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Periodate Oxidation Study of Hemicelluloses of *Erianthus asundinaceus*

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Periodate oxidation reaction is one of the most important reactions used in structural study of noncellulosic polysaccharides. The periodate oxidation study was done using sodium metaperiodate as oxidant. In analysis the method proposed by Fleury and Lange was used. The mole of periodate consumed during periodate oxidation reaction of hemicellulose was determined volumetrically. The composition and probable structure have also been elucidated with the informations obtained from periodate oxidation on purified fraction of *Erianthus asundinaceus* hemicellulose.

INTRODUCTION

Periodate oxidation reaction is used in carbohydrate chemistry and it is also applicable to wood polysaccharides. This reaction was first discovered by Malaprade[1]. Fleury and Lange[2] have given a better method for more extensive use of periodic acid for oxidation of glycol. Pigman[3] has given two important cleaving reagents: periodic acid and lead tetraacetate. Chatterjee[4], Kumar[5] and Sarkar[6] have used the periodate oxidation method to determine the structure of polysaccharides. The central atom of oxidation reagent must be able to coordinate at least two hydroxyl groups. Glycol groups undergo cyclic ester formation with the oxidant. The reaction is considered to be dialdehyde type of oxidation[3].

EXPERIMENTAL

The method proposed by Fleury and Lange[2] was used for periodate oxidation of noncellulosic polysaccharides of *Erianthus asundinaceus* (Ramsar, Sarkanda). Purified hemicellulose was weighed about 0.15 g and suspended in 250 mL of 0.02 M sodium metaperiodate solution. The measuring flask was shaken to form a colloidal solution and kept in dark in refrigerator maintained at low temperature range of 8–15°C. The reaction mixture (5 mL) was drawn at intervals and excess periodate was estimated by arsenite method as follows. To each aliquot 2 mL saturated solution of sodium bicarbonate was added and then about 25 mL of 0.01 N sodium arsenite solution and 2 mL of 20% potassium iodide were added. The reaction mixture was shaken and kept in dark for about 15 minutes and then 5 mL 0.01 N iodine solution was added to it. The excess of iodine was titrated against sodium thiosulphate (hypo) solution, 0.1 N, using starch as indicator near the end point. A blank titration was also carried out in a similar way. Results are recorded in Table-1 and graphically represented in Figure 1.

During periodate oxidation, released formic acid was determined by the procedure proposed by Halsall and coworkers[7]. Aliquots (5 mL) were taken out from each flask at different intervals. To each aliquot about 10 mL of freshly distilled ethylene glycol was added to destroy excess of periodate present in reaction mixture. After keeping the flask for ten minutes, the formic acid produced was estimated by titration aginst alkali (0.0120 N) using methyl red as an indicator. The results are given in Table-2 and graphically represented in Figure 2.

RESULTS AND DISCUSSION

TABLE-1
PERIODATE CONSUMPTION PER ANHYDROSE SUGAR UNIT

Time of oxidation h	Vol. of hypo used with blank V_2 (mL)	Vol. of hypo used sample V_1 (mL)	Vol. of hypo solution used $(V_2 - V_1)$ (mL)	Moles of iodate consumed per anhydrose unit (mole)
0.5	10.45	10.40	0.05	0.11
1.0	10.45	10.36	0.09	0.20
2.0	10.45	10.30	0.15	0.33
4.0	10.45	10.25	0.20	0.44
8.0	10.45	10.21	0.24	0.53
16.0	10.45	10.17	0.28	0.61
24.0	10.45	10.14	0.31	0.68
32.0	10.45	10.11	0.34	0.75
48.0	10.45	10.03	0.42	0.92
72.0	10.45	10.03	0.42	0.92
96.0	10.45	10.03	0.42	0.92

$$\text{Moles of periodate consumed per anhydrose unit} = \frac{N \times (V_2 - V_1) \times 132 \times A.F.}{1000 \times w \times 2}$$

Here,

0.1 N = N = normality of thiosulphate solution

V_2 = volume of hypo used with blank

V_1 = volume of hypo used with sample

0.15 gm = W = weight of hemicellulose (on O.D. basis)

$$50 = \text{A.F. (Aliquot factor)} = \frac{\text{Total volume of periodate taken}}{\text{Periodate volume withdrawn for each titration}}$$

$= 250/5 = 50$

$$\text{Moles of periodate consumed per anhydrose} = \frac{0.1 \times (10.45 - 10.03) \times 132 \times 50}{1000 \times 0.15 \times 2}$$

$= 0.92$ mole

A graph has also been plotted against amount of oxidant consumed in the reaction and the time of oxidation as given in Fig. 1.

