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THE ELEMENTARY COMPOSITION OF THE PENTOSAN XYLAN[1,2]

BY KARL PAUL LINK

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Introduction

When it was demonstrated by Wheeler and Tollens[3] that xylose, the sugar which Koch[4] had originally described and isolated from the products of hydrolysis of wood gum, was a pentose sugar with the empirical composition $C_5H_{10}O_5$, it became very probable that the corresponding anhydride, xylan, had the composition $(C_5H_8O_4)_n$. Soon after the relationship of xylan to xylose was established, a controversy arose with respect to the elemental composition of xylan. In 1896 Johnson[5] reviewed the controversy initiated by the conflicting analyses of Thomsen, Koch, Schuppe, Wheeler and Tollens. The analyses reported, with the exception of those by Schuppe, agreed with the formula $(C_5H_{10}O_5)_n$. Schuppe's analyses for the most part gave higher figures for carbon and hydrogen. The analyses reported by Johnson were on a xylan preparation from corn (*Zea Mays*) cobs. He concluded that xylan has the empirical formula $(C_5H_8O_4)_n$ and that the discrepancies and disagreements reported by other investigators were mainly attributable to the fact that xylan is a very hygroscopic substance, difficult to maintain at a constant moisture content. Although the analyses reported by Johnson appear to have been conducted with the necessary precaution, the conclusion that he reached with respect to the empirical formula of the pentosans was apparently not accepted. The third edition of the late B. Tollens'[6] excellent treatise on the carbohydrates published in 1914 still gave the empirical formula

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[2] The major part of this research was done during 1925–1927 while the author was a Fellow of the International Education Board posted at the University of St. Andrews, Scotland, and the University of Graz, Austria. The author wishes to acknowledge his indebtedness to Sir James Irvine, D.Sc., F.R.S., Principal and Vice Chancellor of the University of St. Andrews, for the privilege of extending the research while a student in his laboratory. The author is particularly indebted to Professor Fritz Pregl, Director of the Medico-chemical Institute of the University of Graz, under whose personal direction the micro-analytical analyses were conducted. To the Board of Directors of the International Education Board, New York City, the author wishes to extend his thanks for the Fellowship grant which enabled him to complete the work in the laboratories mentioned.

[3] Wheeler and Tollens, *Ann.*, **254**, 316 (1889).

[4] Koch, *Ber.*, **20**, Ref., 145 (1887).

[5] Johnson, THIS JOURNAL, **18**, 214 (1896).

[6] B. Tollens, "Kurzes Lehrbuch der Kohlenhydrate," Barth, Leipzig, **1914**, p. 474.

for xylan as $(C_{10}H_{18}O_9)_n$ or $(C_5H_9O_{4.5})_n$. In fact the old controversy on the question of the elemental constitution of the pentosans still persists at the present time.

The expression $(C_{10}H_{18}O_9)_n$ has again been advanced by Schorsch,[7] who formulates the expression $(C_{10}H_{18}O_9)_n$ for the formula of the pentosans on the evidence that: (1) a quantitative recovery of the corresponding pentose sugar is not attainable; (2) the purest preparations available when distilled with 12% hydrochloric acid by the Kröber–Tollens method never give an amount of furfural estimated as the phloroglucide compound corresponding to more than 92–96% pentosan; (3) no sugar other than a pentose has ever been isolated from a pentosan. According to Schorsch the formula $(2C_5H_{10}O_5{\cdot}H_2O)_n$ equivalent to $(C_{10}H_{18}O_9)_n$ is in accord with the experimental results. However, it must be borne in mind that it is not possible to hydrolyze pentosans with weak acids without the formation of some decomposition products, and that attempts at a quantitative crystallization of the free pentose sugar are always accompanied by mechanical losses and some retention of sugar in the mother liquors. In addition, it is well known that the Kröber–Tollens method never gives quantitative results even with the free pentoses.

Heuser and Schorsch[8] have advanced evidence that under certain conditions xylan retains sodium hydroxide and appears to form the compound $((C_5H_8O_4)_2{\cdot}NaOH)_n$ corresponding to the formula of the hydrate $((C_5H_8O_4)_2—H_2O)_n$, the formula implicated in the expression $(C_{10}H_{19}O_9)_n$. It should be noted, however, that the union formed with xylan and alkali is an exceedingly labile one, since the sodium hydroxide can readily be eliminated. In addition, it is important to take cognizance of the fact that specimens of anhydrous xylan can be readily obtained by desiccation at 115° in a vacuum of 15 mm., or over phosphorous anhydride at a lower temperature.

In a recent paper from the laboratory of Professor Haworth in Birmingham, England, methylation studies have been extended to the pentose polysaccharides. In this research Haworth and co-workers[9] used a xylan preparation obtained from esparto cellulose. By the method of estimating separately the carbon and hydrogen, and then the moisture content of an air-dried xylan sample, they concluded that their work substantiated the empirical formula $(C_5H_8O_4)_n$. It is apparent that a definite empirical formula for the pentosans is essential for a critical consideration of the molecular constitution of the pentose polysaccharides. In 1926, while the writer was at the laboratory of Professor Fritz Pregl, Graz, Austria, engaged in elementary micro-organic analyses, it was possible to investigate

[7] Schorsch, *Papier-Fabr. Tech. Wiss., Teil,* **1927**, 576–577; *C. A.*, **22**, 4478 (1928).

[8] Heuser and Schorsch, *Cellulosechemie,* **9**, 109 (1928).

