XVI.—*The Chemistry of Bast Fibres.*

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At the time of publication of the first account of our researches on this subject,* we had established the following points:—

(a.) The chemical similarity between the “non-cellulose” constituents of monocotyledonous and dicotyledonous fibres. (b.) The resolution of the jute fibre by the action of chlorine, into cellulose† on the one hand, and an aromatic body on the other, which was isolated

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† In respect to the term cellulose we would observe that we attach to it only a general significance, analogous, *e.g.*, to that of the term alcohol. It is probable, as has been held by certain chemists, and confirmed by our observations, that there are numerous celluloses standing probably in both polymeric and isomeric relations to one another, and that jute cellulose may be a mixture of these. We apply the term to the aggregate isolated by any particular method, which gives the reactions generally accepted as those of pure cellulose.

in the form of the chloro-derivative, $n(\text{C}_{19}\text{H}_{18}\text{Cl}_4\text{O}_9)$, a similar derivative being obtained from all the bast fibres (flax, hemp, manilla, &c.) examined by us, and likewise from esparto. (c.) A sufficient resemblance of the reactions of these derivatives to tetrachlorquinone to lead to the hypothesis of their being complicated derivatives of this body. (d.) The resolution of the jute fibre by boiling with dilute hydrochloric and sulphuric acids into a soluble carbohydrate, and an insoluble compound of the aromatic body, in the form of a condensed modification, with the more stable form of the cellulose. (e.) The action of dilute nitric acid on the other hand, in resolving the fibre into cellulose and a nitro-derivative of the aromatic constituents, which we investigated by way of the similar product of nitration of the esparto constituents, and found to possess the formula $n\text{C}_{25}\text{H}_{31}(\text{NO}_2)\text{O}_{23}\text{H}_8$, eight of the hydrogen-atoms being replaceable by metals. (f.) The absence of any constituent of the nature of pectose, which we established by the study of the action of boiling dilute alkalis (see page 99). (g.) By inference from these facts, under the guidance of analogy, we had further established the hypothesis that the jute fibre consists of cellulose intimately associated with a complicated body allied to the quinones, that it is in fact a "cellulide" constituted after the type of the glucosides, the aromatic body being united in this case to a cellulose in place of glucose.

In addition to these main features, the following points were incidentally observed:—

(h.) The brilliant colour-reactions of the chlorinated derivatives when freshly prepared, and their application to the detection of bast or bast constituents. (i.) The homogeneity of the jute fibre as regards the relative distribution of cellulose and aromatic bodies, and on the other hand the non-homogeneity of the cellulose isolated from the fibre by the usual methods. (k.) The advantage of substituting for the estimation of cellulose, in place of Müller's method, that of chlorination and removal of the chlorinated bodies by solution in alkalis; and (l) the increase of yield which follows from the further modification of exposing the chlorinated fibre to the action of sulphurous acid previously to the alkaline treatment.

This general view of the chemistry of bast fibres has been substantiated by our subsequent work, and in the solution of the more important special problems which it involves we have made sufficient progress to be able to lay before the Society a fairly adequate account of this branch of plant chemistry.

To the aromatic constituent of the jute fibre we may assign the formula $n(\text{C}_{19}\text{H}_{22}\text{O}_9)$. The resemblance of this to that of catechin,

is so close, that a comparative investigation of the suggested relationship to this body was necessary. Catechu was treated in the usual way for the separation and isolation of catechin and catechutannic acid. The crude products were severally treated with HCl and KClO_3 until the action was complete, and the chlorinated derivatives were isolated by the usual process of purification, *i.e.*, alternate solution in alcohol and precipitation with water, finally dissolving in absolute alcohol, filtering, and distilling off the alcohol. The analysis of these bodies gave the following results: (α) catechin derivative; (β) catechutannic acid derivative.

(α .)	0.2570	gram	yielded	0.2350	gram	AgCl	and	0.0132	gram	Ag.
(β .)	0.3240	"		0.2980	"	AgCl	"	0.0107	"	Ag.
(α .)	0.3010	"		0.4420	"	CO_2	"	0.0860	"	H_2O .
(β .)	0.3000	"		0.4375	"	CO_2	"	0.0845	"	H_2O .

	(α .)	(β .)	Calc. $\text{C}_{20}\text{H}_{19}\text{Cl}_4\text{O}_{12}$.
Cl	24.3	23.8	23.8
C	40.0	39.8	40.2
H	3.2	3.1	3.1

The products were therefore identical, and their resemblance to the before-mentioned derivatives was unmistakeable. In addition, the freshly prepared bodies gave a brilliant magenta reaction with sodium sulphite.

In the light of these results we examined a specimen of jute, rotted by shipment in the damp state, which fortunately came to hand at the moment. The aqueous extract was brown, astringent to the taste, and, at the same time, strongly acid to test-paper. It was concentrated by evaporation, digested with barium carbonate, and filtered. To the filtrate an equal bulk of strong alcohol was added, by which a flocculent precipitate was formed: this was purified by fractional precipitation with alcohol, washed with alcohol and dried, first over sulphuric acid, lastly in the air-bath at 105° . The analysis of this salt gave the following results:—

0.3735 gram gave 0.1582 gram BaSO_4 .
 0.4095 " " 0.4280 " CO_2 , 0.1477 BaCO_3 , and 0.1430 H_2O .

		Calc. $\text{C}_{29}\text{H}_{42}\text{O}_{29}\text{Ba}_2$.
C	30.6	30.8
H	3.9	3.7
Ba	24.9	24.3

It was quite insoluble in boiling alcohol, and gave no reaction with chlorine and sodium sulphite. On boiling for some time with water, it dissolved, partly separating on cooling in a gelatinous form. The

solution of the salt was accompanied by change, the gelatinous body, *i.e.*, the free acid, having no action on alkaline copper solution, whereas the portion remaining dissolved exerted a reducing action. Analysis of the latter showed it to be similar to the above, but somewhat richer in oxygen. The ratio of carbon to oxygen is that which is characteristic of the pectic group. These facts are sufficient to establish the identity of the acid.

