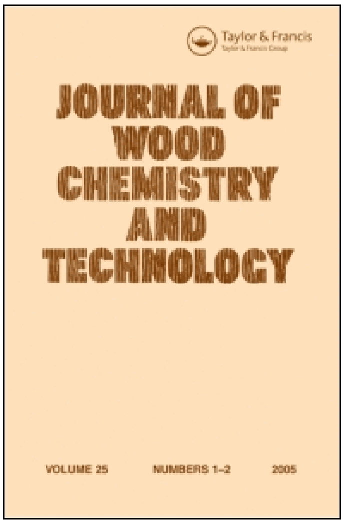

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Substituent Effects on C-13 Chemical Shifts of Aromatic Carbons in Biphenyl Type Lignin Model Compounds

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SUBSTITUENT EFFECTS ON C-13 CHEMICAL SHIFTS OF AROMATIC CARBONS IN BIPHENYL TYPE LIGNIN MODEL COMPOUNDS

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ABSTRACT

Simple 5-5 type lignin model compounds have been synthesized from dehydro-divanillin and its ether derivatives by decarbonylation, hydrogenation, and reduction with metal hydride. The chemical shifts for the aromatic carbons of these compounds were assigned, and the substituent effects have been elucidated from ^{13}C NMR spectra of guaiacyl-type monomeric and 5-5 type lignin model compounds. In addition, evaluation of the observed values of substituent chemical shift (SCS) for the aromatic carbons leads to formulation of a generalized SCS additivity rule for the aromatic carbons in 5-5 type substructures. The rule is complementary to the similar rule formulated earlier for the β-O-4 and β-5 type lignin substructures. The rule can be used for the estimation of the chemical shifts of aromatic carbons in lignin model compounds and lignin preparations with reasonable accuracy. On the basis of the observed ^{13}C NMR spectral data for aromatic

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carbons of the 5-5 type substructure, the quantity of this substructure in Spruce Milled Wood Lignin (MWL) was estimated from a quantitative ^{13}C NMR spectrum of the lignin obtained using the inverse gated decoupling (IGD) sequence. About 24-26 units of guaiacylpropane per 100 C_9-units were estimated to be involved in 5-5 type substructures in Spruce MWL, of which about 18-20 units were present as etherified 5-5 type substructures.

INTRODUCTION

Since Lüdemann and Nimz[1,2] introduced ^{13}C NMR spectroscopy for characterization of lignins one and a half decades ago, ^{13}C NMR spectroscopy has become one of the most important techniques for characterization of lignins[3-6]. In spite of the progress made in this field, there are still several unsolved problems in characterization of lignins by ^{13}C NMR spectroscopy. One of these problems is the absence of ^{13}C NMR data for aromatic carbons in the biphenyl (5-5) type moiety in lignin, which is the second most abundant substructure next to that of the β-O-4 type[7] in guaiacyl lignins.

The objectives of this work are as follows: a) to synthesize simple model compounds related to the 5-5 substructures in lignins; b) to study ^{13}C NMR spectroscopic characteristics of the synthesized compounds; c) to study the effects on the chemical shift (SCS) caused by the introduction of substituents at C-1 on the aromatic carbons in the model compounds; d) to examine whether the generalized substituent chemical shift additivity rule developed for the β-O-4 type substructure[8] is applicable to the biphenyl type substructure and related compounds; and finally, e) to elucidate the importance of the 5-5 substructure in spruce milled wood lignin (MWL) by analyzing its ^{13}C NMR spectrum.

EXPERIMENTAL

Synthesis of Lignin Model Compounds

2,2'-Dihydroxy-3,3'-dimethoxybiphenyl (I)

A mixture of 0.5 g (1.7 mmol) of dehydro-divanillin and 0.02 g (4%) of 5% Pd-C was heated in a sand bath, under a CO_2

atmosphere. The reaction mixture was distilled and the resulting colorless viscous oil was immediately solidified. An examination by TLC showed that the crude colorless crystals were pure, m.p. 135-137°C, yield 0.14 g (0.57 mmol, 33.7%), NMR ($CDCl_3$): δ 3.90 (6H, s, $2ArOCH_3$), 5.80 (2H, broad band, D_2O exchangeable, 2ArOH), 6.90 (6H, m, 2ArH).

2,2',3,3'-Tetramethoxybiphenyl (II)

This compound was prepared from dehydro-diveratraldehyde (1.5 mmol) and 5% Pd-C (1%) in the same manner described for the preparation of compound I. The product has m.p. 72-73°C, yield 0.26 g (0.95 mmol, 62.7%), NMR ($CDCl_3$): δ 3.62 (6H, s, $2ArOCH_3$), 3.87 (6H, s, $2ArOCH_3$), 6.72-7.02 (6H, m, 2ArH).

Diethyldehydro-divanillin (IIIa)

This compound was prepared by ethylation of dehydro-divanillin with EtI in DMF in the presence of anhydrous K_2CO_3, according to the procedure of Hassi and coworkers[8]. Colorless crystals were obtained, m.p. 140-141°C, yield 1.7 g (4.75 mmol, 47%), NMR ($CDCl_3$): δ 1.07 (6H, t, J_{A2X3}=7.5 Hz, $2ArOCH_2CH_3$), 3.96 (6H, s, $2ArOCH_3$), 4.0 (4H, q, J_{A2X3}=7.5 Hz, $2ArOCH_2CH_3$), 7.43 (2H, d, J_{AB} = 1.5 Hz, 2ArH-4), 7.49 (2H, d, J_{AB} = 1.5 Hz, 2ArH-6), 9.9 (2H, s, 2ArCHO).

