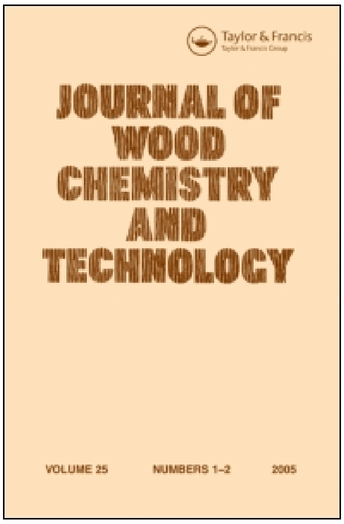

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SUBSTITUENT EFFECTS ON ^{13}C CHEMICAL SHIFTS OF AROMATIC CARBONS IN β-*O*-4 AND β-5 TYPE LIGNIN MODEL COMPOUNDS

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Dedicated to Dr. D. A. I. Goring on the occasion of his retirement from the Pulp and Paper Institute of Canada.

ABSTRACT

Substituent effects on the chemical shifts of aromatic carbons in lignin model compounds have been elucidated from ^{13}C NMR spectra of guaiacyl and syringyl type monomeric and β-*O*-4 model compounds and guaiacyl type β-5 model compounds. Evaluation of the observed values of substituent chemical shift (SCS) for the aromatic carbons leads to elucidation of a generalized SCS additivity rule, for estimation of the chemical shifts of aromatic carbons in ring A of β-*O*-4 and β-5 type substructures in model compounds and in ring B of β-*O*-4 substructures in lignin preparations, with errors of less than 1 ppm. The rule is applicable to substructures of both guaiacyl and syringyl types, using an appropriate parent compound as reference instead of

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benzene. Signals in the aromatic region of the ^{13}C NMR spectra of β-<u>O</u>-4 and β-5 type model compounds are reassigned on the basis of the observed SCS's as well as APT spectra of the compounds.

INTRODUCTION

Since Ludemann and Nimz[1,2] applied ^{13}C NMR spectroscopy for structural analysis of lignin preparations a decade ago, the method has become a powerful tool for the characterization of lignin preparations.[2-6] In spite of the progress made in this field during the past decade, no unambiguous interpretation of signals in some regions of lignin ^{13}C NMR spectra, particularly in the quarternary aromatic carbon region, has been attained. The major constraints in the interpretation of lignin ^{13}C NMR spectra are traceable to the complex nature of lignin in terms of chemical structure causing overlap of signals and, most importantly, the absence of suitable methods to discriminate between signals in order to ascertain the correctness of signal assignment. It is, therefore, desirable to elucidate a generalized ^{13}C NMR substituent chemical shift (SCS) additivity rule by which the chemical shift of a particular aromatic carbon in a lignin substructure can be predicted with a reasonably narrow margin of error, for example, an error of less than ±1 ppm.

The observed SCS additivity rule of benzene to estimate ^{13}C NMR chemical shifts of aromatic carbons in disubstituted benzenes[7,8] cannot be directly applied to lignin model compounds which are typically derivatives of either guaiacol (II; R = H) or syringol (V; R = H), (i.e. 2-methoxyphenol or 2,6-dimethoxyphenol), with an oxygenated propyl group substituted <u>para</u> to the phenolic hydroxyl group, because the rule cannot accurately predict chemical shifts of aromatic carbons in tri- and polysubstituted benzenes. However, it was demonstrated recently in our laboratory that chemical shifts of aromatic carbons in guaiacyl type lignin model compounds could be estimated by the SCS additivity rule when guaiacol and its ethers were used as parent compounds instead of benzene.[9,10] Investigations have been, therefore, conducted in our laboratory to determine whether the SCS additivity rule can also be applied to estimate chemical shifts of aromatic carbons in the syringyl type lignin model compounds. This will lead to the elucidation of a generalized SCS additivity rule by which chemical shifts of aromatic carbons in lignin model compounds and substructures in lignin preparations can be accurately predicted. This paper describes substituent effects on the chemical shifts of aromatic carbons in lignin model compounds, a generalized SCS additivity rule for estimation of the chemical shifts of aromatic carbons in β-*O*-4 and β-5 type lignin model compounds, and the reassignment of signals in the aromatic region of the ^{13}C NMR spectra of these compounds on the basis of the observed SCS data as well as APT spectra of the compounds.

EXPERIMENTAL

Synthesis of Lignin Model Compounds

β-(4-Methyl-2-methoxyphenoxy)-α-hydroxy-α-(4-hydroxy-3-methoxyphenyl)ethane (15)

Compound 15, colorless rhombics (from EtOH), m.p. 93-94°C, was prepared from α-bromo-4-acetoxy-3-methoxyacetophenone and creosol by way of β-(4-methyl-2-methoxyphenoxy)-α-oxo-α-(4-hydroxy-3-methoxyphenyl)ethane (15a), colorless microcrystals (from MeOH), m.p. 95-96°C, according to the procedure of Kratzl *et al.*[11]

β-(4-Methyl-2-methoxyphenoxy)-α-hydroxy-α-(4-ethoxy-3-methoxyphenyl)ethane (16)

Compound 16, colorless rhombics (from MeOH), m.p. 74-75°C, was synthesized from α-bromo-4-ethoxy-3-methoxyacetophenone and creosol by way of β-(4-methyl-2-methoxyphenoxy)-α-oxo-α-(4-ethoxy-3-methoxyphenyl)ethane (16a), colorless scales (from EtOH), m.p. 78-79°C, according to the procedure of Kratzl *et al.*[11]

β-(4-Methyl-2-methoxyphenoxy)-α-hydroxy-α-(4-hydroxy-3,5-dimethoxyphenyl)ethane (17)

Compound 17, colorless rhombics (from MeOH), m.p. 121.5-122.5°C, was synthesized from α-bromo-4-acetoxy-3,5-dimethoxyacetophenone and creosol by way of β-(4-methyl-2-methoxyphenoxy)-α-oxo-α-(4-hydroxy-3,5-dimethoxyphenyl)ethane (17a), pale yellow rhombics (from MeOH), m.p. 121.5-123°C, in the same manner described for the synthesis of compound 15.

β-(4-Methyl-2-methoxyphenoxy)-α-hydroxy-α-(4-ethoxy-3,5-dimethoxyphenyl)ethane (18)

Compound 18, colorless needles (from Me_2CO-EtOH), m.p. 114-116°C, was synthesized from α-bromo-4-ethoxy-3,5-dimethoxyacetophenone and creosol by way of β-(4-methyl-2-methoxyphenoxy)-α-oxo-α-(4-ethoxy-3,5-dimethoxyphenyl)ethane (18a), colorless needles (from Me_2CO), m.p. 121-123°C, in the same manner described for the synthesis of compound 16.

