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On the Celluloses from Different Natural Sources

By

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I Introduction

Colourless non-nitrogenous substances obtained from the plant world insoluble in all simple solvents, generally but variably resistant to processes of oxidation and hydrolysis, are designated celluloses; they have usually the empirical constitution characteristic of the carbohydrate, i.e. $C_6H_{10}O_5$. These substances forming the characteristic component of the cell wall, are usually associated with lignin, pectic substance or hemicellulose in a state of compound¹ or adsorption².

As to the nature of cellulose, there are two different opinions among investigators. E. Heuser³ holds the opinion that cellulose isolated from wood and straw is chemically very similar to cellulose obtained from the seed hairs of the cotton plant. He reached this conclusion from his study of the chemical nature of acetyl derivatives of purified-cellulose and of their hydrolytic substances by the methods of Irvine, Ost and Wilkening. Heuser's hypothesis has been accepted by L. E. Wise and W. C. Russel¹, who confirmed that cotton cellulose

1. H. Wislicenus and M. Klinstück: *Kolloid Zeitschrift*, **6**, **17**, **87**, (1910). L. E. Wise: *Journ. Ind. and Eng. Chem.* **15**, 711 (1923). E. Heuser and A. Hang: *Z. angew. Chem.* **15**, 166 (1918).

2. E. Winterstein: *Z. physiol. Chem.* **17**, 381 (1893). E. Schultze and B. Tollens: *Ann. d. Chem.* **10**, 271 (1892). H. Schermann: *Journ. Am. Chem. Soc.* **19**, 300 (1897). B. Rasso and E. Dörr: *Journ. prak. Chem.* **108**, 113 (1924).

3. E. Heuser and A. Hang: *Z. angew. Chem.* **31**, 99, 166 (1918). E. Heuser and S. S. Aiyer: *Ibid.*, **37**, 27 (1924). E. Heuser and Bödeker: *Ibid.*, **34**, 361 (1921).

4. L. E. Wise and W. C. Russel: *Journ. Ind. and Eng. Chem.* **14**, 285 (1922); **15**, 815 (1923).

and cellulose from the sulphite pulp obtained from spruce wood and purified with 17.5% caustic soda solution are identical substances by transforming them into cellobiose octacetate. I. C. Irvine and E. L. Hirst¹ have also shown that a pure cellulose from esparto pulp is chemically identical with cotton cellulose.

Similar statements as to the identity of all celluloses from plants are also made by R. W. Rigby² in his chemical study of flax-cellulose, and by R. O. Herzog & W. Jancke in the report on their investigation of the X-ray diffraction of cotton cellulose, ramie cellulose and wood pulp³.

It is a question whether the formation of cellobiose octacetate or glucose is a sufficient proof of the chemical identity of all celluloses. As a matter of fact, the lichenin from Iceland moss (*Cetraria islandica*) gives a triacetate having a rotatory power $[\alpha]_D^{19} = -23.8^\circ$ very similar to cellulose triacetate and also cellobiose octacetate. Lichenin, nevertheless, is soluble in dilute alkali and gives a colloidal solution with boiling water, and this readily hydrolyzed to glucose by the enzyme lichenase⁴.

Cross and Bevan⁵ thought of celluloses from different sources as chemically related but by no means identical substances, and the same opinions was also held by D. Krüger⁶.

Hawley & Wise studying the identity of celluloses have concluded on page 147 of their book "The Chemistry of Wood (1926)" that "accumulating experimental data serve to show that the α -cellulose from wood and normal cellulose from cotton probably contain the same cellulose unit. The fact that α -cellulose still retains small quantities of furfural-yielding material does not militate against this hypothesis, despite the criticisms of some recent investigators. In the opinion of the writers, the question is still an open one with preponderating experimental evidence in favor of the chemical identity of the larger part of the substance of α -cellulose of wood with α -cellulose isolated from cotton."

1. J. C. Irvine and L. E. Hirst: Journ. Chem. Soc. **121**, 1585 (1922); **125**, 15 (1924).
2. R. W. Rigby: Journ. Am. Chem. Soc. **50**, 3364 (1928).
3. R. O. Herzog & W. Jancke: Ber. D. Chem. Ges., **53**, 2162 (1920).
4. P. Karrer and Joos: Helv. chim. Acta, **6**, 800 (1923). P. Karrer and K. Nishida: *Ibid.*, **7**, 363 (1924). P. Karrer and M. Staub: *Ibid.*, **7**, 928 (1924).
5. C. F. Cross and J. C. Bevan: Cellulose. (1898). 219
6. D. Krüger: Pap. Fabr. **23**, 767 (1925).

II Experimental Materials and Methods for Preparation of Celluloses.

The writer hesitates to accept the hypothesis that the celluloses from different sources are composed of the same chemical units in the same aggregation or combining way without experiments on celluloses from different sources, and has therefore engaged in the present investigation. The sources of the celluloses studied were wood pulp from Todomatsu (*Abies saccharinensis*, Masters), grown at Naibuchi, Karafuto and prepared by cooking with sulphite liquor on a manufacturing scale at the Hokuetsu Seishi Co., Nagaoka; kaoliang culms (*Andropogon Sorghum*, Broth) grown in Manchuria; and the crude fibres from ramie or China grass (*Boehmeria nivea*, Hook & Arn.) grown in Taihoku, Formosa. The methods which were chosen in the preparation of bleached celluloses from these raw materials, were Cross and Bevan's¹ method and the chlorine dioxide method proposed by C. Schmidt², which are recommended by chemists as the most reliable methods of getting cellulose in a pure state without any destructive action on it.

III Comparative Study of the Crude Cellulose Fibers.

The raw materials used for the preparation of bleached celluloses were analysed, and the moisture content ascertained by drying to a

Table I

	Method	Wood	Ramie	Kaoliang
Water-content		7.5	7.0	11.0
Ash- „		0.4	3.1	4.5
Cellulose- „	Cross and Bevan's —	88.3	90.2	47.2
Water extract	boiling for 3 hours.	1.8	2.2	6.2
Alcohol- „	boiling for 8 hours.	0.8	3.3	6.1
Ether- „	boiling for 8 hours.	1.1	0.31	0.61
Total nitrogen	Kjehldahl's —	0.01	0.56	0.32
Methyl value	Zeisel's —	0.38	0.23	1.69
Lignin	from CH ₃ -Value	7.3	4.3	31.9
	by H ₂ SO ₄ method	7.3	6.1	24.7
Pentosan	Kroebe-Tollens' —	4.6	5.8	24.6

1. C. F. Cross and E. J. Bevan: Journ. Chem. Soc. **55**, 199 (1907).

2. E. Schmidt and E. Graumann: Ber. D. Chem. Ges. **54**, 1862 (1921); E. Heuser and O. Merlau: Cellulosechemie **4**, 101 (1923).

constant weight at 105°C. The ash and cellulose content was determined by Cross-Bevan's method; water-soluble matter and alcohol- and ether-soluble matters were extracted by boiling for 8 hours with these solvents; total nitrogen was measured by Kjehldahl's method, the methoxyl-group by Zeisel's method, lignin by the direct and indirect methods, and pentosan by Kroebe-Tollens' method, and the results were as shown in Table I.

As well be seen in the foregoing table, the wood pulp differs in composition from the ramie fibre-substance which was assumed to be composed mostly of α -cellulose, and the second characteristic ingredient of kaoliang fibre is a furfural-yielding complex which appears to be hemicellulose composed mostly of xylan but not of an oxy-cellulose.

IV The Comparative Study of the Bleached Celluloses.

1 *The chemical constituents and properties*

The impurities or associated substances which occur in cellulose-fibres together with α -cellulose, shown in Table I, might have some influence on the physical and chemical properties of α -cellulose, and therefore of these various cellulose fibers, the specific viscosity in Schweizer's solution, absorption of a direct or basic dyestuff, and the action of alkali-solutions were investigated.

The viscosity of 1% cuprammonium solutions of the various cellulose fibers was determined at 20°C, following the directions given by W. H. Gibson¹, and the results are shown in the following table with the content of α -cellulose and pentosan in comparison, and these substances were regarded to connected intimately with the viscosity of the fibers.

The experimental results indicate that kaoliang gives products the viscosity of which is about half that of ramie. There is also a marked difference in the viscosity obtained with bleached celluloses from ramie by different method, due chiefly to the content of α -cellulose and the transformation of it produced during the process of bleaching and the latter substance will indicate its presence by its effect on the copper-value.

The differentiation in the chemical and physical properties of these

1. W. H. Gibson: Journ. Chem. Soc. 117, 479 (1920); M. Nakano: Journ. Chem. Ind. (Japan), 25, 899 (1922).

Table II

	Cross & Bevan's method (C & B)			Chlorine dioxide method (ClO ₂)		
	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Sp. Vis.	5.80	7.10	3.73	5.33	12.16	5.02
α -Cellulose-content	82.9	95.8	76.6	84.9	96.5	73.2
Corr. Hydrolysis V.	3.5	2.75	14.52	2.88	2.96	19.09
Cu-value	3.25	1.53	6.25	2.87	0.89	1.59
β -Cellulose-content	6.03	2.63	15.70	3.45	1.09	7.11
Pentosans	4.06	0.33	11.95	4.17	0.53	21.47

bleached fibers may be attributed to the occurrence of the secondary characteristic substances associated with α -cellulose, mentioned in the table. The treatment of cellulose fibers with a 17.5% solution of caustic soda, or the so-called "mercerization" of fibers, causes pentosan and other furfural-yielding substances or β -cellulose to dissolve away from the cellulose proper, and the undissolved portion of the fibers, being composed mostly of α -cellulose, should remain in proportion with the baryta resistance value, as will be seen in the experimental results. In wood pulp, however, there is seen a great difference between α -cellulose-content and the baryta resistance value, due to the occurrence of lignin or some reducing substances which are affected by the baryta treatment.

The occurrence of reducing substances in cellulose fibers is indicated by the copper value which is marked in bleached celluloses obtained from wood and kaoliang, especially those prepared by Cross-Bevan's method; the copper value of wood cellulose is due chiefly to lignin and that of the kaoliang to a substance other than lignin such as oxycellulose, since the chlorine method proposed by Cross-Bevan is admitted by numerous experiments to produce a reducible substance by oxidation from α -cellulose. Hydrolysis value, which is taken as a measure of the content of hemicellulose and hydrocellulose, is greater in kaoliang than in wood and ramie.

The dyeing capacity of cellulose fibres¹ is supposed to relate not only to an active group in the molecule of fibre-substances but also to their physical state. For comparison of the dyeing capacity of

1. C. G. Schwalbe: Die Chem. d. Zell. (Berlin) (1911), 93. E. Knecht and E. Hibbert: New Reduction methods in Volumetric analysis (1925) 62, 100.

these bleached celluloses, benzopurpurin-4B, and methylene blue were used in the experiments.

The results indicate that the capacity for dyeing by the direct dye is proportional to the α -cellulose-content of the fibres, while they show some marked difference in their behaviour towards the basic dye.

2 Comparative study of the action of caustic alkali on bleached celluloses

1 Absorption of Alkali¹

Although there has been much dispute as to whether caustic soda forms a definite compound with cellulose, the absorption capacity of bleached celluloses may be taken as a measure of the difference between the constituents of bleached celluloses in their chemical nature.

When air-dry, bleached celluloses were dipped in a caustic soda solution for a time and then separated. The filtered solution and the alkali remaining in the celluloses of wood and kaoliang, as will be seen in the experimental results, were found to agree with the formula $(C_6H_{10}O_5)_2 : NaOH$, a compound which by many previous investigators have been stated is given rise to by this treatment, while the absorption of sodium hydroxide by ramie-cellulose corresponds to a molecular ratio of $(C_6H_{10}O_5)_2 : 2NaOH$. Cotton cellulose gave the same result with regard to alkali-absorption as ramie cellulose in contact with a conc. solution of sodium hydroxide.

According to Vieweg², the amount of alkali absorbed by cotton-cellulose, which depends on the concentration of the alkali solution, corresponds to a molecular ratio of $(C_6H_{10}O_5)_2 : NaOH$, which agrees with an absorption of 13% of alkali by the cellulose and at higher concentrations with an absorption of 24% of sodium hydroxide, which corresponds to a molecular ratio of $(C_6H_{10}O_5)_2 : 2NaOH$.