2,2'-Diethoxy-3,3'-dimethoxybiphenyl (III)

This compound was obtained from diethyldehydro-divanillin (IIIa) (1.4 mmol) and 5% Pd-C (1%) as described for the synthesis of compound I. The product, a colorless oily substance, did not crystallize, but was pure on TLC, yield 0.27 g (0.89 mmol, 63.3%), NMR ($CDCl_3$): δ 1.02 (6H, t, J_{A2X3}=7.5 Hz, $2ArOCH_2CH_3$), 3.83 (6H, s, $2ArOCH_3$), 3.83 (4H, q, J_{A2X3}=7.5 Hz, $2ArOCH_2CH_3$), 6.76-7.08 (6H, m, 2ArH).

2,2'-Dihydroxy-3,3'-dimethoxy-5,5'-dimethylbiphenyl (9)

A mixture of 50 ml of absolute ethanol and 0.2 g of 10% Pd-C was added to a solution of 0.4 g (1.3 mmol) of dehydro-divanillin in 45 ml of DMF. The mixture was subjected to hydrogenation and was shaken for 13 hours under a hydrogen pressure of 60 psi. The reaction mixture was filtered to remove the palladium charcoal.

The residue was washed with ethanol and the solvent was removed under reduced pressure to give a solid mass of beige crystals. The crude product was recrystallized from hexane to give colorless crystals, m.p. 123-124°C, yield 0.069 g (0.25 mmol, 19%), NMR ($CDCl_3$): δ 2.20 (6H, *s*, $2ArC\underline{H}_3$), 3.78 (6H, *s*, $2ArOC\underline{H}_3$), 5.80 (2H, *s*, D_2O exchangeable, $2ArO\underline{H}$), 6.57 (4H, *s*, $2Ar\underline{H}$).

2,2',3,3'-Tetramethoxy-5,5'-dimethylbiphenyl (10)

The compound was prepared from hydrogenation of a solution of dehydro-diveratraldehyde in absolute ethanol in the presence of 5% Pd-C for 6 hours under a hydrogen pressure of 30 psi using the same procedure described for the preparation of compound *9*. The colorless viscous oil which was obtained crystallized after being kept at 0°C for 3 days. The crude product was recrystallized from ethanol to give colorless crystals, m.p. 97-98°C, yield 0.54 g (1.8 mmol, 58.7%), NMR ($CDCl_3$): δ 2.37 (6H, *s*, $2ArC\underline{H}_3$), 3.68 (6H, *s*, $2ArOC\underline{H}_3$), 3.91 (6H, *s*, $2ArOC\underline{H}_3$) 6.69 (2H, *d*, J_{AB}=1.5 Hz, $2Ar\underline{H}$-4), 6.76 (2H, *d*, J_{AB}=1.5 Hz, $2Ar\underline{H}$-6).

2,2'-Diethoxy-3,3'-dimethoxy-5,5'-dimethylbiphenyl (11)

The compound was prepared by adding 10% Pd-C and a few drops of acetic acid to a solution of IIIa in ethanol, following the same procedure described for the preparation of compound *9*. The product has m.p. 104-105°C, yield 0.34 g (1.0 mmol, 73%), NMR ($CDCl_3$): δ 1.06 (6H, *t*, J_{A2X3}=8.7 Hz,$2C\underline{H}_3CH_2OAr$), 2.28 (6H, *s*, $2ArC\underline{H}_3$), 3.76 (4H, *q*, J_{A2X3}=8.7 Hz, $2CH_3C\underline{H}_2OAr$), 3.83 (6H, *s*, $2ArOC\underline{H}_3$), 6.64 (4H, *s*, $2Ar\underline{H}$).

4-Propylguaiacol (12a)

The compound was prepared by hydrogenation of a solution of 8.22 g (50.1 mmol) of isoeugenol in 100 ml of absolute ethanol and 0.6 g of 5% Pd-C for 6 hours, under a hydrogen pressure of 30 psi, as described for the preparation of compound *9*. The product, a colorless viscous oil, did not crystallize, but was pure on TLC, yield 8.27 g (49.8 mmol, 99.4%), NMR ($CDCl_3$): δ 0.93 (3H, *t*, J_{M2X3}=8.0 Hz, $C\underline{H}_3CH_2CH_2$-), 1.63 (2H, *m*, J_{M2X3}=8.0 Hz, J_{A2M2}=7.5 Hz, $CH_3C\underline{H}_2CH_2$-), 2.53 (2H, *t*, J_{A2M2}=7.5 Hz, $ArC\underline{H}_2$-), 3.90 (3H, *s*, $ArOC\underline{H}_3$), 5.55 (1H, *s*, D_2O exchangeable, $ArO\underline{H}$), 6.68-6.97 (3H, *m*, $Ar\underline{H}$).

2,2'-Dihydroxy-3,3'-dimethoxy-5,5'-dipropylbiphenyl (12)

A solution of 4.94 g (29.8 mmol) of 4-propylguaiacol in 60 ml of 95% ethanol and an aqueous solution of 62.3 ml (17.4 mmol) of ferric chloride were mixed and stirred for 2 hours. The crude cyrstals were filtered off and recrystallized from ethanol to give colorless crystals, m.p. 142-145°C, yield 0.5 g (1.5 mmol, 5.12%), NMR ($CDCl_3$): δ 0.90 (6H, t, J_{M2X3}=8.0 Hz, $2CH_3CH_2CH_2-$), 1.62 (4H, m, J_{M2X3}=8.0 Hz, J_{A2M2}=7.5 Hz, 2 $CH_3CH_2CH_2-$), 2.53 (4H, t, J_{A2M2}=7.5 Hz, $2CH_3CH_2CH_2-$), 3.90 (6H, s, $2ArOCH_3$), 6.03 (2H, s, D_2O exchangeable, 2ArOH), 6.77 (4H, s, 2ArH).

