

XXVI.—*Contributions to the Chemistry of Lignification. Constitution of the Jute Fibre-substance.*

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SINCE the publication of earlier papers on this subject (Trans., 1882, 90; 1883, 18) we have continued to prosecute our researches in various directions, certain of which have led to results from which more positive conclusions may be drawn as to the molecular constitution of this group of compound celluloses. Of these we proceed to give a short account. The investigations have been, for the most part, confined to the jute-fibre, than which we have found no better representative of the group of lignified celluloses. With regard to the term lignocellulose, we should, perhaps, explain at this point, that it recommends itself as being a sufficient description, without containing any suggestion as to the nature of the process by which they are formed, and which we do not think, speaking from the chemical point of view, is by any means completely elucidated.

Although from its nature the jute-fibre is an aggregate, it exhibits, notwithstanding, the constancy in composition and properties which

denote a chemical individual. The simplest expression of its elementary composition is the empirical formula $C_{12}H_{18}O_9$ ($C = 47.0$, $H = 6.0$, $O = 47.0$); whilst its proximate resolution into *cellulose* (78—80 per cent.) and *non-cellulose* (20—22 per cent.), may be represented by the formula $3C_6H_{10}O_5, C_6H_6O_3$. For the moment, we advance this as a statistical rather than a molecular expression, leaving it to the experimental evidence to be adduced to show in what degree it is established in the latter and more definite aspect. We shall show, in the first instance, that the more oxidisable constituents of the jute-fibre, to which is applied the neutral term non-cellulose, are compounds, or a compound characterised by an atomic ratio,* approximating to $C_6 : H_6 : O_3$, and associated with the cellulose in chemical rather than mechanical union.

The intimate nature of this union is shown *first* in its resistance to the action of all simple hydrolytic agents. The alkalis in aqueous solution, the dilute mineral acids, such as have neither oxidising nor reducing properties, attack the fibre in proportion to temperature and duration of action. The result is a solution of the fibre substance, in quantity from 1 to 30 per cent. of its weight, according to the conditions, but without producing any essential chemical change in the insoluble residue (Trans., 1882, 100). In illustration of this point, we cite here the results of the "mercerising" treatment (*Watts's Dictionary*, New Edition, "Cellulose"), as applied to the jute-fibre.

Solution.	Temp.	Loss of weight.	Time.	Percentage cellulose† in product.		
1 per cent. NaOH..	boiling	7 per cent.	10 mins.	79.1	77.8	78.7
33 " " ..	18°	7.9	1 hour	78.5	78.7	—
33 " " ..	18	9.6	48 hours	79.1	—	—
33 " " ..	18	14.3	7 days	78.9	—	—
33 " " ..	18	14.8	14 "	78.7	—	—
33 " " ..	80	13.2	1 hour	78.5	79.8	—
50 " KOH..	18	14.2	7 days	79.9	—	—

The structural changes attending the action are profound, as they are in the case of cotton. The individual fibrils increase in thickness at the expense of length to the almost entire obliteration of the central canal; at the same time the union of the fibrils into bundles is more or less completely resolved, and the splitting up of the bundles is accompanied by the development of a wavy outline. So

* The empirical formula actually deduced from the experimental results given in this paper is $C_{76}H_{80}O_{37}$ (see pp. 207 and 213).

† The cellulose in these determinations serves as a constant to which to refer possible variations of the non-cellulose.

that, with the increased softness, the increased fibre has an external resemblance to wool. This increased softness is to be noted as a distinction from the pectic fibres or pecto-celluloses, which are hardened by such treatment. Reverting to the chemical features of these hydrolytic changes, the product does not differ in any essential point from the original fibre; the aggregate composition (C, H, O), the proportion of cellulose to non-cellulose, and the characteristic properties of the latter persist unchanged.

The structural changes determined by the dilute acids, on the other hand, are opposite in character. The fibre substance surviving undissolved is converted into a hard friable modification, fracture taking place across the fibre bundles which are not resolved by the treatment. But the chemical feature of resistance of the combined molecule to hydrolytic resolution is equally characteristic in relation to this group of reagents.

The dissolution of the fibre substance in the ammonio-copper reagent, when carried out fractionally, also fails to *resolve* the compound molecule in question. In short, the fibre-substance is to be regarded as an aggregate, only in the sense that some portions (or molecules) are more susceptible of hydration than others, and although these may be attacked and dissolved wholly or in part by hydrolytic agents, they are not decomposed, but preserve intact their essential characteristics, which are those of the original fibre-substance.

