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The contribution to kappa number from hexeneuronic acid groups in pulp xylan

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Abstract

The kappa number of chemical pulps is widely used both in mill operation and in laboratory work as a measure of the degree of delignification in pulping, oxygen delignification, and prebleaching. Recently, it has been shown that the kappa number reflects not only lignin but also carbohydrate structures sensitive to oxidation by permanganate, notably hexeneuronic acid groups linked to xylan. In the present work, the kappa number units originating from hexeneuronic acid groups calculated on a molar basis have been determined in two different ways, viz. by permanganate oxidation of model compounds and by selective elimination of hexeneuronic acid groups from a series of kraft pulps. The results are in good agreement with each other and demonstrate that 10 μ mol of hexeneuronic acid correspond to 0.84–0.86 kappa units. From kappa number determinations combined with hydrolysis of the pulp with mercuric acetate, it is possible to calculate the amount of hexeneuronic acid groups present in a pulp. © 1997 Elsevier Science Ltd.

Keywords: 4-Deoxy-L-threo-hex-4-enopyranosyluronic acid; Kappa number; Kraft pulps; Xylan

1. Introduction

The lignin content in a chemical pulp is an important parameter for process control in both pulping and bleaching. One way of estimating the residual lignin content in pulp fibers is by determining the kappa number (e.g. according to SCAN-C1:77). In this test, the consumption of potassium permanganate during oxidation of the pulp under standardised conditions is measured, and the resulting value is used as an indirect measure of the lignin content [1].

In previous work [2], it was found that the amount of residual lignin present in birch kraft pulps was much smaller than was indicated by a recalculation of kappa number to lignin content. It was therefore assumed that structures originating from the pulp polysaccharides were able to contribute to the consumption of permanganate (kappa number) and were thus calculated as 'lignin'. In later work [3], it was further confirmed that a substantial portion of the kappa number in a birch kraft pulp was related to carbohydrates and particularly to material present in xylan chains.

Recently, it was shown that kraft pulping of pine wood gives rise to hexeneuronic acid groups in the xylan by elimination of methanol from 4-O-methyl-D-glucuronic acid groups [4] (cf. Ref. [5]). The analytical method involved enzymatic hydrolysis of the

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pulp with xylanase followed by ¹H NMR studies of the resulting liquor [4]. As an alternative, mild hydrolysis of the pulp with mercuric acetate can be used to selectively remove the hexeneuronic acid groups [6]. The finding that hexeneuronic acid groups are present in kraft pulps provides an explanation of the fact that birch pulps (in particular) show a discrepancy between the amount of isolated lignin and the amount calculated on the basis of the kappa number [2], since hexeneuronic acid groups can be expected to consume permanganate in the kappa number determination.

A quantitative determination of hexeneuronic acid groups present in pulps can now be achieved by NMR spectroscopy [4], anion-exchange chromatography [7], capillary zone electrophoresis [8], or colorimetry [6]. The exact consumption of potassium permanganate by hexeneuronic acid groups is a matter of interest, since a more accurate estimation of lignin content based on kappa number could be achieved if it were possible to subtract the contribution associated with hexeneuronic acid groups. Recently, kappa number measurement combined with mild acid hydrolysis with formic acid was applied to hexenuronoxylo-oligosaccharide and pulp samples in order to determine the contribution to the kappa number associated with hexeneuronic acid groups [9]. In the present work, the permanganate consumption of selected model compounds was determined and used to calculate the kappa number contribution of hexeneuronic acid groups. The value obtained was checked by kappa number measurements on pulps before and after a mild hydrolysis with mercuric acetate.

2. Experimental

Materials.—All the model compounds were of 'pro analysis' or equivalent grade, and α -terpineol was redistilled before use. Industrial unbleached and OQP-bleached birch kraft pulps were obtained from Swedish mills and air dried after a thorough washing with distilled water. They were subsequently extracted with acetone for 12 h in order to remove all extractives.

Permanganate oxidation of model compounds.— The standard method for kappa number determination was applied (SCAN-C1:77), but the reaction time with permanganate was varied as follows: 0, 0.5, 2, 3.5, 5, 10, and 20 min. Preliminary experiments to determine the amount of model compound which would consume approximately 50% of the permanganate soln were carried out with all the model compounds, viz. α -terpineol, 2-ketoglutaric acid, Dglucose, and a mixture of D-glucose and 2-ketoglutaric acid (2:1 mol ratio). In each experiment, the required amount of model compound was weighed out with an accuracy of ± 0.001 g and dissolved in a small amount of distilled water. (α -Terpineol was dissolved in a small amount of acetone.) After the addition of water to the required standard volume, the permanganate oxidation was carried out as described in SCAN-C1:77. When acetone was used as cosolvent, the permanganate consumption was corrected by carrying out a blank determination.