2,2',3,3'-Tetramethoxy-5,5'-dipropylbiphenyl (13)

The compound was prepared by methylation of compound 12 with $(CH_3)_2SO_4$ in an alkaline solution. The product, a colorless oil, did not crystallize but was pure on TLC, yield 0.48 g (0.87 mmol, 59.5%), NMR ($CDCl_3$): δ 0.93 (6H, t, J_{M2X3}=8.0 Hz, $2CH_3CH_2CH_2-$), 1.66 (4H, m, J_{M2X3}=8.0 Hz, J_{A2M2}=7.5 Hz, $2CH_3CH_2CH_2-$), 2.56 (4H, t, J_{A2M2}=7.5 Hz, $2CH_3CH_2CH_2-$), 3.63 (6H, s, $2ArOCH_3$), 3.90 (6H, s, $2ArOCH_3$), 7.16 (4H, s, 2ArH).

2,2'-Diethoxy-3,3'-dimethoxy-5,5'-dipropylbiphenyl (14)

The compound was prepared from compound 12 (2.75 mmol) and diethyl sulfate (7.48 mmol) in an alkaline solution. The product, a resinous oil, did not crystallize but was pure on TLC, yield 1.03 g (2.66 mmol, 96.7%).

Dehydro-divanillyl alcohol (15)

To a solution of 0.24 g (0.79 mmol) of dehydro-divanillin was added 1 g of 5% Pd-C in 30 ml of 0.5N NaOH. The mixture was subjected to hydrogenation for 5 hours under a hydrogen pressure of 25 psi. The reaction mixture was acidified to pH 2 with concentrated HCl. The crude product was filtered off and recrystallized from ethanol to give colorless crystals, m.p. 157-158°C, yield 0.14 g (60%, 0.48 mmol), NMR (DMSO-d_6): δ 3.10-3.53 (2H, broad band, D_2O exchangeable, $2ArCH_2OH$), 3.7 (6H, s, $2ArOCH_3$), 4.30 (4H, s, $2ArCH_2OH$), 6.57 (2H, d, J_{AB}=2 Hz, 2ArH-2), 6.78 (2H, d, J_{AB}=2.0 Hz, 2ArH-6), 8.1 (2H, s, D_2O exchangeable, 2ArOH).

Dehydro-diveratryl alcohol (16)

Under a dry N_2 atmosphere, with magnetic stirring, 1.0 g (3.0 mmol) of dehydro-diveratraldehyde was added to a suspension of 0.46 g (12.0 mmol) of $LiAlH_4$ in 20 ml of dry THF. The reaction mixture was stirred for 3 hours at reflux temperature. The excess of lithium aluminum hydride was decomposed by a dropwise addition of water. The insolubles were filtered off and the ethereal solution was washed with water, dried over anhydrous $MgSO_4$, and the solvent removed under reduced pressure to give a colorless oil, yield 0.89 g (2.66 mmol, 88%), NMR ($CDCl_3$): δ 2.60-3.0 (2H, broad band, D_2O exchangeable, $2ArCH_2O\underline{H}$), 3.63 (6H, s, $2ArOC\underline{H}_3$), 3.92 (6H, s, $2ArOC\underline{H}_3$), 4.56 (4H, s, $2ArC\underline{H}_2$-), 6.75 (2H, d, J_{AB}=3 Hz, Ar$\underline{H}$-2), 6.93 (2H, d, J_{AB}=3 Hz, 2Ar$\underline{H}$-6).

4,4'-O-Diethyldehydro-divanillyl alcohol (17)

The compound was prepared from compound (IIIa) (2.7 mmol) and $LiAlH_4$ (10.8 mmol) in THF in the same manner described for the preparation of compound 16. A colorless oil was obtained, yield 0.99 g (2.7 mmol, 97.5%). NMR ($CDCl_3$): δ 1.03 (6H, t, J_{A2X3}=7.5 Hz, $2C\underline{H}_3CH_2OAr$), 2.66-3.16 (2H, broad band, D_2O exchangeable, $2ArCH_2O\underline{H}$), 3.83 (4H, q, J_{A2X3}=7.5 Hz, $2CH_3C\underline{H}_2OAr$), 3.87 (6H, s, $2ArOC\underline{H}_3$), 4.66 (4H, s, $2ArC\underline{H}_2OH$), 6.83 (2H, d, J_{AB}=2 Hz, 2Ar$\underline{H}$-2), 6.93 (2H, d, J_{AB}=2 Hz, 2Ar$\underline{H}$-6).

Routine ^{13}C NMR Spectra

The routine ^{13}C NMR spectra of lignin model compounds were recorded with a Bruker-IBM AF FT spectrometer operating at 25.2 MHz for the ^{13}C nuclei frequency with the broadband-noise decoupling technique. Deuterated dimethylsulfoxide (DMSO-d_6) was used as solvent. The spectra were run in 5 mm (O.D.) sample tubes (concentration of the sample ca. 100 mg in 0.5 ml of DMSO-d_6 (ca. 20% w/v)) with a 30° or 60° pulse angle corresponding to a 8 or 12 sec pulse width, pulse repetition time of 2 sec., and an average number of scans of ca. 1,000. Tetramethylsilane (TMS) was used as the internal chemical shift (δ in ppm) reference. The APT spectra [9,10] of the compounds were also obtained to discriminate signals from primary and tertiary carbons from those of secondary and quaternary carbons.

