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Periodate oxidation of *Ceiba pentandra* and *Morus nigra* purified non-cellulosic polysaccharides

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ABSTRACT: Periodate oxidation reaction is used in carbohydrate chemistry and is also applicable to wood polysaccharides. Periodic acid is mainly capable of cleaning alpha and beta glycols quantitatively from wood polysaccharides. Compounds containing an aldehyde or ketonic group adjacent to an alcoholic group are also attacked by periodic acid in similar manner as glycols. The estimation of the periodic acid used and the formic acid or formaldehyde produced will indicate the number, in pairs, of free oxidizable groups (-CHOH, -CHO or =CO). Since periodic acid can easily be estimated volumetrically, oxidations with H_5IO_6, or $HIO_4.2H_2O$ are very useful in analytical chemistry.

Keywords: Periodate oxidation; oxidizable groups; non-cellulosic polysaccharides; *Ceiba pentandra* and *Morus nigra.*

INTRODUCTION

In this study non-cellulosic polysaccharides (hemicelluloses)[7, 23 & 24] of *Ceiba pentandra* and *Morus nigra*[7 & 13] are used to study their periodate oxidation. Periodate oxidation reaction was first discovered by Malaprade[2], who observed that periodic acid is capable of cleaning alpha and beta glycols quantitatively from wood polysaccharides. The cis-glycols attacked more rapidly than the trans-glycol but both glycols yield two aldehydes, if more than two adjacent -CHOH groups are present, they are converted into formic acid.

Fluery and Lange have given a better method for more extensive use of periodic acid for oxidation of glycol, specific for 1, 2-diols also given various clearing reagents, particularly periodic acid and lead tetra acetate. These reagents exhibit relatively sharp efficiency for the cleavage of bonds between adjacent carbon atoms containing hydroxyl groups. Chatterjee *et al.*, Kumar [5] and Sarkar *et al.*[6] have used the periodate oxidation method to determine the structure of polysaccharides, this oxidation reagent has the following required properties: the suitable diameter of central atom of oxidation reagent is about 2.5 to 3.0×10^{-8} cm, because this is capable to be large enough to bridge the gap between the hydroxyl groups in a 1,2-diol; the central atom of oxidation reagent must be able to coordinate at least two hydroxyl groups, inspite of groups already attached to it; the valancy state of central atom must be exceeded by two units rather than by one or three valancy of next lowest stable state; the oxidation reagent must have oxidation potential in the neighborhood - 1.7 Volts as compared to the next lowest stable valancy state and Periodic acid[8] split 1,2 glycols and one molecule of acid is used for each pair of adjacent alcoholic groups.

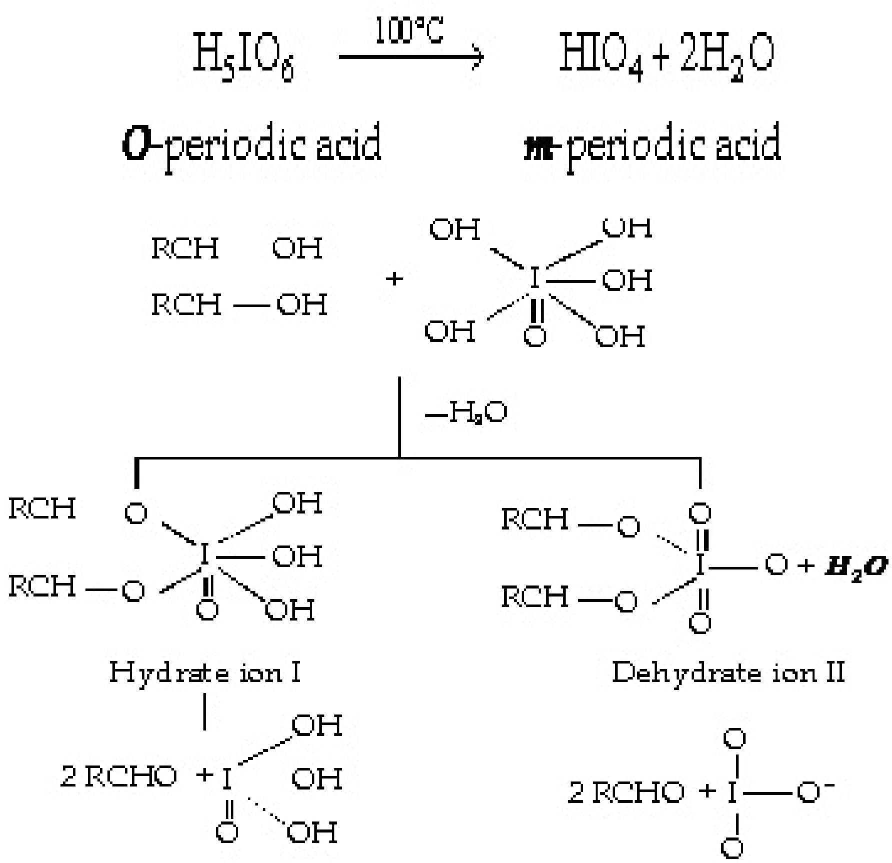
Compounds containing an aldehyde or ketonic group adjacent to an alcoholic group are also attacked by periodic acid in similar manner as glycols. Thus an aldopentose if it had an open chain structure would require four molecules of periodic acid and the products would be four molecules of formic acid and one molecule of formaldehyde (from the terminal $-CH_2OH$ group). The estimation[9] of the periodic acid used and the formic acid and or formaldehyde produced will indicate the number, in pairs, of free oxidizable groups (-CHOH, -CHO or =CO). Since periodic acid can easily be estimated volumetrically, oxidations with H_5IO_6, or $HIO_4.2H_2O$ are very useful in analytical chemistry.

