394. *Polysaccharides. Part XXXVII. Oxycellulose.*

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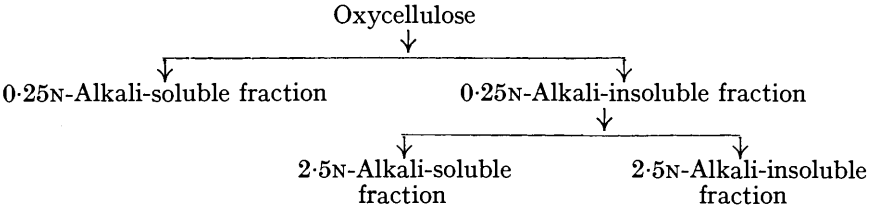
The action of alkali upon oxycellulose has been studied. The oxycellulose, which was prepared by the action of acid permanganate on linters, had a high copper number (14) and contained uronic acid residues. Alkali (0·25N) dissolved 50% of the oxycellulose and the soluble portion was shown to have undergone decomposition of the type suffered by oligosaccharides in the presence of alkali. The moiety insoluble in 0·25N-alkali had a low copper number (0·27) and contained no acidic groups. It was acetylated and methylated with ease and its molecular size (by end-group assay) corresponded to a chain of 90 glucose units. This insoluble fraction of oxycellulose was treated with 2·5N-alkali, in which half of it dissolved. The soluble portion had a chain length of 35 glucose units (by end-group assay) and the insoluble part, a chain length of 60 units (by viscosity measurements on the acetate).

Cold acid hydrolysis of the oxycellulose led to the isolation of an aldobionic acid which has not been further characterised.

The oxycellulose was prepared from cotton linters by oxidation in cold acid solution by means of potassium permanganate (0·25N) (cf. Knecht and Thomson, *J. Soc. Dyers and Col.*, 1920, **36**, 251). The product retained the fibrous cellulose appearance but had a copper number of 14 (linters had 0·1) and it was soluble to the extent of 50% in boiling 1% sodium hydroxide solution. Furthermore, uronic acid residues were present in oxycellulose. Estimation of carboxyl groups by direct and by conductimetric titration, by furfural estimation, and by estimation of carbon dioxide liberated on boiling with acid, gave an average figure of 1·5%.

The solubility of the oxycellulose in alkali is indicative of the change induced in cellulose by the oxidising agent, an alteration which is manifested also by the great difficulty experienced in the acetylation of oxycellulose by methods which are appropriate for cellulose itself. The action of alkali on oxycellulose was more closely examined and, by a graded extraction with alkali of different strengths, the following fractionation was achieved:



In the first place, the oxycellulose was exhaustively extracted by boiling 0·25N-sodium hydroxide. The soluble portion represented 50% of the oxycellulose. The insoluble fraction was now submitted to exhaustive extraction with 2·5N-sodium hydroxide. The material insoluble in alkali of this strength represented 25% of the oxycellulose taken.

The material not dissolved by 0·25N-alkali had lost the properties peculiar to oxycellulose. Its reducing power (Cu No., 0·27) had fallen and uronic acid residues were no longer detectable in it. Moreover, it was no longer resistant to the usual acetylation process and it was easily methylated by treatment of the acetate with methyl sulphate and 30%

sodium hydroxide solution. The 0·25N-alkali-insoluble fraction was not homogeneous, for it was possible to separate the acetate and the methylated derivative into fractions which showed different viscosities. Thus, the methylated derivative (OMe, 44·6%) was separated by precipitation from chloroform solution with light petroleum into three fractions which showed viscosities in *m*-cresol solution corresponding to apparent chain lengths of 110, 92, and 55 glucose units. An assay of the chain length of the main fraction (representing 60% of the whole) by the end-group method gave the value 90 glucose units. In the course of this assay, crystalline tetramethyl glucose and 2 : 3 : 6-trimethyl glucose were isolated in excellent yield. It is clear that this fraction of the oxycellulose is constituted on the same plan as the hydrocellulose described in the preceding papers. If abnormalities of structure did exist in this moiety of the oxycellulose, they were of such a nature that reversion to the normal cellulose type occurred under the action of weak alkali. We prefer to regard the peculiarities of the original oxycellulose as confined to that part which is soluble in weak alkali and which is examined below as 1%-alkali-soluble fraction. The material insoluble in weak alkali is constituted of chain-molecules of glucose units united as in the original cellulose molecule and the average length of these chains corresponds to 90 glucose units.

