[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 37]

THE CONSTITUTION OF FLAX CELLULOSE

BY GEORGE W. RIGBY[1]

RECEIVED AUGUST 16, 1928 PUBLISHED DECEMBER 10, 1928

A convenient hypothesis employed for many years by those investigating natural carbohydrates has been to assume cellulose to be a definite compound common to all plants. Cotton, however, containing relatively large percentages of easily purified cellulose, has been accepted quite generally as the source of material to be used as a "standard cellulose." The properties of the cellulose obtained from cotton have been determined with considerable accuracy and these properties have been assumed, in turn, for "cellulose" derived from other sources.

Although there is considerable evidence to justify the assumption that cellulose is a definite compound universally present in plant tissues, as yet no proof has been offered and many contradictory statements are found as to the properties of cellulose when isolated from various sources. In an attempt to aid in clarifying some of the confusion in regard to the universal occurrence of one cellulose and in order to afford a sound basis for the future investigations of the cell walls of the flax fiber,[1a] it was thought worth while to undertake the present research.

Throughout the present investigation each step has been duplicated with both flax and cotton cellulose, thus affording an accurate check on the results and a dependable basis of comparison for the cellulose derived from both sources.

Before proceeding to a discussion of the results of the present investigation, it is well to recall the outstanding researches which have a direct bearing on the present question. No work, however, has been done on the *Constitution of Flax Cellulose.*

As early as 1819 Braconnot[2] prepared glucose from fully bleached linen by the action of sulfuric acid. Blondeau de Caroles[3] isolated a compound to which he ascribed the formula $C_{18}H_{36}O_{18}(SO_3)_2BaO{\cdot}2H_2O$ which, incidentally, corresponds to a compound of a trisaccharide and H_2SO_4. H. Fehling[4] claimed isolation of a compound $C_{90}H_{180}O_{90}(SO_3)_2BaO$, which would correspond to 15 glucose residues. It has been a common observation[5] that mineral acids effect a weakening of linen cloth, with the forma-

---

[1] From the thesis of George W. Rigby presented in partial fulfilment of the requirements for the degree of Master of Science, 1928.

[1a] As for example, those of A. E. Cashmore, *J. Chem. Soc.*, 718 (1927).

[2] H. Braconnot, *Ann. chim. phys.*, [2] **12,** 172 (1819).

[3] Blondeau de Caroles, *Ann.*, **52,** 412 (1844).

[4] H. Fehling, *ibid.*, **53,** 134–136 (1845).

[5] J. Kolb, *Bull. Mulhouse*, **38,** 922 (1868); A. Girard, *Compt. rend.*, **81,** 1105–1108 (1875); *Ann. chim. phys.*, **24,** 337–384 (1881); *Bull. soc. d'encourg.*, [3] **9,** 176–198 (1882).

tion of "hydrocellulose" in the same way that these acids affect cotton. H. de Mosenthal[6] has shown the "recovered" cellulose obtained by denitration of cellulose nitrate obtained from wood, ramie, flax and cotton to have approximately the index of refraction n_D, 1.5310. The specific heat[7] of linen is given as 0.321 and of cotton as 0.319, while the rotation of a copper–ammonium solution of the cellulose obtained from both sources is identical at $(\alpha)_D^{20} = 1000°$.[8] Furthermore, Schwalbe ("Die Chemie der Cellulose") has found highly purified flax cellulose and highly purified cotton cellulose to have practically no reducing properties.

Experimental

In order to secure the purest possible flax cellulose it was found entirely satisfactory to employ the general procedure recommended by the American Chemical Society for use with cotton.[9]

Flax fibers (obtained through courtesy of the Stevens Linen Works of Boston and of the Miles Linen Company of Salem, Oregon) were procured which previously had been retted, scutched and hackled. These fibers were thoroughly combed to remove all adhering woody tissue. At this stage the fibers showed a moisture content of 8%, which, however, is roughly proportional to the relative humidity. Analysis showed an ash content of 0.78% and an amount of wax extractable with hot petroleum ether of 1.65%, after which ethyl ether extracted 0.67% of wax. The same samples extracted with alcohol were found to contain 1.45% of a substance having the odor of burned sugar. (All of the alcohol extract was soluble in dilute alkali.) By the Cross and Bevan method 80.1% of cellulose was found.