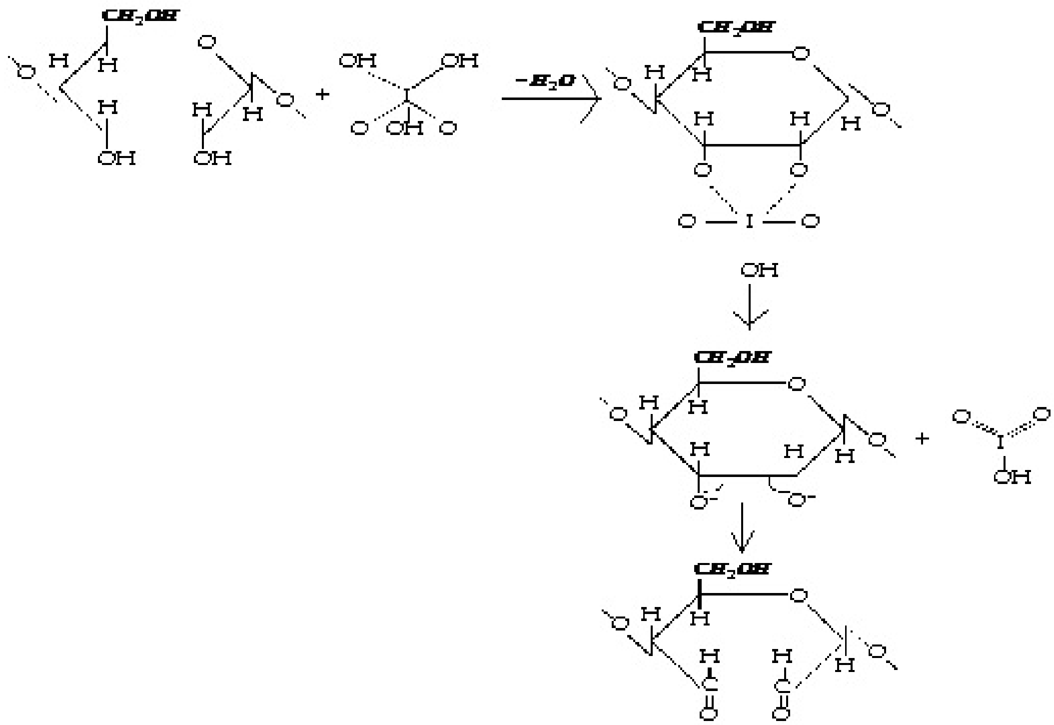
The amount of periodic acid consumed can easily be determined by titration against a standard iodine solution. Simultaneously, the reaction products, viz. HCHO, HCOOH etc. are estimated and thus we may know the complete structure[5] of the compound.

