

filtration of the hydrolysate it was concentrated *in vacuo* at room temperature to a volume of 100 cc. To the cooled concentrate was then added 11.2 g. of liquid hydrogen cyanide and the mixture was allowed to stand for ten minutes, after which an aqueous solution of 7.0 g. of ammonia was added slowly with stirring. The solution was then placed in the ice-box overnight. The reaction product was filtered off and recrystallized from 95% alcohol, in which it is sparingly soluble, to yield a crop of yellow needles. The yield is 17 g. or 50%. It melts with decomposition at 192°.

Anal. Calcd. for $C_6H_9ON_3S$: C, 42.1; H, 5.25; N, 24.5; S, 18.7. Found: (Schoeller) C, 42.2; H, 5.44; N, 23.5; S, 18.7.

This substance is insoluble in cold water and all organic solvents tried except boiling alcohol, but soluble in concentrated hydrochloric or sulfuric acid. When boiled with concentrated sodium hydroxide it gives off exactly two-thirds of its nitrogen as ammonia. When boiled with 0.05 *N* sodium hydroxide, one-third of the nitrogen appears as ammonia in twenty minutes. The second nitrogen is much slower to hydrolyze, only half of it appearing as ammonia in two hours. This behavior, coupled with its high insolubility, is interpreted as confirming the assigned structure.

Thiazane-3,5-dicarboxylic Acid.—Ten grams of the above nitroamide was refluxed for three hours with concentrated hydrochloric acid. At the end of that time it was evaporated to dryness on a water-bath, taken up in water and made *just* alkaline to Congo red with ammonia, whereupon the thiazane-3,5-dicarboxylic acid came out in white needles which can be recrystallized from water and which contain one mole of water of crystallization. The yield was 6 g. or 56%. When heated it first deprecipitates then melts with decomposition at 253–254°.

Anal. Calcd. for $C_6H_9O_4NS \cdot H_2O$: H_2O , 8.6; C, 34.5; H, 5.26; N, 6.7; S, 15.3. Found: (Schoeller) H_2O , 8.7; C, 34.4; H, 5.35; N, 6.3; S, 15.3.

Summary

A new application of the Strecker reaction, ring closure, has been used to enter the thiazane series.

Thiazane-3,5-dicarboxylic acid has been synthesized by means of this method. This substance can serve as a starting point for the synthesis of many new thiazane derivatives.

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White Oak Holocellulose²

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Holocellulose, the carbohydrate fraction in wood freed of its extraneous materials, has proved within the last three years a promising material for the study of the composition of wood.^{3,4} It is similar in composition to the wood fraction, "skeletsubstanz,"⁵ that is isolated by means of an aqueous solution of pyridine and chlorine dioxide.

Since the results on holocellulose from maple³ and spruce⁴ were published, others have been collected on the holocellulose from white oak. They are considered in the present paper.

Materials Used.—White oak sawdust (60–80 mesh) was used in this study. It was first extracted consecutively with alcohol, alcohol-benzene solution, and hot water to remove extraneous materials.

Alcohol-pyridine solution, consisting of 85 parts of 95%

alcohol and 15 parts of pyridine (by volume), was used as the solvent.

A bleach solution was employed that was made by dissolving commercial chlorinated lime in distilled water. The supernatant liquor was removed from any undissolved residue by filtration and diluted so as to contain 1.6% of available chlorine. It was cooled to 10° and was made just acid to litmus by means of acetic acid immediately before using.

Isolation of Holocellulose.—The method developed by Ritter and Kurth³ was employed for the isolation of holocellulose. Briefly, it consists of repeated alternate treatments of the wood with gaseous chlorine and alcohol-pyridine solution.

Four chlorinations were required to remove the maximum amount of lignin from the wood before carbohydrates began dissolving as was shown by determining⁶ the lignin content of a control sample. In general, at this stage of delignification about 1.0% of lignin still remained in the residue. The residual lignin was removed by means of the bleaching solution at 10°.

Physical Properties of White Oak Holocellulose.—Unbleached white oak holocellulose is grayish tan in color; the bleached material is light-cream. It can be bleached

(1) Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

(2) To be presented before the Cellulose Division of the American Chemical Society at Chapel Hill, N. C., April 12, 1937.

(3) G. J. Ritter and E. F. Kurth, *Ind. Eng. Chem.*, **25**, 1250 (1933).

(4) E. F. Kurth and G. J. Ritter, *THIS JOURNAL*, **56**, 2720 (1934).

