ON THE HEMICELLULOSE OF ALLIUM CEPA, L.

By

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Introduction.

Hemicellulose is found generally in the cell-membranes of plant seeds. The study of hemicellulose was first undertaken by E. Schulze[1] and his associates. He ascertained the presence of a substance in cell-membranes, from which sugars of the hexose and pentose groups are produced by hydrolysis with a dilute mineral acid. He called the substance hemicellulose.

E. Schulze divided hemicellulose into two groups according to its function :—

a) A kind of reserve carbohydrates, contained in the endosperms of seeds. At the time of germination, it is used by plants like starch. It is called reserve cellulose. By hydrolysis with dilute mineral acid galactose and sometimes also fructose are produced.

b) The hemicelluloses, belonging to this group, have mechanical functions and serve as building materials, consist chiefly of galactane and pentosane.

It is clear from the studies of E. Schulze and his associates, that hemicellulose has a function as reserve material on the one hand, and a mechanical function on the other hand, serving as a building element.

The principal kinds of seeds in which the occurrence of hemicellulose was ascertained thus far are as follows :—

Pinus Cembra, Soja hispida, Helianthus annuus, Cucurbita Pepo, Ricinus communis, Amygdalus communis, Corylus Avellana, Juglans regia, Fagus sylvatica, etc.

As for the onion, special study has never been made either on hemicellulose or other carbohydrate groups. Further studies along this line are therefore nesessary and desirable.

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1) E. Schulze u. Ch. Godet ; Hoppe-Seyler's Zeitschr. physiol. Chem., 1909, **61**, 279-35. E. Schulze u. Pfennizer; Ibid, 1910, **68**, 93-108. Ibid, 1910, **69**, 366-382.

At the suggestion of Prof. K. Oshima the present investigation was undertaken. The results are presented in the following.

Experimental Part.

A. General Analysis.

The material used in the present investigation was cultivated on the experimental field of the College of Agriculture at Sapporo. It is the so called Sapporo-yellow onion. Its origin is the Yellow Damber imported first from the United States of America.

The air dried substance was finely pulverized in the usual manner.

The result of the analysis is as follows :—

TABLE I.

	Water-free subst. (%)	Original subst. (%)
Water	—	92.320
Ash	5.376	0.413
Crude protein	14.327	1.100
Crude fat	1.382	0.106
Crude fiber	5.815	0.447
N. fr. extrct	73.100	5.614
	100.000	100.000
Reducing sugar	7.201	0.553
Non-reducing sugar	1.475	0.113
Pentosane	6.166	0.474
Methyl pentosane	2.700	0.207

The method of Ellet and Tollens was applied for the determination of pentosane, and the rest of the analysis was carried out in usual manner.

B. Studies on Hemicellulose.

I. PREPARATION OF SAMPLE.

The inedible parts and roots of onion were removed just as for

cooking and then were cut into small pieces. The losses amounted to 16.55 per cent in weight.

5.4 kilograms of the substance were extracted with hot water which was kept at 40–50°C. and filtered. This was repeated several times. Then the substance was extracted twice with 95 per cent boiling alcohol in a flask provided with a reflux condenser. This was immersed for 24 hours in 0.25 per cent solution of sodium hydroxide, filtered through linen, and then washed well with water till no alkali reaction was observed. The residue consisted largely of hemicellulose and cellulose.

II. Qualitative Test.

The sample prepared in the manner above described, gave the following qualitative reactions :—

1. Galactane.

By oxidation with nitric acid of 1.15 sp. gr., mucic acid was produced.

2. Pentosane.

The sample was distilled with hydrochloric acid (1.06 sp. gr.) and the presence of furfurol was confirmed by the characteristic reactions with aniline acetate as well as with phloroglucine and hydrochloric acid.

3. Methyl pentosane.

The method of Tollens and Oshima[1] was made use of, to determine the presence of methyl pentosane.

To the distillate, which was obtained by the same method as for pentosane determination, was added concentrated hydrochloric acid and phloroglucine. After 5 minutes it was filtered. The filtrate gave the characteristic absorption spectrum of methyl furfurol.

III. Quantitative Analysis.

The result of the analysis of the hemicellulose sample is as follows :—

1) Oshima u. Tollens ; Ber. d. Deutsch. Chem. Ges., 1901, 34, 1425–1426.

	Air-dry subst. (%)	Water-free subst. (%)
Water	5.245	—
Galactane	13.398	14.564
Pentosane	12.710	13.820
Methyl pentosane	3.040	3.304
Ash	3.485	3.788

It is thus seen that hemicellulose of onion consists chiefly of galactane and pentosane with a small quantity of methyl pentosane.

C. Products of Hydrolysis.

I. Method of Hydrolysis.

About 90 grams of the sample prepared in the manner as described under B. were heated in a porcelain jar in a boiling water bath, with 3 liters of 3 per cent sulphuric acid for about 18 hours. At the end of the stated time the solution was filtered and the filtrate was neutralized with pure calcium carbonate and filtered again through a "Nutsch" filter. With a small quantity of calcium carbonate the filtrate was concentrated in a partial vacuum and purified with 80 per cent alcohol. The clear solution was concentrated again and then purified with 95 per cent alcohol. The evaporation and purification with strong alcohol was repeated until no more gummy substance was separated out. The decanted solution was concentrated to a syrup which was about 10 grams. The syrup thus obtained is designated as syrup A.