β-(4-Carboxy-2-methoxyphenoxy)-α-hydroxy-α-(4-hydroxy-3-methoxyphenyl)ethane (19)

Compound 19, colorless rhombics (from MeOH), m.p. 156-157°C, was prepared from α-bromo-4-acetoxy-3-methoxyacetophenone and vanillic acid methyl ester by way of β-(4-carboxy-2-methoxyphenoxy)-α-oxo-α-(4-hydroxy-3-methoxyphenyl)ethane (19a), colorless rhombics (from EtOH), m.p. 147-148°C, according to the procedure of Chen *et al.*[3]

β-(4-Carboxy-2-methoxyphenoxy)-α-hydroxy-α-(4-ethoxy-3-methoxyphenyl)ethane (20)

Compound 20, colorless rhombics (from MeOH), m.p. 146-148°C, was prepared from α-bromo-4-ethoxy-3-methoxyacetophenone and vanillic acid methyl ester by way of β-(4-carboxy-2-methoxyphenoxy)-α-oxo-α-(4-ethoxy-3-methoxyphenyl)ethane (20a), colorless needles (from MeOH), m.p. 162-164°C, according to the procedure of Chen *et al.*[3]

β-(4-Carboxy-2-methoxyphenoxy)-α-hydroxy-α-(4-hydroxy-3,5-dimethoxyphenyl)ethane (21)

Compound 21, colorless rhombics (from MeOH), m.p. 179.5-180.5°C, was prepared from α-bromo-4-acetoxy-3,5-dimethoxyacetophenone and vanillic acid methyl ester by way of β-(4-carboxy-2-methoxyphenoxy)-α-oxo-α-(4-hydroxy-3,5-dimethoxyphenyl)ethane (21a), pale yellowish needles (from Me_2CO), m.p. 157-159°C, in the same manner described for the synthesis of compound 19.

β-(4-Carboxy-2-methoxyphenoxy)-α-hydroxy-α-(4-ethoxy-3,5-dimethoxyphenyl)ethane (22)

Compound 22, colorless rhombics (from MeOH), m.p. 175-177°C, was prepared from α-bromo-4-ethoxy-3,5-dimethoxyacetophenone and vanillic acid methyl ester by way of β-(4-carboxy-2-methoxyphenoxy)-α-oxo-α-(4-ethoxy-3,5-dimethoxyphenyl)ethane (22a), colorless needles (from Me_2CO), m.p. 162-164°C, in the same manner described for the synthesis of compound 20.

β-(4-Carboxy-2-methoxyphenoxy)-α-hydroxy-α-(4-hydroxy-3-methoxyphenyl)ethane (23)

Compound 23, colorless rhombics (from MeOH), m.p. 178-180°C, was prepared from α-bromo-4-acetoxy-3-methoxyacetophenone and syringic acid methyl ester by way of β-(4-carboxy-2,6-dimethoxyphenoxy)-α-oxo-α-(4-hydroxy-3-methoxyphenyl)ethane (23a), colorless needles (from Me_2CO), m.p. 170-172°C, in the same manner described for the synthesis of compound 19.

β-(4-Carboxy-2,6-dimethoxyphenoxy)-α-hydroxy-α-(4-ethoxy-3-methoxyphenyl)ethane (24)

Compound 24, colorless needles (from MeOH), m.p. 172-174°C, was prepared from α-bromo-4-ethoxy-3-methoxyacetophenone and syringic acid methyl ester by way of β-(4-carboxy-2,6-dimethoxyphenoxy)-α-oxo-α-(4-ethoxy-3-methoxyphenyl)ethane (24a), colorless needles (from Me_2CO), m.p. 171-173°C, in the same manner described for the synthesis of compound 20.

β-(4-Carboxy-2,6-dimethoxyphenoxy)-α-hydroxy-α-(4-hydroxy-3,5-dimethoxyphenyl)ethane (25)

Compound 25, colorless needles (from MeOH), m.p. 192-194°C, was prepared from α-bromo-4-acetoxy-3,5-dimethoxyacetophenone and syringic acid methyl ester by way of β-(4-carboxy-2,6-dimethoxyphenoxy)-α-oxo-α-(4-hydroxy-3,5-dimethoxyphenyl)ethane (25a), colorless rhombics (from Me_2CO), m.p. 191-193°C, in the same manner described for the synthesis of compound 19.

β-(4-Carboxy-2,6-dimethoxyphenoxy)-α-hydroxy-α-(4-ethoxy-3,5-dimethoxyphenyl)ethane (26)

Compound 26, colorless rhombics (from MeOH), m.p. 165.5-166.5°C, was prepared from α-bromo-4-ethoxy-3,5-dimethoxyacetophenone and syringic acid methyl ester by way of β-(4-carboxy-2,6-dimethoxyphenoxy)-α-oxo-α-(4-ethoxy-3,5-dimethoxyphenyl)ethane (26a), colorless needles (from Me_2CO), m.p. 162.5-163.5°C, in the same manner described for the synthesis of compound 20.

Dehydrodiisoeugenol (27) was synthesized from isoeugenol according to the procedure of Erdtman[12], colorless needles (from MeOH), m.p. 131-132°C. 4-O-Methyldehydrodiisoeugenol (28) was prepared by methylation of compound 27 with $(CH_3)_2SO_4$ in alkaline solution, colorless needles (from EtOH), m.p. 113-115°C. 4-O-Ethyldehydrodiisoeugenol (29) was prepared by ethylation of compound 27 with EtI in DMF in the presence of anhydrous K_2CO_3, pale brownish rhombics (from MeOH), m.p. 124-125.5°C. α',β'-Dihydrodehydrodiisoeugenol (30), 4-O-Methyl-α',β'-dihydrodehydrodiisoeugenol (31) and 4-O-Ethyl-α',β'-dihydrodehydrodiisoeugenol (32) were prepared from compounds 27, 28 and 29, respectively, by catalytic hydrogenation in EtOH in the presence of 10% Pd/C and few drops glacial AcOH with Adam's hydrogenation apparatus at room temperature. Compound 30, colorless needles (from n-hexane), m.p. 91.2-92.5°C. Compound 31, colorless needles (from n-hexane), m.p. 93-94°C. Compound 32, colorless needles (from n-hexane), m.p. 95-96°C.

Guaiacol Ethyl Ether (IV; R = H), Syringol Ethyl Ether (VII; R = H) and Ethoxybenzene (3) were prepared from guaiacol, syringol and phenol by treatment with EtI in DMF in the presence of K_2CO_3, respectively. Compound VII (R = H), colorless rhombics (from EtOH), m.p. 42-44°C. Syringyl alcohol (7), colorless needles (from EtOH), m.p. 130-131°C, was prepared from syringaldehyde by catalytic hydrogenation in the same manner described for the synthesis of compounds 30-32.

