Studies on the Mucilage of the Root of "Tororo-aoi" (Abelmoschus manihot, MEDIC). I. On the Characteristic Colloidal Nature of the Mucilage

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Japanese hand-made paper, as is well known, is very elegant and refined, strong and tenacious, and is considered as a piece of work of Japanese characteristic arts. It is said that its elegance and strength mainly depend upon the properties of "*Neri*" which is indispensable for making Japanese hand-made paper.

"*Neri*" is a plant mucilage, and the mucilage obtained from the root of "*Tororo-aoi*" (*Abelmoschus manihot*, MEDIC) is most widely used. The chemical constituent of this plant mucilage was first investigated by Ozawa[1], and later Oguri[2] studied its distribution in cellular tissue. Oguri et al.[3,4], Machida et al.[5], and Oshibuchi et al.[6] reported that this plant mucilage was mainly made of polyrhamnogalacturonide, which contained rhamnose and galacturonic acid in the ratio of 1:1 or 1:2, and was accompanied by small quantities of araban, xylan, galactosan, and glucosan. However, concerning the colloidal behavior of this plant mucilage, little work has been done[7,8]. Taking an interest in this mucilage, we have been studying it for several years[9-13]. In this paper, such a purification method in which colloidal characteristics are kept well, was studied and then some colloidal characteristics of the purified mucilage were observed.

Experimental

Material. — Roots of "*Tororo-aoi*" were stored in 0.5% formalin.

Crude Mucilage.—The roots were washed with water, ground with a hammer, extracted with distillated water at 0°C for 24 hrs. and the extracted mucilage was filtered through a piece of cotton cloth.

Viscosity.—Viscosity determinations were carried out at 20°C by an Ostwald viscometer.

Intrinsic Viscosity. — Intrinsic viscosity determinations were carried out at 20°C in 1% sodium chloride solution.

Spinnability.—Spinnability was expressed by the maximum length (cm.) of the mucilage threads spun by a rod (7 mm. diameter) raised out of the mucilage. The determinations were carried out at 20°C and the velocity of the ascending of a testing rod was controlled at 4 cm./sec.

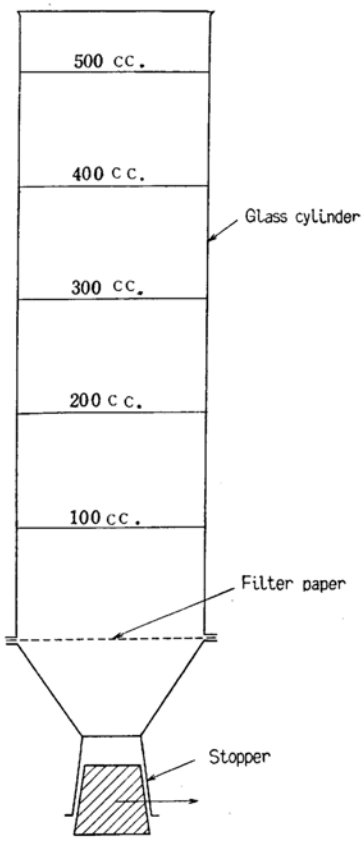

Fig. 1. Apparatus for the measurement of filterability.

1) T. Ozawa, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **24**, 389 (1922).
2) S. Oguri and H. Kawasaki, ibid., **45**, 307 (1942).
3) S. Oguri and K. Tomamezi, ibid., **46**, 146 (1943).
4) S. Oguri and K. Tomamezi, ibid., **47**, 432 (1944).
5) S. Machida and N. Uchino, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **74**, 615 (1954).
6) T. Oshibuchi and H. Kusunose, *J. Agr. Chem. Soc. Japan* (*Nippon Nogei-kagaku Kaishi*), **31**, 481 (1957).
7) S. Machida and N. Uchino, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **74**, 183 (1953).
8) I. Shinohara, T. Ono and S. Oguri, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **61**, 877 (1958).
9) S. Inokawa and R. Goto, *Wood Research* (*Japan*), **No. 14**, 50 (1955).
10) S. Inokawa and R. Goto, ibid., **No. 17**, 50 (1956).
11) S. Inokaxa, R. Goto and A. Takatsuki, ibid., **No. 21**, 26 (1959).
12) S. Inokawa and R. Goto, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 409 (1958).
13) S. Inokawa, R. Goto and I. Morimoto, ibid., **81**, 783 (1960).

Filterability. — Filterability means the rate of clogging up a filter paper. The determinations were carried out at 20°C as follows. A filter paper was fitted at the end of a glass cylinder (500 cc.) as in Fig. 1. a) Five hundred cc. of distilled water were poured into the cylinder and the times to filter 100 cc., 200 cc., 300 cc. and 400 cc. of water were measured (respectively, t_1, t_2, t_3 and t_4 sec.). b) Five hundred cc. of mucilage were poured into the cylinder, 400 cc. of the mucilage were filtered, and the residual mucilage (100 cc.) was discarded. c) Again, 500 cc. of distillated water were poured into the cylinder, and the times to filter 100 cc., 200 cc., 300 cc. and 400 cc. of water were measured (respectively, T_1, T_2, T_3 and T_4 sec.). Mean values of T_1/t_1, T_2/t_2, T_3/t_3 and T_4/t_4 are indicated as values for filterability.