About 200 g. of the thoroughly combed flax was placed in a large container filled with 1% Ivory soap solution on a steam table. The soap solution was changed daily and the fibers were thoroughly washed before being placed in a new solution. The preliminary soap treatment was deemed complete when, after being in contact with the fibers for a day, the solution remained colorless and the fibers themselves were leached to a very light yellow color. The washed and air-dried material showed: moisture, 7 to 8%; ash, 0.13%; petroleum ether extract, 1.28%; ethyl ether extract, 0.32%; alcohol extract, 0.84%; cellulose (Cross and Bevan), 90 to 95%.

In order to remove all extraneous material before the final purification, the soap-leached fibers were treated directly with 10% sodium hydroxide

---

[6] H. de Mosenthal, *J. Soc. Chem. Ind.*, **26**, 447 (1907).

[7] O. Dietz, *Wachbl. papier fabr.*, **43**, 3119 (1912).

[8] A. Levallois, *Compt. rend.*, **99**, 1122 (1884); *ibid.*, **100**, 456 (1885); K. Hess and E. Messmer, *Ber.*, **55**, 2432 (1922).

[9] Report of Committee of the American Chemical Society, *J. Ind. Eng. Chem.*, **15**, 748 (1923).

and gaseous chlorine, as in the Cross and Bevan method for estimating cellulose. Bleaching was best effected by using 100-g. samples and continuing the bleach for fifteen-minute intervals, followed by washing and treatment with sodium bisulfite, the process being repeated until a perfectly white, homogeneous material was obtained. The air dry fibers were then subjected to extraction in a Soxhlet apparatus with ethyl ether for eighteen hours, followed by a similar treatment with ethyl alcohol.

Final purification was effected in an apparatus exactly similar to that recommended for making "standard cellulose," the alkali treatment being continued for as much as a week without interruption.[9] In the case of flax the chlorine bleach was found necessary since experiments performed without bleaching, as recommended by Corey and Grey,[10] did not give a homogeneous product. In passing it is significant to note, however, that fibers purified without bleaching yielded cellobiose octa-acetate in spite of their obvious impurity. This result is striking since L. E. Wise[11] has claimed the formation of cellobiose octa-acetate from wood pulp to be an indication of the identity of wood cellulose and cotton. Furthermore, J. C. Irvine[12] points out that with esparto-cellulose "in no case was cellobiose octa-acetate obtained from material which had not been fully exhausted with alkali."

Purified flax cellulose was perfectly white, soft and very lustrous. All of the original long bast fibers were disintegrated into short lengths due to removal of the intercellular matter. The pure flax cellulose was entirely a hexose cellulose, since distillation with 12% hydrochloric acid and subsequent calculation of the phloroglucide by Kröber's tables gave only 1.13% of pentosans, while purified cotton gave 0.95% calculated as pentosans. The pure cotton showed a moisture content of 4.0% when dried at 100° to a constant weight and also when dried over phosphorus pentoxide, while flax cellulose under similar conditious showed 3.5% moisture. Halides, sulfur, phosphorus and nitrogen were definitely absent. The ash content in both cases was negligible.

Having obtained a highly purified flax cellulose and a generous supply of purified cotton (furnished by the Eastman Kodak Company, copper reduction value 0.001, ash content 0.0001%, α-cellulose 99%), the next problem was to compare the structure of flax cellulose with that of cotton cellulose. This was accomplished first by the method of methylation.

The method adopted was essentially the same as was used by Denham.[13] In no case was copper-ammonium used to remove lower methylated derivatives. The first four methylations were made using 30% aqueous

[10] A. B. Corey and H. L. Grey, *Ind. Eng. Chem.*, **16**, 853, 1130 (1924).