The force of this conclusion is not diminished by the consideration of the resolutions effected by hydrolytic agents other than those above mentioned, or by these agents under extreme conditions of temperature. Thus, dilute nitric acid at 60° , sulphurous acid (7 per cent. solution) at $90-100^{\circ}$, and the aqueous alkalis at high temperatures, *resolve* it into cellulose and non-cellulose (soluble), at the same time attacking the cellulose more or less. But in these cases other conditions, whether of oxidation, reduction, or dehydration (condensation), are superadded, and our conclusion as to resistance of the lignocellulose molecule to simple hydrolysis, is unaffected by the results.

Secondly. In those reactions of the fibre substance which depend on its alcoholic characteristics (OH-groups), its molecular homogeneity is equally manifest. We give the statistics of the conversion of the lignocellulose into nitrates under varying conditions.

(a.) Nitrating acid: mixture of equal volumes of nitric acid (sp. gr. 1.43) and sulphuric acid (sp. gr. 1.8). Temp. 18° .

Duration of exposure.	Yield per 100 pts. fibre.
1 min.	125·2
2 mins.	129·2
3 "	140·0
4 "	149·0
15 "	146·0 secondary actions with con-
16 hours	131·0 version into soluble products.

(b.) Nitrating acids: I. As in (a). II. Nitric acid of 1·5 sp. gr., 1 vol.; sulphuric acid, sp. gr. 1·8, 1 vol. III. Nitric acid of 1·5 sp. gr., 1 vol.; fuming sulphuric acid, 0·75 vol.

In addition to the raw fibre (A), the modification resulting from the action of hot dilute hydrochloric acid (B) was included.

Duration of exposure in all cases 30 minutes at 18°.

Results: yield of nitrate per 100 parts dry fibre:—

	I.	II.	III.
A	144·4	153·3	154·4
B	143·8	152·8	152·7

A reaction according to the equation $C_{12}H_{18}O_9 + 3HNO_3 = 3H_2O + C_{12}H_{15}O_6(NO_3)_3$, is equivalent to a gain in weight of 44 per cent.: the conversion into the tetranitrate, 58 per cent. The formation of the latter appears, therefore, to be the limit of nitration of the jute-fibre; in other words, if we represent the lignocellulose molecule by a C_{12} formula, it will contain four alcoholic OH-groups, or two less than cellulose similarly represented.

To confirm the composition of these products and the equations above given, the specimen IIIA was analysed by Eder's method (*Ber.*, 13, 169), with the following result:—

0·453 gram gave 82·0 c.c. NO at 19° and 770 mm.; whence—

$$N \dots 10\cdot5 \text{ per cent. } \text{Calc. } \begin{cases} C_{12}H_{15}O_6(NO_3)_3 & 9\cdot5 \text{ p. c.} \\ C_{12}H_{14}O_5(NO_3)_4 & 11\cdot5 \text{ ,,} \end{cases}$$

These nitrates resemble those of cellulose in all essential points. There is no evidence of any resolution of the molecule attending its combination with the acid radicle; the product is a nitrate of the lignocellulose, which again manifests itself as a chemical individual.

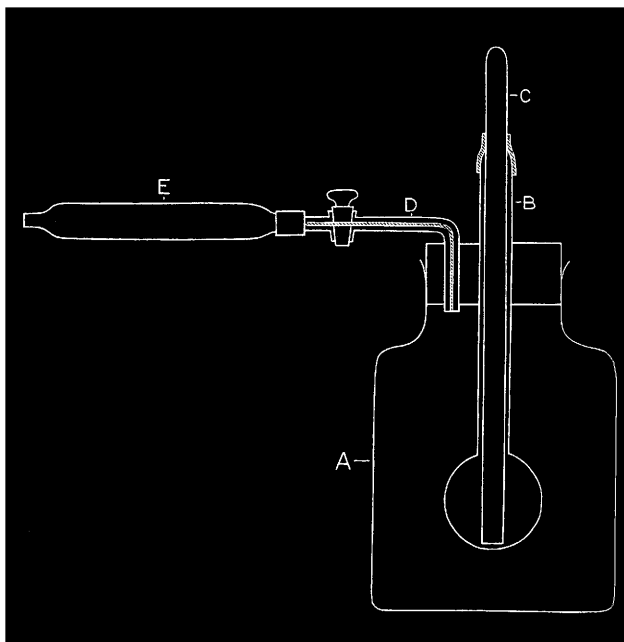
But, as we have previously pointed out (*loc. cit.*), the most characteristic reaction of the fibre substance is that with chlorine (in presence of moisture). The product of chlorination is not homogeneous, however, as are the nitrates: alcohol removes a chlorinated derivative of the non-cellulose, leaving, at the same time, after exhaustive treat-

ment, a certain proportion—about one-fourth—combined with the cellulose in such a way as to resist the action of solvents.

