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On the Carbohydrates of the Shoots of *Sasa paniculata*.

By

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Bamboo shoots are widely consumed in Japan as an article of food, in spring time. The species of bamboo used in warmer provinces are *Phyllostachys mitis* Riv. and *Phyllostachys Quilivoi* Riv.. In northern districts, however, the shoots of *Sasa paniculata* Shibata et Makino are largely used for food.

Investigations on the constituents of bamboo shoots, up to the present time, have been only to show their general composition, except the papers by Kozai¹⁾ and Tōtani²⁾ who studied their non-protein nitrogenous constituents and proved the presence of asparagin, tyrosin, guanin, xanthin, hypoxanthin, adenin, cholin and betain. In regard to the chemical nature of carbohydrates, which compose the greater part of the bamboo shoots no special investigation has been reported. Moreover, the researches which have been made hitherto were exclusively on the shoots of the species of *Phyllostachys* and nothing was known about the shoots of *Sasa paniculata*. Consequently, we selected the *Sasa* shoot for the material of our study and examined its composition, particularly its carbohydrates.

1) Bull. Imp. Coll. Agric. and Dendrol., Tokyo, 1 (1890), 7, pp. 37-46.

2) Hoppe-Seyler Zs. physiol. Chem., Strassburg, 62 (1909), pp.113-114; *ibid.*, 70 (1911), pp. 388-390.

The results obtained are as follows:

	Fresh substance.	Water-free substance.
	%.	%.
Water	91.35
Ash	1.13	13.06
Protein	2.72	31.49
Fat	0.22	2.54
Crude fiber	1.44	16.68
Nitrogen-free extracts	3.14	36.68
Total nitrogen	0.44	5.04
Non-protein nitrogen	0.13	1.79
Reducing sugar	0.53	6.10
Non-reducing sugar	0.15	1.69
Starch	None	None
Cellulose	1.19	13.71
Lignin	Present	Present
Galactan	None	None
Pentosan	1.77	20.45
Methyl Pentosan	None	None

A general analysis was made of the edible part of the shoots by the Weende method, commonly adopted for food stuff. Sugars, cellulose and pentosan were estimated respectively according to the method of Allihn, König¹⁾ and Tollens. The absence of starch was determined by a micro-chemical test with iodine solution. The galactan was tested by oxidizing the fat-free sample with nitric acid of 1.15 sp. gr., as in the usual manner, with negative result. The absence of methyl pentosan was confirmed by the method of Oshima and Tollens²⁾.

As will be seen in the above table, the principal constituents of the shoot are carbohydrates, which form about one half of its total dry matter. Among the carbohydrates, pentosan is a prominent substance, its amount

1) Zs. Unters. Nahrungsmittel., Berlin, 12 (1906), pp. 386-395.

2) Ber. D. Chem. Ges., Berlin, 34 (1901), pp. 1425-1426.

attaining to 20.45% of the dry matter. Sugars are present in no slight quantity, reaching the amount of 7.79% of the dry matter. The absence of starch is apparently striking, when compared with the results of Kozai (l. c.), Nagai and Murai¹⁾ who detected its presence in the shoots of *Phyllostachys*. But it must be remembered that the *Sasa* shoots are generally gathered by breaking off the shoot above the soil and not by digging up, as in the case of other bamboos, and that even in *Phyllostachys* according to Shibata²⁾ starch exists only in the lower part of the underground portion of the shoots, in the neighbourhood of the rhizome.

To determine the nature of pentosan and sugar of the *Sasa* shoots, the following investigation was undertaken and will here be described in detail.

Pentosan of the shoots.

(1) Method of hydrolysis.

280 grams of finely pulverized shoots were washed with water and 2% ammonia successively, until the washings in each case were no more colored. Next, the sample was extracted with 10 L. of 5% caustic soda solution for about 48 hours and filtered. After the filtrate was neutralized with hydrochloric acid, a gummy substance was precipitated by the addition of 95% alcohol, and its amount weighed about 30 grams after drying. Then, 500 c.c. of 5% sulphuric acid were added to this substance and heated in a boiling water bath for 20 hours. When cooled, it was filtered through "Nutsch" filter with suction. The yellowish brown filtrate was neutralized with pure calcium carbonate and allowed to stand overnight. On the following morning, the calcium sulphate produced was filtered off by means of suction and the filtrate was concentrated, with the addition of a little calcium carbonate, to about 100 c.c. in a partial vacuum. The warm solution thus obtained was put into a dry flask with 500 c.c. of 85% alcohol and allowed to stand

1) Japan International Health Exhibition. London, 1884, A. Descriptive Catalogue, pp. 3-6.

2) Journ. Coll. Sc. Imp. Univ., Tokyo, 8 (1900), pp. 427-496.

for about 12 hours, when a blackish gummy substance adhered to the sides and bottom of the flask. The fluid was decanted and concentrated again in a partial vacuum to about 80 c.c.. To the remaining syrup, about 500 c.c. of 95% alcohol were added. This produced a second precipitate of a yellowish gummy substance. After standing for a few hours, the clear solution was decanted and concentrated to a small volume in a partial vacuum. The syrup was once more purified by shaking with about 200 c.c. of absolute alcohol. A clear solution was decanted and evaporated down to about 50 c.c..

