[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, PURDUE UNIVERSITY]

Action of Alkaline Hypochlorite on Methyl 2-*O*-Methyl-α-D-glucopyranoside[1]

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Oxidation of methyl 2-*O*-methyl-α-D-glucopyranoside with alkaline sodium hypochlorite forms an intermediate product or products which upon acid hydrolysis produces up to 0.54 mole of glyoxal per mole of glucoside. The glyoxal is isolated as the 2,4-dinitrophenylosazone and its high yield suggests preferential oxidation at the C3 and C4 positions of the D-glucopyranosidic ring.

In an investigation directed toward the establishment of the oxidative action of alkaline hypochlorite on starch and cellulose, initial examination has been made of the action of hypochlorite on corn amylose[2] and on the α- and β-forms of methyl 4-*O*-methyl-D-glucopyranoside.[3] From the oxidative products of the latter compounds glyoxal has been isolated as the 2,4-dinitrophenylosazone. The presence of the glyoxal fragment has been explained[3] as being derived from a 2-carboxyglycolic aldehyde by treatment of this 3-carbon component under acidic conditions with 2,4-dinitrophenylhydrazine. The 2-carboxyglycolaldehyde is envisioned to represent carbon atoms of C1, C2, and C3 of the methyl 4-*O*-methyl-D-glucopyranoside from which it is derived by oxidation of the glucoside at carbon atom C3 with introduction of a keto group and oxidative cleavage of the resultant 3,4-enediol. Since the hydroxyl group on C4 is blocked by a methyl group, there is a definite limitation to the transformation of this carbon to a carbonyl and hence to its increasing the concentration of 3,4-enediol. To obtain further information on this hypothesis, the yield of glyoxal from the alkaline hypochlorite oxidation of methyl 2-*O*-methyl-α-D-glucopyranoside has now been investigated. According to the hypothesis positions C3 and C4 should both now be available as primary oxidative sites with consequent greatly increased probability of 3,4-enediol formation and subsequent cleavage to 2-carboxy-2-methoxyacetaldehyde. Blocking the hydroxyl at C2 should reduce the oxidative attack on this carbon atom. Thus, the eventual yield of glyoxal osazone should be considerably increased. When each glycoside is oxidized under comparable conditions with 10.6 equivalents of hypochlorite at *p*H 9, it is found that there is a 0.10 molar yield of glyoxal from the 4-*O*-methyl-D-glucopyranoside but a 0.44 molar yield from the 2-*O*-methyl-D-glucopyranoside. This observed 340% increase in yield from the latter compound supports the belief that the glyoxal may derive from a 3 carbon fragment which in turn is derived by oxidative cleavage from a 3,4-enediol structure in the sugar ring.

EXPERIMENTAL

Oxidation of methyl 2-O-methyl-α-D-glucopyranoside. Methyl 2-*O*-methyl-α-D-glucopyranoside[4] (3.0 g.) was treated with 300 ml. of sodium hypochlorite solution buffered with sodium bicarbonate to *p*H 9, at 25°, and containing 10.6 equivalents of oxidant per mole of sugar. Duplicate samples were analyzed for oxidant consumed[5] and for glyoxal. In the latter analysis a 5-ml. sample was diluted to 100 ml. with water, acidified to *p*H 1 with *N* hydrochloric acid, and aerated until free of chlorine to the potassium iodide-starch test. Then 100 ml. of 2,4-dinitrophenylhydrazine reagent was added and the solution was refluxed on a steam-bath for two hours. The osazone was filtered, washed, dried and weighed; m.p. 330–331°; reported m.p. 330–332°. The precipitates were compared to authentic glyoxal 2,4-dinitrophenylosazone as to mixture melting point, x-ray pattern, and infrared spectra and found to be the same. The results are shown in Table I.

TABLE I

GLYOXAL RECOVERED FROM HYPOCHLORITE-OXIDIZED D-GLUCOSIDE

(10.6 equivalents of oxidant per mole of glucoside)

Oxidation Period Hours	Moles of Glyoxal Per Mole Glucoside	Equivalents of Oxidant Consumed Per Mole Glucoside
2	0.05	0.69
4	.09	1.4
8	.14	2.4
24	.29	4.8
48	.40	6.9
72	.44	7.8
96	.44	8.0
168	.42	8.1
264	.42	7.5
(34.5 equivalents of oxidant per mole of glucoside)		
20 minutes	0.11	1.3
1	.27	3.6
2	.46	5.9
4	.50	8.7
8	.52	12.3
12	.52	13.7
26	.54	14.9
48	.54	14.0

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(1) Journal Paper No. 947 of the Purdue Agricultural Experiment Station, Lafayette, Indiana.

(2) Whistler and Linke, Abstract of Papers, 129th meeting, American Chemical Society, Dallas, Texas, April, 1956, p. 4D.

(3) Whistler and Kazeniac, Abstract of Papers, 129th meeting, American Chemical Society, Dallas, Texas, April, 1956, p. 4D.

(4) Whistler and Kazeniac, *J. Am. Chem. Soc.*, **76**, 5812 (1954).

(5) Bradstreet, *The Standardization of Volumetric Solutions*, Chemical Publishing Co., Inc., New York, 1944, p. 106.

In another experiment examination was made of the oxidation effected by 34.5 equivalents of oxidant per mole of the D-glucoside.

Effect of sodium hypochlorite on glyoxal. Glyoxal (99 mg.) was treated with 50 ml. of 0.50 *N* sodium hypochlorite at *p*H 9 and 25°. Within two minutes 85% of the glyoxal underwent conversion to a product or products which did not react with an acidic solution of 2,4-dinitrophenylhydrazine. After 24 hours, no glyoxal could be detected with 2,4-dinitrophenylhydrazine. A control sample showed no change in glyoxal content after 120 hours.

Effect of sodium bicarbonate on glyoxal. Glyoxal (90 mg.) was treated with 50 ml. of 2% aqueous solution of sodium bicarbonate. After 24 hours, 21% of the glyoxal was converted to a product or products which did not react with 2,4-dinitrophenylhydrazine. After 120 hours treatment only 28% of the glyoxal was recovered as the 2,4-dinitrophenylosazone derivative.

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