On the Role of 2,3-Dihydro-3,5-dihydroxy-6-methyl-4(*H*)-pyran-4-one in the Maillard Reaction

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To investigate the thermal degradation pathways of 2,3-dihydro-3,5-dihydroxy-6-methyl-4(*H*)-pyran-4-one (**1**) in the Maillard reaction, the ^{13}C-labeled and unlabeled **1** were synthesized and heated in model systems of food processing. The extent and position of the labeling of the reaction products were interpreted by the mass spectroscopy data. The volatiles identified were, among others, 2,4-dihydroxy-2,5-dimethyl-3(2*H*)-furanone (**2**), 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone, cyclotene, maltol, 5-hydroxymaltol, and some acyclic carbonyls. Under roasting conditions, **2** was formed as a major product. It was concluded that **1** might be transferred to highly reactive open-chain intermediates like the enolic forms of 1-deoxyosone. The further reaction pathways varied with the reaction conditions. Possible degradation pathways of **1** that resulted from the labeling experiments as well as the formation of the described products are discussed.

Keywords: *Maillard reaction; isotopic labeling experiments; 2,3-dihydro-3,5-dihydroxy-6-methyl-4(H)-pyran-4-one; acetylformoin; 2,5-dimethyl-4-hydroxy-3(2H)-furanone; cyclotene*

INTRODUCTION

The thermal generation of aromas is primarily influenced by the Maillard reaction. By reaction of sugars with amino acids, a great many decomposition reactions take place that are responsible for the large number of aroma compounds in thermal aromas. To gain knowledge about the reaction mechanisms, we carried out some model reactions of sugars with selected amino acids, which were heated under the conditions of cooking, roasting, and autoclaving of food (Baltes and Knoch, 1993; Kunert-Kirchhoff and Baltes, 1990).

In the course of some model reactions, we obtained relatively large amounts of 2,3-dihydro-3,5-dihydroxy-6-methyl-4(*H*)-pyran-4-one (**1**; Reese and Baltes, 1992), which was formed via the 1-deoxyosone pathway (Mills and Hodge, 1976), has been identified by Mills et al. (1970), and is found in many heated and stored foods (Tatum et al., 1967; Ledl et al., 1976). Therefore, we supposed that **1** might be a relatively stable degradation compound of hexoses. To investigate the role of **1** during the Maillard reaction, we synthesized it from glucose and used it in model reactions as described. To confirm the degradation pathways as well as the formation mechanisms of products formed (Nyhammar et al., 1983), we also carried out isotopic labeling experiments with ^{13}C-labeled **1**.

EXPERIMENTAL PROCEDURES

Synthesis of 2,3-Dihydro-3,5-dihydroxy-6-methyl-4(*H*)-pyran-4-one (1). Compound **1** was synthesized according to the procedures of F. Ledl (personal communication) with the following slight modifications. A mixture of 0.2 mol of α-D-glucose, 0.2 mol of piperidine, and 150 mL of ethanol was refluxed for 1.5 h. Then, 0.2 mol of acetic acid in 30 mL of ethanol was added slowly, and the mixture was heated at 90 °C for 22 h. Ethanol was evaporated under reduced pressure to one-third the original volume. The insoluble piperidinoreductone was filtered and washed with isopropanol, and the solvent was evaporated under reduced pressure. The residue was dissolved in 40 mL of water and extracted with ethylacetate for 3 h, and the organic layer was evaporated. The yellow oil of **1** was distilled at 120−140 °C and 0.1 torr. The oil was recrystallized twice from ether:pentane. The purified sample was stored in a refrigerator, and its purity was always examined by gas chromatography (GC) prior to use: yield, 0.9 g (3% of theory); mp 73−74 °C (67−70 °C; Shaw et al., 1971); ^{1}H NMR (in $CDCl_3$) 2.10 (3H, s), 4.45 (1H, q), 4.38 (1H, q), and 4.04 (1H, q) ppm.

Synthesis of 2,3-Dihydro-3,5-dihydroxy-6-(^{13}C)methyl-4(*H*)-pyran-4-one. ^{13}C-Labeled **1** was synthesized from 27 mmol of (1-^{13}C)-α-D-glucose and 27 mmol of piperidine as described for **1**.

Synthesis of 2,4-Dihydroxy-2,5-dimethyl-3(2*H*)-furanone (2). Compound **2** was synthesized according to the procedures of Goto et al. (1963).

Degradation of 2,3-Dihydro-3,5-dihydroxy-6-methyl-4(*H*)-pyran-4-one (1). First, 0.7 mmol of **1** was dissolved in 1 mL of sodium phosphate buffer solution (0.4 M, pH 5.8) or in 1 mL of distilled water in an ampule and heated either under reflux for 1−5 h or at 150 °C in the drying oven for 1 h. The reaction mass was then extracted with diethylether and treated with $NaHCO_3$ solution. After drying the diethylether by freezing and removal of the water at −18 °C, the extract was concentrated by careful distillation on a Vigreux column and analyzed by capillary GC-MS. Another sample was prepared in a similar manner, except the initial pH of solution was adjusted to 7.5 with 10% Na_2CO_3 solution.

Degradation of 2,3-Dihydro-3,5-dihydroxy-6-(^{13}C)-methyl-4(*H*)-pyran-4-one. First, 0.3 mmol of ^{13}C-labeled **1** was dissolved in 0.3 mL of sodium phosphate buffer solution (0.4 M, pH 5.8) in an ampule and heated at 150 °C in the drying oven for 1 h. The reaction mass was then extracted with diethylether and treated as described for **1**.