Quantitative ^{13}C NMR Spectrum of Spruce Milled Wood Lignin (MWL)

The quantitative ^{13}C NMR spectrum of the spruce MWL was recorded with a Bruker WM 250 NMR spectrometer operating at 62.9 MHz for the ^{13}C nuclei frequency, using the Inverse Gated Decoupling (IGD) sequence[11] and quadrature detection. Deuterated dimethylsulfoxide (DMSO-$\underline{d}_6$) was used as solvent. The spectrum was run in a 10 mm (O.D.) sample tube (concentration of the sample ca. 350 mg in 1.8 ml of DMSO-$\underline{d}_6$ (ca. 17.5%, w/v)) at 50°C with a 90° pulse angle corresponding to a 22 sec pulse width, 14285 Hz sweep width, 11 sec pulse delay and the number of scans about 15,000. Tetramethylsilane (TMS) was used as the internal chemical shift (δ in ppm) reference.

RESULTS AND DISCUSSION

Parent Compounds

All biphenyl-type lignin model compounds synthesized belong to symmetry species point group C_2[12]. The C_2 axis passes through the bond between the two aromatic rings and bisects the angle between the two planes containing those rings. Although the molecule is dissymetric with respect to the C_2 axis, the axis bisects the molecule into two equivalent parts: hence the corresponding nuclei in rings A and B are chemically equivalent. Thus, the six aromatic carbons of one ring have identical chemical shifts to their corresponding carbons in the other ring.

Study of ^{13}C NMR spectra of these 5-5 type dimeric lignin model compounds has been facilitated by the fact that both rings have the same substituent groups.

Except for C-5, the sequence of the observed chemical shifts for aromatic carbons in the parent compounds I-III (Table 1) is in agreement with the observed chemical shifts of guaiacol and its methyl and ethyl ethers given in Table 2. Thus, in the ^{13}C NMR spectra of these biphenyl parent compounds, the signals for C-3 also appear downfield of the signal for C-4. The C-3 carbons are more deshielded by the presence of the substituents, as is seen in the ^{13}C NMR spectra of all biphenyl model compounds synthesized.

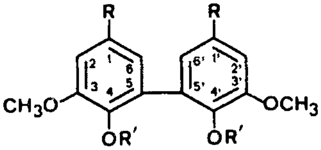
TABLE 1.

^{13}C Chemical Shifts of Aromatic Carbons in Parent Compounds in DMSO-d_6.*

Compound (R = H)	C-1	C-2	C-3	C-4	C-5	C-6
I	118.7	110.8	147.9	143.8	126.2	123.5
II	123.6	112.3	152.6	146.5	132.7	122.9
III	123.0	112.0	152.6	145.7	133.0	122.8

Chemical Shift (δ in ppm)

* Numbering here refers to assignment of signals only.



I, R' = H

II, R' = CH_3

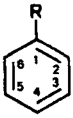
III, R' = CH_2CH_3

TABLE 2.

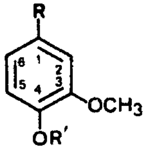
^{13}C Chemical Shifts of Aromatic Carbons in Parent Compounds in DMSO-d_6[8].

Compound (R = H)	C-1	C-2	C-3	C-4	C-5	C-6
IV	128.3	128.3	128.3	128.3	128.3	128.3
V	119.5	112.7	147.9	146.8	115.8	121.4
VI	120.8	112.1	149.2	149.2	112.1	120.8
VII	120.7	113.5	149.3	148.3	113.5	120.7

Chemical Shift (δ in ppm)



IV



V, R' = H

VI, R' = CH_3

VII, R' = CH_2CH_3

This is in good agreement with the new chemical shift assignments for C-3 and C-4 in the spectra of guaiacyl-type model compounds proposed previously[8,13].

As compared to the monomeric model compounds V-VII, the C-5 carbons are strongly deshielded by the presence of the second aromatic ring in the biphenyl type dimeric model compounds I-III. For example, the chemical shifts for C-5 of monomeric model compounds V and VII are 115.8 and 113.5 ppm, respectively (Table 2), while the chemical shifts of the same carbon for the corresponding biphenyl type model compounds I and III are δ 126.2 and 133.0 ppm, respectively. Thus, the substituent effects of aryl group at C-5 on the chemical shift of this carbon are deshielding of about 10 ppm for the 2-hydroxy-3-methoxyphenyl group and about 20 ppm for the 2,3-dimethoxyphenyl and 2-ethoxy-3-methoxyphenyl groups. It is therefore evident that the deshielding of C-5 carbons in biphenyl-type model compounds increases about twofold with respect to the corresponding parent compounds when the substituent at C-5 is converted from 2-hydroxy-3-methoxyphenyl group into 2-alkoxy-3-methoxyphenyl group by 2-O-alkylation.

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

Substituent effects on the chemical shift of aromatic carbons of 5-5 type dimeric lignin model compounds have been studied relative to the corresponding dimeric parent compounds 2,2'-dihydroxy-3,3'-dimethoxybiphenyl (I) and its methyl and ethyl ethers (II and III). Tables 1 and 2 summarize chemical shifts of the 5-5 type and corresponding monomeric parent compounds, respectively. Table 3 shows the substituent effects caused by introduction of a substituent at C-1 observed in monomeric model compounds, while Table 4 summarizes those observed in the following 5-5 type dimeric model compounds: 2,2'-dihydroxy-3,3'-dimethoxy-5,5'-dimethylbiphenyl (9) and its methyl and ethyl ethers (10 and 11), 2,2'-dihydroxy-3,3'-dimethoxy-5,5'-dipropylbiphenyl 12 and its methyl and ethyl ethers (13 and 14),

TABLE 3.

^{13}C Chemical Shifts Observed and Substituent Chemical Shifts of Aromatic Carbons in Monomeric Lignin Model Compounds in DMSO-d_6^{*,8}.

