**36**).

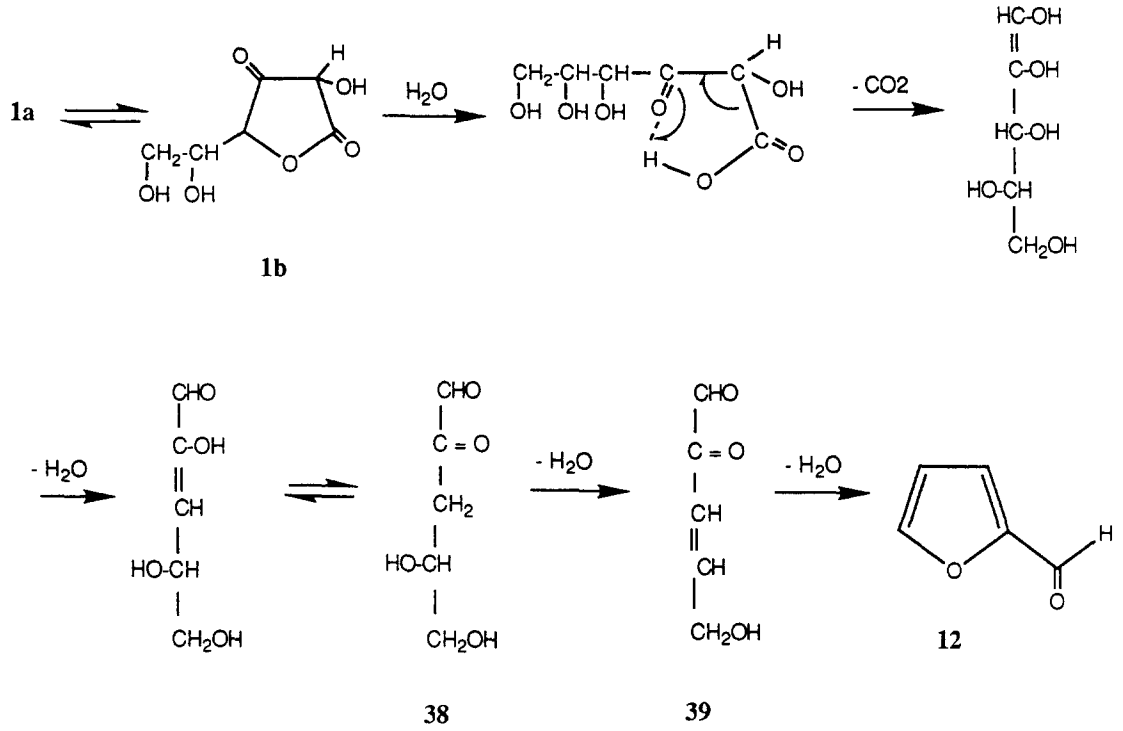
In future studies, positive chemical ionization (PCI/NH_3 or $PCI/iso\text{-}C_4H_{10}$) may permit the generation of quasimolecular ions of unidentified products and the determination of their structures.

It is noteworthy that the decomposition products of ascorbic acid are the same as those found among the degradation products of reducing sugars (in the presence or in the absence of amino acids) and in roasted food products (coffee). The principal reaction product is furfural (**12**, ca. 70%, followed by 2-hydroxy-2-cyclohexen-1-one (**20**, ≈ 10%) and furoic acid (**25**, ≈ 8%) which is formed by oxidation of furfural. Other products are present in smaller amounts.

Mechanism of formation of the principal reaction products. The suggested mechanism of formation of the principal reaction products is shown in several