Mechanism of periodate oxidation: Oxidation[10] with ortho-periodic acid is carried out in neutral or faintly room temperature.

The reaction proceeds through a cyclic intermediate either hydrate ion I or dehydrate ion II.

Glycol groups undergo cyclic ester formation with the oxidant. The reaction is considered to be aldehyde type of oxidation[11].





MATERIALS AND METHODS

The method proposed by Fleury and Lange[12] was used for periodate oxidation of non-cellulosic polysaccharides (hemicelluloses) of *Ceiba pentandra* and *Morus nigra*. The dried purified hemicellulose[7] of both samples were weighed about 0.1450 gm and suspended in 250 ml of 0.02M sodium meta-periodate solution. The measuring flask was shaken to form a colloidal solution which was kept in dark, in refrigerator and at low temperature range of 10 to 15^0 C. From this 5.0 ml reaction mixture solution was drawn at intervals using Arsenite method and estimated the excess of periodate. The Arsenite method is as follows - To each aliquote 2.0 ml saturated solution of sodium bicarbonate was added than about 25.0 ml of 0.01N sodium arsenite solution and 2.0 ml of 20% potassium iodide were added. The reaction mixture was shaken and kept in dark for about 15 minutes and then 5.0 ml of 0.01N solution of iodine was added to it. Then the excess of iodine was titrated against 0.1N hypo solution, 0.1N starch was used as indicator near the end point. Parallel a blank titration was also made in similar way.

$$\text{Moles of periodate consumed per anhydrose unit} = \frac{N \times (V2 - V1) \times 132 \text{ X A.F.}}{1000 \times w \times 2}$$

Here: N = Normality of thio sulphate solution; V_2 = Volume of thio used with blank; V_1 = Volume of thio used with sample and w = Weight of hemicellulose (on O.D. basis)

$$\text{A. F.} = \frac{\text{Total Volume of periodate taken}}{\text{Periodate volume withdrawn for each titration}}$$

RESULTS AND DISCUSSION

The experiment described as above on applying for the dried purified hemicelluloses of both *Ceiba pentandra* and *Morus nigra* and results so obtained are recorded in Table 1 and Table 2.

Table 1: Periodate consumption per anhydrose sugar unit of hemicelluloses of *Ceiba pentandra*.

Time of oxidation (hrs)	Volume of thio used with blank (V_2) ml	Volume of thio used with sample (V_1) ml	Volume of thio solution used (V_2 - V_1) ml	Mole of iodate consumed per anhydrose unit mole.
16.0	10.55	10.27	0.28	0.61
24.0	10.55	10.24	0.31	0.68
32.0	10.55	10.22	0.33	0.72
48.0	10.55	10.19	0.36	0.79
72.0	10.55	10.15	0.40	0.88
96.0	10.55	10.11	0.44	0.96
120.0	10.55	10.05	0.50	1.10
168.0	10.55	10.05	0.50	1.10
216.0	10.55	10.05	0.50	1.10

Table 2: Periodate consumption per anhydrose sugar unit of hemicelluloses of *Morus nigra*.

Time of oxidation (hrs)	Volume of thio used with blank (V_2) ml	Volume of thio used with sample (V_1) ml	Volume of thio solution used (V_2 – V_1) ml	Mole of iodate consumed per anhydrose unit mole
16.0	10.55	10.31	0.24	0.52
24.0	10.55	10.29	0.26	0.57
32.0	10.55	10.27	0.28	0.61
48.0	10.55	10.25	0.30	0.66
72.0	10.55	10.23	0.32	0.70
96.0	10.55	10.20	0.35	0.77
120.0	10.55	10.17	0.38	0.83
168.0	10.55	10.17	0.38	0.83
216.0	10.55	10.17	0.38	0.83