The affinity of celluloses for alkali, which is said to be proportional to the colloidal activity produced by moisture and other reagents and seems to have some connection with the absorption of dyestuffs as already mentioned, and accordingly the difference between bleached celluloses in their affinity for alkali or dyestuffs, in the present case,

1. G. W. Blanco: *J. Ind. and Eng. Chem.* **20**, 926 (1928). W. von Neuenstein: *Sonderheft d. Kolloid-Zeitschrift.* **43**, (3) 241 (1928).

2. *Ber. D. Chem. Ges.*, **40**, 3876 (1907); **41**, 3269 (1908).

may be explained by the difference in the physical state of the surface of the celluloses.

2 Action of Caustic Soda on Bleached Celluloses¹

The effect of the treatment of the fibers with strong caustic soda solution, which is called "mercerization" of celluloses, is to remove β -cellulose, some hexosans other than cellulose and pentosans associated with α -cellulose, and to produce some physical and chemical changes on the surface of the fibers, such as shrinkage. The portion of the bleached fibers undissolved by the strong solution of sodium hydroxide was, therefore, employed to decide the identity of the wood- and kaoliang-celluloses with ramie cellulose by comparing the physical and chemical properties.

The values of the water-content for various gelatinized celluloses, as will be seen in the table, are higher, in general, than those of the bleached celluloses, due to the presence of hydrocellulose and also to the colloidal activity of the surface produced by the shrinkage caused by the contact with alkali. Of the three celluloses, the water-content of ramie-cellulose is highest, and the water content in both ramie and kaoliang maintains constant value irrespective of the time of contact with alkali, while the wood-cellulose shows irregularity in the water-content depending on the time of contact.

The wood and ramie fibers which contain equally 96 per cent of α -cellulose determined by Cross-Bevan's method, show a similar hydrolysis value but a different copper value, as indicated in the experimental results.

It was a well known fact that gelatinized celluloses differ from hydrocelluloses in having a lower copper value, and in our experiments, the order is kaoliang > wood > ramie, with regard to the copper value, which is inversely proportional to the water-content. Schwalbe² suggests that this is due to the presence of oxy-cellulose.

Although the α -cellulose-content is invariably increased in kaoliang fibre by mercerization, the mercerized kaoliang cellulose remains rich in the furfural-yielding substances such as pentosans and oxy-celluloses.

The celluloses mercerized with caustic soda solution are, in general, characterized by their high content of α -cellulose and hydrocellulose,

1. C. W. Blanco: *J. Ind. & Eng. Chem.*, **20**, 926 (1928).

2. *Ber. D. Chem. Ges.*, **40** 4523 (1907).

and the ramie cellulose is distinguished from the other ones by its high content of oxy-cellulose, wood cellulose by its high lignin content as indicated by the reducing action, and kaoliang by the furfural-yielding substances.

Will these mercerized celluloses be characterized by associated substances which behave differently towards dyestuffs, or will the difference be shown by the capillary phenomenon?

The specific viscosity of these three celluloses in a standard Schweizer's solution was measured at 20°C, and differs, as will be seen in the table, from that of the bleached celluloses. The mercerized celluloses from wood, kaoliang and ramie arrange themselves in that order with respect to the specific viscosity. It is interesting to note that these celluloses when in contact with alkali for a short time show a different specific viscosity, but when mercerized for 70 hours, they retain almost the same specific viscosity.

The impurities such as oxy-cellulose which occurs in these celluloses may have some effect on the nature of α -cellulose, especially on its capacity for absorbing basic dyes. As will be seen from the experimental results, the order of the celluloses with regard to their absorption of direct dyes, is ramie > kaoliang > wood, while with regard to the strength of their affinity for basic dyes, the order is kaoliang > wood > ramie.

3 Comparative study of the action of superheated water on bleached celluloses

Gelatinized celluloses may be produced through mechanical comminution in the presence of water, and the action of superheated water¹ is regarded as an agency comparable to that at work in nature. The action of superheated water on bleached celluloses was therefore investigated in order to get some idea of the difference among α -celluloses obtained from the different fibers.

In the experiment, air-dry bleached celluloses were heated in an autoclave with water at 150°C for 5, 10 and 15 hours, and the aqueous solution was separated by filtration from the insoluble part.

1. S. Komatsu & C. Tanaka: *The Sexagint.* 1 (1927) and also to refer: Mulder: *Journ. prak. Chem.* 63, 565 (1855); Hoppe-Seyler: *Ber. D. Chem. Ges.* 4, 15 (1880); C. G. Schwalbe: *Chem. News.* 265, 281; M. Robinoff: *Ueber die Einwirkung von Wasser und Natronlauge auf Baumwolle.* 1912; A. E. Cashmore: *Journ. Chem. Soc.* 718 (1927); E. Berl and A. Schmidt: *Ann. d. Chem.* 461, 192 (1928).

The filtrate separated from the insoluble part, was light yellow in colour; the content of solid matter, reducing substance and furfural-yielding substance were estimated by the usual methods.

The solid matter in the aqueous solutions is largest amount in the case of kaoliang, and is the same in wood and ramie. The chief constituent of the solid matter is a reducing substance and not a furfural-yielding substance, as is indicated in the experimental results.

The portion of the celluloses undissolved by the superheated water, was separated from the solution and washed with water, and was found to consist mostly of α -cellulose. It was analysed and the results were compared with those obtained in the case of the mercerized celluloses.

The water-content of the insoluble residues is not the same in the three celluloses, the copper value being almost in inverse proportion to it. Such a numerical relation between the water-content and the copper value of the insoluble residues is never met with in celluloses mercerized with caustic soda.

The most marked difference noticed in these insoluble residues from three bleached fibers is in the content of α -cellulose and furfural yielding substance, and the same is also met within the alkali-mercerized celluloses.

The alkali-mercerized celluloses show a greater similarity in the specific viscosity of their cuproammonical solutions to the celluloses treated by superheated water, owing to the high content of α -cellulose in each sample and also to the diminution in the substances associated with α -celluloses in the bleached fibers.

V Comparative study of the α -Celluloses

1 *The preparation and properties of α -celluloses*

The bleached celluloses and the mercerized celluloses from three different sources are concluded from the experimental results to be different from each other in their physical and chemical properties, and the difference among these celluloses, which is shown in the viscosity of their cuproammonium solutions, their alkali-absorption and the effect on them of the action of superheated water, is dependent in part at least upon the difference in the chemical composition of these celluloses. The presence of lignin or hemicellulose in the cellulose fibers depends chiefly upon the methods by which the celluloses are

prepared and purified, and the occurrence in the celluloses of some degradation products such as oxycellulose may be attributed to the chemical nature of the α -celluloses, since, in order that the fibers examined should be as nearly comparable with each other as possible, an uniform procedure was adopted in the preparation of the bleached celluloses and in their treatment.

For the purpose of the present study, pure α -cellulose is required.

In the preparation of α -cellulose from the three bleached celluloses, some ingredients contaminating it and having some influence on its properties should be removed, and the process by which the pure substance is obtained, should be modified according to the materials, which are supposed to differ from each other in the minor characteristics of the non-cellulose portion.

For the elimination of the non-cellulose constituents from bleached ramie cellulose and wood cellulose, they were treated with 12.5% cold caustic soda solution, and then with 4% caustic soda solution for 30 minutes, washed with water acidified with dilute acetic acid, washed again with water and dried. By this means, α -cellulose of high purity was obtained with 5.9% loss of weight. Bleached kaoliang cellulose was treated with 4%, 12.5% and 17.5% caustic soda solution in succession to eliminate the non-cellulose components, and the yield of α -cellulose was about 84%. By this treatment, hemicellulose and other furfural-yielding substances which constitute the minor characteristics of kaoliang fibres, were hydrolysed and converted into soluble forms in the alkali solutions.

The purity of these samples¹, as will be seen from the content of water, ash, and α -cellulose shown in the table, is about the same in each sample, and they show similar behavior towards dye stuffs and strong alkali solutions, and also similar results with regard to the specific viscosity and the specific rotatory power of Schweizer's solution and the hydrolytic velocity by strong hydrochloric acid². Although the furfural-yielding complex is comparatively great in the kaoliang-cellulose, this may have no marked influence upon the chemical characters of the α -cellulose, and in fact, the three α -celluloses treated from 1 to 3 hours with 18 per cent sodium hydroxide solution, contained the same amount of NaOH (average 0.15 mol per cent).

1. C. G. Schwalbe: *Pap. Fabr.* **24**, 769 (1926); A. B. Corey and H. Le B. Gray: *Ind. & Eng. Chem.* **15**, 748 (1923); **16**, 853 (1924).

2. R. Willstätter & Zeichmeister: *Ber. D. Chem. Ges.* **46**, 2401 (1913).

This value is approximately that calculated for $(C_6H_{10}O_5)_2NaOH$ (being 1 : 0.12 in mols per cent ratio). The mercerized α -celluloses, however, formed by treating the α -celluloses with 17.5 per cent caustic soda at 20°C. for 2 hours, were found to differ from each other in the content of the furfural-yielding complex and this content, as may be inferred from the experimental results shown in the table, is independent of the time of treatment (5~70 hours). It was noted that the kaoliang α -cellulose, which consists of 99% of α -cellulose, is especially marked in its resistance to the action of oxidation and hydrolytic agents.

The specific viscosity of α -celluloses was decreased by mercerization, and on the contrary, the capacity for absorbing direct dye was increased.

Table III

	Yield of furfural (%)					
	Wood		Ramie		Kaoliang	
	(C & B)	ClO ₂	(C & B)	ClO ₂	(C & B)	ClO ₂
α -Cellulose	0.13	0.34	0.10	0.29	1.42	1.78
Mercerized α -cellulose	0.42	0.50	0.45	0.45	1.15	1.20

These facts indicate that the α -celluloses obtained from the different sources have undoubtedly suffered in a different degree some changes during the mercerization. A proof for the view that α -celluloses undergo partly a chemical change by mercerization is noticed in the result of their treatment by means of superheated water.

By the action on α -celluloses of water heated to 150°C in a closed vessel, one part of the substances was transformed into water soluble substances which yielded furfural on distillation with strong hydrochloric acid and reduced Fehling's solution. The insoluble part separated from the aqueous solution was examined so as to find the content of water, ash and α -cellulose, the furfural yield, the copper value, the hydrolysis value, the specific viscosity, the dye absorption, and also the specific rotation in Schweizer's solution, the velocity of hydrolysis with conc. hydrochloric acid, and the alkali absorption, and the results were compared with each other and with those obtained from the original samples and the mercerized celluloses.

When the properties of those celluloses treated with superheated water are compared with those of the original samples the special

Table IV

Wood	α -Cellulose		Mercerized		Acted with H ₂ O	
	(C & B)	ClO ₂	(C & B)	ClO ₂	(C & B)	ClO ₂
H ₂ O	6.7	5.8	7.2	7.5	7.5	8.8
α -Cellulose	99.3	99.5	99.5	99.6	95.1	98.0
Furfural	0.13	0.34	0.4	0.5	0.86	1.0
Cu-value	0.86	0.61	0.6	0.4	2.0	1.2
Hydrolysis Value	5.4	5.7	6.5	5.8	5.2	5.4
Sp. V.	6.0	16.0	4.0	6.0	2.8	4.1
Direct dye	0.99	1.1	2.5	2.6	2.2	2.6
Basic dye	1.1	1.1	1.0	1.0	0.6	0.5
Ramie						
H ₂ O	6.2	6.1	6.2	7.7	10.9	9.7
α -Cellulose	99.9	99.9	99.6	99.9	96.4	99.4
Furfural	0.10	0.29	0.5	0.47	0.8	0.8
Cu-value	0.98	0.64	0.74	0.23	1.58	0.75
Hydrolysis Value	5.6	4.6	6.8	5.4	5.5	4.9
Sp. V.	6.1	23.3	4.7	14.5	2.8	8.7
Direct dye	0.5	0.5	2.0	1.9	1.1	1.2
Basic dye	0.5	1.4	0.2	0.3	0.7	0.7
Kaoliang						
H ₂ O	6.02	6.40	6.8	8	7.3	6.8
α -Cellulose	99.53	99.71	72.5	95.6	98	99
Furfural	1.42	1.78	1.9	2.5	1.1	1.3
Cu-value	0.69	0.44	5.0	2.4	0.5	0.4
Hydrolysis Value	5.57	6.27	2.8	5.1	6	6
Sp. V.	13.20	24.1	1.6	3.7	4	6
Direct dye	1.01	0.81	1.9	2.4	2.3	2.4
Basic dye	1.11	1.11	0.3	0.4	1	1

features are the so-called α -cellulose-content, the specific viscosity and capacity for absorption of direct dye.