A statistical study of this reaction has enabled us to make some progress towards elucidating the problem of the constitution of the fibre substance.

First, with regard to the quantity of chlorine combining, 1.613 gram was chlorinated and dried in a vacuum over potassic hydrate (it was necessary to remove the hydrochloric acid in this way, as the chlorinated compound is appreciably soluble in water), and lastly, in the air-bath at 105°. We obtained 1.765 gram of dry chlorinated fibre; or 0.152 in excess of the original weight. The chlorine, estimated in the usual way, was found equal to 0.1511 gram; or 9.4 per cent., calculated on the original weight of fibre. This result was confirmed by other similar experiments. The numbers obtained we judged to be somewhat high, owing to the evidence of the presence of residual hydrochloric acid, in the chlorinated fibre blackening somewhat on heating. We therefore decided to measure the volume of chlorine disappearing in the reaction, and constructed an apparatus for the purpose already described in a note communicated to the *Chem. News*, 58, 215.

The essential portion of this apparatus is the reaction flask or bottle A. This is closed by a cork, through which pass two tubes.



The first, B, is blown out below to a thin bulb; it carries an outer tube of india-rubber above, through which is inserted a rod, C, of somewhat less diameter, and reaching nearly to the bottom of the bulb. The prepared fibre is introduced into the bulb, and at the required moment the bulb is shattered by a blow on C, and at once freely exposed to the chlorine atmosphere in A. A second tube, D, of narrow internal diameter, serves to connect the bottle with any convenient gas-measuring apparatus. The tube E contains a small quantity of the prepared fibre, and serves to indicate any diffusion of the chlorine outwards; which, however, we have never found to occur. It is as well to keep the gas atmosphere in A under a somewhat diminished pressure during the experiment; the absorption of the gas being followed (when an ordinary U-tube with mercury reservoir is used) by continual additions of mercury from the reservoir.

We need not enter in detail into the other precautions necessary to be observed, beyond remarking that the containing vessel was filled over warm water, and, on reinverting, a small quantity of water (5—10 c.c.) was allowed to remain in the bottom of the vessel, in order to provide for the complete absorption of the hydrochloric acid formed in the reaction.

We give the results of two, from amongst many concordant determinations.

(1.) 1·062, fibre; temp. 18°; bar., 758—18.

Duration in minutes....	10	15	30	40	45
Cl combining, c.c.....	52·5	53·5	59·0	60·0	60·0

Volume of Cl corrected to 0° and 760 mm.; 55 c.c. = 0·1764 gram.

At the conclusion of the experiment water was added to the containing vessel, the excess of chlorine expelled, and the hydrogen chloride formed was determined by titration, and found equivalent to 2·5 c.c. normal alkali; we have, therefore—

Cl in combination with fibre substance ..	0·0876
Cl as HCl formed in the reaction.....	0·0888
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	0·1764

The quantity of chlorine as hydrogen chloride in excess of the equivalent in combination is 0·0012.

The chlorinated fibre resulting from this experiment was boiled in solution of sodium sulphite, and the cellulose thus isolated, after washing and drying, was found equal to 0·846 gram, or 79·7 per cent. of the original.

(2.) 1·387 fibre; temp., 18·5; bar., 752 — 18·6.

Duration in minutes. 5 10 15 20 25 30 45 60 90 120 135 145 155
 Cl combining, c.c.... 47 53 57 59 62 63 69 72 75 78 80 82 82

Vol. of Cl corrected to 0° and 760 mm., 74·5 c.c. = 0·2390 gram.

Cl as HCl by titration..... 0·1221 gram.

Whence Cl in combination..... 0·1169 „

0·2390 „

The chlorine as hydrogen chloride in excess of the equivalent in combination is 0·0052 gram. Cellulose isolated 1·094 = 80·5 per cent. The percentage of chlorine combined with the fibre substance, and calculated on its original weight, is in (1) 8·2 per cent. in (2) 8·4 per cent.

