ANALYSIS OF ^{1}H-NMR SPECTRA OF CINNAMALDEHYDE TYPE MODEL SUBSTANCES OF LIGNIN

Tibor LIPTAJ[a], Milan REMKO[b] and Ján POLČIN[c]

[a] *Central* NMR *Laboratory,*
Slovak Institute of Technology, 880 37 Bratislava,
[b] *Scientific Research Institute of Pharmaceutical Faculty,*
Comenius University, 880 34 Bratislava and
[c] *Pulp and Paper Research Institute, 890 20 Bratislava*

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^{1}H-NMR spectra of the following lignin model substances have been analyzed: cinnamaldehyde, 2-methoxycinnamaldehyde, 3-methoxycinnamaldehyde, 4-methoxycinnamaldehyde, 3,4-dimethoxycinnamaldehyde, 3-methoxy-4-hydroxycinnamaldehyde and 3,4,5-trimethoxycinnamaldehyde. From the NMR spectra analysis it follows that the studied compounds exist in solutions as *trans* isomers. Theoretical (PCILO) calculations in agreement with the NMR data have shown that the more stable conformer has *trans* orientation of C=O group with respecet to the double bond of the conjugated side chain.

Cinnamyl structures play an important role in lignin chemistry. The present generally accepted concept of lignin is based on a polymer formed by dehydrogenation of mixture of three *p*-hydroxycinnamyl alcohols[1] (*p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol). As the lignin macromolecule with varying combinations of the structural units is too complicated for definitive conclusions about its structure by means of current identification methods, these conclusions first have to be verified with suitable models. Cinnamaldehyde models with oxy substituents at various positions of the benzene ring are chiefly important in colour of lignified materials. The cinnamaldehyde structures are present in the lignin macromolecule and, with respect to their absorption in visible region[2], are significant chromogens which must be destructed during bleaching of woodpulps[3-6]. In ref.[2] electronic spectra of some cinnamaldehyde structural units of lignin were studied both experimentally and theoretically. Conformation of *cis*-cinnamaldehyde was studied by quantum-chemical methods CNDO/2 and PCILO in ref.[7].

The present paper deals with analysis of ^{1}H-NMR spectra of cinnamaldehyde type model substances of lignin (cinnamaldehyde, 2-, 3- and 4-methoxycinnamaldehyde, 3,4-dimethoxycinnamaldehyde, 3-methoxy-4-hydroxycinnamaldehyde and 3,4,5-trimethoxycinnamaldehyde) and effect of oxy substitution on NMR spectra of the compounds studied. Furthermore, conformation of *trans* cinnamaldehyde has been studied by semi-empirical PCILO method[16,17].

EXPERIMENTAL

A commercial sample of cinnamaldehyde (Loba-Chemie, Wien) was used for the NMR measurements. The other studied substituted cinnamaldehydes were synthetized according to the procedures in ref.[10].

^{1}H-NMR spectra were measured with a Jeol FX-100 spectrometer operating in FT mode. For the measurements the substances were dissolved in $CDCl_3$ (0·1M solutions) using tetramethylsilane (TMS) as the internal standard. The spectra were analyzed by the Castellano and Bothner–By method[8] using the LAOCOON 3 programme[9].

As in the studied systems there exists a number of small long-range and spin-spin interactions resulting merely in broadening of spectral lines, some coupling constants could not be determined from the analysis of the spectra, *viz.* those between the protons in the side chain and the protons in aromatic nucleus as well as between the aromatic protons in *para* positions. This means that the subspectra both of the side chain and the aromatic protons could be analyzed independently.

RESULTS AND DISCUSSION

The results of ^{1}H-NMR spectra analysis of cinnamaldehyde and its hydroxy- and methoxy derivatives are summarized in Table I and II. In all the systems analyzed the calculated probable errors of the parameters given in the Tables were less than 0·04 Hz. The real errors are approximately 2 to 3 times higher[11], *i.e.* about 0·1 Hz. From Tables I and II it can be seen that changes in substitution of the aromatic ring have only a small effect on the spectral parameters of the side chain protons. The only exception is 2-methoxycinnamaldehyde having the substituent in ortho position to the side chain. However, even in this case the substituent effect is demonstrated only in a chemical shift of the proton H_α (due obviously to the direct sterical effect of the substituent).

