On the Chemistry of Japanese Plants, I.

The Proximate Composition of Karafuto Wood.

By

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Yezo-matsu (*Picea ajanensis, Fisch.*) and Todo-matsu (*Abies sachalinensis, Masters.*) which are the principal constituents of the forests of Karafuto island, are regarded as the most important pulp material in Japan.

The cellulose-content of the wood was studied by I. Morioka,[1] from the point of view of paper manufacture. According to his report, the cellulose-content in Karafuto wood and European spruce is equal. The yield of sulphite pulp, however, which was made by the present author from our wood on a manufacturing scale at the Nippon Chemical Pulp Co., Karafuto, was small in comparison with that from European spruce, the yield being 10·5 and 9·7 tons of pulp from 22 tons of Yezo-matsu and Todo-matsu respectively, in the case of indirect cooking.

The present investigation, therefore, was undertaken in connection with the study of the manufacture of wood pulp, to the proximate composition of the wood.

The sample used in the experiment were sawdust from 130 years old trees grown at the Naibuchi, Karafuto, which are used in pulp manufacture, and were sifted with a 50-mesh sieve to get uniform size to avoid the effect of size of particle on yield of cellulose and other things.[2]

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1 Sapporo Norin Gakuho, **30** (1915); **40** (1920).

2 S. A. Mahood: J. Ind. & Eng. Chem., **12**, 833 (1920).

1. DRYING.

The sample was dried at 98° to constant weight, and the moisture was determined from the loss of weight.[1]

2. EXTRACTION WITH 95% ALCOHOL.

The etherial oil in the wood was studied by Shinozaki[2] and confirmed to consist mainly of pinene and phellandrene.

Wax, fat and resinous matter in the sample were estimated by extracting the dried substance with 95% alcohol boiling for three hours,[3] and the content calculated from the loss weight in Yezo-matsu and Todo-matsu is 3·1% and 3·8% respectively.

3. WATER EXTRACT.

Although cotton cellulose and filter paper, as obserbed independently by Robinoff[4] and Tauss,[5] are partially attacked by water on heating under pressure, pure cellulose is generally regarded by many investigators as insoluble in hot water.[6] However, pentosans and hexosans, according to S. Komatsu and his co-operators' experiments,[7] by heating with water under pressure were partially hydrolysed into simple sugars. It is, therefore, proper to ascribe the origin of simple sugars in the water extract of woods obtained under pressure to the hemicellulose which is composed of cell-wall.

Spruce heated with water under a pressure of five atmospheres for three hours, yields 1·18% reducing sugar, and the increased yield of the sugar in water extract results from increased pressure as seen in J. Konig and E. Rump's experiment.[8]

To determine the hydrolytic degree of the woods by water, 25 grm. of air-dried Yezomatsu, were heated with 300 c.c. water in autoclave for two hours, and the extract, separated from the insoluble matter by filtration, was diluted with water to 500 c.c. The reducing sugar in the

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1 M. Renker: U. Bestim. d. Cellulose, 1910, 10–20.

2 J. Chem. Ind. Japan., **15**, 730 (1912).

3 P. Klason: Beitrage z. Kent. d. Chem. Zusam. d. Fichtenholz, 1911, 34.

4 U. Einwirk. u. Wasser u. Natronlauge a. Baumwollcellulose, 1912, 21.

5 G. Schwalbe: Chem. d. Cellulose, 21–25.

6 G. Schwalbe: Chem. d. Cellulose, 1911, 19; H. Pringsheim: Die Polsach, 1919, 12

7 This memoirs, **5**, 308 (1922).

8 Chem. u. Struktur d. Pflanzen-zellmembran, 1914, 23; G. Schwalbe: Chem. d. Cell., 54, 396; P. Klason: Beitrag. z. Kennt d. Chem. Zusam. d. Fichtenholz, 1911, 29.

extract was estimated by means of the Fehling solution, and, as shown in Fig. 1., increased with temperature.

