phenanthrene, and a second ketone which is probably 2-hydroxy-6- or 7-acetylphenanthrene.

9-Hydroxyphenanthrene gives a mono- and a diacetyl derivative. The former is 9-hydroxy-10-acetylphenanthrene, the latter 9-hydroxy-10,3-(or 6-)diacetylphenanthrene.

UNIVERSITY, VIRGINIA
RECEIVED FEBRUARY 28, 1933
PUBLISHED JULY 6, 1933

[CONTRIBUTION FROM FOREST PRODUCTS LABORATORY,[1] FOREST SERVICE, U. S. DEPARTMENT OF AGRICULTURE]

Some Factors that Influence the Conversion of Cellulosic Materials to Sugar[2]

BY GEO. J. RITTER, R. L. MITCHELL AND R. M. SEBORG

When cellulosic materials are treated with strong sulfuric acid at room temperature and then with boiling dilute sulfuric acid, the sugar yields that are obtained vary considerably among different investigators.[3,4,5,6]

Results described in this paper indicate that with a given concentration of acid such variations in sugar yields may be due to differences in (a) the temperature of the strong acid during its contact with the cellulose, (b) the time during which the cellulose remains in the strong acid, and (c) the cellulosic materials.

Materials Used.—Spruce cellulose, isolated from sawdust by means of the modified chlorination method,[7] was used for the study.

Experimental Procedure

Spruce cellulose was treated with 72% sulfuric acid (20 cc. of acid to 1 g. of cellulose) for periods of both two and six hours at temperatures ranging from 8 to 45°. The solution was then diluted with water to 4% acid concentration and hydrolyzed for four hours at boiling temperature. The reducing number of the sugar solution was determined according to the standard method[8] using the electrolytic procedure for the deposition of the reduced copper from a nitric acid solution. The glucose equivalent of the reducing number found was divided by the theoretical glucose yield (hexosan $\times$ 1.1) to obtain the efficiency of the conversion. In reporting the sugar yields in terms of glucose equivalent no correction has been applied for a small percentage of xylan and mannan that was present in the cellu-

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

(2) Presented before the joint meeting of the Divisions of Organic Chemistry and Cellulose Chemistry at the 84th meeting of the American Chemical Society, Denver, Colo., August 22–26, 1932.

(3) Braconnot, *Ann. chim. phys.*, **25**, 81 (1827).

(4) Flechsig, *Z. physiol. Chem.*, **7**, 528 (1883).

(5) Monier-Williams, *J. Chem. Soc.*, **119**, 803 (1921).

(6) Ost and Wilkening, *Chem.-Ztg.*, **34**, 461 (1910).

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TABLE I

PERCENTAGE OF THEORETICAL SUGAR YIELDS OBTAINED BY TREATING CROSS AND BEVAN CELLULOSE FROM WHITE SPRUCE WITH 72% SULFURIC ACID PREVIOUS TO HYDROLYSIS IN 4.0% SULFURIC ACID FOR FOUR HOURS

Hours with 72% H_2SO_4	8°	16°	20°	25°	35°	45°
2	55.6	92.3	95.0	95.0	98.1	95.4
	55.7	92.0	94.8	95.5	97.9	95.1
	56.7	92.3	94.8	95.2	97.7	94.3
	56.5	92.9	94.4	96.1	98.4	93.7
			94.6	95.6		
Av..........	56.1	92.4	94.7	95.5	98.0	94.6
6	95.1	100.0	97.7	96.0	90.0	87.7
	97.1	98.8	97.7	95.8	91.7	86.8
	97.4	100.0	96.5	95.4	91.5	86.8
	97.1	100.0	97.8	96.0	91.6	87.6
			97.7	96.6		87.8
Av..........	96.7	99.7	97.5	96.0	91.2	87.3

lose material because the error is less than the experimental accuracy of the determination of sugar yields. The results are shown in Fig. 1.