Elasticity.—Elasticity determinations were carried out at 30°C by Schwedoff's method[14].

Results and Discussion

Effect of Heat Treatment on Spinnability, Filterability, Elasticity, and Viscosity, of the Mucilage.—Although spinnability, filterability, elasticity, and viscosity, of the crude mucilage were considerably large, spinnability, filterability, and elasticity decrease very rapidly by heating at 80°C, as shown in Fig. 2. These are the characteristic properties of the mucilage.

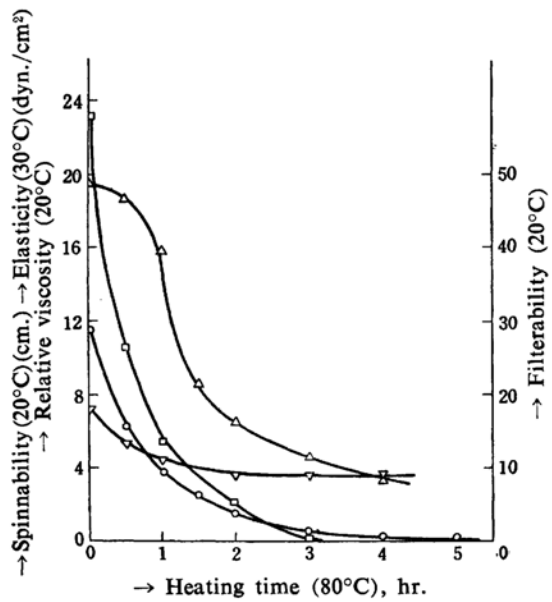

Fig. 2. Effect of heat treatment on the crude mucilage. Concentration of mucilage: 0.20%; 3.2×10^{-5}% (filterability).
○, Spinnability △, Filterability
□, Elasticity ▽, Relative viscosity

Effect of Mixer Treatment on Spinnability, Filterability, Elasticity, and Viscosity, of the Mucilage.—The crude mucilage in the original state was difficult to filter through a filter paper, but by homogenizing with a mixer, it was made easily filterable. Starch and other impurities contained in the crude mucilage could be removed by the filtration. The change of colloidal properties by mixer treatment is shown in Fig. 3. The spinnability and filterability almost disappeared by mixer treatment but the high elasticity remained. However, the high elasticity decreased considerably by heating or by longer standing in the similar way to that of the crude mucilage. The viscosity decreased rapidly also in the first 1 hr. of heating, the initial rapid fall being followed by a further slow reduction. The white precipitates obtained by the addition of alcohol-ether (8 : 2) mixture to the mucilage, were composed mainly of rhamnose and galacturonic acid and the mucilage prepared by redissolving the precipitates in water, had nearly equal elasticity to the original mucilage treated by a mixer. The mucilage thus obtained was used in subsequent studies as purified mucilage.

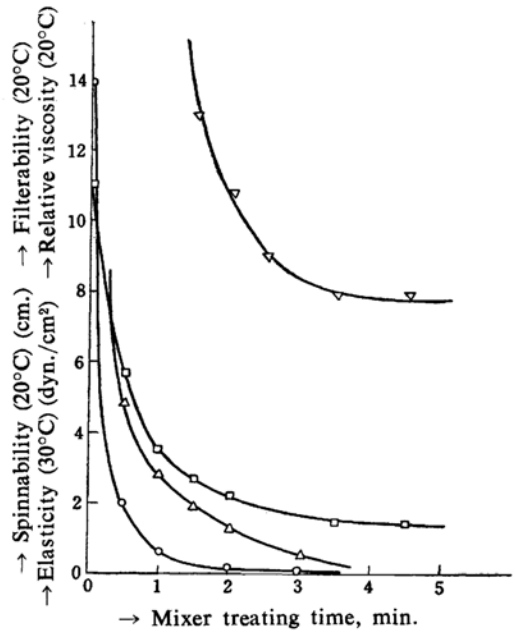

Fig. 3. Effect of mixer treatment on the crude mucilage. Concentration of mucilage: 0.16%; 1.1×10^{-5}% (filterability).
○, Spinnability △, Filterability
□, Elasticity ▽, Relative viscosity

Effect of Heat Treatment on Elasticity and Intrinsic Viscosity of the Purified Mucilage.—By heating at 80°C for varying periods of time, the elasticity of the purified mucilage fell down very rapidly to nearly zero. The intrinsic viscosity decreased rapidly in the first 30 min. of heating, the initial rapid fall being followed

14) Th. Schwedoff, *J. de Phys.*, [2] 8, 341 (1889).