α-Hydroxyphenylethane (9), α-Hydroxy-α-(4-hydroxy-3-methoxyphenyl)ethane (10), α-Hydroxy-α-(3,4-dimethoxyphenyl)ethane (11), α-Hydroxy-α-(4-ethoxy-3-methoxyphenyl)ethane (12), α-Hydroxy-α-(3,4,5-trimethoxyphenyl)ethane (13) and α-Hydroxy-α-(4-ethoxy-3,5-dimethoxyphenyl)ethane (14) were prepared from acetophenone, 4-hydroxy-3-methoxyacetophenone, 3,4-dimethoxyacetophenone, 4-ethoxy-3-methoxyacetophenone, 3,4,5-trimethoxyacetophenone and 4-ethoxy-3,5-dimethoxyacetophenone by reduction with $NaBH_4$ in alkaline EtOH solution.

Other Chemicals -- Other chemicals were reagent grade, obtained from commercial sources.

^{13}C NMR Spectra

The ^{13}C NMR spectra of the model compounds were obtained with a Bruker-IBM 100 AF Fourier transform spectrometer at 25.2 MHz with broadband-noise decoupling technique. Deuterated dimethylsulfoxide (DMSO-d_6) was used as solvent. The spectra were run in 5 mm (O.D.) glass tubes with concentrations of the samples ca. 100 mg in 0.5 ml of DMSO-d_6 (ca. 20% w/v). The signal for the CD_3-group of DMSO-d_6 was locked to the spectrometer. The signal has a δ value of 39.6 ppm relative to tetramethylsilane. Pulse width was 8 or 12 μsec. (30° or 60° pulse) with data acquisition time of 0.745 sec., pulse repetition time of 1 or 2 sec., an average number of scans being ca. 1000. Selection of the operational parameters depended on the nature of compound to be investigated. The APT spectra[13,14] of the compounds were also obtained in order to discriminate signals from primary and tertiary carbons from those for secondary and quaternary carbons.

RESULTS AND DISCUSSION

Parent Compounds

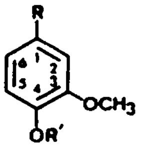
Among the parent compounds, benzene (I; R = H) belongs to symmetry species point group D_{6h}, while guaiacol methyl ether (III; R = H), syringol and its methyl and ethyl ethers (V-VII; all, R = H) belong to symmetry species point group C_{2v}.[15] The C_2 axis of guaiacol methyl ether passes through the bond between C-3 and C-4 with the vicinal methoxyl groups (for numbering, see Table 1) and the opposite bond between C-1 and C-6, bisecting the molecule into two equivalent parts, while the C_2 axis of syringol and its methyl and ethyl ethers passes through C-1 and C-4, bisecting the molecules into two equivalent parts. Thus, as shown in Table 1, six aromatic carbons of benzene have an identical chemical shift, while C-1, C-2 and C-3 of guaiacol methyl ether have chemical shifts identical to C-6, C-5 and C-4, respectively, and chemical shifts for C-2 and C-3 of syringol and its methyl and ethyl ethers are identical to those for C-6 and C-5, respectively. In contrast, guaiacol (II; R = H) and its ethyl ether (IV; R = H) belong to symmetry species point group C_1. The compounds are, therefore, asymmetric, and their aromatic carbons do not have chemical shifts identical to one another, except when additional contributions by steric interaction and other effects of substituents affect the distribution of electronic charge density for the aromatic carbons. For example, the chemical shifts for C-1 and C-6 in compound IV (R = H) are the same. This probably arises synergistically from the +M effects of C-3 methoxyl and C-4 ethoxyl groups in the compound on their *para* carbons, i.e. C-6 and C-1, resulting in a shielding of the same magnitude for C-6 and C-1, respectively.[7,8]

On the basis of the observed substituent chemical shifts (SCS's) for the aromatic carbons of phenol (1), methoxybenzene (2)

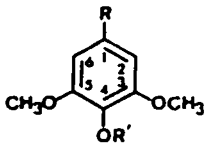
TABLE 1. ^{13}C Chemical Shifts of Aromatic Carbons in Parent Compounds in DMSO-$\underline{d}_6$

Compound (R = H)	Chemical shift (δ in ppm)					
	C-1	C-2	C-3	C-4	C-5	C-6
I	128.3	128.3	128.3	128.3	128.3	128.3
II	119.5	112.7	147.9	146.8	115.8	121.4
III	120.8	112.1	149.2	149.2	112.1	120.8
IV	120.7	113.5	149.3	148.3	113.5	120.7
V	118.3	105.8	148.3	135.9	148.3	105.8
VI	123.6	105.6	153.3	137.8	153.3	105.6
VII	123.4	105.5	153.5	136.6	153.5	105.5

I



II, R' = H
III, R' = CH_3
IV, R' = CH_2CH_3



V, R' = H
VI, R' = CH_3
VII, R' = CH_2CH_3

and ethoxybenzene ($\underline{3}$) as shown in Table 2, the chemical shifts of aromatic carbons in the parent compounds were estimated and summarized in Table 3. In general, the estimated chemical shifts are not in good agreement with the observed values for the corresponding carbons and have errors in the range of 0-7.4 ppm. The errors are particularly large for quaternary aromatic carbons with oxygenated substituents <u>ortho</u> to each other, except for C-3 of compound II (R = H) and C-3/C-5 of compound V (R = H). In di-polysubstituted benzenes, the presence of bulky <u>ortho</u> substituents

TABLE 2. ^{13}C Chemical Shifts and Substituent Chemical Shifts of Aromatic Carbons in Phenol and Its Methyl and Ethyl Ethers in DMSO-d_6*

Substituent at C-1 (R)	Parent	Comp'd	*ipso* (C-1)		*ortho* (C-2/C-6)		*meta* (C-3/C-5)		*para* (C-4)	
			δ	SCS	δ	SCS	δ	SCS	δ	SCS
-OH	I	1	157.5	+29.2	115.4	-12.9	129.4	+1.1	118.9	-9.4
$-OCH_3$	I	2	159.4	+31.1	113.8	-14.5	129.3	+1.0	120.3	-8.0
$-OCH_2CH_3$	I	3	158.6	+30.3	114.3	-14.0	129.2	+0.9	120.2	-8.1

* Chemical shift: δ in ppm.

Substituent Chemical Shift (SCS): Δδ in ppm, relative to benzene.

