

# CXXI. THE COMPOSITION OF SOME VEGETABLE FIBRES WITH PARTICULAR REFERENCE TO JUTE.

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THE vegetable fibres commonly met with find very diverse uses according to their physical characteristics and chemical composition. Very few comparable analyses are, however, to be found in the literature, and the wide differences which exist in composition are not generally known. Cross and Bevan [1895] originally devised methods for the study of many fibres and carried out much experimental work on jute. Jute they considered to be a typical example of the "lignocellulose" group of "compound celluloses" and a very convenient material for the investigation of the cellulose-lignin relationship in the cell wall and the chemistry of lignin itself. In some respects their views are not acceptable today, and particularly is this the case with the concept of "compound celluloses". Analytical methods too, have been improved or their shortcomings recognised. Methods which have recently been devised for whole plant materials are applicable directly to a study of isolated fibres.

Through the courtesy of Dr S. G. Barker, and members of the Indian Jute Mills Association, samples of jute of known history and quality, covering the entire commercial range, were available (Jute 6-22). For other samples, I am indebted to Messrs Darragh Smail and Co. Ltd. (coir), the Linen Industry Research Association (flax), Messrs F. Ashton (hemp, manilla hemp, sisal), the Imperial Institute (sisal, jute), Messrs Landauer and Co. (ramie), Messrs Myles and Stewart (jute), Messrs Wigglesworth and Co. Ltd. (hemps), the New Zealand Government (*Phormium tenax*), and Dr S. G. Barker (Pita grass, Chinese hemp, coir and *Calatropis gigantea*).

## METHODS.

The following determinations were made on samples previously ground, wherever possible, in a high speed mill. (The coir samples were very resistant and in this case the determinations had to be carried out on material of very variable particle size.) The method of sampling adopted was to select at random a considerable number of small groups of fibres, which, collected together, formed the composite sample for analysis.

I. *Cellulose* by the Norman and Jenkins [1933] modification of the Cross and Bevan [1918] procedure. Chlorination is carried out in solution by acidified hypochlorite. No pretreatment is given, owing to serious effects on one component of the cellulose aggregate.

II. *Lignin* by the Norman and Jenkins [1934] modification of the Ost and Wilkening [1910] process employing 72%  $H_2SO_4$ . The modification involves the pretreatment of the material with 5%  $H_2SO_4$  for 1 hour to remove pentose-containing polysaccharides, it being found that pentose groups in the presence of strong acid slowly give rise to furfuraldehyde, which condenses with the lignin.

III. *Furfuraldehyde yield* by distillation with 12% HCl and precipitation as the phloroglucide. The yield of furfuraldehyde from the isolated cellulose is also determined.

IV. *Uronic anhydride content* by the yield of CO<sub>2</sub> on boiling with 12% HCl. This determination was made on only a few samples.

The analytical figures expressed on the oven-dried material are given in Table I.

Table I. *Analyses of some vegetable fibres.*

All results expressed on 100 g. oven-dried material.