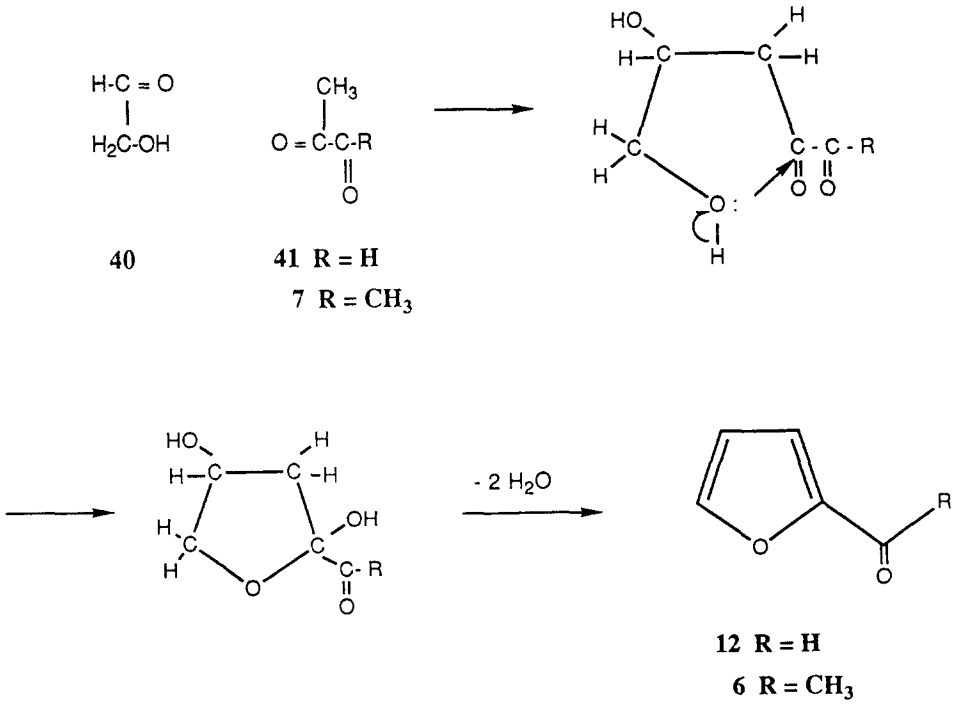


Scheme 1.



Scheme 2.

schemes. Scheme 2 presents the possible formation of furfural (**12**) via 3-deoxyopentosulose (**38**) and 3,4-dideoxypentos-3-en-ulose (**39**). However, furfural (**12**) can also be formed from hydroxyacetaldehyde (**40**) and pyruvaldehyde (**41**) (Scheme 3). Similarly, 2-acetylfuran (**6**) results from the condensation of hydroxyacetaldehyde (**40**) and butanedione (**7**) (Scheme 3). In both cases, the starting materials in Scheme 3 arise from thermal degradation of dehydroascorbic acid (**2**). Once formed, furfural (**12**) can participate in aldol reactions with other carbonyl compounds, such as hydroxyacetaldehyde (**40**).

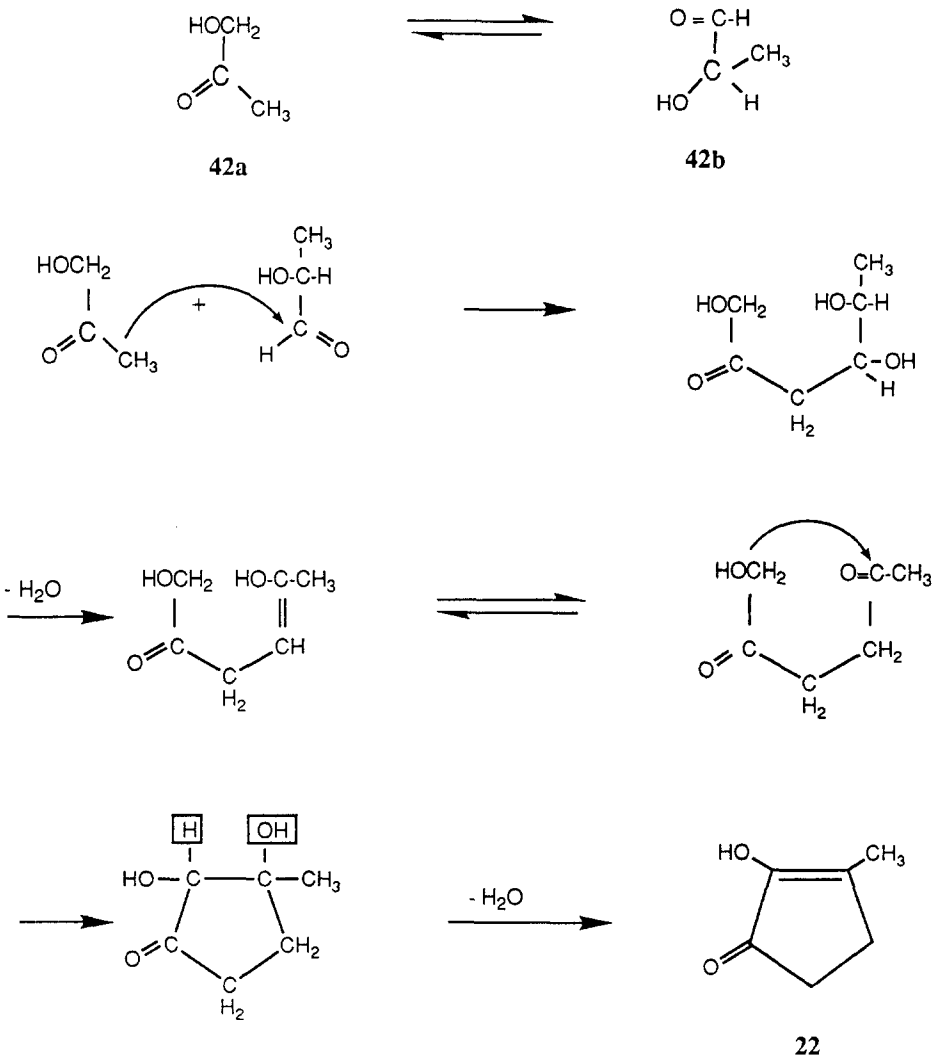


Scheme 3.

