LXV. THE STONE CELLS OF THE PEAR.

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IN the course of an investigation into the nature of lignocellulose it was thought that the curious woody concretions commonly found in the fleshy parenchyma of the pear might offer possibly a new type of lignocellulose. These structures, termed by de Bary "stone cells," have long been known to botanists and are distributed throughout the whole of the fleshy portions of ripe pears, being especially numerous near the core. Each concretion is situated in the centre of a radiating mass of elongated cells, which are strikingly dissimilar to the rest of the parenchyma. They give all the reactions of a typical lignocellulose with the usual microchemical reagents, such as phloroglucinol and hydrochloric acid (bright red) and chlorine and sodium sulphite (magenta).

Erdmann [1867], who first isolated the stone cells, regarded them as composed of a substance $C_{24}H_{36}O_{16}$, to which he gave the name glycodrupose. He considered the following reactions to occur on hydrolysis:

This drupose on fusion with caustic potash gave aromatic derivatives including pyrocatechol. On boiling with dilute nitric acid the glycodrupose gave rise to "pure" cellulose. These results were repeated by Bente [1875] and in general confirmed.

Cross and Bevan [1895], who also made a brief examination of the material, considered the complex to be a lignocellulose closely allied to jute and pointed out that the empirical formulae of glycodrupose and jute differ only by one atom of oxygen:

On analysis they obtained the following values for glycodrupose:

Ash	...	...	...	...	...	0.91 %
Cellulose	...	...	...	...	...	26-34
Furfural	...	...	...	...	...	18.0
Loss on boiling with 12 % HCl	...	...	...	...	...	53.0

In the absence of other information we have examined the material of the stone cells in the light of modern methods of analysis. The technique in general employed was that elaborated by Dore [1920] for the investigation of hard and soft woods and in Table I a comparison is given of the values

obtained by Dore for a hard wood (oak) and for a soft wood (*Sequoia sempervirens*, Redwood) with the values similarly obtained by us for the stone cells isolated in the manner to be described. The cells were obtained as pale brown, very hard, spherical masses resembling millet seed. The yield from 88 lb. of pears was 97 g. or 0.3 %. The ash content, 0.6 %, was low, the natural moisture was 7.76 %. The analytical figures given have been calculated in each case on the original weight of material dried at 100°.

Table I. *Composition of typical woods and the stone cells.*

				<i>Quercus</i> <i>agrifolia</i> (Hard wood)	Stone cells (Glycodrupose)	<i>Sequoia</i> <i>sempervirens</i> (Soft wood)
Extracted by	benzene	...	...	0.52	0.23	0.34
	alcohol	...	...	4.52	0.38	4.39
	water	...	...	3.82	0.00	0.00
	5 % NaOH	...	...	19.53	12.20	3.45*
Cellulose	...	...	...	47.48	57.18	54.83
Lignin ...	...	...	...	21.14	20.00	34.50
Mannan	...	...	...	0.00	4.62	3.17
Galactan	...	...	...	1.55	0.00	0.49
				98.56	94.61	101.17
Natural moisture				4.20	7.76	11.62

* Estimated as soluble pentosan.

There was no water extract in the case of the stone cells as they had already been boiled with water in the course of isolation. The cellulose figure is almost certainly low owing to the drastic chlorination treatment necessary to remove lignin. To confirm the value obtained, the cellulose was also estimated by the method of Cross and Bevan, but again four chlorinations were necessary before a lignin-free product was obtained. The following values calculated as percentages of dry material were found by this method:

Loss with boiling 1 % NaOH (5 minutes)	...	14.25 %
Cellulose	...	54.82
HCl formed during chlorination	...	11.56

The true value for the cellulose is most probably 60 % accounting partly for the deficiency of the total constituents from 100 %. It contained 73 % of α -cellulose (insoluble in 17.5 % NaOH) and 27 % of β - and γ -cellulose. It will be noted that the alcohol extract, stated by Mehta [1925] to be "free lignin," is very low compared with that of either soft or hard wood. In its high alkali-soluble fraction and small lignin content the wood of the stone cells resembles a hard wood. On the other hand, in its percentage of cellulose and mannan it resembles rather the soft woods. As the growth period is very short it is interesting to find so close a resemblance in composition to that of the mature forest woods.

Distribution of the furfural-yielding components.

The furfural values obtained for the stone cells are compared below with those given by Dore for soft and hard woods respectively. The numbers given are percentages of each particular fraction. No methylfurfural was found.