Determinations of cellulose in specimens of the rotted fibre yielded the following percentages: 57, 58.5, 64, 66, showing that the cellulose-yielding constituent has been degraded with formation of the soluble bodies in question.

The alcoholic filtrate from the original precipitate was evaporated to dryness, and the residue exhausted with strong alcohol. From the solution, filtered and evaporated, a substance was obtained whose aqueous solution gave the following reactions: a dark brownish-green precipitate with ferric chloride; an orange-coloured flocculent precipitate with bromine-water; the characteristic magenta reaction with chlorine and sodium sulphite; a copious precipitate with gelatin;—it was moreover strongly astringent to the taste and mordanted cotton, *i.e.*, imparted the property of dyeing fast colours with aniline dyes. The substance dried at 105° was analysed with the following results:—

0.2040 gram gave 0.3831 CO₂ and 0.1045 H₂O.

		Calc. C ₂₆ H ₃₄ O ₁₆ .
C	51.7	51.8
H	5.7	5.6

This body is therefore proved to be a member of the tannin group. In indirect confirmation of this conclusion, we fused a quantity of the esparto resin previously described (*Chemistry of Bast Fibres*, p. 22) with potash, and isolated the products in the usual way. Phloroglucol was obtained in sufficient quantity for qualitative identification only; on the other hand, a considerable quantity of protocathechuic acid was formed. The recrystallised product was analysed with the following result:—

0.1580 gram gave 0.3150 gram CO₂ and 0.0525 H₂O.

		Calc. C ₇ H ₆ O ₄ .
C	54.4	54.5
H	3.7	3.8

The reactions and melting point were moreover those of pure protocathechuic acid.

The general identity of these non-cellulose constituents with the class of astringent substances, or tannins, is thus fully established.

In what relationship they stand to the prototype, gallo-tannin or digallic acid, is a problem which remains to be solved for them as for the entire group. All that can be said with certainty, is that the molecule of these bodies is extremely large. Their existence in plants in the closest union with cellulose, we shall discuss hereafter.

In connection with the foregoing, we have to describe certain observations on the halogen-derivatives of these bodies, additional to those previously discussed.

Determinations have been made of the yield of the chlorinated product ($C_{22}H_{23}Cl_4O_{10}$) of the action of $KClO_3$ and HCl upon pure esparto resin. Previously to the determinations, the specimen was dissolved in hot glacial acetic acid; the portion (β) which separated out on cooling was collected separately, redissolved, and precipitated with water, then washed and dried. The portion (α) remaining dissolved in the acetic acid was also precipitated with water, washed, and dried.

$(\alpha.)$ { 0.5000 yielded 0.3350 gram Cl compound.				
	0.5000	„	0.3380	„ „
$(\beta.)$	0.5000	„	0.3370	„ „

The percentage yielded in the three cases is uniformly 67.

The crude esparto resin, *i.e.*, as precipitated from the alkaline liquors of the paper-maker and washed with cold water, gives up a certain quantity of substance to boiling water. The first extract, in one experiment, gave with bromine-water an orange-coloured precipitate of a highly brominated body, $n(C_{17}H_{14}Br_4O_6)$ (α); the third extract gave a similar product, $n(C_{15}H_{12}Br_4O_6)$ (β).

The analysis of these bodies is appended.

$(\alpha.)$ 0.6855 gram gave 0.8085 AgBr and 0.0032 Ag.				
	0.2487	„ „	0.2905 CO_2	„ 0.0475 H_2O .

Calc. $C_{17}H_{14}Br_4O_6$.

C	31.8	32.1
H	2.1	2.2
Br.....	50.5	50.4

$(\beta.)$ 0.3185 gram gave 0.3995 AgBr and 0.0032 Ag.				
	0.1225	„ „	0.1370 CO_2	„ 0.0235 H_2O .

Calc. $C_{15}H_{12}Br_4O_6$.

C	30.5	30.4
H	2.1	2.0
Br.....	54.1	54.0

A second portion of this third extract was evaporated to a small bulk; and the brown plastic substance which separated was dissolved

in alkali and precipitated as a chlorinated body, by a stream of chlorine gas (α). The residue from the repeated extraction was treated with KClO_3 and HCl (β). Both products were dissolved in glacial acetic acid and filtered, and the solution was poured into a large quantity of a clear solution of bleaching powder: the precipitates collected, purified, and analysed after drying at 100° .

(α.) 0.4365 gram gave 0.4085 AgCl and 0.0080 Ag.			
0.2300	"	"	0.0795 H_2O " 0.3830 CO_2 .
(β.) 0.5745 " " 0.5665 AgCl " 0.0045 Ag.			
0.2470	"	"	0.0995 H_2O " 0.4090 CO_2 .
Calc. $\text{C}_{22}\text{H}_{28}\text{Cl}_4\text{O}_{10}$.			
C	45.4	45.1	44.7
H	3.8	4.4	3.9
Cl	23.8	24.6	24.1

These products are therefore identical with one another and with the derivative described in our original paper. The results are interesting for their uniformity, as showing that constant results are obtainable, at least in what are end-products, even although the physical properties of the substances dealt with are difficult of definition.