From 55 grams of the sample 13 grams of syrup were obtained by exactly the same treatment as above described, but with less frequent purification with strong alcohol, the syrup obtained in this case is referred to as syrup B.

II. Qualitative Tests on the Syrup.

The syrup gave the following reactions:—

1) The α-naphtol reaction for the carbohydrates was positive.
2) It reduced Fehling's solution strongly.
3) It rotated the plane of polarization to the right.

4) The solution of one gram of the syrup in 25 c. c. of water evolved carbon dioxide as the result of fermentation by yeast.

5) Mucic acid was produced by oxidation of syrup with nitric acid of sp. gr. 1.15.

6) The mucic acid was produced when two grams of syrup oxidized with nitric acid 1.15 sp. gr. The mucic acid was separated by filtration and the filtrate was evaporated nearly to dryness and treated with potassium carbonate and acetic acid in usual manner, but production of saccharic acid could not be observed, even after standing for several days.

7) To one gram of syrup, 5 c.c. of water, and 5 drops of phenylhydrazine were added and the mixture was well stirred at the room temperature. But the characteristic mannose phenyl-hydrazone was not formed. Therefore the absence of mannose is confirmed.

8) Seliwanoff's as well as Pinoff's reaction for ketose was negative.

9) Bertrand's reaction was made use of to determine the presence of xylose. About one gram of the syrup was dissolved in a little water and then a few drops of bromine water and 0.5 gram of cadmium carbonate were added. The mixture was warmed in a water bath a little while, and the next day poured into a porcelain basin and dried. Then a little of water was added and it was filtered. After the filtrate was nearly dried up, a little alcohol was added, the characteristic crystals of cadmium bromoxylonate was formed.

10) Two grams of syrup were dissolved in 6 grams of 70 per cent alcohol and 1.1 grams of benzylphenyl-hydrazine, which was dissolved in two grams of absolute alcohol was added to it, but the formation of hydrazone was negative. This proves the absence of arabinose.

11) According to the method of Tollens and Oshima, the presence of methyl pentose was positive.

From the qualitative tests made above it seems warranted to conclude the presence of pentose, methyl pentose, and galactose or the substance containing galactose molecule in the syrup.

III. Isolation of Galactose.

The syrup A was left untouched for about a fortnight, when, upon examination, the syrup was found to be thickly laden with fine crystals. After a small quantity of 75 per cent alcohol was added and mixed well, the crystals was separated from the solution by filtration with

suction. 1.5 grams of crystals were obtained from 10 grams of syrup.

The crystals showed the following properties :—

1) The crystal form was found largely to be needles.

2) They reduced Fehling's solution.

3) The specific rotatory power was determined and found to be $[\alpha]_D = \frac{4.7 \times 0.346 \times 25}{1 \times 0.5} = 81.°77$. Where 0.5 g. of the sugar was dissolved in 25 c. c. of water and polarized in a 100 m. m.-tube in a Schmidt and Haensch half-shadow polariscope, and it rotated 4.7 on the scale to the right.

4) The melting point was 165°C.

5) From 0.2 gram of the crystal, mucic acid was produced with the melting point of 215–216°C, the quantity of the acid being 0.1409 gram or 70.45 per cent of the sugar.

The physical constants and other properties observed point to the conclusion, that the sugar in hand is no other than galactose. Upon further examination of the sugar, the reaction for pentose with phloroglucine and hydrochloric acid was observed. It produced, however, no arabinose benzylphenyl-hydrazone nor cadmium bromoxylonate, evidently showing that pentose is admixed with galactose but in a very slight amount.

The syrup B crystallized as soon as it was cooled. On the next day 2.16 grams of crystal was obtained by the same treatment as above. A week after the first separation of crystal, 0.290 gram of crystal was separated again.

The crystal form, the melting point, and the specific rotatory power etc. of the crystals obtained in three cases were found to coincide well with each other. Therefore, there is no doubt, that they are all galactose.

Two grams of the mother liquor from which the crystals of galactose were separated twice before, were treated with 60 c.c. of nitric acid of 1.15 sp. gr. and produced 0.193 gram of mucic acid, or 0.257 gram as galactose. It is evident that the mother liquor contained still some galactose but further crystallization was not possible.

SUMMARY.

Among the hydrolysis products of hemicellulose of onion are found

galactose, xylose and methyl pentose, but not mannose, fructose, glucose nor arabinose.

The hemicellulose of onion consists chiefly of galactane and xylane with a small quantity of methyl pentosane whose nature could not be determined because of its small quantity.

In conclusion, I wish to express my hearty thanks to Prof. K. Oshima, to whom I am indebted for much valuable advice and kindness received during the present study.
