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OXIDATION AND DEGRADATION OF MALTOSE AND ISOMALTOSE BY PERSULFATE

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ABSTRACT

Maltose and isomaltose were oxidized and degraded by ammonium persulfate in 66.7 mmol aqueous phosphate buffer (pH 7.1). Product and e.s.r. studies suggested that radicals formed by C–H abstraction at C-1 and C-4 were predominant for oxidation of maltose, whereas C–H abstraction of isomaltose proceeded preferentially at C-5 of the reducing glucose group.

INTRODUCTION

Persulfate, a well-established initiator, has been exploited in the graft polymerization of poly(vinyl alcohol)[1], cellulose[2], and pullulan[3]. Recently, we have succeeded in grafting several vinyl monomers onto pullulan by using ammonium persulfate. However, a serious drawback was that pullulan was degraded by persulfate[3]. Such degradation has been overlooked in graft polymerization of polysaccharides because most polysaccharides used in this field, such as cellulose and starch, are insoluble in the solvents. This degradation, however, is considered to take place to an appreciable extent in the graft polymerization of such water- or Me_2SO-soluble polysaccharides as pullulan or dextran.

Although persulfate is known to oxidize methanol[4,5], ethanol[5], 2-propanol[5–7], and glucose[8], only limited knowledge is available concerning the degradation of carbohydrates by persulfate. This degradation has been suspected to be an oxidative degradation in the case of *O*-(hydroxyethyl)cellulose[9], but details regarding the degradation mechanism remain ambiguous.

In order to investigate the degradation of carbohydrates in the presence of persulfate, we selected here two disaccharides of D-glucose, maltose [α-D-Glc*p*-(1→4)-D-Glc*p*] and isomaltose [α-D-Glc*p*-(1→6)-D-Glc*p*] as substrates. These are regarded as model compounds for pullulan (+α-D-Glc*p*-(1→4)-α-D-Glc*p*-(1→4)-α-

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D-Glc*p*-(1→6)$\}_n$), starch ($\{\alpha$-D-Glc*p*-(1→4)$\}_n$), and dextran ($\{\alpha$-D-Glc*p*-(1→6)$\}_n$).

Two methods, product analysis and electron spin resonance (e.s.r.), were employed in this work to examine the degradation and oxidation of maltose and isomaltose by ammonium persulfate. Acetylated oxidation products were separated by high-performance liquid chromatography (l.c.) and identified by 400-MHz ^{1}H-n.m.r. and fast-atom-bombardment (f.a.b.) mass spectroscopy.

Several e.s.r. investigations on free-radical generation in carbohydrates under various conditions have been reported[10–17], in which the flow techniques[10–13] and freezing method[14–17] have been used. The spin-trapping technique has received considerable attention in the past few years because it does not require any special apparatus[18–21]. Although spin trapping has been applied to carbohydrates[22,23], to our knowledge, no satisfactory data are available for the adducts of carbohydrate radicals. Therefore, we demonstrate here that the spin-trapping method may be applied in the carbohydrate chemistry.

On the basis of these results, the mechanism of oxidation and degradation of maltose and isomaltose by ammonium persulfate is discussed.

EXPERIMENTAL

Materials. — Maltose and isomaltose were kindly supplied by Hayashibara Biomedical Laboratories, Inc. (Okayama, Japan). Ammonium persulfate was of guaranteed grade and its purity (99%) was determined by idometric titration. Phenyl *N-tert*-butylnitrone [PhCH=N(O)Bu^t] and 2-methyl-2-nitrosopropane (Bu^{t}NO) were obtained commercially from Aldrich Chemical Co. Ltd.