From the aromatic constituent of the esparto fibre, two other halogen-derivatives have been prepared as follows:—*Bromine compound*: by heating the purified resin in acetic acid solution with bromine, precipitating with water, redissolving in acetic acid, and heating again with bromine, precipitating, and purifying in the usual way. *Chlorine compound*: by heating esparto, cut into small pieces, with chlorine gas; extracting with alcohol and purifying as in previous cases. The analyses gave the following results:—

0.3115 gram gave 0.2755 AgBr and 0.0047 Ag.			
0.2350	"	"	0.3335 CO_2 " 0.0735 H_2O .
0.1910	"	"	0.2750 CO_2 " 0.0565 H_2O .
Calc. $\text{C}_{27}\text{H}_{28}\text{Br}_4\text{O}_{10}$.			
C	38.7	39.2	38.9
H	3.5	3.3	3.4
Br	38.7	—	38.4

Chlorine compound:—

0.3055 gram gave 0.2480 AgCl and 0.0090 Ag.			
{ 0.2515	"	"	0.4335 CO_2 " 0.1220 H_2O .
{ 0.1650	"	"	0.2825 CO_2 " 0.0715 H_2O .

			Calc. $C_{27}H_{33}Cl_4O_{12}$.
C	47.0	46.7	46.8
H	5.4	4.8	4.8
Cl	21.0		20.6

The action of chlorine on the jute fibre has been discussed at length in our original paper. We have since investigated the action of caustic alkalis upon the resulting derivative, $C_{19}H_{18}Cl_4O_9$. A specimen of the pure preparation was dissolved in a warm solution of potassium hydrate, the solution acidified with hydrochloric acid, and the resulting precipitate collected, washed, and dried. It was purified by solution in absolute alcohol and precipitation with water: it was lastly dried at 105° and analysed, with the following results:—

0.3620 gram gave	0.2310 AgCl	and	0.0077 Ag.
0.2940 „ „	0.1750 AgCl	„	0.0190 Ag.
0.2920 „ „	0.5345 CO_2	„	0.1300 H_2O .
0.2445 „ „	0.4410 CO_2	„	0.0990 H_2O .
			Calc. $C_{18}H_{20}Cl_2O_8$.
C	49.9	49.2	49.6
H	4.9	4.5	4.6
Cl	16.5	16.8	16.3

By the action of potash, therefore, two of the chlorine-atoms have been removed, as in the case of chloranil. The further slight incidental changes in composition which prevent our representing the reaction by the symmetrical equation of saponification, are characteristic of these complex amorphous bodies.

The action of bromine on the jute fibre we had investigated only as a method (Müller's) of preparing pure cellulose, and we found that it was characterised by the formation of brominated derivatives of the aromatic constituents; but it was impossible to isolate them in any quantity. A portion of the fibre was therefore treated with dilute nitric acid (5 per cent.) at 60° , washed, and exhausted with caustic soda solution. The solution was acidified with hydrochloric acid, the precipitate collected, washed, and dissolved in alcohol. Bromine was then added, and the solution allowed to stand some time. On adding water, a flocculent precipitate of the brominated derivative was obtained; this was purified in the usual way and then analysed.

{ 0.2880 gram gave	0.1555 AgBr	and	0.0052 Ag.
{ 0.2780 „ „	0.1500 AgBr	„	0.0032 Ag.
0.2465 „ „	0.4210 CO_2	„	0.0940 H_2O .
			Calc. $C_{26}H_{28}Br_2O_{11}$.
C	46.6		46.2
H	4.2		4.1
Br (mean of 2) ..	23.9		23.7

The similarity of this to the derivatives of the esparto constituent is noteworthy: that only two atoms of bromine have been introduced is due to the fact that the action took place in the cold.

In regard to the actual constitution of these derivatives we have no very direct evidence: all our efforts to resolve them proximately into bodies of known constitution have hitherto failed. The action of nitric acid, though interesting, is too destructive to throw light on the problem: the chlorinated compounds yield chloropicrin in some quantity, and an amorphous nitro-body resembling that described in our original paper. The colour-reactions of many of them are remarkably pure, and, as we have often observed, so closely similar to those of chloranil, that, taken in conjunction with the fact that they contain 4 atoms of the halogen, the conclusion is almost inevitable that the molecule is built up around this body as a centre. Nor is this supposition without other foundation (see also p. 109) (*f*). An inspection of the constitutional formula proposed for catechin by Etti,

$$\text{C}_6\text{H}_2(\text{OH})_2 < \begin{array}{c} \text{CO} \cdot \text{C}_6\text{H}_7(\text{OH})_2 \\ \text{O} \cdot \text{C}_6\text{H}_3(\text{OH})_2 \end{array}$$
 shows that the formation of quinone-

derivatives by the chlorination of these astringent bodies is, *à priori*, most probable. If chloranil is boiled with sugar or even cellulose and water, it dissolves to a violet liquid; this solution is astringent to the taste, gives a copious precipitate with gelatin, and a dark brownish-green precipitate with ferric chloride. Moreover, on evaporation, it deposits a brown substance, which, after solution in ammonia, is precipitated by bromine-water as orange-coloured flocks of a compound exactly resembling those before described. If the action of the chloranil upon the sugar takes place in sealed tubes at 100° , there is a considerable yield of this brown substance, which behaves with alkalis and chlorine exactly like the aromatic substances obtained from bast fibres. The complexity of these bodies, which is certainly greater than that indicated by the proportional formula given above, and the absence of any strongly marked physical characteristics, are the difficulties which impede our progress.

We have now to consider the wider problem of the relation of the cellulose to the non-cellulose constituents of bast fibres, and the relation of both to the life of the plant. In these points, as might have been expected, we have been to a certain extent anticipated by the investigations and inferences of physiological botanists, notably in respect of the origin of the tannins. On this occasion we do not think it expedient to enter into an exhaustive discussion of this aspect of the subject, but must content ourselves with giving a brief account of the current theories of the biologists, for which we have referred to the works of Sachs (*Handb. der Exper. Phys. der Pflanze* [1865]) and Sachsse (*Farbstoffe, Kohlehydrate und Proteinsubstanzen* [1877]).