The increased absorptive capacity of the α -celluloses treated with superheated water for direct dyes may be attributed to physical causes resulting from the swelling of the surface of the celluloses by the treatment, and the lowering of the specific viscosity in the Schweizer's

solution is probably caused by some chemical changes occurring in the molecule of α -cellulose¹.

The α -cellulose-content is decreased markedly when the samples are treated with superheated water, and the fact is explained by assuming that α -cellulose behaves differently toward superheated water and caustic soda solution.

The main difference among the α -celluloses from wood pulp, ramie and kaoliang is in the resistance to hydrolysis and oxidation, which seems independent of the presence of the furfural-yielding residue left in the pulps even after severe cooking and bleaching treatment, as will be seen from the table. A small quantity of the furfural-yielding substances remains in the kaoliang pulp, unaffected by bleaching, compared to which the loss of α -cellulose owing to the action of superheated water is too great, and kaoliang cellulose especially is greatly affected by this treatment to convert it into a soluble substance.

Thus, α -celluloses from three different sources show quite different behavior toward superheated water notwithstanding that they contain the same quantity of the major characteristic constitution of α -cellulose (99.5—99.8%).

The attempt to prove that purified celluloses therefore, are chemically identical, fails since α -celluloses differ in their resistance against the action of superheated water, though they have been proved identical in regard to their ultimate composition and their behavior towards solvents and dye stuffs as previously described.

Is this difference in the chemical reaction of α -celluloses to superheated water to be attributed to a difference in the mode of aggregation or combining way of the chemical unit $C_6H_{10}O_5$ in the molecule or to a difference in the configuration of the atomic groups in the unit?

2 Comparative Study of Regenerated α -Celluloses and α -Cellulose Derivatives

1 Comparison of the α -celluloses generated from the Schweizer's solution of α -celluloses

In the previous chapter, the writer has pointed out that α -cellulose isolated from Todomatsu most closely approaches ramie α -cellulose in

1. Refer: M. Robinoff: Über die Einwirkung von Wasser und Natronlauge auf Baumwolle, 1912.

its chemical properties, while that from kaoliang is different from the latter, and that the fact that kaoliang α -cellulose still retains small quantities of furfural-yielding material would not be accounted an irrefutable argument against the hypothesis of the chemical identity of celluloses from various sources.

But the questionable identity of the mode of aggregation of the chemical unit $C_6H_{10}O_5$ in the molecule of α -celluloses remains as an explanation of the difference between the celluloses in their chemical behavior towards superheated water.

In this chapter, therefore, α -celluloses dissolved in a cuproammonium solution¹, containing 12.3 gms. of copper and 153 gms. of ammonia in 1 litre, and then precipitated by dilute sulphuric acid from the solution, and the chemical study of the regenerated α -celluloses was carried out, from which some idea of the mode of aggregation of the chemical unit will be gained.

The regenerated α -celluloses all show a smaller value in rotatory power than the original α -celluloses², and this fact may be partly explained by assuming the accumulation of hydrate- and oxy-celluloses in the precipitate, formed at the expense of the α -cellulose in the cuproammonium solution; and such a view harmonizes with the fact that copper value, hydrolysis value and dye-absorption capacity are high in the regenerated celluloses.

All the regenerated α -celluloses show similar results for the hydrolysis value, specific viscosity, dye-absorption capacity, velocity of hydrolysis with mineral acids and rotatory power in the Schweizer's solution, but the furfural-yielding substance is still retained in some measurable quantity (about 2%) in kaoliang cellulose.

By subjecting the regenerated α -celluloses to the action of superheated water, 2.5% of the weight of the kaoliang cellulose was removed as a water-soluble substance composed partly of a compound which reduces the Fehling's solution.

These α -celluloses regenerated from their Schweizer's solutions, while they closely approach to each other in their chemical and physical

1. C. F. Cross and E. J. Bevan: Cellulose (1895), 57; G. Bumcke and R. Wollfenstein: Ber. D. Chem. Ges., **32**, 2501 (1899); E. Heuser: Lehrbuch der Cellulosechemie, 176 (1927); K. Hess and E. Messmer: Ber. D. Chem. Ges., **54**, 834 (1921); Ann. d. Chem., **435**, 1 (1923).

2. A. Levallois: Compt. rend. **99**, 1122 (1884); **100**, 456 (1885); K. Hess and E. Messmer and E. Jagla: Ber. D. Chem. Ges., **55**, 2432 (1922); K. Hess & E. Messmer: Ann. d. Chem., **435**, 1 (1923).

properties, behave toward superheated water in a different manner, and this fact serves to show that the mode of aggregation of the chemical unit $C_6H_{11}O_5$ in the kaoliang cellulose molecule is not the same as that in the α -cellulose from wood and ramie nor as that in normal cellulose from cotton.

2 Triacetyl α -Celluloses¹

In order to see the chemical nature of the unit $C_6H_{11}O_5$ of pure α -celluloses, triacetyl- α -celluloses were prepared from the α -celluloses by the method proposed by Burnet, and separated into fractions by means of acetone and glacial acetic acid—the acetone-soluble fraction and the acetone-insoluble fraction—and the latter was again divided into two parts—the glacial acetic acid soluble and insoluble fractions. The yield of all of these three fractions, m.p. rotatory power in chloroform solution, and their molecular weight in acetic acid were estimated, and the results were compared with each other. The properties far studied were noticed to be identical, to a great extent, with those of all the α -celluloses from different sources.

Tables V

	(C & B)			(ClO ₂)		
	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
M. W.	299	324	302	342	352	325
Yield %	98	99	99	99	98	99
Acetone sol.	8	7	8	5	6	5
Insol.	90	92	91	93	92	94
Acetone sol. $[\alpha]_D$	-11°	-11°	-13°	-11°	-10°	-11°
Insol. $[\alpha]_D$	-23°	-23°	-23°	-23°	-22°	-22°
Glacial acetic acid sol.	14%	20	6	20	22	10
M. p.	250-7°	248-59°	252-8°	251-8°	249-58°	253-9°
$[\alpha]_D^{21}$	-23°	-23°	-22°	-23°	-23°	-22°
M. W.	299	324	302	342	353	532

3 The α -celluloses generated from acetyl celluloses

α -celluloses regenerated from acetyl- α -celluloses by saponification with alcoholic potash, show the following properties.

1. K. Hess und Mitarbeiter: Ann. d. Chem., **448**, 99 (1926); Ibid., **450**, 33 (1926); Ibid., **55**, 81 (1927).

Table VI

Acetone soluble acetyl celluloses

	Wood		Ramie		Kaoliang	
	C & B	ClO ₂	C & B	ClO ₂	C & B	ClO ₂
Yield of α -cellulose	83	70	77	76	79	86
$[\alpha]_{\text{blue}}^{20}$	-449°	-619°	-698°	-453°	-572°	-417°

Acetone insoluble & chloroform soluble acetyl- α -cellulose

Yield of α -cellulose	99	99	99	99	99	99
$[\alpha]_{\text{blue}}^{20}$	-945°	-907°	-950°	-904°	-1050°	-974°

α -celluloses from the different natural sources, prepared from their acetyl derivatives by saponification are the same in their properties so far as they have been studied, but they show a different optical rotatory power according to the fractions of the acetyl-celluloses from which the α -celluloses are derived.

These experimental facts are favorable to the idea that the unit $C_6H_{10}O_5$ in the α -cellulose molecule is chemically identical in all the α -celluloses.

The experimental data accumulated in the previous chapters, for the consideration of the general characters of celluloses, justify the conclusion that the α -celluloses from ramie, Todomatsu and kaoliang probably do not contain the cellulose unit in the same state of aggregation. The characters considered as a whole are in favor of the view that the α -cellulose isolated from ramie is made up of a group or unit more resistant and the greater part of the α -cellulose isolated from kaoliang of a group less resistant to the action of oxidation and of superheated water.

The fact that α -cellulose from kaoliang still contains small quantities of furfural-yielding substance is not accounted by the writer as an important argument against the hypothesis that the α -celluloses isolated from different natural substances are chemically identical.

Preparation of Bleached Celluloses from Three Forms of Raw Material

A. By Cross-Bevan's Method

100 gms. of air-dried sample was placed in 2 litres of 1% caustic soda solution and kept boiling for 30 minutes, when it was filtered and washed with water. The water was then pressed out and dry chlorine gas passed over it for 30 minutes, after which it was again washed with water and then placed in 2 litres of 2% sodium sulphite solution and 250 c.c. of 1% caustic soda solution and kept boiling for 5 minutes. It was then filtered, and washed with water. This process was repeated three times, and the bleached cellulose was dried at 30°C to a constant weight.

B. By the Chlorine dioxide Method

500 gms. of air-dried sample was placed in a large cylinder, the soluble matter having been previously extracted with 1% caustic soda solution, and 3 litres of 0.6—0.8% chlorine-dioxide solution were added. After standing for 12 hours at ordinary temperature, the solution was decanted out, and the residue was washed with water, and then placed in 10 liters of 2% sodium sulphite solution to which 1250 c.c. of 1% caustic soda was added, and boiled for 5 minutes. It was then filtered and washed with water. The process was repeated 3 times and the bleached cellulose was dried at 30°C in a current of dry air to a constant weight.

The yield of the bleached celluloses was as follows:

Table VII

Cross and Bevan			Chlorine dioxide		
Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
87.0	78.2	42.7	92.0	79.4	47.6

The yield of the bleached celluloses depends largely on the α -cellulose-content of the raw materials, and partly on the methods employed in their preparation.

The analytical results of these bleached samples are given in the following table (Tab. VIII).

Table VIII

	Cross and Bevan			Chlorine dioxide		
	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Water-content	7.48	9.08	9.78	5.74	11.78	7.63
Ash- „	0.18	0.08	1.48	0.19	0.18	0.72
α -Cellulose- „ ¹⁾	82.94	95.79	76.64	84.93	96.47	73.18
β -Cellulose „ ¹⁾	6.03	2.63	15.70	3.45	1.09	7.11
Barytaresistance ²⁾ Value	81.88	93.37	75.34	83.53	94.99	72.87
Copper Value ³⁾	3.29	1.57	6.32	2.92	0.93	1.63
Cellulose Value ⁴⁾	0.048	0.04	0.07	0.05	0.04	0.04
Hydrolysis „ ⁵⁾	6.79	4.32	20.84	5.78	3.87	20.70
Corr. Copper Value ⁶⁾	3.24	1.35	6.25	2.87	0.89	1.59
Corr. Hydrolysis Value ⁵⁾	3.50	2.75	14.52	2.88	2.96	19.09
Furfural-yield ⁶⁾	2.53	0.19	7.02	2.45	0.31	12.81
Pentosans ⁶⁾	4.06	0.33	11.95	4.17	0.53	21.47
Water-soluble matter ⁸⁾	0.54	0.39	0.25	0.65	0.27	0.30
Alcohol-soluble matter ⁹⁾	0.73	0.54	0.61	0.73	0.57	0.73
Ether-soluble- matter ¹⁰⁾	0.15	0.25	0.50	0.33	0.15	0.35
Lignin ⁷⁾	0.34	trace	—	0.28	trace	—

Lignin-Content: This was determined by a calculation based on the methoxyl value as estimated by the method of Benedikt and Bamberger, and also by treating the samples with conc. sulphuric acid

1. C. G. Schwalbe: Die Chem. d. Zellulose (1911) s. 637.
- „ „ und R. Sieber: Die Chemische Betriebskontrolle in der Zellstoff u. Pap. Ind (1922). s. 221.
2. „ „ und H. Wenzl: Zellstoff u. Pap. 11, 75 (1922).
3. „ „ und R. Sieber: Die Chemische Betriebskontrolle in der Zellstoff u. Pap. Ind. (1922), s. 230.
4. „ „ : Die Chem. d. Zellulose (1911), s. 634.
5. „ „ : „ „ „ „ „ „ 635.
6. „ „ : Zeitschr. f. angew. Chem., 32, 229 (1919).
7. König u. Rump: Zeitschr. für Untersuchung der Nahrungsmittel 28, 184 (1914); Ost u. Wilkening: Chem. Ztg., 34, 461 (1910).
- 8, 9, 10. A. W. Schorger: Chem. of Cellulose and Wood (1926) s. 506.

according to the directions of König.

Pentosan: The content of pentosan was estimated as usual by Tollens & Krüger's method.

α -Cellulose: The portion of the cellulose fibers undissolved by a 17.5 per cent solution of sodium hydroxide was taken as α -cellulose.