*These results lead to the conclusion that the reaction is one of simple substitution of hydrogen by chlorine.** We may extend this statistical inquiry by including what we had previously determined in regard to the composition of the chlorinated derivative. Our analytical results were as under:—

		Calculated for $C_{19}H_{18}Cl_4O_9$.
C	42·8	42·85
H	3·4	3·38
Cl	26·8	26·69

The fibre, on chlorination, we now find increases from 100 to 108·1, and from the above contains $\frac{100 \times 8\cdot1}{26\cdot8}$, that is, 30·2 of the chlorinated derivative of the non-cellulose. Subtracting this from the 108·1 we get 78, which agrees sufficiently well with the percentage of cellulose obtained. From this, we infer also that the chlorinated fibre contains no other compound, in addition to cellulose, but the chlorinated derivative of the above composition.

This is confirmed by the following experiments, in which the chlorinated derivative was investigated in fractions: 4·218 fibre chlorinated, washed, and exhausted with hot alcohol, the solvent always employed by us in isolating the chlorinated derivative for analysis. After exhaustion, the fibre weighed 3·635 = 86·2 per cent. of the original, still giving the brilliant colour re-action with sodium sulphite characteristic of the compound in question. Of this residual fibre, 1·232 grams was analysed for chlorine and found to contain 0·0225. This is equivalent to

* We leave out of consideration, while admitting the possibility of combinations of chlorine without substitution as with $CH-CH$ -groups.

$0.0225 \times \frac{100}{26.8} = 0.084$ of the chlorinated compound, of which, therefore, continuing the assumption, the fibre contains 6.8 per cent. Subtracting this from 86.2, the percentage of fibre remaining after the original exhaustion, leaves 79.4 for cellulose. This agreement with the percentage estimated confirms the assumption, and supports the conclusion previously drawn as to the composition of the chlorinated fibre.

We must now consider, by way of parenthesis, one or two points of subsidiary and general bearing on the main argument, and the observations upon which it is founded. First, with regard to the errors in the method of determining the amount of chlorine combining, by observing the decrease in volume. We need not enter into a minute discussion of all the probable errors, for the reason that the decrease in volume in c.c. is a large multiple (>7) of the percentage on the fibre to be calculated therefrom, and therefore the only error of moment is that resulting from the absorption of chlorine by the moist fibre.

The quantity of water introduced by the fibre in experiments (1) and (2) was less than 1 gram in either case; the corresponding absorption (solution) of chlorine would be from 1 to 2 c.c. This absorption would affect the percentage of Cl. calculated in the fibre by an amount equal to 0.2—0.3. This error requires further to be distributed between the chlorine as hydrogen chloride, and that in combination with the fibre substance. The former being taken as the difference between the observed absorption, and the chlorine as hydrogen chloride determined independently by titration, it will be seen that the error falls entirely on the former quantity.

The determinations of hydrochloric acid are subject to an error arising from the solubility of the chlorinated derivative in water and to its possessing an acid reaction. Washing the chlorinated fibre with saturated salt solution, in which the derivative is only slightly soluble, enabled us to minimise this error, which by direct observation of the "acidity" of the derivative—using litmus as the indicator as in the above titrations—we found could not exceed 0.1 c.c. of normal alkali in the second of the experiments detailed above. One other point remains to be noticed, viz., the work done by the chlorine used up in excess of the equivalent of that combining with the fibre substance. We carefully determined the quantities of carbonic acid formed in chlorinating the fibre, and in three experiments in which 4.5 grams of fibre was employed the quantities determined were 0.0156, 0.0210 and 0.0213, that is, from 0.003 to 0.005 per gram of fibre. The excess of chlorine in question would thus appear to be accounted for in the occurrence of a certain slight destructive oxidation.

$$19[3C_6H_{10}O_5, C_6H_6O_3] + 24Cl_2 = 6C_{19}H_{17}Cl_4O_9 + 57C_6H_{10}O_5 + 3H_2O + 24HO.$$

The equation leaves us with a plus of 18 atoms H on the right hand side.

$$\text{C}_{114}\text{H}_{120}\text{O}_{55} + 24\text{Cl}_2 = 6\text{C}_{19}\text{H}_{17}\text{Cl}_4\text{O}_9 + \text{H}_2\text{O} + 24\text{HCl},$$

With regard to the molecular proportion of chlorine taken up in the subsidiary reactions, it is easy to see that it equals 2Cl_2 , that is, in terms of the quantities represented by the above equations.

