[CONTRIBUTION FROM THE DIVISION OF AGRICULTURAL BIOCHEMISTRY AND THE DEPARTMENT OF BOTANY, UNIVERSITY OF MINNESOTA]

Analyses of Glacial and Preglacial Woods[1]

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Minnesota has been subjected to five glaciations. The Nebraskan glaciation (*ca.* 700,000–1,000,000 years ago),[2] the Kansan glaciation (*ca.* 500,000 years ago), the Illinoian glaciation (*ca.* 175,000 years ago), the Iowan glaciation (*ca.* 75,000 years ago) and the Wisconsin glaciations. The late Wisconsin ice sheet probably retreated from the middle part of Minnesota about 20,000 years ago. The advance must have taken place considerably earlier and the Peorian interglacial period probably came to an end in northern Minnesota 40,000–50,000 years ago.

In each of the interglacial periods forests developed only to be overridden by the ensuing ice sheets. In certain instances the wood from the interglacial or preglacial forests has been so preserved in the underlying clays as to be readily identifiable as to species and to be truly "wood," *i. e.*, fossilization had not taken place. The present communication deals with the chemical analyses of certain such specimens and supplements and extends similar analyses by Mitchell and Ritter[3] on three fossil woods from gravels of Miocene age in California.

Experimental

Materials. Specimen A—Pre-Nebraskan Spruce Wood.—This wood was secured *in situ* in the Nebraskan glacial till exposed in a highway cut 1.8 miles east of St. Charles, Minnesota. Figure 1 shows the specimens which were selected for analysis. All samples selected for analysis floated on water and after washing free of clay were dried and ground.

Specimen B—Pre-Nebraskan Spruce Wood.—This specimen was found in 1932 at a depth of 55 feet on the south bank of the Cottonwood River near New Ulm, Minnesota. It is shown in Fig. 2.

Specimen C—Peorian (last interglacial) Age Spruce Wood.—This was found at the bottom of a well sunk through 17 feet of lacustrine "clay" which formed in the bed of glacial Lake Agassiz and 70 feet of glacial till (ground moraine of late Wisconsin) in southeastern Kittson County near Bronson, Minnesota. It is shown in Fig. 2.

Specimen D—Peorian Age Spruce Wood.—This specimen was part of a larger "log" found beneath the Wisconsin gravel stratum at a depth of eleven feet, three miles north of Bottineau, North Dakota. It is shown in Fig. 2.

Methods.—The methods used are for the most part those recommended by Bray[4] with such modifications as were necessitated by the nature of the samples. All woods were reduced in a Wiley mill to pass a 40-mesh screen. Ash was determined on 3-g. samples. The alcohol–benzene soluble portion, pentosans, lignin (72% sulfuric acid method), and Cross and Bevan cellulose techniques followed procedures previously described.[5]

Certain of the glacial woods did not respond to the Cross and Bevan cellulose methods, since the lignin chloride formed a jelly-like mass. Mitchell and Ritter also noted this phenomenon in their fossil woods. In the present series of analyses the cellulose content of such woods was determined by a "hypochlorite method" in which the sample was extracted with a sodium hypochlorite solution in a centrifuge tube followed by extracting with 3% sulfurous acid, then with water, then with 2% sodium sulfite solution with repeated extractions, washing and centrifuging until a pure white fiber mat of cellulose was obtained. As an alternative method the cellulose was hydrolyzed with sulfuric acid and the resulting glucose determined volumetri-

TABLE I

SHOWING THE AVERAGE ANALYSES OF THE DIFFERENT WOOD SAMPLES

All Calculations on Basis of Oven-Dry Material

	Wood analyzed				
Approximate age in years	Modern white spruce 0 %	Peorian age (Specimen D) 40,000 %	Peorian age (Specimen C) 40,000 %	Preglacial (Specimen B) 800,000 %	Preglacial (Specimen A) 800,000 %
Ash	0.24	2.98	2.37	5.97	10.47
Lignin	29.73	39.03	53.38	79.23	66.41
Pentosans	9.63	7.21	7.77	2.23	2.10
Alcohol–benzene soly.	1.38	0.71	1.49	1.07	2.91
Cross and Bevan cellulose	60.70	42.30	[a]	[a]	[a]
"Hypochlorite" cellulose	....	35.07	27.10	[b]	[b]
"Sugar" cellulose	65.50	54.75	31.45	4.01	12.21
Holocellulose	70.92	53.79	44.88	13.30	23.68
Total of lignin + ash + holocellulose	100.89	95.80	100.63	98.50	100.56

[a] Not run for these three woods, due to formation of a lignin–chloride jelly which prevented chlorination or washing.

