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REACTION OF PERIODIC ACID ON THE DIFRUCTOSE ANHYDRIDES

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ABSTRACT

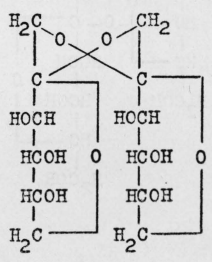
Diheterolevulosan, difructose anhydrides I, III, and II react, respectively, with 4, 2, 1, and 1 moles of periodic acid per mole of sugar. These results are in keeping with the known structures of the first three sugars. It is suggested that difructose anhydride II is a 1,2′-2,4′-difructofuranose.

CONTENTS

I. INTRODUCTION

Four difructose anhydrides are known as crystalline compounds. Diheterolevulosan was first prepared by Pictet and Chavan [1] by the action of hydrochloric acid on levulose at 0° C. Difructose anhydrides I, II, and III were obtained by Jackson [2] [3] and his coworkers from the residues after the removal of levulose when inulin was hydrolyzed with acid.

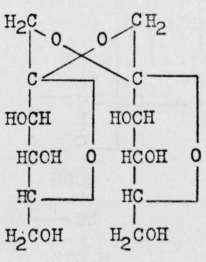
It has been shown that diheterolevulosan,[4] difructose anhydride I,[5] and difructose anhydride III [6] have the following structures:



I

Diheterolevulosan

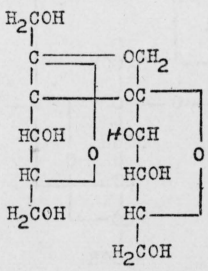
1,2′-2,1′-Difructopyranose anhydride



II

Difructose Anhydride I

1,2′-2,1′-Difructofuranose anhydride



III

Difructose Anhydride III

1,2′-2,3′-Difructofuranose anhydride

*Richard F. Jackson, deceased.

[1] A. Pictet and J. Chavan, Helv. Chim. Acta **9**, 807 (1926).
[2] R. F. Jackson and S. M. Goergen, BS J. Research **3**, 27 (1929) RP79.
[3] R. F. Jackson and E. J. McDonald, BS J. Research **6**, 709 (1931) RP299.
[4] H. H. Schlubach and C. Behre, Liebigs Ann. Chem. **508**, 16 (1933).
[5] W. N. Haworth and H. R. L. Streight, Helv. Chim. Acta **15**, 693 (1932).
[6] E. J. McDonald and R. F. Jackson, J. Research NBS **24**, 181 (1940) RP1277.

II. DISCUSSION

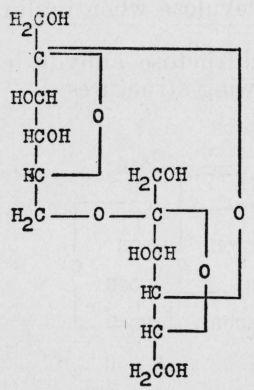
In the present investigation the reaction between periodic acid and the difructose anhydrides has been quantitatively studied. This acid has been used by many investigators [7] [8] [9] in structural studies because of its ability to react selectively with hydroxyls on adjacent carbon atoms.

In keeping with their known structures, diheterolevulosan reduces four moles of periodic acid per mole of anhydride, difructose anhydride I reacts with two moles, and difructose anhydride III with one mole of this acid.

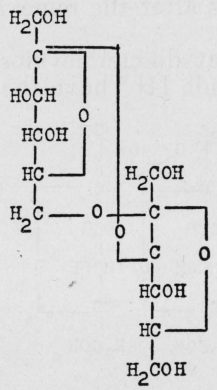
Haworth and Streight [10] have suggested that the stability of difructose anhydride I to acid might be attributed to the presence of the dioxane ring. The stability of diheterolevulosan and difructose anhydride III, both of which contain this dioxane grouping, is in keeping with this explanation.

In a previous investigation (see footnote 6) it has been shown that hexamethyl difructose anhydride II, upon hydrolysis, yields a product having a positive specific rotation of about 25 degrees. This appears to be composed of two trimethyl fructoses. The separation and purification of these partially methylated fructoses are being further studied.

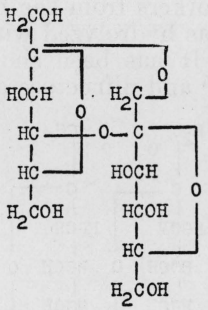
It is now shown that difructose anhydride II reacts with one mole of periodic acid. If we assume that, like the other two prepared from inulin, it is composed of fructofuranose units, there are 10 possible structures for this difructose anhydride. Only four of these would be expected to react with one mole of periodic acid. One of the four has been identified as difructose anhydride III. The remaining three are represented by formulas IV, V, and VI.