Measurements. — Fast-atom-bombardment mass spectrometry was performed with a JEOL JMS-DX 300 mass spectrometer. The compounds were dissolved in 1:1 methanol–chloroform and added to a drop of glycerol on the target. Sodium iodide was added to the matrix to enhance the formation of quasimolecular ions. The atom gun operated at 6 keV with xenon as the bombarding gas. Spectra were recorded at an acceleration voltage of 3 keV. The 400-MHz ^{1}H-n.m.r. spectra were recorded for solutions in $CDCl_3$ with a JEOL GX-400 spectrometer. Specific rotations were determined with a PM-101 automatic, digital polarimeter (Union Giken, Osaka). Gas–liquid chromatography was performed with a Hitachi 063 gas chromatograph equipped with a flame-ionization detector and a fused-silica capillary column (FFAP, 0.25 mm × 25 m, Gasukuro Kogyo, Tokyo). E.s.r. spectra were recorded for phosphate buffer solutions (66.7mM, pH 7.1, 1 mL) of substrate (0.171 g, 0.5 mmol), ammonium persulfate (11.4 mg, 50 μmol), and spin-trapping reagent (2 mg) by a JEOL JEX-FEIX spectrometer (X band) with 5 mV of microwave power at 50°.

Reaction of maltose and isomaltose with ammonium persulfate. — A flask containing a mixture of maltose (3.0 g, 8.77 mmol) and ammonium persulfate (1.73 g, 7.5 mmol) in 66.7mM phosphate buffer (150 mL, pH 7.1 at 20°) was kept for 2 h at 60° under nitrogen. After the reaction, when the pH of the solution was 6.45

(20°), potassium iodide (1.3 g) was added to decompose the remaining oxidant. The pH of the mixture was adjusted to 7.0 by adding NaOH (0.01M). The solution was evaporated to dryness under diminished pressure and dried at 50° *in vacuo*. The residue was acetylated with acetic anhydride (50 mL)–pyridine (50 mL) for 2 h at 100°. The mixture was then evaporated and acetic anhydride was removed by distillation of toluene from the residue. The residue was dissolved in 100 mL of $CHCl_3$ and the solution washed twice with 300 mL of water. The organic phase was dried over sodium sulfate and evaporated to dryness; yield, 3.45 g.

The acetylated product was then introduced onto preparative gel-permeation columns (TSK-Gel G2000HG, 60 × 2.2 cm × 2) that were eluted with $CHCl_3$ to give two fractions, the first (0.37 g) having a molecular weight larger than that of maltose octaacetate, and the second (2.46 g) of lower molecular weight. A portion (1.3 g) of the lower-molecular weight material was chromatographed on a reversed-phase column (TSK-Gel LS-410, ODS-silica, TOYO SODA, 250 × 8 mm). The chromatographic conditions are described in the legend to Fig. 1.

The reaction of isomaltose (1.2 g, 3.5 mmol) and ammonium persulfate (0.69

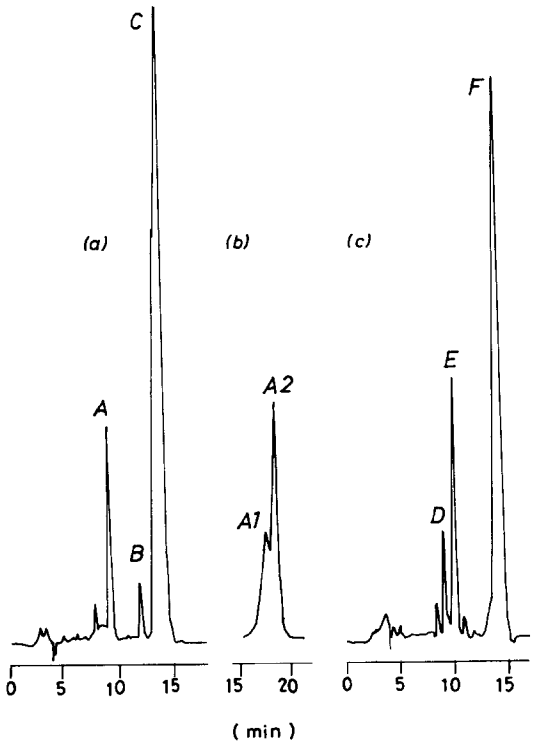


Fig. 1. Reversed-phase l.c. diagram of acetylated oxidation products of (see experimental section) (*a*) maltose and (*c*) isomaltose. Conditions: column, ODS-silica gel (TSK-Gel, LS-410, TOYO SODA, 250 × 8 mm); eluent, 1:1 (v/v) CH_3CN–H_2O, flow rate, 2.2 mL/min; detection, r.i. G.p.c. diagram of compounds from peak A (*b*), conditions: column, GElKO A-120 and A-110 (Hitachi Chemicals); eluent, $CHCl_3$; flow rate, 1 mL/min; detection, r.i.

g, 3 mmol) (in the same molar ratio as with the maltose–ammonium persulfate reaction) was processed in the same manner.