[b] No further determinations by this method; lignin–chloride jelly formed.

(1) Presented before the Division of Cellulose Chemistry at the General Meeting of the American Chemical Society, Cleveland, Ohio, September, 1934.

(2) (a) G. F. Kay, *Bull. Geol. Soc. Amer.*, **42**, 425–466 (1931); (b) F. Leverett, U. S. Geol. Survey, Professional Paper 161, 5–39 (1932).

(3) R. L. Mitchell and G. W. Ritter, THIS JOURNAL, **56**, 1603–1605 (1934).

(4) W. M. Bray, *Paper Trade J.*, **87**, 59–68 (1928).

(5) S. I. Aronovsky and R. A. Gortner, *Ind. Eng. Chem.*, **22**, 264–274 (1930).

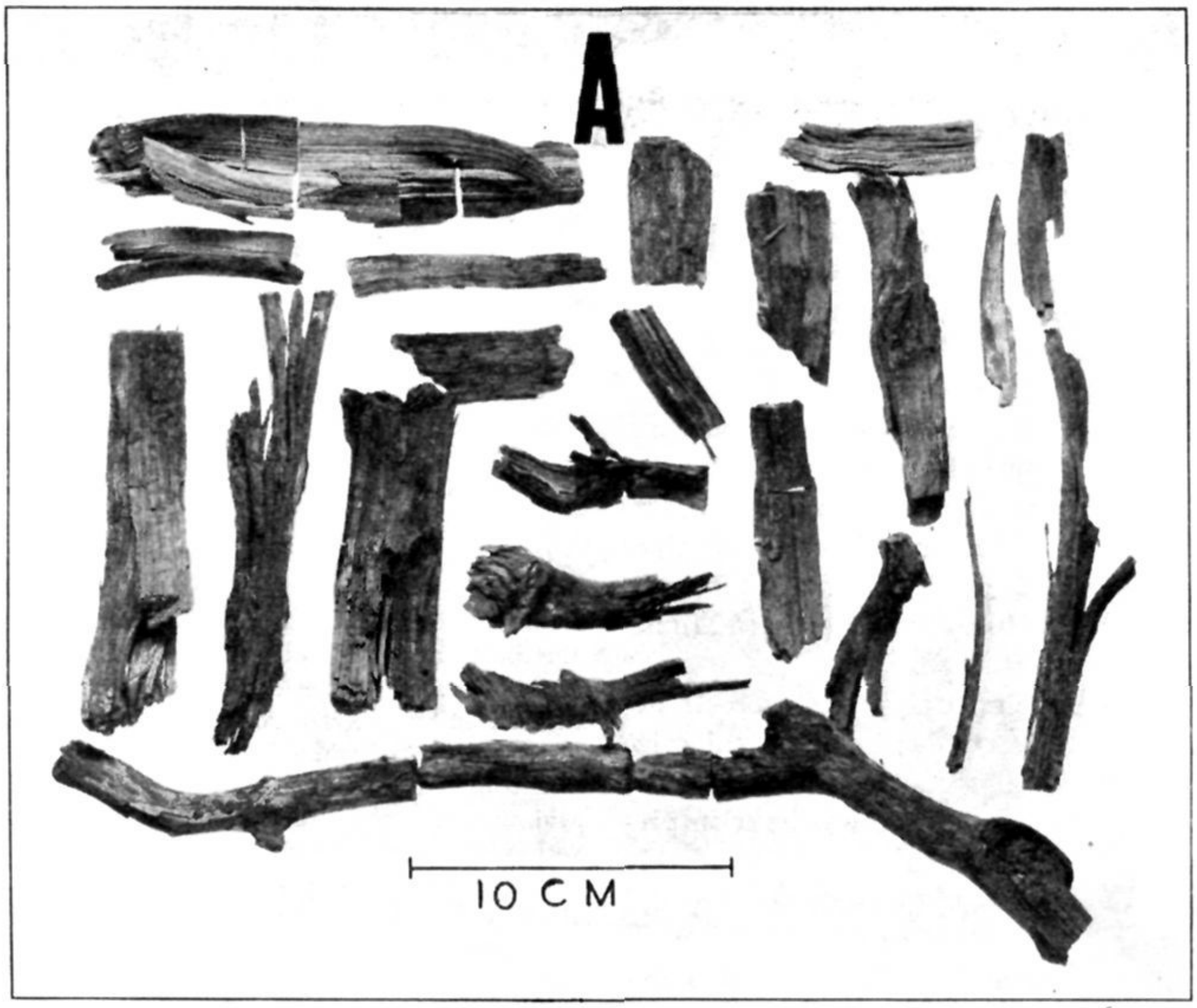

Fig. 1.—Specimen A, preglacial spruce wood.

cally.[6] This value was converted to "cellulose" by the appropriate factor. All woods were also analyzed for total carbohydrates by the "holocellulose" method of Ritter and Kurth.[7]

The Experimental Data.—Table I shows the analytical data and includes for comparison purposes parallel analyses of wood from a recently cut white spruce. These data represent the averages of closely agreeing triplicate or duplicate determinations. The range in duplicate or triplicate analyses for the glacial woods was within the limits allowable for comparable analyses in the pulp and wood-using industries.

Discussion

Ash.—The ash content increases with the age of the wood. This is probably due to the infiltration of mineral matter during the long periods that the wood was buried in the earth.