According to these observers, cellulose is directly derived from starch, or from its physiological equivalents, sugar, fat, or inulin, and is not a product of resolution of a proteid molecule. This conversion of starch into cellulose is always accompanied by the evolution of carbonic anhydride (Sachsse, p. 113), and the interdependence of these phenomena has been clearly demonstrated by the researches of Sachsse on the germination of *Pisum sativum*. The chemical changes attending this transformation are expressed by the following statistical equation (Sachsse),

$$n(\text{C}_6\text{H}_{10}\text{O}_5) = n(\text{C}_5 + \text{O}_4 + \text{H}_{10-x} + \text{CH}_x\text{O}),$$

or more explicitly as a result of the observations that $\frac{5}{6}$ ths of the carbon of the starch underwent complete combustion :

$$n(\text{C}_{36}\text{H}_{60}\text{O}_{30} + 30\text{O}) = n(30\text{CO}_2 + 24\text{H}_2\text{O} + \text{C}_6\text{H}_{12}\text{O}_6).$$

The molecule, $n\text{C}_6\text{H}_{12}\text{O}_6$, is then further transformed, probably by dehydration, into substances having the atomic ratio $\text{C}_6\text{H}_{10}\text{O}_5$. By these researches it is also shown that the growth of the plant, i.e., the formation of cellular tissue, and its respiration, are parallel phenomena. As regards the relation of these transformations to the chlorophyll of the plant, and those functions with which it is more especially associated, the explanation here given is entirely in harmony with the observations that, in the majority of cases, the formation of cellulose occurs in those portions from which chlorophyll is absent, whereas the formation of the parent substance, starch, is associated with the presence of chlorophyll and the evolution of oxygen. The lignification of fibres originally consisting of pure cellulose, is held by Sachs (*ibid.*, p. 369) to consist of a modification of the cell-substance (cellulose) itself, and not of infiltration of substances from the contents of the cell. The chemistry of such metamorphoses is indicated by a comparison of the composition of lignin ($\text{C}_{18}\text{H}_{24}\text{O}_{10}$) with that of cellulose ($\text{C}_{18}\text{H}_{30}\text{O}_{15}$), showing that there must occur, in addition to dehydration ($3\text{H}_2\text{O}$), a loss of oxygen (O_2). This latter probably takes the form of a more highly oxidised carbon-compound, the resolution being expressed by the following equation (Sachsse) :—

Sachsse is of opinion that it is to this more highly oxidised molecule that the origin of the tannins may be referred; this conclusion, however, is scarcely warranted by the equations, and as we shall presently show a much more probable mode of formation of these bodies, it must give way before a more consistent hypothesis. This is afforded by the observation of the presence in plant-structures of the pectic

group of compounds, the composition of which is much more in harmony with the equation given.* In our first paper we drew attention to a paper of Kolb's (*Bull. Soc. Ind. Mulh.*, June, 1868, and *Ann. Chim. Phys.* [4], **14**, 348) on the linen fibre, in which he established the presence of a substance (about 20 per cent.) in the fibre, removable by alkalis in the form of pectic acid. On further examining his statements we find that the fibre used by him was a specimen of raw Russian flax, having the following aggregate composition (CH):—

C	43·7
H	5·9

It is obvious from these numbers that this particular fibre represented a different class from that to which jute belongs, viz., one in which the development has taken the course of converting the cellulose into bodies of lower carbon percentage. It is therefore easy to see that the results of Kolb's researches on the one hand, and our different experience with jute bast on the other are reconcilable, both with one another, and with the hypothesis given above, which is thereby strengthened.

We may here mention that that portion of the fibre known as jute "cuttings," that is to say, the root ends, containing a considerable proportion of bark, yields pectic acid when treated under pressure with a dilute solution of sodium sulphite. It is probable therefore that in the development of the jute fibre, pectous substances are likewise formed, but are transferred from the bast to the other portions of the plant.

In respect of the origin of the astringent bodies, so widely distributed throughout plant-structures, Sachs maintains, on physiological grounds, that they are degradation-products, probably of cellulose, which when formed take no further part in the metabolism of the plant, but, like urea in the animal body, are to be regarded as excreta.

If now the celluloses and the tannins are extreme terms of developmental series, it devolves upon the chemist to throw light upon the intermediate stages of the transformation, and so complete the demonstration of the biologists.

The chemical composition of the jute fibre contributes very much to the elucidation of this point, and therefore of the whole problem. The action of chlorine has been already described as effecting the resolution of the fibre into extreme products: the study of the intermediate terms of the natural series, as well as the condition of existence of the fibre substance, must be approached through the action of less drastic reagents; of these dilute sulphuric acid (5 per

* Metapectic acid is represented by the formula $C_8H_{14}O_9$.

cent.) at 80—90° C. is the most important. We have already described the soluble product of resolution of the fibre by this reagent, as a neutral body, soluble in alcohol, and, according to analysis, a carbohydrate. We have since prepared and analysed a further quantity of this substance (or mixture of substances) with the following result:—

(α .) Dried at 90°—

0.2805 gram gave 0.4575 CO₂ and 0.1580 H₂O.

		Calc. C ₁₂ H ₂₀ O ₁₀ .
C	44.4	44.4
H	6.2	6.2

(β .) Dried at 105°—

0.2460 gram gave 0.4220 CO₂ and 0.1350 H₂O.

		Calc. C ₁₂ H ₁₈ O ₉ .
C	46.8	47.0
H	6.1	5.9

(It will be observed that the aggregate composition of this substance differs but little from that of the jute itself.) The ratio H₂ : O is maintained; the substance also evinces the strong tendency to dehydration (condensation) which is characteristic of bodies of this class. Observations showed that it was not susceptible of alcoholic fermentation, and was without action on polarised light. On boiling this substance with dilute sulphuric acid in a retort it was resolved into acetic acid and furfural, which distilled, the yield of the latter being considerable, and a residue, which separated in the insoluble form, of substances yielding characteristic chlorination-products. We then made observations upon sugar, and found that when it was treated with strong sulphuric acid, and afterwards diluted and distilled, we obtained precisely the same products of resolution, confirming the conclusion therefore that a carbohydrate was present in the soluble modification of the jute fibre.

