

389. *Formation of Furfural from Methylated Pentoses.*

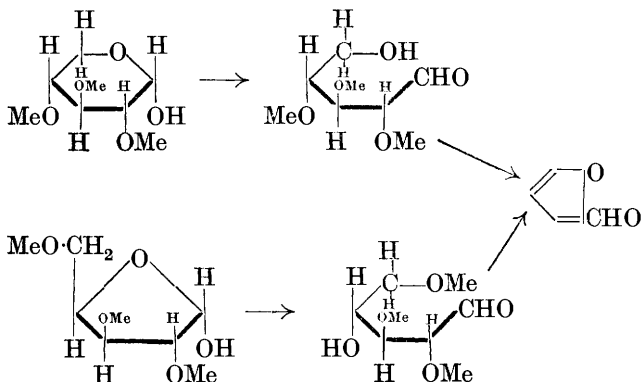
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THE conversion of the unsubstituted pentoses into furfural by the action of boiling aqueous hydrochloric acid has long been known, and has been used as the basis of several methods of estimation of these substances. On the other hand, glucose and its methylated derivatives (in particular, those derivatives obtained on hydrolysis of di- and poly-saccharides) are notably stable towards hydrochloric acid. In the pentose series, however, Carruthers and Hirst observed (*J.*, 1922, 121, 2299) that the hydrolysis of trimethyl methylxyloside by aqueous hydrochloric acid is accompanied by the formation of furfural, and Neher and Lewis (*J. Amer. Chem. Soc.*, 1931, 53, 4411) have now found that trimethyl arabopyranose can be made to lose methyl alcohol under the influence of cold dilute alkali. In the present paper it is shown that fully methylated derivatives of arabofuranose, arabopyranose, xylofuranose, and xylopyranose are readily decomposed by hydrochloric acid with formation of furfural, the rates of reaction and the amounts of furfural produced being directly comparable with those found with the free sugars. The times required to reduce the concentration of sugar to one-half of the original value, using boiling 12% aqueous hydrochloric acid, and the maximum obtainable yield of furfural are shown in the accompanying table.

Sugar.	Time (hrs.) to reduce conc. by 50%.	Max. yield of furfural, %.
Trimethyl arabofuranose	3.4	93
Trimethyl arabopyranose	12.0	66
Trimethyl xylofuranose	2.4	34
Trimethyl xylopyranose	1.2	80
Arabinose	2.8	76
Xylose	1.6	92

The results show that loss of methyl alcohol occurs with extraordinary ease, but the mechanism of the reactions which lead to the formation of furfural remains obscure. These changes take place under the influence of hydrogen chloride either in aqueous solution or in methyl-alcoholic solution in the absence of water. It would appear that under appropriate conditions the sugar assumes the aldehyde form and is subsequently transformed into furfural by loss of water and methyl alcohol. The occurrence of an intermediate enolic modification which readily loses methyl alcohol has been suggested in explanation of the transformation of tetramethyl fructofuranose into methoxymethylfurfural (Haworth, Hirst, and Nicholson, *J.*, 1927, 1514), and it is not impossible that a similar mechanism involving the first and second carbon atoms is operative

in the present instances. An intermediate enolic form has been suggested also by Neher and Lewis (*loc. cit.*) in connexion with the formation of furfural from trimethyl arabopyranose by the action of alkali. Whatever be the mechanism, the remarkable fact that



trimethyl pentoses of both pyranose and furanose structure yield furfural with almost equal readiness indicates that the presence or absence of a methyl ether group in position 5 is immaterial as regards the ease of reaction. On the other hand, great stability towards hydrochloric acid is conferred by the addition of a sixth carbon atom. Tetramethyl glucopyranose, for instance, which differs from trimethyl xylopyranose only in the terminal group, is almost unaffected by boiling 8% hydrochloric acid.

The stereochemical nature of the molecule is of considerable importance in connexion with the formation of furfural, arabinose and its methylated derivatives being more stable than the corresponding xylose compounds (cf. Hurd and Isenhour, *J. Amer. Chem. Soc.*, 1932, 54, 317). Another example of the ease with which xylose derivatives lose methyl alcohol is provided by 2 : 3 : 4-trimethyl *d*-xylonolactone, which gives a furancarboxylic acid when heated with aqueous pyridine (Haworth and Long, *J.*, 1929, 349).

EXPERIMENTAL.

Trimethyl Arabofuranose.—Trimethyl arabofuranose (Baker and Haworth, *J.*, 1925, 127, 367) was boiled with 12% aq. HCl, the procedure being similar to that employed in the estimation of pentoses. The furfural in the distillate was weighed as the phloroglucinol compound. Under standard conditions, the vol. of distillate collected is 400 c.c., and the wt. of furfural is obtained from the wt. of phloroglucide by the formula $F = (a + 0.0052) \times 0.5185$, in which F is the wt. of furfural, a that of the phloroglucide compound, and 0.0052 is a correction factor to compensate for the solubility of the latter. In the present expts. this factor has been proportionately increased in those cases where decomp. was not complete until more than 400 c.c. of distillate had

been collected. From 0.1297 g. of trimethyl arabofuranose, 0.1091 g. of phloroglucide was obtained, the vol. of distillate being 600 c.c. The wt. of furfural was therefore 0.0605 g. (calc., 0.0649 g.; 93% transformation).