For comparison of the results obtained from Yezo-matsu and Todo-matsu, 5 grm. of each sample extracted with alcohol and dried, were digested with 70 c.c. water at 120–123° in a sealed tube for one hour, and the loss of weight of the sample and the reducing sugar-content in the water extract were found to be:

1·54 % loss of weight and 0·19 % sugar in Yezo-matsu.

1·65 % loss of weight and 0·29 % sugar in Todo-matsu.

Pentose in the water extract prepared from Yezo-matsu by heating with water at 145–148° for one hour, was determined by converting it into furfurol with hydrochloric acid by Tollens and Kruger's method.[1]

It amounted to 39·8 % of the reducing sugars.

4. HYDROLYSIS WITH DILUTE HYDROCHLORIC ACID.

Of the polysaccharides occurring in plant cell-walls, only pentosans and hexosans of which hemi-cellulose is composed were hydrolysed by digestion with dilute hydrochloric and sulphuric acids, into simple sugars.[2] Such digestion, however, evidently had some effect upon the yield of sugars, cellulose being partially attacked by the acids. Klason[3] has reported that when spruce is digested with mineral acid at high temperature, it yields 22–23% of reducing sugar which consists of 25% xylose, 6% mannose, 64 % unknown sugar and a trace of galactose.

25 grm. of Yezo-mutsu sawdust were heated with 300 c.c. one per-cent hydrochloric acid for one hour in autoclave. The acidic solution was filtered and neutralised with sodium carbonate, and the reducing sugar content was determined by the Fehling solution. This reducing sugar content showed a gradual increase with temperature as shown in Fig. 1.

To compare the sugar content in the acid extracts obtained from both Yezo-matsu and Todo-matsu, 5 grm. of each sample were digested with 70 cc. 1 % hydrochloric acid in a sealed tube at 148–152° for one

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1 Tollens: Handbuch der Kohlenhydrat III Aufl. s. 137; Browne: Handbook of Sugar Analysis p. 459.

2 G. Schwalbe: p. 54; M. Renker: p. 37; J. König and Rump: **23**, 73; Lunge: Chem. Tech. Unter. method., II, 453 (1904); E. Hägglund: D. Hydroly d. Zellulose u. d. Holzes, 430, 450; Kuhn: Zs. Physiol. Chem., **14**, 244 (1890).

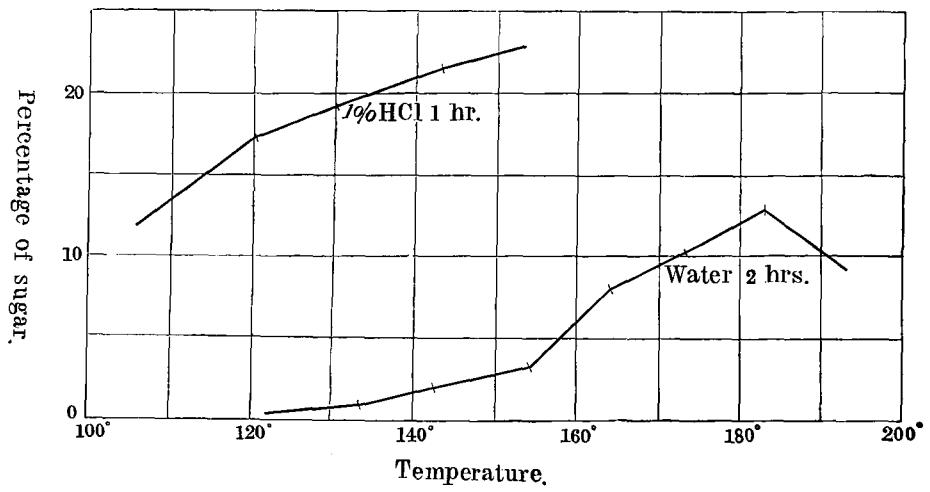
3 Papier Zeit., **35**, 2518 (1910); also compare Simonsen: Zs. angew. Chem., **111**, 195 (1898).

hour, and the following results were obtained:

37·7% (1·583 grm.) loss of weight and 21% sugar calculated as *d*-glucose in Yezomatsu.