Reverting now to the action of the dilute acid upon the normal fibre, it is remarkable that the formation of the soluble modification occurs at so low a temperature as 80—90°. Moreover we found that, by successive digestions with the acid at temperatures below 100°, the greater portion of the fibre could be dissolved away in the form of this compound, and that when nine-tenths of its substance had been so removed, exposure to chlorine still caused the characteristic resolution into cellulose and chlorinated aromatic bodies. As regards the structural changes which accompany this modification, it is remarkable that the union of the fibrils into bundles remains unresolved, the appearance being that figured in our original paper (Fig. *d*). On examining this disintegrated fibre, we found that it yielded on analysis

the same percentage of cellulose as the normal fibre; thus from three specimens we isolated severally 74.4, 76.3, and 78 per cent. This result is remarkable, and is confirmed by the following additional observations:—

Four specimens of the same fibre were exposed to the action of 10 per cent. sulphuric acid at 95°. The loss sustained after 16 hours' treatment was 27.7, 28, 26.4, and 26.6 per cent. respectively. Determinations of cellulose in two of the specimens thus modified gave the numbers 75.2 and 74.7 per cent. On combustion the modified fibre was found to contain 48.1 per cent. C and 5.9 per cent. H. Not only therefore was the yield of cellulose unchanged from that of the normal fibre, but the jute had undergone no alteration in respect of its aggregate composition. Putting all these facts together—(1) the resolution of the fibre at so low a temperature as 80–90° C. by a dilute acid, *i.e.*, under conditions which are practically without influence on cellulose; (2) the identity as regards aggregate composition, (CH), of the dissolved and undissolved portions both with one another and with the original fibre; (3) the unchanged yield of cellulose; (4) the absence of perceptible variation in composition of the fibre throughout its entire length;* and (5) the absence of disintegrating action on the bundles of fibrils—we are led to the conclusion that the jute fibre is composed for the most part, *not* of cellulose, but of a transition form of cellulose from that of the original carbohydrate to its ultimate modification of a soluble astringent. It is impossible to say, supposing this transformation to be accomplished through an infinite series of terms, how many of such terms may be represented in the fibre; it is possible that cellulose is present as such, a small quantity of a soluble astringent is always found in the normal fibre; and hence it is not unlikely that the entire series may be represented. The most rational view of the jute fibre is therefore, perhaps, that it is an average aggregate of the intermediate terms of this developmental series.

The uniform disposition of the fibre constituents is shown by the following determinations of the aggregate composition and yield of cellulose from different portions of the fibre.

Aggregate composition—

(α .) Extreme upper ends. (β .) Extreme root ends.†

	(α .)	(β .)
C	47.7	47.1
H	5.9	5.7

* Negatives the hypothesis of the constitution of the fibre out of a mixture of cellulose and “encrusting” substances. See also next page.

† The extreme lower portions of commercial jute, representing a distance of about 18 inches from the actual root.

Cellulose isolated from—

(a.)	(β.)
80.6 per cent.	79.9 per cent.

This uniformity of composition is visibly demonstrated, as we observed in our original paper, by treating entire lengths of the fibre (84 in.) with solutions of the aniline dyes, or of aniline sulphate. In either case a perfectly even distribution of the colour is observed, a fact which has very important technological* bearings; for as in the preparation of the fibre for spinning, very little of the averaging is resorted to, to which so much importance is attached in the manufacture of silk and wool yarns, it would be impossible to dye jute yarns successfully but for the regularity in composition of the fibre. The alternative view that it is made up of cellulose *mixed* with so-called encrusting matters is inconsistent with the foregoing chemical investigations; and a microscopic examination of the fibre mounted, after chlorination, in a solution of sodium sulphite, will satisfy every observer of the uniform distribution of the "potential tannin" throughout the fibre substance, which could scarcely obtain if it were present as an encrusting substance.

To sum up and give definiteness to the view which we have thus developed as more consistent with facts, as well as with the deductions of biologists, we propose to give the name of *Bastose* to this transition modification of cellulose, at the same time observing that as there are many celluloses, so there would be necessarily corresponding forms of bastose. This nomenclature may be extended to the aromatic derivatives, to which we propose to give the generic term *Bastin*. Both of these terms may be made specific by means of prefixes derived from the name of the plant from which the fibres are obtained: thus, e.g., we should use the names *Linobastose*, *Corchorobastose*, &c., &c.

It may be urged that we have as yet given no direct proof of the possible conversion of carbohydrates into aromatic bodies. There is, however, no lack of evidence on this point. Hoppe-Seyler (*Berl. Ber.*, 4, 15) for instance, found that by heating starch to high temperatures in presence of water, catechol was formed. The nitrocelluloses have been so often observed to degrade spontaneously into bodies of the pectic class, that Abel says on this point: "These substances have been so frequently obtained that they must be regarded as general products of the gradual decomposition of guncotton;" and meta-pectic acid, the last member of the series, has recently been shown to be resolved by fusion with potassium hydrate (Rochleder, *Zeitschr. f. Chem.* [2], 4, 381) into formic and protocatechuic acids.

* The technological bearings of these researches will be found treated by Dr. O. Witt and C. F. Cross in papers recently communicated to the *Soc. Ind. Mulhouse*.