Q 2

We have now to resolve the non-cellulose molecule, which, up to the present, has been dealt with as a homogeneous aggregate.

Following the lines of our previous communications (*loc. cit.*), we assume, as our starting point, the probable connection of the chlorinated compound with the derivative obtained by the action of this halogen on pyrogallol. The original suggestion of this line of research, we would remind the Society, is due to Dr. Armstrong.

We had previously shown (*loc. cit.*) that there was evidence of the presence of *mairogallol* in the chlorinated fibre, its reactions with sodium sulphite and with ferric chloride being indistinguishable from those of the phenol-derivative. Similarly, also, the isolated chloro-derivative yields chloroquinones by sublimation. Mairogallol yields trichloropyrogallol on reduction with zinc and sulphuric acid (Webster, *Proc.*, 1887, p. 131; Hantzsch and Schniter, *Ber.*, 20, 2033). The chlorinated fibre similarly treated yields to ether a substance giving the deep blue reaction with barium hydrate, characteristic of this derivative. It has, however, been found impossible to isolate either trichloropyrogallol or mairogallol from the chlorinated fibre.

Taking the qualitative and *à priori* evidence before us as a basis for the hypothesis of the formation of the former in the chlorination of jute, we will again have recourse to the statistical method of proof.

As mairogallol contains 50·5 per cent. of chlorine, and the derivative under discussion 26·7 per cent., we conclude, on our assumption, that the latter contains 52 per cent. of the former, associated with a chlorine-free compound or compounds, amounting, therefore, to 48 per cent. of its weight. Or, taking the formulæ for these compounds in such multiples respectively that the numbers for chlorine shall be equal, and subtracting, we arrive at the result as follows:—

$$\begin{array}{rcl}
 (a.) & 11\text{C}_{19}\text{H}_{17}\text{Cl}_4\text{O}_7 & = \text{C}_{209}\text{H}_{187}\text{Cl}_{44}\text{O}_{99} = 5841 \\
 (b.) & 4\text{C}_{18}\text{H}_7\text{Cl}_{11}\text{O}_{10} & = \text{C}_{72}\text{H}_{28}\text{Cl}_{44}\text{O}_{40} = 3094 \\
 (c.) & \text{By difference} \dots & \text{C}_{137}\text{H}_{159} \quad \text{O}_{59} \quad 2747
 \end{array}$$

The proportion of the difference—that is, the chlorine-free hypothetical molecule (*c*)—to the original 11 mols. of chlorinated derivative (*a*) is 48 : 100. We have now to confirm this deduction by the experimental diagnosis of the hypothetical molecule in question.

In our earlier work (*loc. cit.*) we had observed that the chlorinated derivative had a powerfully reducing action on cupric oxide in alkaline solution, and concluded that it was a compound of a chlorinated body with a non-chlorinated derivative of aldehydic nature. That it was a compound and not a mixture we showed by the invari-

able results of the analyses of the compound prepared from various sources and variously fractionated. The aldehydic constituent we subsequently found to be *furfural* (Trans., 1883, 20). To liberate this aldehyde, alkaline hydrolysis of the chlorinated derivative is necessary; on then acidifying and distilling it is obtained in quantity. Thus, from 2 grams of jute chlorinated and treated in this way, we obtained 250 c.c. of distillate, giving a deep rose-red reaction with aniline acetate. Jute-cellulose, treated similarly, gives no furfural. This aldehyde is, moreover, a characteristic product of hydrolysis (acid) of all the lignocelluloses. We made an estimate of the yield of furfural from the jute fibre-substance, when decomposed by boiling with strong acids, using the approximate method proposed by V. Meyer (*Ber.*, 11, 1870), and based upon the colour reaction with aniline acetate. The quantities estimated in two experiments were 10.0 and 11.2 per cent. respectively (*Jour. Soc. Chem. Ind.*, 4, 11; *Watts's Dictionary*, New Edition, "Cellulose"). On the other hand, the isolated celluloses from such substances as jute, pinewood, and other fully-elaborated lignified fibres or tissues, yield no furfural, or at the most traces of it, under severe treatment. We have now to compare the composition of furfural with that of the hypothetical chlorine-free constituent of the chlorinated derivative expressed by the statistical formula, viz., $C_{137}H_{159}O_{59}$, as follows:—

	Furfural. $C_5H_4O_2$.	Hypoth. body. $C_{137}H_{159}O_{59}$.
C.....	62.5	59.8
H.....	4.1	5.8

It would appear, therefore, that the furfural is associated in the hypothetical molecule with a body containing a relatively high proportion of hydrogen. This body we have had no difficulty in showing to be an acetic residue.