The rate of decomp. was much slower with more dil. acid. An estimate of the rate with various concns. of acid was obtained by following the change polarimetrically. The rotations were measured on cooled samples of the solution removed at the times specified in parentheses, which are given in hours throughout, 0 representing the initial value.

(a) *With boiling 12% aq. HCl.* $[\alpha]_D^{20} - 35^\circ$ (c, 1.3; 0); 30° (1); 27° (2); 14° (4.5); 4° (6); 0° (8).

(b) *With boiling 9% aq. HCl.* $[\alpha]_D^{20} - 35^\circ$ (c, 1.2; 0); 33° (1.5); 29° (5); 12° (13); 6° (19); 2° (27); 0° (36).

(c) *With boiling 6% aq. HCl.* $[\alpha]_D^{20} - 28^\circ$ (c, 1.2; 0); 21° (12); 18° (22); 15° (28); 9° (37); 6° (46); 4° (55); 1.5° (61); 0° (70).

Trimethyl Arabopyranose.—When boiled with 20% aq. HCl, trimethyl arabopyranose (Purdie and Rose, J., 1906, 89, 1204) (0.2327 g.) gave furfural (0.0763 g.; 66% of theo.). The rate of decomp. with acid of various strengths is shown below.

(a) *With 20% aq. HCl.* $[\alpha]_D^{20} + 113^\circ$ (c, 1.3; 0); 73° (1); 43° (2); 14° (4); 7° (5.5); 4° (6.5); 2° (7.5).

(b) *With 12% aq. HCl.* $[\alpha]_D^{20} + 116^\circ$ (c, 1.0; 0); 112° (0.5); 89° (5); 76° (8); 67° (10); 44° (15); 32° (18.5); 18° (24); 10° (26.5); 6° (30); 0° (37).

(c) *With 9% aq. HCl.* $[\alpha]_D^{20} + 109^\circ$ (c, 1.2; 0); 101° (2); 93° (6); 77° (13); 56° (20); 48° (24); 33° (29); 23° (33).

(d) *With 6% aq. HCl.* $[\alpha]_D^{20} + 108^\circ$ (c, 1.6; 0); 107° (7); 99° (14); 93° (26); 86° (34); 71° (44); 66° (53).

Trimethyl Xylofuranose.—Trimethyl xylofuranose (Haworth and Westgarth, J., 1926, 880) decomposed rapidly when heated with 12% aq. HCl, giving optically inactive products, but the amount of furfural formed was comparatively small (0.0135 g. from 0.0797 g.; 34% yield). The rate of decomp. with acid of various concns. is indicated below.

(a) *With 12% aq. HCl.* $[\alpha]_D^{20} + 32^\circ$ (c, 1.2; 0); 24° (0.5); 23° (1); 17.5° (2); 12° (4); 7.5° (6); 6° (8); 1.5° (11.5); 0.4° (13.5).

(b) *With 9% aq. HCl.* $[\alpha]_D^{20} + 32^\circ$ (c, 1.1; 0); 28° (0.5); 26° (1); 20° (3); 13° (6); 11° (9); 5.4° (13); 3° (15); 1.5° (19); 0.5° (20).

(c) *With 6% aq. HCl.* $[\alpha]_D^{20} + 34^\circ$ (c, 1.1; 0); 28° (1); 25° (3); 21° (8.5); 14.5° (18); 10° (25); 7° (34); 5° (39); 3° (47).

(d) *With 3% aq. HCl.* $[\alpha]_D^{20} + 34^\circ$ (c, 1.2; 0); 30° (4); 29° (6); 28° (11); 27° (27); 23° (36).

Trimethyl Xylopyranose.—This sugar, prep. by Carruthers and Hirst's method (*loc. cit.*), readily gave furfural when boiled with 12% aq. HCl (0.0485 g. from 0.1211 g.; 80% yield). The rate of decomp. at the b. p. was as follows:

(a) *With 12% aq. HCl.* $[\alpha]_D^{20} + 21^\circ$ (c, 1.3; 0); 15° (0.5); 13° (1); 9.5° (1.5); 8.5° (2); 6° (2.5); 3° (4); 0° (5).

(b) *With 9% aq. HCl.* $[\alpha]_D^{20} + 20.5^\circ$ (c, 1.2; 0); 17.5° (1); 15° (2); 10° (4); 7° (6); 5° (8); 3° (12); 1.3° (15); 0.4° (17).

(c) *With 6% aq. HCl.* $[\alpha]_D^{20} + 20.5^\circ$ (c, 1.1; 0); 19.4° (1); 17.5° (4); 13° (7); 11° (10); 8° (16); 5° (22); 4° (26); 1.4° (37).

(d) *With 3% aq. HCl.* $[\alpha]_D^{20} + 19.5^\circ$ (c, 1.0; 0); 18.5° (1); 17.5° (4.5); 13.5° (18.5); 10.5° (38); 9° (50).

Action of Boiling 12% Aqueous HCl on Xylose and Arabinose.—For comparison with the above, the rate of decomp. of the free sugars in the presence of boiling 12% aq. HCl was studied.

(a) *Xylose*. $[\alpha]_D^{20} + 22.4^\circ$ (c, 1.0; 0); 16° (1); 9.5° (2); 7° (2.5); 2.4° (4); 2° (5); 0° (6).

(b) *Arabinose*. $[\alpha]_D^{20} + 108^\circ$ (c, 0.9; 0); 93° (0.5); 85° (1); 63° (2); 50° (3); 24° (6); 6° (10); 2° (12).

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