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by

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Free Phenolic Hydroxyl and 4-Keto-Guaiacol Groups In Lignin

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In a previous paper on the estimation of the free phenolic hydroxyl content of soft-wood lignin, a method based on the colour reaction between 1-nitroso-2-naphthol and the free phenolic groups of the guaiacyl nucleus was described and 0.255mole free phenolic hydroxyl groups per OCH_3 group was reported. Since it was found that the lignin model compounds containing an α - carbonyl group on the side chain of the guaiacyl nucleus did not react with 1-nitroso-2-naphthol to give a colour, the previously reported value for the free phenolic hydroxyl content of lignin should be somewhat lower.

To find the free phenolic hydroxyl group content of lignin, the colour reaction was carried out after the removal of the α - carbonyl groups present in lignin by reduction with $NaBH_4$. The results obtained indicate the presence of 0.287 moles of free phenolic hydroxyl groups per OCH_3 group.

Consequently, the difference between these values gives the 4-keto-guaiacol group content of lignin.

INTRODUCTION

The results obtained from the reactions between hydroxylamine and milled-wood lignin indicated the presence of a relatively large number of carbonyl groups (0.18 - 0.21 CO/OCH_3) [1]. A knowledge of their actual positions on the propyl side chain would give further information on lignin structure.

To determine the location of carbonyl groups on the propyl side chain, the reduction of lignin with $NaBH_4$ in alkaline solution was carried out afterwhich the difference in the absorbance was determined. From the experimental results it was possible to draw some conclusions as to the location of carbonyl groups [2].

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The present method is limited to the determination in soft wood lignins of α-carbonyl groups in the side chain of those guaiacyl nuclei which contain phenolic hydroxyl, i. e., 4-keto-guaiacol groups (Fig 1).

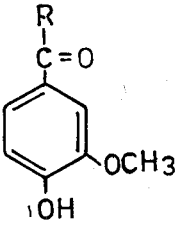

Fig. 1

In a previous communication from this laboratory a method for the estimation of the free phenolic content of soft wood lignin was reported [3]. The method was based on the colour reaction between 1-nitroso-2-naphthol and the free phenolic hydroxyl group of the p-substituted guaiacol nucleus [4]. In studies on the colour reaction with various lignin model compounds, it was found that compounds containing an α-carbonyl group on the side chain of the guaiacyl nucleus did not react with 1-nitroso-2-naphthol.

Thus, since lignin contains α-carbonyl groups on the side chain an increase of absorbance of the colour formed after the reduction of lignin with $NaBH_4$ would have been expected. From the difference in absorbance, the 4-keto-guaiacol group content of soft wood lignin preparations may be calculated.

RESULTS AND DISCUSSION

For ease of preparation, lignin solutions were made in a mixture of glycol and ethyl alcohol.

Experiments which were carried out with lignin model compounds in the ethyl alcohol- glycol mixture revealed that the molar absorptivity of the colour formed from the reaction with1-nitroso-2-

naphthol did not differ from that obtained when the colour reaction was carried out in alcoholic solutions [5].

To examine the reduction of α-carbonyl groups with $NaBH_4$ experiments were performed with model compounds containing a carbonyl group in the α-possition of the side chain, i. e., vanillin and acetovanillone. Both compounds, after reduction with $NaBH_4$ in a solution containing 40 volumes of glycol and 60 volumes of ethyl alcohol gave a colour reaction with 1-nitroso-2-naphthol, as was expected.

The colours formed showed molar absorptivities of about 1670 which was in accordance with earlier results obtained from model compounds containing one free phenolic hydroxyl group on a guaiacyl nucleus [3].

The reduction of milled-spruce wood lignin with $NaBH_4$ was carried out under conditions similar to those used for vanillin and acetovanillone.

Table I. Absorption Characteristic of Colour Formed with 1-Nitroso-2-Naphthol.

	Absorbance*	λmax
Milled-wood lignin 100 mg/1000 ml	0.204	505 mμ
Reduced milled-wood lignin 100 mg/1000 ml	0.226	505 mμ

* Optical path was 1 cm.

As can be seen from Table I, the absorbance values of the colour formed during the reaction of 1-nitroso-2-naphthol with milled-wood lignin and $NaBH_4$ reduced milled-wood lignin are 0.204 and 0.226 respectively.

The difference between these values is due to the presence of the α-carbonyl groups in lignin.

The free phenolic hydroxyl group content of the milled-wood lignin can be calculated from the absorbance value of the colour obtained with reduced milled-wood lignin and the average ε_{max} value obtained from the model compounds containing one free phenolic hydroxyl group.

Mmoles of phenolic hydroxyl group per 100 mg of milled-wood lignin: (0.226 x 1000)/ 1670 = 0.135.

Since the methoxyl content of the lignin sample used in the experiment was 14.79 % or 14.79 /31 = 0.47 Mmole per 100 mg lignin, then the lignin contained 0.135 /0.47=0.287 moles of free phenolic hydroxyl group per OCH_3 group.

Similar calculations indicate the presence of 0.255 moles of free phenolic group per OCH_3 group in the unreduced milled-wood lignin.

The difference between these two values corresponds to the 4-keto-guaiacol group content of the lignin which according to the results obtained above is 0.032 mole per OCH_3 group.

EXPERIMENTAL

Apparatus: A Beckman Model DU spectrophotometer with 5 cm matched cells was used.

Procedure:

To prepare the solution of model compounds and of the lignin sample a mixture of 40 volumes of glycol and 60 volumes of ethanol (96 %) was used as solvent.

Test solutions:

Solution of Model compounds: Vanillin and acetovanillone were purified by recrystallisation. After disolving 2.5 - 3 mg of model compound in 50 ml of solvent, 50 mg $NaBH_4$ was added and the volume was made to 100 ml with the same solvent. Solution of milled-spruce wood lignin: 10 mg of lignin was dissolved in 50 ml of solvent. After adding 50 mg of $NaBH_4$ the volume was made up to 100 ml with the same solvent.

The 1-nitroso-2-naphthol colour reaction was carried out according to the procedure described earlier [4]. To a pyrex test tube, 5 ml of test solution, 1 ml of 1-nitroso-2-naphthol (0.1 % ethanolic solution), 0.25 ml nitric acid (2.5 N), and 1.5 ml of concentrated hydrochloric acid were added.

The contents of the tubes were well mixed by shaking and then heated in a water bath maintained at 85.0 $\pm$ 0.5 °C. Subse-

quent to the beginning of the development of the orange-red colour the tubes were kept in the bath for an additional 30 seconds, after which they were kept at room temperature for 30 seconds and then cooled in a ice-water bath.

For the measurment of the absorbance, the same mixture, without test substance, treated identically was used as a referance.

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ÖZET

Ligninde serbest fenolik hidroksil gruplarının tayininde kullanılan 1-nitroso-2-naftolün,guayakol halkasında hidroksil grubuna nazaran 4-yerinde karbonil grubu ihtiva eden lignin model bileşikleri ile renk reaksiyonu vermediği tesbit edildiğinden, lignin numunesi $NaBH_4$ ile muamele edilerek karbonil grubunun indirgenmesi temin edilmiştir. Böylece indirgenmiş ve indirgenmemiş lignin numuneleri ile 1-nitroso-2-naftol arasındaki reaksiyondan elde edilen rengin absorbansları arasındaki farktan ligninde mevcut 4-keto-guayakol grubu miktarı tayin edilmiştir.

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