Blank experiment. — Maltose (or isomaltose) (0.2 g, 0.6 mmol) was dissolved in 33.3 mM phosphate buffer (10 mL, pH 6.40, 20°) and the solution was kept for 2 h at 60°. Potassium iodide (0.2 g) was added to the solution, which was then evaporated to dryness. The residue was acetylated as already described.

RESULTS

As the purpose of this work was to investigate the degradation of maltose and isomaltose by ammonium persulfate, it was important to employ neutral media in which no hydrolysis of disaccharides could occur. Because the aqueous solution of oxidant is acidic, we used 66.7mM phosphate buffer (pH 7.1, 20°) as solvent. The pH of the reaction mixture was found to become 6.45 at [ammonium persulfate] = 0.05M after 2 h at 60°. A blank experiment was carried out in 33.3mM phosphate buffer (pH 6.40, 20°). By examination of the acetylated products from the blank experiment, no new compounds were obtained except the substrates (maltose or isomaltose octaacetates), confirming that the degradation did not occur in the absence of ammonium persulfate at pH 6.40.

For separation and identification of the oxidation product, acetylation was

TABLE I

CHARACTERISTICS OF PRODUCTS

Compound[a]	%	*I.r. (neat)* cm^{-1}	$[\alpha]_D^{25}$ *($CHCl_3$)*	*m.p.* (°)	*U.v. (EtOH)* *nm*
Higher-molecular weight substances	20				
1 (peak A1)	3.5	1640, 1700–1740	+151° (*c* 0.7)		205 (ε 3200)
D-Glucose pentaacetate (peak A2)	5.5	1740			
2 (peak B)	3.0	1670, 1700–1740	+133° (*c* 0.3)		205 (ε 4100)
Maltose octaacetate (peak C)	65	1740			
Higher-molecular weight substances	18				
D-Glucose pentaacetate (peak D)	5	1740			
3 (peak E)	16	1580, 1650, 1740	+132° (*c* 2.8)	142–143	292 (ε 7400)
Isomaltose octaacetate (peak F)	55	1740			

[a]See Fig. 1.

