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Pyrolysis of inulin, glucose, and fructose [†]

Glenn R. Ponder and Geoffrey N. Richards *
Wood Chemistry Laboratory, University of Montana, Missoula, Montana 59812 (USA)

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ABSTRACT

The pyrolytic behavior of inulin, a (2 → 1)-linked fructofuranan, is described. Parallel investigations of the pyrolysis of glucose and of fructose were conducted to supplement the inulin results and to aid comparison with previous results from glucans. Effects of neutral and basic additives are emphasized. As with glucans, the addition of such additives (especially basic) increases the yields of the one-, two-, and three-carbon products (as well as of hexosaccharinolactones), while generally decreasing the yields of anhydro sugar and furan derivatives. The former products include glycolaldehyde, acetol, dihydroxyacetone, acetic acid, formic acid, and lactic acid. Mechanistic speculations are made regarding the origins of these compounds, as well as of furan derivatives and saccharinic acid lactones. Parallels with alkaline degradation are considered.

INTRODUCTION

Previous pyrolytic studies of a variety of aldoglycans, both natural and synthetic, have revealed significant parallels in their behavior[1–3]. In the pyrolysis of such polysaccharides, anhydro sugar formation is favored by the absence of inorganic contaminants. When traces of such contaminants are present, either indigenously or introduced, pathways leading to one-, two-, and three-carbon compounds are favored. Typical of these latter products are glycolaldehyde (GA), acetol (hydroxypropanone), acetic acid, and formic acid.

The present study seeks to determine whether such general pyrolytic behavior applies to ketoglycans as well as to aldoglycans. To this end, the pyrolytic behavior of inulin, a naturally occurring fructan, has been investigated. Inulin is a food reserve glycan which is found in various higher plants such as in the tubers of dahlias and of Jerusalem artichokes and in some green algae[4]. It is a linear (2 → 1)-linked β-D-fructofuranan, the molecules of which contain ~30 monomer units[5] and terminate in a molecule of sucrose. Inulin thus differs from the previous polysaccharides whose pyrolysis has been investigated in that it is a polyketose

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* Corresponding author.

rather than a polyaldose. Interest in the pyrolytic behavior of inulin derives also from the fact that coffee substitute extracts are produced by roasting chicory roots, composed largely of inulin and fructose[6]. In the present study, inulin from dahlia tubers was acid-washed to remove indigenous metal ions, and the effects of some neutral salts and bases on its pyrolytic behavior were found in general to be analogous to previously observed effects on glucans.

Recognizing that hexoglycans consist of glycosidically linked hexose residues, and as an extension of the investigation of pyrolytic similarities between glucans and fructans, we have included glucose and fructose in the present study. Previous pyrolytic studies of these monosaccharides[7–11] have often neglected to investigate the effects of additives, have failed to identify some significant products, and have generally not been conducted under conditions suitable for comparison with the present study.

RESULTS AND DISCUSSION

Inulin from dahlia tubers was acid-washed as described in the Experimental section. Vacuum pyrolyses were conducted for 1 h at 240°C, the temperature being chosen on the basis of preliminary thermogravimetric analysis. The untreated sample melted quickly and appeared to boil gently during the early stages of pyrolysis. Samples with additives also melted and generally formed a brown-black voluminous foam. In some cases foaming out of the sample boat prevented determination of char yields. Table I gives the percent yields based on starting materials of the major organic components found in the pyrolysis fractions of acid-washed inulin treated with various inorganic additives. Additive concentrations are 1% (w/w) except in the case of $Ca(OH)_2$ which is 5%. The increased amount of the latter additive was used because it was added as a solid by mechanical mixing with the inulin, whereas the more water-soluble additives were mixed with inulin in aqueous solution and freeze-dried. Therefore, it was assumed that in the latter cases mixing would be more efficient. Three fractions from the pyrolysis products are considered: the tar fraction (room-temperature condensate), the distillate fraction (−60°C condensate after removal of tar), and the char fraction (residue remaining in sample boat after pyrolysis).

Glucose and fructose were similarly pyrolyzed with and without the additives listed in Tables II and III. Vacuum pyrolyses for these hexoses were conducted for 30 min at 275°C. Untreated and NaCl-treated samples became reddish, boiling melts that darkened and, to a small extent, spattered and/or foamed as the pyrolysis progressed. NaOH-treated samples appeared to boil more vigorously and darken more rapidly. Tables II and III give the percent yields (based on starting hexose) of the major organic components found in the pyrolysis fractions. Additive concentrations are 1% (w/w) unless otherwise stated.

Tables II and III reveal an increasing similarity in the pyrolytic behaviors of glucose and fructose as the pyrolysis matrix becomes more basic, a result which is

TABLE I

Vacuum pyrolyses of acid-washed inulin

	Untreated	NaCl	NaOH	$Ca(OH)_2$	$Ca(OAc)_2$
Distillate	22	15	31	11	21
GA	–	0.4	2.2	0.8	2.5
Acetol	–	0.2	4.9	0.2	1.5
HOAc	–	0.1	3.9	0.1	1.2
HCO_2H	–	tr	0.3	tr	1.0
Furfural	1.8	0.2	–	–	0.4
Tar	41	29	15	59	52
HMF [a]	8.9	1.7	0.5	1.4	4.5
Lactic acid	–	0.1	2.0	–	?
DHA [b]	–	0.2	3.4	0.2	2.1
2,6-AFru*f* [c]	2.2	0.3	1.6	3.3	1.8
Unknown A	0.4	0.1	–	0.1	0.4
2,5-AMan [d]	0.7 [c]	nd	nd	nd	nd
2,5-AGlc [f]	0.9 [e]	nd	nd	nd	nd
Gluco-MSL	–	0.4	1.8	0.3	–
Disaccharides [g]	> 4	> 5	> 1	> 13	> 3
Char	35	50	nd	nd	nd

[a] 5-Hydroxymethyl-2-furaldehyde. [b] Dihydroxyacetone. [c] 2,6-Anhydrofructofuranose. [d] 2,5-Anhydromannose. [e] Yield of reduced anhydroaldose. [f] 2,5-Anhydroglucose. [g] See text. –, not detected. nd, not determined. tr, trace (< 0.05%).

understandable in light of base-catalyzed carbonyl migration, a key step in the Lobry de Bruyn–Alberda van Ekenstein transformation, whereby glucose, fructose and mannose equilibrate in aqueous solution[12]. Results of work by Shafizadeh and Lai[10] have shown that such equilibrations also occur in pyrolysis melts. These workers melted glucose with $Ca(OH)_2$ or Na_2CO_3, and subsequently found that the melt contained not only various ring forms of fructose and mannose, but also forms of allose, altrose, and *ribo*-hexosulose, indicating that the carbonyl group had migrated two carbons down the chain and back in some cases.

