COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES
DE L'UNIVERSITÉ D'ANKARA

Série B : Chimie

TOME 16 B ANNÉE 1969

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by

ARAL OLCAY

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Faculté des Sciences de l'Université d'Ankara
Ankara, Turquie

Communications de la Faculté des Sciences de l'Université d'Ankara

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Aryl-alkyl Ether Linkages in Lignin

ARAL OLCAY

*Department of Industrial Chemistry, Faculty of Science University of Ankara, Ankara - Turkey**

(Received July 15, 1969)

The increase in the number of free phenolic hydroxyl groups during the acidolysis of lignin has been investigated using the colour reaction of 1- nitroso - 2- naphthol with compounds containing free phenolic hydroxyl on p-subtituted guaiacyl nuclei.

After the sodium borohydride reduction of any α-carbonyl groups which may have resulted during the acidolysis, the determination of free phenolic hydroxyl groups indicated that milled-spruce wood lignin contained 0.30 moles of arylglycerol units per methoxyl group. These units were linked through an ether linkage in the β-or γ-position of the side chains.

INTRODUCTION

It has been found, using the 1–nitroso-2–naphthol colour reaction, that milled spruce wood lignin contains 0.29 moles of free phenolic hydroxyl per methoxyl group [1]. This result is in good agreement with the earlier results of Aulin-Erdtman [2] and Goldschmied [3] using the spectrophotometric ΔE method. Consequently the remainder -0.71- of the phenolic hydroxyl in guaiacyl propane monomers, the basic structural units of coniferous lignin, must be present in blocked phenolic groups.

There seems to be general agreement that in lignin aryl oxygen is linked to the β-carbon atom of the propane side chain of the adjacent monomer [4,5]. Evidence has also been obtained which supports the presence of phenylcoumaran structures in milled -wood lignin [6]. If lignin indeed contains building stones linked through aryl-alkyl ether linkages, then hydrolysis of the ether

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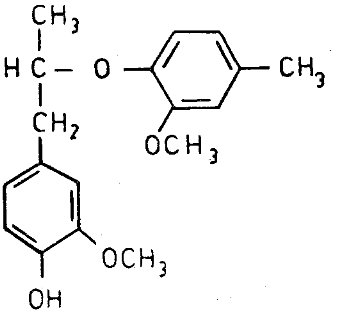
* Mailing address: A. Ü. Fen Fakültesi, Ankara, Turkey.

linkages could give rise to guaiacyl propane derivatives containing free phenolic groups.

Since one objective of the studies on lignin is to gain information about the linkages which unite the guaiacyl propane building stones of lignin, the increase in C–CH_3 groups and in free phenolic hydroxyl groups as the result of acidolysis was investigated [7].

The present study is also concerned with the determination of the types of aryl-alkyl ether linkages which join the guaiacyl propane moieties together in soft wood lignin. Thus dihydroeugenol-β-4-methyl-guaiacyl ether (I) was chosen as a lignin model compound. Model compound and milled-spruce wood lignin were each subjected to acidolysis and the increase in the number of free phenolic hydroxyl groups was investigated.

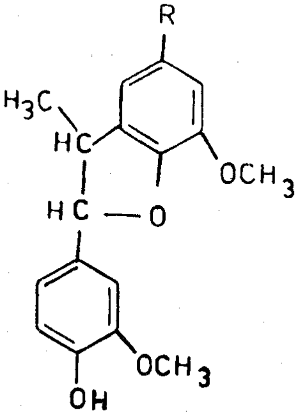


I

The colour reaction of 1-nitroso-2-naphthol has been proved [8] to be a rapid and accurate method for the determination of the free phenolic content of p-substituted guaiacyl compounds. Therefore this reaction was used for the estimation of free phenolic hydroxyl groups.

