SOLUBILITIES OF SUGARS AT 20° (*continued*).

Sugar.	Formula.	Solvent.	Grams of anhydrous sugar in 100 cc. solution.	
			Init. sol.	Final sol.
α-Lactose hydrate	$C_{12}H_{22}O_{11}.H_2O$	40% alcohol	1.1	2.4
α-Lyxose	$C_5H_{10}O_5$	90% alcohol	5.4	7.9
β-Maltose hydrate	$C_{12}H_{22}O_{11}.H_2O$	60% alcohol	3.0	4.75
β-Mannose	$C_6H_{12}O_6$	80% alcohol	2.4	13.0
β-Mannose	$C_6H_{12}O_6$	Methyl alcohol	0.78	4.4
β-Melibiose dihydrate	$C_{12}H_{22}O_{11}.2H_2O$	80% alcohol	0.76	1.3
α-Rhamnose hydrate	$C_6H_{12}O_5.H_2O$	Absolute alcohol	8.6	9.5
α-Rhamnose hydrate	$C_6H_{12}O_5.H_2O$	70% alcohol	8.2	9.6
α-Xylose	$C_5H_{10}O_5$	80% alcohol	2.7	6.2
Sucrose	$C_{12}H_{22}O_{11}$	80% alcohol	3.7	3.7
Trehalose dihydrate	$C_{12}H_{22}O_{11}.2H_2O$	70% alcohol	1.8	1.8
Raffinose pentahydrate	$C_{18}H_{32}O_{16}.5H_2O$	50% alcohol	1.4	1.4

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[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE.]

THE PREPARATION OF XYLOSE.

BY C. S. HUDSON AND T. S. HARDING.

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The pentose sugar xylose has not been readily accessible to most investigators because it has been sold only at a very high price and its preparation has been a matter of considerable uncertainty. Since it was needed in large quantities in this laboratory, its isolation from various natural sources was studied in order to obtain, if possible, an inexpensive and accessible source and a dependable method for its preparation.

The Best Source for Xylose.—The sugar does not appear to have been noticed in the free state in nature, but it is very widely distributed among plants in the form of a condensation product, the gum xylan. By the acid hydrolysis of xylan the pentose is liberated and may be readily crystallized from the solution by the usual methods for isolating sugars. Beginning with the isolation of xylose from wood by its discoverer Koch[1] in 1886, it has been obtained also from brewer's grain,[2] straw,[3] corn cobs,[4] jute,[5] hay,[6] flax,[6] the alkaline cook liquor obtained by the action of hot

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[1] *Pharm. Z. Russland*, **25**, 619 (1886).

[2] Stone and Tollens, *Ann.*, **249**, 238 (1888).

[3] Hebert, *Ann. Agron.*, **16**, 364 (1890); Bertrand, *Compt. rend.*, **114**, 1492 (1892); and *Bull. soc. chim.*, [3] **5**, 555 (1891); Schulze and Tollens, *Ann.*, **271**, 40 (1892).

[4] Stone and Lotz, *Am. Chem. J.*, **13**, 348–50 (1891); *Chem. News*, **64**, 29 (1891); *Ber.*, **24**, 1657 (1891).

[5] Wheeler and Tollens, *Ann.*, **254**, 304 (1889); *Ber.*, **22**, 1046 (1889); *Z. Ver. Zuckerind.*, **26**, 848 (1889).

[6] Hebert, *Ann. Agron.*, **18**, 261 (1892).

calcium hydroxide on straw in paper making,[1] cocoanut shells,[2] certain tragacanth gums,[3] apricot stones,[4] and from *Psyllium gallicum* or "fleawort," a species of plantain found in South Europe.[5] The method which was used to prepare the sugar from most of these materials consists in first extracting the xylan from the wood or other source with a weak caustic soda solution, precipitating it with alcohol, and hydrolyzing it to xylose. In 1891, however, Bertrand[6] showed that xylose can be prepared by the direct hydrolysis of oat straw, the isolation of the xylan not being necessary. Maquenne used this direct process later with apricot stones. This simplification of the preparation left little to be desired in the way of a procedure for isolating xylose, and our present investigation has been directed principally to learning what common raw material would give the best yield of crystalline xylose by direct acid hydrolysis. The largest yield by far which has been reported is Maquenne's preparation of 12–13% xylose from apricot stones. In a recent book by Euler[7] it is mentioned that xylose "can now be made commercially from cottonseed hulls." We have been unable to find any other reference to this source in the literature and our efforts to communicate with Prof. Euler have been unsuccessful, but our experiments have shown that xylose can indeed be very readily prepared from the easily obtainable and inexpensive cottonseed hulls with a yield of 8–12%. Since this yield is nearly as large at that which Maquenne obtained from the less commonly available aprico stones, it appears that cottonseed hulls constitute the best source for the preparation of xylose.