No.	Fibre and description	Cellu- lose	Lignin	Total furfur- ald. yield	Cellu- lose in furfur- ald. yield	Xylan cellu- lose	Furfur- ald. from hemi- cell.	Uronic acid anhy- dride
F. 1	Flax (Sandringham)	92.26	6.04	1.86	1.37	2.37	0.5	—
F. 3	Flax (Irish)	91.20	3.27	2.32	1.93	3.01	0.4	—
Cg. 1	<i>Calatropis gigantia</i>	91.10	0.67	1.99	1.19	1.85	0.8	—
R. 1	Ramie 1	85.97	1.01	2.39	0.84	1.80	1.6	—
R. 2	Ramie 2	84.12	1.26	2.39	0.78	1.21	1.6	—
H. 1	Hemp (Italian)	89.23	5.32	1.11	1.12	1.73	0.0	—
H. 6	Hemp (Czechoslovakian)	81.63	5.51	3.13	0.99	1.54	2.1	—
H. 5	Hemp (Chinese)	75.86	4.12	3.87	2.47	3.84	1.4	—
H. 2	Hemp (Indian)	77.27	7.28	2.83	1.15	1.79	1.7	—
Pg. 1	Pita grass 1	90.26	3.13	9.73	7.78	12.07	2.0	—
Pg. 2	Pita grass 2	90.83	2.40	9.75	7.61	11.80	2.1	—
J. 1	Jute (lightening)	74.95	11.70	10.60	7.34	11.39	3.3	—
J. 2	Jute (Dacca Tossa)	78.02	11.22	10.96	7.67	11.90	3.3	—
J. 3	Jute (ordinary Tossa)	75.84	11.29	9.76	7.64	11.85	2.1	—
J. 4	Jute (Daisee)	74.56	11.38	9.75	7.43	11.53	2.3	—
J. 15	Jute (best Jat Suti)	74.20	11.01	9.72	7.16	11.12	2.6	4.00
J. 16	Jute (good Jat Suti)	70.87	12.08	10.00	7.39	11.47	2.6	5.12
J. 18	Jute (average Jat Suti)	73.59	11.26	10.19	7.49	11.62	2.7	5.04
J. 17	Jute (good Suti-Eastern)	74.05	12.02	9.64	7.26	11.26	2.4	4.80
J. 19	Jute (average Suti-Eastern)	69.81	12.64	9.93	7.68	11.93	2.3	6.32
J. 22	Jute (discoloured Suti)	72.55	12.35	10.04	7.05	10.94	3.0	5.04
J. 21	Jute (average rejection Suti)	67.61	14.05	10.30	7.85	12.17	2.5	6.68
J. 20	Jute (stick rejection Suti)	64.78	13.79	10.00	6.90	10.72	4.1	7.20
J. 13	Jute (good soft district Tossa)	74.40	10.37	9.56	7.76	12.04	1.8	4.60
J. 14	Jute (average soft district Tossa)	74.32	11.53	11.07	8.27	12.82	2.8	4.72
J. 6	Jute (good Jat Bogi)	74.54	10.57	10.62	7.48	11.61	3.1	4.36
J. 7	Jute (medium Jat Bogi)	71.91	12.12	10.27	7.99	12.40	2.3	5.56
J. 10	Jute (low Bogi)	73.96	11.79	10.01	8.01	12.42	2.0	4.80
J. 8	Jute (low soft district Bogi)	76.00	11.22	11.17	8.25	12.80	2.9	4.84
J. 9	Jute (very low soft district Bogi)	71.89	13.91	10.00	7.70	11.94	2.3	5.68
J. 12	Jute (average Bogi rejection)	71.87	13.10	10.69	7.51	11.65	3.2	5.28
J. 11	Jute (Bogi stick rejection)	68.74	12.47	10.47	7.32	11.36	3.2	6.36
MH. 1	Manilla hemp	74.14	8.51	9.07	9.04	14.01	0.0	—
Pt. 1	<i>Phormium tenax</i>	72.04	11.13	13.33	9.74	15.09	3.6	—
S. 1	Sisal 1 (African)	74.95	6.04	13.63	11.97	18.56	1.7	—
S. 2	Sisal 2	79.43	6.57	12.81	10.54	16.35	1.3	—
C. 1	Coir (bristle fibre—good)	55.69	30.59	14.98	8.52	13.21	6.5	—
C. 2	Coir (bristle fibre—bad)	51.28	29.75	13.62	6.65	10.32	7.0	—
C. 3	Coir (mattress fibre—good)	54.48	32.63	13.92	9.08	14.08	4.8	—
C. 4	Coir (mattress fibre—bad)	56.97	31.50	14.18	8.91	13.80	5.3	—
C. 5	Coir (Cochin fibre—good)	54.29	28.56	13.90	8.44	13.07	5.5	—
C. 6	Coir (Cochin fibre—bad)	50.52	29.45	13.85	7.48	11.64	6.4	—