TABLE 3. Estimated ^{13}C Chemical Shifts of Aromatic Carbons in Parent Compounds, Using Observed ^{13}C Substituent Chemical Shifts of Phenol and Its Methyl and Ethyl Ethers in DMSO-d_6*

Compound (R = H)	C-1		C-2		C-3		C-4		C-5		C-6	
	δ	Error	δ	Error	δ	Error	δ	Error	δ	Error	δ	Error
II	119.9	+0.4	114.9	+2.2	146.5	-1.4	143.0	-3.8	116.4	+0.6	121.4	0.0
III	121.3	+0.5	114.8	+2.7	144.9	-4.3	144.9	-4.3	114.8	+2.7	121.3	+0.5
IV	121.2	+0.5	114.7	+1.2	145.4	-3.9	144.1	-4.2	115.3	+1.8	121.2	+0.5
V	120.9	+2.6	106.9	+1.1	147.5	-0.8	128.5	-7.4	147.5	-0.8	106.9	+1.1
VI	122.3	-1.3	106.8	+1.2	145.9	-7.4	130.4	-7.4	145.9	-7.4	106.8	+1.2
VII	122.2	-1.2	106.7	+1.2	146.4	-7.1	129.6	-7.0	146.4	-7.1	106.7	+1.2

* Chemical Shift: δ in ppm.

Error: Δδ in ppm, relative to the observed chemical shift of the corresponding carbon.

gives rise to distortions of the molecular geometry through sterically produced bond angle changes, and neighboring group anisotropy. These affect the substituent effects on the aromatic carbons, particularly on the ipso carbons.[7,8] Thus the rather large discrepancy between the estimated and observed chemical shifts for the oxygenated quaternary aromatic carbons of syringol and its methyl and ethyl ethers are attributable mainly to the steric interaction of three vicinal oxygenated substituents at C-3, C-4 and C-5, and the neighboring group anisotropy.

As demonstrated above, it is evident that the observed SCS's of monosubstituted benzenes cannot be directly applied to estimate chemical shifts of aromatic carbons in lignin model compounds and substructures in lignin preparations. However, it can be observed that the sequence of the estimated chemical shifts for aromatic carbons in the symmetric parent compounds is in agreement with the observed signal sequence in the ^{13}C NMR spectra of the compounds. Conceivably, this could also be true for the asymmetric parent compounds. Thus, in the ^{13}C NMR spectrum of compound IV (R = H), the signals at δ 149.3 and 148.3 ppm are assigned to C-3 and C-4 respectively, according to the sequence of the estimated chemical shifts for the carbons. The corresponding signals in the ^{13}C NMR spectra of 4-O-alkylated guaiacyl type model compounds are also assigned in the same manner. This is a reversal of previous signal assignments,[2-4] and required further elaboration.

As given in Table 4, the ^{13}C NMR spectra of benzyl alcohol (4) and α-hydroxyphenylethane (9) show that hydroxymethyl and α-hydroxyethyl groups cause shielding of ortho-, meta- and para-carbons. The effects of the substituents on the ortho- and para-carbons are more pronounced than those on the meta-carbons. In both cases, the observed SCS for meta- and para-carbons are -0.3 ppm and -1.8 ppm, relative to benzene, respectively. Consequently, C-4 of parent compound III (R = H) should experience an appreciably greater shielding effect than C-3 upon introduction

TABLE 4. ^{13}C Chemical Shifts and Substituent Chemical Shifts of Aromatic Carbons in Monomeric Lignin Model Compounds in DMSO-$\underline{d}_6$*

Substituent at C-1 (R)	Parent	Comp'd	C-1 (ipso)		C-2 (ortho)		C-3 (meta)		C-4 (para)		C-5 (meta)		C-6 (ortho)	
			δ	SCS	δ	SCS	δ	SCS	δ	SCS	δ	SCS	δ	SCS
$-CH_2OH$	I	4	142.6	+14.3	126.5	-1.8	128.0	-0.3	126.5	-1.8	128.0	-0.3	126.5	-1.8
	II	5	133.7	+14.2	111.3	-1.4	147.6	-0.3	145.5	-1.3	115.3	-0.5	119.4	-2.0
	III	6	135.5	+14.7	111.0	-1.1	149.1	-0.1	148.2	-1.0	111.9	-0.2	119.1	-1.7
	V	7	132.7	+14.4	104.4	-1.4	148.0	-0.3	134.4	-1.5	148.0	-0.3	104.4	-1.4
	VI	8	138.5	+14.9	103.7	-1.9	153.0	-0.3	136.4	-1.4	153.0	-0.3	103.7	-1.9
$-\underset{\mathrm{CH_3}}{\underset{\mid}{\mathrm{C}}}\mathrm{HOH}$	I	9	147.4	+19.1	125.3	-3.0	128.0	-0.3	126.5	-1.8	128.0	-0.3	125.3	-3.0
	II	10	138.6	+19.1	110.0	-2.7	147.5	-0.4	145.3	-1.5	115.2	-0.6	117.9	-3.5
	III	11	140.4	+19.6	109.8	-2.3	149.0	-0.2	147.9	-1.3	111.9	-0.2	117.5	-3.3
	IV	12	140.3	+19.6	109.9	-3.6	149.0	-0.3	146.8	-1.5	113.2	-0.3	117.3	-3.4
	VI	13	143.4	+19.8	102.8	-2.8	152.9	-0.4	136.5	-1.3	152.9	-0.4	102.8	-2.8
	VII	14	143.0	+19.6	102.7	-2.8	153.0	-0.5	135.2	-1.4	153.0	-0.5	102.7	-2.8

* Chemical Shift: δ in ppm.

Substituent Chemical Shift (SCS): $\Delta\delta$ in ppm, related to the corresponding carbon of parent compound.

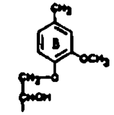
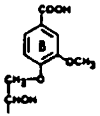
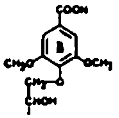
of a C-α oxygenated alkyl group on C-1. Because chemical shifts of C-3 and C-4 in the parent compound are identical, both δ 149.2 ppm, the signal for C-4 should undergo an up-field shift in greater magnitude than the signal for C-3. The same should be true for parent compound IV (R = H), since the chemical shifts of C-3 and C-4 in the parent compound are δ 149.3 and 148.3 ppm, respectively. Thus, in the 4-O-alkylated guaiacyl type model compounds, the signal for C-4 should appear up-field of the signal for C-3 in the ^{13}C NMR spectra of the compounds.