Cellulose.—The trends in "holocellulose" and "sugar" cellulose are essentially parallel, although no explanation is available for the marked decrease of "sugar" cellulose (4–12%) for the preglacial woods which show a holocellulose content of 13–23%. Possibly the reducing sugars titrated were not glucose, or some other change had taken place so that other compounds than reducing sugars were formed by hydrolysis of the "cellulose" residue. In general, there is a parallelism in the trends shown by all the "cellulose" methods, although the absolute values for any particular sample are not exactly alike.

Pentosans.—Pentosans decrease with age in about the same ratio as cellulose decreases. Possibly these residual "pentosans" are in reality uronic acids which are calculated as pentosans in the methods of analysis. In any event both cellulose and pentosan-like compounds have shown remarkable stability.

Lignin.—There is an apparent increase in lignin. This is probably largely the result of a loss of other wood constituents and is probably not due to an actual increase in lignin *per se*. Assuming a constant lignin value (no change in lignin with age of burial) of 30%, there would remain in the preglacial woods only 7–15% of the holocelluloses and only 9–10% of the pentosans which were present when the glacier overthrew and buried

(6) J. J. Willaman and F. R. Davison, *J. Agr. Research*, **28**, 479–488 (1924).

(7) G. F. Ritter and E. F. Kurth, *Ind. Eng. Chem.*, **25**, 1250–1253 (1933).