54·9% (2·338 grm.) loss of weight and 22·8 % sugar in Todo-matsu.

To estimate quantitatively the simple sugars in the acid extract obtained from both Todo-matsu and Yezo-matsu by boiling sawdust, after extracted with alcohol and dried, with 3% sulphuric acid for three hours, the acid extract was neutralized with barium carbonate to remove sulphuric acid, and then treated with basic lead acetate solution. The solution freed from lead salts by means of hydrogen sulphide was concentrated unner reduced pressure to small volume. One part of the solution was used for the estimation of pentoses by Tollens and Krugers's method.[1] The amount of mannose in the solution was determined by precipitating it as mannophenylhydrazone as usual. The amount of galactose was determined by oxydising another part of the solution with nitric acid into mucic acid, which was weighed after being separated from other sugar acids formed simultaneously from other hexoses associated with mannose in the solution, by repeated precipitation with hydrochloric acid from their sodium salts solution. The results were as follows:



[1] Loc. cit.

	Yezo-matsu			Todo-matsu
	Water 145–148°, 1h.	1% HCl 146–152°, 1h.	3% H_2SO_4 boil 4h.	3% H_2SO_4 boil 4h.
Mannose	——	——	45·57%	43·04%
Galactose	——	——	9·67%	8·89%
Xylose	39·79%	16·03%	29·00%	24·59%
Pentose	48·87%		32·32%	27·04%

The proportion of the simple sugars in the acid extracts as seen from the above table, was quite different from that obtained by Klason.[1]

Referring to the investigation by E. Hägglund[2] on the compositions of the waste liquors from the sulphite process, the author's results seem to explain the real nature of the hemi-cellulose occuring in the wood. An experiment for alcoholic fermentation of the acid extract of the wood was undertaken with one main object to determine the fermentable sugar and consequently to ascertain whether the author's view on the composition of hemi-cellulose was correct.

The sawdust was boiled with 3% sulphuric acid for four hours, the acid extract was treated with basic lead acetate and the filtrate separated from lead salts was treated again with hydrogen sulphide to remove lead salts remaining in the solution. The filtrate from the precipitate of lead sulphide, amounting to 2000 c.c., contained 98 grm. of reducing sugar calculated as *d*-glucose. The solution, thus obtained, was found to ferment freely on adding bottom yeast obtained from the Nippon Brewery Co., Suita. The solution after being fermented and after the alcohol was distilled off, was treated with basic lead acetate. The quantity of sugar remaining in the solution without fermentation was estimated by means of the Fehling solution, to be equal to about 30% of the original sugar, amounting to 22 grm. of sugar.

5. PENTOSANS AND HEXOSANS.

It has already been mentioned that pentosan such as xylan occur in lignified cell-walls, either mixed or in combination with some hexosans such as mannan and galactan.

Pentosans in the samples were determined by Tollens and Kruger' method: the samples, extracted with alcohol and dried, were distilled

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1 Loc. cit.

2 D. Sulfitablauge u. ihre Verarbeitung auf Alkohol, 1921, 15, and also compare G. Schwalbe: Chem. d. Cellulose, 419.

after digesting with hydrochloric acid, and furfurol in the distillate was precipitated with phloroglucin. Pentosans were calculated from the weight of furfurol phloroglucide as usual. The weight remaining after subtracting pentosans from the total reducing sugar, was designated as hexosans. The results are shown in table.

6. MANNOSE, GALACTOSE AND XYLOSE.

It was tried to isolate these sugars from the acid extract in the crystalline state, by which to give strong support to the theory of the existence of mannan, galactan and xylan in the wood cell-wall.