Substituent Effects on ^{13}C Chemical Shift of Aromatic Carbons

Substituent effects on the chemical shifts of aromatic carbons in lignin model compounds, relative to the corresponding carbons of the appropriate parent compound, were elucidated from the ^{13}C NMR spectra of the compounds. In the case of dimeric lignin model compounds, only the substituent effects on the aromatic carbons in ring A were studied. The substituent effects observed in monomeric model compounds are summarized in Table 4, while those observed in β-O-4 and β-5 type dimeric model compounds are given in Tables 5 and 6, respectively.

In all the cases, the observed SCS's are near constant for each aromatic carbon in model compounds of the same class. Moreover, the observed SCS's for the aromatic carbons in monomeric model compounds of the same class are in rather good agreement with the observed SCS's for the corresponding carbons of their benzene analogue. If the assignment of signals for C-3 and C-4 in the ^{13}C NMR spectra of 4-O-alkylated guaiacyl type model compounds are reversed, then the observed SCS's for C-3 and C-4 in the model compounds of the same class would no longer remain near constant. In addition, the revised SCS's for C-3 and C-4 in the compounds would no longer be in agreement with the observed SCS's for C-3 and C-4 of their benzene analogue. This can be interpreted as further evidence for the correctness of the new signal assignment for C-3 and C-4 in the spectra of 4-O-alkylated guaiacyl type model compounds, as discussed previously.

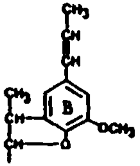
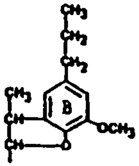
TABLE 5. ^{13}C Chemical Shifts and Substituent Chemical Shifts of Aromatic Carbons in β-$\underline{O}$-4 Type Dimeric Lignin Model Compounds in DMSO-$\underline{d}_6$*

Substituent at C-1 (R)	Parent	Comp'd	Ring	C-1 (ipso)		C-2 (ortho)		C-3 (meta)		C-4 (para)		C-5 (meta)		C-6 (ortho)	
				δ	SCS	δ	SCS	δ	SCS	δ	SCS	δ	SCS	δ	SCS
	II	15	A	133.3	+13.8	110.6	-2.1	146.9	-1.0	145.4	-1.4	114.8	-1.0	118.5	-2.9
			B	129.9		113.2		148.6		145.8		113.8		120.6	
	IV	16	A	135.3	+14.6	110.7	-2.8	148.8	-0.5	147.2	-1.1	112.9	-0.6	118.4	-2.3
			B	130.2		113.5		149.0		146.1		114.1		120.8	
	V	17	A	132.4	+14.1	103.7	-2.1	147.4	-0.9	134.5	-1.4	147.4	-0.9	103.7	-2.1
			B	129.8		113.1		148.6		145.7		113.5		120.5	
	VII	18	A	138.2	+14.8	103.9	-1.6	153.0	-0.5	135.7	-0.9	153.0	-0.5	103.9	-1.6
			B	130.2		113.7		149.1		146.2		114.2		120.9	
	II	19	A	133.5	+14.0	111.1	-1.6	147.6	-0.3	146.0	-0.8	115.3	-0.5	119.1	-2.3
			B	123.3		112.5		148.7		152.3		112.7		123.5	
	IV	20	A	135.1	+14.4	110.9	-2.6	149.0	-0.3	147.5	-0.8	113.1	-0.4	118.6	-2.1
			B	123.3		112.5		148.7		152.3		112.7		123.4	
	V	21	A	132.7	+14.4	104.3	-1.5	148.0	-0.3	135.0	-0.9	148.0	-0.3	104.3	-1.5
			B	123.2		112.5		148.7		152.3		112.6		123.5	
	VII	22	A	137.9	+14.5	103.9	-1.6	153.0	-0.5	135.7	-0.9	153.0	-0.5	103.9	-1.6
			B	123.1		112.5		148.5		152.0		112.6		123.3	
	II	23	A	133.0	+13.5	110.8	-1.9	147.4	-0.5	145.8	-1.0	115.1	-0.7	119.0	-2.4
			B	125.8		106.9		152.5		140.9		152.5		106.9	
	IV	24	A	134.6	+13.9	110.6	-2.9	148.8	-0.5	147.3	-1.0	112.9	-0.6	118.7	-2.0
			B	125.7		106.9		152.5		140.9		152.5		106.9	
	V	25	A	132.2	+13.9	104.3	-1.5	147.9	-0.4	135.0	-0.9	147.9	-0.4	104.3	-1.5
			B	125.9		107.0		152.6		141.1		152.6		107.0	
	VII	26	A	137.6	+14.2	103.8	-1.7	152.9	-0.6	135.6	-1.0	152.9	-0.6	103.8	-1.7
			B	125.7		106.9		152.4		140.9		152.4		106.9	

* Chemical Shift: δ in ppm.

Substituent Chemical Shift (SCS): Δδ in ppm, relative to the corresponding carbon of parent compound.

TABLE 6. ^{13}C Chemical Shifts and Substituent Chemical Shifts of Aromatic Carbons in β-5 Type Dimeric Lignin Model Compounds in DMSO-$\underline{d}_6$*

Substituent at C-1 (R)	Parent	Comp'd	Ring	C-1 (ipso)		C-2 (ortho)		C-3 (meta)		C-4 (para)		C-5 (meta)		C-6 (ortho)	
				δ	SCS	δ	SCS	δ	SCS	δ	SCS	δ	SCS	δ	SCS
	II	27	A	131.0	+11.5	110.7	-2.0	147.7	-0.2	146.8	0.0	115.3	-0.5	119.3	-2.1
			B	131.5		109.8		146.2		143.7		133.4		113.4	
	III	28	A	132.5	+11.7	110.2	-1.9	149.0	-0.2	149.0	-0.2	111.8	-0.3	118.9	-1.9
			B	131.6		110.0		146.2		143.8		133.4		113.4	
	IV	29	A	132.7	+12.0	110.8	-2.7	149.2	-0.1	148.1	-0.2	113.2	-0.3	118.5	-2.2
			B	131.4		110.4		146.1		143.4		133.1		113.6	
	II	30	A	131.0	+11.5	110.6	-2.1	147.7	-0.2	146.8	0.0	115.9	+0.1	119.3	-2.1
			B	133.0		112.4		145.0		143.4		135.4		115.3	
	III	31	A	132.7	+11.9	110.6	-1.5	149.0	-0.2	149.0	-0.2	112.3	+0.2	118.6	-2.2
			B	132.9		112.8		145.0		143.2		135.3		115.4	
	IV	32	A	132.7	+12.0	110.7	-2.8	149.2	-0.1	148.0	-0.3	113.6	+0.1	118.5	-2.2
			B	132.9		112.8		144.9		143.1		135.0		115.4	

* Chemical Shift: δ in ppm.