β -Cellulose: The precipitate formed on acidifying the alkaline filtrate from the α -cellulose was taken as β -cellulose.

Baryta Resistance Value: This was estimated by the method of C. G. Schwalbe & H. Wenzl. The air-dry sample was boiled with a saturated solution of barium hydroxide in a flask with a reflux condenser for 1 hour. The insoluble pulp was then filtered, washed with water, dilute hydrochloric acid, and again with water, and dried at 105°C. to a constant weight. The percentage of the insoluble pulp was taken to represent the baryta resistance value, which agreed approximately with the α -cellulose-content.

Copper Value: This value of the cellulose fibers was estimated by the method proposed by C. G. Schwalbe, the Fehling's solution being used for the determination of the reducing capacity of the fibers. The occurrence of oxycellulose and other ingredient contaminating β -cellulose will be apparent in the copper value.

Hydrolysis Value: The air-dry samples were heated with 5% sulphuric acid to boiling for 1/4 hour and neutralized with caustic soda solution, and the amount of reducing substance in the solution was estimated by Fehling's solution. Hemicellulose and some hexosans other than cellulose are hydrolysed by this treatment into reducing substances.

Specific Viscosity: The viscosity of a 1% bleached cellulose cuproammonium solution was measured at 20° according to the directions of W. H. Gibson and the results are as follows:

Table IX.

	Cross and Bevan			Chlorinedioxide		
	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Sp. Vis.	5.80	7.110	3.73	5.33	12.16	5.02

Dye-Absorption Capacity

In the experiment, about 2 gms. of the air-dried samples were

placed in 100 c.c. of 0.05—0.1% solution of dye at 25°C for 12 hours, and 50 c.c. of the solution pipeted out and the content of the dye was estimated by means of a standard solution of titanous chloride, according to the directions given by E. Knecht & E. Hippert. The results are as follows:

Table X

	Origin	Method	Sample in gram	Dye in gram in 100 c.c. sol.	Absorbed Dye in gram	%
Direct Dye	Wood	C & B	1.8132	0.07308	0.0088	0.48
	"	ClO ₂	1.8031	"	0.0059	0.33
	Ramie	C & B	2.9256	"	0.0167	0.57
	"	ClO ₂	2.9162	"	0.0186	0.63
	Kaoliang	C & B	1.7060	"	0.0044	0.28
	"	ClO ₂	1.4912	"	0.0040	0.27
Basic Dye	Wood	C & B	2.0294	0.1055	0.0152	0.75
	"	ClO ₂	2.0172	"	0.0152	0.75
	Ramie	C & B	2.8124	"	0.0220	0.78
	"	ClO ₂	2.8973	"	0.0169	0.58
	Kaoliang	C & B	1.5667	"	0.0106	0.67
	"	ClO ₂	1.5949	"	0.0140	0.88

Alkali-absorption

50 gms. of air-dried samples were immersed in 1 litre of 17.28% caustic soda solution at 20°C. and the amount of alkali absorbed was measured from time to time, the solution being titrated with $\frac{N}{I}$ SO₄H₂-solution.

Table XI

Hours.	Wood		Ramie		Kaoliang	
	C & B	ClO ₂	C & B	ClO ₂	C & B	ClO ₂
1	0.155	0.160	0.181	0.214	0.158	0.140
2	0.161	0.155	0.207	0.219	0.198	0.16
3	0.153	0.160	0.190	0.230	0.158	0.149
4	0.153	0.151	0.220	0.198	0.176	0.169
5	0.130	0.143	0.179	0.186	0.147	0.153
Mean	0.150	0.154	0.195	0.209	0.167	0.155

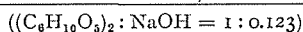


Table XII

Method		Cross and Bevan			Chlorine dioxide		
Origin	Hours	N-H ₂ SO ₄ c.c.	Conc. of mother liquor	grm. % of absorbed NaOH	N-H ₂ SO ₄ c.c.	Conc. of mother liquor	grm. % of absorbed NaOH
Wood	1	24.30	19.44	0.64	24.26	19.41	0.67
"	2	24.27	19.41	0.67	24.30	19.44	0.64
"	3	24.32	19.45	0.63	24.27	19.41	0.67
"	4	24.31	19.45	0.63	24.32	19.46	0.62
"	5	24.45	19.56	0.54	24.37	19.50	0.59
Ramie	1	24.18	19.34	0.73	23.93	19.15	0.89
"	2	24.03	19.22	0.83	23.92	19.13	0.91
"	3	24.13	19.30	0.76	23.84	19.06	0.97
"	4	23.94	19.15	0.89	24.04	19.23	0.82
"	5	24.19	19.35	0.72	24.11	19.29	0.77
Kaoliang	1	24.33	19.47	0.61	24.44	19.55	0.55
"	2	24.11	19.29	0.77	24.30	19.44	0.64
"	3	24.34	19.47	0.61	24.39	19.51	0.58
"	4	24.24	19.39	0.68	24.26	19.42	0.65
"	5	24.40	19.52	0.57	24.37	19.49	0.60

As will be seen in the experimental results shown in Table XI, the quantity of alkali remaining in the cellulose fibers from wood and kaoliang, of which the molecular ratio is 1:0.15, agreed with the formula $(C_6H_{10}O_5)_2 NaOH$, (1:0.123), while the amount of sodium hydroxide absorbed by the ramie fiber, the ratio being 1:0.2, is approximately that calculated for $(C_6H_{10}O_5)_2 2NaOH$ (1:0.23).

Action of Caustic Soda on Bleached Celluloses

So-called mercerization of celluloses with concentrated solution of caustic soda will have some physical effect on the surface of α -cellulose which constitutes the major part of cellulose fibers, and also exert a chemical action on the substances associated with α -cellulose.

For the mercerization, 100 gms. of the bleached fibers were immersed in 1800 c.c. of 17% caustic soda-solution at 20°C for 2 hours.

The fibers were then separated and the adhering solution was partly pressed out so as to leave its weight equal to that of the fibers. The samples were divided into 5 parts and kept separately in stoppered flasks at 20°C. Each sample was placed in 400 c.c. of 5% sulphuric acid solution for 15 minutes at intervals of 5, 10, 15, 40 and 70 hours, and the fibers separated from the solution, washed with water and dried at 30°C to a constant weight. Then the content of water (Table XIII), ash (Table XIV), α -cellulose (Table XV), and cellulose-value (Table XVI), copper-value (Table XVII), hydrolysis value (Table XVIII), furfural yield (Table XIX), specific viscosity (Table XX) and dye-absorption capacity (Table XXI) were determined, and the experimental results are shown in the Tables.

Table XIII

Method	Cross and Bevan			Chlorine dioxide		
	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Origin						
Hours						
5	8.35	13.86	7.35	8.62	12.59	8.56
10	11.46	13.80	7.24	11.23	12.64	9.49
15	6.37	15.97	5.86	6.69	13.73	6.98
40	7.71	12.21	9.35	7.21	12.81	9.27
70	11.63	15.27	8.76	11.53	12.28	8.80
Mean	9.10	14.22	7.71	9.06	12.81	8.62

Table XIV

Method	Cross and Bevan			Chlorine dioxide		
	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Origin						
Hours						
5	0.16	0.08	0.71	0.13	0.08	0.30
10	0.18	0.09	0.58	0.15	0.12	0.29
15	0.16	0.08	0.46	0.18	0.09	0.28
40	0.13	0.12	0.78	0.14	0.08	0.32
70	0.14	0.11	0.66	0.17	0.13	0.41
Mean	0.15	0.096	0.64	0.15	0.10	0.32

Table XV

Method	Cross and Bevan			Chlorine dioxide			
	Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Hours							
5		96.31	97.37	88.15	95.30	93.74	91.67
10		95.10	95.33	85.10	96.08	96.96	91.76
15		95.67	94.02	90.30	98.66	96.76	90.80
40		95.32	95.50	78.73	95.21	96.17	89.72
70		95.29	93.43	81.35	95.11	96.30	89.38
Mean		95.54	95.13	84.73	96.07	95.90	90.67

Table XVI

Method	Cross and Bevan			Chlorine dioxide			
	Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Hours							
5		0.056	0.080	0.074	0.038	0.082	0.045
10		0.055	0.076	0.058	0.048	0.081	0.051
15		0.060	0.072	0.078	0.052	0.080	0.059
40		0.058	0.089	0.068	0.052	0.075	0.067
70		0.063	0.058	0.075	0.047	0.067	0.057
Mean		0.058	0.075	0.071	0.047	0.077	0.056

Table XVII

	Method	Cross and Bevan			Chlorine dioxide		
	Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
	Hours						
	5	1.02	0.86	2.33	1.01	0.52	1.01
	10	1.05	0.71	2.42	1.04	0.43	1.01
	15	1.09	0.80	2.32	0.75	0.74	0.92
	40	1.04	0.75	2.40	0.97	0.78	1.45
	70	0.98	0.74	2.53	1.00	0.71	1.53
Corr. Copper value	5	0.96	0.78	2.24	0.97	0.44	0.96
	10	0.99	0.62	2.36	0.97	0.36	0.96
	15	1.03	0.73	2.24	0.70	0.65	0.86
	40	0.98	0.66	2.33	0.92	0.70	1.38
	70	0.92	0.68	2.45	0.95	0.65	1.47
	Mean	1.01	0.73	2.36	0.93	0.60	1.16

Table XVIII

	Method	Cross and Bevan			Chlorine dioxide		
	Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Corr. Hydrolysis value	Hours						
	5	10.60	7.14	20.98	10.21	6.23	23.10
	10	10.37	8.02	21.73	10.53	7.03	25.85
	15	9.46	8.22	21.28	10.01	8.01	24.81
	40	9.16	7.71	19.15	8.74	7.65	22.81
	70	9.61	7.12	19.34	8.57	7.04	24.48
	5	9.60	8.02	18.65	9.20	5.80	22.09
	10	9.32	7.40	19.31	9.51	6.66	24.84
	15	8.37	7.50	18.96	9.26	7.36	23.89
	40	8.12	7.05	16.75	7.77	6.94	21.36
	70	8.63	6.44	16.81	7.57	6.40	22.95
	Mean	9.50	7.46	19.30	9.13	6.91	23.62

Table XIX

Method	Cross and Bevan					
Origin	Wood		Ramie		Kaoliang	
Hours	Furfural	Pentosan	Furfural	Pentosan	Furfural	Pentosan
5	0.84	1.44	0.36	0.62	7.21	12.19
10	0.68	1.17	0.32	0.56	6.62	11.25
15	0.66	1.14	0.15	0.26	6.26	11.20
40	0.66	1.14	0.31	0.54	4.04	6.94
70	0.70	1.19	0.24	0.42	5.91	10.10
Mean	0.70	1.22	0.28	0.48	6.01	10.34

Chlorine dioxide						
5	0.92	1.55	0.30	0.52	10.91	18.62
10	0.69	1.20	0.33	0.39	10.35	17.67
15	0.76	1.31	0.29	0.50	9.92	16.92
40	0.50	0.86	0.57	0.91	8.56	14.61
70	0.48	0.82	0.16	0.28	9.44	16.60
Mean	0.67	1.15	0.33	0.54	9.86	16.88

Table XX

Method	Cross and Bevan			Chlorine dioxide		
Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Hours						
5	7.50	3.83	5.50	9.87	6.35	5.75
10	6.79	3.47	4.69	6.84	4.61	6.30
15	7.15	3.79	4.47	7.15	4.84	6.31
40	4.58	3.13	3.11	4.97	2.89	4.36
70	3.72	3.07	2.86	4.49	3.06	3.57
Mean	5.95	3.46	4.13	6.66	4.35	5.26

Table XXI

Method	Cross and Bevan					
Origin	Wood		Ramie		Kaoliang	
Dyes	Direct	Basic	Direct	Basic	Direct	Basic
Hours						
5	0.68	0.40	2.34	0.42	1.50	1.40
10	0.48	0.37	2.60	0.19	1.23	1.57
15	0.63	0.53	3.22	0.29	1.45	1.61
40	0.67	0.60	3.43	0.52	1.06	1.76
70	0.64	0.50	2.90	0.16	1.12	1.57
Mean	0.62	0.48	2.90	0.32	1.27	1.58

Chlorine dioxide

5	0.68	0.54	1.98	0.59	1.35	1.40
10	0.53	0.49	2.52	0.45	1.10	1.59
15	0.66	0.66	3.40	0.37	1.83	1.61
40	0.67	0.71	3.25	0.44	1.55	1.85
70	0.51	0.61	3.30	0.16	1.26	1.65
Mean	0.61	0.60	2.89	0.40	1.42	1.62

Table XXV

Method	Cross and Bevan			Chlorine dioxide		
	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Origin						
Hours						
5	6.06	6.31	4.84	5.65	6.95	4.80
10	5.91	7.79	5.41	5.61	8.15	5.00
15	5.71	6.27	4.19	6.94	5.89	3.94
Mean	5.89	6.79	4.81	6.07	7.00	4.58

Table XXVI

Method	Cross and Bevan			Chlorine dioxide		
	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Origin						
Hours						
5	0.09	0.05	0.63	0.13	0.14	0.18
10	0.12	0.04	0.83	0.15	0.14	0.29
15	0.10	0.02	0.75	0.15	0.04	0.23
Mean	0.10	0.04	0.74	0.14	0.11	0.23

Table XXVII

Method	Cross and Bevan			Chlorine dioxide		
	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Origin						
Hours						
5	83.32	93.95	83.02	86.41	96.14	79.72
10	92.05	92.96	79.57	97.27	94.87	81.18
15	92.50	89.70	74.38	98.05	90.89	73.18
Mean	89.29	92.20	78.99	93.91	93.97	78.03

Action of Superheated Water on Bleached Celluloses

1 part of air-dried celluloses with 7.5 parts of water was heated in an autoclave at 150°C for 5, 10 and 15 hours and then in an oil bath heated to 160°C, and the samples were then separated from the aqueous solution, and dried at 30°C to a constant weight. In the aqueous solutions the amount of solid matter (Table XXII) and of reducing

substance (Table XXIII), and the yield of furfural and digesting the solid matter with conc. hydrochloric acid (Table XXIV) were estimated, and the results are shown in the tables.