Table II shows that both mutarotation[13] and glucose–fructose isomerization occurs even in uncatalyzed melts. The untreated glucose before pyrolysis was shown by Me_3Si-GLC-FID analysis to be 95% α-pyranose, 5% β-pyranose, and < 1% α-furanose, but the glucose detected in the melt was shown by similar analysis to be 43% α-pyranose, 53% β-pyranose, and 4% α-furanose (glucose listed in Table II is the sum of these forms). The additional occurrence of glucose–fructose isomerization is made evident by the presence of both fructose and 2,6-anhydrofructofuranose (2,6-AFru*f*) in the tar fraction of glucose pyrolysis. In addition to traces of fructose found in the glucose pyrolysates, there were also traces of glucose in the fructose pyrolyzates. Significant amounts of fructose were detected in the fructose pyrolyzates, but these were not quantified because Me_3Si-fructose did not demonstrate satisfactory GLC behavior.

For both hexoses, addition of inorganic additives increases distillate yield at the expense of tar yield. Formation of compounds in the distillate fraction is catalyzed

TABLE II

Vacuum pyrolyses of glucose

	Untreated	NaCl	NaOH		Ca(OH)$_2$
			1%	5%	10%
Distillate	22	30	39	44	39
GA	0.6	1.6	2.9	3.0	3.5
Acetol		0.3	0.5	1.3	1.3
HOAc		0.3	2.0	4.1	1.8
HCO$_2$H		0.1	1.7	3.5	2.6
Furfural	0.1	0.1			
Tar	46	33	34	22	31
HMF	1.3	4.0	0.3		
Lactic acid			0.5	1.9	?
DHA		0.4	4.0	4.3	5.0
1,6-AGlc*p* (LG)	6.6	0.8			
1,6-AGlc*f*	5.0	0.7			
2,6-AFru*f*	0.6	tr [b]			
Unknown A [a]	0.2	0.1			
Gluco-MSL		0.9	1.7	1.7	2.2
Gluco-ISL				tr	0.3
Gluco-SL			tr	0.1	0.5
Glucose	5.4	0.9	0.6	0.5	0.2
Disaccharides	4.5	4.8	0.5		
Char	26	27	24	24	23

[a] Probably 2,5-anhydroglucose. [b] tr, trace.

TABLE III

Vacuum pyrolyses of fructose

	Untreated	NaCl	NaOH		Ca(OH)$_2$
			1%	5%	10%
Distillate	24	30	41	50	40
GA		0.6	2.3	2.7	3.4
Acetol		0.3	0.7	1.2	1.4
HOAc		0.3	2.0	3.8	2.7
HCO$_2$H		0.2	1.6	3.2	3.3
Furfural	0.8	0.5			
Tar	54	43	32	23	31
HMF	3.2	6.4			
Lactic acid		0.1	0.8	2.1	?
DHA		0.4	3.4	5.1	5.9
2,6-AFru*f*	2.6	0.1	tr [b]		
Unknown A [a]	0.4	0.1			
Gluco-MSL		0.5	1.5	2.1	1.8
Gluco-ISL				tr	0.3
Gluco-SL			tr	0.1	0.6
Disaccharides	6.7	4.3	0.2		
Char	16	23	23	25	23

[a] Probably 2,5-anhydroglucose. [b] tr, trace.

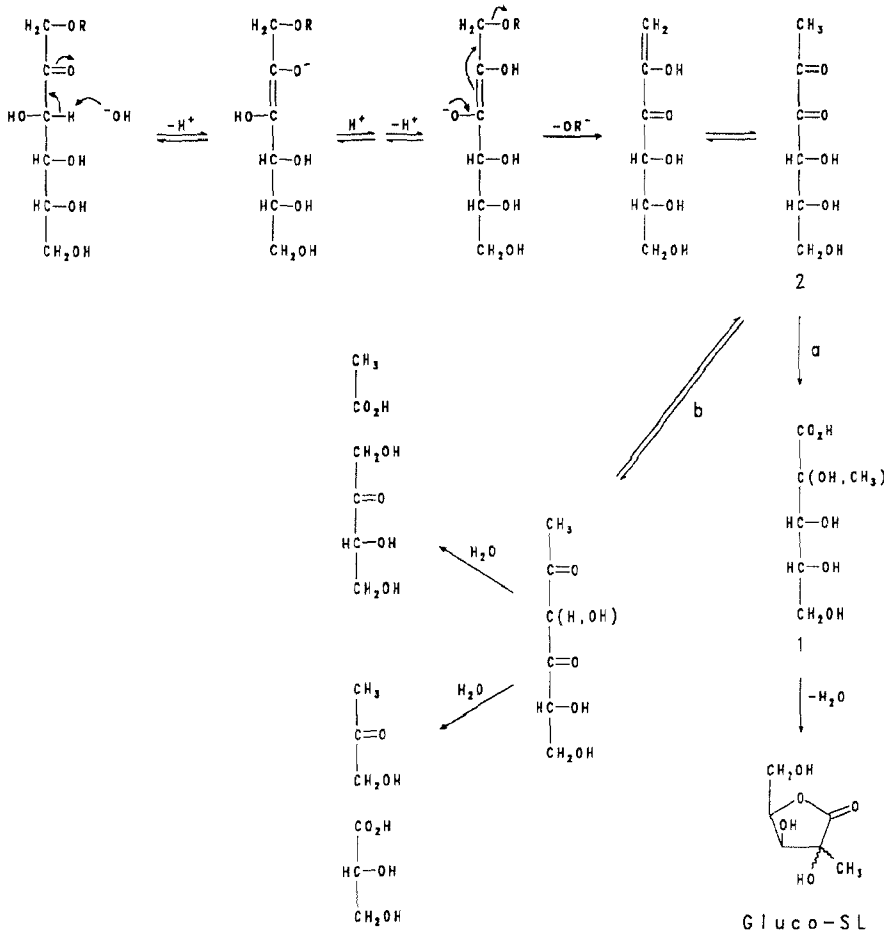
by addition of NaCl, with concomitant decrease in yields of anhydro sugars in the tar fraction. This is identical to the pyrolytic behavior of glucans, and these are the same compounds as those produced in glucan pyrolysis[1].

GA, acetol, HOAc, and HCO_2H.—Table I shows that the addition of 1% NaCl to inulin results in the increased production of the distillate components at the expense of the principal anhydro sugar (2,6-AFru*f*). This behavior parallels that of glucans, in which the addition of NaCl enhances the yields of the same compounds at the expense of levoglucosan (LG) yield[1]. Of particular interest is the dramatic increase in yields of compounds in the distillate when NaOH is used as the catalyst; NaOH has similar effects on the pyrolytic behavior of cellulose[14].