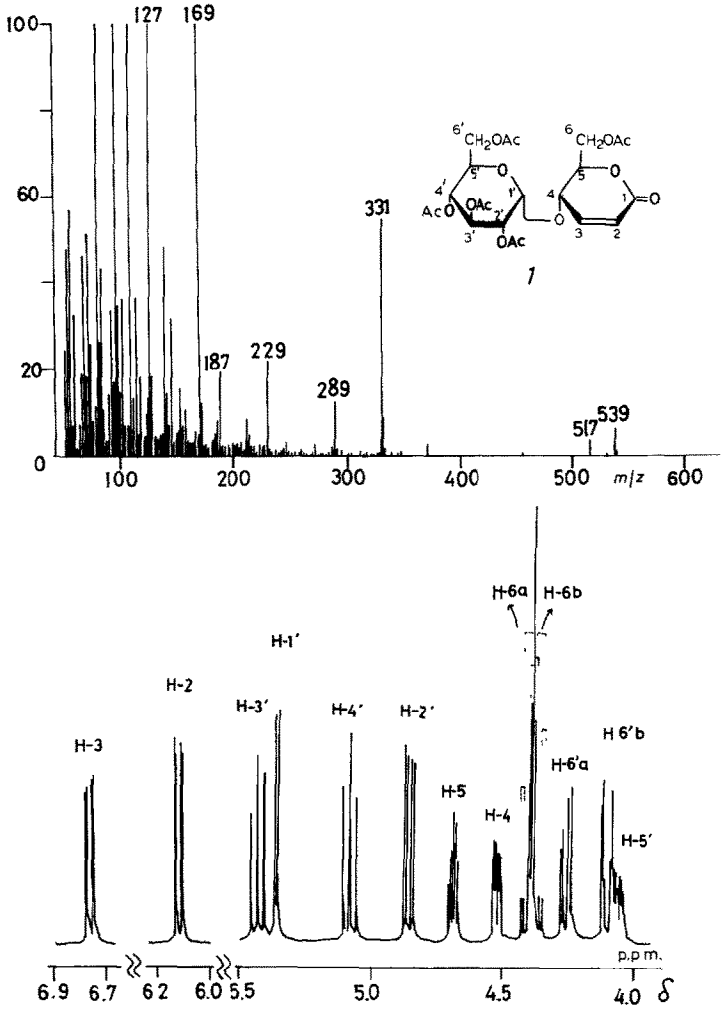


Fig. 2. F.a.b.m.s. and 400-MHz ^{1}H-n.m.r. spectra of **1** (from peak A1).

carried out. Through g.p.c., substances of higher molecular-weight were removed, and a fraction having molecular weight equal to or smaller than that of maltose (isomaltose) octaacetate was further subjected to a reversed-phase liquid chromatography to give chromatograms shown in Fig. 1a and Fig. 1c for maltose and isomaltose, respectively. Peak A of Fig. 1a is further resolved into two peaks by g.p.c. (Fig. 1b).

Characteristics for all fractions are listed in Table I.

The compounds in peaks A2 and D were readily identified as penta-*O*-acetyl-α,β-D-glucopyranose by comparison with an authentic sample in gas–liquid chromatography, and by 400-MHz ^{1}H-n.m.r. spectroscopy. It was determined that

TABLE II

^{1}H-N M R PARAMETERS OF COMPOUNDS **1, 2,** AND **3**[a]

Compound	*Chemical shifts at 400 MHz in $CDCl_3$*													
	H-1'	*H-2'*	*H-3'*	*H-4'*	*H-5'*	*H-6a'*	*H-6b'*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6a*	*H-6b*	*OAc*
1	5 35d	4.85dd	5.42dd	5.07dd	4.05m	4.25dd	4.10dd	6.11dd	6.75dd	4.52m	4.69m	4.41dd	4.35dd	2.02, 2.05, 2.08, 2.11, 2.12
2	5.33d	4.84dd	5.42dd	5.06dd	4.05m	4.25dd	4.10dd		6.41dd	4.65dd	4.81m	4.40d	4.40d	2.03, 2.05, 2.07, 2.10, 2.12, 2.29
3	5 18d	4.90dd	5.49dd	5.08dd	4.04m	4.27dd	4.10dd	6.26d	7.09d			4.46d	4.37d	2.31, 2.09, 2.01
	Coupling constants in Hz[b]													
	$J_{1',2'}$	$J_{2',3'}$	$J_{3',4'}$	$J_{4',5'}$	$J_{5',6'a}$	$J_{5',6'b}$	$J_{6'a,6'b}$	$J_{2,3}$	$J_{2,4}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$J_{6a,6b}$
1	3.97	10.07	9.76	10.07	4.57	2.54	12.51	10.07	1.53	3.05	4.58	4.57	4.57	12.50
2	3.96	10.07	9.77	10.07	4.88	2.44	12.51			3.66	5.04	4.27	4.27	
3	3.97	10.38	9.46	9.77	4.28	2.44	12.21	7.02						14.04

[a]The ring protons in the non-reducing ring are designated by primed numbers; d doublet, dd doublet of doublets, m multiplet. [b]The coupling constants are expressed in absolute values.