Removal of hexeneuronic acid groups by mercuric acetate hydrolysis.—A soln of 60 mM mercuric acetate at pH ~ 5.4 was prepared by dissolving 4.84 g of mercuric acetate in 60 mL of 0.2 M CH₃COOH containing 4.66 g of NaOAc, and diluting to 250 mL. Acetone extracted pulp (1–4 g, O.D. weight) was mixed with water (60 mL/g) and allowed to swell at room temperature for 1 h with stirring. An equal vol of the mercuric acetate soln was added and the mixture was kept at room temperature for 20 min with continuous stirring. After filtration, the pulp was washed overnight with running deionised water, and collected for the kappa number measurement.

Determination of hexeneuronic acid groups in pulps.—The colorimetric method described in Ref. [6] was applied.

Determination of kappa number in pulps.—The standard procedure described in SCAN-C1:77 was applied on pulps before and after the mercuric acetate hydrolysis. According to this standard, the kappa number is defined as the number of mL of 20 mmol/L (0.1 N) KMnO₄ soln consumed by one gram of moisture-free pulp under the conditions specified in the standard.

3. Results and discussion

Theoretical permanganate consumption by hexeneuronic acid groups.—Permanganate reacts with carbon-carbon double bonds and, under the acidic conditions prevailing in the standard kappa number measurement, a ketol pathway for the reaction of the double bond in hexeneuronic acid should be favoured [10]. This is outlined in Scheme 1 and starts by the addition of permanganate to the double bond in 1. Subsequent hydrolysis leads to the ketol structure 2 containing an unstable hemiketal group which in turn



Scheme 1. Oxidation of the hexeneuronic acid group by KMnO₄.

is rearranged. The resulting α , β -diketo acid (3), is further oxidised and decarboxylated in two consecutive steps into structure 5. The hemiacetal group in 5 is then rearranged, resulting in liberation of the xylan chain. Finally the aldehyde acid (6) formed is oxidised to the end product 7. (Rearrangement of the hemiacetal group may also occur at the earlier stage, i.e. from structure 3).

The complete reaction sequence giving compound 7 from the starting structure 1 can thus be separated into four individual oxidation steps, viz. oxidation A: $1 \rightarrow 2$, oxidation B: $3 \rightarrow 4$, oxidation C: $4 \rightarrow 5$, and oxidation D: 5 or $6 \rightarrow 7$ (Scheme 1). If it is assumed that the overall reaction ends with compound 7, and that each oxidation step in the sequence A-D goes to completion during the standard reaction conditions employed in the kappa number determination, 10 μ mol of hexeneuronic acid would theoretically be equal to 1.0 kappa number units. By calculation of the number of electrons transferred in each step (A-D), this value can be divided into 0.4, 0.2, 0.2, and 0.2 units, respectively.

Permanganate consumption of model compounds. — The permanganate consumption by a hexeneuronic acid group can be calculated if the extent of each individual reaction step in the sequence A–D is known. For this purpose, a series of model compounds, assumed to be representative of the oxidation steps, A–D, were oxidised with permanganate under standard conditions, and the extents of oxidation were determined. Reaction A was calculated with α terpineol as a model compound, reactions B and C with 2-ketoglutaric acid, and reaction D with D-glucose (Scheme 2). In order to support the assumption that compound 7 was the end product in the oxidation of 1 (Scheme 1), glycolic acid and DL-glyceric acid were also subjected to the permanganate treatment.

In Fig. 1, the rates of oxidation of the various model compounds are shown based on the consumption of permanganate. For α -terpineol, the permanganate consumption has been calculated as 100% for the conversion to the ketol structure **8** (Scheme 2), and a higher consumption thus means that further oxidation occurs. The results shown in Fig. 1 demonstrate that α -terpineol and 2-ketoglutaric acid are immediately oxidised to **8** and succinic acid **9**, respectively. Glucose, on the other hand, gave a degree of oxidation of only about 7% after the standard 10 min reaction time with permanganate.

The oxidation with acidic permanganate is autocat-



Scheme 2. Oxidation of different model compounds by KMnO₄.

alytic and it has been shown that the lower oxidation states of manganese, i.e. Mn(IV) and Mn(III), are much more effective as oxidants than Mn(VII) [11]. A separate permanganate oxidation experiment with a mixture of D-glucose and 2-ketoglutaric acid was therefore carried out to see whether the oxidation of glucose was increased by the presence of Mn(IV) or Mn(III), the latter originating from the fast oxidation of 2-ketoglutaric acid. Glucose was indeed oxidised more rapidly, and after 10 min a conversion of about 19% was obtained.