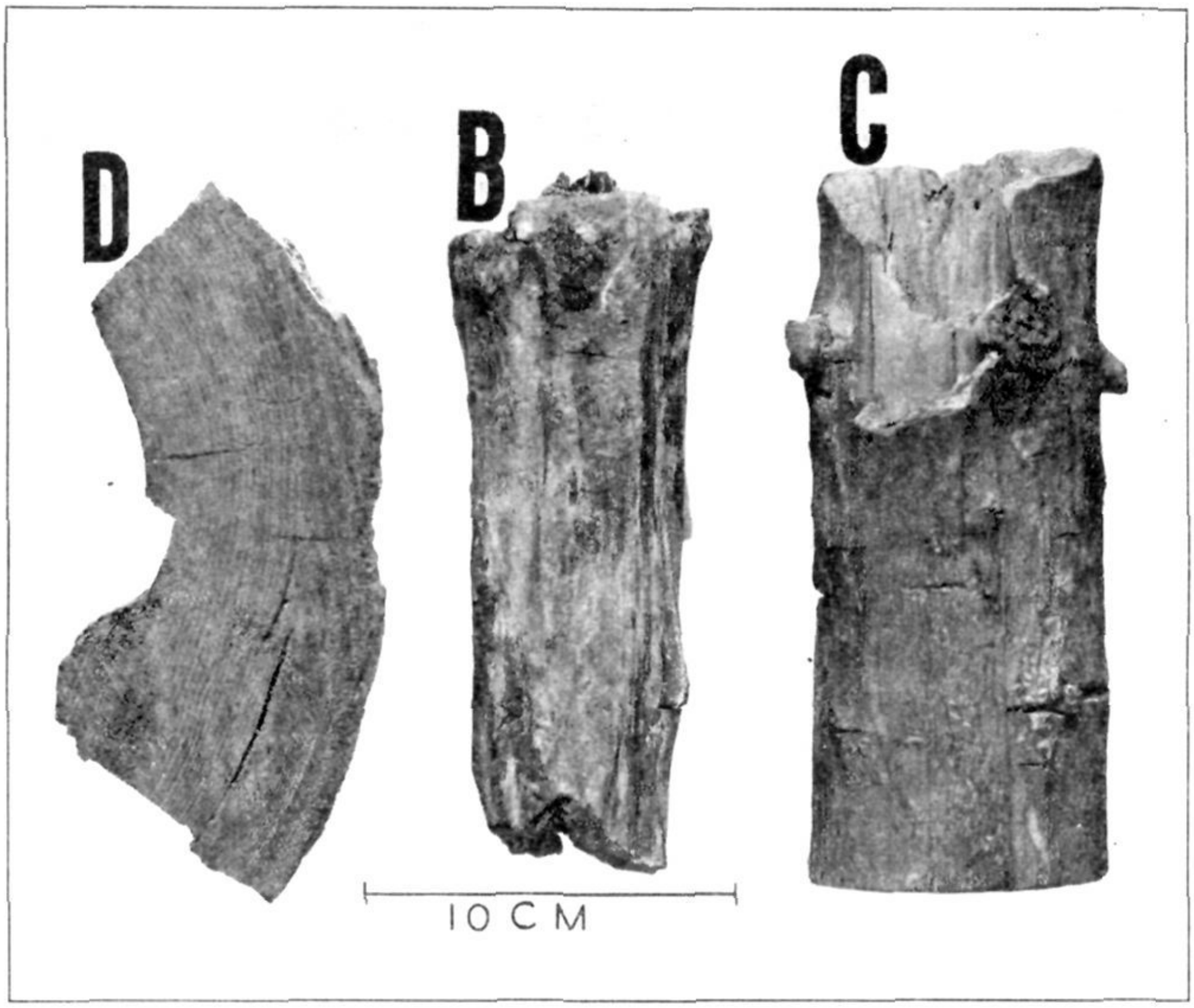

Fig. 2.—Specimen B, preglacial spruce wood; specimens C and D, Peorian age spruce wood.

the forest. It is therefore evident that lignin, or lignin-like complexes, are much more stable than are the cellulose–pentosan complexes.

The above analyses and conclusions parallel in a remarkable degree the analyses and conclusions of Mitchell and Ritter[3] in their studies of the fossil pine and cedrus woods of Miocene age. Apparently after being buried for a few hundreds of thousands of years wood reaches somewhat of an equilibrium with its environment, so that subsequent changes take place extremely slowly. Our analyses of wood of Peorian age indicate an intermediate degree of alteration.

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Summary

Two samples of preglacial spruce wood (Pre-Nebraskan) and two samples from the Peorian interglacial period were analyzed in comparison with modern white spruce.

The analyses show an increased ash content with age of burial, presumably due to the infiltration of inorganic salts from the earth. The pentosans and cellulose decrease with increase in age of the wood, with lignin showing an apparent increase. It is believed that this lignin increase is only apparent and is due to the decrease in the cellulosic constituents. Correcting to a constant lignin basis, there still remain in the wood which has been buried in the earth for 700,000–1,000,000 years approximately 7–15% of the original "holocelluloses" and 9–10% of the original "pentosans."

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