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Elucidation of Sugars Structure through Periodic Acid Oxidation Cleavage

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Abstract: ***In this work the periodic acid was used to elucidate the structure of sugars. When a sugar is reacted with excess periodic acid attacks the vicinal diols in sugar (carbohydrates) and oxidizes these groups to form carbonyl compounds. Method was carried out by dissolving one mole of sugars in 50 ml of distilled water. Then excess periodic acid was added. The mixture was left for about an hour and titrated against 0.1M Na_2CO_3, solution instead of (thiosulfate method) using screen methyl orange as an indicator to determine excess periodic acid remains. One equivalent of periodic acid corresponds to one carbon-carbon bond cleavage. The results obtained, practical molar ratio of sugars to periodic acid and theoretical molar ratio of sugars to periodic acidwere found to be in good accordance with expected and were in agreement with these reported in the literature.***

Keywords: Periodic acid, oxidation cleavage, elucidate structure, sugar and titration

1. Introduction

One important method of elucidating the structure of carbohydrates is using periodic acid degradation. Periodic acid (HIO4) is a reagent that cleaves the carbon-carbon bonds in a sugar through oxidation cleavage.[1-5]Periodic acid attacks the vicinal diols in carbohydrates and oxidizes these groups to form carbonyl compounds.[6] The mechanism of this reaction involves a cyclic periodate ester that reacts with two neighboring alcohol functional groups which are oxidized to carbonyl functional groups.[5-8]
Periodic acid is the highest oxidizing acid of iodine, in which the iodine exists in oxidation state VII. Like all periodates it can exist in two forms: orthoperiodic acid, with the chemical formula H_5IO_6 and metaperiodic acid, which has the formula HIO_4.

Like all periodates periodic acid can be used to cleave various 1,2-difunctional compounds.[9]

Theperiodic acid can be useful in determining the structure of carbohydrates, alsoit can be used to open saccharide rings. This process is often used in labeling saccharides with fluorescent molecules. [1-4, 8]

When a sugar is reacted with excess periodic acid, each carbon-carbon bond is broken, forming a characteristic composition of one-carbon compounds that can provide some information about the structure of carbohydrate[7,8]. Therefore, each broken bond will be replaced with an OH group. If there is any carbon with two OH groups, it will lose water and become a carbonyl group. The final product will be either a ketone or an aldehyde.[7,8]

For example, an aldehyde has one carbon-carbon bond and will react to form formic acid. Secondary alcohols will break 2 carbon-carbon bonds and will be oxidized twice, also forming formic acid. Primary alcohols will break one carbon-carbon bond and will be oxidized once to formaldehyde. Ketones will break into two carbon-carbon bonds and form carbon dioxide (CO2).[7,10, 11]

This method can provide several clues to elucidate the structure of an unknown carbohydrate,[7]by analyzing the ratios of the products mentioned above, some information about the types of functional groups present can be obtained[7]. Specifically, ketones oxidize to carbon dioxide when they are reacted with periodic acid,which can provide clues as to whether the carbohydrate is an aldose or a ketose.[10, 11] Also, the size of the carbohydrate can be revealed by the amount of periodic acid that is consumed. One equivalent of periodic acid corresponds to one carbon-carbon bond cleavage.For example of periodic acid cleavage involves the degradation of one equivalent of D-glucose into five equivalents of formic acid and one equivalent of formaldehyde[1-4, 7,8,12,13]

Another example of periodic acid cleavage involves the degradation of one equivalent of D-fructose to three equivalents of formic acid, two equivalents of formaldehyde, and one equivalent of carbon dioxide.[10, 11]

The mild conditions of the reaction are especially well adapted for application to the sensitive carbohydrate structures.[1-4] The development and wide application of the reaction have been occasioned by a number of factors, the principal one being the high degree of selectivity shown by the periodate reaction when applied under the proper conditions. Thus, the oxidation can be limited to 1,2-glycols, 2-amino alcohols, α-hydroxy ketones and aldehydes, α-amino aldehydes, 1 2-diketones, and certain activated methylene groups.[6,14,15]

The oxidative cleavage with periodic acid has been successfully applied in the constitutional analysis of sugars. The presence of several pairs of vicinal diols during oxidation with periodic acid can lead to the formation of complex product mixtures. For example, reaction of glucose with 5 equivalents of HIO_4 gives five equivalents of formic acid and one equivalent of methanal (formaldehyde)*Fig.1*.[12,13, 16]