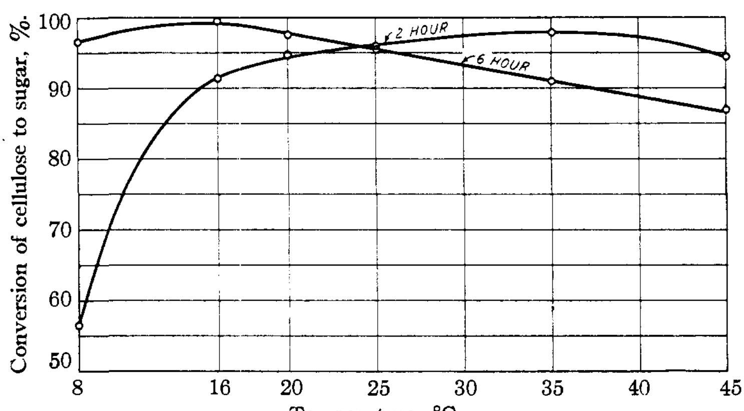

Fig. 1.—Effect of time and temperature of sulfuric acid on the conversion of cellulose to sugar.

Results and Discussion

Two-Hour Treatment.—The two-hour treatment of the cellulose with 72% sulfuric acid showed a minimum sugar yield at 8°. Reasons for the low yield are: (1) the removal from the system of considerable cellulose dextrins which precipitated during dilution of the acid-cellulose solution to 4.0% concentration and which failed to redissolve during the final hydrolytic treatment; (2) incomplete hydrolysis of the dissolved cellulose. At 16° the sugar yield increased over that at 8°. This rapid increase may be explained (1) by the fact that the small amount of cellulose dextrins which precipitated during dilution of acid-cellulose solution redissolved during the final hydrolytic treatment, and (2) by more hydrolysis of the dissolved cellulose. At 20, 25 and 35°, respectively, the progressively increased sugar yields are entirely due to more complete hydrolysis of the dissolved cellulose, since no cellulose dextrins were precipitated. At 45° the sugar yields decreased from the maximum because some of the cellulose was transformed into partially charred products, as was indicated by a brown discoloration of the solution from which a brown precipitate separated during dilution and the final hydrolytic treatment.

Six-Hour Treatment.—The six-hour treatment of the cellulose with 72% acid shows 96.4% sugar content at 8°, rising to a maximum of 99.7% at 16°, with a gradual decrease through 45°. The solutions prepared at 8 and 16° remained clear with no discoloration, at 20 and 25° there occurred a slight brown discoloration, progressively increasing to a brown precipitate at 35 and 45°. The apparent increasing amounts of cellulosic material thus destroyed account for accompanying decrease in sugar yields.

Charring of Cellulosic Materials.—These optimum conditions for the conversion of Cross and Bevan cellulose to reducing sugars do not correspond to those for obtaining minimum lignin residues from wood.[9] In the latter case charring of some carbohydrates apparently began slightly above 8° in six hours and slightly above 20° in two hours, whereas with Cross and Bevan cellulose charring first began above 16° in six hours, and above 35° in two hours. The results indicate that the non-cellulose carbohydrate portion in wood chars at lower temperatures than the Cross and Bevan cellulose. This conclusion is confirmed in studies on the carbohydrates not in the Cross and Bevan cellulose now under way at the Forest Products Laboratory.

Summary

1. With the two-hour treatment of Cross and Bevan cellulose with 72% sulfuric acid, the optimum temperature for the maximum yields of reducing sugars is 35°; with the six-hour treatment the optimum temperature for the maximum yields of reducing sugars is 16°.

2. Below the optimum temperatures the yields of reducing sugars from Cross and Bevan cellulose are lower because of insufficient hydrolysis; above the optimum temperatures the yields of reducing sugars are lower because of a partial charring of some of the hydrolytic products.

3. Some cellulose materials char more readily than others and require different temperature and time treatments to produce maximum sugar yields.

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RECEIVED MARCH 1, 1933
PUBLISHED JULY 6, 1933

(9) Ritter, Seborg and Mitchell, *Ind. Eng. Chem., Anal. Ed.*, **4**, 202 (1932).