As with inulin and glucans, addition of NaOH to the hexoses results in an increase in yields of small carbonyl compounds and carboxylic acids, accompanied by suppression of furan derivatives and anhydro sugars. For both hexoses, addition of NaOH elevates the yields of the two carboxylic acids relative to GA and acetol, and an increase in the basicity of the pyrolysis matrix appears to further decrease the relative importance of GA (Tables II and III). This significant change in the relative proportions of these distillate components is not observed with addition of NaOH to cellulose, and although the relative proportions do change for inulin, the change is different, the yields of acetol and acetic acid exceeding those of GA and formic acid (Table I).

Table I shows that $Ca(OH)_2$ (added as a mechanically mixed powder) appears to act as a weak base, its effect on the yields of the distillate components being similar to that of NaCl. This may be due to the relative insolubility of $Ca(OH)_2$ in the melt, which would decrease its catalytic activity as a base [the inulin pyrolyzed as though no additive was present when only 1% $Ca(OH)_2$ was added]. Table I also shows that $Ca(OAc)_2$ (added as an aqueous solution) results in yields and relative proportions of distillate components which are typical for a glucan (although some of the acetic acid could derive from decomposition of the salt). Thus for a fructan, this salt is apparently superior to NaCl for effecting increased yields of these compounds. $Ca(OAc)_2$ does not have this effect on cellulose. Note that it also has less effect in diminishing yields of anhydro sugar (2,6-AFru*f*) and of the furan derivatives than does NaCl. The reasons for these phenomena are unknown.

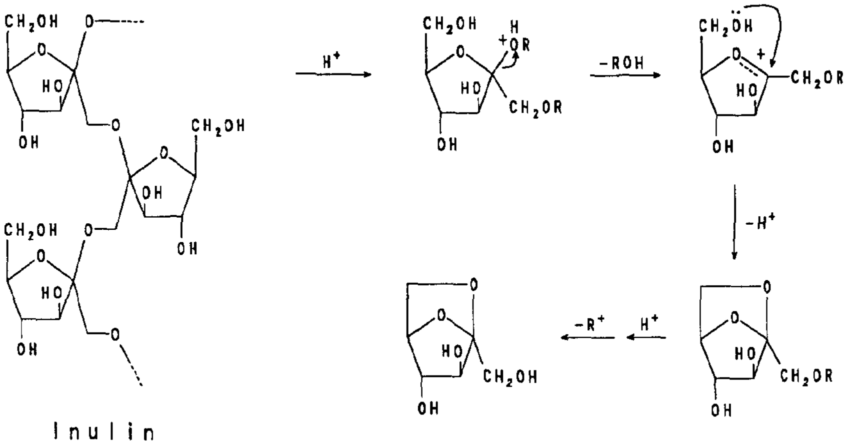
Comparison of Tables I and III shows that NaOH-treated inulin produces several times more acetol upon pyrolysis than does NaOH-treated fructose. This is analogous to the "remarkably rapid formation of acetol from 1-*O*-methyl-D-fructose[15]", as compared to acetol formation from fructose itself during thermal degradation in aqueous solution. Hayami and co-workers studied the acetol produced from thermal decomposition of isotopically labeled pentoses[16] and hexoses[17], and of various hexose derivatives[15] in aqueous solution. The results of the labeling work show that most of the acetol derives from contiguous terminal carbons, C-1–C-2–C-3 or C-4–C-5–C-6, the former being favored, and that most of the methyl carbons of acetol derive from a terminal carbon, C-1 or C-6. Based on the results of this study, Hayami[15] proposed the mechanism illustrated in



Scheme 1.

Scheme 1b. The greater acetol yield from 1-substituted fructose derivatives as compared to acetol yield from fructose is thus accounted for by the greater rate of β-elimination of an alkoxyl group as compared to a hydroxyl group. In a (2 → 1)-linked fructan, glycosidic scission followed by hydration of the fructosyl cation end-group would convert that end-group into a 1-substituted fructose derivative, subject to the mechanisms of Scheme 1. Pathway b of that scheme might therefore be operating pyrolytically, although the fate of the byproduct glyceric acid is unclear. This acid has not been reported as a product of glycan pyrolysis.

Monomeric anhydro sugars.—2,6-Anhydro-β-D-fructofuranose (2,6-AFru*f*) was identified by matching the mass spectrum of the Me_3Si derivative to that of published data[18]. The bicyclic structure of 2,6-AFru*f* involves fusio of a furanose ring and a pyranose ring, so that an alternative name for it is 2,5-anhydro-α-D-fructopyranose (2,5-AFru*p*). It is an expected product, being also formed in pyrolyses of sucrose and of fructose. The mechanism of its formation is probably



Scheme 2.

analogous to that of levoglucosan (LG) formation in glucans[19]. Thus the fructofuranosyl cation (Fruf^+), formed by heterolytic scission of fructosidic bonds, is the key intermediate (Scheme 2). As in the case of glucans, addition of ionic catalysts suppresses anhydro sugar formation. An exception to this is $Ca(OH)_2$, which appears to enhance formation of 2,6-AFru*f*. The cause of this effect is unknown. It is not observed in glucans (e.g., pyrolysis of CF11 cellulose with 5% $Ca(OH)_2$ results in a three-fold decrease in LG yield).

The yields of 2,6-AFru*f* (and that of unknown A) given in Table I are based on the FID response of 1,6-AGlc*p* (LG) relative to glucitol internal standard. 1,6-AGlc*p* and 1,6-AGlc*f* are present in small amounts in the tar but not listed in Table I. They are expected products, since inulin chains terminate in glucopyranose end-groups.