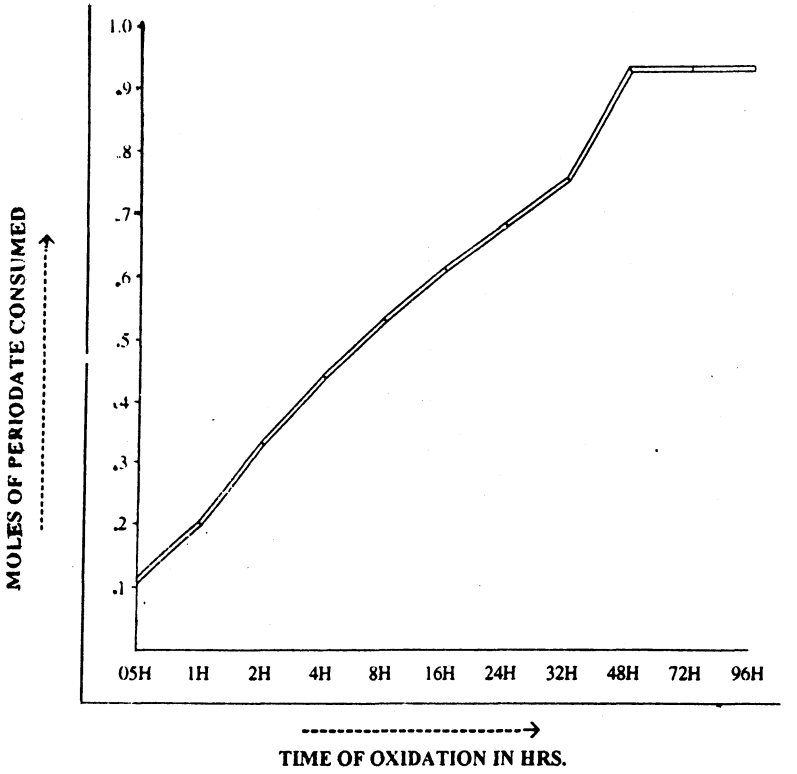


Fig. 1. Periodate consumption of hemicellulose *Erianthus asundinaceus*

TABLE-2
DETERMINATION OF RELEASED FORMIC ACID DURING PERIODATE OXIDATION OF HEMICELLULOSE

Time of oxidation h.	Formic acid released mole/1000 g hemicellulose
0.5	0.10
1.0	0.36
2.0	0.58
4.0	0.71
8.0	0.82
16.0	0.94
24.0	1.05
32.0	1.05
48.0	1.05
72.0	1.05
96.0	1.05

A graph has been plotted against amount of oxidant consumed in the reaction and the time of oxidation as given Fig. 2.