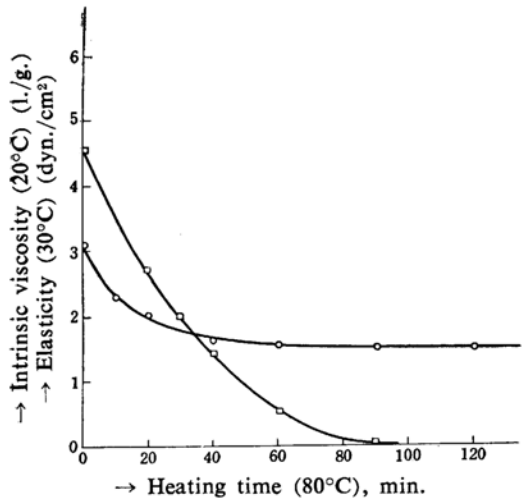

Fig. 4. Effect of heat treatment on the purified mucilage. Concentration of mucilage: 0.37%.
○, Intrinsic viscosity (in 1% NaCl solution)
□, Elasticity

by a slow reduction over a period of some hours as shown in Fig. 4. It seems that the fall of the elasticity does not always depend upon degradation of molecules of the mucin.

Effect of Electrolytic Groups in the Mucin on Elasticity of the Purified Mucilage. — 1) Effect of sodium chloride, calcium chloride, disodium ethylenediaminetetraacetate, and sodium oxalate on the elasticity of the purified mucilage was observed (Fig. 5). The elasticity

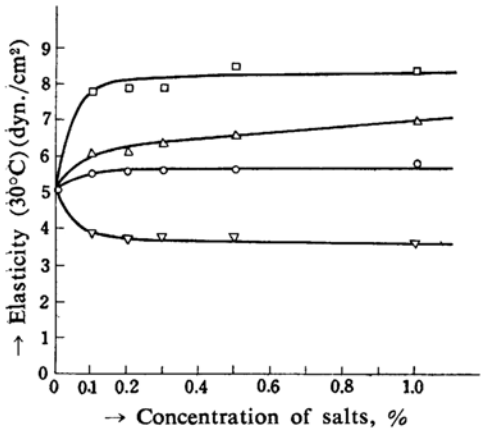

Fig. 5. Effect of addition of salts on the elasticity of the purified mucilage. Concentration of mucilage: 0.37%
○, Sodium chloride
△, Disodium ethylenediaminetetraacetate
□, Sodium oxalate ▽, Calcium chloride

was hardly influenced at all by the addition of sodium chloride, but increased by the addition of disodium ethylenediaminetetraacetate and sodium oxalate which are able to interchange calcium (about 40%) contained in ash of the mucilage, with sodium, and decreased by the addition of calcium chloride. 2) Electrodialysis experiments were carried out. By electrodialysis of the purified mucilage, pH of the mucilage changed from 6.1 to 2.9 and the value for the elasticity of 0.35% mucilage changed from 4.3 (dyn./cm²) to 10 (dyn./cm²). The change of the elasticity of the electrodialyzed mucilage is plotted against the change of pH with the addition of sodium carbonate in Fig. 6. The addition of calcium oxide to

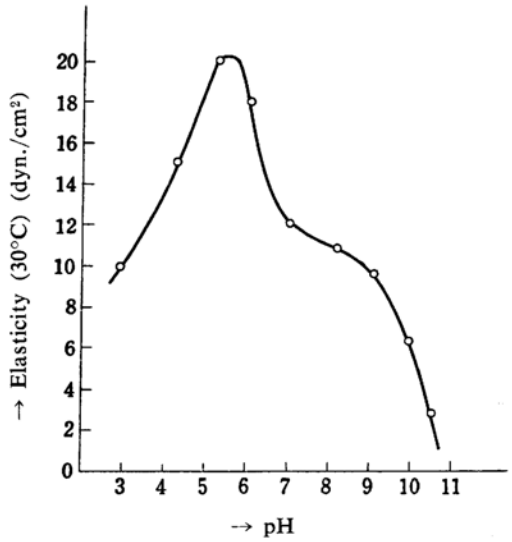

Fig. 6. Effect of pH on the elasticity of the electrodialyzed mucilage. Concentration of mucilage: 0.35%

the electrodialyzed mucilage always decreased the elasticity and at pH 4.2, the value for the elasticity fell to 4.2 (dyn./cm²). From results of above two experiments, it is considered that electrolytic groups in the mucin have effect on the elasticity but are not a major cause for the elasticity.

Summary

1) The crude mucilage could be filtered after homogenizing by a mixer. By the addition of alcohol-ether mixture to the filtrate, the precipitates were obtained, which gave purified mucilage on redissolving in water.

2) The purified mucilage had noticeable elasticity and could be used for the research work instead of crude mucilage.

3) Some colloidal behavior of the purified mucilage was observed.

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