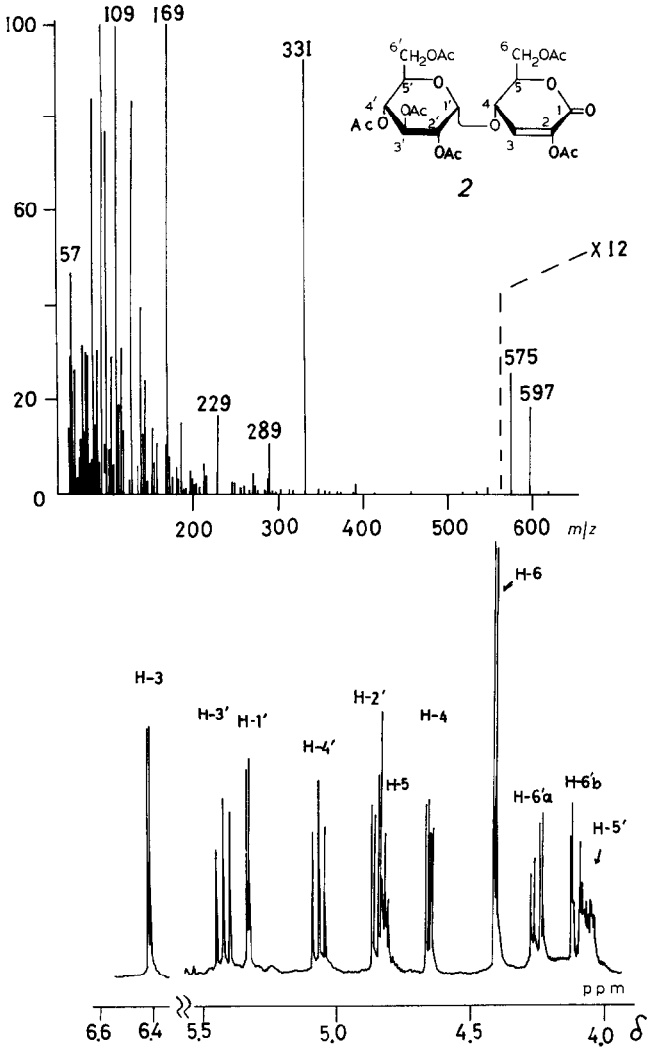


Fig. 3. F.a.b.m.s. and 400-MHz ^{1}H-n.m.r. spectra of **2** (from peak B).

D-glucose was liberated from maltose and isomaltose in a yield of ~5% by persulfate under the experimental conditions used.

For determination of structures of the other compounds, the ability to obtain precise molecular weight was of great help in deciding alternative, plausible structures. Because of the high-temperature instability of acetylated carbohydrates, the molecular ion was only occasionally traced in electron-impact, chemical-ionization, and field-desorption mass spectrometry. However, fast-atom bombardment spectrometry (f.a.b.m.s.)[24] enabled us to determine the precise molecular weights of compounds under consideration.

In the f.a.b. mass spectrum of A1 (Fig. 2), the quasimolecular ions having

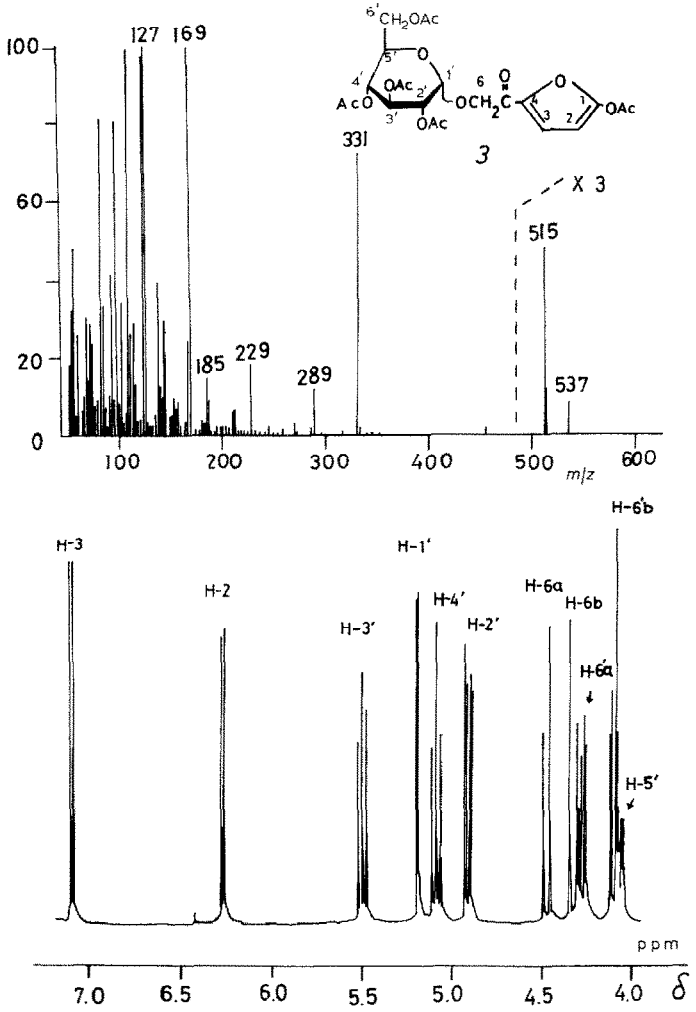


Fig. 4. F.a.b.m.s. and 400-MHz ^{1}H-n.m.r. spectra of **3** (from peak E).