Substituent Chemical Shift (SCS): Δδ in ppm, relative to the corresponding carbon of parent compound.

TABLE 7. Evaluated ^{13}C Substituent Chemical Shifts of Lignin Model Compounds in DMSO-$\underline{d}_6$*

Substituents	ipso	ortho	meta	para
	C-1	C-2/C-6	C-3/C-5	C-4
Hydroxymethyl [$-CH_2OH$]	+14.6	-1.6	-0.3	-1.3
α-Hydroxyethyl [$-CH(CH_3)OH$]	+19.5	-3.0	-0.4	-1.4
β-(4-Methyl-2-methoxyphenoxy)- α-hydroxyethyl	+14.3	-2.2	-0.8	-1.2
β-(4-Carboxy-2-methoxyphenoxy)- α-hydroxyethyl	+14.3	-1.8	-0.4	-0.9
β-(4-Carboxy-2,6-dimethoxyphenoxy)- α-hydroxyethyl	+13.9	-2.0	-0.5	-1.0
3-Methyl-5-(1-propenyl)- coumar-2-yl	+11.7	-2.2	-0.3	-0.2
3-Methyl-5-propyl- coumar-2-yl	+11.8	-2.2	-0.1	-0.2

* Substituent Chemical shift (SCS): $\Delta\delta$ in ppm, relative to the corresponding carbon of an appropriate parent compound.

As shown in Table 7, all of the substituents investigated cause strong deshielding of the ipso-carbon, and shielding of the ortho-, meta- and para-carbons. The meta-effects are, in general, insignificant. Thus, the results are in agreement with the electron-releasing nature of these substituents, and the Karplus-Pople theory.[16,17]

Monomeric Lignin Model Compounds

The following model compounds were investigated: benzyl alcohol (4), vanillyl alcohol (5), 4-O-methylvanillyl alcohol (6), syringyl alcohol (7), 4-O-methylsyringyl alcohol (8), α-hydroxyphenylethane (9), α-hydroxy-α-(3-methoxyphenyl)ethane (10), α-hydroxy-α-(3,4-dimethoxyphenyl)ethane (11), α-hydroxy-α-(4-ethoxy-3-methoxyphenyl)ethane (12), α-hydroxy-α-(3,4,5-trimethoxyphenyl)ethane (13) and α-hydroxy-α-(4-ethoxy-3,5-dimethoxyphenyl)-ethane (14)

Effects of Hydroxymethyl Group

The spectral data of compounds 5-8 (Table 4) show that the ipso-carbons (C-1) are deshielded by 14.2-14.9 ppm relative to C-1 of the corresponding parent compounds II, III, V and VI (R = H), when a hydroxymethyl group is introduced into C-1 of the parent compounds. In contrast, C-2/C-6, C-3/C-5 and C-4 undergo shielding of 1.1-2.0, 0.1-0.5 and 1.0-1.5 ppm, respectively. It is apparent that the meta-effects are insignificant. On the basis of the observed SCS data, the effects of a hydroxylmethyl group on the chemical shift of aromatic carbons in the compounds of this class are given in Table 7. The evaluated SCS's are reasonably in good agreement with the observed SCS's for the aromatic carbons of benzyl alcohol (4) caused by the effects of hydroxymethyl group, given in Table 4.

Effects of α-hydroxyethyl group

The SCS data of compounds 10-14 (Table 4) show that ipso-carbons (C-1) undergo deshielding of 19.1-19.8 ppm relative to C-1 of the corresponding parent compounds II-IV, VI and VII (all, R = H) on introduction of an α-hydroxyethyl group into C-1 of the parent compounds. In addition, C-2/C-6, C-3/C-5 and C-4 are shielded by 2.3-3.6, 0.2-0.6 and 1.3-1.5 ppm, respectively. Here again, the *meta*-effects are insignificant. The observed values of the SCS for the C-1 and C-2/C-6 are generally larger by about 5 ppm and 1 ppm than the corresponding substituent effects of the hydroxymethyl group. Thus, the terminal methyl group in the α-hydroxyethyl group affects only C-1 and C-2/C-6. The effects of the α-hydroxyethyl group on the chemical shift of aromatic carbons in the compounds of this class are given in Table 7. The evaluated SCS's are reasonably similar in magnitude to the observed SCS's for the corresponding carbons of α-hydroxyphenylethane (9) caused by the effects of an α-hydroxyethyl group, given in Table 4.

Dimeric Lignin Model Compounds

The following dimeric model compounds were investigated: the twelve β-*O*-4 type compounds 15 - 26 given in Table 5, and the six β-5 type compounds 27 - 32 given in Table 6.

Effects of β-(4-methyl-2-methoxyphenoxy)- -hydroxyethyl group

Compounds 15-18 correspond to introduction of a β-(4-methyl-2-methoxyphenoxy)-α-hydroxyethyl group into C-1 of parent compounds II, IV, V and VII (all, R = H), respectively. The observed SCS data (Table 5) show that *ipso*-carbons (C-1) undergo deshielding of 13.8-14.8 ppm relative to C-1 of the corresponding parent compounds. In contrast, C-2/C-6, C-3/C-5 and C-4 are shielded by 1.6-2.9, 0.5-1.0 and 0.9-1.4 ppm, respectively. The evaluated SCS's for the aromatic carbons of ring A in the compounds of this class are given in Table 7. The evaluated SCS's are similar in magnitude to the evaluated SCS's for vanillyl alcohol homologues, compounds 5-8, rather than those for α-hydroxy-α-(4-hydroxy-3-methoxyphenyl)ethane homologues, compounds

10-14. Thus, the effects of a β-(4-methyl-2-methoxyphenoxy)-α-hydroxyethyl group on the aromatic carbons are similar to the effects of hydroxymethyl group rather than those of an α-hydroxyethyl group, although the substituent has somewhat greater *ortho*- and *meta*-effects than the hydroxymethyl group, probably due to the effects of 4-methyl-2-methoxyphenoxymethyl group, substituent on the carbon of the hydroxymethyl group.

Effect of β-(4-carboxy-2-methoxyphenoxy)-α-hydroxyethyl group

Compounds 19-22 differ from compounds 15-18 in the substituent at C-4 of ring B, carboxyl group instead of methyl group, respectively. The observed values of SCS (Table 5) show that the *ipso*-carbons (C-1) are deshielded by 14.0-14.5 ppm, whereas C-2/C-6, C-3/C-5 and C-4 undergo shielding of 1.5-2.6, 0.3-0.5 and 0.8-0.9 ppm, respectively, all relative to the corresponding carbons of their parent compounds. While the substituent effects on the *ipso*-carbons are similar, the effects of the β-(4-carboxy-2-methoxyphenoxy)-α-hydroxyethyl group on the *ortho*-, *meta*- and *para*-carbons are generally smaller by about 0.6 ppm than the effects of the β-(4-methyl-2-methoxyphenoxy)-α-hydroxyethyl group, indicating that the effects of methyl and carboxyl groups at C-4 on the β-(2-methoxyphenoxy)-α-hydroxyethyl group are different, probably due to the +I effect and -M effect, respectively. The *meta*-effects are insignificant. The evaluated SCS's for the aromatic carbons of ring A in the compounds of this class are given in Table 7.