Table II. *Percentage furfural content of the constituents of wood and stone cells.*

	<i>Sequoia sempervirens</i>	Stone cells	<i>Quercus agrifolia</i>
(a) Untreated material	5.84	21.05	12.00 %
(b) Solvent-extracted material ...	5.71	21.23	6.83
(c) After treatment with 5 % NaOH	—	13.61	6.50
(d) In the cellulose	2.52	20.03	6.11
(e) In the chlorination liquors ...	—	—	1.10

It will be seen that both the stone cells and the cellulose isolated from them yield an unusually high amount of furfural. By combining the values given in Tables I and II, we can calculate that

100 parts of the stone cells yielding 21.23 parts of furfural consist of:

- (a) 88 parts insoluble in alkali, which contribute 11.97 parts of furfural;
- (b) 12 parts soluble in alkali, which contribute 9.26 parts of furfural.

The alkali-soluble fufuroid (b) therefore gives 77 % of its weight of furfural. Of the 88 parts insoluble in alkali 60 are cellulose, 20 lignin and the remainder mannan, etc. The whole of the furfural-yielding complex in this insoluble portion is combined with cellulose, since direct estimation shows that the cellulose yields 20 % of furfural, so that 60 parts would contribute 12 parts of furfural, in good agreement with the 11.97 calculated under (a) above. Further, the cellulose contains 27 % of β -cellulose, and if, as is usual, the β -cellulose is the source of the furfural the β -cellulose must be capable of yielding 74 % of furfural.

It follows from these values that the stone cells contain two fufuroid complexes, one of which is readily removable by caustic soda, while the other remains firmly attached to the α -cellulose.

The fraction (b) is of the nature of a hemicellulose and owing to the large yield of furfural obtained from it no doubt consists partly of pentosan, but in the light of the work of Nanji, Paton and Ling [1925], who have shown that "uronic" acids of the type of galacturonic acid are widely distributed in the plant world, the presence of these furfural-yielding substances is not excluded. "Uronic" acids do not give a quantitative yield of furfural on decarboxylation, but the carbon dioxide evolved is an exact measure of their amount. In a qualitative experiment on the alkali-soluble fraction from the stone cells we found a considerable evolution of carbon dioxide, so that "uronic" acids are present, as well as pentosan, in this hemicellulose constituent.

The composition of the stone cells may therefore be given as follows:

Extractives and ash	1.20 %
Mannan	4.62
Fufuroid soluble in NaOH	12.00*
Lignin	20.00
β -Cellulose	16.20†
α -Cellulose	43.80

* Yielding 77 % of furfural.

† Yielding 74 % of furfural.

EXPERIMENTAL.

The complete separation of the concretions from adherent parenchyma proved very difficult and after a number of attempts it was found best to allow the pears to rot. The method worked out finally was as follows.

(i) *Ripe Pears*. The core and skin were carefully removed and the clean pieces were passed twice through a mincing machine. The mass thus produced was allowed to rot in a large dish (4–5 days).

(ii) *Rotten Pears*. The contents of rotten pears cleaned from skin and core were placed in an enamel-lined bucket in which they were stirred and pulped with a wooden rod. The ensuing treatment was the same for (i) and (ii).

The mass was boiled for 3–4 hours with a large volume of water with constant stirring. After straining through muslin the pulp was covered with glacial acetic acid. The acid and pulp were well mixed by vigorous stirring, diluted with twice their volume of water and again boiled for 3–4 hours. The pulp was washed by decantation, the process being repeated till the water was no longer milky. The pulp was now transferred to a bottle in small quantities at a time, covered with 6–8 times its own bulk of water and well shaken. The crude “glycodrupose” sank to the bottom, while the upper layer of liquid containing parenchyma was poured away.

When a considerable quantity of the glycodrupose had been obtained, further purification was effected by filtering at the pump and drying at 100°. The mass was then ground up in a mortar and shaken with cold water in a bottle. The process of drying, grinding and shaking was repeated several times till the concretions were free from parenchyma.

It was found best to employ a common variety of cooking pear obtained from France, rather than a “table” variety, which contains a smaller quantity of the concretions.

Lignin. The lignin was estimated by the method of Willstätter. The glycodrupose was treated for 12 hours with hydrochloric acid (sp. gr. = 1.2), the whole was then poured into water, filtered and washed. There was still a small quantity of cellulose present and the material was again treated with the acid for 2 hours, diluted with water, filtered and washed free from acid with hot water.

SUMMARY.

(i) The stone cells of the pear are a lignified cellulose resembling in composition the forest woods rather than the annual lignocelluloses such as jute.

(ii) They consist as to 80 % of a lignocellulose, which contains 60 parts of cellulose and 20 parts of lignin. The cellulose contains 73 % of α -cellulose and 27 % of β -cellulose, which latter yields 74 % of its weight of furfural.

(iii) The remaining 20 % consists of extractives 1.2 %, mannan 4.62 %, and an alkali-soluble furfuroid 12 %, which yields 77 % of its weight of furfural, and contains “uronic” acids.

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