m/z of 539 $(M + Na)^+$ and 517 $(M + 1)^+$ were found. Fragment-ions observed at *m/z* 331, 289, 187, 169 and 127 were derived from the glycosyl ions (*m/z* 331), and these are consistent with those described for the electron-impact mass spectrum[25]. These fragments result from cleavage of the interglucosidic linkage of the disaccharide peracetate. The ^{1}H-n.m.r. spectrum of A1 exhibited resonances of 5 acetyl groups. By intensive decoupling experiments, each peak was assigned, as shown in Table II. Consequently, A1 was identified as 6-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-2,3-dideoxy-D-*erythro*-hex-2-enono-(1→5)-lactone (**1**). A long-range coupling constant (1.53 Hz) between H-2 and H-4 and u.v. absorption[26] at 205 nm were consistent with this structure.

In the f.a.b. mass spectrum of B, quasimolecular ions of *m/z* 597 $(M + Na)^+$

and 575 $(M + 1)^+$ were detected, as well as fragment-ions for the glycosyl ion (*m/z* 331) (Fig. 3). Six acetyl-group resonances and those of protons in the non-reducing glucopyranosyl residue were detected in the ^{1}H-n.m.r. spectrum, and a u.v. absorption at 205 nm similar to that of A1 was also found. The remaining n.m.r. resonances were assigned as listed in Table II by decoupling experiments. Compound B was identified as 2,6-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-3-deoxy-D-*erythro*-hex-2-enono-(1→5)-lactone (**2**).

In the f.a.b. mass spectrum of E (Fig. 4), the quasimolecular ions of *m/z* 537 $(M + Na)^+$ and 515 $(M + 1)^+$ and fragment-ions attributable to glycosyl ion (*m/z* 331) were detected. In the ^{1}H-n.m.r. spectrum, resonances of protons from 5 acetyl groups and protons of the non-reducing glucopyranosyl residue were observed, and two resonances at 7.09 and 6.26 p.p.m. (coupling constant, 7.02 Hz) indicated the existence of an alkenic group. The intense u.v. absorption at 292 nm is ascribed to a furan ring[27]. Compound E was thereby identified as 2-acetoxy-5-[2-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyloxy)acetyl] furan (**3**).

DISCUSSION

It is known[28,29] that the persulfate ion decomposes to produce the sulfate ion–radical in aqueous solution. The sulfate radical may react with water to produce the hydroxyl radical (·OH) and oxygen according to Eqs. *1–3*:

$$S_2O_8 = \rightarrow 2SO_4^- \cdot \qquad (1)$$

$$SO_4^- \cdot + H_2O \rightleftharpoons HSO_4^- + \cdot OH \qquad (2)$$

$$2 \cdot OH \rightarrow H_2O + 1/2\ O_2 \qquad (3)$$

Therefore, oxidation may be initiated by either the sulfate ion–radical or ·OH.

We used two spin traps, PhCH=N(O)Bu^t and Bu^{t}NO, for e.s.r. studies. The nitrone compound, PhCH=N(O)Bu^t was added to a solution of the substrate and ammonium persulfate in phosphate buffer, and the e.s.r. measurement was executed at 50°. The observed e.s.r. spectrum arises (Fig. 5a) from a primary triplet splitting by the α-nitrogen (a_N 15.5 G) and a secondary doublet splitting from the β-hydrogen (a_H 2.0 G). The spectra obtained by using PhCH=N(O)Bu^t show no significant differences according to the presence or absence of the substrate. The observed coupling-constants compare favorably with those reported elsewhere for the ·OH adduct[19]. Consequently, only the hydroxyl radical was captured by PhCH=N(O)Bu^t.

