SHORT COMMUNICATIONS

The Polarography of 3, 6-Anhydro-galactose

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As 3, 6-anhydro-galactose is so unstable in acid that it decomposes readily to 5-hydroxymethyl furfural and then to levulic acid and formic acid, it is difficult to obtain this sugar by the methods usually used for the hydrolysis of polysaccharides. Using methanolysis, Araki and Hirase[1,2] first isolated the dimethyl acetal of this sugar and thus confirmed the natural occurrence of anhydro-sugars. Later O'Neil and Stewart[3] developed an indirect procedure for the detection of anhydro-sugars in polysaccharides. This procedure was based on the fact that, when polysaccharide is treated with N/50 sulfuric acid, only anhydro-sugar is converted to 5-hydroxymethyl furfural, and the latter can be determined photometrically. Because the pyranose ring of 3, 6-anhydro-sugar tends to open, giving aldehyde much more easily than do any other hexoses, the authors applied a polarographic method in studies of this sugar. In polarographic studies of various monosaccharides, Cantor and Peniston[4] reported that reduction waves could be detected with ketoses, even in 10^{-3} M in a phosphate buffer. On the other hand, under the same conditions as aldoses, these could only be at much higher concentrations, such as 10^{-1} M. Our studies of 3, 6-anhydro-L-galactose (AG)* and agarobiose (AGB)**, 4-D-galactopyranosyl-anhydro-L-galactose, showed that these compounds showed perceptible waves in the neutral and basic range, even in 10^{-3} M. (Fig. 1); this character was different from that of other aldoses. AG showed triplet and AGB, double waves; in each case, only the last wave changed in height with a change in pH value, (Fig. 2). To judge from the results of

1) C. Araki, *J. Chem. Soc. Japan (Nippon Kwagaku Kwaisi)*, 65, 725 (1944).
2) C. Araki and S. Hirase This Bulletin, 26, 463 (1944); 27, 109 (1954).
3) A. N. O'Neil and D. K. R. Stewart, *Can. J. Chem.*, 34, 1700 (1956).
4) S. M. Cantor and Q. P. Peniston. *J. Am. Chem. Soc.*, 62, 2113 (1940).

* Hydrolyzate of 3, 6-anhydro-L-galactose dimethylacetal with N/50 H_2SO_4 at 100°C for 1hr. Concentration: 1.87×10^{-3} M. The 3, 6-Anhydro-L-galactose dimethylacetal (b. p. 158~160°C/0.023 mmHg $[\alpha]_D^{15}$ −28.7 (H_2O) used was prepared from agarobiose dimethylacetal by Araki (1).

** Hydrolyzate of agarobiose dimethylacetal (m. p. 165~166°C $[\alpha]_D^{15}=-29.3$, H_2O) with N/50 H_2SO_4 at 100°C for 1hr.). Concentration: 1.36×10^{-3} M.

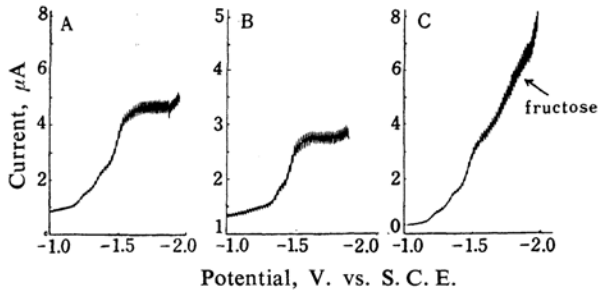

Fig. 1. Polarograms of anhydro-sugars at pH 9.0 (0.2 M NH_3-NH_4Cl buffer).

A) 3,6-Anhydro-L-galactose, 5.3×10^{-3} M, 3rd wave: $E_{1/2}=-1.42$ V, $i_d=1.77$ μA.
B) Agarobiose, 1.36×10^{-3} M, 2nd wave: $E_{1/2}=-1.38$ V, $i_d=0.66$ μA.
C) A mixture of 3,6-anhydro-L-galactose (4.8×10^{-3} M) and D-fructose (4.1×10^{-3} M), 3rd wave: $E_{1/2}=-1.42$ V, $i_d=1.44$ μA.

The procedures were carried out at 20~25°C using a Shimadzu RP-2 type polarograph. The capillary had an *m*-value of 1.227 mg./sec. and the drop time was 5.6 sec. in 0.2 N potassium chloride at a potential of 0.0 V. vs. S. C. E. with a mercury head of 58 cm.

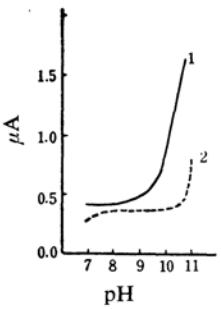

Fig. 2. Relation of wave height and pH for 10^{-3} M. 3,6-anhydro-L-galactose and agarobiose.

1: 3rd wave of 3,6-anhydro-L-galactose
2: 2nd wave of agarobiose

Cantor and Peniston, these waves may be presumed to be reduction waves of the aldehyde of the sugar. The height of the last wave was proportional to the concentration of AG in around 1×10^{-3} M in a Michaelis buffer (0.2 M NH_3-NH_4Cl) at pH 9.0, in which the most typical wave pattern was observed. The half-wave potentials of both sugars were about −1.4 V. vs. S. C. E. respectively (Table I) this value is smaller than those of any other sugars, but larger than that of 5-hydroxymethyl furfural (−1.3 V. vs. S.C.E.), as judged from our preliminary tests. It was also found that 3,6-anhydro-sugars are detectable by polarograpy, even in the presence of fructose (Fig. 1-c). In this case the figure of the wave was partially changed, but the potential of the waves remained unchanged. In conclusion, it may be said that as little 3,6-anhydro-sugar as about 3×10^{-3} M can be determined easily and rapidly by polarography.

TABLE I. HALF-WAVE POTENTIALS OF 3,6-ANHYDRO-L-GALACTOSE AND AGAROBIOSE (V. vs. S. C. E.)

pH	3,6-Anhydro-L galactose[1] 3rd wave	Agarobiose[2] 2nd wave
8.0	−1.41	−1.37
9.0	−1.42	−1.38
10.1	−1.42	−1.40
10.9	−1.46	−1.42

1) Concn. 1.87×10^{-3} M
2) Concn. 1.36×10^{-3} M

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