Scheme 4 shows dimerization of hydroxyacetone (**42**) and its tautomer leading to the cyclopentene derivative **22** by a consecutive loss of two molecules of water. In a similar fashion, it is possible to explain the formation of 4-alkyl-2-hydroxy-1-cyclopenten-1-ones from hydroxy α-carbonyl compounds, and (2*H*)-

Table 2
Mass-spectral characteristics (electron impact) of the products obtained by degradation of ascorbic acid in propylene glycol at 180 °C[a]

No. (listing)[b]	Scans[c]	Mol wt[d]	*m/z*[e]
1. 2-Substituted 4-methyl-1,3-dioxolanes (different substituents)			
4	236	102	87, 43, 58, 51, 59
7/8	305/312	116	87, 31, 41, 59, 57, 72
15/16	571/587	132	87, 31, 59, 41, 43
17/18	595/610	132	87, 31, 43, 59, 57
30/31	1933/1753	188?	43, 87, 42, 59, 31, 101
38/39	2216/2372	?	87, 42, 43, 57, 115, 129
40	2396	202?	87, 42, 43, 57, 115, 129
41	2490	170?	43, 87, 95, 42, 101, 126
49	3223	228?	42, 87, 100, 144, 173
52/53	3921/3960	228	87, 59, 56, 114
55/56	4281/4329	228	69, 87, 42, 59, 145, 115
57/58	4387/4424	230	69, 42, 59, 87, 145, 115
62/63	5494/5572	286	87, 187, 59 87, 43, 56, 187
68/69	6555/6645	288	87, 85, 143, 212, 59, 41, 31
2. 2-Substituted 2,4-dimethyl-1,3-dioxolanes			
5	261	118	43, 101, 42, 40, 72
14/15	549/571	132	43, 101, 58, 41, 31
22/23	798/818	146	43, 101, 41, 87, 59
27/28	1571/1802	144	43, 101, 87, 59
29/30	1621/1693	144/146	43, 101, 41, 87, 59
3. 1,3-Dioxolanes and other compounds[f]			
19	650	132	57, 29, 43, 87, 102
20	662	132	57, 29, 43, 88, 87, 102
21	684	132	57, 29, 43, 87, 102
25/26	1218/1238	154	95, 100, 81, 154
32/33	1827/1871	188	43, 101, 87
41/42	2490/2564	170	95, 43, 10
43	1732	202?	71, 129, 43
44/45	2773/2860	214	100, 42[g]
46/47	3001/3092	214	100, 42[g]
47	3092	228	114, 96, 41
48/49	3181/3223	214	100, 42
48	3181	228	57, 115, 87, 173
51	3741	?	41, 127, 69
54/55	4150/4280	280	69, 42, 59, 95
59	4942	224	43, 83, 57, 97, 69[h]
61	5288	248	95, 153
64/65	6282/6392	288	85, 87, 201[g]
66/67	6418/6465	288	85, 87, 201[g]
70/71	6804/6852	276–298?	114, 56, 41, 56, 127, 242, 127, 187
72/73	6906/6980	264?	114, 41, 56, 127, 242, 187
77/78	7694/7726	290?	151, 209, 95
79	7993	296	95, 151, 42, 110, 173, 238
80	9802	298	43, 98, 57, 118, 267, 298



Scheme 4.

Notes to Table 2:

[a] GC–MS analysis was carried out on a nonpolar column DB-1 programmed from 70 to 200 °C at 2 °C/min and/or from 20 to 300 °C at 5 °C min.

[b] These correspond to the numbers of the spectra in the listing (from *1* to *80*). Isomer pairs (*Z* and *E*) giving the same mass spectra are placed together.

[c] Number of scans of mass spectra.

