THE OCCURRENCE OF FREE PENTOSE IN BAMBOO SHOOTS. (STUDIES ON JAPANESE PLANTS. VIII.)[1]

By Shigeru KOMATSU and Yasuo SASAOKA.

Received January 15, 1927. Published February 28, 1927.

On the occurrence of free pentoses in plants, the evidence was offered by Davis and Sawyer,[2] as suggested by the work of de Chalmot,[3] from the Kröber-Tollens determination of pentoses in the extract of some vegetables, prepared with ammoniacal alcohol, and the contribution which supports this view was reported by A. G. Spoehr,[4] studying the carbohydrate economy of cacti. However, the treatment of the plant materials, employed by Davis and his co-workers, and Spoehr, as these were pointed out by D. T. Englis and C. Hale,[5] would then throw some doubt as to the conclusiveness of the evidence, owing to the fact that the desiccation of plant materials at high temperature,[6] and the use of ammonia and other weak alkalis for the extraction of sugars, could have given rise to a product which would lead to the

(1) The articles I, II, III, IV, V, and VII have been published in *The Mem. Coll. Sci. Kyoto Imp. Univ.*, **6** (1923), 295; **7** (1923), 7; **9** (1925), 1; **8** (1925), 59; 223; 253.

(2) *J. Agr. Sci.*, **6** (1914), 406.

(3) *Am. Chem. J.*, **15** (1893), 21; **16** (1894), 16; *J. Am. Chem. Soc.*, **15** (1893), 618.

(4) "The Carbohydrate Economy of Cacti," (1919), p. 41.

(5) *J. Am. Chem. Soc.*, **47** (1925), 446.

(6) K. P. Link, ibid., **47** (1925), 470 and refer W. Stiles, "Photosynthesis," (1925), p. 145.

formation of furfural-like compounds by some intramolecular changes or some degradation of hexoses.

In view of these facts, it appears that the only reliable method for the evidence of the occurrence of free pentoses, must be based upon the isolation of these sugars of the expressed juice which was prepared on the spot where the plant materials were freshly gathered.

In the phytochemical study of bamboo shoots, one of the writers (S. K.) and Ch. Tanaka[1] have reported that the pentose-content, which was determined by Kröber-Tollens' method, was constant throughout the bamboo shoot life, and the conviction of the occurrence of pentose in the free state came to the writers from a consideration of the origin of the sugars in plant tissues, ascribing them to the metabolism of hexoses, but not to the photosynthesis of carbon dioxide. The endeavours by which free pentose was isolated, will open the way for some suggestion as to the provenance of pentoses in nature.

The material used in this experiment was the shoots of the Madake (*Phyllostachys quilioli, F. M.*), which were obtained from a bamboo grove in Yamanouchi, Kyoto, located two miles from the laboratory. The shoots were minced in a mincing machine within an hour of gathering, and the minced mass was pressed by means of a hydraulic press. The juice thus obtained was poured into absolute alcohol. The manipulation was carried out as rapidly as possible in order to avoid all danger from enzyme actions on the carbohydrates.

13 Kg. of shoots yielded 10 litres of the expressed-juice of a density of 1.02; and this juice contained 160 gr. of reducing sugar calculated to be d-glucose from its power of reducing Fehling's solution.

To the juice a sufficient quantity of alcohol (30 litres) was added, whereon a voluminous precipitate was formed, which was filtered, washed well with alcohol and the filtrate subjected to distillation under reduced pressure to distill off the alcohol, and then diluted with water. To get sugars only, a slight excess of basic lead acetate was added to precipitate glucuronic acid with some organic acids which occur in the juice and the precipitate was filtered off, the excess of lead was removed by hydrogen sulphide gas. The colourless solution was evaporated to syrup under reduced pressure and the reducing sugars were extracted with absolute alcohol, evaporated again to a thick syrup and treated with alcohol. The operation was repeated three times, and the final extract containing 111.68 gr. of d-glucose and 12.88 gr. of l-xylose calculated from the reducing power of Fehling's solution and from the quantity of furfural measured by Kröber-Tollens' method, was evaporated under reduced pressure to a thick syrup. After clarifying with basic lead

(1) Loc. cit.