Table XXII

Method	Cross and Bevan			Chlorine dioxide		
Origin	% Wood	% Ramie	% Kaoliang	% Wood	% Ramie	% Kaoliang
5	0.70	1.04	3.52	0.67	0.66	4.65
10	0.79	1.24	4.99	1.05	0.83	6.81
15	2.05	1.35	5.42	1.22	1.06	7.76
Mean	1.18	1.21	4.64	0.98	0.85	6.41

Table XXIII

Method	Cross and Bevan			Chlorine dioxide		
Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Hours	%					
5	0.12	0.01	5.15	0.07	0.07	6.47
10	0.19	0.07	8.59	0.07	0.24	10.69
15	0.17	0.19	9.12	0.08	0.15	10.95
Mean	0.16	0.09	7.62	0.07	0.15	9.37

Table XXIV

Method	Cross and Bevan			Chlorine dioxide		
Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Hours						
5	—	—	0.59	—	—	0.23
10	—	—	0.72	—	—	0.39
15	—	—	1.09	—	—	0.57

The substance soluble in water, which was separated from cellulose proper by the action of superheated water, is estimated to be contaminated in a larger amount with the kaoliang cellulose and to consist partly of the furfural yielding substance.

The air-dry insoluble residue separated from the soluble substance was analysed and its physical and chemical properties studied, and the content of water (Table XXV), ash (Table XXVI), α -cellulose (Table XXVII), and also the cellulose-value, copper value, hydrolysis value (Table XXVIII), furfural yield (Table XXIX), specific viscosity (Table XXX), capacity for absorbing direct and basic dyes (Table XXXI) were investigated and the results obtained from the three cellulose fibers were compared with each other and also with those of the bleached and mercerized celluloses.

Table XXVIII

Method		Cross and Bevan			Chlorine dioxide		
Hours		Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
5	Cellulose value	0.059	0.04	0.083	0.05	0.04	0.063
10		0.056	0.057	0.062	0.055	0.056	0.074
15		0.054	0.076	0.08	0.053	0.066	0.069
5	Copper value	2.75	2.07	8.20	2.13	1.22	7.67
10		3.52	3.27	9.01	2.58	1.44	8.20
15		2.78	1.96	9.92	2.53	2.17	6.36
5	Hydrolysis value	5.41	4.48	15.01	4.63	4.14	13.80
10		6.13	5.10	15.72	4.70	4.56	12.38
15		4.75	4.33	12.87	4.35	3.95	12.31
5	Corr. Copper value	2.69	2.03	8.12	2.08	1.18	7.60
10		3.46	3.21	8.95	2.52	1.39	8.12
15		2.72	1.89	9.84	2.47	2.11	6.20
5	Corr. Hydrolysis value	2.66	2.41	6.80	2.40	2.92	6.13
10		2.61	1.83	6.71	2.12	3.12	4.18
15		1.97	2.36	2.95	1.82	1.77	5.93

Table XXIX

Method	Cross and Bevan					
Origin	Wood		Ramie		Kaoliang	
Hours	Furfural	Pentosan	Furfural	Pentosan	Furfural	Pentosan
5	2.26	3.87	0.34	0.59	11.38	19.41
10	2.12	3.63	0.41	0.71	10.18	18.12
15	2.18	3.72	0.54	0.93	8.45	14.40
Mean	2.19	3.74	0.43	0.74	10.00	17.31

Chlorine dioxide

5	2.53	4.50	0.37	0.63	10.73	18.27
10	2.25	3.87	0.57	0.99	10.17	17.28
15	2.17	3.73	0.56	0.97	10.21	17.38
Mean	2.32	4.03	0.50	0.86	10.37	17.64

Table XXX

Method	Cross and Bevan			Chlorine dioxide		
	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Origin						
Hours						
5	4.17	8.80	3.87	6.28	9.85	3.80
10	4.22	7.54	3.51	5.43	9.02	3.48
15	4.82	5.88	3.68	6.34	8.44	4.19
Mean	4.40	7.41	3.69	6.02	9.10	3.82

Table XXXI

Method	Origin	Cross and Bevan			Chlorine dioxide		
		Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
	Dyes						
Hours							
5	Direct	3.05	2.06	2.20	2.96	3.16	3.28
10		2.74	1.58	2.89	2.99	2.72	3.45
15		2.72	1.54	2.88	3.00	2.60	3.19
5	Basic	0.72	0.19	0.72	1.89	0.35	1.36
10		1.57	0.16	1.10	1.54	0.34	0.90
15		1.11	0.12	1.41	1.50	0.28	1.38

	ClO ₂ Method								
	Wood			Ramie			Kaoliang		
	B	M	H	B	M	H	B	M	H
H ₂ O	5.7	9	6	11.8	12.5	7	7.6	8.9	4.3
Ash	0.19	0.15	0.14	0.18	0.10	0.1	0.72	0.31	0.23
α-Cellulose	84.9	95	93	96.5	96	94	73.2	90	78
Cu-value	2.9	0.9	2.3	0.9	0.58	1.8	1.6	1.0	7.5
Hydrolysis value	2.9	8.2	2.0	3.0	6.3	2.4	19.1	23	5.3
Furfural yield	2.5	0.7	2.3	0.3	0.3	0.4	12.6	10	10.3
Sp. V.	5.33	7.2	6	12.16	4.2	9.2	5.02	5	3.9
Direct dye	0.33	0.62	3.0	0.63	3.4	2.8	0.27	1.3	3.2
Basic dye	0.75	0.60	1.6	0.58	0.4	0.32	0.88	1.5	1.2

B—Bleached Cellulose.

M—Mercerized with caustic soda solution.

H „ „ superheated water.

	(C & B)								
	Wood			Ramie			Kaoliang		
	B	M	H	B	M	H	B	M	H
H ₂ O	7.5	8.7	5.9	9.1	13	6.7	9.8	7.8	4.9
Ash	0.18	0.15	0.1	0.08	0.10	0.04	1.5	0.60	0.75
α -Cellulose	82.9	95.9	90	95.8	95	92	76.6	87	80
Cu-value	3.2	0.98	2.7	1.5	0.7	2	6.3	2.3	9.2
Hydrolysis value	3.5	8.5	2.3	2.8	7.5	2.2	14.5	18	4.3
Furfural yield	2.5	0.6	2.1	0.2	0.3	0.4	7.0	6.5	9.5
Sp. V.	5.8	6.7	4.3	7.1	3.7	7.1	3.7	4.5	3.6
Direct dye	0.48	0.6	2.7	0.57	2.9	1.6	0.28	1.3	2.5
Basic dye	0.75	0.4	1.1	0.78	0.3	0.15	0.67	1.5	1.1

The water-content is high in the ramie cellulose, and is parallel to that of ash. The high content of water in the mercerized cellulose is partly due to the colloidal nature of the cellulose surface. The content of α -cellulose is obviously great in the ramie celluloses and poor in kaoliang celluloses. Both copper value and hydrolysis value are greatest in kaoliang celluloses but they show no intimate connection with oxy- and hydro-cellulose-content. The chemical change which produced in the cellulose constituents by the mercerization is very evident in wood cellulose, as is indicated by the hydrolysis value. To our surprise, the content of α -cellulose in the different bleached celluloses and their mercerized ones, has no apparent relation with specific viscosity and dye-absorption capacity.

When the wood pulp bleached by the processes introduced by Cross and Bevan, and Schmidt, the resulting substance shows similar properties to the bleached ramie cellulose, but with kaoliang celluloses some differences were noticed in the content of α -cellulose, copper value and hydrolysis value, which are partly due in this case to the methods employed.

These differences, however, were greatly lessened by mercerization of the bleached celluloses with caustic soda solution and also with superheated water.

As a matter of fact, crude fibers prepared from different sources were diverse in their properties and on purifying they tend to approach, to some extent, a chemically identical substance.

Preparation of α -Celluloses¹

Ramie- α -Cellulose and Wood- α -Cellulose.

A bleached ramie-cellulose was treated with 20 times its weight of 12.5% caustic soda solution at ordinary temperature for 40 minutes, separated from the solution by filtration and pressed to remove the mother liquor, washed with 4% caustic soda solution and with water, and then treated with 25 times its weight of 2% acetic acid solution for 15 minutes, washed thoroughly with water and dried at 30°C to a constant weight. The yield and analytical results of α -cellulose are as shown in the tables (Tables XXXII—XXXVIII).

Kaoliang- α -Cellulose.

After many trials, the writer succeeded in getting pure α -cellulose from kaoliang fibers by the following procedure.

7 parts of bleached kaoliang cellulose were treated successively with 50 parts of 4% caustic soda solution at 25°C for 24 hours, 20 parts of 12.5% caustic soda solution for 30 minutes and 20 parts of 17.5% caustic soda solution for 30 minutes and finally with 25 parts of 2% acetic acid solution for 15 minutes, and washed with water and dried at 30°C. to a constant weight.

Table XXXII

	Ramie		Wood		Kaoliang	
	(C & B)	ClO ₂	(C & B)	ClO ₂	(C & B)	ClO ₂
Yield	94.69	96.71	92.07	90.86	80.84	85.10
H ₂ O	6.22	6.09	6.73	5.80	6.02	6.40
Ash	0.12	0.12	0.13	0.09	0.22	0.11
Cu-value	0.98	0.64	0.86	0.61	0.69	0.44
Hydrolysis value	5.57	4.63	5.44	5.74	5.57	6.27
Furfural yield	0.10	0.29	0.13	0.34	1.42	1.79
α -Cellulose	99.90	99.93	99.28	99.41	99.53	99.71

Of these α -celluloses, the specific viscosity (Table XXXVI), the

1. A. B. Corey and H. Le B. Gray: Ind. Eng. Chem., **16**, 853, 1130 (1924); C. G. Schwalbe: Pap. Fabr. **24**, 769 (1926); H. Hibbert: Ind. Eng. Chem., **15**, 748 (1923).

absorption of benzopurpurine 4 B, and methylene blue (Table XXXVIII, XXXIX), alkali absorption (Table XL), hydrolytic velocity with conc. hydrochloric acid (Table XLI), and the specific rotatory power in Schweizer's solution (Table XLII) were measured; the action on them of caustic soda (Table XLVII—LI) and of superheated water were also studied.

The specific viscosity of α -celluloses¹ was estimated with a 1% cuproammonium solution containing 1.18% of copper and 20.1% of ammonia (Table XXXVI).

In the experiment on the dye-absorption capacity², 2 gms. of the α -celluloses were placed in 100 c.c. of 0.057% benzopurpurine 4 B at 28° for 12 hours, and the content of the dye in 25 c.c. of the solution was estimated as usual (Table XXXVIII).