Substituent at C-1(R)	Parent	Comp'd	C-1(ipso) δ	C-1(ipso) SCS	C-2(ortho) δ	C-2(ortho) SCS	C-3(meta) δ	C-3(meta) SCS	C-4(para) δ	C-4(para) SCS	C-5(meta) δ	C-5(meta) SCS	C-6(ortho) δ	C-6(ortho) SCS
CH_3	IV	1	137.2	+8.9	128.7	+0.4	128.0	-0.3	125.1	-3.2	128.0	-0.3	128.7	+0.4
	V	2	128.3	+8.8	113.4	+0.7	147.6	-0.3	144.6	-2.2	115.7	-0.1	121.3	-0.1
	VI	3	129.9	+9.1	113.2	+1.1	149.3	+0.1	147.5	-1.7	112.1	0.0	120.7	-0.1
$CH_2CH_2CH_3$	IV	4	142.8	+14.5	128.4	-0.1	128.6	+0.3	125.8	-2.5	128.6	+0.3	128.4	-0.1
	V	5	133.2	+13.7	112.7	0.0	147.6	-0.3	144.6	-2.2	115.4	-0.4	120.6	-0.6
CH_2OH	IV	6	142.6	+14.3	126.5	-1.8	128.0	-0.3	126.5	-1.8	128.0	-0.3	126.5	-1.8
	V	7	133.7	+14.2	111.3	-1.4	147.6	-0.3	145.5	-1.3	115.3	-0.5	119.4	-2.0
	VI	8	135.5	+14.7	111.0	-1.1	149.1	-0.1	148.2	-1.0	111.9	-0.2	119.1	-1.7

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

TABLE 4.

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

Substituent			C-1(ipso)		C-2(ortho)		C-3(meta)		C-4(para)		C-5(meta)		C-6(ortho)	
at C-1(R)	Parent	Comp'd	δ	SCS	δ	SCS	δ	SCS	δ	SCS	δ	SCS	δ	SCS
CH_3	I	9	127.4	+8.7	111.6	+0.8	147.7	-0.2	141.3	-2.5	126.0	-0.2	123.5	0.0
	II	10	132.3	+8.7	112.9	+0.6	152.0	-0.6	144.2	-2.3	132.3	-0.4	122.9	0.0
	III	11	131.4	+8.4	113.0	+1.0	152.0	-0.6	143.5	-2.2	132.5	-0.5	123.1	+0.3
$CH_2CH_2CH_3$	I	12	132.4	+13.7	110.8	0.0	147.7	-0.2	141.5	-2.3	126.0	-0.2	122.9	-0.6
	II	13	137.0	+13.4	112.1	-0.2	152.1	-0.5	144.3	-2.2	132.0	-0.7	122.4	-0.5
	III	14	136.6	+13.6	112.0	0.0	152.2	-0.4	143.6	-2.1	132.6	-0.4	122.6	-0.2
CH_2OH	I	15	133.0	+14.3	109.8	-1.0	147.9	0.0	142.7	-1.1	126.0	-0.2	121.8	-1.7
	II	16	137.8	+14.2	110.5	-1.8	152.2	-0.4	145.2	-1.3	132.4	-0.3	120.7	-2.2
	III	17	137.4	+14.4	110.7	-1.3	152.6	0.0	144.7	-1.0	133.0	0.0	121.1	-1.7

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

dehydro-divanillyl alcohol (15) and its methyl and ethyl ethers (16 and 17). In both cases, the observed SCS's are generally similar in magnitude for each aromatic carbon in model compounds having the same substituent at C-1 of different guaiacyl-type parent compounds.

In the ^{13}C NMR spectra of all 5-5 type dimeric model compounds analyzed here, the signal for C-4 appears upfield of the signal for C-3, and a larger shielding effect has always been observed for the *para* carbon as compared to that for the *meta* carbon. If signal assignments for C-3 and C-4 are reversed, the observed SCS's for C-3 and C-4 in the biphenyl type model compounds of the same class would no longer remain near constant because the chemical shifts of aromatic carbons in the parent compounds are fixed. These results are in good agreement with the ^{13}C NMR data of β-*O*-4 type model compounds[8,13].

In guaiacyl-type monomeric and β-*O*-4 dimeric lignin model compounds, the ^{13}C NMR signal for C-5 always appears upfield of the signal for C-1. In contrast, C-3/C-5 carbons of syringyl-type model compounds are strongly deshielded, and the signal for C-3/C-5 always appears downfield of the signal for C-1. Except for model compounds 10 and 11, the signal for C-5 in 5-5 type model compounds appears generally upfield of the signal for C-1, as given in Table 4. For compound 10, the chemical shifts for C-1 and C-5 are the same, while for compound 11, the chemical shift for C-5 and C-1 are 132.5 and 131.4 ppm, respectively.

As shown in Table 4, all the substituents investigated cause strong deshielding of the *ipso*-carbon, but shielding of the *meta*- and *para*-carbons. The *meta*-effects are insignificant. *Ortho*-carbons are shielded when the substituents at C-1 are N-propyl or hydroxymethyl groups, whereas introduction of a methyl group at C-1 results in deshielding of *ortho*-carbons.

Effects of Methyl Group

As given in Table 4, the SCS data of compounds 9 to 11 show that C-1 (*ipso* carbon) and C-2 (*ortho* carbon) undergo deshielding

TABLE 5.
Average ^{13}C Substituent Chemical Shifts of Biphenyl (5-5) Type Lignin Model Compounds in DMSO-$\underline{d}_6$*

Substituents	C-1 (ipso)	C-2/C-6 (ortho)	C-3/C-5 (meta)	C-4 (para)
$-CH_3$ (Methyl)	+8.6	+0.6	-0.4	-2.3
$-CH_2CH_2CH_3$ (n-propyl)	+13.6	-0.3	-0.4	-2.2
$-CH_2OH$ (Hydroxymethyl)	+14.3	-1.7	-0.2	-1.1

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

of 8.4-8.7 ppm and 0.6-1.0 ppm, respectively. The signals for C-6 (ortho) of compounds 9 and 10 are not shifted, whereas in compound 11 C-6 is deshielded by 0.3 ppm. In contrast C-3/C-5 and C-4 are shielded by 0.2-0.6 and 2.2-2.5 ppm, respectively, by introduction of a methyl group into C-1 of the parent compounds I-III. The meta effects observed are insignificant. On the basis of the observed SCS data, the effects of a methyl group on the chemical shift of aromatic carbons of these model compounds can be calculated and are summarized in Table 5. These values are in good agreement with the observed SCS's for the aromatic carbons in monomeric lignin model compounds given in Table 3.