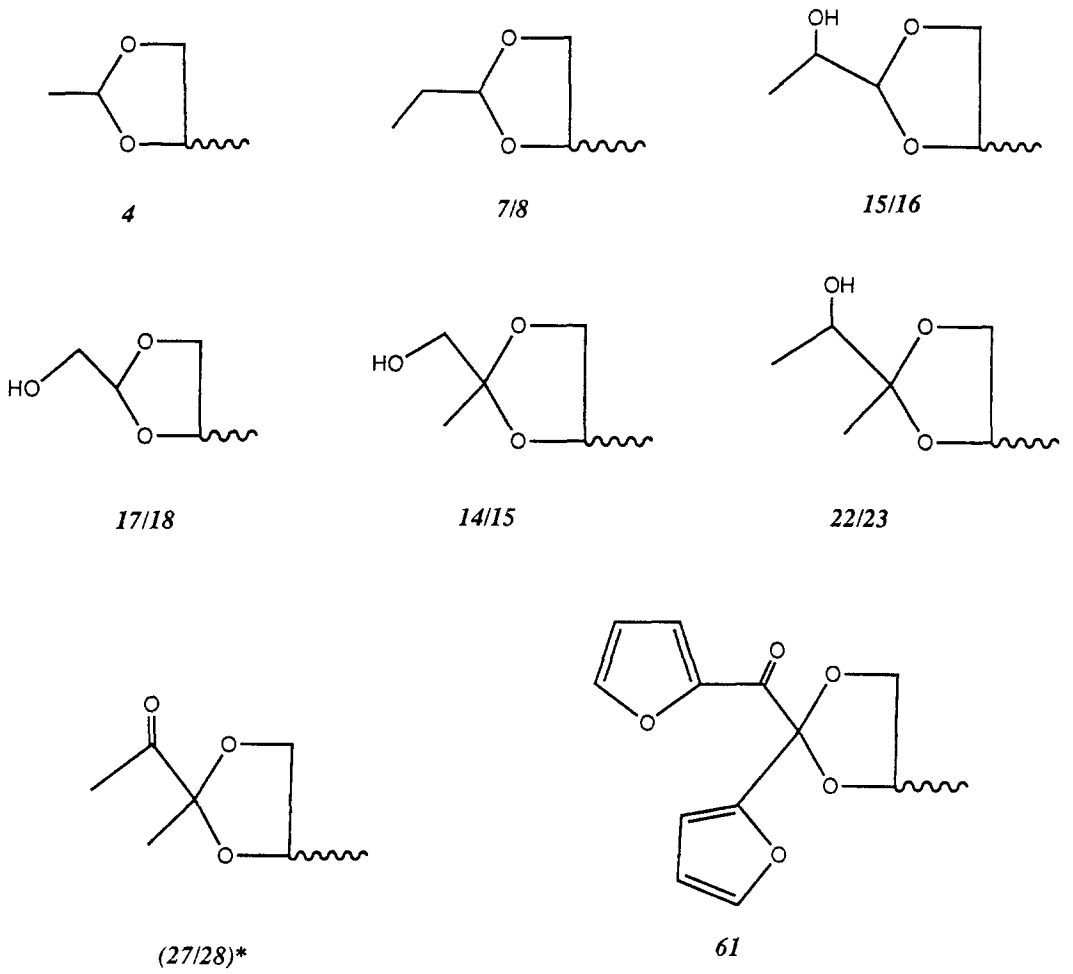
[d] Observable molecular weights are shown. In the case of 2-substituted 1,3-dioxolanes a very low intensity fragment at $(M-1)^+$ or $(M-15)^+$ can be seen.

[e] Principal fragments are shown in the order of decreasing intensity.

[f] The following additional compounds were identified: acetaldehyde (mol wt 44, BP 44), butanedione (mol wt 86, BP 43), propylene glycol (mol wt 76, BP 45), propionic acid (mol wt 74) in a mixture, furfural (mol wt 96, BP 39), 2-acetylfuran (mol wt 110, BP 95), C_{12} and C_{14} linear alkanes, dibutyl phthalate, etc.

[g] Four isomers.

[h] Hexadecene.



Scheme 5. The numbers are listing numbers (Table 2).

and (3*H*)-4,5-dehydrofuranones by ring enlargement from 3-methyl-2-cyclopenten-1-ones (**14**) formed from glyoxal, CHO · CHO, and butanedione (**7**) [2].

Thermal degradation of ascorbic acid in propylene glycol at 180 °C. Dry degradation of ascorbic acid described above takes place under relatively drastic conditions. Thermal degradation of ascorbic acid in propylene glycol at 180 °C, takes place at a temperature analogous to that used in baking of various foods. The results were unexpected: Only a few furan derivatives [e.g., furfural (**12**), 2-acetylfuran (**6**)] were found among the eighty separated products (Table 2). Most products can be characterized by base peaks at *m/z* 87 and 101 and, in some cases, at *m/z* 115 and 129. These fragments are characteristic of the cations based on 2-mono- and 2,2-disubstituted 4-methyl-1,3-dioxolanes, with the *Z*- and *E*-isomers in most cases.

The products shown in Table 2 are divided into three groups. The first group (24 compounds) includes the various 2-substituted 4-methyl-1,4-dioxolanes (R^1 = H). The second group (15 products) are most likely 2-substituted 2,4-dimethyl-1,3-dioxolanes ($R^1 = CH_3$; *m/z* 43 and 101). The third and most important group (37 products) are compounds which have not been positively identified (no reference spectra are available). In some cases, four different isomers were observed (for listing nos. *64*, *65*, *66*, *67*, and for *70*, *71*, *72*, and *73*). Assuming that these products are substituted 1,3-dioxolanes, they should contain a double bond in position 2 of the side chain. The structures of some identified compounds are presented in Scheme 5. The respective precursors of these compounds are acetaldehyde (for listing No. *4*), propanal (for listing Nos. *7/8*), 2-hydroxypro-

[2] Additional schemes with the proposed mechanisms of formation of these compounds are available from the authors.