Degradation of Acetylformoin (2), 1-Hydroxy-2-propanone (22), and Glyceraldehyde (39). First, 0.7 mmol of **2** was dissolved in 1 mL of sodium phosphate buffer solution (0.4 M, pH 5.8) in an ampule and heated at 150 °C in the drying oven for 1 h. In another experiment, 0.04 mol of 1-hydroxy-2-propanone (**22**) or glyceraldehyde (**39**) in 60 mL of sodium phosphate buffer solution (0.4 M, pH 5.8) was heated in a laboratory autoclave (Berghof, Germany) at 150 °C for 1 h. The reaction mixtures were treated as already described.

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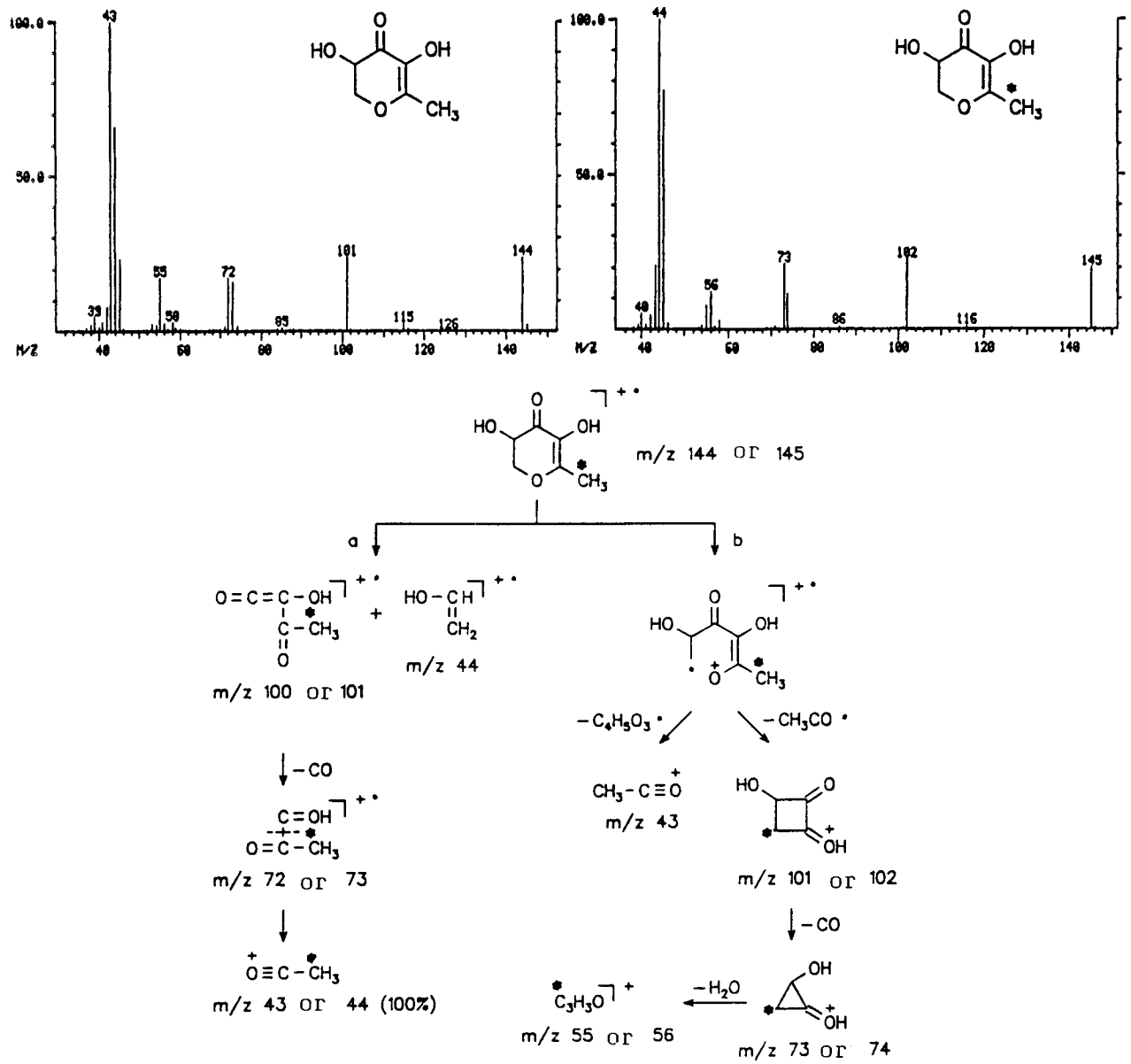


Figure 1. Mass spectra (EI) and fragmentation patterns of labeled and unlabeled **1**.

Roasting. Compound **1** or ^{13}C-labeled **1** at 0.7 mmol, the same mass of sea sand, and 0.02 mL of sodium hydrogen phosphate buffer solution (0.4 M, pH 5.8) were mixed homogeneously, placed into a tube with quartz wool, and heated at a rate of 20 °C/min to a final temperature of 220 °C and held for 20 more min. The volatile compounds were swept out by a nitrogen stream of 50 mL/min and trapped at 20, 0, and −196 °C. The condensates were dissolved in diethyl ether and treated as described previously.

Esterification. Some acids were identified by esterification with diazomethane (Black, 1983).