An observation of some interest was made when the 0·25N-alkali-insoluble fraction was further extracted with boiling 2·5N-sodium hydroxide. Approximately half of the material dissolved and the dissolved substance recoverable by acidification retained the characteristics of a cellodextrin. The 2·5N-alkali-soluble fraction (representing 25% of the oxycellulose) had copper number 0·23 and underwent acetylation and methylation with the usual reagents. The methyl derivative (containing OMe, 44·6%) was fractionated from chloroform–light petroleum, and viscosity determinations on the fractions showed that the substance, unlike the parent 0·25N-alkali-insoluble fraction, was constituted of chain-molecules of approximately uniform size. The chain length, determined by the end-group method, was 35 glucose units.

It is obviously impossible for the 0·25N-alkali-insoluble fraction with an average chain length of 90 units to consist of a mixture, half of which is a cellodextrin with a chain length of 35 glucose units. The conclusion is inescapable that the shorter chain cellodextrin is produced by the fragmentation, under the influence of 2·5N-alkali, of the longer chain molecules of the 0·25N-alkali-insoluble fraction.

The amount of the 2·5N-alkali insoluble fraction available was insufficient for a determination of its molecular size by the end-group method. It was, however, possible to acetylate this material and the viscosity of the acetate corresponded to an apparent chain length of 60 glucose units. It is probable that this figure approximates to that which would be found by the end-group method, since in the hydrocellulose and oxycellulose series the molecular size as determined by the two methods is of the same order. This being so, it becomes apparent that the whole of the 0·25N-alkali-insoluble substance has been further degraded by boiling with 2·5N-sodium hydroxide.

The structure of that part of the oxycellulose which is soluble in weak alkali can only be conjectured, for an examination of the 0·25N-alkali-soluble material reveals that profound and extensive decomposition has occurred. The soluble product proved to be a mixture of acids and as some difficulty was experienced in the isolation of these acids from the sodium salts the procedure of extraction of the oxycellulose was modified in that 3% barium hydroxide solution was used instead of 0·25N-sodium hydroxide. There was no essential difference in the type of substance extracted by the two methods.

The nature of the products of extraction of oxycellulose with 3% barium hydroxide solution was unaltered by the exclusion of air during the extraction. Thus, the extraction of 2 g. of oxycellulose (*a*) in air and (*b*) in a nitrogen atmosphere led to the same loss in weight (40%), gave the same weight of mixture of barium salts (0·88 g.), and the reducing powers of the extracts were identical.

The acids regenerated from the barium salts fell into two categories—those volatile in steam and those which were non-volatile. The volatile acids were formic and acetic acids and the yield of the former represented 5% of the weight of the 0·25N-alkali-soluble fraction. The non-volatile fraction was methylated by treatment with methyl iodide and silver oxide

and the mixture of methyl esters so obtained was fractionally distilled. The chief constituent of the first fraction was methyl *d*-α-methoxypropionate (characterised by conversion into the crystalline amide), which could only have been derived, by methylation, from *d*-lactic acid. It was shown that the remaining fractions consisted of the methylated esters of an acid, $C_3H_5(OH)_2 \cdot CO_2H$, and a mixture of saccharinic acids of formula $C_5H_7(OH)_4 \cdot CO_2H$.

The products of the action of weak alkali on oxycellulose which have been identified are therefore formic acid, acetic acid, lactic acid, a dihydroxybutyric acid, and a mixture of C_6-saccharinic acids. It is significant that the same acids are formed when a monosaccharide (or a disaccharide) is treated with alkali (cf. *Ann. Reports*, 1937, **34**, 286).

The uronic acid residues in oxycellulose were destroyed not only by weak alkali but also by boiling mineral acid. Thus, oxycellulose was hydrolysed by treatment first in the cold with 72% sulphuric acid and thereafter with boiling 1% sulphuric acid. No uronic acid could be detected in the hydrolysate, from which crystalline glucose and crystalline α-methylglucoside were isolated in a yield of 81% of the oxycellulose taken. In a comparative hydrolysis of the 0·25N-alkali-insoluble fraction of the oxycellulose (which was free from acidic groups), 90% was isolated as crystalline glucose and α-methylglucoside. When, however, the oxycellulose was hydrolysed with 72% sulphuric acid in the cold and the boiling with weak mineral acid was omitted, the acidic groups persisted and a barium salt was isolated which appeared to have the composition of the barium salt of an aldobionic acid. This product is under investigation.