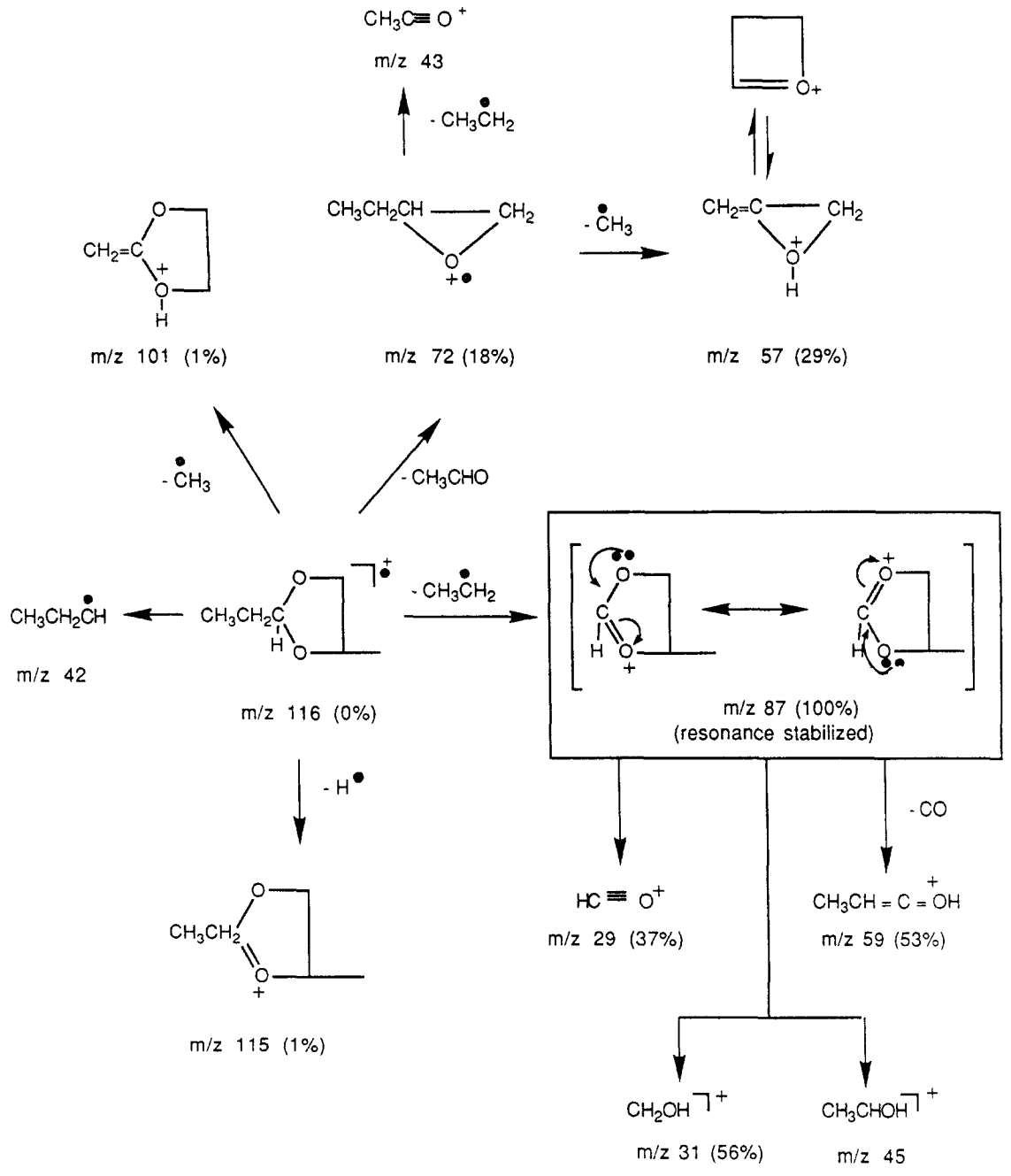
panal (listing Nos. *15/16*), hydroxyacetaldehyde (listing Nos. *17/18*), hydroxyacetone (listing Nos. *14/15*), acetoin (listing Nos. *22/23*), butanedione (listing Nos. *27/28*), and furil (listing No. *61*). All these precursors arise from degradation of ascorbic acid (Scheme 5). Retroaldol reactions lead to pyruvaldehyde, glyoxal, hydroxyacetaldehyde, and 2,3-dihydroxypropanal.