Gas Chromatography−Mass Spectrometry (GC-MS). The column used was a J&W fused silica column (DB Wax, 60 m, 0.25 mm i.d., 0.25 μm film thickness); the carrier gas was helium at 2 mL/min; the temperature program was heating for 5 min at 40 °C, 40−210 °C at 2 °C/min, and 210 °C isotherm; and the injection temperature was 250 °C. The gas chromatograph was a Carlo Erba 4130 with FID. Modified Kovats indices were calculated by the method of van den Dool and Kratz (1963). The gas chromatograph−mass spectrometer apparatus consisted of a quadrupole mass spectrometer (Finnigan-MAT 4500) coupled with a Finnigan GC 9610 (direct coupling) and data system INCOS 2100. Electron-impact ionization was conducted at a transline temperature of 240 °C, an ion source temperature of 120 °C and an ionization energy of 70 eV. Chemical ionization was performed with methane as a reactant gas (0.7 Torr; ion source pressure, 3.5 $\times$ 10^{-5} Torr), a cyclic scan of 0.8 s, and a mass range of 80−350 amu.

MS Data Interpretation of Labeled Compounds. The locations of labeling were determined by interpretation of MS fragmentations compared with those of unlabeled compounds. The extents of labeling were calculated from the ratios of molecular mass ion intensities, which were corrected to natural contents of isotopes and to protonation.

Quantification of the Reaction Products. The peak areas of individual compounds were calculated from data of a computer-assisted program (INCOS data system) according to the 100% method.

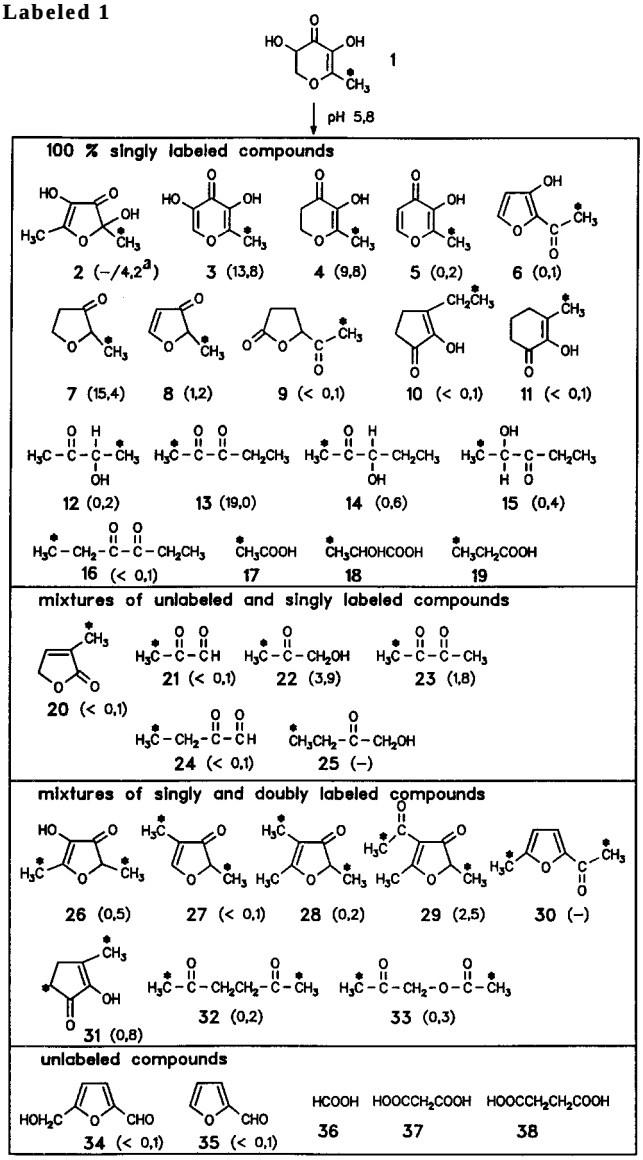
^{1}H NMR Spectroscopy. A Bruker WM 400 NMR spectrophotometer was used, with $CDCl_3$ as a solvent and tetramethylsilane as an internal standard.

Melting Points. Melting points are uncorrected (determined in capillary tubes).

RESULTS AND DISCUSSION

Compound **1** is a white crystalline compound that is stable in the refrigerator for a few months. The solutions of **1** were rather acidic. After heating, the reaction

Table 1. Reaction Products from Degradation of Labeled 1



Abbrevation: a= relative amounts after roasting, * = point of labeling

mixture had a sweet, caramel, and melted butter flavor, whereas **1** was odorless. Heating of aqueous solutions of **1** at 100−120 °C (pH 5.8) resulted in decomposition of only 20−30%. On the other hand, **1** was decomposed rather quickly at pH 7.5 or 11.0. After treatment of **1** under the conditions of food processing, 56 volatile compounds were identified (19 acyclic carbonyls, 8 cyclic carbonyls, 6 furanes, 14 furanones, 3 pyranones, and 6 carboxylic acids). To gain information on their formation mechanisms, we extended our investigations to 2,3-dihydro-3,5-dihydroxy-6-(^{13}C)methyl-4(*H*)-pyran-4-one, which we synthesized by reaction of (1-^{13}C)glucose. Compound **1** was fully labeled at the methyl group, which must be derived from the C-1 position of glucose. The mass spectra and fragmentation patterns of labeled and unlabeled **1** are shown in Figure 1. The mass spectrometric fragmentations of labeled **1** [*m*/*z* 102 (M − CH_3CO), 73 (M − CH_2CHOH − CO), 56 (M − CH_3CO − CO − H_2O)] and the base peak at 44 (M − 101) clearly indicate a ^{13}C-labeled methyl group.