Table XXXIII

Origin	Method	Water in %	Ash in %	Method	Copper-number	Hydrolysis-value
Ramie	C & B	6.22	0.12	C & B	0.98	5.57
	ClO ₂	6.09	0.12	ClO ₂	0.64	4.63
Wood	C & B	6.73	0.13	C & B	0.86	5.44
	ClO ₂	5.80	0.09	ClO ₂	0.61	5.75
Kaoliang	C & B	6.02	0.22	C & B	0.69	5.57
	ClO ₂	6.40	0.11	ClO ₂	0.44	6.27

Table XXXIV

Origin	Method	Sample in g.	Phloroglucide in gms.	Furfural %
Ramie	C & B	3.0370	0.0006	0.10
	ClO ₂	3.3373	0.0133	0.29
Wood	C & B	3.3353	0.0029	0.13
	ClO ₂	3.3005	0.0160	0.34
Kaoliang	C & B	2.0439	0.0506	1.42
	ClO ₂	1.9732	0.0622	1.78

1. W. H. Gibson: Journ. Chem. Soc., **117**, 479 (1920); M. Nakano: Journ. Chem. Ind., **25**, 899 (1922).

2. E. Knecht: Journ. Soc. Dyers & colourists, **24**, 107 (1908); C. G. Schwalbe: Die Chemie d. Zellulose, (1911) 93—129

Table XXXV

Origin	Method	α -Cellulose in %	Mean
Ramie	C & B	99.98 99.82	99.90
	ClO ₂	99.87 99.98	99.93
Wood	C & B	99.30 99.25	99.28
	ClO ₂	99.42 99.50	99.46
Kaoliang	C & B	99.50 99.55	99.53
	ClO ₂	99.65 99.77	99.31

Table XXXVI

Origin	Method	Sp. gr. of soln.	Second	V
Ramie	C & B	0.9462	106.5	6.07
	ClO ₂	0.9473	407.9	23.29
Wood	C & B	0.9475	105.2	6.01
	ClO ₂	0.9476	280.2	16.00
Kaoliang	C & B	0.9475	230.6	13.17
	ClO ₂	0.9481	421.6	24.09
Schweizer's sol.		0.9447	17.6	

Table XXXVII

Origin	Method	Water- content	Ash- content	Furfural yield	α -Cellulose content	Copper- value	Hydrolysis value	Specific viscosity
Wood	C & B	6.73	0.13	0.13	99.28	0.86	5.44	6.01
	ClO ₂	5.80	0.09	0.34	99.46	0.61	5.75	16.00
Ramie	C & B	6.22	0.12	0.10	99.90	0.98	5.57	6.07
	ClO ₂	6.09	0.12	0.29	99.29	0.64	4.63	23.29
Kaoliang	C & B	6.02	0.22	1.42	99.53	0.69	5.57	13.17
	ClO ₂	6.40	0.11	1.78	99.71	0.44	6.27	24.09

Table XXXVIII

Origin	Method	Sample in gms.	Absorbed dye in gms.	Absorbed dye in %
Wood	C & B	2.2961	0.00569	0.99
	ClO ₂	2.3226	0.00655	1.12
Ramie	C & B	2.0811	0.00351	0.53
	ClO ₂	2.1287	0.00259	0.49
Kaoliang	C & B	1.8633	0.00474	1.01
	ClO ₂	1.9360	0.00396	0.81

Table XXXIX

Origin	Method	Sample in gms.	Absorbed dye in gms.	Absorbed dye in %
Wood	C & B	1.9834	0.0222	1.07
	ClO ₂	2.0048	0.0222	1.07
Ramie	C & B	2.0038	0.0248	0.54
	ClO ₂	1.9387	0.0208	1.37
Kaoliang	C & B	1.9957	0.0218	1.11
	ClO ₂	1.9985	0.02197	1.11

The absorption of methylene blue was studied with a 0.11% solution (Table XXXIX). The amount of dyestuffs taken up is greatest with ramie celluloses.

Alkali absorption of α -celluloses¹

12 gms. of air-dried α -celluloses were kept in 20 times its weight of 18.0 L caustic soda solution at 28°C. for 1, 2 & 3 hours respectively and the content of alkali absorbed by the celluloses was estimated by means of $\frac{N}{I}$ SO₄H₂ solution. In the table (Table XL), the alkali-content absorbed is calculated in mol per cent.

1. W. von Neuenstein: Sonderheft. d. Koll. Zeitschr. **43**, 241 (1928); Galo W. Blanco: Ind. and Eng. Chem., **20**, 926 (1928).

Table XL

hours	α -Celluloses.	Wood		Ramie		Kaoliang	
		C & B	ClO ₂	C & B	ClO ₂	C & B	ClO ₂
1		0.16	0.22	0.14	0.13	0.16	0.14
2		0.19	0.18	0.16	0.14	0.18	0.15
3		0.14	0.13	0.14	0.15	0.13	0.13
	Mean	0.16	0.18	0.15	0.14	0.16	0.14

Table XLI

Origin	Method	Time in hours	Sample in gms.	$\frac{N}{10}$ KM ₁₁ O ₄ c.c.	Cu mg.	Glucose mg. in 500 c.c.	Glucose mg. in total c.c.	Glucose percent for sample	Glucose percent for theory
Wood	C & B	2	1.9486	6.50	41.3	20.6	824	42.28	38.09
		4	"	10.35	65.8	33.6	1344	68.97	62.13
		6	"	10.70	87.1	45.3	1812	92.99	83.77
		8	"	15.15	96.3	50.5	2020	103.66	93.39
		10	"	15.65	99.5	52.3	2092	107.36	97.00
		13	"	16.50	104.9	55.4	2216	113.72	102.45
	ClO ₂	2	1.9573	7.70	49.0	24.7	988	50.48	45.48
		4	"	10.90	69.3	35.5	1420	72.55	65.36
		6	"	13.80	87.7	45.7	1828	93.39	84.13
		8	"	15.25	97.0	51.0	2040	104.22	93.89
		10	"	16.25	103.3	54.5	2180	111.38	100.34
		13	"	17.05	108.4	57.4	2296	117.30	105.67
		Ramie	C & B	2	1.9527	6.55	41.6	20.7	828
4	"			10.10	64.2	32.8	1312	67.19	60.53
6	"			13.15	83.6	43.3	1732	88.70	79.91
8	"			15.40	97.9	51.4	2056	105.28	94.85
10	"			15.90	101.1	53.2	2128	108.97	98.17
13	"			16.05	102.1	53.9	2156	110.41	99.47
ClO ₂	2		1.9235	7.00	44.5	22.3	892	46.37	41.77
	4		"	10.15	64.5	33.0	1320	68.62	61.82
	6		"	13.00	88.4	46.0	1840	95.66	86.18
	8		"	15.20	96.7	50.8	2032	105.64	95.17
	10		"	16.00	101.7	53.6	2144	111.46	100.41
	13		"	16.85	107.1	56.7	2268	117.91	106.22
	Kaoliang		C & B	2	1.9101	6.90	43.9	22.0	880
4		"		10.45	66.4	34.0	1360	71.20	64.14
6		"		13.25	84.3	43.8	1752	91.72	82.63
8		"		15.55	98.9	52.0	2080	108.89	98.10
10		"		15.60	99.2	52.1	2084	109.10	98.29
13		"		17.00	108.1	57.2	2288	119.78	107.81
ClO ₂		2	1.9610		44.5	22.3	892	45.48	40.97
		4	"		68.7	35.2	1408	71.80	64.68
		6	"		88.1	46.0	1840	93.83	84.53
		8	"	15.75	100.2	52.8	2112	107.70	97.93
		10	"	16.50	104.9	55.4	2216	113.00	101.80
		13	"	16.55	105.2	55.6	2224	113.41	102.17

The content of alkali absorbed by the three α -celluloses being in agreement with the formula $(C_6H_{10}O_6)_2 : NaOH = 1 : 0.12$, shows no marked difference.

Hydrolysis of α -Celluloses

α -Celluloses were hydrolysed completely with conc. hydrochloric acid according to Willstätter and Zechmeister's directions, and the amount of d-glucose formed was estimated from time to time by the usual method, and the reaction velocity was measured in each case, which gave similar results as follows:— (Table XLI).

Specific Rotation of α -Celluloses¹

The specific rotatory power of α -celluloses in Schweizer's solution (Cu-content 1.21 gms. & NH_3 -content 17.32 gms. in 100 c.c.) was measured at 20°C with a 2 cm. tube. They show the same rotatory power as will be seen from Table XLII.

Table XLII

Origin	Method	Concentration of cellulose solution	Observed angle	$[\alpha]_{blue}^{20^\circ}$
Wood	C & B	1.1700	-2.23°	-953°
	ClO ₂	0.9990	-1.84°	-921°
Ramie	C & B	0.9964	-2.15°	-1079°
	ClO ₂	1.0830	-2.33°	-1076°
Kaoliang	C & B	1.1660	-2.50°	-1072°
	ClO ₂	0.9630	-2.08°	-1080°

Action of Caustic Soda on α -Celluloses

The action of 17.5% caustic soda solution on 100 gms. of air dried celluloses at 20°C for 2 hours was studied. The celluloses, separated from the solution, were kept in a bottle for 5, 10, 15, 40 & 70 hours respectively and the content of water (Table XLIII), ash (Table XLIV), α -cellulose (Table XLV), and furfural-yield (Table XLVI)

1. K. Hess and E. Messmer: Ber. D. Chem. Ges. **54**, 834 (1921); K. Hess and E. Messmer: Ber. D. Chem. Ges., **55**, 2432 (1922); E. Haeggelund and F. W. Klingstedt Ann. d. Chem., **459**, 26 (1927); M. Nakano: Cellulose Ind. **1**, 13 (1922).

of the products were estimated and the copper-value (Table XLVII), hydrolysis value (Table XLVIII), specific viscosity of 1% Schweizer's solution (Table XLIX), and the absorption of direct & basic dyes (Tables I.—LI), were investigated.

Table XLIII

Method	Cross and Bevan			Chlorine dioxide		
Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Hours						
5	6.38	6.18	7.12	7.84	7.71	8.70
10	11.46	7.43	9.12	7.18	5.49	11.89
15	7.73	7.20	7.60	6.03	5.97	6.79
40	6.58	8.01	7.67	5.96	5.21	6.59
70	7.82	5.85	6.94	6.57	6.34	5.85

Table XLIV

Method	Cross and Bevan			Chlorine dioxide		
Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Standing hours						
5	0.08	0.08	0.14	0.08	0.08	0.13
10	0.12	0.06	0.22	0.11	0.08	0.20
15	0.13	0.08	0.20	0.12	0.05	0.19
40	0.12	0.06	0.14	0.11	0.05	0.17
70	0.11	0.07	0.26	0.11	0.06	0.21

Table XLV

Method	Cross and Bevan			Chlorine dioxide		
Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Standing hours						
5	99.77	99.56	99.64	99.96	99.93	99.95
10	99.66	99.62	99.74	99.91	99.88	99.91
15	98.78	98.43	98.74	88.96	99.51	98.51
40	98.62	99.35	98.42	99.23	99.73	99.13
70	99.69	99.33	98.26	99.66	99.49	99.24

Table XLVI

Method	Cross and Bevan			Chlorine dioxide		
Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Standing hours						
5	0.42	0.52	1.10	0.52	0.47	1.44
10	0.47	0.59	1.17	0.54	0.58	1.33
15	0.49	0.35	1.30	0.53	0.38	1.36
40	0.51	0.46	1.14	0.49	0.39	1.21
70	0.36	0.33	0.94	0.41	0.35	1.15

Table XLVII

Method	Cross and Bevan			Chlorine dioxide		
Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Hours						
5	0.67	0.74	0.52	0.43	0.23	0.30
10	0.67	0.68	0.42	0.44	0.19	0.34
15	0.73	0.70	0.55	0.49	0.33	0.41
40	0.62	0.48	0.63	0.49	0.69	0.57
70	0.57	0.69	0.73	0.51	0.42	0.56

Table XLVIII

Method	Cross and Bevan			Chlorine dioxide		
Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Standing hours						
5	7.21	6.77	6.63	5.78	5.30	5.99
10	6.80	6.29	5.74	5.83	5.41	6.62
15	5.72	6.08	6.48	6.09	5.58	5.73
40	5.02	5.93	6.96	5.29	5.14	5.79
70	6.56	6.00	6.49	4.64	5.28	6.44

Table XLIX

Method	Cross and Bevan			Chlorine dioxide		
Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Standing hours						
5	4.86	4.71	5.65	8.44	14.52	9.72
10	4.32	4.62	5.35	8.31	7.30	8.86
15	4.28	3.75	4.89	6.24	12.46	6.98
40	3.86	4.21	3.51	5.06	6.42	4.50
70	3.21	3.01	3.23	4.40	6.33	3.81

Table L

Method	Cross and Bevan			Chlorine dioxide		
Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Standing hours						
5	3.40	2.02	2.80	3.14	1.94	2.98
10	2.26	2.02	2.36	2.14	1.74	2.54
15	2.36	1.20	2.30	2.20	1.30	2.26
40	2.46	1.04	2.36	2.68	1.00	2.40
70	2.40	1.18	2.22	2.64	1.30	2.22

Table LI

Method	Cross and Bevan			Chlorine dioxide		
Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Standing hours						
5	0.56	0.24	0.32	0.26	0.26	0.22
10	0.42	0.30	0.74	0.86	0.70	0.88
15	0.46	0.76	0.84	0.36	0.20	1.02
40	1.84	1.86	1.70	1.84	1.50	1.72
70	2.34	2.06	1.72	1.78	1.32	1.94

Action of Superheated Water on α -Celluloses

one parts of air-dried α -celluloses were heated with 7.5 parts of water in a sealed tube at 150°C for 5, 10 & 15 hours respectively, and the solution separated from the insoluble residue was analysed to find the content of solid matter, reducing substance with Fehling's solution and furfural-yielding substance; the results are shown in Table LII—LIV.