On the other hand, Bu^{t}NO could not trap ·OH under the same conditions as for PhCH=N(O)Bu^t. The e.s.r. spectrum of a solution of maltose and ammonium persulfate in phosphate buffer (Fig. 5b) showed a triplet–triplet splitting having a 1:2:1 intensity (a_N 15.3 G, a_H 1.1 G) after 10 min at 50°. Another triplet–doublet

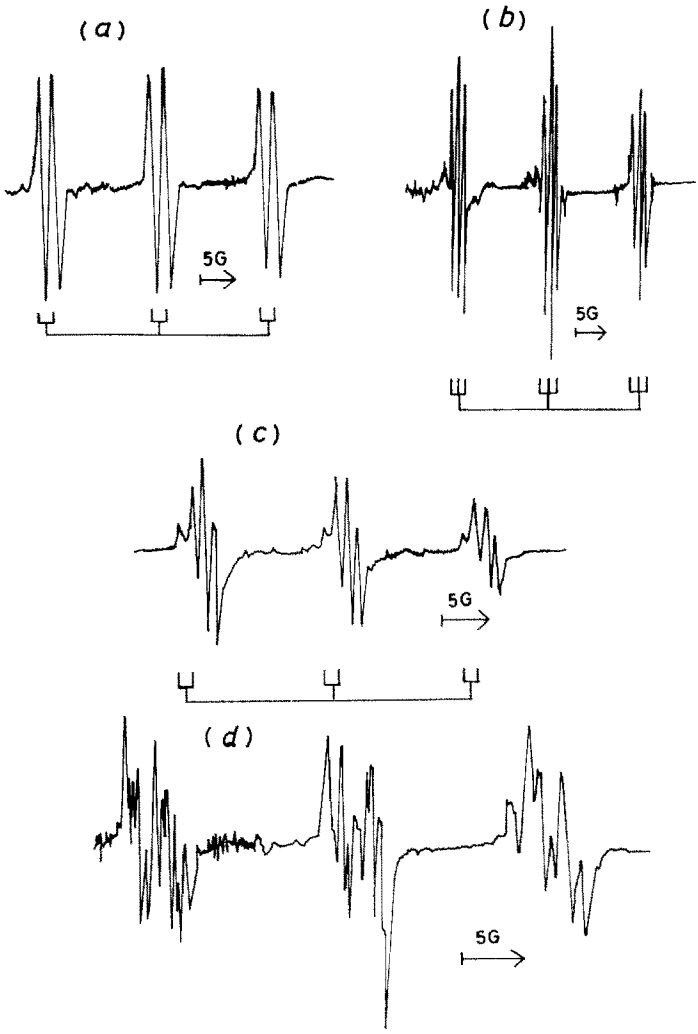
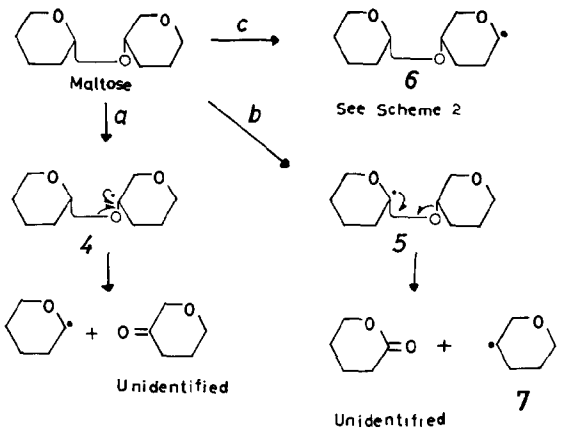


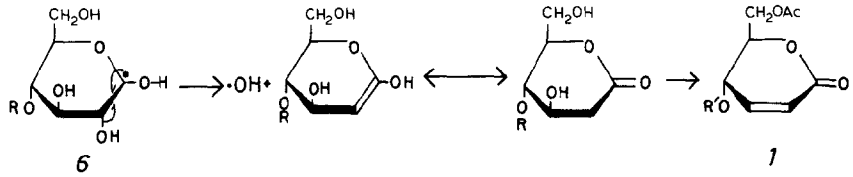
Fig. 5. E.s.r. spectra of spin-trapped radicals from 66.7mM phosphate buffer solutions (1 mL) of (*a*) maltose (0.1M), ammonium persulfate (0.01M), and PhBu^{t}NNO (2 mg) after ~15 min at 50°; (*b*) maltose (0.5M), PhBu^{t}NNO (0.05M) and Bu^{t}NO (2 mg) after ~10 min at 50°; (*c*) the same sample of (*b*) after ~30 min at 50°, and (*d*) isomaltose (0.5M), PhBu^{t}NNO (0.05M) and Bu^{t}NO (2 mg) after ~20 min at 50°. The modulations for spectra (from *a*–*d*) were 1, 0.2, 1, and 0.2 G, respectively.