In Table 1, the formulas, labelings, and relative amounts (given in parentheses) of the most important compounds from degradation of **1** at 150 °C and 1 h in aqueous solution or after roasting (220 °C, 20 min) are listed. As indicated, there are both compounds whose methyl group is fully labeled as well as those with incomplete (<100%) or a double labeling. The first group contains compounds with a labeled methyl group that was directly transfered from **1**. On the other hand, the mass spectra of compounds from the second group showed two molecular masses, indicating that the marked methyl group was labeled only to some extent. In this case, there was more than one possible path of formation. The third group contains compounds that possess two labeled methyl groups. The formation of the latter must include condensations of two fragments from **1**, each containing its labeled methyl group. About 50% of the compounds have a cyclic structure. The most important of them, which are formed in the highest amounts, are 2,3-pentanedione (**13**), 2-methyl-4,5-dihydro-3(2*H*)-furanone (**7**), 1-hydroxy-2-propanone (**22**), cyclotene (**31**), and 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone (**26**, Furaneol). Two gas chromatograms of the decomposition reactions of these compounds are shown in Figure 2.

Only 13 compounds were identified after roasting of **1**, 67.8% of which were recovered. The most important compounds were 5-hydroxymaltol (**3**, 12.7%), 2,4-dihydroxy-2,5-dimethyl-3(2*H*)-furanone (acetylformoin, **2**, 4.2%), and maltol (**5**, 1.7%).

Hydration of 1. When an aqueous solution of **1** was heated, cyclic enolones like 5-hydroxymaltol (**3**), dihydromaltol (**4**), and maltol (**5**) were formed to some extent, the latter has been described as the major compound after heating of 1,4-disaccharides (Hodge et al., 1963). The postulated pathways that were confirmed by the extent of labeling are shown in Figure 3. The pyranones **3**, **4**, and **5** were fully labeled at the marked position, which obviously indicates formation from the intact skeleton of **1**. We propose that in aqueous medium, **1** was transferred to the highly reactive intermediates **1a**−**1e**, in which numerous possibilities of keto−enol tautomerizations were included. In neutral and in weak basic medium, **1** formed an enolic semi-ketale structure **1a** by hydration. Then, by tautomerization, **1a** formed the semi-ketale structure **1b**. Compound **1b**, by elimination of 2 mol of water, can be transferred to maltol. On the other hand, **1b** formed **4** after reduction and **3** by additional oxidation. Although **3** and **4** are dominant in neutral and weak alkaline media **4** represents the main product after thermal degradation of **1** in acidic solution (relative amounts, 6.9%). This result indicates that water elimination occured more readily at a lower pH. Simultaneously, traces of isomaltol (**6**), which is a characteristic product of lactose, were formed. For formation of **6**, cleavage of the cyclic structure is necessary. After hydration, cleavage of the C-2—O bond of **1** yielded **1c**, which formed **6** by cyclization with subsequent water elimination.

The Role of Acetylformoin. Acetylformoin (**2**) is a major degradation product of **1** under roasting conditions. When an aqueous solution of **2** was heated as described, nearly the same degradation products as from **1** were formed. This result makes the interpretation probable that **2** or some of its isomers (e.g., diacetylformoin; Figure 4), are intermediates of the thermal degradation of **1**. This idea has already been proposed by Helak (1987). In Figure 5, the postulated pathway of the degradation of **1** is demonstrated. As was already described, **1** yields **1d**, which can split off H_2O and form the dimethyl derivative **1h**, which can be transferred