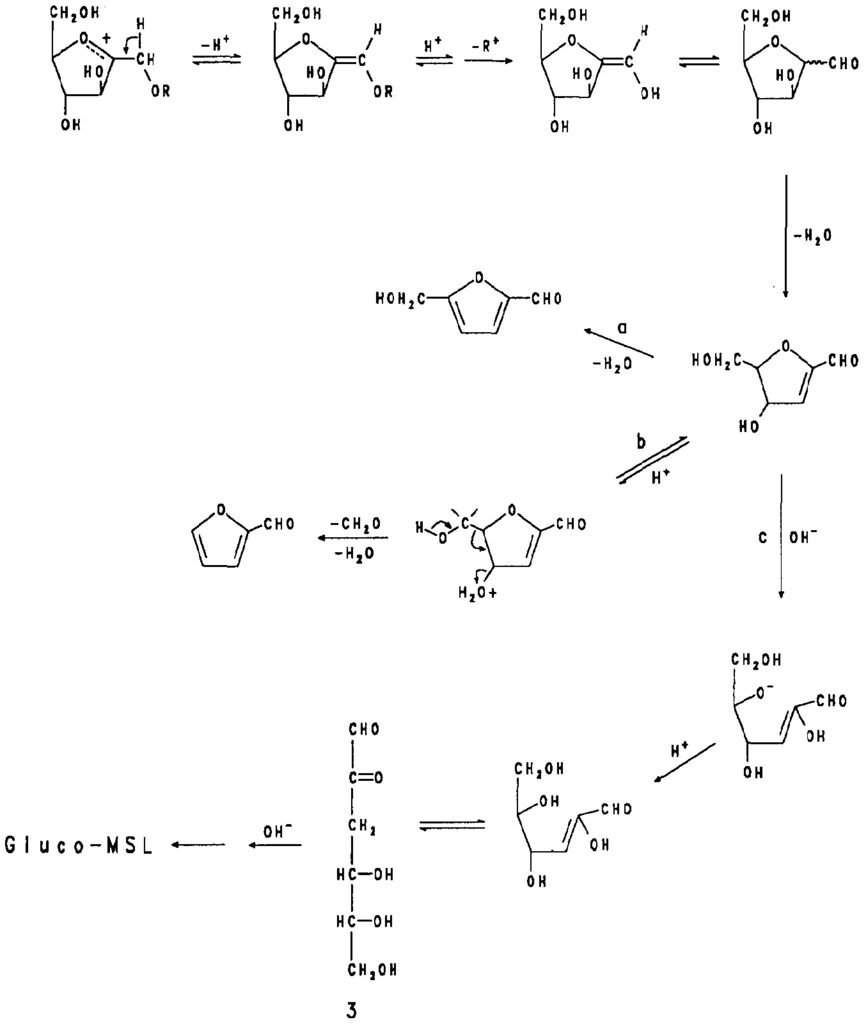
As expected, pyranose and furanose isomers of 1,6-anhydroglucose are major products from pyrolysis of untreated glucose. Of interest is the high proportion (43%) of the furanose isomer. Glucan pyrolysis in comparison, results in 1,6-AGlc that is only 5-15% furanose[1]. This effect is evidently due to mutarotation of glucose in the melt[13], forming glucofuranose ring forms (note also that in neutral aqueous solution the proportion of furanose forms of glycoses in mutarotation equilibria increases at higher temperatures[20]). Protonation of the anomeric hydroxyl group and its subsequent elimination as water results in a glucofuranosyl cation, which then "stabilizes" internally to form volatile 1,6-AGlc*f*. These steps, along with the analogous steps leading from pyranose ring forms to 1,6-AGlc*p* (LG), constitute a system of equilibria in the melt. Volatilization of the anhydro sugar removes it from the system and shifts the equilibria toward 1,6-AGlc. The increase in relative yield of 1,6-AGlc*f* is also probably due in part to the fact that cation formation (the rate-determining step) is more facile for the furanose isomer, by analogy to the known facile acid hydrolysis of furanosidic linkages[21]. Thus, despite the preference for pyranose ring forms in the mutarotation equilibria[13], a large proportion of the 1,6-AGlc is furanose. Application of these concepts to galactose, which forms furanose rings much more easily than glucose, leads to the expectation that pyrolysis of galactose should result in a high proportion of 1,6-AGal*f* relative to 1,6-AGal*p*, and this has indeed been found to be the case. Gardiner[8] subjected galactose to vacuum pyrolysis, analyzed the products by Me_3Si-GLC, and found that the 1,6-anhydrogalactose thus produced was 60% furanose.

These effects are also observed in acid-catalyzed reversion of glucose (i.e., inter- and intra-molecular elimination of water in acidic aqueous solution). Peat and co-workers[22] heated glucose in aqueous H_2SO_4 and found that the major products were 1,6-AGlc*p*, 1,6-AGlc*f*, and several disaccharides. After 2 h, the 1,6-AGlc was found to be 47% furanose (after 10 h, 34%). In comparison, Richtmyer[23] heated galactose in aqueous H_2SO_4 and thus formed 1,6-AGal which was 57% furanose.

Authentic 2,5-anhydromannose (2,5-AMan) was considered to be a possible pyrolysis product from inulin and was synthesized from 2-amino-2-deoxy-D-glucose hydrochloride[24]. It was, however, found to be unstable to trimethylsilylation and was reduced[24] with $NaBH_4$ to 2,5-anhydromannitol for indirect identification and analysis. The inulin tar was also reduced, resulting in the disappearance of unknown A in Me_3Si-GLC analysis (see Table I) and the appearance of two new peaks, the mass spectrum of one of which matched that of the authentic 2,5-anhydromannitol. The spectrum of the other was similar and is presumably that of the expected diastereomer 2,5-anhydroglucitol. This was confirmed by heating 2,5-AMan with acid, thus generating 2,5-anhydroglucose (2,5-AGlc) via keto–enol tautomerism. Neutralization, reduction, trimethylsilylation and GLC–MS resulted in a retention time and mass spectrum of 2,5-anhydroglucitol which matched that of the putative 2,5-anhydroglucitol in the reduced inulin tar.

The above results strongly suggest that unknown A in the nonreduced tar is the Me_3Si derivative of 2,5-AGlc. The mass spectrum of unknown A is interpretable as 2,5-AGlc, and yields of unknown A appear to follow the same trend as those of hydroxymethylfurfural (HMF) (Table I), a result to be expected if unknown A is an HMF precursor (Scheme 3). The yields of 2,5-AMan and 2,5-AGlc given in the table are actually the yields of the corresponding 2,5-anhydroalditols obtained after reduction of the tar and are based on the FID response of 3,6-anhydroglucitol relative to inositol internal standard.

Furan derivatives.—5-Hydroxymethyl-2-furaldehyde (HMF, 5-hydroxymethyl-furan-2-carboxaldehyde) is a common product of pyrolysis of various glycans and glycoses, although significant yields are generally obtained only from substrates containing fructofuranose units. The mechanism by which HMF is generated from inulin pyrolysis probably involves dehydration of 2,5-AMan and/or its diastereomer 2,5-AGlc as shown in Scheme 3a. This mechanism is analogous to the one recently proposed by Antal et al.[25] for the formation of HMF from fructose in water at high temperature.



Scheme 3.

As expected, higher pyrolytic yields of the furan derivatives 2-furaldehyde (furfural, furan-2-carboxaldehyde) and HMF were obtained from fructose than from glucose, this situation being also the case for degradation of these hexoses in aqueous solution[26]. Interestingly, NaCl catalyzes the formation of HMF from fructose, whereas it suppresses HMF formation from inulin. This result might be caused by NaCl having a decelerating effect on the enol ether hydrolysis step of Scheme 3 (not a rate-determining step in aqueous acid degradation[27]), but an accelerating effect on the subsequent dehydration steps. HMF from glucose, which probably arises in part via isomerization to fructose, is similarly affected. Tables II and III show that significant yields of unknown A are found with HMF in the tars from both hexoses. As discussed above, unknown A is probably 2,5-anhydroglucose, a precursor of HMF.