#### INTERPRETATION OF ANALYSES.

I. *Cellulose*. Cotton cellulose, which is taken as the standard for all work on cellulose fibres, is unique in two respects. In the first place, a pure product may be obtained by very mild treatments, since it is neither encrusted nor infiltrated with other constituents, and in the second place, the cellulose itself corresponds

more or less to chemically "ideal" cellulose, being composed solely of polyglucose anhydride molecules. The ordinary cellulosic framework of plant materials, woods and fibres is encrusted with other cell wall constituents, and while consisting largely of "true" cellulose, as typified by that of cotton, is not exclusively so and may contain polysaccharides of other sugars. Such associated polysaccharides or cellulosans are retained tenaciously and must be regarded as an integral part of the cellulosic aggregate.

The cellulosan associated with most celluloses is xylan, though in *Gymnosperms* mannan also is found. The nature of the association between cellulose and cellulosans is under investigation and will be reported elsewhere. The molecule of cellulosan polysaccharides is undoubtedly very much shorter than that of cellulose, and their presence has a considerable influence on the properties of the cellulose aggregate as a whole. The xylan content is obtained from the furfuraldehyde yield of the isolated cellulose by reference to Kröber's tables.

II. *Lignin*. The determination of lignin is deceptively difficult, and a method satisfactory for all types of material has yet to be elaborated. The principle of all procedures is the same—to dissolve cellulose and other polysaccharides by strong acid and to weigh the residue after hydrolysis as lignin. Two serious sources of error exist in the determination, due to the presence of pentose groups in the polysaccharides and to the presence of proteins. The disturbance caused by pentose is minimised by the hydrolytic pretreatment with 5%  $H_2SO_4$  which removes the disturbing polysaccharides, and that caused by proteins did not arise in these fibre samples. The results given may therefore be regarded as approximately accurate and comparable.

III. *Furfuraldehyde yield*. The furfuraldehyde obtained on distillation with 12% HCl may come from two groupings, pentoses and uronic acids. In such materials as were used in this work, the uronic acid content (in encrusting hemicelluloses and pectin) is relatively low, so that the major part of the furfuraldehyde arises from the xylan in the cellulose and the pentose units in the encrusting hemicelluloses or polyuronides. The difference between the total yield and that from the cellulose therefore represents that from the pentose and uronic groups in the encrusting hemicelluloses and pectin, if present. No satisfactory method of direct determination of the encrusting hemicelluloses is known. All methods so far suggested, whether dependent on hydrolysis or extraction, include to a greater or lesser extent the cellulosan fraction of the cellulose and are therefore objectionable. Until a procedure which distinguishes between these two important polysaccharide groups is elaborated, the best that can be done for comparative purposes is to take the furfuraldehyde yield of the encrusting hemicelluloses as a measure of the total amount present. No extra precision is gained by calculating separately the furfuraldehyde from uronic acid groups, unless the material happens to have a high content of pectin or polyuronides, a circumstance that was not met with in the fibre samples described here.

IV. *Uronic acids*. Uronic acid anhydride groups are found in pectin and the encrusting hemicelluloses as mentioned above. In retted fibres the pectin content is quite small and the  $CO_2$  yield is therefore almost exclusively due to hemicelluloses.

#### DISCUSSION OF RESULTS.

Flax, ramie, *Calatropis gigantia* and Italian hemp are fibres with very high cellulose contents and contain only small amounts of lignin. The yields of furfuraldehyde which they give are also low, being mainly derived in flax and hemp from xylan in the cellulose with the implication that in these fibres there