When these results are viewed as a whole, certain suggestions as to the constitution of oxycellulose may be made. In the first place it is clear that the fragmentation of the cellulose chain which normally occurs under the action of alkali is greatly accelerated if the cellulose is first treated with an acid oxidising agent. The latter effects the conversion of a proportion ($6\frac{1}{2}$% in this case) of the terminal primary alcohol groups of the glucose units into carboxyl groups, but it is doubtful if this conversion is the cause of the apparent decreased stability towards alkali of the glycosidic links. The high reducing power of the oxycellulose suggests indeed that the fragmentation of the cellulose chain has already occurred during the oxidation with the formation to the extent of 50% of very short chains of glucose units (the average size of these small molecules cannot be determined at present, but the maximum chain length would seem to be 30—35 glucose units, for the 2·5N-alkali-soluble fraction, which is recovered unchanged from alkali, has a chain length of 30—35 units). The short-chain molecules dissolve in weak alkali and undergo degradation of the kind suffered by the reducing sugars under the same conditions. The newly formed uronic residues would appear to be confined to the postulated molecules of oligosaccharide dimensions and hence are not found in the 0·25N-alkali-insoluble fraction.

Experimental.

Preparation of Oxycellulose.—Cellulose (cotton linters) was oxidised in acid solution with potassium permanganate (0·25N) by the method of Knecht and Thompson (*loc. cit.*). Oxycellulose was obtained in 95% yield after washing with water until free from mineral acid and drying in a vacuum at 45°. A comparison of certain properties of this oxycellulose with those of the cellulose from which it was prepared are shown below :

	Copper number.	Methylene-blue absorption.	% Moisture.	% Ash.	Ash. alkalinity.	Loss in weight on boiling with 1% NaOH.
Oxycellulose	14·0	32·1	6·0	0·7	7·9	44·1
Cellulose	0·1	1·0	2·5	0·15	2·2	1·7

In addition, the following properties of the oxycellulose were recorded. On boiling with 12% hydrochloric acid the percentage yield of furfural by the barbituric acid method (Jäger and Ungar, *Ber.*, 1903, **36**, 1222) was 1·2 and by the phloroglucinol method (Schorger, *J. Ind. Eng. Chem.*, 1923, **15**, 748) 1·8. On the basis of the furfural estimation, the carboxyl content of the oxycellulose was 1·4%; it was 1·2% by carbon dioxide estimation (method of Nanji, Paton, and Ling, *J. Soc. Chem. Ind.*, 1925, **44**, 253T); 1·8% by direct titration and by conductimetric titration (method of Callen and Horrobin, *J. Soc. Chem. Ind.*, 1928, **47**, 329T).

Oxycellulose Acetate.—Oxycellulose (50 g.) was stirred for 30 minutes with glacial acetic acid

(500 c.c.) containing a little chlorine and to the cooled mixture acetic anhydride (250 c.c.), containing sulphur dioxide equivalent to the chlorine, was added. The temperature was then kept at 35° for 6 days. Even at the end of this period, a part of the oxycellulose remained undissolved. This residue was filtered off, the clear filtrate, after dilution with acetic acid, was poured into a large volume of water, and the precipitated acetate was washed with water until free from acid. Yield, 68%. The oxycellulose acetate so prepared contained ash 0·44, $CH_3{\cdot}CO$ 43·7% (by distillation with benzenesulphonic acid) and showed $[\alpha]_D^{20°}$ — 21·0° in chloroform. A viscosity estimation in *m*-cresol solution corresponded, on Staudinger's formula, to an apparent chain length of 60—70 glucose units. Attempts to regenerate oxycellulose from the acetate were abandoned because of the marked effect of alkali on the oxycellulose, which for the same reason was not submitted to methylation.

Extraction of Oxycellulose with 0·25N-*Sodium Hydroxide.*—Oxycellulose (40 g.) was heated under reflux with 0·25N-sodium hydroxide (4 l.) for 4 hours. The residue—0·25N-alkali-insoluble substance—was washed successively with a little dilute acetic acid, water, alcohol, and ether, and finally dried at 45° in a vacuum. Yield, 58%. When this residue was submitted to further repeated extraction with 0·25N-sodium hydroxide, the total material extractable by alkali of this dilution was removed in four operations, the total loss in weight approaching a maximum value of 52%. Cotton linters under similar conditions showed a loss in weight of 1·9%. The 0·25N-alkali-insoluble substance had copper number 0·27 and contained no carboxylic groups.