(5) E. Schmidt, K. Meinel and W. Jandebaur, *Cellulosechem.*, **13**, 129 (1932).

(6) G. J. Ritter and J. H. Barbour, *Ind. Eng. Chem., Anal. Ed.*, **7**, 238 (1935).

white but in doing so a small percentage of the acetyl groups is apt to be removed.

White oak holocellulose resembles the untreated wood structurally in that the fibers cling together. The clinging tendency of the fibers indicates the presence of carbohydrate material in the middle lamella and confirms findings by Bailey.⁷ These physical properties are similar to those of maple and spruce holocellulose.^{3,4}

Chemical Composition of Holocellulose.—The chemical composition of the holocellulose was determined by the following analyses: lignin was determined by the 72% sulfuric acid method,⁸ methoxyl by the Zeisel method,⁸ carbon dioxide by the 12% hydrochloric acid method,⁹ acetyl by the toluene-sulfonic method¹⁰ and pentosans by Tollens' method.⁸

The following three materials were analyzed by one or more of the foregoing methods: (1) white oak sawdust freed of its extraneous materials; (2) bleached holocellulose isolated from Material 1; (3) lignin isolated from Material 1 by means of the 72% sulfuric acid method. Table I shows the yields and composition of the three materials. Table II records the composition of the materials calculated on the basis of the extractive-free wood so as to reveal the proportion of the substituent groups in each of the three materials.

TABLE I

YIELDS AND RESULTS OF ANALYSIS OF EXTRACTIVE-FREE WOOD, HOLOCELLULOSE AND LIGNIN

Yields of materials based on oven-dry weight of extracted wood; results of analysis based on oven-dry weight of materials.

Material	Yields, %	Lignin 72% Sulfuric acid, %	Methoxy, %	Carbon dioxide, %	Acetyl, %	Pentosans, %
Extracted white oak wood	100.0	23.40	6.44	1.20	2.37	18.70
White oak holocellulose	75.6	0.00	1.64	1.56	3.07	23.40
White oak lignin	23.4	...	22.44

White oak holocellulose is free from lignin (Table I). Its methoxyl content is about 25% of that of the extracted wood; it liberates considerably higher percentages of car-

(7) A. J. Bailey, *Ind. Eng. Chem., Anal. Ed.* **8** (1), 52 (1936).

(8) M. W. Bray, *Paper Trade J.*, **87**, 59 (1928).

(9) A. D. Dickson, H. Otterson and K. P. Link, *THIS JOURNAL*, **52**, 775 (1930).

(10) K. Freudenberg, *Ann.*, **433**, 230 (1923).

TABLE II

COMPOSITION OF EXTRACTED WOOD, HOLOCELLULOSE AND LIGNIN

Results based on oven-dry weight of extracted wood.

Material	Yields, %	Lignin 72% Sulfuric acid, %	Methoxy, %	Carbon dioxide, %	Acetyl, %	Pentosans, %
Extracted white oak wood	100.0	23.40	6.44	1.20	2.37	18.70
White oak holocellulose	75.6	0.00	1.23	1.18	2.32	17.70
White oak lignin	23.4	...	5.25

bon dioxide than the wood; and it contains higher percentages of acetyl groups and pentosans than the wood. The carbon dioxide evolved from the holocellulose is believed to be a decarboxylation product of uronic acids. These acids and high percentages of pentosans render holocellulose especially prone to hydrate quickly in a pulp beater. As a result, it is converted to a stuff excellent for glassine paper by a sixty-minute processing treatment as compared with a ten-hour treatment for a refined pulp.

One per cent. of the holocellulose was lost during the isolation procedure (Table II), the sum of the holocellulose and the lignin being 99.0% (75.6 + 23.4 = 99.0). The loss occurs in pentosans as is shown in the last column. About 20.0% of the methoxyl groups are located in the holocellulose and 80.0% in the lignin. Within experimental error the results indicate that the carbon dioxide forming material and the acetyl groups of the wood are located in the holocellulose. These results on the location of the methoxyls, carboxyls and acetyls, are in agreement with those on maple and spruce holocellulose.^{3,4}

Summary

White oak holocellulose has been isolated by means of alternate treatments with chlorine gas and alcohol-pyridine solution. It has physical properties similar to those of holocellulose from maple and spruce reported previously. Its substituent groups are also distributed similarly to those in maple and spruce; about 20% of the methoxyls and all the carboxyls and the acetyls are located in the white oak holocellulose.

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