can be little encrusting hemicellulose. Ramie, with a lignin content of about 1%, contains considerably more hemicellulose, as the major part of the furfuraldehyde is not associated with the cellulose. Chinese hemp and Indian hemp have lower cellulose and higher hemicellulose contents than Italian hemp, which represents the best quality fibre of this group. The remaining fibres may be clearly distinguished from those already mentioned by the relatively high content of xylan which is to be found in the cellulose. Roughly then, isolated vegetable fibres seem to fall into two groups, those which have a high content of cellulose, free or almost free of xylan, and those which contain appreciable amounts of other constituents such as lignin and hemicelluloses, and the celluloses of which contain much xylan. Jute, sisal, manilla hemp and coir are the most important members of the second group. The distinction between these two groups is not sharp in respect to cellulose content, though, with the one notable exception of Pita grass (a Brazilian fibre from the leaf of an agave), the members of the first group tend to be higher in this constituent. With lignin the reverse is the case, Pita grass again being an exception. The lignin of some members of the second group, particularly jute, seems to be intimately concerned with the fibre structure, whilst in the first group, a portion of it at least arises from woody elements not wholly removed in isolation. Flax and ramie, for example, give only weak general colour reactions for lignin.

Whereas in most cases the fibre samples analysed were supplied as typical, in the case of jute and coir, fibres of various qualities and sources were examined. The grading of jute depends almost solely on appearance, which may not be related directly to the amounts of the chief structural constituents present. The grading of coir, on the other hand, is based on the suitability of the fibres for certain rather different uses and is based on stiffness or flexibility. In jute, no clear differences in analysis were found between the two main types, *Corchorus capsularis* ("white jute") and *C. olitorius* ("brown jute"—the Bogi and Tossa samples), but within each group the better samples tended to have the higher cellulose contents. The uronic acid present, being a measure of encrusting hemicelluloses, increased considerably as quality decreased, probably indicating in-different retting and poor separation from the softer tissues, or over exposure to sunlight with the production of oxycellulose. The xylan in the cellulose of jute, expressed as a percentage of the whole fibre, varied surprisingly little (10.72 to 12.82% being the limits). Omitting "rejection" and discoloured samples the average analysis of jute is cellulose 73.9%, lignin 11.6%, xylan in cellulose 11.9%. No generalisation is possible from the results obtained on the coir samples, the lignin content of which was higher than that of many woods. The variation in amount of xylan in cellulose was greater than expected in view of the fact that each of the grades of coir fibre comes from the same part of the plant, namely the husk. The figures for furfuraldehyde from hemicelluloses indicate the presence of considerable amounts of this group, approaching the quantity found in mature straws.

In Table II the xylan content of the cellulose of all the samples is calculated as a percentage of the total cellulose containing it. The xylan must not be considered as an impurity or contaminant in the cellulose but as an integral and structural part of the cellulosic fabric forming the fibre bundles. The relationship of the cellulosan fraction to the cellulose containing it is under investigation by Astbury and Norman (unpublished). The view has been put forward that the xylan molecules in the cellulose participate in the micellae, are oriented in the same direction as the cellulose chains and are retained by the same forces as are responsible for the lateral stability of the cellulose chains. The molecules of xylan

Table II. *Xylan content of fibre celluloses.*

Expressed as % on the cellulose.			
Fibre	Xylan	Fibre	Xylan
Flax 1	2.6	Jute 21	18.0
Flax 3	3.3	Jute 20	16.5
<i>Calatropis</i>	2.0	Jute 13	16.2
Ramie 1	1.5	Jute 14	17.2
Ramie 2	1.4	Jute 6	15.6
Italian hemp	1.9	Jute 7	17.2
Hemp 6	1.9	Jute 10	16.8
Chinese hemp	5.0	Jute 8	16.9
Indian hemp	2.3	Jute 9	16.6
Pita grass 1	13.4	Jute 12	16.5
Pita grass 2	13.0	Jute 11	16.5
Jute 1	15.2	Manilla hemp	18.9
Jute 2	15.2	<i>Phormium tenax</i>	20.9
Jute 3	15.6	Sisal 1	24.7
Jute 4	15.5	Sisal 2	20.6
Jute 15	15.0	Coir 1	23.8
Jute 16	16.2	Coir 2	20.1
Jute 18	15.8	Coir 3	25.9
Jute 17	15.2	Coir 4	24.2
Jute 19	17.1	Coir 5	24.2
Jute 22	15.1	Coir 6	23.0

are undoubtedly much shorter than the long cellulose chains which may contain 100–300 glucose units. The presence of the xylan in the cellulose must have an important influence on the properties of the aggregate, so that a cellulose high in xylan might be expected to be less perfect in many respects than pure cotton cellulose. It is significant in this connection that the high quality textile fibres are those low in xylan, and that between the two groups there is almost as wide a gap in valuation as in xylan contents. The difference is also reflected in commercial uses and market prices.