Acetylated 0·25N-*Alkali-insoluble Substance.*—The residue left after the alkali extraction was acetylated with great ease by the method already described, 4 hours at room temperature being sufficient to complete the reaction. The acetate so obtained contained only 40% of acetyl. It was separated into five fractions by precipitation from a chloroform solution by addition of light petroleum. Viscosity measurements on the fractions in *m*-cresol demonstrated that the substance was not homogeneous: the average apparent chain length of the fractions varied from 48 to 70 glucose units.

Methylated 0·25N-*Alkali-insoluble Substance.*—The acetate prepared as above was insoluble in acetone but it became soluble in this solvent after a preliminary swelling in carbon tetrachloride. The acetate so pretreated was then simultaneously deacetylated and methylated by the usual method. After eight successive treatments with the methylating agents, the product (purified by precipitation from chloroform) contained OMe 44·6% ($C_9H_{16}O_5$ requires OMe, 45·6%). The methylated product (95 g.) was separated by solution in chloroform (1000 c.c.) and ether (400 c.c.) and precipitation with light petroleum into the following fractions:

Fraction.	Wt. (g.).	% OMe.	$\eta_{sp.}$ in *m*-cresol.	$\eta_{sp.}/c.$
1	5		Discarded	
2	19	43·5	0·442	0·110
3	55·5	44·0	0·378	0·092
4	15·1	44·2	0·222	0·055

An estimation of the chain length of fraction 3 was made by the method of Haworth and Machemer (*loc. cit.*). Hydrolysis was effected with fuming hydrochloric acid in the cold; the resulting sugars were converted into the methylglucosides, and the latter separated by distillation from a Widmer flask at 0·1 mm. pressure. The following fractions were collected:

Fraction.	Wt. (g.).	$n_D^{15°}$.	% OMe.
1	0·380	1·4460	60·0
2	0·330	1·4522	55·5
3	1·972	1·4572	51·3
4	1·583	1·4580	50·3

Fraction 1 was pure tetramethyl methylglucoside, and fraction 4 pure trimethyl methylglucoside. It was estimated on this basis that the yield of tetramethyl methylglucoside was 0·672 g. from 55 g. of methylated cellulose. Applying the usual correction (J., 1938, 1244) the percentage yield of tetramethyl methylglucoside is 1·39, corresponding to an average chain length of 90 glucose units. The tetramethyl methylglucoside and the trimethyl methylglucoside were characterised by conversion into crystalline tetramethyl glucopyranose and 2 : 3 : 6-trimethyl glucopyranose respectively.

Further Extraction with 2·5N-*Sodium Hydroxide Solution.*—Oxycellulose which had been exhaustively extracted with 0·25N-sodium hydroxide was now submitted to the action of boiling 2·5N-sodium hydroxide; a further loss in weight then occurred, reaching a maximum of 25% (calculated on the weight of original oxycellulose) in four extractions. The total loss in weight of oxycellulose under the successive actions of 0·25N- and 2·5N-sodium hydroxide was thus

75%. The extraction of the 0·25N-alkali-insoluble substance with 2·5-sodium hydroxide was not accompanied by decomposition, for on acidification of the extract the 2·5N-alkali-soluble substance was precipitated apparently unchanged. The 2·5N-alkali-insoluble substance had copper number 0·23. In a comparative experiment, cotton linters lost 9% of its weight on exhaustive extraction with 2·5N-sodium hydroxide.

Acetylation of the 2·5N-Alkali-soluble Substance.—The products extracted by four successive treatments of 0·25N-alkali-insoluble substance (10 g.) with boiling 2·5N-sodium hydroxide together with the insoluble residue were each converted into the corresponding acetate by the method already described. The properties of these acetates are tabulated below :

Acetate	1st extract	2nd extract	3rd extract	4th extract	2·5N-Alkali-insoluble substance
% $CH_3{\cdot}CO$	40·7	44·0	38·2	41·2	41·9
$\eta_{sp.}$ (*m*-cresol)	0·108	0·087	0·137	0·093	0·221
$\eta_{sp.}/c$	0·026	0·021	0·033	0·022	0·056