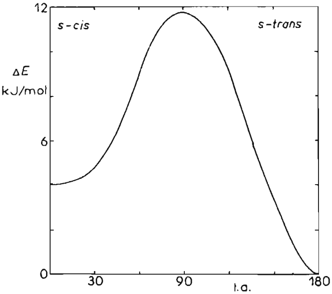
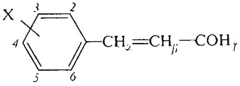


FIG. 1

PCILO Potential Energy Curve for Rotation of Aldehydic Group in Cinnamaldehyde

TABLE I

Chemical Shifts of the Studied Cinnamaldehydes in δ Scale (ppm)



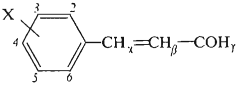
I

X	α	β	γ	2	3	4	5	6
$3,4,5\text{-}(OCH_3)_3$	7·34	6·61	9·64	6·77	3·89[a]	3·89[a]	3·89[a]	6·77
$3\text{-}OCH_3$, $4\text{-}OH$	7·37	6·57	9·60	7·05	3·93[a]	—	6·92	7·10
$3,4\text{-}(OCH_3)_2$	7·38	6·59	9·61	7·05	3·93[a]	3·92[a]	6·87	7·14
$2\text{-}OCH_3$	7·74	6·71	9·58	3·82[a]	6·87	7·33	6·91	7·45
$3\text{-}OCH_3$	7·33	6·61	9·56	7·00	3·75[a]	6·91	7·24	7·06
$4\text{-}OCH_3$	7·35	6·55	9·57	7·46	6·89	3·82[a]	6·89	7·46
H[b]	7·36	6·60	9·59					

[a] Chemical shifts of OCH_3 groups; [b] only the side chain was analyzed.

TABLE II

Interaction Constants (in Hz) of the Studied Cinnamaldehydes



II

X	$J_{\beta\gamma}$	$J_{\alpha\beta}$	J_{23}	J_{24}	J_{26}	J_{34}	J_{35}	J_{45}	J_{46}	J_{56}
$3,4,5\text{-}(OCH_3)_3$	7·8	16·0	—	—	—	—	—	—	—	—
$3\text{-}OCH_3$ $4\text{-}OH$	7·7	15·8	—	—	1·8	—	—	—	—	7·9
$3,4\text{-}(OCH_3)_2$	7·7	15·8	—	—	2·1	—	—	—	—	8·2
$2\text{-}OCH_3$	7·9	16·1	—	—	—	7·6	1·1	7·9	1·8	7·3
$3\text{-}OCH_3$	7·6	16·0	—	1·6	1·4	—	—	8·6	1·1	7·8
$4\text{-}OCH_3$	7·8	15·8	8·7	—	2·2	—	2·7	—	—	8·7
H[a]	7·6	16·0	—	—	—	—	—	—	—	—

[a] Only the side chain was analyzed.

The spin-spin coupling constants of the side chain protons were almost the same within the whole series of the compounds studied, which means that the side chain conformation of the systems analyzed is independent of the aromatic ring substitution. According to Table II the interaction constants $J_{\alpha\beta}$ lie within 15 to 16 Hz in all the analyzed systems. Comparison of these values with those of similar systems[12] shows that the protons H_α and H_β are in a *trans* position. Similarly, the $J_{\beta\gamma}$ values found within the interval 7·6 to 7·9 Hz (Table II) indicate that also the H_β and H_γ, protons have a *trans* arrangement[13].

Experimental studies[14,15] of *cis* and *trans* isomers of the simpler structure of acrylaldehyde ($CH_2{=}CH{-}CH{=}O$) showed that this molecule is planar with two preferred conformations: *s-cis* and *s-trans*, the latter being somewhat more stable. For a more detailed study of conformation structure of aldehydic group in the side chain of the analyzed systems we used the semi-empirical PCILO method[16,17] and applied it to the simplest non-substituted cinnamaldehyde. Previous studies[7,18-20] showed that the PCILO method was successfully used in the study of stable conformations of conjugated compounds. Figure 1 presents the dependence of potential energy on rotation angle of the cinnamaldehyde aldehydic group. According to these calculations and in accordance with our experimental NMR data the more stable conformer is *s-trans* having the H_β and H_γ hydrogens in *trans* position. However, energy difference between the *s-trans* and *s-cis* forms is so small (4·01 kJ/mol) that they probably coexist.

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