The highest contents of xylan in cellulose have been found in cereal straws and hard woods (*vide* Table III), the celluloses of which are notoriously of poor quality. Coir cellulose seems to be similar in composition to the straws. No claim

Table III. *Xylan content of some other celluloses.*

Expressed as % on the cellulose.	
Material	Xylan
Oat straw	29.3
Barley straw	23.5
Wheat straw	28.6
Rye straw	29.4
Oak wood	26.5
Beech wood	24.0

is made that there is an absolute relationship between xylan content and quality, but only that the xylan content is an indication of the type of cellulose present. The percentage of xylan in the cellulose of any given material is not constant, but varies, within limits, with age and environmental conditions. Xylan has been found in the cellulose of extremely young cereal seedlings, but is present to a greater extent in cellulose produced later. It is presumably laid down by the same mechanism as synthesises true cellulose, the balance between the two components changing with age.

From the practical aspect, the division of fibres into two broad groups on the basis of xylan content is of some importance since statements have frequently

been made to the effect that if certain coarser fibres could only be delignified and softened, they could replace the more expensive fine fibres. Even if this were achieved the celluloses would be of different types and possess different properties.

The extraction and hydrolysis of celluloses containing a high percentage of xylan has been investigated and will be reported elsewhere. Such celluloses are far more susceptible than cotton. Apart from the loss of xylan on treatment with acid or alkali, a portion of the cellulose, or a hexosan fraction associated with the cellulose, comes into solution concurrently. The existence of a less resistant portion of the cellulose has long been known, and in the arbitrary method of estimation of  $\alpha$ -cellulose (cold extraction with 17.5% NaOH) the  $\beta$ - and  $\gamma$ -fractions together represent approximately the amount of xylan *plus* less resistant hexosan. The figure is only approximate since the  $\alpha$ -cellulose residue is rarely pentose-free. The nature and amount of the less resistant hexosan fraction in fibre celluloses is a subject calling for investigation. Some observations that have been made on the effect of hot dilute alkalis on fibre celluloses show that generalisation is not possible. The celluloses were prepared and extracted without drying

Table IV. *Extraction of celluloses with hot alkali.*

Results expressed as % oven-dry cellulose.

	Conc. of NaOH %	Residue	Xylan in residue	Xylan loss	Hexosan loss	$\frac{\text{Xylan loss}}{\text{Hexosan loss}} \times 100$
Flax	0.1	94.9	2.5	0.0	5.1	—
	1.0	86.6	1.6	0.9	12.5	7
Ramie	0.1	98.1	1.5	0.0	1.9	—
	1.0	90.7	0.9	0.7	8.6	8
Italian hemp	0.1	96.4	1.3	0.6	3.0	20
	1.0	85.5	1.2	0.7	13.8	5
Jute	0.1	94.2	12.4	2.3	3.5	40
	1.0	88.7	10.8	3.9	7.4	35
Manilla hemp	0.1	95.1	15.8	2.6	2.4	52
	1.0	93.3	14.8	3.5	3.2	53
Sisal	0.1	92.7	16.3	4.0	3.3	55
	1.0	90.7	14.4	5.9	3.3	64
Barley straw	0.1	82.2	12.3	12.3	5.5	69
	1.0	73.4	8.5	16.1	10.5	60

with 0.1 and 1.0% NaOH at the boiling-point for 1 hour (Table IV). The high-xylan fibres are not notably more affected by these extractions than the low-xylan fibres. In the former group, jute cellulose stands out from manilla hemp and sisal in that the xylan removed forms a lower proportion of the total loss, and that 1.0% NaOH removes a considerably greater amount of the less resistant hexosan than does 0.1%, whereas in the other two cases little difference was found. The barley straw cellulose, typical of all cereal celluloses, is far more susceptible to extraction, a high proportion of the loss being xylan. That jute cellulose contains more of a hexosan fraction easily removed by alkali than sisal or manilla hemp celluloses may also be seen from Table V. Samples were treated in the cold with 0.5 to 10% NaOH. From sisal or manilla hemp, concentrations above 4% result in the removal of little additional hexosan material. In jute, the amount increases progressively with concentration.