Some of these compounds are quite unstable and undergo ready oxidation to the respective acids or polymerization. Propanal is formed by dehydration of propylene glycol:

$$CH_3CH(OH)CH_2OH \rightarrow CH_3CH{=}CHOH \rightarrow CH_3CH_2CHO$$

Aldol reaction of the latter gives 2-methyl-2-pentenal (**5**). Acetylation is also one of the processes to be considered.

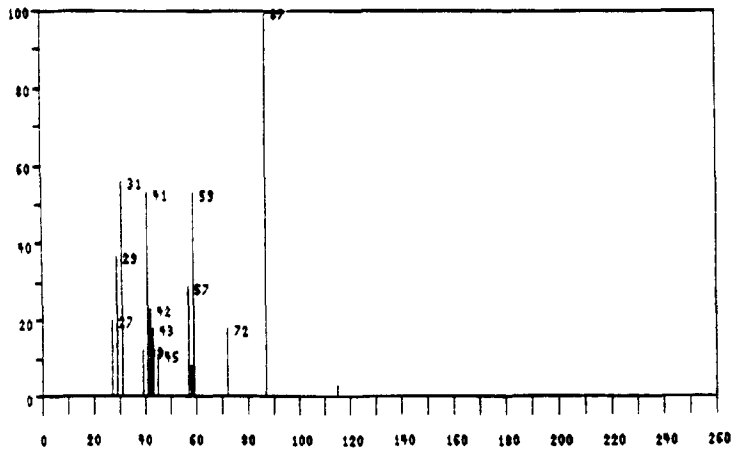
The two most important reaction products are the *Z*- and *E*-isomers with the molecular ion with *m/z*



Scheme 6.

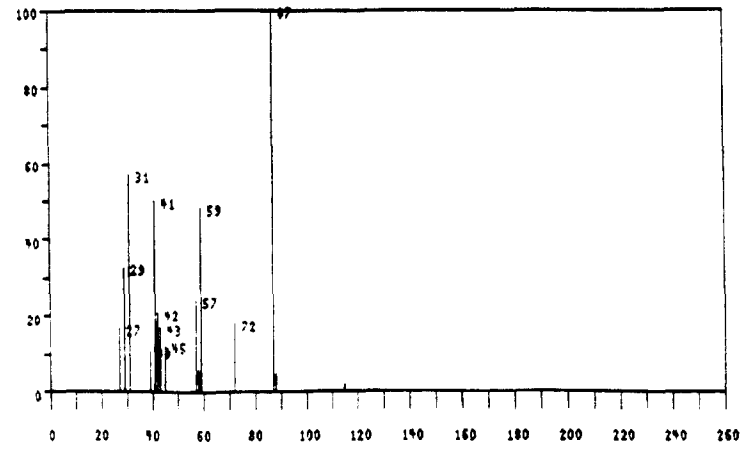
144 and an important fragment at *m/z* 101, characteristic of 2-substituted 2,4-dimethyl-1,3-dioxolanes. It follows from the base peak at *m/z* 43 (144 − 43 = 101) that the substituent is an acetyl group. Thus, the structures assigned to these products are *27* and *28* (listing Nos., Table 2). As an example, Scheme 6 shows the fragmentation of the two isomeric 2-ethyl-4-methyl-1,3-dioxolanes (*Z* and *E*, **3** and **4**, respectively). We have synthesized these two compounds and used the GC–MS data for their positive identifi-

Name: (Z)-2-ETHYL-4-METHYL-1,3-DIOXOLANE
Mol. formula: $C_6H_{12}O_2$ Mol. wt. 116
Origin: VITAMIN C/PROPYLENE GLYCOL; VERNIN & CHAKIB, 1995.
IK_a = 0 IK_p = 0 DIK = 0 Ref.: 0: 0



Electron impact spectrum: 87(100)
31(56), 41(53), 59(53), 29(37), 57(29), 42(23), 27(20), 43(18), 72(18), 39(12), 45(11), 58(8), 115(3)

Name: (E)-2-ETHYL-4-METHYL-1,3-DIOXOLANE
Mol. formula: $C_6H_{12}O_2$ Mol. wt. 116
Origin: VITAMIN C/PROPYLENE GLYCOL; VERNIN & CHAKIB, 1995.
IK_a = 0 IK_p = 0 DIK = 0 Ref.: 0: 0