The Method of Procedure.—Cottonseed hulls may be obtained from manufacturers of cottonseed oil. One kilo of the hulls is first covered with 2% ammonium hydroxide solution and allowed to stand overnight. The following morning the ammonia is washed out with hot tap water. The hulls are then boiled for two hours with eight liters of 7% sulfuric acid under a reflux condenser, the insoluble residue is filtered off through a piece of cheesecloth placed in a Büchner funnel, and the filtrate is carefully neutralized with pure calcium hydroxide, care being taken that the reaction never becomes alkaline. As the solution nears neutrality but while still acid it changes in color from reddish to greenish. The calcium sulfate precipitate is filtered off and washed with hot water and the washing combined with the filtrate The solution is made just acid

[1] Stone and Test, *Am. Chem. J.*, 15, 195 (1893).

[2] Tromp de Haas and Tollens, *Ann.*, 286, 303 (1895).

[3] Widtsoe and Tollens, *Ber.*, 33, 132 (1900).

[4] Maquenne, *Ann. chim. phys.*, 24, 401 (1901).

[5] Bauer, *Ann.*, 248, 140 (1888).

[6] *Bull. soc. chim.*, [3] 5, 555 (1891).

[7] H. Euler, "Grundlagen und Ergebnisse der Pflanzenchemie," Braunschweig, 1, 44 (1908).

with about 5 cc. syrup phosphoric acid and ten to fifteen grams of active decolorizing carbon are added and the solution is stirred for a few minutes, usually by passing a current of air through it. The filtrate from the carbon should be perfectly clear and of a greenish color. . It is concentrated to about 750 cc. and 6 to 10 g. decolorizing carbon are added and filtered off, after which twice its volume of 95% ethyl alcohol is added to precipitate the remaining calcium sulfate. After filtration the solution is boiled under reduced pressure to a very thick sirup of 90–95% solids. To this sirup sufficient 95% ethyl alcohol is added to cause the sirup to be nearly saturated with alcohol after the homogeneous mixture is cooled to room temperature. The mixing of the alcohol with the very thick sirup may be accomplished by heating on the steam bath or by careful heating of the flask over a flame. The sirup must not contain so much alcohol that a separation into two liquid phases will occur when the mixture is cooled to room temperature. This saturation requires approximately 50–75 cc. ethyl alcohol. As crystallization proceeds at room temperature or lower more alcohol may be added to prevent the mass becoming too solid, but care should be taken that sirup is not precipitated. Crystallization is usually complete in from two to three hours, but the solution is ordinarily allowed to stand overnight at 0°. The crystals are filtered off in a Büchner funnel, washed with 75 and then with 95% ethyl alcohol, followed by absolute alcohol, and dried in a vacuum oven. The sugar is almost colorless, nearly pure, and the yield is 80–120 g., or 8–12%, depending upon the quality of the hulls used. Glacial acetic acid may be used for washing the crystals, and it may also be used instead of alcohol in the original crystallization. By either method the xylose crystallizes very readily. Xylose may be recrystallized so readily that it is not necessary to give accurate directions.

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[CONTRIBUTION FROM THE FOREST PRODUCTS LABORATORY, U. S. DEPT. OF AGRICULTURE.]

THE OLEORESIN OF DOUGLAS FIR.

BY A. W. SCHORGER.

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The Douglas fir (*Pseudotsuga taxifolia* Britt.) apparently is the chief source of "Oregon balsam," which made its first appearance in commerce over forty years ago. The oleoresin is obtained mainly from natural cavities in the wood of the tree in which it has gradually collected.

Blasdale[1] appears to have first mentioned the volatile oil. He only states that the oil obtained from the "hardened natural exudation collected in Mendocino Co." (California) consisted of terpenes. In 1904,

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[1] THIS JOURNAL, 23, 163 (1901).