(2) Qualitative tests of the syrup.

The syrup gave the following reactions:-

- a) It reduced Fehling's solution very strongly.
- b) It rotated the plane of polarization toward the right.
- c) It gave the characteristic absorption-spectrum of pentose with phloroglucin and hydrochloric acid.
- d) Two drops of the syrup were placed on an object glass and were seeded respectively with a crystal of xylose and arabinose. After 36 hours, the drop which had been seeded with xylose showed the formation of new crystals, while that with arabinose remained unchanged.

From the above reactions it is safe to conclude that the syrup contained pentose and that the presence of xylose was highly probable.

(3) Isolation of xylose.

When the purified syrup was left untouched nearly one week, it was found thickly laden with fine crystals. A small amount of 85% alcohol was added to the syrup, well mixed, filtered with suction and washed with absolute alcohol and ether. The sugar thus obtained was slightly yellowish in colour but upon recrystallization from alcohol with the use of animal charcoal, it became perfectly white and left no ash on ignition. The pure air-dry sugar thus obtained was 3 grams in weight.

0.425 gram of the carefully dried sugar was dissolved in water and made up into 25 c.c. and polarized in 100 mm. tube, in Schmidt and Haensch half shadow polariscope. Strong bi-rotation was observed. After 24 hours

the rotation was 0.9 on the scale toward the right. The specific rotatory power is

$$(\alpha)D = \frac{0.9 \times 0.346 \times 25}{0.425 \times 1} = +18.3^\circ \text{ (at } 20^\circ\text{)}$$

0.5 gram of the pure dried sugar was mixed with 1. gram of phenylhydrazin hydrochloride, 1.5 grams of sodium acetate and 10 c.c. of water and heated in the boiling water bath for one and a half hours, according to Fischer's method¹⁾. The yellowish needle-shaped crystals were produced. After the recrystallization from alcohol, their melting point was found to be 157°.

According to Tollens²⁾, the calculated specific rotatory power of 1.7% xylose solution at 20° is

$$(\alpha)D = 18.095 + 0.06986 p = 18.24^\circ$$

Melting point of xylosephenylosazone, according to Bauer³⁾ is 154°, according to Stone and Test⁴⁾ is 158°.

Consequently, the sugar under examination is xylose.

(4) Isolation of arabinosebenzylphenylhydrazone.

The mother-liquor filtered off from the crystals of xylose was evaporated to a syrup. It did not show any sign of forming new crystals of its own accord, after one week's standing. Trial was made to induce the formation of crystals by seeding with xylose or arabinose, but the effort was in vain in both cases. An attempt was then made to separate and detect arabinose by the use of benzylphenylhydrazin, according to the method of Ruff and Ollendorf⁵⁾.

3.5 grams of the syrup were dissolved in 10 grams of 70% alcohol, to which a solution of 2.5 grams of benzylphenylhydrazin in 4.5 grams of absolute alcohol, was added and the mixture well shaken. The fluid soon became turbid and in the course of 6 hours crystalline precipitates were

1) Ber. D. Chem. Ges., Berlin, 17 (1884), pp. 579—584.

2) Hand. d. Kohlenhydrate. II, Breslau, 1895, p. 70.

3) Lippmann:—Chemie d. Zuckerarten. I, Braunschweig, 1904, p. 140.

4) Ber. D. Chem. Ges., Berlin, 32 (1897), pp. 3234—3237.

formed. The crystals were separated by filtration with suction, washed with a small amount of 75% alcohol and finally recrystallized from 95% alcohol. The product obtained in this manner was perfectly white and weighed 0.392 gram when dried over sulphuric acid in vacuum. The melting point was found to be 170° which coincides with that of arabinosebenzylphenylhydrazone.

0.2035 gram of the substance was dissolved in 50 c.c. of methyl alcohol and polarized in a 200 mm. tube. A laevo-rotation of 0.3 on the scale was observed. The specific rotatory power is

$$(\alpha)D = \frac{0.3 \times 0.346 \times 50}{0.3035 \times 2} = -12.7^\circ \text{ (at } 16^\circ \text{)}$$

The specific rotatory power of arabinosebenzylphenylhydrazone according to van Ekenstein and de Bruyn¹⁾ is -14.6°, while Brown and Tollens²⁾ as well as Oshima³⁾ found it to be -12.1°, -12.6°. Consequently, it will be clear that the isolated benzylphenylhydrazone is that of arabinose.

From the above tests, it is evident that in the hydrolysis products of the shoots, both xylose and arabinose are present and consequently, that the pentosan of the shoots is made up of both xylan and araban, which are anhydrous condensation products of the pentoses.

Sugar of the shoots.

Although the amounts of sugar in bamboo shoots have been given in nearly every analysis hitherto reported, its nature⁴⁾ has been left untouched for future study. With a view of elucidating this phase of the question, the following experiments were undertaken.