Effects of n-propyl group

For model compounds 12-14, the observed SCS data show that C-1 is deshielded by 13.4-13.7 ppm relative to C-1 of the corresponding parent compounds I-III. In addition, C-2/C-6, C-3/C-5 and C-4 are shielded by 0.2-0.6, 0.2-0.7 and 2.1-2.3 ppm, respectively. The ortho and meta effects are insignificant. Only the chemical shift of C-1 was substantially affected by the substitution of the methyl group, in compounds 9-11, by the N-propyl group in compounds 12-14, shifting by about +5 ppm from the corresponding substituent effects of the methyl group. The averaged effects of the n-propyl group are registered in Table 5 and are very similar in magnitude to the observed SCS's for n-propyl guaiacol 5 as given in Table 3.

Effects of Hydroxymethyl Group

Compounds 15-17 correspond to the introduction of a hydroxymethyl group into C-1 of parent compounds I-III. As a result, the *ipso*-carbons (C-1) undergo deshielding of 14.2-14.4 ppm relative to C-1 of the corresponding parent compounds, while C-2/C-6, C-3/C-5 and C-4 are shielded by 1.0-2.2, 0.2-0.4 and 1.0-1.3 ppm, respectively. Once again, the *meta* effects are insignificant.

The substituent effects on C-1 are larger by about 6.0 and 1.0 ppm than the corresponding substituent effects of the methyl and N-propyl groups, respectively. For C-4, these effects are smaller by about 1.0 ppm than the effects of the alkyl groups, while the observed values of the SCS's for C-2/C-6 are different for the three analyzed substituents. The averaged SCS's for the aromatic carbons are given in Table 5, and they agree with the observed assignments for compounds 7 and 8 in Table 3.

Estimation of Biphenyl (5-5) Type Substructure in Spruce Milled Wood Lignin (MWL)

Figure 1 shows a quantitative ^{13}C NMR spectrum of spruce milled wood lignin (MWL), obtained by using the inverse gated decoupling (IGD) sequence.[11] The quantitative nature of the spectrum is shown by the fact that the signal at δ 55.6 ppm, aromatic methoxyl carbon, integrates at about 0.98 carbons/phenyl group, as shown in Tables 6 and 7. This corresponds to about 0.98 moles $-OCH_3/C_9$-unit for the MWL. The elemental analysis of the MWL gave a methoxyl content of 0.94 moles $-OCH_3/C_9$-unit for the MWL[14]. Thus, the methoxyl content estimated from the ^{13}C NMR spectrum has approximately a 4% deviation from the value obtained from the elemental analysis. This is well within a ±5% deviation from the latter value, the limit of error allowed for the ^{13}C NMR spectroscopic estimation.

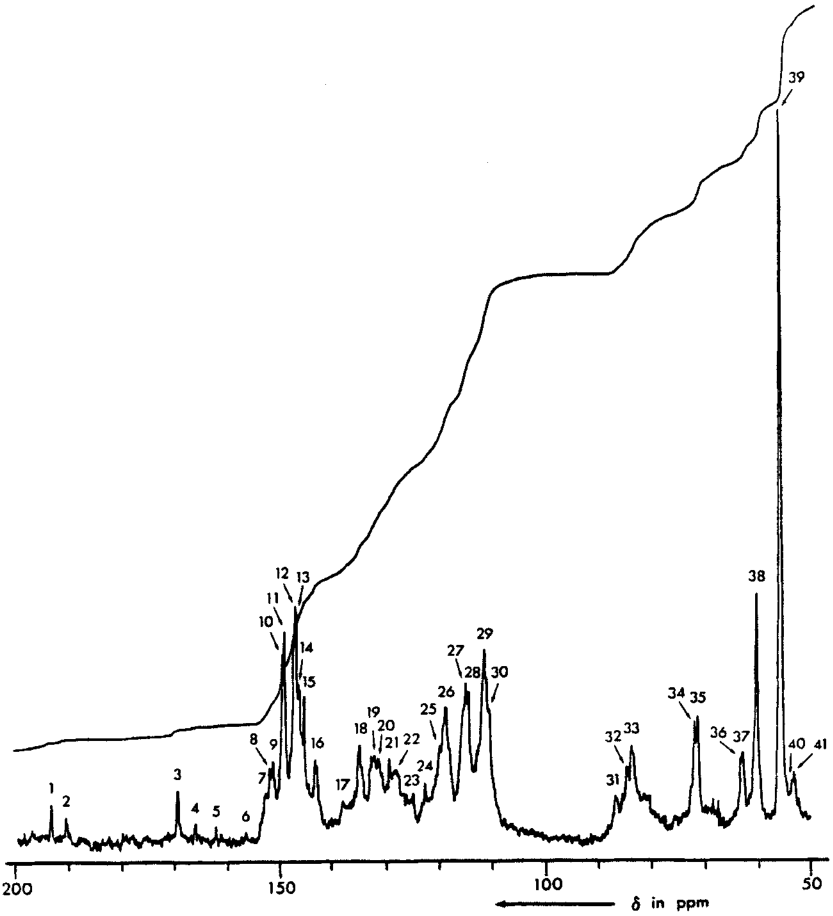


Figure 1. Quantitative ^{13}C NMR Spectrum of Milled Wood Lignin (MWL) from Spruce (Picea glauca) by Inverse Gated Decoupling (IGD) Pulse Sequence. Solvent: DMSO-$\underline{d}_6$.