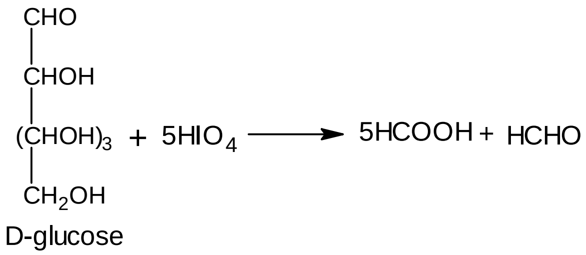

Figure 1

An analogous degradation of fructose yields three equivalents of formic acid, two equivalents of formaldehyde and one equivalent of carbon dioxide*Fig.2.*[16]

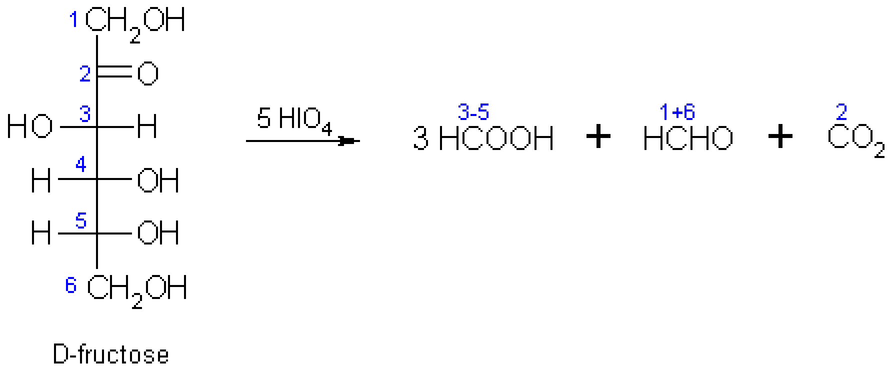

Figure 2

Products of the oxidation of terminal aldehydes are derived from the corresponding hydrated forms, vicinaldiols, which are in equilibrium with the aldehydes. The oxidation yields formic acid and a one-carbon atom less aldoseshown in fig.3, [14, 6]

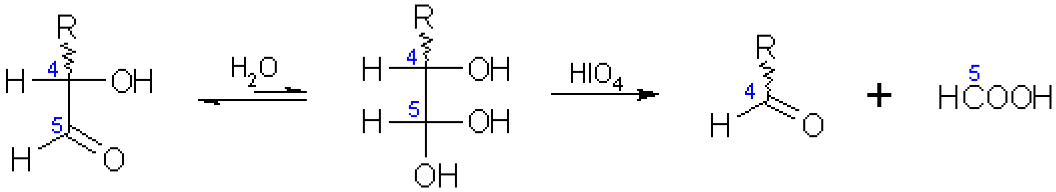

Figure 3

In the case of a terminal hydroxymethyl group adjacent to a carbonyl function (fructose), oxidative cleavage proceeds also through a vicinaldiol and produces formaldehyde and carboxylic acid asshown in fig., (4).[6, 11]

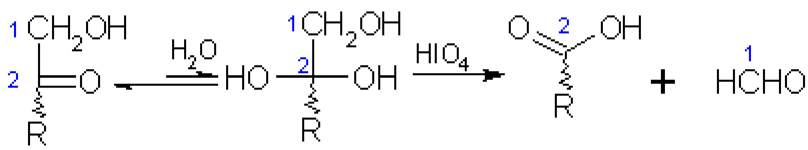

Figure 4

If the generated acid contains an α-hydroxyl group, oxidation produces carbon dioxide and an aldehyde that can be degraded further shown in fig., (5).[16]

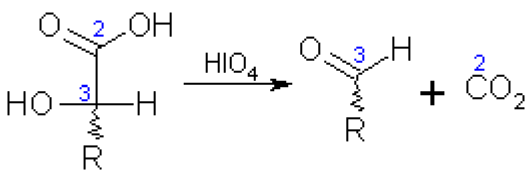

Figure 5

In summary, the basic skeleton of sugars is degraded during oxidative cleavage with periodic acid into formic acid, formaldehyde and carbon dioxide. The ratio of the individual fragments depends on the constitution of the sugar.[1-4,13,16]