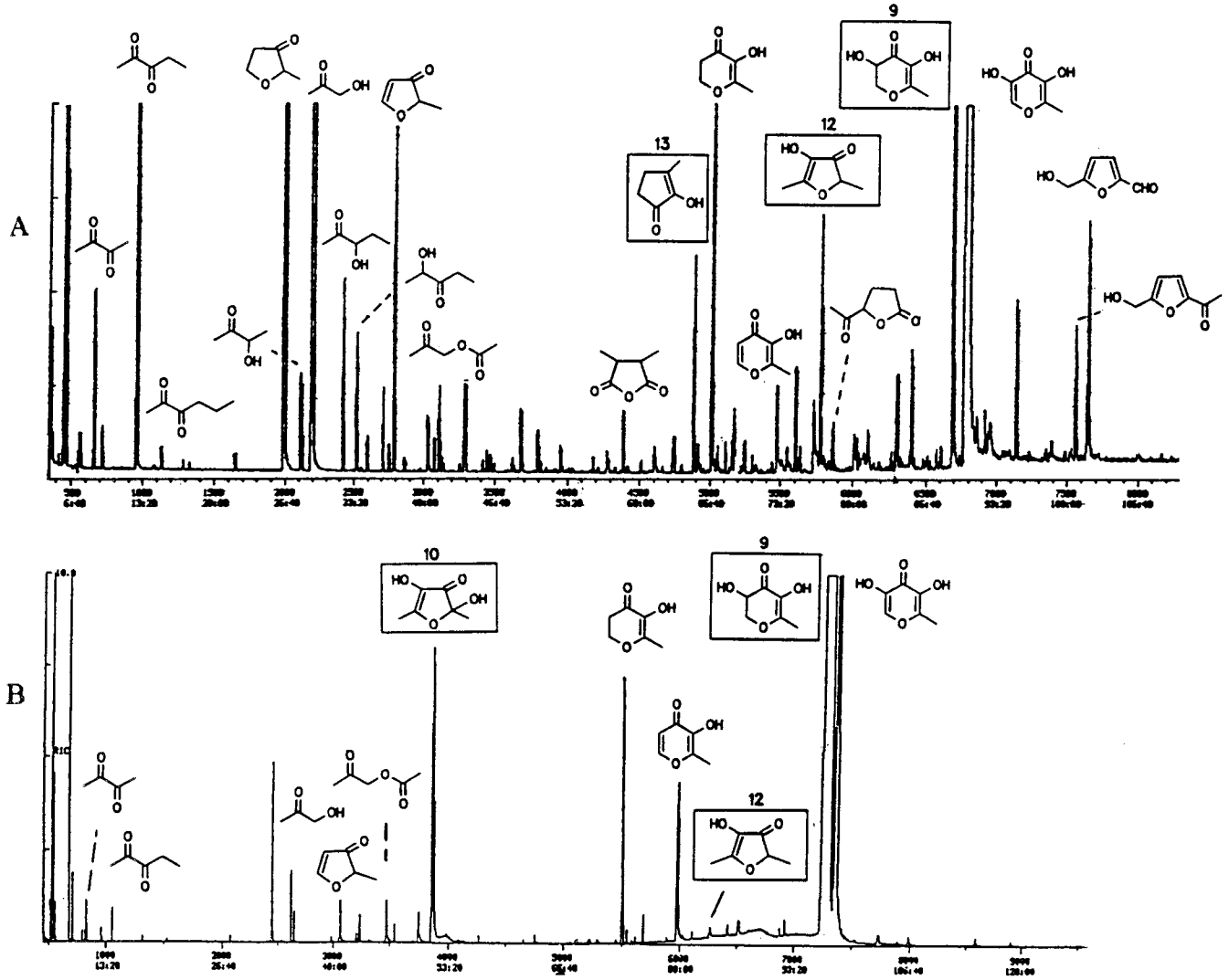


Figure 2. Gas chromatograms of degradation products from **1**: (A) pH 5.8, 150 °C, 2 h; (B) 220 °C, 20 min.

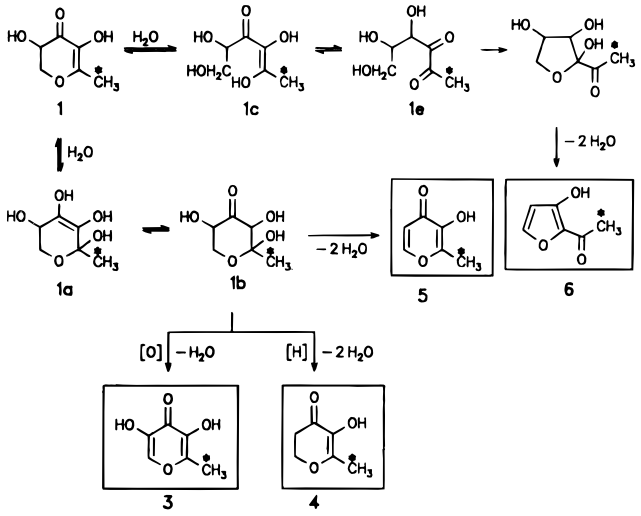


Figure 3. Possible formation pathways of labeled 5-hydroxymaltol (**3**), dihydromaltol (**4**), maltol (**5**), and isomaltol (**6**) from labeled **1**.

to yield **2** by tautomerization and cyclization. Simultaneously, **26** and **31** were formed by reduction with subsequent dehydration. The formation mechanism of **2** is confirmed by the exclusive full labeling of the marked methyl group. On the other hand, ~20% of the second methyl group of **26** and of the methylene carbon atom in **31** were also labeled. The reason for this

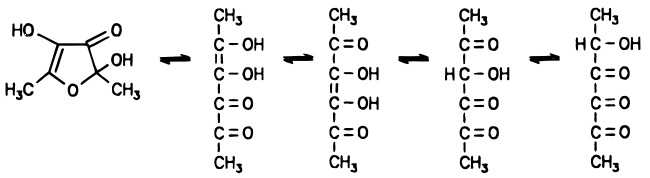


Figure 4. Possible structures of acetylformoin (**2**).

additional labeling might be the easy formation of **31**. In contrast, **26** was predominantly formed in strong alkaline medium (Shaw et al., 1986) from **22**, which we identified as a degradation product of **1** after heating (Figure 6). On the other hand, labeled acetylformoin (**2**) can be transferred directly to labeled **26** and **31** by reduction (Figure 5). From degradation of **2** at 150 °C for 1 h, **26** was identified as a main product, among others, whereas **31** was only formed in a trace amount. This result indicates that **2** was more easily reduced to **26** than **1**. In addition, aldol condensation of **2** with acetaldehyde could lead to the formation of 2,5-dimethyl-4-acetyl-3(2*H*)-furanone (**29**), which was also identified after heating of **1**. This reaction agrees with the results of the labeling experiment, which indicated that the labelings of **29** were located in a methyl group and in an acetyl carbon atom.

Formation of Furanes. Most of the formations of furanes are postulated to occur via the 3-deoxyosone

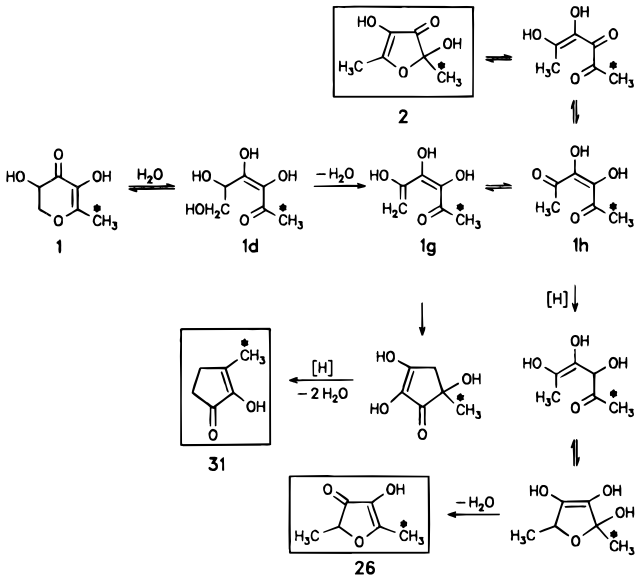


Figure 5. Possible formation pathways of labeled acetylformoin (**2**), 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone (**26**), and cyclotene (**31**) from labeled **1**.