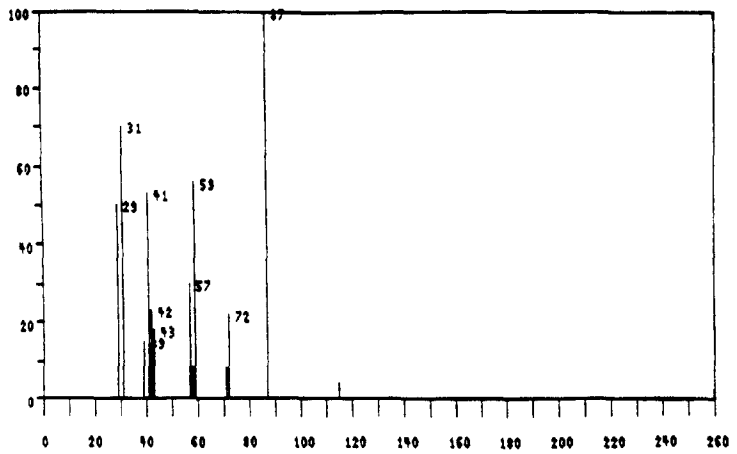
Electron impact spectrum: 87(100)
31(57), 41(50), 59(48), 29(33), 57(24), 42(21), 72(18), 27(17), 43(17), 45(12), 39(11), 58(6), 88(5), 115(2)

Fig. 2. Mass spectra of (*Z*)-2-ethyl-4-methyl-1,3-dioxolane (**3**) (top) and (*E*)-2-ethyl-4-methyl-1,3-dioxolane (**4**) (bottom) obtained by thermal decomposition of ascorbic acid (**1**) in propylene glycol.

cation. The major process in the fragmentation scheme is a loss of the ethyl radical in position 2 giving a base peak at *m/z* 87. This fragment then gives additional fragments with *m/z* 59, 31, and 45. The second important pathway is the ring cleavage with a loss of acetaldehyde and the formation of fragments at *m/z* 72, 57, 43, 42, and 29. Additional low-intensity peaks are observed at *m/z* 115 $(M-H)^+$ and 101 $(M-CH_3)^+$. The molecular ion is not seen.

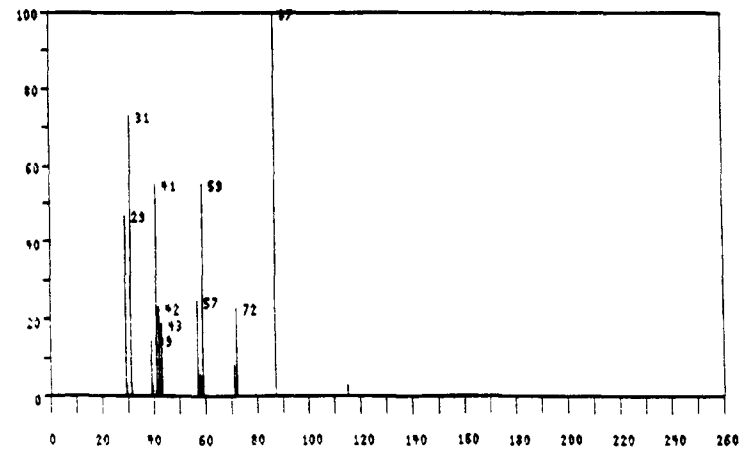
The formation of acetals is not unexpected.

Name: (Z)-2-ETHYL-4-METHYL-1,3-DIOXOLANE
Mol. formula: $C_6H_{12}O_2$ Mol. wt. 116
Origin: SYNTHETIC (PROPANAL/PROPYLENE GLYCOL); VERNIN & CHAKIB, 1995.
IK_a = 0 IK_p = 0 DIK = 0 Ref.: 0: 0



Electron impact spectrum: 87(100)
31(70), 59(56), 41(53), 29(50), 57(30), 42(23), 72(22), 43(18),
39(15), 58(8), 71(8), 115(4), 101(1)

Name: (E)-2-ETHYL-4-METHYL-1,3-DIOXOLANE
Mol. formula: $C_6H_{12}O_2$ Mol. wt. 116
Origin: SYNTHETIC (PROPANAL/PROPYLENE GLYCOL); VERNIN & CHAKIB, 1995.
IK_a = 0 IK_p = 0 DIK = 0 Ref.: 0: 0