TABLE 6.
Number of Carbons in Chemical Shift Range of the ^{13}C NMR Spectrum of Spruce Milled Wood Lignin (MWL)

Chemical Shift Range (δ in ppm)	Integral*	Number of Carbons** per Phenyl Group
194-193	1.1	0.06
192-191	0.7	0.04
158-154	0.8	0.04
154-150.5	6.4	0.34
150.5-145	26.0	1.37
145-140	5.8	0.31
140-124	28.4	1.50
124-103	48.6	2.56
90-57	44.0	2.32
57-54.5	18.6	0.98
54.5-52.5	3.4	0.18

* Total integral for chemical shift range δ 160-100 ppm = 116. Thus, the integral for one aromatic carbon = 116/6.12 = 18.95, assuming that spruce MWL contains 3 units of Ar-CH=CH-CHO and 3 units of Ar-CH=CH-CH_2OH substructures per 100 C_9-units.

** Type of carbons in each chemical shift range see Table 7.

TABLE 7.
^{13}C Chemical Shifts and Signal Assignments for Spruce Milled Wood Lignin (MWL). Solvent: DMSO-$\underline{d}_6$.

Signal Number	Chemical Shift (δ in ppm)	Intensity*	Assignment**
1	193.4	w	C=O in Ar-CH=CH-CHO C=O in Ar-CO-CH(-OAr)-C-
2	191.6	vw	C=O in Ar-CHO
3	169.4	w	Ester C=O in R'-O-CO-CH_3
4	166.2	vw	C=O in Ar-COOH Ester C=O in Ar-CO-OR
5	162.3	vw	Unknown
6	156.4	vw	C-4 in H-units
7	152.9	w	C-3/C-3' in etherified 5-5 units C-α in Ar-CH=CH-CHO units

Table 7 (continued)

Signal Number	Chemical Shift (δ in ppm)	Intensity*	Assignment**
8	152.1	w	C-3/C-5 in etherified S-units and B-ring of 4-*O*-5 units
9	151.3	w	C-4 in etherified G-units with α-C=O group
10	149.4	s	C-3 in etherified G-units
11	149.1	s	(β-*O*-4 type)
12	146.8	s	C-4 in etherified G-units
13	146.6	s	C-3 in non-etherified G-units (β-*O*-4 type)
14	145.8	m	C-4 in non-etherified G-units
15	145.0	m	C-4/C-4' of etherified 5-5 units
16	143.3	m	C-4 in ring B of β-5 units C-4/C-4' of non-etherified 5-5 units
17	138.0	w	unknown
18	134.6	w	C-1 in etherified G-units
19	132.4	w	C-5/C-5' in etherified 5-5 units
20	131.1	m	C-1 in non-etherified G-units
21	129.3	w	C-β in Ar-CH=CH-CHO
22	128.0	w	C-α and C-β in Ar-CH=CH-CH_2OH
23	125.9	w	C-5/C-5' in non-etherified 5-5 units
24	122.6	vw	C-1 and C-6 in Ar-CO-C-C units
25	119.9	m	C-6 in G-units
26	118.4	s	C-6 in G-units
27	115.1	s	C-5 in G-units
28	114.7	s	C-5 in G-units
29	111.2	s	C-2 in G-units
30	110.4	m	C-2 in G-units
31	86.6	vw	C-β in G type β-*O*-4 units(*threo*)
32	84.6	w	C-β in G type β-*O*-4 units(*erythro*)
33	83.8	m	C-β in G type β-*O*-4 units(*erythro*)
34	71.8	m	C-α in G type β-*O*-4 units(*erythro*)
35	71.2	m	C-α in G type β-*O*-4 units(*threo*) C-γ in G type β-β units
36	63.2	w	C-γ in G type β-*O*-4 units w/ α-C=O
37	62.8	w	C-γ in G type β-5, β-1 units
38	60.2	s	C-γ in G type β-*O*-4 units
39	55.6	vs	C in Ar-OCH_3
40	53.9	vw	C-β in β-β units
41	53.4	vw	C-β in β-5 units

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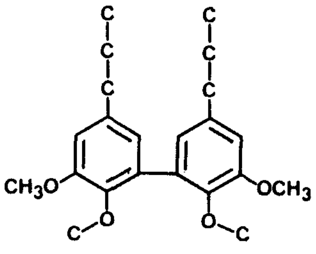
* vw=very weak; w=weak; m=moderate; s=strong; vs=very strong;

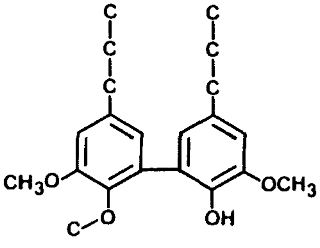
** H=*p*-Hydroxyphenylpropane; G=Guaiacylpropane; S=Syringylpropane