The presence of methyl-groups is proved by the evolution of methyl chloride from the chlorinated derivative when heated. We also obtained this gas in large quantity from the similar derivative which we prepared from esparto and described in our first paper (Trans., 1882, 94).

The fibre, when boiled with chromic acid, yields acetic acid in small quantity, but the most effectual way of isolating the acid is by dissolving the fibre in concentrated sulphuric acid in the cold, diluting and distilling; from 4.5 grams thus dissolved, after the solution was diluted to 250 c.c. and distilled,* we obtained a distillate of 160 c.c.,

* We treated in this way the same weights of both cotton and jute cellulose. In neither case did we obtain any volatile acid. The source of the acetic acid in the above experiment is therefore in the non-cellulose constituents of the fibre.

containing 0.180 gram of acetic acid, together with furfural. The distillate was redistilled from chromic acid, the second distillate boiled with silver oxide, filtered, and evaporated to dryness. Silver acetate crystallised out, and the crystalline residue yielded, on ignition, 64.7 per cent. Ag (calc. $C_2H_3O_2Ag$ 64.6). Acetic acid was thus proved to be the only volatile acid formed.

Reverting to the statistical comparison of the hypothetical molecule with furfural with our determinations of the proportion of this aldehyde to the fibre substance, and assuming that the acetyl radicle is present in the form of acetaldehyde, we infer, from the carbon percentages, that these aldehydes are associated in the proportion by weight of six of the former to five of the latter.

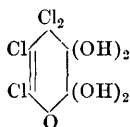
We may sum up our inferences as to the composition of the chlorinated derivative of the non-cellulose as follows:—

100 parts of fibre combine with 8 of chlorine; 108 of chlorinated fibre thus produced are made up of 78 of cellulose and 30 of chlorinated fibre. The 30 of chlorinated non-cellulose is made up approximately of 16 parts of mairogallol and 14 of the hypothetical molecule. 14 of the hypothetical molecule are made up of 7.6 parts of furfural and 6.4 of acetaldehyde.

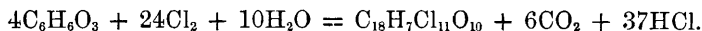
Having no further experimental evidence to adduce on the main subject of our inquiry, we would close our communication at this point, but we may, perhaps, be allowed to discuss certain of its general bearings.

With regard to the statistical method pursued, it is unnecessary to point out its imperfections. It must be judged by the exigencies of the case and by its results. We have made many ineffectual attempts to resolve the chlorinated derivative. We have closely studied mairogallol and the group of halogen-derivatives of the trihydric phenols, of which it is a member, with the view of finding a means of isolating it, or a product of its decomposition from the derivative. Our failure, it will be admitted, is in harmony with the conclusions drawn from the statistical investigation as to the nature of this complex molecule, that is the association of mairogallol—itself a very unstable molecule—in combination with such active molecules as furfural and acetic residues.

Hantzsch and Schniter regard mairogallol (*loc. cit.*) as a condensed derivative of a typical quinone-chloride molecule—



It is formed from pyrogallol by a destructive chlorination, which Stenhouse and Groves formulated as under :—



We made an approximate determination, by the absorption method described above, of the chlorine required to chlorinate pyrogallol in presence of cellulose. We dissolved 0.100 of the phenol in a little water, and added the solution to a pure cellulose fibre, which was then exposed to chlorine, as described. The absorption measured was 87 c.c. (at 18° and 756 mm.), from which, neglecting the CO_2 formed, which we assume to be absorbed by the water present, we conclude that 0.25 of Cl was taken up; the quantity required by the equation being 0.33. We cite this in contrast to the chlorination of jute, which we have shown to be non-destructive, and in support of the conclusion that mairagallol being formed by the simple combination with chlorine, the non-cellulose of jute contains carbon-rings of similar arrangement to the typical molecule of mairagallol formulated above.