Methylation of the 2·5N-Alkali-soluble Substance.—0·25N-Alkali-insoluble substance (100 g.) was boiled with 2·5N-sodium hydroxide (9 l.) for 5 hours. After keeping at room temperature over-night, the supernatant liquid was decanted and acidified with acetic acid, and the precipitate separated by the centrifuge. This precipitate was dissolved by stirring with 30% sodium hydroxide solution (3 l.) and to the solution were added methyl sulphate (300 c.c.) and dioxan (300 c.c.). After the mixture had been stirred at room temperature for 20 hours, second portions of methyl sulphate (300 c.c.) and dioxan (50 c.c.) were added and the stirring was continued for 20 hours. The upper dioxan layer was separated by decantation and the lower, aqueous, layer was submitted to remethylation in the above manner. After five such treatments almost the whole of the methylated product had accumulated in the dioxan layer, which was now evaporated to dryness and the residue exhaustively extracted with chloroform (2 l.). Yield, 13 g. Purification was effected by solution in chloroform and precipitation by the addition of light petroleum. A small first fraction containing 28·1% of mineral matter was discarded. The main fraction (10·1 g.) contained ash 0·4, OMe 44·6% and had $[\alpha]_D^{20°}$ — 2° and $\eta_{sp.}$ 0·13 in *m*-cresol, corresponding to an apparent chain length of 33 glucose units. The product appeared to be homogeneous, for 1 g. was separated into two fractions (0·61 and 0·35 g.) by precipitation from chloroform solution with light petroleum and these fractions showed $\eta_{sp.}$ 0·137 (equiv. to 34 units) and $\eta_{sp.}$ 0·123 (equiv. to 30 units) respectively.

The methylated 2·5N-alkali-soluble substance (9·54 g.) was simultaneously hydrolysed, and the sugars converted into the glucosides by boiling with methyl alcohol (200 c.c.) containing 3·5% of hydrogen chloride for 90 hours. The filtered solution was neutralised with silver carbonate, filtered, and concentrated to a syrup. The latter was fractionated in the usual way by distillation from a Widmer flask at 0·1 mm. pressure.

Fraction.	Weight (g.).	$n_D^{19·5°}$.	% OMe.	Fraction.	Weight (g.).	$n_D^{19·5°}$.	% OMe.
1	0·078	1·4431	61·2	4	0·773	1·4567	—
2	0·272	1·4498	—	5	1·394	1·4570	52·0
3	0·601	1·4551	—				

Crystalline tetramethyl glucopyranose (m. p. 85°) and 2 : 3 : 6-trimethyl glucopyranose (m. p. 117°) were obtained by the hydrolysis of fractions 1 and 5 respectively. The estimated total yield of tetramethyl methylglucoside was 0·31 g., corresponding, after correction, to a percentage yield of 3·5%. The average chain length of the 2·5N-alkali-soluble substance is thus 35 glucose units.

Examination of the Material Soluble in Dilute Alkali Solution.—(a) *0·25N-Sodium hydroxide extract.* By methylation of the extract it was established that the principal products of the action of 0·25N-sodium hydroxide on oxycellulose were hydroxy-monocarboxylic acids. As it was found impossible to recover by this method more than 30% of the weight of oxycellulose dissolved, a modified procedure was adopted in which the extraction was made with 3% barium hydroxide solution; the loss in weight suffered by the oxycellulose was the same with each extracting medium.

(b) *Extraction with 3% barium hydroxide solution.* Oxycellulose (800 g.) was boiled for 4 hours with 3% barium hydroxide solution (10 l.), and the dark brown solution, after filtration, neutralised at 70° with carbon dioxide. The neutral solution was filtered through charcoal and evaporated to dryness under diminished pressure. The residue, a hard glass (380 g.), contained 35·1 and 34·4% of barium (duplicate estimations). The insoluble oxycellulose residue weighed 460 g. The loss in weight was thus 42%.

The free acids were liberated from the barium salts (230 g. in 400 c.c. of water) by the addition of 10N-sulphuric acid in sufficient quantity to precipitate all but a trace of the barium. The solution was evaporated to dryness at 50°, without removal of the precipitated barium sulphate, and the whole of the distillate (water and volatile acids) was collected in a receiver cooled in ice and salt (distillate A). The residue (non-volatile acids and barium sulphate) will be referred to as B.