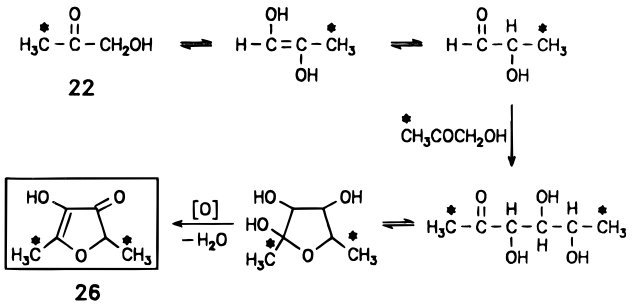


Figure 6. Possible formation pathway of doubly labeled 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone (**26**) from labeled 1-hydroxy-2-propanon (**22**).

pathway (Anet, 1964). Therefore, we were very surprised to identify low amounts of furanes in the reaction mixture after thermal degradation of **1**. These low amounts of furanes were accompanied by relatively high amounts of furanones, which might be active as precursors. The most important representatives are listed in Table 2. For the formation of 2-acetylfuran, a reaction mechanism was postulated that included 1,4-dideoxyosone, which might be formed by ring opening at pH 7.5, with subsequent reduction (Figure 7). 5-(Hydroxymethyl)furfural (**34**) and 2-furfural (**35**), which have been described as common degradation products of 3-deoxyosone (Feather and Harris 1973), were unexpected in the reaction mixture but were identified as unlabeled compounds. We suppose that glyceraldehyde (**39**), which could be formed from an unlabeled fragment of **1** (Figure 8), could form **34** and **35** by condensation with subsequent elimination of water or formaldehyde. To confirm this idea, we heated glyceraldehyde under the same conditions. As expected, **34** and **35** were obtained as major compounds in the reaction mixture.

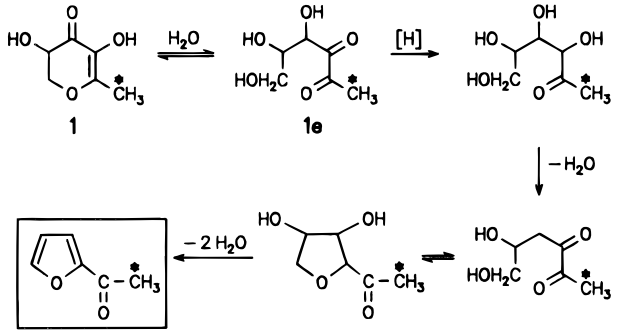


Figure 7. Postulated formation pathway of 2-acetylfuran from **1**.

Formation of Acyclic Carbonyls. In the course of the degradation via the 1-deoxyosone pathway, the acyclic carbonyls are formed via retroaldol reactions, mostly at higher pH. After heating of **1**, 19 acyclic carbonyls and six carboxylic acids, which were identified as methyl esters, were identified. As already mentioned, the hydrolytic ring cleavage of **1** produces open-chain intermediates **1c**−**1e**, which subsequently undergo a retroaldol reaction and/or carbonyl decomposition at pH 5.8 to produce a group of primary acyclic carbonyls, which can also lead to the formation of long-chain

Table 2. Furans and Furanones Identified after Heating of 1[a]

compound	relative amount (%)[a]			
	150 °C, pH 5.8	150 °C, pH 2.5	150 °C, pH 7.5	180 °C, pH 5.8
2-methylfuran	–[b]	–	Tr[c]	–
2-furfural	Tr	–	0.5	0.1
2-acetylfuran	–	–	Tr	–
3-acetyl-2,5-dimethylfuran	–	0.7	–	–
2-acetyl-5-methylfuran	–	0.4	–	–
1-(2′-methyl-3′-furyl)-1-butanone	–	0.3	–	–
2-acetyl-3-hydroxyfuran	0.1	–	–	–
1-(5′-methyl-2-furyl)-2-butanone	–	Tr	–	–
1-(2′-furyl)-1,2-propanedione	–	0,5	–	–
1-(5′-methyl-2′-furyl)-1,2-propanedione	–	0,2	–	–
5-(hydroxymethyl)-2-furfural	T	–	–	–
2-methyl-4,5-dihydro-3(2*H*)-furanone	15.4	10.4	11.2	–
2-methyl-3(2*H*)-furanone	1.2	1.3	2.3	0.8
2,4-dimethyl-3(2*H*)-furanone	Tr	Tr	Tr	Tr
2,5-dimethyl-3(2*H*)-furanone	–	–	–	0.3
2,4,5-trimethyl-3(2*H*)-furanone	0.2	Tr	–	0.5
2-ethyl-5-methyl-3(2*H*)-furanone	–	–	–	0.5
3,5-dimethyl-2(5*H*)-furanone	Tr	–	0.3	Tr
3-methyl-2-(5*H*)-furanone	Tr	0.9	0.5	Tr
3,4-dimethyl-2,5-furandione	Tr	0.2	0.3	Tr
5-ethyldimethyl-2(5*H*)-furanone	–	–	Tr	–
2,5-dimethyl-4-acetyl-3(2*H*)-furanone	2.5	2.4	–	0.4
2,5-dimethyl-4-hydroxy-3(2*H*)-furanone	0.5	Tr	Tr	0.2
5-acetyldihydro-2-furanone	–	0.2	0.5	–

[a] All were heated for 1 h. [b] –, not determined. [c] Tr, trace amount.