This fact of the passage of cellulose into pectin,* we may also observe, is in harmony with the interpretation which we have given of Sachsse's equation for the chemical changes involved in lignification. There are also several observations of the direct transformation of cellulose into pectic bodies in nature which have been made by Frémy (*Compt. rend.*, **48**, 203), and Vogt (*Sitz. ber. Kais. Acad.*, **48**, 689). But perhaps the most conclusive proof of this transformation of carbohydrates into aromatic derivatives, is that which we recently communicated to the British Association (*Chem. Section Reports*, 1881). We found that by the action of concentrated sulphuric acid at 70°, cellulose (dextrin) was converted into a black substance containing 64.4 per cent. C and 4.4 per cent. H.† By the action of chlorate of potash and hydrochloric acid it was converted into the derivative $C_{21}H_{16}Cl_4O_{10}$,‡ exactly resembling in properties as well as in composition the chlorobastin previously described. The formation of the original black substance was attended by that of acetic and carbonic acids, and furfural. This transformation would appear to be closely similar to the resolution of the soluble modification of bastose on distillation with dilute acid, and completes therefore the chemical proof of the possible occurrence of such a resolution of cellulose during and by reason of the life of the plant, as would lead to the formation of astringent substances together with certain more highly oxidised bodies (probably aldehydes, pectic bodies, &c.).

As we indicated, these observations throw light on the formation and composition of coal and other so-called carbonaceous products. Berthelot (*Ann. Chim. Phys.* [5], **17**, 139), in discussing the proximate composition of a charcoal formed from cellulose, which he found to contain 20 per cent. of oxygen, uses the following language: "J'ai déjà insisté sur l'existence de ces composés humiques et charbonneux formés par la voie des condensations successives et dont les divers carbones représentent la limite extrême." In corroboration of this view we have obtained from wood-charcoal§ by heating it with nitric acid in a sealed tube, a nitro-compound exactly resembling that obtained from esparto, and from coal (Wigan cannel) a chlorinated derivative containing 26.3 per cent. Cl, and in every respect similar to the compound previously described.

Berthelot has formulated (*Ann. Chim. Phys.* [4], **9** and **19**) the laws under which these so-called "carbons" of pyrogenic origin may

* Reichardt maintains (*Arch. Pharm.* [3], **10**, 116) the close connection of the pectous substances with the carbohydrates.

† This black substance dries up to a hard compact mass with a shining fracture, and almost indistinguishable from coal.

‡ This body gives a large yield of chloropicrin (10 per cent.) when distilled with nitric acid.

§ This observation was made by Hatchett (*Phil. Trans.*, 1805, 211, 285).

be supposed to be formed, but has not extended his theories to the consideration of the chemistry of coal. Into this subject we do not consider it at present expedient to enter at any length, but would remark that it is at least probable that coals constitute the limiting terms of the series (comp. Balzer, *Vierteljahresschrift Zürich. Naturf. Ges.*, **17**, 1, 1872) of successive transformations of cellulose, developed according to the laws which Mills (*Watts' Dict.*, III Supp., p. 593; *Phil. Mag.*, June, 1877) has formulated as those of "Cumulative Resolution."

Reverting to what we term the bastose series of the jute fibre, it is important to consider the evidence as to its being simple or complex. In our original paper we gave several analyses of the chlorobastin, all of which proved singularly constant, although the several preparations were obtained from different specimens of jute, and in one case the fibre had been profoundly modified (structurally) by long boiling with dilute sulphuric acid. Moreover, the remarkable purity of the colour reaction of this derivative, and its invariable characteristics, point to the uniformity in composition of this extreme product of the resolution of the fibre. On the other hand, the isolated cellulose will appear from what follows to be a mixture. In the first place it is different in aggregate composition from the more ordinary forms, (linen, cotton, &c.). The following are the percentages of carbon and hydrogen, determined by combination of different specimens.

- (α .) Specimens obtained as a yield of 80 per cent. of the fibre (chlorine method).
- (β .) Specimens obtained as a yield of 70 per cent. of the fibre (bromine method).
- (γ .) Specimens obtained from fibre previously disintegrated by boiling with HCl, and subsequent treatment by chlorine method.
- (δ .) Specimens obtained from Swedish filter-paper.

	(α)		(β .)	(γ .)	Calc. $3C_6H_{10}O_5, H_2O$.	(δ .)
C	42.7	43.2	43.5	43.0	42.8	44.0
H	6.2	6.2	6.0	5.9	6.3	5.8

An examination of jute cellulose by means of the Schweizer-Pelouze reagent, showed that it differed from ordinary cellulose in another important particular, viz., in being only imperfectly precipitated by mineral acids from its solution in this reagent, whereas linen cellulose was found by Schlossberger (*Lieb. Ann.*, **7**, 21), and by Boussingault (*Ann. Chim. Phys.* [4], **13**, 231) to be completely precipitated. Three specimens of jute cellulose were dissolved and precipitated, the percentages recovered being 81.7, 89.0, and 89.2 respectively.* The

* On boiling the solution there occurs a still further transformation into the

precipitated cellulose gave on oxidation with alkaline permanganate a large yield of oxalic acid; and the body remaining in solution was isolated and found to be a carbohydrate closely resembling dextrin.

In our original paper we give the results of experiments, showing that jute cellulose, unlike ordinary cellulose, was in part readily transformed into soluble bodies by the action of bromine-water in the cold, and by dilute mineral acids at 60°. On the other hand we showed that if in our chlorination method of estimating cellulose, the action of the gas was followed by treatment with dilute sulphuric acid, before boiling off in alkali, the yield was uniformly increased 3—5 per cent. Subsequent experiments have fully confirmed this: we find moreover that the yield can be still further augmented by allowing the chlorination to proceed at as low a temperature as possible, *e.g.*, by placing the fibre in contact with powdered ice. By the method thus modified we have succeeded in isolating the following percentages of cellulose* :—

80.9	80.6	79.9	82.0	81.3	84.5
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By otherwise varying the process, different percentages can be isolated, which exhibit corresponding variations. From these observations we infer that the isolated cellulose is a mixture of two or more forms, which differ either in aggregation, degree of hydration, or even more fundamentally, and are either wholly or partially products of resolution of the parent substances, *i.e.*, the bastose constituents of the normal fibre.