The aqueous distillate (*A*). The acid distillate was neutralised by the addition of barium hydroxide, the excess of which was removed with carbon dioxide. The filtered solution was evaporated to dryness, and the partially crystalline residue (25 g.) dissolved in water (200 c.c.). Four fractions were obtained by the gradual addition of ethyl alcohol to this solution. The first fraction (crystalline needles) contained Ba, 60·7% (Calc. for $C_2H_2O_4Ba$: Ba, 60·4%) and gave an ammonium salt, m. p. 115—117°. It reduced Fehling's solution, ammoniacal silver nitrate, and mercuric chloride, evolved carbon monoxide on heating with sulphuric acid and ethyl formate with sulphuric acid and ethyl alcohol. The substance was thus barium formate. The fourth fraction contained barium acetate (ethyl acetate test; formation of cacodyl with arsenious oxide). The amount of formate in each fraction was estimated by permanganate titration.

Fraction	1	2	3	4
Weight (g.)	21·2	1·32	2·70	1·61
% Barium formate	99·0	76·6	60·8	16·5

The yield of barium formate was 24 g. (from 480 g. of oxycellulose).

The non-volatile acids. The residue (B) was heated at 45° with methyl iodide (250 c.c.) and dry silver oxide (200 g.) for 24 hours. Thereafter the excess of methyl iodide was removed by distillation, and the residue exhaustively extracted with ether (2500 c.c.). Evaporation of the ether left a syrup, which was submitted to further treatment with the methylating agents, the process being repeated until the methoxyl content of the product reached a constant value. The methylated esters so obtained (94·4 g.) were submitted to fractional distillation :

Fraction.	Wt. (g.).	Bath temp.	Pressure, mm.	$[\alpha]_D$.	Equiv. wt.	% OMe.	% C.	% H.	$n_D^{20°}$.
1	2·0	138°	20	Inactive	127	52·1	50·8	8·6	1·4005
2	4·0	86	0·03	Inactive	162	51·0	51·6	8·5	1·4226
3	23·0	103	0·03	+45·0°	198	49·6	53·1	8·3	1·4465

Fraction 1 on treatment with methyl-alcoholic ammonia gave a crystalline amide, m. p. 81°, which in admixture with authentic *O*-methyl-lactamide (m. p. 82°) showed no depression (Found : C, 46·6; H, 8·7; N, 13·5; OMe, 30·0. Calc. for $C_4H_9O_2N$: C, 47·0; H, 8·7; N, 13·6; OMe, 30·1%). Fraction 1 was thus methyl *d*-α-methoxypropionate, which came from the methylation of *d*-lactic acid.

Fraction 2 was identical with a fraction obtained by methylating and distilling the material extracted from oxycellulose by 0·25N-sodium hydroxide [see under (*a*) above]. The latter fraction also was optically inactive, had $n_D^{20°}$ 1·4230, OMe 50·1%, and equiv. weight by alkali titration 162. The substance was an ester and contained 16·2% of ester methoxyl. It was found impossible to prepare a crystalline amide and the ester did not condense with phenylhydrazine. From the properties recorded, fraction 2 would appear to be the methyl ester of a methoxy-monocarboxylic acid. The ester $C_3H_5(OMe)_2{\cdot}CO_2Me$ requires total OMe, 57·4; ester OMe, 19·1%; equiv. wt., 162. The ester (1·1 g.) was hydrolysed by heating with 3% barium hydroxide solution (70 c.c.) for 2 hours at 75°. The excess of alkali was neutralised with carbon dioxide, and the solution filtered and evaporated to dryness at 45°. The residual barium salt was dissolved in aqueous alcohol, and an exact equivalent of N-sulphuric acid added. After removal of the barium sulphate by centrifuging and evaporation of the solution, a colourless acid syrup was obtained, which distilled at constant temperature at 0·1 mm. pressure. The distillate (0·8 g.) was optically inactive and had $n_D^{20°}$ 1·4402, OMe 37·5%, and equiv. wt. 155 [$C_3H_5(OMe)_2{\cdot}CO_2H$ requires OMe, 39·2%; equiv. wt., 158].

Fraction 3, also an ester, was hydrolysed, as described, with 3% barium hydroxide solution. The hydrolysis product from 5·1 g. of the ester was separated by distillation at 0·1 mm. pressure into two parts, fraction 3*a* (3·0 g.) and fraction 3*b* (0·4 g.).