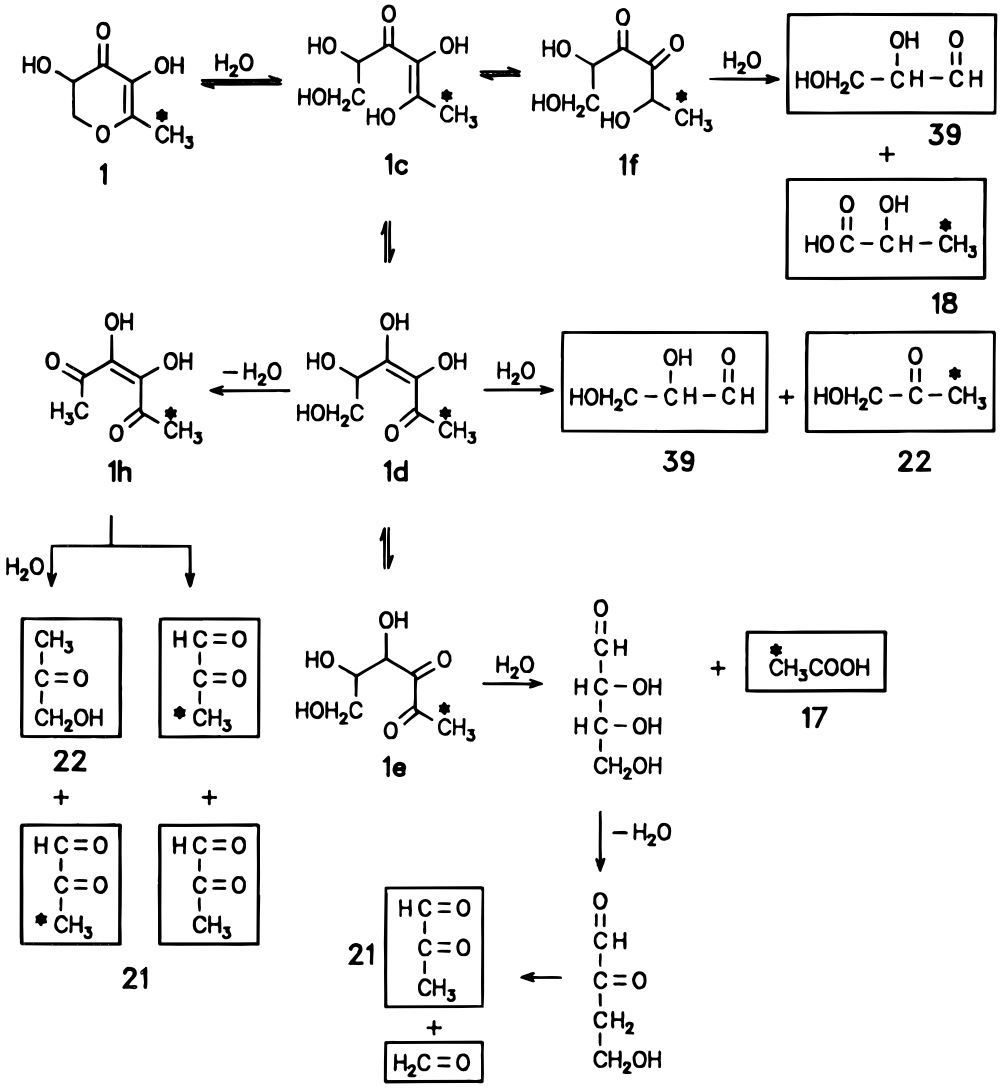


Figure 8. Possible formation pathways of some C-3 acyclic carbonyls and acids.