IV



V



VI

If formula IV represented difructose anhydride II, hydrolysis of the hexamethyl derivative would yield 1,3,6-trimethylfructose and 1,3,4-trimethylfructose. The latter is known as a crystalline product having a specific rotation of −51.4 in water. 1,3,6-Trimethylfructose is unknown, but it seems at least improbable that this derivative

[7] P. Fleury and J. Lange, J. pharm. chem. **17**, 107 (1933).
[8] E. L. Jackson and C. S. Hudson, J. Am. Chem. Soc. **59**, 994 (1937).
[9] E. L. Jackson, Organic Reactions, vol. II, p. 341 (John Wiley & Sons, Inc., New York, N. Y., 1944).
[10] W. N. Haworth and H. R. L. Streight, Helv. Chim. Acta **15**, 693 (1932).

would have a rotation of +100 degrees. Thus, it seems unlikely that IV is the structure of difructose anhydride II.

An anhydride whose structure is represented by V would produce a mixture of 1,4,6- and 1,3,4-trimethylfructose upon hydrolysis of its hexamethyl derivative. Hydrolysis of hexamethyl difructose anhydride III is known to form 1,4,6-trimethylfructose along with 3,4,6-trimethylfructose. Since the latter is known to have a rotation of +30 degrees in water and the combined rotations are approximately this value, it follows that 1,4,6-trimethylfructose has a specific rotation in water solution of approximately +30 degrees. A mixture of 1,3,4-trimethylfructose and 1,4,6-trimethylfructose would rotate at approximately −10 degrees instead of +25 to +30 degrees. Thus, structure V is excluded.

The hydrolysis of the hexamethyl derivative of a sugar whose structure is represented by VI would yield 3,4,6-trimethylfructose and 1,3,6-trimethylfructose upon hydrolysis. Data now available are at least in accord with this structure.

III. EXPERIMENTAL WORK

A solution containing 0.6367 g of diheterolevulosan in 50 ml of 0.2715-*M* HIO_4 was kept at 25° C for 15 hours. To 10 ml of this reaction mixture 1.5 g of Na_2CO_3 was added, followed by 31.008 ml of

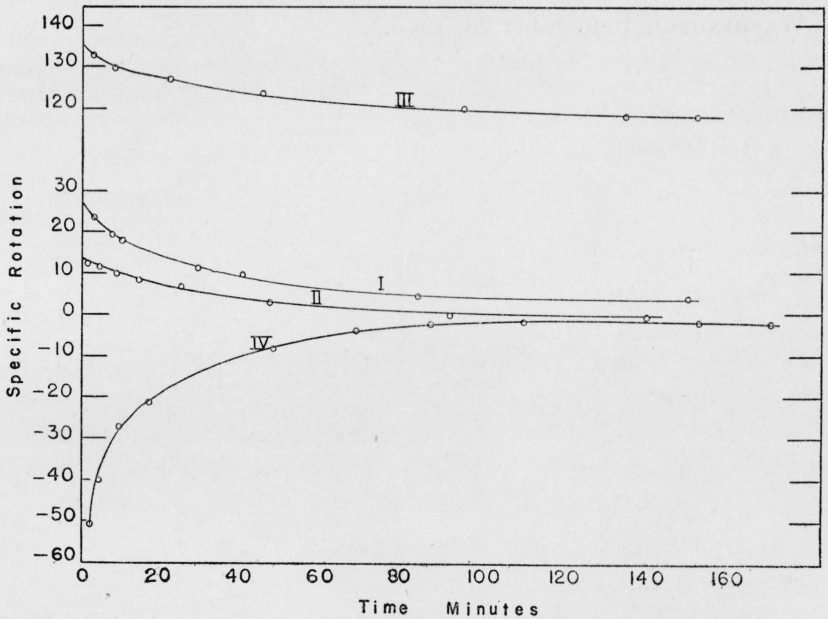


FIGURE 1.—*Rates of reaction of periodic acid and the difructose anhydrides.*
I. Difructose anhydride I. II. Difructose anhydride II. III. Difructose anhydride III. IV. Diheterolevulosan.

0.10095-*N* As_2O_3. One milliliter of 20-percent KI solution was then added, and after 15 minutes the unreacted As_2O_3 was determined by iodine titration. 8.456 ml of 0.1000-*N* iodine was required; thus,

22.629 ml of the As_2O_3 solution had reacted with the iodate present. This is equivalent to 4.188 ml of 0.2715-*M* periodic-acid solution, and hence 5.812 ml, or 0.001578 mole, of acid was consumed by 0.000393 mole of sugar.

The difructofuranoses were treated by the same procedure. The number of moles of iodine reduced by one mole of the difructose-anhydrides is given in table 1.

TABLE 1.—*Reacton of periodic acid and difructose anhydrides*

	Mole of sugar	Time reacted	Mole of HIO_4 consumed	Mole of HIO_4 / Mole of sugar
		Hours		
Diheterolevulosan	0.000393	3	0.00154	3.9
	.000393	15	.00158	4.0
Difructose anhydride I	.000345	15	.000660	1.9
	.000345	18	.000695	2.0
Difructose anhydride II	.000337	4	.000368	1.1
	.000337	24	.000370	1.1
Difructose anhydride III	.000318	17	.000324	1.0
	.000318	44	.000347	1.1

The progress of the reaction was followed polariscopically in each case, and the results are shown in figure 1.

WASHINGTON, September 25, 1945.