[11] L. E. Wise and others, *J. Ind. Eng. Chem.*, **15**, 711–713, 815–818 (1923).

[12] Irvine and Hirst, *J. Chem. Soc.*, **125**, 15 (1924).

[13] W. S. Denham, *J. Chem. Soc.*, **119**, 77 (1921); W. S. Denham and H. Woodhouse, *ibid.*, 111, 244 (1917).

sodium hydroxide and in the later treatments 30% methyl alcoholic potassium hydroxide was used. After three methylations the methoxy content, as determined in a modified Pregl semi-micro methoxy determination outfit, showed 23.6% of methoxy groups. After the fifth treatment, analysis showed 41.1% of methoxy groups. In all treatments the methyl sulfate was dissolved in ether before adding.

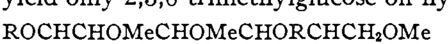
After 18 treatments the methoxy content had risen to 44.7% and continued methylation up to 26 treatments failed to exceed this maximum. The theoretical for trimethylcellulose is 45.6%—this figure, however, having never been reached by any investigator because of experimental difficulties.

Simultaneous hydrolysis and condensation of the methylated cellulose with methyl alcohol in a sealed tube, using 1% hydrochloric acid in methyl alcohol according to the directions of Irvine,[14] gave a clear liquid from which was obtained a golden-yellow sirup of n_D, 1.4632. Since this index of refraction was comparatively low, the sirup was thought to be a mixture of trimethyl- and dimethylglucose. Fractional distillation under 0.003 mm. pressure yielded a perfectly clear and colorless sirup which was collected in three fractions. The first fraction failed to show any tetramethylmethylglucose. This derivative would have been evident by a depression of the index of refraction and an elevation of the methoxy content. The constants obtained for the first and second fractions are compared, for convenience, with the accepted constants for 2,3,6-trimethylmethylglucose in the following tabulation:

Found (first and second fraction) n_D, 1.4592; $(\alpha)_D^{23}$, 67.1° for $c = 0.669$; MeO, 51.6%.
Accepted constants n_D, 1.4583; $(\alpha)_D^{20}$, 66.1° for $c = 1.34$; MeO, 52.6%.

The third fraction was found to be a mixture of 2,3,6-trimethylmethylglucose and of the dimethyl derivative. No 2,3,5-trimethylmethylglucose was found.

The conclusion is therefore drawn that completely methylated cotton and flax cellulose yield only 2,3,6-trimethylglucose on hydrolysis



$$\mathrm{RO\underbrace{CHCHOMeCHOMeCHORCH}_{O}CH_2OMe}$$

The formation of only 2,3,6-trimethylglucose from both cotton and flax cellulose indicated a similarity between the two, but reveals nothing of the size of the molecule. Furthermore, starch has been found to yield only 2,3,6-trimethylglucose, hence the next step was to prepare cellobiose octa-acetate from both cotton and flax and compare the yields.

As early as 1901, Skraup and König[15] noted that filter paper, from which they prepared cellobiose octa-acetate, consisted of a mixture of cotton and linen fibers. This result indicates that the presence of linen fibers did

[14] J. C. Irvine and E. L. Hirst, *J. Chem. Soc.*, **123**, 518 (1923).

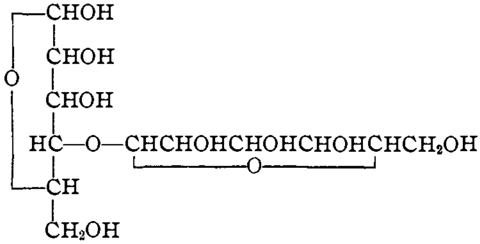
[15] Z. H. Skraup and J. König, *Monatsh.*, **22**, 1011–1036 (1901).

not hinder the formation of cellobiose octa-acetate, but does not necessarily show that cellobiose octa-acetate was actually prepared from flax. In the present investigation the work of Skraup and König was, therefore, repeated, using highly purified flax cellulose.