The experiments described here on the effect of alkali on fibre celluloses show the extreme variability in properties that occurs and also that it is not possible to

Table V. *Extraction of fibre celluloses with cold NaOH.*

2 hours—room temperature.					
Results expressed as % oven-dried original cellulose.					
Alkali conc. %	Total loss	Xylan in residue	Xylan loss	Hexosan loss	Xylan loss / Total loss × 100
<b>Jute:</b>					
0.5	3.52	13.50	1.23	2.29	35
1.0	4.62	13.31	1.42	3.20	31
2	5.74	12.29	2.44	3.30	43
3	10.40	9.60	5.13	5.27	49
4	13.48	7.70	7.03	6.45	52
5	15.13	6.01	8.72	6.41	58
6	16.95	4.35	10.38	6.57	61
7	21.00	2.63	12.10	8.90	58
8	21.28	2.71	12.02	9.26	57
9	22.61	2.56	12.17	10.44	54
10	23.03	2.50	12.23	10.80	53
<b>Sisal:</b>					
0.5	2.16	18.93	1.43	0.73	66
1.0	3.26	18.19	2.17	1.09	67
2	7.40	15.79	4.57	2.83	62
3	11.26	12.84	7.52	3.74	67
4	15.65	9.13	11.13	4.52	72
5	17.22	7.92	12.44	4.78	73
6	18.60	6.40	13.96	4.64	75
7	19.70	5.49	14.87	4.83	76
8	19.76	5.12	15.24	4.52	77
9	20.10	4.56	15.80	4.30	79
10	20.32	4.25	16.11	4.21	79
<b>Manilla hemp:</b>					
1.0	3.95	14.39	3.96	—	100
2	7.39	12.49	5.86	1.53	79
3	10.13	9.31	9.04	1.09	89
4	12.81	7.68	10.67	2.14	84
5	14.59	6.68	11.67	2.92	80
6	15.41	6.03	12.32	3.09	80
7	16.40	4.88	13.47	2.93	82
8	17.90	3.69	14.66	3.24	82
9	18.49	2.51	15.84	2.65	85
10	19.42	1.41	16.94	2.48	87

deduce from xylan content the resistance of the cellulosic aggregate. It has sometimes been the practice to correct the gross cellulose figure for pentosan content to obtain "true" cellulose or "pentosan-free cellulose". The validity of such a correction is questionable, not only on structural grounds but because the residues may apparently contain varying amounts of a less resistant hexosan fraction. The molecular size of the true cellulose chains in these fibres may also be more variable or shorter than those of cotton cellulose, though the evidence on this point obtained by viscosity measurements is not conclusive, as the effect of the other components has not always been given adequate consideration. In any examination of the factors affecting the properties of a cellulosic fibre these points of ultimate composition and micellar structure must be taken into account as well as the nature and distribution of encrusting substances.

#### SUMMARY.

Vegetable fibres of many types fall into two well-defined groups, according as the cellulose of the fibre is low or high in xylan. The first group, low in xylan, includes the high grade fibres such as flax, ramie and Italian hemp. The

second group, high in xylan, consists of fibres of the coarser type, such as jute, manilla hemp and sisal, all of which contain also appreciable amounts of lignin and encrusting hemicelluloses. No direct relationship between quality and xylan content was found in a wide range of jute samples. The resistance or susceptibility of isolated cellulose to such treatments as boiling with dilute alkalis cannot be deduced from the xylan content, owing to the presence of varying amounts of easily extractable hexosan.

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