RESULTS AND DISCUSSION

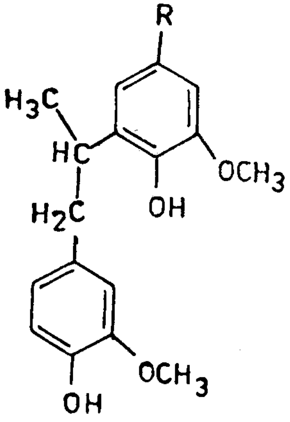
Under the experimental conditions used for the acidolysis of lignin the hydrolysis of aryl-alkyl ether linkages of guaiacyl-glycerol-β-guaiacyl ether units as well as the opening of the ring in phenylcoumaran elements could both give rise to guaiacyl propane derivatives containing free phenolic groups. As the result of the opening of the phenylcoumaran ring (II), 4,6-disubstituted guaiacyl elements containing free phenolic hydroxyl groups arise (III). It has been demonstrated that such structures do not react with 1-nitroso-2-naphthol to give a colour reaction [8]. Thus the increase in the colour formed with 1-nitroso-2-naphthol during the acidolysis of lignin will be caused only by the cleavage of the aryl-alkyl ether bridges of guaiacyl glycerol units present in the lignin.



II

The milled-spruce wood lignin used for the investigation contained 0.29 mole of free phenolic hydroxyl groups per methoxyl group. The solution of the lignin sample in glycol-ethyl alcohol, containing 0.2 N hydrochloric acid was subjected to acydolysis by refluxing.

It has been reported that guaiacyl-glycerol-β-arylether subjected to acidolysis with 0.2 N hydrogen chloride yields guaiacylpropane monomers containing carbonyl groups on the side chain [7]. Therefore the acidolysis products of lignin could be expected to contain similar compounds. Since previous work from this laboratory [8] has established that compounds containing an α-carbonyl group on the propyl-guaiacyl nuclei do not give a colour reaction with 1-nitroso-2-naphthol, the acidolysis products of lignin were first treated with sodium borohydride to reduce the carbonyl groups. After this the 1-nitroso-2-naphthol colour reaction was applied.



III

The colour formed with the model compound (I) after 12 hours acidolysis, showed a molar absorptivity which was twice as high as the value obtained for the absorptivity of the model compound before acidolysis. Thus it may be assumed that the acidolysis of the aryl-alkyl ether linkages was complete after 12 hours refluxion.

The change of phenolic hydroxyl content of lignin after increasing periods of reflux is shown in Fig. 1. As can be seen from the figure, the maximum increase of phenolic hydroxyl group per methoxyl is 0.30 which is obtained after 14 hours refluxion. With prolonged heating no increase of free phenolic hydroxyl content was observed. Accordingly this result indicates the presence of one aryl-alkyl ether linkages for three or four guaiacyl propane units in milled-spruce wood lignin.