The formation of HMF from glucose in acidic aqueous solutions has been explained by invoking a mechanism that involves two initial, successive β-eliminations to produce a 3,4-dideoxy-3-eno-2-hexosulose intermediate, which then cyclizes via internal nucleophilic addition, followed by a final dehydration to form[26] HMF. In the case of glucose pyrolysis, isomerization to fructose in the melt provides additional pathways to both furfural and HMF, accounting for the relatively high yields of these furan derivatives from glucose as compared to their yields from glucans.

Based on results of a pyrolytic study of isotopically labeled glucose, Houminer and Patai[7] concluded that the dominant pathway whereby furfural arises from glucose involves expulsion of C-6, and that another, minor pathway involves expulsion of C-1. For the dominant pathway, these workers proposed loss of C-6 as formaldehyde from HMF, and for the minor pathway, they proposed loss of C-1 as formaldehyde from 2-furylhydroxymethyl ketone, a minor product of cellulose pyrolysis[8]. In a later paper describing another labeling study[28], these workers supplemented their HMF degradation hypothesis by reporting that about 65% of the formaldehyde produced in glucose pyrolysis derives from C-6.

Hydroxymethylfurfural, because of its relative stability and volatility, is an unlikely intermediate for furfural formation, especially under conditions of vacuum pyrolysis. In the present work, HMF was pyrolyzed under a flow of nitrogen at atmospheric pressure, increasing the temperature from 150 to 230°C at a rate of ~ 5°C min, and during that time the HMF melted and darkened while a small amount of a clear liquid condensed at room temperature downstream from the pyrolyzing sample. Subsequent ^{1}H NMR analysis of that clear condensate demonstrated that it was pure HMF. No furfural was detected. In another experiment, HMF was pyrolyzed in a sealed tube for 30 min at 250°C, and the result was an insoluble char containing no furfural. The HMF degradation hypothesis is further opposed by the work of Kato[9], who thermally degraded HMF at different temperatures and reported the products 5-methylfurfural and furfural in ratios of 5 : 1 at 350°C and 10 : 1 at 500°C. Since the yield of 5-methylfurfural is much smaller than the yield of furfural from cellulose pyrolysis, Kato concluded that secondary degradation of HMF could not be an important pyrolytic pathway leading to furfural.

Pyrolytic formation of furfural from hexoses via expulsion of C-6 is reminiscent of its formation (in ~ 30% of theoretical yield) via decarboxylation of hexuronic acids in hot, aqueous acidic solutions[29]. Nearly quantitative yields of carbon dioxide are obtainable from hexuronic acids by either reflux in acidic solution or by pyrolysis[26]. The generally accepted mechanism[26] for furfural formation from degradation of hexuronic acids in acidic aqueous solution involves successive dehydration and decarboxylation reactions, and it is possible that a similar mechanism operates to produce furfural in the pyrolysis of polyhexuronic acids such as pectic acid [poly(galacturonic acid)]. Pyrolysis mass spectrometry experiments conducted by Meuzelaar et al.[30] on pectic acid resulted in mass spectra in which *m/z* 96 was the base peak. It seemed to us that this ion was most likely due to furfural which arises by dehydration and expulsion, via decarboxylation, of C-6 in the galacturonic acid residues. To confirm the presence of furfural in polyhexuronic acid pyrolyzate, pectic acid was pyrolyzed (300°C for 30 min) in the present study. ^{1}H NMR analysis of the distillate fraction (yield, 37%) showed that its principal component after water was furfural, produced in 1.3% yield from the pectic acid. This is a much higher yield of furfural than would be obtained from pyrolysis of an aldohexopyranan, and it is probably due to the operation of the mechanism just described.

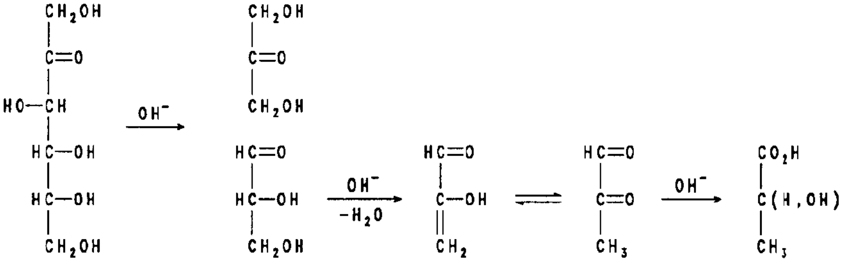
By analogy with the loss of C-6 of a glycuronic acid as CO_2, one can propose a related mechanism whereby C-6 of a glycose is lost as formaldehyde. The closest literature precedent to such a process appears to be the cleavage of alkoxides of tertiary alcohols[31], a reaction that is essentially the reverse of addition of carbanions to ketones. The expulsion of C-6 as formaldehyde would be less efficient than its expulsion as CO_2, which would explain the lower yield of furfural from aldohexoglucans as compared to poly(aldohexuronic acids).

The relatively high yields of furfural from pyrolysis of fructose (and of ketohexoglycans such as inulin) as compared to pyrolysis of glucose (and of glucans) are undoubtedly due to the preexistence of the essential furan framework in the preferred furanosyl ring forms of these substrates. A mechanism similar to that of HMF formation shown in Scheme 3 is, therefore, also probably responsible for furfural formation, with expulsion of the hydroxymethyl group occurring prior to final furan ring formation (e.g., Scheme 3b). To confirm the assumption that the dominant pathway involves loss of C-6, fructose, 20% enriched with ^{13}C at C-1, was pyrolyzed (250°C for 40 min), and the distillate fraction was analyzed by GLC–MS, which showed that 74% of the original label at C-1 had been retained in the furfural, suggesting that the dominant pathway for furfural formation involves expulsion of C-6.