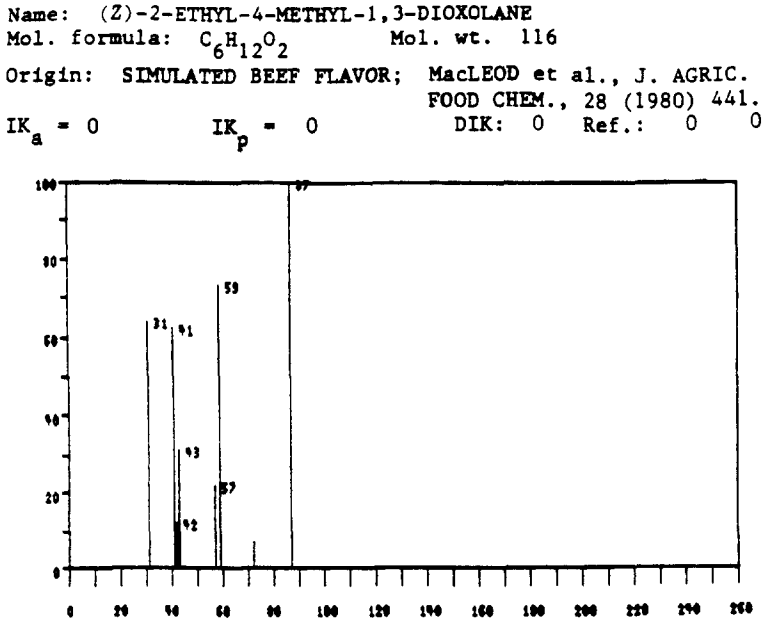


Electron impact spectrum: 87(100)
31(73), 41(55), 59(55), 29(47), 57(25), 42(23), 72(23), 43(19),
39(15), 71(8), 58(6), 115(3), 101(1)

Fig. 3. Mass spectra of (*Z*)-2-ethyl-4-methyl-1,3-dioxolane (**3**) (top) and (*E*)-2-ethyl-4-methyl-1,3-dioxolane (**4**) (bottom) synthesized from propanal and propylene glycol.

MacLeod et al. [29] were the first to describe the interaction of propylene glycol with carbonyl compounds formed in the Maillard reaction and leading to 1,3-dioxolanes. In the beef-flavored commercial products, the use of propylene glycol as the solvent alters the characteristic beef flavor because of the formation of 1,3-dioxolanes [29].

Three 1,3-dioxolanes, namely, 2,4-dimethyl-, 2-isobutyl-4-methyl-, and 2-(1-isopropyl-4-methyl-1-pentenyl)-4-methyldioxolane were identified by Hart-



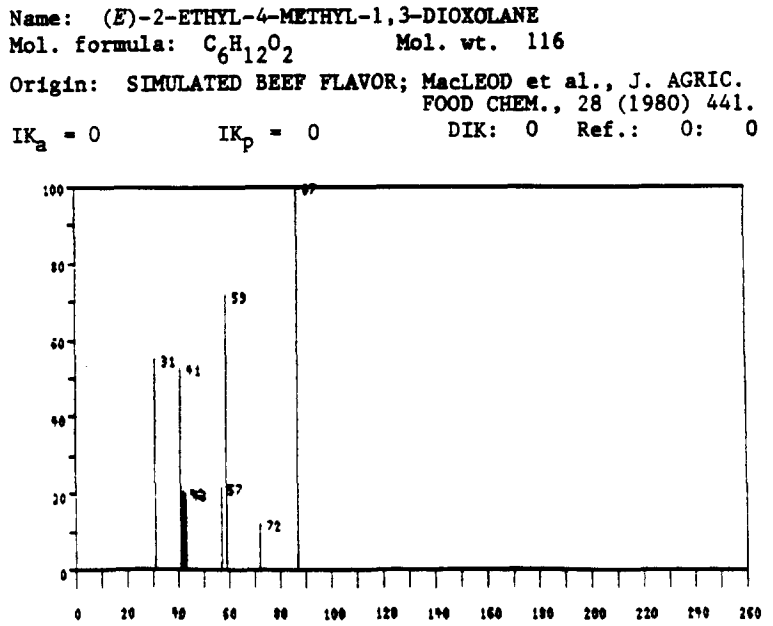


Fig. 4. Mass spectra of (*Z*)-2-ethyl-4-methyl-1,3-dioxolane **(3)** (top) and (*E*)-2-ethyl-4-methyl-1,3-dioxolane **(4)** (bottom) in simulated beef flavor [29].

man et al. [30] among the products of the reaction of leucine and D-glucose in propylene glycol as the solvent. The synthesis of 2-formyl-4,5-dimethyl-1,3-dioxolane was reported by Thiam and Chastrette [31] using glyoxal and glycerol as the starting materials. This is the starting material for the synthesis of chiral acetals. We have not found any 4-methyl derivative in our reaction mixture.

Kantlehner and Gutbrod [28] described the synthesis of a number of 1-alkyl-4-methyl-1,3-dioxolanes in the presence of *N,N*-dimethylformamide and dimethyl sulfate. Finally, MacLeod et al. [29] carried out the synthesis of 1,3-dioxolanes using *p*-toluenesulfonic acid and removing the water formed in the reaction by distillation of an azeotropic mixture with benzene. The products were purified by distillation under diminished pressure. An adaptation of this method was used in our study for the synthesis of several reference compounds.

An example shown in Fig. 2 presents the mass spectra of (*Z*)- and (*E*)-2-ethyl-4-methyl-1,3-dioxolanes synthesized in our laboratory from propanal and propylene glycol. For comparison, Fig. 3 contains the mass spectra of these two compounds identified after thermal decomposition of ascorbic acid in propylene glycol, and Fig. 4 represents their mass spectra in simulated beef flavor [29]. The agreement among the three sets of spectra is excellent.

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