

FURFURALDEHYDE FROM 4-*O*-METHYL-D-GLUCURONIC ACID*

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Quantitative methods of paper chromatography are tending to replace the classical methods for the analysis of fibrous plant materials; nevertheless, proximate methods of analysis are still used for certain applications, for example, in the pulp and paper industry.

Many workers (see Browning 1952) have shown that, during distillation with 12% hydrochloric acid, uronic acids (including polyuronides), and pentoses (including pentosans) yield respectively 33–45% theoretical and more nearly theoretical amounts of furfuraldehyde. Pentosans are often estimated by determining the total yield of furfuraldehyde, the uronic acid content being determined separately and the total furfuraldehyde being corrected by using the data of Norris and Resch (1935).

Sarkar, Mazumdar, and Pal (1952) and Das Gupta and Sarkar (1954) have concluded, on the basis of periodate oxidation studies, that an aldobiouronic acid obtained from the noncellulosic polysaccharides of jute fibre was 3-*O*-(3-*O*-methyl-D-glucopyranosiduronic acid)-D-xylose.

Sarkar, Mazumdar, and Pal (1952) have shown that the yield of furfuraldehyde, obtained by distilling the aldobiouronic acid with 12% hydrochloric acid, is approximately equal to the yield that may be calculated by using the assumption that the *O*-methylhexuronic acid does not yield any furfuraldehyde or methoxyfurfuraldehyde. Also, they have demonstrated that the phloroglucide precipitate, obtained during the determination of the yield of furfuraldehyde, contained no methoxy groups. From this evidence and the fact that no methanol was detected in the distillates, they have concluded that the *O*-methylhexuronic acid unit does not yield furfuraldehyde during distillation with 12% hydrochloric acid.

The aldobiouronic acid component of the noncellulosic polysaccharides of many woods and cereal straws has been isolated and identified as 2-*O*-(4-*O*-methyl- α -D-glucosiduronic acid)-D-xylopyranose. The identification of 3-*O*-methyl-D-glucuronic acid and of 3-*O*-(3-*O*-methyl-D-glucopyranosiduronic acid)-D-xylose by Das Gupta and Sarkar (1954) seemed to suggest the existence of unique biosynthetic processes in the jute plant. Consequently Aspinall and Das Gupta (1958), Srivastava and Adams (1959), and Dutton and Rogers (1959) have reinvestigated the problem and have found that the aldobiouronic acid of jute was in reality 2-*O*-(4-*O*-methyl- α -D-glucosiduronic acid)-D-xylopyranose. Therefore the work of Sarkar, Mazumdar, and Pal may be reinterpreted to indicate that 4-*O*-methyl-D-glucuronic acid units do not yield furfuraldehyde during distillation with 12% hydrochloric acid.

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Because of this rather surprising result it was decided to reinvestigate the matter. The results reported herein show that 4-*O*-methyl-D-glucuronic acid, in the form of its crystalline amide, does indeed yield furfuraldehyde during distillation with 12% hydrochloric acid. The *p*-nitrophenylhydrazones of furfuraldehyde from arabinose and from methyl 4-*O*-methyl- α -D-glucosiduronamide proved to be identical. The yield of furfuraldehyde from the latter substance was similar to that found by Norris and Resch (1935) for the D-glucuronic acid units contained in euxanthic acid. Hence, because of the ubiquitous occurrence of 4-*O*-methyl-D-glucuronic acid in woods and cereal straws, the yield of furfuraldehyde obtained during the pentosan estimation should be corrected for furfuraldehyde from hexuronic acids before calculating the pentosan content of the material being examined.

Since the completion of the above work, Sen and Das Gupta (1962) have shown that the uronic acid component of 2-*O*-(4-*O*-methyl- α -D-glucosiduronic acid)-D-xylopyranose prepared from mesta fibre does yield furfuraldehyde under the conditions of the pentosan estimation; they have calculated that the 4-*O*-methyl-D-glucuronic acid unit of the aldobiouronic acid evolves 15.04% of its weight of furfuraldehyde; the furfuraldehyde-phloroglucide did not contain any methoxy groups.

Experimental

The microanalyses were carried out by the Australian Microanalytical Service C.S.I.R.O. and University of Melbourne. Melting points are uncorrected.

(a) *Preparation of Methyl 4-O-Methyl- α -D-glucosiduronamide.*—The amide was prepared from mesquite gum according to the method described by Smith (1951), except that the amide was prepared directly from the solution of the methyl ester of methyl 4-*O*-methyl-D-glucosiduronic acid without prior vacuum distillation of the ester. Yield of amide, 5% of gum. The amide was recrystallized, m.p. and mixed m.p. 235°C. According to the uronic acid estimation (Whistler, Martin, and Harris 1940) the yield of CO₂ from amide corresponded to a purity of 97%.

(b) *Furfuraldehyde from Methyl 4-O-Methyl- α -D-glucosiduronamide.*—The furfuraldehyde yield was determined according to the method for the estimation of pentosan as described by Dorée (1950), except that thiobarbituric acid was employed instead of phloroglucinol as the precipitant (Mackney and Reynolds 1938).

Yield obtained, 19.7% on weight of amide.

In another experiment the furfuraldehyde was distilled as described above and precipitated as the *p*-nitrophenylhydrazone, m.p. and mixed m.p. (with furfuraldehyde *p*-nitrophenylhydrazone made from L-arabinose) 154°C, with previous sintering at *c.* 140°C.

Analysis of the furfuraldehyde *p*-nitrophenylhydrazone made from methyl 4-*O*-methyl- α -D-glucosiduronamide (Found: C, 56.2; H, 4.1; N, 18.1; OCH₃, 0.0%. Calc. for C₁₁H₉O₃N₃: C, 57.1; H, 3.9; N, 18.2%).

References

- ASPINALL, G. O., and DAS GUPTA, P. C. (1958).—*J. Chem. Soc.* **1958**: 3627.
BROWNING, B. L. (1952).—In "Wood Chemistry." (Eds. L. E. Wise and E. C. Jahn.) pp. 1159-77. (Reinhold Publ. Corp.: New York.)
DAS GUPTA, P. C., and SARKAR, P. B. (1954).—*Text. Res. J.* **24**: 705, 1071.
DORÉE, C. (1950).—"The Methods of Cellulose Chemistry including Methods for the Investigation of Substances Associated with Cellulose in Plant Tissues." (Chapman & Hall Ltd.: London.)

- DUTTON, G. G. S., and ROGERS, I. H. (1959).—*J. Amer. Chem. Soc.* **81**: 2413.
- MACKNEY, A. W., and REYNOLDS, T. M. (1938).—*J. Coun. Sci. Industr. Res. Aust.* **11**: 333.
- NORRIS, F. W., and RESCH, C. E. (1935).—*Biochem. J.* **29**: 1590.
- SARKAR, P. B., MAZUMDAR, A. K., and PAL, K. B. (1952).—*Text. Res. J.* **22**: 529.
- SEN, S. K., and DAS GUPTA, P. C. (1962).—*Canad. J. Chem.* **40**: 572.
- SMITH, F. (1951).—*J. Chem. Soc.* **1951**: 2646.
- SRIVASTAVA, H. C., and ADAMS, G. A. (1959).—*J. Amer. Chem. Soc.* **81**: 2409.
- WHISTLER, R. L., MARTIN, A. R., and HARRIS, M. (1940).—*J. Res. Nat. Bur. Stand.* **24**: 13.