The saccharinic acid lactones.—Glucometasaccharinolactone (Gluco-MSL, 2 epimers; 3-deoxy-D-glucono-1,4-lactone and 3-deoxy-D-manno-1,4-lactone) is a somewhat surprising product from inulin. If any of the three possible types of saccharinic acids were to be formed during inulin pyrolysis, one might expect it to be the one known simply as glucosaccharinic acid (**1**). This would result in the presence of either or both isomers of glucosaccharinolactone (gluco-SL; 2,3,5-trihydroxy-2-methyl-D-erythro-4-pentanolides) in the tar fraction. Glucosaccharinic acid is formed at least partly by benzilic acid rearrangement of the 1-deoxy-2,3-hexodiulose intermediate **2** in the alkaline degradation of (2 → 1)-linked fructans and of 1-linked fructose derivatives[32] as shown in Scheme 1a. Isotopic labeling experiments by Sowden[33] demonstrate that there is also a fragmentation–recombination mechanism involved. One possible explanation for the absence of gluco-SL from the inulin tar is that pathways involving fragmentation of the intermediate **2** strongly compete with benzilic acid rearrangement (e.g., Scheme 1b). The work by Sowden[33] indicates that fragmentation of **2** is very important in alkaline solution, although the nature of the fragments is uncertain. It has been shown[34] that calcium ions catalyze the benzilic acid rearrangement in saccharinic acid formation, and it was this idea that motivated the use of $Ca(OH)_2$ and of $Ca(OAc)_2$ as catalysts in inulin pyrolysis. However, no gluco-SL was detected in any of the tar fractions.

Gluco-MSL is known to be formed from pyrolysis of (1 → 3)-linked glucans in up to 38% yield[35], and the mechanism is almost certainly analogous to the established alkaline-degradation pathway whereby metasaccharinic acids form from 3-substituted glucose derivatives[32]. However, the mechanism by which gluco-MSL arises from the pyrolysis of inulin is unknown. It could perhaps be peculiar to pyrolysis, since refluxing inulin in 1 M NaOH followed by acidification and drying under vacuum did not result in detectable gluco-MSL, although it did produce gluco-SL in 0.9% yield. The appearance of gluco-MSL instead of the expected gluco-SL in the inulin tar fraction is reminiscent of the occurrence of significant gluco-MSL but little or none of the expected glucoisosaccharinolactone (gluco-ISL; 2,5-dihydroxy-2-hydroxymethyl-D-*glycero*-4-pentanolides) in the tars of (1 → 4)-linked glucans[1]. As in that case, one might invoke transglycosylation to form a 3-linkage as the explanation. In the case of the fructosyl residues in inulin, however, migration of the carbonyl group in the open-chain fructose unit from C-2 to C-1 would also be required, and this could occur only after scission of the fructosidic bond at C-1. This seems to be a rather tortuous pathway, and it is tempting to look for a more direct route whereby the 3-deoxyhexosulose precursor **3** of gluco-MSL can arise. One could for example postulate the mechanism of Scheme 3c, in which nucleophilic attack by OH^- upon C-2 of the HMF precursor opens the ring. Equilibration to the keto tautomer then gives rise to the gluco-MSL precursor **3**.

The concurrent pyrolytic formation of all three types of saccharinic acid lactones from each of the two hexoses is noteworthy. In particular, the pyrolytic formation of gluco-SL has not been previously reported. A single isomer of this lactone was identified, and it is assumed to be the α epimer, as this is the one preferentially formed from glucose in alkaline aqueous solution[33]. That these lactones form in a basic pyrolysis matrix leaves little doubt that they arise via the established mechanisms of alkaline degradation, with β-hydroxycarbonyl eliminations occurring in lieu of β-alkoxycarbonyl eliminations, the lower efficiency of the former process being compensated for by the increased availability of acyclic forms in the hot melt. Saturated aqueous solutions of $Ca(OH)_2$ (lime water) have proven to be the most effective medium for converting hexoses into saccharinic acids, fructose being somewhat more efficient than glucose in forming gluco-SL[33]. The treatment of fructose with lime water at 35°C for one week[36], followed by filtration, acidification and drying, resulted in gluco-SL (8.0% yield), gluco-ISL (6.0% yield), and gluco-MSL (4.8% yield) as demonstrated by Me_3Si-GLC. Like-



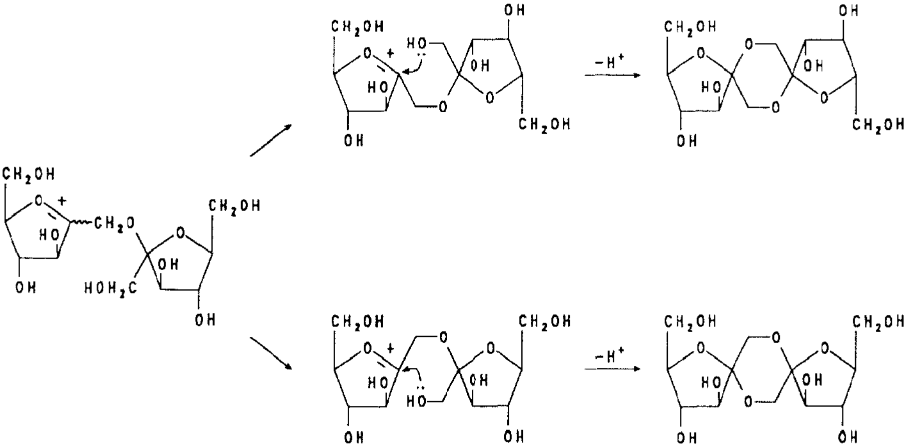
Scheme 4.

wise, highest pyrolytic yields of these lactones were obtained by premixing the hexose with 10% $Ca(OH)_2$ (Tables II and III). The predominance of gluco-MSL in the pyrolytic situation suggests that there may be additional pathways to this lactone which are unique to pyrolysis. A possibility for a pathway involving fructofuranose rings is presented in Scheme 3c. As for glucose, the 3-deoxyhexosulose precursor **3** of gluco-MSL might arise via dehydration of the glucopyranose ring prior to ring-opening[37].

Lactic acid and 1,3-dihydroxy-2-propanone (dihydroxyacetone, DHA).—A significant yield of lactic acid in the tars of the base-catalyzed pyrolyses of inulin and of the hexoses is noteworthy, since lactic acid is a major product of the alkaline degradation of these and other carbohydrates. Moreover, the concurrent formation of DHA suggests that these compounds form by the alkaline degradation pathway shown in Scheme 4 (the scheme shows the mechanism applied to fructose; aldoses must first isomerize to a 2-ketose). In this mechanism, which has been firmly established[26,33], the ketose cleaves into two trioses via reverse aldol reaction. One of these trioses, DHA, can isomerize to the other triose, glyceraldehyde. The latter undergoes β-hydroxycarbonyl elimination to form methylglyoxal (pyruvaldehyde), from which lactic acid arises via the benzilic acid rearrangement.

In alkaline solution there is ample time and opportunity for DHA to isomerize to glyceraldehyde and for the latter to transform into lactic acid. Consequently, alkaline digests of hexoses contain large yields of lactic acid and small yields of DHA. Under conditions of vacuum pyrolysis, however, one would expect this situation to be reversed. The volatility of DHA militates against its further reaction before leaving the heated zone as a gas. Likewise, competing pyrolytic reactions, as well as the volatility of intermediates, militate against the transformation of much of the glyceraldehyde into lactic acid. Thus, both glyceraldehyde and pyruvaldehyde have been reported as significant products of glucan pyrolysis[38] (the latter was reported to be obtained in 3.3% yield from flash pyrolysis of NaOH-treated cellulose[14]). The consistently larger yields of DHA compared to lactic acid in Tables I–III are probably a reflection of these factors.