The mechanism is focused on the actual cleavage step. Prior to this, the vicinal diolsreacts to form a cyclic periodate ester, shown in *Fig.6.*[16,17] The periodate ester undergoes a rearrangement of the electrons, cleaving the C-C bond, and forming two C=O and water is eliminated concurrently[18]. Presumably, the ester dissociates via an aromatic 6-electron-5-center transition state into two carbonyl fragments and iodic acid. Iodine is reduced from +VII to +V. *Fig.7* [19,20,7,13]

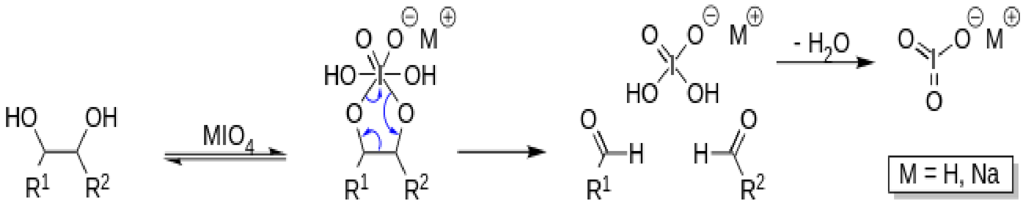

Figure 6

2. Material and Method

Material

Sugar, periodic acid, Na_2CO and methyl orange.

Method

One mole of sugar was dissolved in 50 ml of distilled water. Then excess periodic acid was added. The mixture was left for about half an hour and titrated against 0.1M Na_2CO_3 solution using screen methyl orange as an indicator to determine excess periodic acid remains. The results are given in table.

Calculation

One equivalent of periodic acid corresponds to one carbon-carbon bond cleavage. For example, a six-carbon carbohydrate would consume 5 equivalents of periodic acid to give five equivalents of formic acid and one equivalent of formaldehyde.

Synthetic sugar + n periodic acid = (n-1)formic acid + formaldehyde
For example, a seven-carbon
Weight of C7 = 0.105g
Number of moles of C7 = 0.00005 mole
Weight of periodic acid = 0.772g
Number moles of periodic acid = 0.0038
Volume of moles of (Na_2CO_3) = 25 ml
Number of moles of (Na_2CO_3) = 0.00025 mole
Number moles of periodic acid = 2×0.00025 = 0.00050 mole
Number moles of periodic acid required for oxidation = 0.003885 -0.0005 = 0.002885
Practical molar ratio of sugars to periodic acid = 0.00005÷0.00395 = 1:5.77
Theoretical molar ratio of sugars to periodic acid is 1:6

Table: The structural analysis of synthetic sugars using periodic acid

sugars backbone	Number of moles sugars	Number of moles (periodic acid)	Theoretical molar ratio of sugars to periodic acid)	Practical molar ratio of sugars to periodic acid
C7	0.0005	0.002885	1:6	1:5.77
C8	0.00052	0.00352	1:7	1:6.8
C9	0.00049	0.00395	1:8	1:8.06
C10	0.0005	0.00430	1:9	1:8.76
C11	0.00051	0.00054	1:10	1:10.05
C12	0.0005	0.0004	1:11	1:10.72

3. Results and Discussion

This method can provide several clues to elucidate the structure of an unknown carbohydrate,by analyzing the molar ratios of sugarsto periodic acid.The chemical structure of prepared sugar was determined by reacting it with excess periodic acid. The practical molar ratio of sugar to periodic acid it was found to be (1:5.8; 1:6.8; 1:8; 1:8.8; 1:10; 1:10.72), and theoretical molar ratio it was (1:6, 1:7, 1:8, 1:9, 1:10, 1:11).The results obtained (Practical molar ratio of sugars to periodic acid and theoretical molar ratio of sugars to periodic acid) are in good accordance with expected and were found to be in agreement with these reported in the literature.

The important method of elucidating the structure of carbohydrates was using periodic acid degradation. Periodic acid (HIO4) is a reagent that cleaves the carbon-carbon bonds in a sugar through oxidation cleavage. When a sugar is reacted with excess periodic acid attacks the vicinal diols in sugar (carbohydrates) and oxidizes these groups to form carbonyl compounds, which can provide some information about the structure of that sugar.One example of periodic acid cleavage involves the degradation of one equivalent of D-glucose into five equivalents of formic acid and one equivalent of formaldehyde.

4. Conclusion

In this work the periodic acid was used to elucidate the structure of sugars.The chemical structure of prepared sugars was determined by reacting it with excess periodic acid.The results obtainedwere found to be in agreement with these reported in the literature.

5. Acknowledgements

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