The kaoliang α -cellulose still contains a measurable quantity of furfural-yielding substance which was mostly removed from the cellulose proper by the action of superheated water.

With regard to insoluble residues, their content of water, ash (Table LV) and α -cellulose (Table LVI) was determined and also furfural-yield (Table LVII), copper value (Table LVIII), hydrolysis value (Table I.IX), specific viscosity (Table LX) and absorption of dyestuffs (Tables LXI—LXII) were studied.

Table LII

Method	Cross and Bevan			Chlorine dioxide		
	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Origin						
Hours	%					
5	0.49	0.28	3.38	0.37	0.98	2.42
10	0.63	1.52	1.52	0.31	1.52	1.58
15	1.64	1.23	2.87	0.93	0.97	2.79

Table LIII

Method	Cross & Bevan			Chlorine dioxide		
	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Origin						
Hours						
5	0.009	0.011	0.383	0.018	0.036	0.28
10	0.004	0.05	0.195	0.002	0.028	0.113
15	0.011	0.046	0.744	0.004	0.017	0.143

Table LIV

Method	Cross & Bevan			Chlorine dioxide		
	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Origin						
Hours						
5	0.49	0.28	1.23	0.53	0.34	1.54
10	0.49	0.39	1.24	0.54	0.28	1.30
15	0.51	0.44	1.10	0.69	0.43	1.47

Table LV

Method	Cross and Bevan					
	Wood		Ramie		Kaoliang	
Origin						
Time	Water	Ash	Water	Ash	Water	Ash
5	7.05	0.03	10.95	0.03	7.56	0.10
10	7.65	0.04	7.79	0.05	6.57	0.10
15	7.86	0.06	7.46	0.04	6.83	0.10
Chlorine dioxide						
5	11.66	0.11	9.69	0.03	10.83	0.06
10	7.19	0.08	10.31	0.05	5.61	0.11
15	7.53	0.11	8.05	0.05	8.52	0.22

Table LVI

Method	Cross and Bevan			Chlorine dioxide		
Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Time						
5	93.98	96.43	59.23	98.03	99.44	92.40
10	98.24	98.29	86.63	97.92	99.29	90.51
15	93.40	99.07	72.50	97.25	97.25	95.64

Table LVII

Method	Cross & Bevan			Chlorine dioxide		
Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Hours						
5	0.84	0.47	2.14	0.91	0.75	2.66
10	0.85	0.66	2.14	0.92	0.48	2.25
15	0.88	0.76	1.90	1.19	0.76	2.53

Table LVIII

Method	Cross & Bevan			Chlorine dioxide		
Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Hours						
5	1.99	1.58	5.42	1.11	0.75	2.94
10	0.87	1.22	3.73	1.02	0.55	3.07
15	2.28	1.06	5.21	1.45	0.52	1.79

Table LIX

Method	Cross & Bevan			Chlorine dioxide		
Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Hours						
5	5.16	5.51	2.66	5.45	4.90	3.95
10	6.45	6.63	4.42	5.74	5.11	4.19
15	4.73	6.26	2.90	5.22	5.13	5.12

Table LX

Method	Cross & Bevan			Chlorine dioxide		
	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Origin						
Hours						
5	2.50	2.81	1.69	4.97	8.67	2.11
10	3.79	4.40	1.92	3.98	6.75	2.07
15	2.33	3.81	1.62	3.46	8.11	3.75

Table LXI

Method	Cross-Bevan			Chlorine dioxide		
	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Origin						
Hours						
5	1.74 %	1.10	1.32	2.11	1.18	1.64
10	2.44	1.00	2.38	2.80	0.80	2.34
15	2.77	1.82	1.96	2.84	1.52	2.38

Table LXII

Method	Cross-Bevan			Chlorine dioxide		
	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Origin						
Hours						
5	0.82	0.66	0.80	0.88	0.66	0.80
10	0.76	0.44	0.52	0.76	0.92	0.16
15	0.46	0.40	0.34	0.24	0.12	0.36

Regeneration of Celluloses from Schweizer's Solutions of α -Celluloses¹

30 gms. of air-dried α -celluloses were dissolved in 150 c.c. of Schweizer's solution at 23°C, and left to stand for 12 hours. The solution was then poured into 1.5 litres of 5% sulphuric acid, and the regenerated cellulose was filtered, washed with water and dried at 50°C. The yield of the celluloses as will be seen from Table LXIII was about the same in all cases.

1. K. Hess: Die Chem. d. Zellulose, 1928 p. 320.

The celluloses regenerated from the solution, were analysed, and their physical constants, (Tables LXIV—LXV) absorption of dyes (Table LXVI), and hydrolytic velocity with strong hydrochloric acid & sulphuric acid under pressure (Tables LXVIII—LXX) were estimated.

As will be seen from the experimental results shown in the tables, all the celluloses regenerated from the Schweizer's solution seem to be composed of identically the same unit, though they show somewhat different results in their properties from those of the original α -celluloses.

Table LXIII

Origin	Method	Water-free sample in grm.	Yield in grm.	Yield in per cent
Wood	C & B	27.45	26.6	96.90
	ClO ₂	27.58	27.3	98.98
Ramie	C & B	27.29	26.4	96.74
	ClO ₂	27.53	27.0	98.07
Kaoliang	C & B	27.33	25.9	94.77
	ClO ₂	27.34	26.4	96.56

Table LXIV

Method	Cross-Bevan			Chlorine dioxide		
	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Water-content	5.12	5.29	5.09	4.98	5.83	5.35
Ash-content	0.37	0.37	0.29	0.39	0.37	0.40
Cu-value	3.90	6.34	3.97	4.89	3.67	3.75
Hydrolysis-value	15.10	12.04	14.21	10.64	12.36	17.30
Specific viscosity	4.12	4.00	4.19	4.13	3.85	4.43

Table LXV

Origin	Method	Sample in grm.	Furfural-phloroglucide in grm.	Furfural %	Mean
Kaoliang	C & B	0.4305	0.0081	1.60	1.83
		0.4861	0.0141	2.05	
	ClO ₂	0.4332	0.0132	2.19	2.21
		0.3778	0.0110	2.22	

Table LXVIII

Origin	Method	Time in hours	Sample in gms.	$\frac{N}{10}$ KMnO ₄ c.c.	Cu mg.	Glucose mg. in 5 c.c.	Glucose mg. in total	Glucose % for sample	Glucose % for theory	
Wood	C & B	3	0.6791	7.05	44.84	22.45	224.5	33.06	29.75	
		5	"	11.55	73.46	37.72	377.2	55.54	49.99	
		7	"	14.50	92.22	48.15	481.5	70.90	63.82	
		9	"	16.40	104.30	55.10	551.0	81.16	73.03	
		11	"	17.95	114.16	60.69	606.9	89.37	80.44	
		13	"	18.85	119.88	64.16	641.6	94.48	85.03	
		15	0.5262	15.55	98.90	52.0	520.0	98.82	88.95	
		17	"	16.30	103.67	54.68	546.8	103.91	93.53	
		20	"	16.40	104.30	55.05	550.5	104.62	94.16	
		ClO ₂	3	0.5705	6.00	38.16	19.00	190.0	33.30	29.97
			5	"	9.30	59.15	30.00	300.0	52.58	47.32
			7	"	11.70	74.41	38.31	383.1	67.15	60.43
			9	"	11.90	75.68	39.00	390.0	68.36	61.52
			11	"	15.25	96.99	51.00	510.0	87.39	80.45
			13	"	16.40	104.30	54.03	540.3	94.70	85.23
	15		0.5809	17.45	109.82	59.00	590.0	101.56	91.41	
	17	"	17.50	111.32	59.10	591.0	101.74	91.57		
	20	"	17.70	112.57	59.79	597.9	102.92	92.64		
Ramie	C & B	3	0.5184	5.35	34.02	16.90	169.0	34.53	29.34	
		5	"	8.80	55.97	28.30	283.0	54.59	49.13	
		7	"	11.10	70.59	36.25	362.5	69.92	62.93	
		9	"	12.70	80.77	41.77	417.7	80.57	72.52	
		11	"	13.15	83.63	43.36	433.6	83.64	75.28	
		13	"	15.0	95.40	50.00	500.0	96.45	86.80	
		15	0.5568	16.5	104.94	55.42	554.2	99.53	89.59	
		17	"	17.2	108.12	58.00	580.0	104.16	93.76	
		20	"	17.6	111.92	59.42	594.2	106.71	96.05	
		ClO ₂	3	0.5639	6.25	39.75	19.80	198.0	35.11	31.60
	5		"	9.9	62.96	32.00	320.0	56.75	51.08	
	7		"	11.25	71.55	36.72	367.2	65.11	58.61	
	9		"	13.80	87.77	45.68	456.8	81.00	72.91	
	11		"	15.55	98.90	52.00	520.0	92.21	83.00	
	13		"	16.05	102.08	53.79	537.9	95.39	85.86	
	15		0.6508	19.0	120.84	64.64	646.4	99.32	89.39	
	17		"	19.85	126.24	67.80	678.0	104.18	93.76	
	20	"	20.15	128.15	69.00	690.0	106.02	95.42		
Kaoliang	C & B	3	0.6014	6.8	43.25	21.60	216.0	35.91	32.32	
		5	"	10.35	65.82	33.61	336.1	55.88	50.30	
		7	"	13.10	83.31	43.21	432.1	71.85	64.66	
		9	"	14.75	93.81	49.10	491.0	81.64	73.48	
		11	"	16.25	103.35	54.53	545.3	90.67	81.61	
		13	"	17.40	110.66	58.69	586.9	97.59	87.83	
		15	0.6009	17.20	109.39	58.00	580.0	96.52	86.88	
		17	"	17.85	113.52	60.37	603.7	100.46	90.43	
		20	"	18.00	114.48	61.00	610.0	101.51	91.37	
		ClO ₂	3	0.7176	8.00	50.88	25.65	256.5	35.74	32.17
	5		"	12.40	78.86	40.67	406.7	56.67	51.01	
	7		"	15.10	96.03	50.31	503.1	70.11	63.10	
	9		"	17.75	112.83	60.00	600.0	83.61	75.25	
	11		"	18.50	117.66	62.74	627.4	87.43	78.69	
	13		"	19.15	121.79	65.27	652.7	90.95	81.86	
	15		0.5816	17.20	109.39	58.00	580.0	99.72	89.75	
	17		"	17.55	111.62	59.26	592.6	101.89	91.70	
	20	"	17.75	112.87	60.00	600.0	103.16	92.85		

Table LXVI

Method	Cross-Bevan			Chlorine dioxide		
	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Origin						
Direct dye	2.3	4.2	5.9	4.7	2.8	3.2
Basic dye	3.8	3.8	4.8	3.0	2.8	3.2

Table LXIX

Method	Cross-Bevan			Chlorine dioxide		
	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Origin						
Residue in %	73.24	72.27	74.69	70.00	69.26	73.64
Soluble matter in %	26.76	27.73	25.31	30.00	30.74	26.54

Table LXX

Method	Cross-Bevan			Chlorine dioxide		
	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Origin						
% as Glucose	25.43	25.61	25.62	27.17	27.58	25.39

Table LXXI

Method	Cross Bevan			Chlorine dioxide		
	Wood	Remie	Kaoliang	Wood	Ramie	Kaoliang
Origin						
Observed angle	-1.50°	-1.58°	-1.34°	-1.55°	-1.54°	-1.50°
(α) _{blue} ^{23°}	-750°	-790°	-690°	-775°	-770°	-750°

It was a noteworthy fact that the celluloses regenerated from the kaoliang cellulose solution still contain furfural-yielding substance. This fact seems to contradict the formation of the precipitates formed by acidifying with 10% acetic acid all the cellulose extracts with 2-N-caustic soda solution. The yield of the precipitate dried at 105°C to a constant weight was as follows:¹

1. G. Buncke u. R. Wolfenstein: Ber. D. Chem. Ges., **32**, 2501 (1899); K. Hess., W. Weltzien u. E. Messmer: Ann. d. Chem., **435**, 139 (1923).