Fraction 3*a*, a mobile syrup, had $n_D^{20°}$ 1·4496, $[\alpha]_D^{20°}$ + 64·4°, and equiv. wt. 203. The substance behaved as a γ-lactone. It reacted only very slowly with sodium hydroxide solution to form a sodium salt. The acid produced by acidification of the sodium salt with sulphuric

acid had $[\alpha]_D$ — 7·5°, changing to a constant value + 32·4° in 25 hours [Found : C, 53·1; H, 7·9; OMe, 45·3. $C_6H_7O_2(OMe)_3$ requires C, 53·0; H, 7·9; OMe, 45·6%; equiv. wt., 204].

Fraction 3*b* was a viscous syrup which behaved as a monocarboxylic acid on titration (equiv. wt. 232). It had $n_D^{20°}$ 1·4560, $[\alpha]_D$ — 4·8° [Found : OMe, 51·5. $C_5H_7(OMe)_4 \cdot CO_2H$ requires OMe, 52·5%; equiv. wt., 236].

Fraction 3 would thus appear to be a mixture of a lactone, $C_6H_7O_2(OMe)_3$ and an ester, $C_5H_7(OMe)_4 \cdot CO_2Me$.

The Extraction of Oxycellulose in the Absence of Air.—Comparative experiments were performed in which oxycellulose (2 g.) was extracted with 3% barium hydroxide solution (200 c.c.) in an atmosphere of (*a*) nitrogen and (*b*) air. The following table shows that the action of alkali is not modified by the presence of oxygen.

Extraction.	Loss in wt., %.	Reducing power of extract (c.c. N/25-$KMnO_4$).	Yield of Ba salts from extract (g.).
In air	40·4	16·5	0·88
In nitrogen	40·3	16·65	0·88

The Acid Hydrolysis of Oxycellulose.—The method of Monier-Williams (J., 1921, **119**, 803) being used, oxycellulose (9·730 g.; moisture, 2·92; ash, 1·50%) was treated at room temperature with 72% sulphuric acid (50 c.c.) for 7 days and, after dilution to 5 l. with water, the solution was boiled for 16 hours. The solution was filtered (residue, 0·08 g.) and the filtrate, after neutralisation with barium carbonate, was evaporated to dryness under diminished pressure. During the evaporation, sufficient N/10-sulphuric acid was added at intervals to maintain the p_H at about 4. The residue was exhaustively extracted with boiling methyl alcohol (2 l.) and evaporation of the extract gave a syrup (9·415 g.) which partially crystallised. The syrup gave a negative uronic acid test with naphtharesorcinol. Crystalline glucose (7·35 g.) was separated and the residual syrup converted into the glucoside by boiling for 7 hours with 2% methyl-alcoholic hydrogen chloride (70 c.c.). This product yielded crystalline α-methylglucoside (2·01 g.) and a syrup (0·39 g.). The yield of crystalline material calculated as glucose was thus 8·31 g. from 9·22 g. of oxycellulose, *i.e.*, 90·2 g. from 100 g. of oxycellulose (81·2%).

The Acid Hydrolysis of the 0·25N-*Alkali-insoluble Substance.*—The residue (10·115 g.; moisture, 1·82; ash, 1·15%) after extraction of oxycellulose with 0·25N-sodium hydroxide was hydrolysed by the sulphuric acid method used for oxycellulose. The yield of crystalline material (glucose and α-methylglucoside), calculated as glucose, was 100·0 g. from 100 g. of 0·25N-alkali-insoluble substance (89·7%).

The Cold Acid Hydrolysis of Oxycellulose.—Oxycellulose (10 g.) was treated with 72% sulphuric acid (50 c.c.) for 14 days at room temperature. The solution was diluted with water (5 l.), neutralised immediately with barium carbonate, and evaporated to dryness at 30°. The residual syrup, which gave a positive naphtharesorcinol test, was dissolved in water, filtered, and, after concentration to 20 c.c., mixed with methyl alcohol (150 c.c.). The precipitation was repeated and the precipitate was extracted (Soxhlet) with methyl alcohol until the rotation of the extract reached a constant value. The residue of barium salts was purified by two further precipitations from aqueous solution with alcohol. Yield, 1·42 g. of a colourless amorphous powder, $[\alpha]_D$ + 61·7° [Found : Ba, 16·4. $Ba(C_{12}H_{18}O_{12})_2$ requires Ba, 16·3%]. These constants were unchanged after a further precipitation from aqueous solution by alcohol.

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