Significant amounts of lactic acid appeared also to be present in the tars from the $Ca(OH)_2$-catalyzed pyrolysis of the two hexoses and in the tar from the



Scheme 5.

$Ca(OAc)_2$-catalyzed pyrolysis of inulin, but quantification by ^1H NMR was prevented by interference from other signals. The appropriate ^1H NMR signal for pyruvaldehyde (singlet at 2.25 ppm) was seen in the distillate spectra from the NaOH-catalyzed and $Ca(OH)_2$-catalyzed pyrolyses of both hexoses, and in the distillate spectrum from the NaOH-catalyzed pyrolysis of inulin, corresponding to a yield of 0.2–0.4%.

Disaccharides.—The disaccharides listed in Table I are seen as a cluster of 10–12 late-running peaks in the gas chromatogram. Several of these compounds are undoubtedly isomeric difructose dianhydrides (DFDAs). Scheme 5 shows how two such isomers might form pyrolytically from a dimeric cation. DFDAs are also formed by the action of HNO_3 upon the acetates of fructans such as inulin[39], by the action of HF upon inulin or fructose[40], and by the action of methanolic H_2SO_4 or trifluoroacetic acid upon fructose[40]. In the pyrolytic situation, acidic byproducts of the pyrolysis might serve to induce formation of DFDAs, and the presence of a basic additive might actually favor DFDA formation by slowing the charring reactions which would otherwise be catalyzed by acidic pyrolysis products. Isomerization of furanose to pyranose ring forms would result in additional isomers of these anhydrides. One such isomer has been positively identified in the inulin tar by the mass spectrum of its Me_3Si derivative[41]. Isomers of fructosyl anhydrofructose are also probably included among the disaccharides in the inulin tar. Quantification of the disaccharides listed in Tables I–III was achieved by adding the areas of the peaks and applying the f.i.d. response factor of sucrose relative to glucitol. Further studies, still in progress, indicate that the true yields of the disaccharides are actually greater than shown in Table I, because they are incompletely volatilized from char to tar during the pyrolysis. Further studies of these products will be described at a later date.

The pyrolysis of a glycose inevitably involves to some degree the pyrolysis of a randomly linked glycan resulting from thermal polymerization during early stages of the pyrolysis, such polymerization occurring even without added catalyst. Thus, Sugisawa and Edo[42] heated untreated glucose for 2.5 h at 150 and identified nine disaccharides and two trisaccharides in the resulting caramel, the disaccharides containing all possible linkages and orientations. The disaccharides mentioned in Tables II and III are seen as a cluster of peaks which run in the disaccharide region of the chromatogram. Undoubtedly, these disaccharides include various isomers of glycosyl-anhydroglycose (e.g., "cellobiosan"), and among the disaccharides from fructose, there may be difructose dianhydrides. The tar from untreated fructose was analyzed for possible trisaccharides, and another cluster of peaks, well separated from the disaccharides, was seen running in the trisaccharide region of the chromatogram. Quantification of the total area, using the response factor of raffinose, indicated a yield of 1.3%.

As with the disaccharide yields from the inulin pyrolyses, those from the hexose pyrolyses should be taken as representing only a portion of disaccharides formed, some of which probably remained in the char fraction, which was weighed but not analyzed. However, because the spattering and/or foaming of the hexose sample was minimal in each case, and also because the pyrolysis temperature was 35°C higher in these cases, the disaccharide yields listed in Tables II and III can probably be taken, at least, as a comparative measure of disaccharide formation. Table II shows that the tar fraction from pyrolysis of untreated glucose contains roughly equal amounts of disaccharides and of glucose, this despite the fact that glucose would be expected to be more volatile than the disaccharides. The implication is that the disaccharides form quickly at this temperature. With the addition of NaCl, the disaccharide content of the tar changes little, but the glucose content decreases to less than one-fifth its former value. The monomers thus appear to be subject to new (or faster) degradative pathways in addition to polymerization. Finally, addition of NaOH appears to result in a decreased rate of disaccharide formation. The polymerization probably occurs via a glucosyl cation intermediate[43], and the suppression of such cation formation by OH^- explains the effect of NaOH.

EXPERIMENTAL

Materials and general methods.—Inulin from dahlia tubers (Sigma Chemical Company) was acid-washed by three successive treatments with 1:1 (v/v) acetone-0.1 N HCl for 2 h at 2°C, followed by five successive treatments with 1:1 (v/v) acetone-water for 30 min at 2°C, then two successive washes with acetone, followed by drying under vacuum. This procedure resulted in removal of 95% of the indigenous inorganic ions (measured by inductively coupled argon-plasma spectrometry). Table IV details results of the procedure. Concentrations in ppm of major indigenous ions are listed.

Additives, except for $Ca(OH)_2$, were mixed with the acid-washed inulin by freeze-drying from concentrated aqueous solutions. Additives were mixed with the

TABLE IV

Results of acid-washing inulin

	Ca	Mg	P	Na	K
Inulin	88	376	666	284	508
H^+ washed	5	5	5	0	77

hexoses, and $Ca(OH)_2$ with the inulin, by grinding in a mortar and pestle. Vacuum pyrolyses were conducted on a 0.25-g scale at a pressure of 1.5 mmHg under a flow of N_2 as described previously[44]. ^1H NMR spectra were recorded at room temperature at 90 MHz, using D_2O as solvent and 2-methyl-2-propanol as internal standard (1.20 ppm). Mass spectral analyses were performed with a Hewlett–Packard 5970 mass selective detector interfaced with a Hewlett–Packard 9133 computer. GLC analyses were performed with a Hewlett–Packard 5890A gas chromatograph using He as carrier gas. Hewlett–Packard Ultra-1 (0.20 mm i.d., 25 m, 0.33 μm crosslinked methyl silicone) and Ultra-2 (0.31 mm i.d., 25 m, 0.52 μm crosslinked 5% phenyl methyl silicone) capillary columns were used for the GLC–MS and GLC-FID analyses, respectively. Temperature programs were as follows: for GLC–MS, 160°C for 4 min, then 25°C min to 210°C, then 4°C/min to 260°C; for GLC-FID, 160 to 200°C at 30°C min, then 200°C isothermal.