A graph has also been plotted against amount of oxidant consumed in the reaction and the time of oxidation as given in Figure 1 for purified hemicellulose of *Ceiba pentandra* and *Morus nigra*. From data recorded in Tables 1 and 2 and the results obtained by the analysis of data as well as observations made from Fig. 1, it is evident that the moles of periodate consumption increases from 0.61 to 1.10 and 0.52 to 0.83 by increasing the time of oxidation from 16 to 120 hrs but it becomes constant from 120 to 216 hrs at the values 1.10 and 0.83 of *Ceiba pentandra* and *Morus nigra* respectively. It is also observed that moles of periodate consumption (1.10) of *Ceiba pentandra* is little higher than the value of *Morus nigra* (0.83). The results of periodate oxidation also indicate that the structure of non-cellulosic polysaccharide is linear or branched. These results for *Ceiba pentandra* indicate the presence of linear structure because a straight chain with small amount of branched glucomannan, linked at 1→ 4(β), would consume 1.10 mole of periodate for each anhydro hexose sugar and the same results of *Morus nigra* indicate the presence of linear structure because a straight chain xylan, linked 1→ 4(β), would consume 0.83 mole of periodate for each anhydro-D-xylose units, plus an extra mole of each and of the chain. In long, straight chains the effects of end groups is diminished and periodate consumption approaches one mole per mole of polysaccharide.

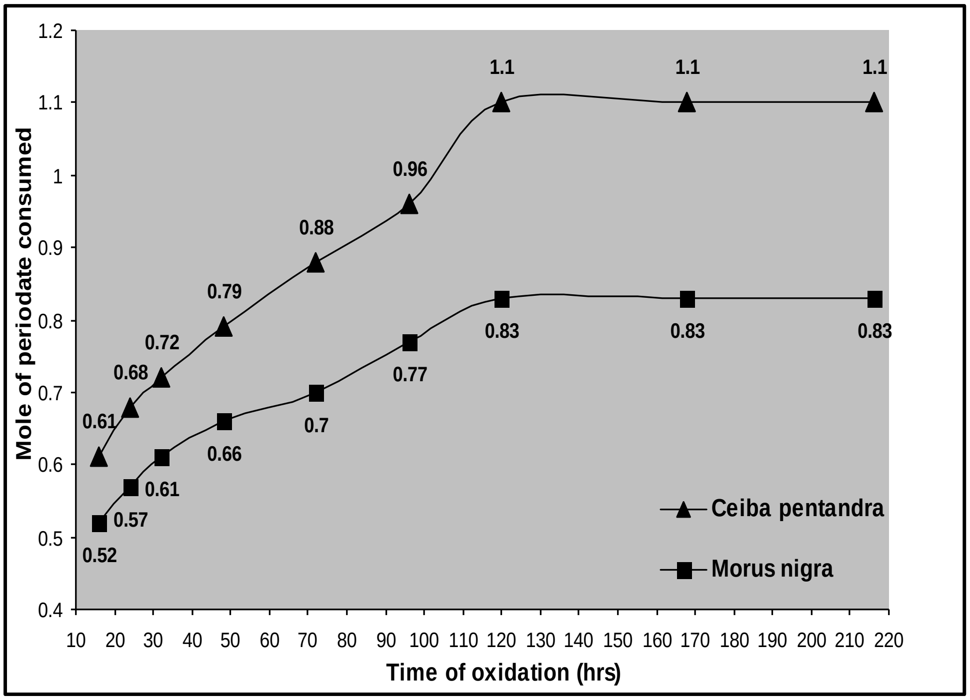


Fig. 1: Periodate consumption – per anhydrose sugar unit of hemicelluloses.

This study also shows that non-cellulosic polysaccharide contain adjacent free hydroxyl groups (because consumption of periodate ions during oxidation reaction). But the approximate 8% of purified hemicellulose of *Ceiba pentandra* not contain adjacent free hydroxyl groups, it is indicating the small amount of branching. These results show similarity with the results of Negi, Singh and Jindal, Guha *et al*, Shukla, Hussain *et al*, Shatalov *et al.*, Lundquist *et al.* and Willfor and Holmbom[22].

CONCLUSION

The structure of non-cellulosic polysaccharide is either linear or branched and the results for *Ceiba pentandra* indicate the presence of linear structure because a straight chain with small amount of branched glucomannan, linked at 1→ 4(β), would consume 1.10 mole of periodate for each anhydro hexose sugar and the same results of *Morus nigra* indicate the presence of linear structure because a straight chain xylan, linked 1→ 4(β), would consume 0.83 mole of periodate for each anhydro-Percival, E.G.V., 1962.

D-xylose units, plus an extra mole of each and of the chain. In long, straight chains the effects of end groups is diminished and periodate consumption approaches one mole per mole of polysaccharide.

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