acetate, and an equal volume of glacial acetic acid was added to the syrup to crystallize the d-glucose, and actually 43 gr. of d-glucose. m.p. 145°, were isolated in a white crystalline state. The filtrate from the crystallized d-glucose, containing 49.5 gr. of reducing sugar, was diluted with water, and the acetic acid was expelled by distillation under reduced pressure, and the solution concentrated to 200 c.c.; it gave a polarization of $\alpha_D = 26°.9$ in a 1 dm. tube. Half of the sugar solution was diluted with water to make approximately a 10% aqueous solution, and about 5 gr. of top yeast were added, together with about 5 gr. of malt sprouts as a nitrogenous yeast food in order to ferment some hexoses remained in the solution with pentose. Fermentation proceeded at room temperature. After four days from the start, the fermentation had ceased and the solution was then cleared with a slight excess of basic lead acetate, the precipitate filtered, the excess of lead in the filtrate was precipitated by hydrogen sulphide gas, decolorized with active carbon and the solution again filtered. The solution freed from hydrogen sulphide, showed a polarization of $\alpha_D = 19°.2$ in a 1 dm. tube, contained 6.11 gr. and 6.13 gr. of l-xylose calculated from the reducing power of Fehling's solution, and the furfural-content by the Kröber-Tollens' method respectively. As concentrating the solution under reduced pressure, sugar was crystallized and the yield of the crude material was 5.4 gr. The sugar purified from its aqueous solution, melted at 145–150°, and showed a dextro-rotation in aqueous solution,

$$[\alpha]_D^{18} = \frac{0.39 \times 100}{2 \times 1.015} = +19.°21$$

Analysis, (C = 39.95; H = 6.65), indicated that the sugar has the formula $C_5H_{10}O_5$ (it requires, C = 40.00; H = 6.66%). For confirmation to be l-xylose, it was transformed into l-xylose osazone, m.p. 159°, and into xylonic acid by oxidation with bromine, and the latter was identified as the double salt of cadmium bromide with cadmium xylonate, following the method suggested by G. Bertrand.(1) It gave on analysis, Br = 20.78; while theory requires Br = 21.32 for $(C_5H_9O_6)_2Cd \cdot CdBr_2 \cdot 2H_2O$.

The isolation of l-xylose in a crystalline state from the pressed juice of bamboo shoots was successful, and this is probably the first example that pentose has been obtained direct in crystalline form from vegetable tissues.

Moreover, it is noteworthy fact that glucuronic acid which was regarded as an intermediate product of glucose metabolism in nature, was isolated from the precipitate by basic lead acetate mentioned above. For the recognition of glucuronic acid,(2) the precipitate which formed by basic lead acetate, suspended in water was decomposed by means of hydrogen sulphide gas, and

(1) *Bull. soc. chim.*, [3] 5 (1891), 556.

(2) Refer C. G. Schwalbe and G. A. Feldtmann, *Ber.*, 58 (1925), 1535.

the free acid in solution was isolated by converting it into barium salt of the phenylosazone[1] (m.p. 192°). The analytical results of the barium salt, $C_{36}H_{38}O_{10}N_8Ba$, are : C=48.98 ; H=4.76 ; N=12.68%.

The discovery of these substances in such a vigorously growing part of the plant, should account for much of formation of pentoses by the metabolic changes of hexoses in plants.

In addition, pectinic substance was isolated in an impure state from the pressed juice of the shoots, which yields pentose by hydrolysis and mucic acid by oxidation.

In fact, pectines and mucilages,[2] their basal molecule consists of xylose, glucose and glucuronic acid or arabinose, galactose and galacturonic acid, have been very generally occured in nature with the pentoses and hexoses. These facts strongly support the hypothesis of pentose formation above mentioned.

In conclusion, the writers desire to express their thanks to Mr. N. Iguchi for furnishing valuable materials used in this investigation.

October 1926.

Laboratory of Organic- and Biochemistry,
Kyoto Imperial University.

---

(1) Goldschmidt, *Monatsh.*, 31 (1910), 477.

(2) F. Ehrlich, *Chem. Ztg.*, 44 (1917), 197; T. von Fellenberg, *Biochem. Z.*, 85 (1918), 82; W. H. Dore, *J. Ind. & Eng. Chem.*, 16 (1924), 1042; S. Komatsu and H. Ueda, *The Mem. Coll. Sci. Kyoto Imp. Univ.*, A, 8 (1925), 51; D. R. Nanji, F. I. Paton and A. R. Ling *J. Soc. Chem. Ind.*, 44 (1925), 253; J. W. Mikinney, *J. Soc. Chem. Ind.*, 45 (1926), 301.