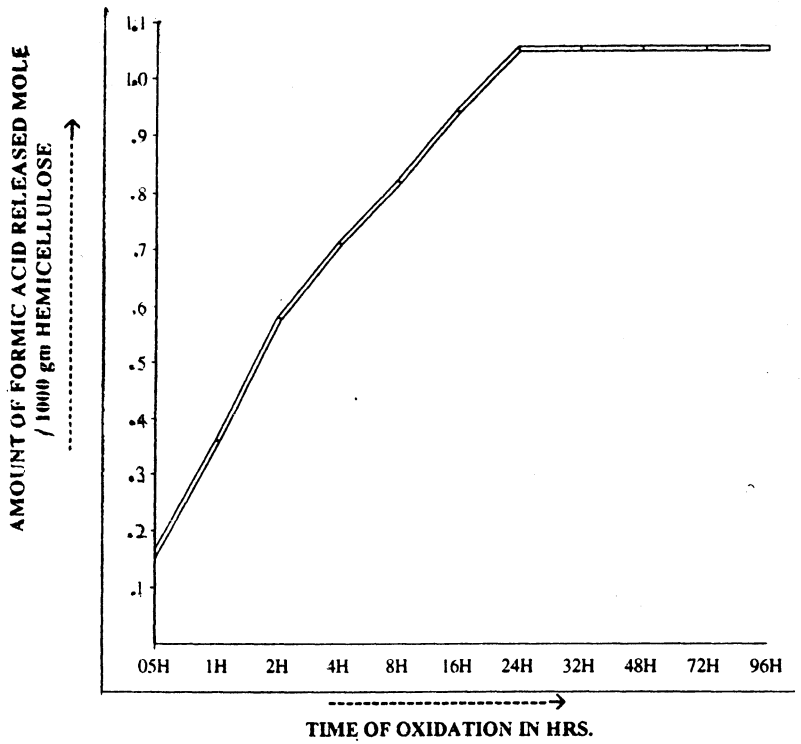
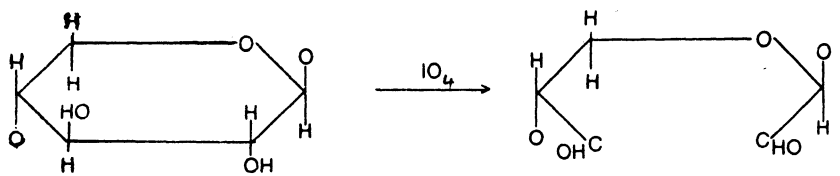


Fig.2. Determination of released formic acid during periodate oxidation of *Erianthus asundinaceus* hemicellulose

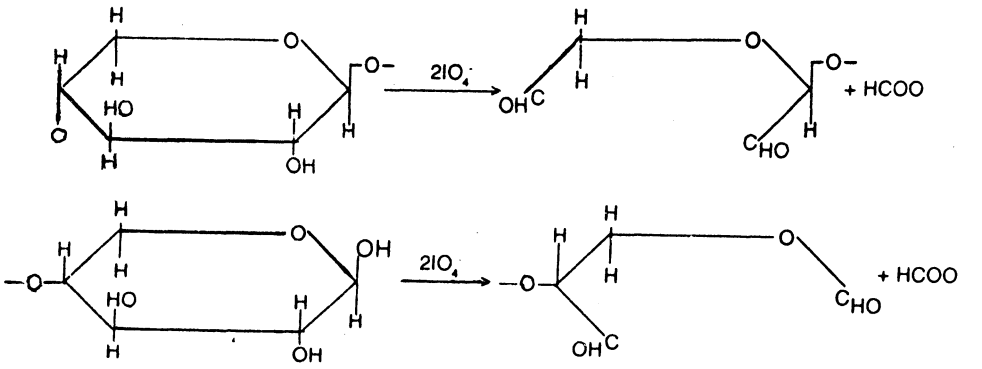
The study showed the consumption of 0.92 moles periodate ions per anhydroxyxylopyranose as determined volumetrically. The probable reaction by which the periodate oxidation of hemicelluloses (xylosepyranose monomer) occurs as under:



This reaction shows that 92% of xylopyranose units were containing adjacent free hydroxyl groups, resulting in the consumptionage of periodate ions during oxidation reaction. The remaining per cent of xylopyranose units were not containing adjacent free hydroxyl groups, indicationg the occurrence of branch-

ing. Finally it is concluded from the above mentioned facts that probably one branching point occurs per eleven repeated units of xylopyranose, constituting the noncellulosic polysaccharides of *E. asundinaceus*. Graph between time of oxidation and moles per iodate (oxidant) consumed indicated that on increasing the time of oxidation from 0.5 h to 48 h. the consumption of moles of periodate increases (from 0.11 to 0.92), but from 48 h. to 96 h. the consumption of moles of periodate becomes constant (0.92 per unit mole).

The formic acid appears to be originating from reducing as well as non-reducing terminal units of xylopyranose as shown in the following reaction.



From the above reaction it may be concluded that the terminal xylopyranose units of hemicellulose are not substituted.

Graph between time of oxidation and amount of formic acid released during periodate oxidation indicates that on increasing the time of oxidation from 0.5 h to 24 h. the amount of released formic acid increases (from 0.16 to 1.05) but from 2 h to 96 h the amount of released formic acid becomes constant (1.05 mole).

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