Table LXVII

Origin	Wood		Ramie		Kaoliang	
Method	C & B	ClO ₂	C & B	ClO ₂	C & B	ClO ₂
%	5.3	4.5	1.7	1.5	4.9	4.7

Action of Superheated Water on Regenerated Celluloses

1 part of regenerated celluloses was heated with 10 parts of water in a sealed tube at 150°C. for 15 hours. The solution was then separated from the insoluble residue by filtration, and the amount of the insoluble residue and of reducing substance in the solution was estimated (Tables LXXII & LXXIII).

Table LXXII

	Cross-Bevan			Chlorine dioxide		
	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Residue in %	99.46	99.35	97.60	99.57	99.44	97.38
Soluble matter in %	0.54	0.65	2.40	0.43	0.56	2.62

Table LXXIII

	Cross-Bevan			Chlorine dioxide		
	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
as Glucose in %	0.12	0.06	0.85	0.09	0.06	0.80

The loss of the regenerated celluloses by the action of superheated water is exceedingly great in kaoliang, and its amount is nearly equal to the content of furfural-yielding substance but not of alkali-soluble substance in these celluloses.

Acetyl α -Celluloses

1 Preparation of Acetyl α -Celluloses

For the preparation of acetyl celluloses, the method proposed by W. L. Barnett¹ was employed.

1. W. L. Barnett: Journ. Soc. Chem. Ind., 40, 8 (1921).

10 gms. of air-dried α -celluloses suspended in 50 c.c. of glacial acetic acid for 12 hours, was mixed with 30 c.c. of acetic anhydride containing 1.5 gms. chlorine and 18.5 c.c. of acetic anhydride containing 1.25 gms. SO_2 . The mixture was kept in a water bath heated to $69-70^\circ\text{C}$. for 2 hours, the cellulose passed into solution, and an equal volume of chloroform was added, and then the solution was poured into water, the chloroform expelled by boiling and the residual precipitate, thus formed, was purified, dried in vacuo. The yield was as follows (Table LXXIV):

The acetyl α -celluloses, thus prepared, are divided by the use of acetone and chloroform, into two parts; the one is soluble and the other is insoluble in acetone, and the latter was purified by recrystallisation from the chloroform solution (Table LXXV).

Table LXXIV

Method	Cross-Bevan			Chlorine dioxide		
	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Dried sample in g.	9.99	10.10	9.94	10.00	10.01	10.00
Yield in g.	17.40	17.80	17.40	17.60	17.50	17.50
Yield in %	98.30	99.16	98.46	99.04	98.42	98.47

Table LXXV

	Method	Cross-Bevan			Chlorine dioxide		
	Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Aceton soluble acetyl- α -cellulose	Yield in grm.	1.4	1.2	1.4	0.9	1.0	0.9
	Yield in %	8.05	6.74	8.04	5.11	5.71	5.14
Aceton insoluble acetyl- α -cellulose	Yield in grm.	15.60	16.3	15.9	16.4	16.1	16.5
	Yield in %	89.65	91.59	91.37	93.13	92.00	94.29
Total gms.		17.0	17.5	17.3	17.3	17.1	17.4
Total %		97.90	98.33	99.41	98.24	97.71	99.43

The acetyl-content of the two fractions was estimated by the method of C. Freudenberg¹, which he used in his experiment with

1. C. Freudenberg and Harder: *Ann. d. Chem.*, **443**, 230 (1923).

acetyl tannin (Table LXXVII).

The rotatory power (m.p.) and the acetyl-content agree with those of triacetyl cellulose derived from pure cotton cellulose¹ (Tables LXXVI, LXXVIII).

Saponification of Tri-acetyl- α -Celluloses

0.2 gms. of triacetyl- α -cellulose were hydrolysed with 20 c.c. of a normal solution of alcoholic potash at 20°C for 18 hours, and the reaction product was treated with 40 c.c. $\frac{N}{I}$ SO₄H₂ for 10 minutes, washed with water and dried in vacuo. The yield is shown in Table LXXIX.

The regenerated α -celluloses

The rotatory power of these celluloses in the Schweizer's solution was studied, the results being as follows²:

Table LXXVI

Origin	Method	Chloroform soluble acetyl- α -cellulose	acetone-soluble acetyl- α -cellulose
Wood	C & B	240-247°	240-250°
Ramie	"	238-246°	244-253°
Kaoliang	"	241-248°	242-252°
Wood	ClO ₂	240-248°	238-248°
Ramie	"	240-247°	242-253°
Kaoliang	"	240-245°	237-252°

Table LXXVII

Method	Cross-Bevan			Chlorine dioxide		
	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
CH ₃ .CO %	45.51	45.33	45.05	45.59	45.92	44.69

1. K. Hess u. G. Schultz: Ann. d. Chem., **455**, 94 (1927); K. Hess: Die Chemie der Zellulose, p. 594 (1928).

2. K. Hess: Chem. Ztg. **50**, 751 (1926); K. Hess: Z. angew. Chem. **39**, 1189 (1926).

Table LXXVIII

Method	Cross-Bevan			Chlorine dioxide		
	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Origin						
Concentration of Chloroform Sol.	1.9456	1.9648	1.9528	1.8884	1.9056	2.0044
Observed angle	-0.2°	-0.2°	-0.25°	-0.19°	-0.19°	-0.21°
$[\alpha]_D^{20}$	-10.82°	-10.71°	-13.47°	-10.59°	-10.49°	-11.02°

Table LXXIX

Method	Cross-Bevan			Chlorine dioxide		
	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Origin						
Sample in gms.	0.1189	0.1710	0.2375	0.1949	0.2006	0.1562
Yield in gms.	0.0555	0.0742	0.1051	0.0763	0.0860	0.0753
Yield in %	82.96	77.13	78.72	69.62	76.24	85.89

Table LXXX

Method	Cross and Bevan			Chlorine dioxide		
	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Origin						
Conc. of solution	0.1780	0.2564	0.3756	0.2904	0.2980	0.2520
Observed angle	-0.14°	-0.36°	-0.43°	-0.36°	-0.27°	-0.21°
$[\alpha]_{\text{blue}}^{20}$	-449.4°	-698.3°	-572.4°	-619°	-453°	-416.6°

Table LXXXI

Method	Cross-Bevan			Chlorine dioxide		
	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Origin						
CH ₃ .CO %	44.87	44.77	45.06	44.86	44.90	49.85

Table LXXXII

Method	Cross-Bevan			Chlorine dioxide		
	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Origin						
Conc. of solution	1.7260	1.7652	1.7624	1.6128	1.7272	1.7482
Observed angle	-0.37°	-0.20°	-0.38°	-0.35°	-0.19°	-0.37°
$[\alpha]_D^{23}$	-22.56°	-22.66°	-22.69°	-22.84°	-22.00°	-22.27°

Table LXXXIII

Method	Cross-Bevan			Chlorine dioxide		
Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Specific viscosity	1.37	1.33	1.38	1.48	1.38	1.36

Table LXXXIV

Method	Cross-Bevan			Chlorine dioxide		
Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Sample in gms.	0.0923	0.1001	0.0896	0.1163	0.0962	0.0817
Yield in gms.	0.0515	0.0559	0.0502	0.0652	0.0535	0.0454
%	99.23	99.30	99.60	99.70	99.40	98.91

Table LXXXV

Method	Cross-Bevan			Chlorine dioxide		
Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Conc. of solution	0.92	1.22	1.10	1.08	1.20	1.16
Observed angle	-1.74°	-2.35°	-2.31°	-1.96°	-2.17°	-2.27°
$[\alpha]_{\text{blue}}^{20^\circ}$	-945.6°	-950.4°	-105.0°	-907.4°	-904.0°	-974.4°

Separation of Triacetyl- α -Celluloses

Separation of triacetyl celluloses in fractions by means of glacial acetic acid, was tried according to the directions given by K. Hess & G. Schultz¹.

5 gms. of the chloroform-soluble acetyl α -cellulose was treated with 100 c.c. of glacial acetic acid at 23°C for 24 hours, the insoluble residue being then separated by filtration, washed with water and alcohol and reprecipitated from the chloroform solution with ether.

The acetyl cellulose, soluble in acetic acid, was regenerated from the solution by pouring into water. The yield of these celluloses and

1. K. Hess u. G. Schultz: Ann. d. Chem. **455**, 81 (1927).

their molecular weight², m.p., acetyl content, and their rotatory power in chloroform solution³ were estimated by the usual methods (Tables LXXXVII—XCIII).

Table LXXXVI

Method	Cross-Bevan			Chlorine dioxide		
Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Residue in gms.	3.8	3.4	4.3	3.6	3.5	4.2
Residue in %	76.0	68.0	86.0	72.0	70.0	34.0
soluble acetyl cellulose in gms.	0.7	1.0	0.3	1.0	1.1	0.5
%	14.0	20.0	6.0	20.0	22.0	10.0

Table LXXXVII

Method	Cross-Bevan			Chlorine dioxide		
Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
M.P.	250—257°	248—259°	252—258°	251—258°	249—258°	253—259°

Table LXXXVIII

Method	Cross-Bevan			Chlorine dioxide		
Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
CH ₃ CO %	44.88	45.42	44.52	45.02	45.82	45.36

Table LXXXIX

Method	Cross-Bevan			Chlorine dioxide		
Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Conc. of solution	1.7264	1.7228	1.8188	1.8816	1.7636	1.9820
Observed angle	-0.37°	-0.36°	-0.38°	-0.41°	-0.38°	-0.42°
$[\alpha]_{\text{blue}}^{21}$	-22.55°	-22.63°	-21.99°	-22.93°	-22.68°	-22.28°

2. K. Hess u. G. Schultz: *Ann. d. Chem.*, **448**, 99 (1926); **450**, 59 (1926); **455**, 81, 104 (1927); H. Pringsheim, E. Kasten u. E. Schapiro: *Ber. D. Chem. Ges.*, **61**, 2019 (1928).

3. K. Hess u. G. Schultz: *Ann. d. chem.*, **455**, 94 (1927);
 „ „ : *Die Chemie der Zellulose*, p. 594 (1927).

Table XC

Method	Cross-Bevan			Chlorine dioxide		
Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Sample in gms.	10.0	10.0	10.0	10.0	10.0	10.0
Soluble portion in gms.	8.7	8.5	8.5	9.0	8.7	8.5
Insoluble portion in gms.	0.1	0.4	0.3	0.1	0.2	0.4

Table XCI

Method	Cross-Bevan			Chlorine dioxide		
Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
CH ₃ CO %	45.11	45.10	44.81	44.51	44.66	44.70

Table XCII

Method	Cross-Bevan			Chlorine dioxide		
Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Conc. of solution	1.8884	2.1048	1.9672	2.0296	1.7728	1.8868
Observed angle	-0.09°	-0.10°	-0.09°	-0.09°	-0.08°	-0.085°
$[\alpha]_D^{20}$	-23.83°	-23.75°	-22.80°	-22.17°	-22.56°	-22.52°

Table XCIII

Method	Cross-Bevan			Chlorine dioxide		
Origin	Wood	Ramie	Kaoliang	Wood	Ramie	Kaoliang
Conc. of solution	0.54	0.63	0.66	0.57	0.59	0.59
Depression fo temp	0.07°	0.075°	0.085°	0.065°	0.065°	0.07°
Mol. wt.	299.3	324.1	302.0	342.2	353.4	325.0

The triacetyl- α -celluloses derived from three different α -celluloses show similar chemical compositions, and physical and chemical properties, and these experimental results so far obtained seem to favour the hypothesis that all the cellulose fibers from different sources are composed of a chemically identical unit.

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