This inference, in conjunction with the ascertained furfural and acetyl groupings of the constituent atoms of the non cellulose, lands us in a region of possibilities, further entry into which would be on the basis of pure speculation. For the present it is sufficient to bear in mind that the conclusions we have arrived at generalise, and in no particular contravene what is known of this typical lignocellulose, the jute-fibre.

Having regard to the results obtained, we shall extend this statistical method of investigation to other members of the group of lignocelluloses. Of these there appear to be two main groups, (1), that of which jute is the type, and which, so far as we have been able to observe, is coextensive with lignification as defined by the physiologists, and as manifested in the earlier stages of growth; (2), the substances composing the fibre elements of perennial stems, that is, the woods proper. Of these, fir-wood (*Pinus abies*) may be taken as the type. Of the former, we have had occasion to investigate a considerable number, and have found the same chemical characteristics, not only in isolated bast-fibres of the same class physiologically as jute, for example, the bast of the various species of *Hibiscus*, of *Sida rhombifolia*, but also in fibres and fibro-vascular bundles of monocotyledons, for example, *Musa* and *Aloe* species, and even in the stony secretions of the pear, which, although of such widely different functions, is closely similar in properties to the jute-fibre substance.

Of results obtained with these various plant products we mention the following :—Chlorinated derivatives isolated from *Musa* (*Paradisica*) and Esparto, closely resembling the compound from jute

(Trans., *loc. cit.*). A quantitative investigation of the chlorination of *Sida* by the method described in this paper, giving 7.2 per cent. on the fibre of chlorine combining, with 7.9 per cent. chlorine as hydrogen chloride. The decomposition of the stony concretions of the pear by chlorination into cellulose and chlorinated non-cellulose, identical with that of jute, and by acid hydrolysis into furfural* on the one hand (not glucose, as stated by Erdmann), and insoluble condensation-products on the other.

With regard to the actual processes of lignification, of which the chemical identity is established for so wide a range of plant elements, we would offer a few observations, based upon our investigations of jute.

We have recently had the opportunity of investigating the development of the fibre in the living plant. We find that from the earliest appearance of the fibre bundles, for example, in sections cut a few centimetres below the growing point, they have all the chemical characteristics of the mature fibre. In the isolated fibre, we find no sensible variation in the proportion of cellulose to non-cellulose, nor in their mode of combination, throughout the entire length of 2 to 3 metres. This evidence appears to carry with it the suggestion that both cellulose and non-cellulose may have a common and simultaneous origin in a parent substance, and that lignification is the result of progressive modifications and differentiations of this original complex molecule.

On this view the chemistry of the second group of lignocelluloses, the woods, would be a continuation of this process of modification. We have reason to hold that, in the earlier stages of growth, they are similar in composition to the members of the first group. In their mature condition, on the other hand, we find them characterised by a higher carbon percentage, 49—51, as compared with 46—48, and a higher proportion of non-cellulose, 50—60, as against 20—30.

The physiologists are accustomed to speak of vegetable matter as "dead" when removed from the sphere of the vitally active cells. To the chemist no such sharp line of demarcation exists. The substances composing the tissues of plants, and notably the lignocelluloses, are, as is evident from their nature, capable of a long series of intrinsic modifications, and we think due weight should be given to such considerations in all endeavours to advance from our present very imperfect knowledge of the chemistry of elaboration.

In conclusion, we would briefly summarise the main points which we have thus endeavoured to establish, with regard to the constitution of the jute fibre-substance.

- (1.) A compound of cellulose and non-cellulose, empirically $C_{12}H_{18}O_9$,

* Or a carbohydrate yielding furfural.

of the general chemical features of the celluloses, resisting hydrolysis and yielding explosive nitrates, of which the highest is the tetra-nitrate.

(2.) The non-cellulose is a complex molecule, from the products of resolution of which, by chlorination and hydrolysis, we infer it to contain the following groups of molecules :—

(a.) $C_{18}H_{18}O_{10}$, ketone transitional to a quinone, chlorinated directly to form mairongallol: (b.) $C_6H_4O_2$, furfural in combination, by condensation with (a), and with (c) an acetic residue. These are combined in the approximate molecular proportion (a) 2, (b) 6, (c) 5, = $C_{76}H_{80}O_{37}$.

(3.) The lignocelluloses in the earlier stages of growth are constituted on this type. The true woods, on the other hand, appear to represent a more condensed type.