Effects of β-(4-carboxy-2,6-dimethoxyphenoxy)-α-hydroxyethyl group

Compounds 23-26 correspond to compounds 19-22 with an additional methoxyl group substituted on the carbon *meta* to the carboxyl group in ring B, respectively. As shown in Table 5, *ipso*-carbons (C-1) undergo deshielding of 13.5-14.2 ppm, whereas C-2/C-6, C-3/C-5 and C-4 are shielded by 1.5-2.9, 0.4-0.7 and 0.9-1.0 ppm, respectively, all relative to the corresponding carbons of parent compounds. As compared to the β-(4-carboxy-2-

methoxyphenoxy)-α-hydroxyethyl group, the substituent effects on the *ipso*-carbons are generally smaller by 0.5 ppm, while the effects on the *ortho*-, *meta*- and *para*-carbons are similar. Thus, the additional methoxy group does not significantly affect the substituent effects on the aromatic carbons. Here again, the *meta*-effects are insignificant. The evaluated SCS's for the aromatic carbons of ring A in the compounds of this class are given in Table 7.

Effects of 3-methyl-5-(1-propenyl)coumar-2-yl group

Compounds *27*-*29* correspond to parent compounds II, III and IV (all, R = H) with a 3-methyl-5-(1-propenyl)coumar-2-yl group substituted on C-1, the carbon *para* to the phenolic hydroxyl and corresponding methoxyl and ethoxyl groups, respectively. The SCS data (Table 6) show that *ipso*-carbons (C-1) are deshielded by 11.5-12.0 ppm, whereas C-2/C-6, C-3/C-5 and C-4 are shielded by 1.9-2.7, 0.1-0.5 and 0-0.2 ppm, respectively, all relative to the corresponding carbons of parent compounds. The substituent effects on both the *meta*- and *para*-carbons are insignificant. As compared to the β-*O*-4 type compounds, the observed values of SCS for the *ipso*- and *para*-carbons are generally smaller by 2 and 1 ppm, respectively. The evaluated SCS's for the aromatic carbons of ring A in the compounds of this class are given in Table 7.

Effects of 3-methyl-5-propylcoumar-2-yl group

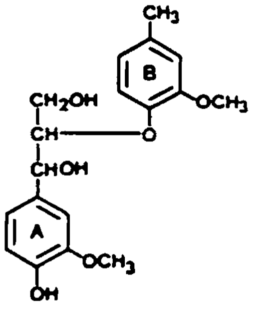
Compounds *30*-*32* are obtained from compounds *27*-*29* on hydrogenation of the double bond in the side chain. As shown in Table 6, *ipso*-carbons (C-1) and C-5 are deshielded by 11.5-12.0 ppm and 0.1-0.2 ppm, respectively, whereas C-2/C-6, C-3 and C-4 are shielded by 1.5-2.8 ppm, 0.1-0.2 ppm and 0-0.3 ppm, respectively, all relative to the corresponding carbons of the parent compounds II, III and IV (all, R = H). In general, the effects of this substituent on the aromatic carbons of ring A are similar in magnitude to the effects of the 3-methyl-5-(1-propenyl) coumar-2-yl group. Thus, the conversion of the 1-propenyl group into a propyl group does not affect the substitutent effects on the aromatic carbons in ring A significantly. The evaluated SCS's for the aromatic carbons in ring A in the compounds of this class are given in Table 7.

Additivity of Evaluated ^{13}C Substituent Chemical Shifts

Table 7 summarizes the evaluated ^{13}C substituent chemical shifts (SCS's) of lignin model compounds, relative to the corresponding carbons of an appropriate parent compound. β-O-(4-Methyl-2-methoxyphenyl)guaiacylglycerol (33) and β-O-(4-carboxy-2-methoxyphenyl)-4-O-ethylguaiacylglycerol methyl ester (34) are used for testing additivity of the evaluated SCS's because their structures are similar to compounds 15 and 20, respectively.

Chemical shifts for the aromatic carbons in ring A of compound 33 were calculated from the evaluated substituent effects of the β-(4-methyl-2-methoxyphenoxy)-α-hydroxyethyl group, using compound II (R = H) as the parent compound. The calculated chemical shifts are δ 133.8, 110.5, 147.0, 145.6, 115.0 and 119.2 ppm for C-1, C-2, C-3, C-4, C-5 and C-6 of ring A, respectively. The observed values for the corresponding carbons are δ 133.4, 111.3, 147.1, 145.5, 114.7 and 119.2 ppm for the *threo* form. The calculated chemical shifts are in good agreement with the observed values with an error of less than 0.8 ppm.

Chemical shifts for the aromatic carbons in ring A of compound 34 were calculated from the evaluated substituent effects of β-(4-carboxy-2-methoxyphenoxy)-α-hydroxyethyl group, compound IV (R = H) being the parent compound. The calculated chemical shifts are δ 135.0, 111.7, 148.9, 147.4, 113.1 and 118.9 ppm for C-1, C-2, C-3, C-4, C-5 and C-6 of ring A, respectively. The observed values for the corresponding carbons of the compound are δ 134.6, 111.0, 148.6, 147.2, 112.4 and 118.9 ppm for the *threo* form.[3] The calculated chemical shifts are in good agreement with the observed values with an error of less than 0.7 ppm.