Frémy (*Compt. rend.*, 48, 862) has endeavoured to establish definite distinctions between certain of the more commonly occurring celluloses. Sachsse (*Farbstoffe*, 150) however points out that any classification of celluloses, based, as Frémy has based his, into “fibre,” “vasculose,” &c.,† upon the behaviour of the substances towards acids and alkalis, is rendered nugatory by the mere consideration of the necessary variations, in constitution and composition of these substances, with the age of the tissue which they go to build up. While agreeing with Sachsse in rejecting Frémy’s classification, we do not feel ourselves in a position to speak definitely as to the lines

soluble form; thus in one case after 10 minutes’ boiling 71.9 per cent., and after 1 hour only 47.1 per cent. was recovered by precipitation.

* The variations exhibited by these numbers are in harmony with our general view of the constitution of the fibre. To increase the yield of cellulose above 75 per cent., the necessary modification of the process must have reference to those constituents, which easily tend to degrade into soluble products, and are therefore far more sensitive to the unavoidable slight variations in the application of the reagents.

† This classification has also reference to the various points or localities of origin of the cellulose within the plant, and is supported by the *à priori* ground for the existence of differentiated celluloses. The differentiations, however, cannot be regarded as affording a basis for *chemical* classification.

upon which a classification of these bodies should be based ; but it is our intention to apply the results of our researches without delay, to the investigation of this important problem.

Miscellaneous.

Under this head we must include an account of certain observations which, while they bear upon the main points at issue, have only a subordinate place in their logical treatment.

(a.) *Glycolignose and Glycodrupose* (Erdmann, *Lieb. Ann.*, **138**, 1 ; and V Suppl., 223).—In our first paper we drew attention in passing to these substances, as calculated to throw light upon our investigations. On examining the stony concretions of pears, we found that they could be resolved in precisely the same way as bastose, into cellulose on the one hand, and an aromatic chlorinated derivative on the other, giving the characteristic colour-reaction with sodium sulphite. We may remark that the experiment of chlorinating a thin section of the fresh fruit, and then plunging it into a solution of this salt, forms a very brilliant demonstration of its structure ; the stony concretions becoming deep purple in colour, while the astringent matters, which towards the peel have a radiating and concentric arrangement, become variously coloured from purple to orange-red ; these colours are beautifully contrasted with the pure white of the cellular substance of the flesh. On further treating a section, thus acted upon, with a dilute solution of ferric chloride, the reds give place to dark olive-greens, the arrangement of which constitutes another beautiful colour effect. On comparing this iron reaction with that afforded by the fresh fruit, a considerable development of tannins will be recognised. The formula given by Erdmann for glycodrupose, $C_{24}H_{36}O_{16}$ (C 49·6 per cent. and H 6·2 per cent.) involves a slightly higher percentage of carbon than is present in normal jute: the drupose ($C_{18}H_{28}O_{12}$) into which, together with glucose, this complex substance is resolved, has a composition similar to that of bastin ($C_{18}H_{24}O_9$).

There can be no doubt therefore that Erdmann's interpretations of his results need correcting by considerations drawn from our researches. The reaction of drupose with dilute nitric acid, whereby it was resolved into cellulose and certain soluble substances (not further examined), is a further proof of its close similarity to bastose, and that the hypothetical equation by which Erdmann represents this proximate resolution, viz. :—

does not adequately represent the chemistry of the change.

(b.) *Origin of Tannins*.—There can be little doubt that Baeyer's

interesting researches (*Berl. Ber.* [5], **25**, 280, 1094) on the reactions of the phenols with the aldehydes, constitute an important advance towards the discovery of the immediate origin of the aromatic constituents of plants, more especially of the astringents and colouring matters. The researches in question led Baeyer to conclude that all aldehydes unite with all phenols to form bodies belonging to the group of phenol colouring matters. The observations which have the most direct bearing upon our subject are: (1) that by the action of furfural upon resorcinol in presence of hydrochloric acid, he obtained a substance dissolving in water to a green solution resembling in its optical properties that of chlorophyll; and (2) that formaldehyde and pyrogallol react to form an amorphous compound closely resembling tannin, which in presence of excess of the aldehyde yielded a fugitive bright-red colouring matter.

Our researches have clearly shown that the resolution of plant-substances is generally attended by the liberation of aldehydes, and there have been numerous observations of the presence of phenols in living plants (Gorup-Besanez, *Berl. Ber.*, **4**, 15; *N. Repert f. Pharm.*, **23**, 180; Kraus, *ibid.*, **22**, 273, &c.). In absence of further observations, however, we withhold discussion of this interesting question, contenting ourselves with indicating this as a direction which our future researches must take.

(c.) *Reactions of the Jute Substance under High Pressure.*—(1.) Heated with water for 12 hours at 110° C.; 2·64 grams fibre. Only slightly attacked. Weight of fibre after washing and drying, 2·411; loss 11 per cent.

(2.) Heated with water 10 hours at 120—130°; 4·43 grams fibre. As before, only slightly attacked. Heating continued for another 10 hours. The fibre was thoroughly disintegrated, dark-brown in colour. Solution acid, smelling strongly of burnt sugar.* Weight of modified fibre 3·212 grams, loss 27·5 per cent.

(3.) Heated with water 9 hours at 140°; 4·52 grams raw fibre. Completely disintegrated. Weight of modified fibre 3·498; loss = 22·6 per cent. After chlorination, &c., it yielded 2·691 = 59·5 per cent. cellulose, or calculated on the modified fibre = 76·8 per cent. The modified fibre gave the following percentages on combustion: C = 48·3, H = 5·16†.