[9] Hampton, Haworth and Hirst, *J. Chem. Soc.*, **130**, 1739 (1929).

the problem of the empirical composition of xylan, by micro-combustion methods.

The results obtained from the analyses of 15 xylan specimens from various sources corroborate the contention of Johnson, Haworth and coworkers in formulating xylan as $(C_5H_8O_4)_n$ and the methylated xylan compounds as derivatives of this parent formula.

Experimentation

Five xylan preparations from corn (*Zea Mays*) seedlings isolated as described in this Journal,[10] four xylan specimens from corn cobs, two from corn stalks and one each from beech wood, cherry wood, rye straw, and esparto grass were subjected to the ultimate carbon and hydrogen analysis by the Pregl micro-combustion method.[11] With the exception of the xylan specimens prepared from the corn seedlings, which were isolated as stated above, the various specimens were prepared by the method of Wheeler and Tollens.[12] After the initial isolation the various specimens were subjected to a further purification using the method of Heuser.[13] The preparations were thrice precipitated from 5.0% sodium hydroxide solution (carbonate free) as the copper–xylan complex, from which the copper was eliminated as already described.[14] All of the freshly precipitated preparations were first dried through the use of organic solvents; the importance and significance of this procedure has already been mentioned.[15] When the moisture content of the various xylan preparations was reduced to less than 3% through the employment of the aforementioned technique, no difficulty was encountered in obtaining an absolutely anhydrous xylan by drying the specimens in the Pregl micro-desiccator block at 100° for eight to ten hours at 15 mm. pressure. While it may not be difficult to produce absolutely dry xylan specimens by drying in the Pregl micro-desicca-

TABLE I

ANALYTICAL RESULTS

Source of xylan specimen	Carbon found,[a] %	Hydrogen found,[a] %
Corn seedlings preparation A	45.23	6.09
Corn seedlings preparation B	45.23	6.08
Corn seedlings preparation C	45.22	6.02
Corn seedlings preparation D	45.24	6.02
Corn seedlings preparation E	45.24	6.06
Beech wood	45.42	6.08
Esparto cellulose	45.22	5.85
Cherry wood	45.10	5.91
Rye straw	45.44	6.06
Corn cobs 1	45.51	6.09
Corn cobs 2	45.48	6.10
Corn cobs 3	45.42	6.04
Corn cobs 4	45.46	6.04
Corn stalks 1	45.47	6.04
Corn stalks 2	45.47	6.10

[a] All figures are the averages of duplicate analyses of the same specimen.

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[10] Link, THIS JOURNAL, **51,** 2506 (1929).

[11] The xylans from beech wood and esparto grass were isolated and purified while the writer was at the St. Andrews Laboratory. All the others had been isolated and purified in the home laboratory.

[12] Wheeler and Tollens, *Ann.*, **254,** 304 (1889).

[13] Heuser, *J. prakt. Chem.*, **104,** 259 (1922). This method is a modification of the original Salkowski method, *Z. physiol. Chem.*, **34,** 162 (1901).

[14] Link, THIS JOURNAL, **51,** 2510 (1929).

[15] Link, *ibid.*, **51,** 2508 (1929).

tor block, it is necessary to employ the utmost care to prevent a re-absorption of water. This difficulty was circumvented by placing enough of the partially dried xylan specimens in a platinum combustion boat to insure a sample of from six to eight milligrams when completely dry. The boat was then quickly transferred to a micro-weighing bottle by holding the mouth of the bottle against the drying tube and tilting the latter to discharge the boat. After weighing the specimen the boat was expeditiously transferred to the combustion tube in the manner described above. Through the use of this technique the absorption of water from the atmosphere was practically nil, as indicated by control weighings made on samples in platinum boats that were transferred back and forth from the combustion tube to the weighing bottle. The carbon and hydrogen values obtained in the highly purified xylan specimens are given below, calculated on the moisture and ash-free basis. Calcd. for $(C_5H_8O_4)_n$: mol. wt., 132.06; C, 45.44; H, 6.11.

In conclusion the writer wishes to express his gratitude to Dr. Arnulf Soltys (Graz) for the generous assistance and helpful suggestions that he contributed to this work.

Summary

The analytical results obtained by subjecting fifteen highly purified xylan specimens from various sources to the ultimate carbon and hydrogen analyses by the Pregl micro-method, indicate that pure xylan has the empirical formula $(C_5H_8O_4)_n$. This is in agreement with the theoretical formula for xylan when formulated as the anhydride corresponding to xylose, $C_5H_{10}O_5$. Judging from the ultimate analyses of xylan preparations reported in the literature, pure xylan has in most cases either not been obtained, or the preparations were analyzed under conditions that did not exclude the absorption or loss of water in the course of the analytical procedure.

Department of Agricultural Chemistry
University of Wisconsin
Madison, Wisconsin

[Contribution from the Chemical Laboratory of Barnard College]

THE STRUCTURAL ISOMERS OF BROMOBENZOYLACRYLIC ACID

By Grace Potter Rice

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In a recent paper published from this Laboratory[1] two pairs of unsaturated bromo-γ-ketonic esters and the pair of acids corresponding in configuration to them were described and shown to be geometrical isomers, but the position of the bromine atoms in these substances was not determined. In 1925 Bogert and Ritter[2] prepared an unsaturated bromo acid of benzoylacrylic acid and stated that the bromine atom in this substance was probably in the α-position because it gave acetophenone on

[1] Rice, This Journal, 50, 1481 (1928).

[2] Bogert and Ritter, *ibid.*, **47**, 526 (1925).