Me_3Si-GLC-FID analyses of tar fractions.—Tar fractions (2–5 mg) containing added D-glucitol internal standard (0.5–1 mg) were trimethylsilylated for 40 min at 90°C using Tri-Sil reagent (Pierce Chemical Company). The resulting solutions were taken to dryness at 40°C in a stream of dry air and the residue extracted with hexane. Retention times of the Me_3Si derivatives on the Ultra-2 column relative to D-glucitol (1.00) and FID response factors relative to D-glucitol (1.00) are listed in Table V. 2,5-Anhydromannose (2,5-AMan) and 2,5-anhydroglucose (2,5-AGlc) are not listed in the table because these components were quantified via their reduced forms. Retention times of the Me_3Si derivatives of these anhydroalditols (0.61 and

TABLE V

GLC of Me_3Si derivatives on Ultra 2 column

	Retention time [a]	FID response [a]
2,6-AFru*f*	0.35	0.7 [d]
Unknown A [b]	0.39	0.7 [d]
Gluco-SL	0.44	0.5 [d]
1,6-AGlc (LG)	0.46	0.7
1,6-AGlc*f*	0.50	0.7 [d]
Gluco-ISL	0.52	0.6
Gluco-MSL	0.60, 0.61	0.4
α-Glc*f* [c]	0.70	0.7 [d]
α-Glc*p* [c]	0.84	0.7 [d]
β-Glc*p* [c]	1.19	0.7

[a] Relative to D-glucitol (1.00). [b] Probably 2,5-anhydroglucose. [c] Isomer of glucose. [d] Estimated.

0.64, respectively) were measured relative to myo-inositol (1.00) (retention time of inositol relative to glucitol, 1.10; FID response factor of inositol relative to glucitol is assumed to be 1.00). Yields were based on FID response of 3,6-anhydroglucitol relative to inositol (0.90).

The disaccharides quantified in the work on pyrolysis of glycoses were associated with a group of peaks that appeared between 7 and 12 min in the chromatogram, using the Ultra-2 column on a temperature program of 160°C initially, then 30°C/min to 280°C (isothermal for 15 min), then 30°C min to 320°C (isothermal). The trisaccharides detected in the tar from fructose pyrolysis were associated with a group of peaks that appeared between 20 and 25 min on the same temperature program. Also on that program, glucitol eluted at 5.7, sucrose at 8.8, and raffinose at 23.9 min. Response factors of the latter compounds (relative to glucitol) are 1.2 and 0.65, respectively.

^{1}H NMR analyses of tar fractions.—HMF yield was determined by ^{1}H NMR of the tar rather than by GLC-FID of the Me_3Si derivative since the latter derivative of HMF is quite volatile, causing some to be lost during workup. Throughout the inulin work, a water-cooled condenser was kept around the tar tube during the pyrolyses to ensure that all HMF would condense there (this might have resulted in a slight decrease in GA yield as measured in the distillate). No such actions were taken for the hexose pyrolyses, however, so a small proportion of HMF occasionally appeared in the distillate. 1,3-Dihydroxy-2-propanone (dihydroxyacetone, DHA) and lactic acid also appeared in both fractions, the former predominantly in the tar. When lactic acid was formed, it would sometimes condense predominantly in the tar and other times predominantly in the distillate, apparently depending on such factors as pyrolysis temperature and rate of formation. In each case where a component appeared in both fractions, the total yield was arrived at by adding yields from the separate fractions as determined by ^{1}H NMR.

^{1}H NMR analyses of distillate fractions.—Upon completion of the pyrolysis, the frozen distillate fraction was allowed to warm to room temperature. After weigh-

TABLE VI

^{1}H NMR chemical shifts in D_2O

Compound	Shift (ppm)
GA[a]	3.48 (d, 5.0), 5.00 (t)
Acetol	2.11 (s), 4.31 (s)
HOAc	2.04 (s)
HCO_2H	8.18 (s)
DHA[b]	4.36 (s)
Lactic acid	1.38 (d, 7.2), 4.34 (q)
HMF[c]	9.40 (s), 7.48 (d, 4.0), 6.62 (d), 4.65 (s)
Furfural	9.41 (s), 7.85 (d, 1.8), 7.49 (d, 3.7), 7.69 (dd)

[a] Hydrated monomer of glycolaldehyde. [b] Dihydroxyacetone. [c] Hydroxymethylfurfural.

TABLE VII

MS data[a] for Me_3Si derivatives of saccharinic acid lactones

Gluco-SL	103 (15), 117 (63), 133 (16), 147 (78), 191 (13), 217 (100), 218 (42), 219 (14), 231 (12), 260 (23), 378 (31)
Gluco-ISL	103 (56), 116 (23), 117 (43), 129 (42), 133 (22), 147 (56), 149 (12), 155 (10), 217 (18), 243 (10), 245 (30), 348 (100)
Gluco-MSL[b]	103 (39), 117 (35), 129 (80), 131 (21), 133 (43), 147 (100), 149 (34), 155 (59), 189 (21), 205 (28), 245 (28), 246 (38), 247 (19), 273 (31), 292 (25), 322 (6), 378 (5)

[a] Mass range: 100–500 amu. [b] Epimers did not resolve on Ultra-1 column.

ing, it was rinsed out of the cold trap with D_2O (0.5 mL) containing internal standard (~ 0.02 mmol). Quantitative analysis was achieved by integration of ^1H NMR signals relative to the internal standard. Table VI lists chemical shifts (ppm) for compounds analyzed by ^1H NMR, with multiplicities and coupling constants (Hz) given in parentheses. The predominant species of glycolaldehyde in dilute aqueous solutions (~ 78%) is the hydrated monomer[45], and the doublet at 3.48 ppm arising from this species was used to quantify the GA yield. Thus, in calculating this quantity, a correction was made to allow for equilibration with the other GA molecular species. A correction was also needed for formic acid, due apparently to the unusually long relaxation time of the proton attached to the carbonyl carbon. ^1H NMR calibrations of the formic acid proton, using D_2O solutions of known concentration, demonstrated that the intensity of this signal (at 8.18 ppm), using a pulse delay of 0.2 s, accounted for only 30% of the actual formic acid present. For this reason, distillate spectra were acquired with a 2-s pulse delay, and this resulted in a formic acid signal accounting for 67% of actual formic acid present.

The saccharinic acid lactones.—"Glucosaccharinolactone" (gluco-SL), "glucoisosaccharinolactone" (gluco-ISL), and "glucometasaccharinolactone" (gluco-MSL) were identified in tar fractions as the Me_3Si ether derivatives by comparison with the GLC retention times and mass spectra of derivatives prepared from authentic samples of the lactones[36,46,47]. Relative retention times of the α isomer of gluco-SL, of the α isomer of gluco-ISL, and of the pair of isomers of gluco-MSL on a Hewlett–Packard Ultra-2 capillary column are given in Table V. Major m/z values (and relative intensities) in the mass spectra of the Me_3Si ether derivatives of these lactones are listed in Table VII.

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