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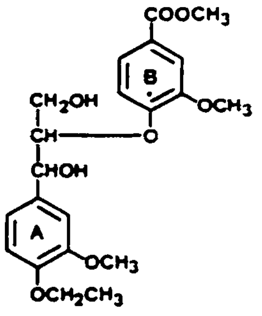

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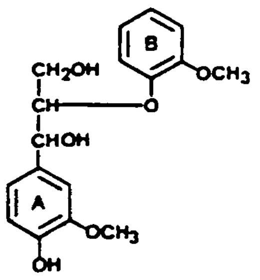

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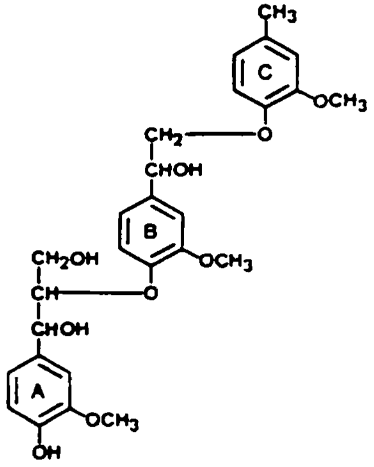

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Similarly, chemical shifts for the aromatic carbons in ring B of β-O-4 type substructures can be estimated by using either threo or erythro form of β-O-(2-methoxyphenyl)-α-guaiacylgylcerol (35) as the parent compound and the substituent effects of an appropriate substituent. The aromatic carbons of ring B in the threo form of compound 35 have chemical shifts of δ 121.1, 112.7, 149.8, 148.5, 115.9 and 120.8 ppm for C-1, C-2, C-3, C-4, C-5 and C-6 in DMSO-d_6, respectively. For the corresponding carbons in the erythro form of compound 35, the values are δ 121.4, 112.8, 149.8, 148.2, 116.0, and 120.7 ppm, respectively. Chemical shifts for the aromatic carbons in ring B in the threo form of trimeric β-O-4 substructure 36 were calculated from the substituent effect of the β-(4-methyl-2-methoxyphenoxy)-α-hydroxyethyl group, using the threo form of compound 35 as the parent compound. The calculated values are δ 135.4, 110.5, 149.0, 147.3, 115.1 and 118.6 ppm for C-1, C-2, C-3, C-4, C-5 and C-6, respectively. Very recently, Bardet et al.[18] determined the chemical shifts of the aromatic carbons in ring B of β-O-4 type substructure in uniformly ^{13}C enriched Aspen milled wood lignin (MWL) from a ^{13}C enriched wood of Aspen (X Populus euramericana), grown under $^{13}CO_2$ enriched atmosphere, through establishing the connectivities between directly bonded ^{13}C-^{13}C by ^{13}C NMR 2D-INADEQUATE technique. The observed values are δ 134.8, 111.8, 149.4, 147.7, 115.7 and 119.4 ppm for C-1, C-2, C-3, C-4, C-5 and C-6, respectively. This result implies that a trimeric β-O-4 substructure of the type 36 is present in the Aspen MWL. In the ^{13}C NMR spectrum of a MWL from wood of Spruce (Picea glauca), signals corresponding to the aromatic carbons of ring B in the β-O-4 substructure were observed at δ 135.0, 111.8, 149.3, 147.2, 115.2 and 119.5 ppm for C-1, C-2, C-3, C-4, C-5 and C-6, respectively. Thus, the calculated chemical shifts are in good agreement with the observed values with an error of less than 0.9 ppm, except for the value for C-2 which has an error of 1.3 ppm.

As demonstrated above, the evaluated SCS's can be applied to estimate chemical shifts of aromatic carbons in ring A of β-O-4 type dimeric model compounds as well as in ring B of the substructure in MWL's by a generalized SCS additivity rule, using an appropriate parent compound as reference instead of benzene. However, it must be noted that the above calculations are only first approximations. The evaluated SCS's of β-(4-methyl-2-methoxyphenoxy)-α-hydroxyethyl and β-(4-carboxy-2-methoxyphenoxy)-α-hydroxyethyl groups are used in the estimation of the chemical shifts of aromatic carbons in ring A of compounds 33 and 34 as well as in ring B of β-O-4 substructures in MWL's, instead of those of β-(4-methyl-2-methoxyphenoxy)-α,γ-dihydroxypropyl and β-(4-carboxy-2-methoxyphenoxy)-α,γ-dihydroxypropyl groups, respectively. It is likely that the chemical shifts of aromatic carbons in ring A of compounds 33 and 34 and in ring B of β-O-4 substructures in MWL's can be predicted even more accurately when evaluated SCS's of the latter two substituents are used in the estimation. At present, our laboratory does not have sufficient ^{13}C NMR spectral data to evaluate SCS's caused by these substituents.

Assignment of Signals in ^{13}C NMR Spectra of DHP's from Coniferyl Alcohol

Ellwardt *et al.*[19] obtained the ^{13}C NMR spectrum of the dehydrogenation polymer (DHP) prepared from coniferyl alcohol specifically ^{13}C-enriched at C-4 (^{13}C-enrichment, *ca.* 5 atomic %). As compared to ^{13}C natural abundance DHP, the spectrum of the DHP specifically ^{13}C-enriched at C-4 exhibits enhanced signals at δ 149.7, 148.2, 147.6, 147.3, 146.3 and 143.6 ppm in the oxygenated quarternary aromatic carbon region. Except for signal at δ 149.7 ppm, the relative intensities of these signals are remarkably strong. However, these signals have not been assigned. According to the generalized SCS additivity rule, the signals at δ 148.2 ppm and 143.6 ppm are assigned to C-4 of rings A and B in a 4-O-alkylated β-5 substructure, respectively, although the latter also corresponds to C-4 of a 4-O-alkylated 5-5 substructure.[20] Similarly, the signals at δ 147.6 and 147.3 ppm are assigned to C-4 of 4-O-alkylated β-O-4 and β-β substructures. The signal at δ 146.3 ppm corresponds to C-4 of ring A in non-etherified β-O-4, β-5 and β-β substructures. The origin of the signal at δ 149.7 ppm is not known. Signals corresponding to C-3 in ring A of either non-etherified or 4-O-alkylated β-O-4, β-5 and β-β substructures are not discernible due to the enhancement of signals corresponding to C-4 of the aforementioned substructures. However, the signals for C-3 of these 4-O-alkylated substructures should be present at δ values around 149 ppm while those for C-3 of the non-etherfied substructures should appear at δ values around 147 ppm. The ^{13}C NMR spectrum of ^{13}C natural abundance DHP exhibits relatively intensive signals at δ 53.6 ppm and 53.1 ppm, corresponding to C-β of β-β and β-5 substructures, respectively.[18] Thus, the spectra of DHP's from coniferyl alcohol indicate that the DHP is structurally quite different from softwood milled wood lignins (MWL's). The former contains considerably greater quantities of β-5 and β-β substructures than the latter.

CONCLUSION

The SCS additivity rule of mono- and disubstituted benzene can be applied to estimate chemical shifts of aromatic carbons in lignin model compounds of the β-O-4 and β-5 types when the evaluated SCS's elucidated in this paper are used with guaiacol, syringol and their ethers as parent compounds. An appropriate parent compound is selected on the basis of the nature of the model compound or lignin substructure to be examined. In addition, the generalized SCS additivity rule can estimate chemical shifts of aromatic carbons in lignin model compounds and lignin preparations with reasonable accuracy.

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