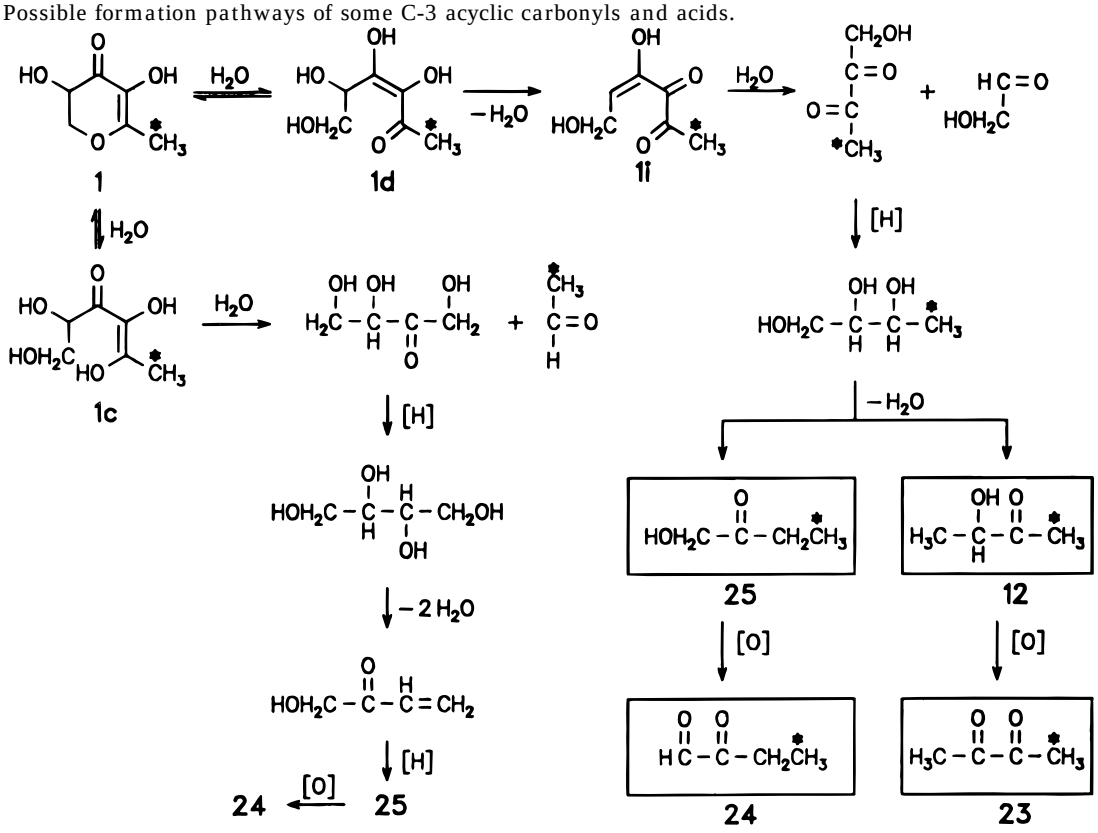


Figure 9. Possible formation pathways of some C-4 acyclic carbonyls.

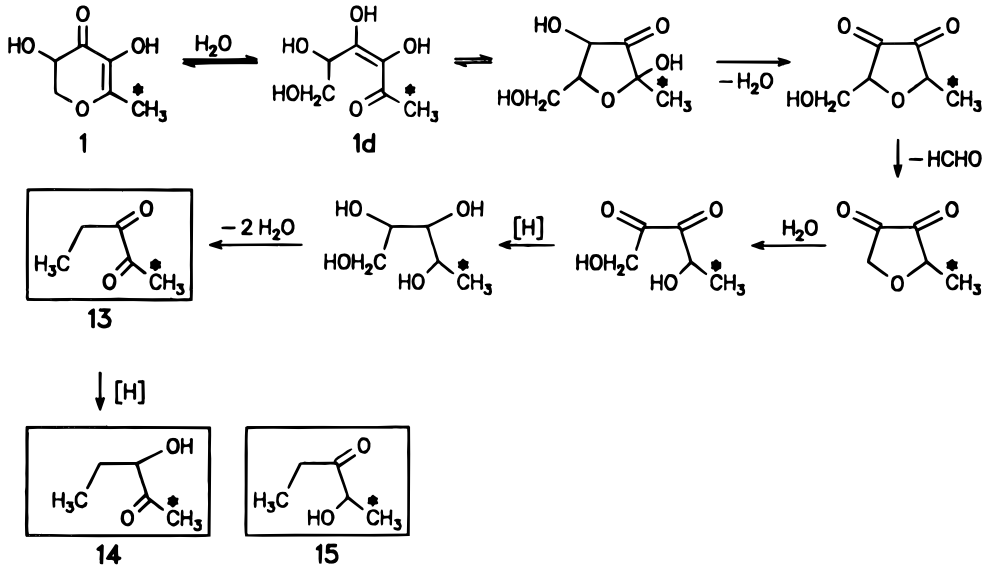


Figure 10. Possible formation pathways of some C-5 acyclic carbonyls.

and cyclic carbonyls via condensation. The postulated pathways of three- and four-carbon acyclic carbonyls and acids that were confirmed by the extent of labeling are shown in Figures 8 and 9, respectively. The hydrolytic carbonyl decomposition could lead to the formation of lactic acid (**18**) and acetic acid (**17**), whose methyl groups are fully labeled. The byproduct was unlabeled glyceraldehyde (**39**). Pyruvic aldehyde (**21**), 1-hydroxy-2-propanone (**22**), 2-ketobutyr-1-aldehyde (**24**), and 1-hydroxy-2-butanone (**25**) had nearly the same distribution of unlabeled and singly labeled isotopomers. Compounds **21** and **22** could be formed from **1h**, which possessed the equivalent possibilities of labeling at C-1 and C-6 atom by retroaldol fragmentation. In addition, **1e** could form the unlabeled **21**, by hydrolytic cleavage of dicarbonyls, yielding labeled acetic acid (**17**). Compound **25**, which yielded **24** by oxidation, could be formed from an unlabeled tetrose fragment of **1c** and labeled fragment of **1i** by retroaldol reaction and by subsequent reduction. In the case of 2-hydroxy-3-butanone (acetoine, **12**), which could be oxidized to yield 2,3-butandione (**23**), the extent of labeling (100%) clearly showed that it was formed by retroaldol fragmentation splitting of the C-4—C-5 bond of **1**.

One of the most important results of the labeling experiments was the identification of labeled five-carbon acyclic carbonyls like 2,3-pentanedione (**13**) and 3(2)-hydroxy-2(3)-pentanone (**14**, **15**), which must be formed by cleavage of the C-1—C-2 bond of **1**. This reaction could lead to the formation of unlabeled formaldehyde, which was determined independently by reaction with 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole. Two pathways for the formation of **13** can be discussed: (*1*) elimination of formaldehyde and water with subsequent reduction via 5-ring intermediates (Figure 10); and (*2*) aldol condensation of **22** with acetaldehyde. The second pathway should require isotopic distribution to unlabeled, singly labeled, or doubly labeled compounds, which was not detected. Therefore, we suggest that the first pathway is more likely; that is, **13** can be easily be reduced to **14** and **15** as described by Shu et al. (1985); and we demonstrated that 1-(2′-oxopropyl)-acetate (**33**) has the same isotopic distribution as singly and doubly labeled compounds, indicating its formation by condensation of **22** and **17**.

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