500 grams of finely chopped edible portion of the fresh shoots were put into a large flask containing 800 c.c. of 95% alcohol. After standing for a

1) Ber. D. Chem. Ges., Berlin, 29 (1897), Ref. pp. 911—913.

2) *ibid.*, 35 (1902), pp. 1457—1467.

3) Journ. Sapporo Agric. Coll., Sapporo, 2 (1906), p. 94.

4) Shibata (l.c.) makes mention of glucose but from the nature of the methods followed by him it is not easy to decide whether the sugar under question is glucose or other reducing sugar.

few hours, the content was examined and found to possess an acid reaction. Hence, it was neutralized with ammonia and heated in a boiling water bath for 2 hours, using a reflux-condenser. When cooled, it was filtered and well washed with 95% alcohol. The filtrate was put in a flask and evaporated in a partial vacuum to a small volume. To this concentrated liquid 95% alcohol was added and allowed to stand for about 10 hours, stirring from time to time, when a brownish gummy substance was seen to adhere to the sides and bottom of the flask. The brown coloured transparent fluid was decanted and concentrated again to a syrupy condition in a partial vacuum. The syrup was once more purified by shaking with about 150 c.c. of absolute alcohol. The clear solution was decanted and evaporated down to about 10 c.c..

(1) Qualitative tests of the syrup.

The syrup gave the following qualitative reactions:—

- a) It reduced Fehling's solution very strongly; after inversion with hydrochloric acid, the reducing power is much enhanced, showing the presence of both reducing and non-reducing sugar.
- b) Molisch-Udransky reaction was positive.
- c) It did not show any pentose reaction by the phloroglucin method.
- d) It produced no characteristic mannose phenylhydrazone. When the mixture was warmed in a boiling water bath with acetic acid, the yellowish crystalline osazone was clearly produced.
- e) No mucic acid was produced upon oxidation with nitric acid.
- f) It gave the characteristic fire red colour of ketose with resorcin and hydrochloric acid.

(2) Phenyllosazone Tests.

The syrup did not show any sign of forming crystals even after standing one week. An attempt was then made to separate and detect the sugar as phenyllosazone.

- a) 1 gram of the syrup, 2 grams of phenylhydrazin hydrochloride, 3 grams of sodium acetate and 20 c.c. of water were mixed and heated in a

boiling water bath. After 10 minutes yellowish crystals had been produced. At the end of one hour and a half, the heat was removed and the crystals examined under the microscope. None of the other forms, besides the stellate form of yellow fine needle-shaped crystals which coincides with that of phenylglucosazone prepared from pure glucose in our laboratory, was observed. When cooled, it was filtered and washed with a little water. Upon recrystallization from dilute alcohol and drying over sulphuric acid in a vacuum the amount was 0.24 gram. The melting point was determined and found to be 204° which coincides with that of phenylglucosazone. Consequently the osazone under question is phenylglucosazone.

b) 1 gram of the syrup was dissolved in 20 c.c. of water and inverted with hydrochloric acid in a boiling water bath for about 30 minutes. After it was neutralized with sodium carbonate, 2 grams of phenylhydrazin hydrochloride and 3 grams of sodium acetate were added and heated in a boiling water bath, exactly in same manner as above described. The yellow crystals had already been produced at the end of 10 minutes. After heating for one hour and a half, the crystals were examined under the microscope, but they were all uniform and quite identical with those of phenylglucosazone which was obtained in the previous experiments. When cooled, it was filtered and washed with a little water. The yellow crystals thus obtained were recrystallized from 60 % alcohol and dried over sulphuric acid in a vacuum. The product weighed 0.3 gram and the melting point was found to be 204° . The crystalline form and melting point indicate that the osazone at hand is no other than phenylglucosazone.

Phenylglucosazone may be formed either from glucose, fructose, mannose or sucrose. The presence of mannose is excluded since no characteristic phenylhydrazone could be obtained in the qualitative experiment already mentioned. Maltose if present, will form an osazone of melting point similar to that of glucosazone but it can easily be distinguished from the latter in its crystalline form. From the results of our experiments maltose can hardly be expected to exist. Taking all these facts into consideration we may safely conclude that the reducing sugar consists chiefly of glucose, while the non-reducing sugar is sucrose. As to whether or not the fructose is present as

such or only in combination with glucose molecule in the form of sucrose, we have not sufficient data to decide and the question remains to be solved in future.

Summary.

- 1) The principal constituents of the shoots are carbohydrates which form about 50 percent of the dry matter.
- 2) The chief carbohydrates of the shoots are pentosan, cellulose and sugar. Galactan, methyl pentosan and starch are not present.
- 3) Pentosan of the shoots is made up of both xylan and araban, the former, however, predominating in amount over the latter.
- 4) Glucose and sucrose seem to compose the principal sugar in the shoots; the former is present in much larger quantity than the latter.

In conclusion, the authors wish to express their hearty thanks to Prof. K. Oshima for the valuable suggestions he has given in carrying out this research.