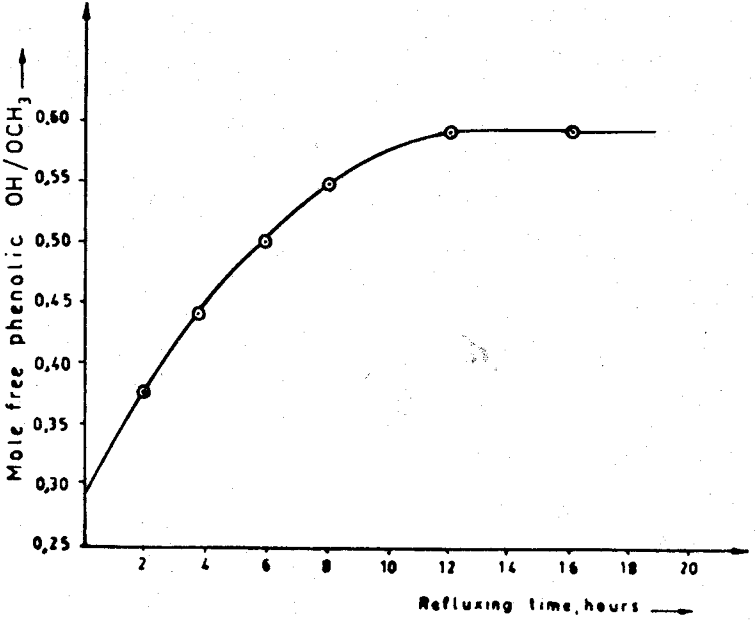


Fig. 1. Acidolysis of milled-spruce wood lignin

EXPERIMENTAL

Acidolysis of dihydroeugenol-β-4-methyl-guaiacyl ether (I). 10 mg of model compound were dissolved in 98.3 ml of glycol-ethanol (4V /6V) mixture. To this solution, 1.7 ml of concentrated hydrochloric acid (sp.gr. 1.19) was added. The resulting solution was refluxed in a water bath. After heating for predetermined periods of time, the mixture was poured quantitatively into a flask.

The preparation of the solution for the 1-nitroso-2-naphthol colour reaction: The mixture obtained after acidolysis was neutralized with a concentrated solution of sodium hydroxide and treated with sodium borohydride. The volume was then made up to 500 ml with glycol-ethanol and allowed to stand for 12 hrs. at room temperature. The 1-nitroso-2-naphthol colour reaction was then applied to the solution according to the procedure described in a previous paper [9].

Acidolysis of milled-spruce wood lignin.

The solution of 10 mg of lignin in glycol-ethanol containing 0.2 N HCl was subjected to acidolysis under the same conditions as those used for the model compound. After acidolysis the mixture was again treated in an identical manner to that used for the model compound and the final volume was made up to 100 ml.

The absorbances were measured at 505 nm with a Beckmann quartz Model DU spectrophotometer using 5 cm cells.

REFERENCES

[1] A. Olcay, Commun. Fac. Sci. Univ. d'Ankara, **XVI B,** (1969).

[2] Aulin-Erdtman, Svensk Papperstidn., **57,** 745 (1954).

[3] O. Goldschmid, Anal. Chem., **26,** 1421 (1954).

[4] E. Adler, B. O. Lindgren, Svensk Papperstidn., **55,** 563 (1952).

[5] E. Adler, S. Yllner, Svensk Papperstidn. **57,** 78 (1954).

[6] E. Adler, S. Delin and K. Lundquist, Acta Chem. Schand. **13,** 2149 (1959).

[7] E. Adler, J. M. Pepper and E. Eriksoo, Ind. Eng. Chem. **49,** 1391 (1957).

[8] A. Olcay, to be published in Holzforschung.

[9] A. Olcay, Commun. Fac. Sci. Univ. d'Ankara, **XV B, 7,** 85 (1968).

ÖZET

Milled-wood ligninde bulunan aril-alkil eter bağlarının miktarını tayin etmek üzere, lignin numunesinin glikol-etanol karışımındaki çözeltisi 0.2 N hidroklorik asit ile asidolize tabi tutulmuştur.

Asidoliz sırasında aril-alkil eter yapısındaki dimerlerde aril-alkil bağlarının kopması sonucu, serbest fenolik hidroksil grubu ihtiva eden p-sübstitü guayakol türevleri teşekkül edebileceğinden, serbest fenol gruplarının artışı, mevcut olabilecek α-karbonil gruplarının sodyum borhidrür ile indirgenmesinden sonra, 1- nitroso - 2- naftol renk reaksiyonu ile spektrofotometrik olarak tayin edilmiştir.

Böylece "milled-spruce wood lignin" numunesinde asidoliz sırasında serbest fenolik hidroksil grubunun maksimum artma miktarı, her bir metoksil grubuna mukabil 0.30 mol olarak bulunmuştur. Dolayısı ile bu netice, ligninde her bir metoksil grubuna mukabil 0.30 mol aril-alkil eter yapısı olduğunu göstermiştir.

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Ankara Üniversitesi Basımevi - 1969