splitting emerged after 30 min, with low intensity (a_N 15.3 G, a_H 1.4 G) (Fig. 5c). The former spin-adduct may be tentatively assigned as radical **4** (Scheme 1), and the latter radical-adduct may be attributable to radical **5** or **6**. Radicals **4** and **5** are precursor radicals for degradation. Pathways a and b in Scheme 1 may be considered as possible routes for radical degradation of maltose, but pathway b seems implausible because the degraded monosaccharide radical **7** is expected to couple with ·OH at C-4 to give the C-4 epimer, D-galactose, which was not obtained in the product studies. A similar mechanism may be considered for the radical degradation of isomaltose.

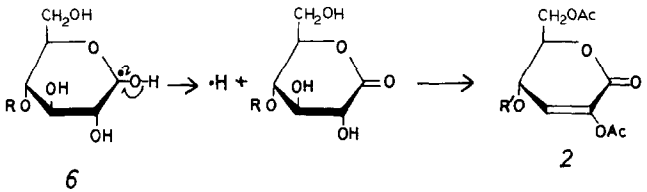


Scheme 1

Formation of 1



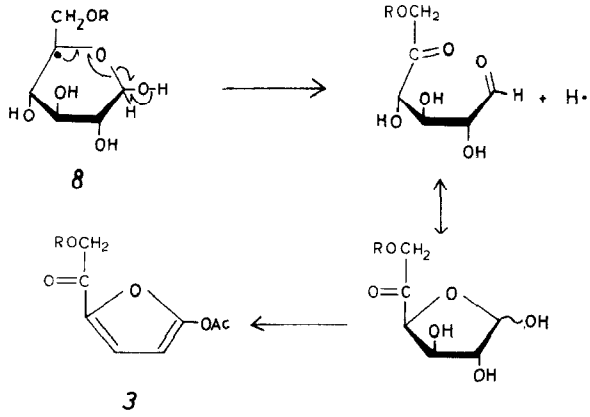
Formation of 2



Scheme 2

Radical **6** may lead to the formation of **1** and **2** (Scheme 2). Product **1** was formed by dehydration, tautomerization, and additional dehydration during the course of acetylation[30]. Compound **2** was obtained by oxidation at C-1 and dehydration during the acetylation process.

The e.s.r. spectrum of a solution of isomaltose and ammonium persulfate was more complicated than that of maltose (Fig. 5d). It is not clear what kind of radicals may form. The abstraction from C–H and subsequent oxidation at C-5 (Scheme 3) seem to be necessary for the formation of **3**. The formation of double bonds may occur during the course of acetylation[31]. The radical adduct from radical **8** may be involved in the e.s.r. spectrum, but the expected splitting-interactions



Scheme 3

with two protons at C-6 and one proton at C-4 are too intricate to assign unambiguously.

Although ·OH is known to be responsible for degradation of polysaccharides[13,32,33], attack on the substrates by ·OH seems to be of little importance in this system because of two major reasons. First, indiscriminate attack by ·OH would form radicals at all positions of the substrates[13], and this was not found in the present studies. Second, in the absence of substrates, the rate of the reaction (Eq. *2*) is very low except in alkaline solution[29]. Furthermore, it has been shown that the reaction (Eq. *2*) becomes less significant in the presence of scavengers for sulfate ion–radicals[34,35]. Based on the foregoing discussion, the regioselective C–H abstraction at C-1 and C-4 for maltose, and at C-5 and probably at C-6 for isomaltose, involve mainly by $S_2O_8^{2-}$ and $SO_4^{\cdot-}$ ·. Their oxidative susceptibility has been demonstrated in the reaction with alcohols[5].

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