Sawdust from Yezo-matsu was hydrolysed with 3% sulphuric acid, and the acidic solution, separated from insoluble residue, was treated with basic lead acetate solution to remove sulphuric acid and lignin yielded by hydrolytic decomposition of ligno-cellulose. An excess of lead salt in the solution was removed completely by means of hydrogen sulphide, and the filtrate from the lead sulphide was then concentrated under reduced pressure after being decolourised with norite. Mannose in the solution was precipitated with phenylhydrazine hydrochloride and sodium acetate, and the hydrazone thus obtained was decomposed with benzaldehyde into mannose and benzalphenylhydrazone. The mannose solution freed from the hydrazone, was concentrated under reduced pressure to a thick syrup and an equal volume of hot glacial acetic acid was added. Standing the solution after seeding with *d*-mannose crystals, in an ice-box for a few days, *d*-mannose was crystallised, which was filtered from the mother liquor. To purify, the crystals were dissolved in water and concentrated under reduced pressure to a thick syrup, left in the ice-box to crystallise. The crystals were dried in the vacuo and their physical and chemical properties were studied, with the following results:

It melts at 132–133°, and having an initial rotatory power $[\alpha]_D = \frac{-18 \times 100}{2{\cdot}88} = -10°{\cdot}4$ (after 7 minutes) which on standing, becoming constant when $[\alpha]_D = +13°{\cdot}9$.

0·1489 grm. the substance gave 0·216 grm. CO_2, 0·0916 grm. H_2O and 0·0002 grm. ash.

	Calc. for $C_6H_{12}O_6$.	Found.
Carbon	40·00	39·88
Hydrogen	6·66	6.89
Ash	——	0·13

Another part of the solution which contained *d*-mannose, *d*-galactose *l*-xylose but no lignin, was oxidised with nitric acid, and mucic acid formed by the oxydation was isolated as usual from other sugar acids. It melts at 212°, and showed optically inactive in its boric acid solution.

0·1031 grm. of the acid gave 0·1287 grm. CO_2, 0·048 grm. H_2O.

	Calc. for $C_6H_{10}O_8$.	Found.
Carbon	34·29	34.06
Hydrogen	4·76	5·19

l-Xylose in the solution was confirmed by transforming into xylonic acid by oxydation with bromine, which was identified as the double salt of cadomium bromide with cadomium xylonate[1]

1). 0·2768 grm. sub. gave 0·1515 grm. $CdSO_4$.
2). 0·2504 grm. sub. gave 0·1276 grm. AgBr.

	Calc. for $(C_5H_9O_6)_2Cd + CdBr_2 + 2H_2O$.	Found.
Cd.	29·86	29·50
Br.	21·32	21·01

7. LIGNIN.

In old trees the cell-wall usually become lignified partially, and the presence of ligno-cellulose in wood affects the yield of pulp and also the consumption of the sulphite liquor in the course of the cooking of the wood.

Various methods have been proposed for the determination of lignin in wood, and the author used in this experiment the methods of J. Kõnig,[2] Benedict and Bamberger.[3]

Sawdust extracted with alcohol and dried, was treated with 72% sulphuric acid at ordinary temperature according to the directions of Ost and Wilkennig,[4] where lignin only remains unaffected by the acid. Lignin insoluble in the acid was filtered in Gooch's crucible, washed with hot water and alcohol successively and then dried at 110° to constant weight. To confirm whether the substance insoluble in sulphuric acid, consisted of pure lignin, the methoxy group of the substance was estimated fol-

1 G. Bertrand, Bull. soc. chim., (3), **5**, 556 (1891)
2 Chem. u. struktur d. Pflanzen-Zell., 1914, 50.
3 Monat. Chem., **11**, 260 (1885).
4 Chem. Zeitung, **52**, 461 (1910).

lowing the Zeisel direction[1], using the apparatus modified by S. Zeisel and R. Fanto,[2] and the quantity of lignin was shown to be equal to 96% of the theoretical on the basis of the methoxy value.

0·1295 grm. of the sub. gave 0·299 grm. CO_2, 0·0572 grm. H_2O and 0·0029 grm. ash.