Cellobiose octa-acetate was prepared from flax cellulose both according to the directions of Skraup and König[16] and after the method of Haworth and Hirst.[17]

Five grams of flax cellulose yielded, after four recrystallizations from hot 95% alcohol, two grams of cellobiose octa-acetate. This yield is exactly comparable with that obtained from pure cotton under parallel conditions.

Eighteen successive crystallizations from 95% alcohol yielded a material, m. p. 233.9° (corr.), showing no depression when mixed with an authentic sample prepared from cotton. In chloroform solution the rotation was found to be $(\alpha)^{23}_{\mathrm{D}} + 40.9°$ for $c = 5.452$ and $(\alpha)^{23}_{\mathrm{D}} + 41.4°$ for $c = 7.834$ in chloroform. C. S. Hudson[18] reports $(\alpha)^{20}_{\mathrm{D}} + 41.95°$ for $c = 9.87$ and $(\alpha)^{20}_{\mathrm{D}}$, $+ 40.87°$ for $c = 5.85$ in chloroform. As further identification the acetate was saponified in the cold with alcoholic sodium hydroxide and the phenylosazone of the liberated cellobiose prepared, m. p. 207–208°. Schliemann[19] gives 208–211° (corr.) as the melting point. Thus the cellobiose residues may be considered as integral parts of the flax cellulose molecule, as surely as of the cotton cellulose molecule.



Finally it was found that the flax cellulose molecule must contain at least three glucose residues. The method adopted was graded acetolysis after the directions of Irvine.[20] There was obtained by this method at the end of 168 hours a mixture of acetates of a trisaccharide and of an anhydro-trisaccharide, just as in the case of cotton after 100 hours. Six recrystallizations produced by dissolving the acetate in alcohol and precipitating with water yielded a material showing $(\alpha)^{23}_{\mathrm{D}} +19.6°$ for $c = 10.608$ and $(\alpha)^{23}_{\mathrm{D}} +19.2°$ for $c = 1.721$ in chloroform. Irvine reports $(\alpha)^{20}_{\mathrm{D}} +19.4°$ for $c = 2.58$ in chloroform solution. The acetate

[16] H. Skraup and J. König, *Ber.*, **34**, 1115–1118 (1901).

[17] W. N. Haworth and E. L. Hirst, *J. Chem. Soc.*, **119**, 197 (1921).

[18] C. S. Hudson and J. M. Johnson, This Journal, **37**, 1276 (1915).

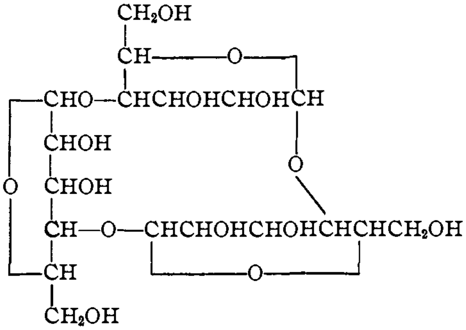
[19] W. Schliemann, *Ann.*, **378**, 366–381 (1910).

[20] J. C. Irvine and G. J. Robertson, *J. Chem. Soc.*, **128**, 1496 (1926).

is very soluble in cold 95% alcohol. Cellulose triacetate gives $(\alpha)_D^{20}$ $-22.3°$ with $c = 0.8092$ in chloroform solution and is insoluble in hot 95% alcohol. Cellobiose octa-acetate α-form is soluble in hot alcohol, but insoluble in the cold and gives a specific rotation of $(\alpha)_D^{20}$ $+41°$. The β-form is more soluble in cold alcohol, but has $(\alpha)_D^{22}$ $-14.48°$ for $c = 10.88$ and m. p. 202°.

The above described acetates were also obtained by fractional crystallization of the alcohol mother liquor from preparations of cellobiose octa-acetate, after the method of Bertrand and Benoist.[21] Parallel experiments using pure cotton completed the evidence that graded acetolysis yielded the same product from both cotton and flax cellulose.