The permanganate oxidation of glycolic acid or DL-glyceric acid showed a negligible consumption of permanganate (~0.004 mL/10 μ mol), and no increase in the permanganate consumption was obtained when the glycolic acid was oxidised in the presence of 2-ketoglutaric acid. Obviously, the kappa number measurement conditions do not lead to any further oxidation of glycolic acid.

From these model compound experiments, it was found that 10 μ mol of α -terpineol, 2-ketoglutaric acid, D-glucose in the presence of 2-ketoglutaric acid and glycolic acid consumed, respectively, 0.4, 0.2, 0.04, and 0.00 mL of potassium permanganate when subjected to oxidation under the standard kappa number measurement conditions. Therefore, 10 μ mol of hexeneuronic acid present in 1 g of pulp should contribute 0.84 kappa number units, with 0.4 units coming from the oxidation step A (Scheme 1), 0.2 units from B, 0.2 units from C, and 0.04 units from D. In this calculation, compound 7 is the end product of the oxidation.

Kappa number measurement combined with mer-



Fig. 1. Relative degree of oxidation for different model compounds.

curic acetate hydrolysis .--- Following the method reported in [6], a mercuric acetate solution, buffered at pH \sim 5, was used to completely remove all hexeneuronic acid groups from a series of unbleached and bleached birch kraft pulps (Table 1). After a thorough washing of the pulp samples, recovery yields of about 99% were obtained indicating that only the hexeneuronic acid groups had been removed. In the pulps, traces of mercuric ion could be found after washing. The amount was of the order of 2 μ mol per gram of pulp and, in a separate experiment, it was shown that this amount has no measurable influence on the kappa number determination. Thus, the kappa number reductions resulting from the hydrolysis are considered to be due to the elimination of the hexeneuronic acid groups.

Mercuric acetate hydrolysis of the pulps in combination with colorimetric analysis as described in Ref. [6] gives a quantification of the hexeneuronic acid groups present. The amounts are given in Table 1. When the reduction in kappa number due to the

Table 1 Analytical data for industrial unbleached and OQPbleached birch kraft pulps

No.	Pulp type ^a	Original kappa No.	Reduction in kappa No.	Hexeneuronic acid (μmol/gram of pulp)
1	Ī	12.5	3.4	43
2	Ι	11.2	3.3	43
3	I	11.1	3.2	38
4	I	16.9	4.9	58
5	I	15.2	5.4	65
6	Ι	15.8	4.3	48
7	Ι	16.0	5.9	69
8	Ι	16.4	5.4	65
9	Ι	19.2	5.6	67
10	Ι	14.9	5.0	58
11	Ι	17.1	5.4	58
12	Ι	14.0	3.4	45
13	II	6.0	4.5	53
14	II	4.5	3.5	39
15	II	8.5	3.8	50
16	II	8.4	3.9	46
17	II	8.1	3.6	48
18	II	7.6	3.1	39
19	II	7.9	3.4	41
20	II	8.3	3.7	48
21	II	8.0	3.3	36
22	II	9.0	3.9	49
23	II	7.9	3.3	38
24	II	8.1	3.8	44

^a I: unbleached; II: OQP bleached.



Fig. 2. Correlation between kappa number reduction of different kraft pulps and hexeneuronic acid content.

mercuric acetate hydrolysis was plotted versus the amount of hexeneuronic acid in each pulp, a linear relationship was obtained (Fig. 2). The relationship indicates that every 10 μ mol of hexeneuronic acid will give a difference of 0.86 kappa number units, i.e. a value very close to the value obtained from the model compounds. The values obtained in this work are much lower than those reported in the literature [9]. In the latter work, values greater than 1.0 were obtained and it seems reasonable to believe that other oxidation reactions contributed to the overall values in that case since, theoretically, 10 μ mol of hexeneuronic acid per gram of pulp cannot yield more than a maximum of 1.0 kappa number unit if the final product is compound **7**.

4. Conclusions

The kappa number contribution of hexeneuronic acid groups present in kraft pulps has been determined in two different ways, viz. by a series of model experiments and by a combination of mercuric acetate hydrolysis and colorimetric quantification of hexeneuronic acid groups. The former method gave a contribution of 0.84 kappa number units per 10 μ mol of hexeneuronic acid, whereas the latter gave a value of 0.86. A kappa number which better represents the pulp lignin content can thus be obtained after subjecting the pulp to mercuric acetate hydrolysis. It is also possible to calculate the amount of hexeneuronic acid groups in a pulp by determining the kappa number before and after mercuric acetate hydrolysis.

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