(4.) Heated with water and barium carbonate for 9 hours at 135°; 4·457 grams raw fibre. Colour changed to dark-brown, fibre *not* disintegrated. Some quantity of barium in solution. Yield of modified fibre 3·565 grams = 80 per cent. Cellulose 2·837 = 63·5, or calculated on modified fibre, 79·3 per cent.

* Compare *Report on Rhea Fibre*, Dr. Forbes Watson.

† Compare action of dilute acids, p. 100.

(5.) Heated with 1 per cent. NaOH solution for 10 hours at 120—130°; 4.43 grams raw fibre. Fibre yellowish-brown, but not disintegrated. Yield of modified fibre $3.77 = 85.1$ per cent. Cellulose $3.044 = 68.7$, or calculated on modified fibre, 80.7 per cent.

(6.) Heated with dilute hydrochloric acid (5 per cent.) for 10 hours at 120—130°. The jute was converted into a brownish-black powder, which on chlorination yielded the orange-coloured derivative, giving the characteristic reaction with sodium sulphite; but on boiling with alkali it was completely dissolved, showing that no cellulose survived this treatment. The solution contained only traces of aromatic bodies.

(7.) Heated with dilute sulphuric acid (7 per cent.) 12 hours at 110°. 2.659 gram raw fibre. Entirely disintegrated. Yield of modified fibre $1.857 = 698.6$. Cellulose $1.232 = 46.3$ per cent., or, calculated on modified fibre = 80.7 per cent.

(8.) Heated with solution of acid sodium sulphite (2.6 per cent. SO_2) for 10 hours at 115°. 4.482 grams raw fibre. Perfectly bleached, and somewhat disintegrated. Yield of modified fibre 89 per cent. Cellulose 2.93 grams = 65.4, or, calculated on modified fibre, 73.5 per cent.

(9.) Heated with neutral sodium sulphite (5 per cent.) for 10 hours at 120—130°. 4.444 grams raw fibre. No pressure on opening; solution faintly alkaline; fibre disintegrated. Perfectly bleached; became rose-coloured on exposure to air. Yield of modified fibre 3.609 grams = 81.2 per cent. Cellulose 3.050 grams = 68.7 per cent., or, calculated on modified fibre, 84.6 per cent.

It is not necessary specially to discuss the above results, as without raising any new point, they are in full accord with what has gone before.

(d.) *Reduction of Indigo by Jute.*—It is an interesting observation, as showing the presence in the jute fibre, or perhaps rather the ready development from the parent substance, of strongly deoxidising agents, that powdered indigo-blue is converted into the soluble hydrogenised compound by suspension in a solution of potassium hydrate in contact with raw jute. Pectic acid has previously been observed to exert the same action, and has been successfully employed in the dyeing of wool (Leuchs, *Polytech. Notizblatt*, 1865, 277; *Crookes's Dyeing and Calico Printing*, p. 481). The reduction of indigo by means of bran and lime, which is the principle of the ordinary "vat" used in wool-dyeing, is probably best explained by the presence in the former of the furfural-yielding constituent, especially as the temperature at which the vat is maintained (50° C.) and its general conditions point to this rather than to any fermentation action as the efficient cause of the reduction.

(e) *Reaction of Linseed Oil with Sulphuric Acid.*—When linseed oil is mixed with oil of vitriol, a violent reaction ensues, resulting in

the formation of a viscous black substance, from which water dissolves the substance known as *Hatchett's artificial tannin* (*Watts' Dict.*, 3, 703; *Phil. Trans.*, 1806, 109—146). We found, on examining this black substance, that it was converted by the action of potassium chlorate and hydrochloric acid into a golden-yellow chlorinated derivative, melting below 100°. This body resembles the chlorobastin in properties and reactions, and affords a verification of the close chemical connection which biologists have assumed to exist between the physiologically equivalent carbohydrate and fats.

(f.) *Additional Observations on the Chlorobastins.*—On carefully heating the crude product from esparto, a small sublimate of golden-yellow plates was obtained, which gave a dark purple-blue coloration (compare Wichelhaus, *Berl. Ber.*, 14, 952) with dimethylaniline; this reaction is known to be characteristic of the chloroquinones, and gives support to our view of the probable constitution of the chlorobastins.

We have made observations on the absorption spectrum of the coloured solution obtained by treating the freshly prepared chlorobastin with sodium sulphite, but were unable to distinguish any characteristic feature.

It may be further observed that bastose, treated with chromic acid solution, gives with sodium sulphite a colour reaction similar to that of the chlorobastin.

Chlorobastin when strongly heated evolves a “permanently” gaseous chlorine-compound, which was found to burn with a green flame. This body is still under investigation.

Conclusion.

We have attempted to give, in the accompanying sketch, a diagrammatic survey of the main results of our researches. It is of course very imperfect, but the main feature of the passage of cellulose into aromatic bodies allied to the tannins, for the actual occurrence of which in the life of the plant we have adduced so much evidence, is clearly represented.

The imperfections are due to the dynamic condition of the transformation considered in relation to the statical observations by which alone it can be investigated, and to the insufficient nature of these.

That these, moreover, are statistical rather than molecular, needs no further explanation or justification. Neither need we allude specially to the fact that nitrogen plays no essential part in this chapter of plant chemistry, *i.e.*, so far as our observations are concerned.

Our researches are a further contribution, however meagre, to the ideal arrangement of the carbon-compounds, *viz.*, according to their synthesis and transformations in that most marvellous laboratory, the living plant.

* Isolated jute cellulose contains 43 p.c. C and 6 p.c. H, and is represented by the formula $n(3C_6H_{10}O_5H_2O)$.