	Calc. for $C_{36}H_{40}O_{12}$.	$C_{38}H_{38}O_{12}$.	Found.
Carbon	65·06	66·47	64·40
Hydrogen	6·02	5·54	5·22
Methyl	5·88		5·08
Ash	——		2·24

Lignin content in the wood was also determined indirectly by estimating the methoxy value, following Benedikt and Bamberger's proposal,[3] and and the results were as shown in the table.

8. CELLULOSE.

Cellulose both in Yezo-matsu and Todo-matsu has already been determined by Morioka using Cross and Bevan's method. His results show fair agreement with the data obtained by the present author by the same method as seen in the table.

On the other hand, the author has treated the sawdust with dilute sulphuric acid and caustic potash solution successively, following Henneberg's directions,[4] and the cellulose content, thus obtained, is too large compared with others as shown in the table.

It is true that an absolutely accurate method of cellulose determiation as Renker[5] has already commented in his article, has not yet been devised. The method which has given the highest yield of pure cellulose, with ascertained minimum of change in the cellulose attending the process of isolation, so far as we can judge, is J. König's hydrogen peroxide method.[6]

To get a satisfactory result and to compare it with the other mentioned above, 3 grm. of air-dried sawdust after digesting with glycerol and sulphuric acid mixture, was treated with 120 cc. of 3% hydrogen peroxide and 10 c.c. of 24% ammonia solution.

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1 Monat. Chem., **6**, 989 (1885).

2 Zeitschrift. f. Anal. Chem., **42**, 549 (1903).

3 Monatsheft Chem. **15**, 509 (1894).

4 Lieb. Ann., **146**, 130 (1868).

5 U. Bestimmung. methoden d. Cellulose, 1910, 86.

6 Ibid., 73.

After 12 hours, it was treated with 10 c.c. of 30% hydrogen peroxide, warmed in a water bath and then the residue was dried at 110° to constant weight. The substance thus obtained consisting of cellulose, cutin and ash, was ignited, and weighed. The differenee in the weighings corresponds with the amount of cellulose with some cutin. The percentage of cellulose and cutin in the dry sample was as shown in the table.

The content of nitrogenous matter determined by the Kjeldahl method and of ash in the sample, are shown in the table.

		Yezo-matsu.	Todo-matsu.
Water		15·50%	14·85%
Ash		0·78%	1·17%
Protein N.		0·59%	0·55%
Alcohol soluble matter		3·10%	3·78%
Pentosans		9·46%	9·57%
Polysoccharides (cal. as *d*-glucose)		21·79%	22·83%
Cellulose, by	Henneberg's method	71·94%	68·90%
	Cross & Bevan's m.	56·97%	56·41%
	Konig's m.	52·30%	47·52%
Lignin, by	72% H_2SO_3	35·23%	34·15%
	Methoxy value	43·52%	46·17%

	Materials.	temp.	hour.	loss. %	sugar %
Yezo-matsu	5 grm. 60 c.c. H_2O	120°	1	1·54	0·19
	5 grm. 70 c.c. 1% HCl	148–151°	1	37·7	21·79
	4 grm. 40 c.c. 72% H_2SO_4	ord. temp.	1	64·77	44·20
Todo-matsu	5 grm. 60 c.c. H_2O	120°	1	1·65	0·29
	5 grm. 70 c.c. 1% HCl	148–151°	1	54·92	22·83
	4 grm. 40 c.c. 72% H_2SO_4	ord. temp.	1	65·85	44·95

9. SUMMARY.

The content of moisture, ash, nitrogenous matter, resinous matter, lignin, pentosans, hexosans and cellulose both in Yezo-matsu and Todo-matsu was determined.

2. Todo-matsu contains much more pentosan, hexosan and less cellulose than Yezo-matsu.

3. *d*-Mannose was isolated from the dilute mineral acid extract in

a crystalline state, and *d*-galactose and *l*-xylose were confirmed to exist in the extract by converting into mucic and xylonic acids respectively.

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