Hence the unit structure for both cotton and flax cellulose, to the best of our present knowledge, may be represented by an anhydro-trisaccharide formula as proposed by Irvine.



Summary

From the above reported results the following general conclusions are proposed:

1. Flax bast fibers consist of cells composed of pure cellulose and an intercellular material containing a furfural-yielding constituent.
2. The glucose residues in flax cellulose are joined together in positions one and four by glucoside linkages, as are those in cotton.
3. Cellobiose is obtained from flax cellulose in yields equivalent to those from cotton. This assures that at least two glucose residues are combined in the cellulose and suggests that probably at least three are combined in a unit from which the cellulose molecule is constructed—as proposed by J. C. Irvine.
4. Acetates of a trisaccharide and of an anhydro-trisaccharide may be obtained from flax cellulose. This supports the proposed anhydro-trisaccharide unit formula.
5. The above submitted results point to the chemical identity of cotton

---

[21] G. Bertrand and S. Benoist, *Compt. rend.*, **177**, 85–87 (1923); *ibid.*, **176**, 1583–1587 (1923).

and flax cellulose, without reference to the relative states of polymerization.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORIES OF SHARP AND DOHME]

CATALYTIC REDUCTION OF NITRILES AND OXIMES

BY WALTER H. HARTUNG

RECEIVED AUGUST 30, 1928 PUBLISHED DECEMBER 10, 1928

In a study undertaken in this Laboratory it became desirable to reduce oximes and nitriles catalytically to pure primary amines. A review of the available literature showed that a large amount of research has been done on this type of reduction but that invariably a mixture of primary and secondary bases was obtained, with the latter often predominating.

Benzonitrile and benzaldoxime when reduced by gaseous hydrogen with palladium or nickel catalysts gave mixtures of benzylamine, dibenzylamine and ammonia.[1] From α- and β-naphthonitriles, phenylacetonitrile and β-phenylpropionitrile, Rupe and his coworkers obtained mixtures of the corresponding primary and secondary amines with ammonia. From acetaldoxime and propionaldoxime triethyl- and tripropylamines, respectively, and ammonia were obtained, while from benzophenone-oxime Paal and Gerum isolated a 57% yield of primary amine. Mignonac[2] obtained ketimines from the oximes of cyclohexanone, acetophenone and propiophenone. Braun, Blessing and Zobel,[3] by reducing nitriles in various non-aqueous solvents, found that they obtained both primary and secondary amines, the amount of each depending on the concentration and on the nature of the solvent. Vavon and Berton[4] report that cyclic ketoximes reduced with platinum from hydroxylamines.

Rosenmund and Pfankuch[5] were the first to forestall the formation of secondary amine by using the acetate of the oxime and an acetic acid solution of the nitrile. Thus benzaldoxime acetate gave a 91% yield and benzonitrile an 80% yield of benzylamine, benzylcyanide gave a 73% yield of phenylethyl amine, while *p*-hydroxybenzylcyanide again formed secondary amine.

Hence it appears that except for the methods of Rosenmund and Pfankuch and Carothers and Jones,[6] there is no known general procedure for

---

[1] (a) Paal and Gerum, *Ber.*, **42**, 1553 (1908); (b) Rupe and Beckerer, *Helv. Chim. Acta*, **6**, 880 (1923); (c) Rupe and Glenz, *ibid.*, **5**, 937 (1922); (d) Rupe and Hodel, *ibid.*, **6**, 865 (1923); (e) Gulewitsch, *Ber.*, **57**, 1645 (1924).

[2] Mignonac, *Compt. rend.*, **170**, 936 (1920).

[3] Braun, Blessing and Zobel, *Ber.*, **56**, 1988 (1923).

[4] Vavon and Berton, *Bull. soc. chim.*, **37**, 296 (1925).

[5] Rosenmund and Pfankuch, *Ber.*, **56**, 2258 (1923).

[6] Carothers and Jones, THIS JOURNAL, **47**, 3051 (1925), using platinum catalyst in acetic anhydride solvent, reduced several nitriles to the corresponding primary amines,