The signals in the chemical shift range δ 154-150.5 ppm integrate at about 0.34 carbons/phenyl group. The carbons giving rise to the signals in this region are those of the following classes: (a) C-3/C-3' of etherified biphenyl (5-5) substructures of the type VIII; (b) C-3/C-5 in ring B of diphenyl ether (4-O-5) substructures of the type XI; (c) C-4 of 4-O-alkylated, uncondensed guaiacyl groups with α-carbonyl; (d) C-3/C-5 of 4-O-alkylated, uncondensed syringylpropane units; and finally (e) C-α of Ar-CH=CH-CHO substructures. In general, spruce MWL contains about 3 units of 4-O-alkylated coniferyl aldehyde substructures, 3 units of 4-O-alkylated coniferyl alcohol substructures, 2 units of 4-O-5 substructures of the type XI, and 1 unit of 4-O-alkylated uncondensed syringylpropane substructure per 100 C_9-units.[15] Since the signal at δ 194 ppm integrates at about 0.06 carbons/phenyl ring, and consists of the -CHO of 4-O-alkylated coniferyl aldehyde groups and -C=O of 4-O-alkylated, uncondensed guaiacylpropane substructures with α-carbonyl group, the number of the latter can be estimated to be about 3 units per 100 C_9-units. In addition, the signal at δ 191 ppm is comprised of about 0.04 carbons/phenyl group, and corresponds to -CHO of 4-O-alkylated vanillin substructures. Thus, the total number of 4-O-alkylated, uncondensed guaiacyl groups with α-carbonyl is about 7 units per 100 C_9-units.

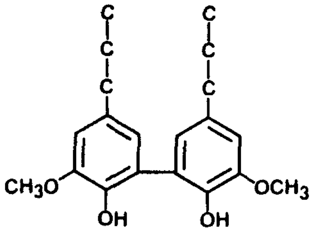
The number of carbons of the classes b, c, d, and e can then be estimated to be about 0.04, 0.07, 0.02 and 0.03/phenyl ring, respectively. The total number of the C-3/C-3' of etherified 5-5 substructures (class a) is therefore about 0.18/phenyl group, implying that about 18 guaiacylpropane units per 100 C_9-units are involved in 5-5 substructures of the type VIII. An inspection of the ^{13}C NMR spectrum of spruce MWL further reveals that 5-5 substructures of the type VIII are predominant over those of the types IX and X. This is evidenced by the presence of signals at δ 145-143 ppm and the absence of a signal at δ 141 ppm. The former corresponds to C-4/C-4' of VIII and C-4 in ring A of IX, while the



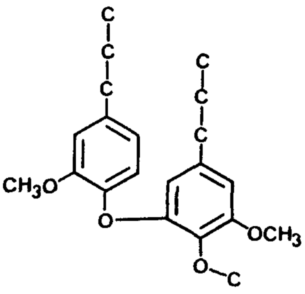
VIII



IX



X



XI

latter corresponds to C-4/C-4' of X and C-4' in ring B of IX. The C-4' in ring B of phenylcoumaran (β-5) substructures also gives rise to the signal at δ 143 ppm[13]. However, the signal at δ 53.4 ppm which corresponds to C-β of β-5 substructures[16] integrates at less than 0.05 carbons/phenyl group. In contrast, the chemical shift region δ 145.5-140 ppm is comprised of about 0.31 carbons/phenyl group. The carbons giving rise to the signals in this region include C-4/C-4' of both VIII and X, and C-4 of β-5 substructures. Thus, even considering the possible experimental error, the spruce MWL contains about 24-26 guaiacylpropane units/100 C_9-units involved in the 5-5 type substructures. Of these about 18-20 units are present as non-phenolic substructures of the type VIII. The remainder, about 6-8 units, are phenolic moieties in substructures of the types IX and/or X. The value of about 26 units/100 C_9-units for 5-5 type substructures in spruce MWL is slightly higher than that of about 22 units/100 C_9-units derived from the results of potassium permanganate oxidation by Erickson and coworkers[15].

CONCLUSION

The observed ^{13}C NMR spectral data show that the generalized SCS additivity rule for estimation of the ^{13}C NMR chemical shifts of aromatic carbons in β-O-4 and β-5 type lignin substructures can also be applied to 5-5 type substructures in lignin preparations, when the parent compounds used are 2,2'-dihydroxy-3,3'-dimethoxybiphenyl and their O-alkylated derivatives. The parent compound must be chosen according to the nature of the model compound or lignin substructure in the study. This allows chemical shifts of aromatic carbons in lignin compounds and lignin preparations to be predicted with reasonable accuracy. In addition, it has been estimated that about 24-26 units of guaiacylpropane units/100 C_9-units are involved in 5-5 type substructures in spruce MWL. Of these about 18-20 units are associated with etherified 5-5 substructures of the types VIII and IX, and the remainder with phenolic 5-5 substructures of the types IX and X.

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REFERENCES

1. H.-D. Ludemann and H. Nimz, Makromol. Chem. 175, 2393 (1974).

2. H.-D. Ludemann and H. Nimz, Makromol. Chem. 175, 2409 (1974).

3. C.-L. Chen, M.G.S. Chua, J. Evans, and H-m. Chang, Holzforschung, 36, 239 (1982).

4. K.P. Kringstad and R. Morck, Holzforschung, 37, 237 (1983).

5. C. Lapierre, B. Monties, E. Guittet, and J.Y. Lallemand, Holzforschung, 38, 333 (1984).

6. M. Bardet, M.-F. Foray, and D. Robert, Makromol. Chem. 186, 1495 (1985).

7. E. Adler, Wood Sci. Technol., 11, 169 (1977).

8. H.Y. Hassi, C.-L. Chen, and J.S. Gratzl, Proc. TAPPI 1984 Research and Development Conference, p. 249-260.

9. D.L. Robenstein and T.T. Nakashima, Anal. Chem., 51, 1465 (1979).

10. S.L. Patt and J.N. Shoolery, J. Magn. Reson., 46, 535 (1982).

11. D. Robert, Proc. Can. Wood Chem. Symp., 1982, p. 63.

12. M. Orchin and H.H. Jaffe, Symmetry, Orbitals, and Spectra, p. 91-136, Wiley-Interscience, New York, 1971.

13. H.Y. Hassi, M. Aoyama, D. Tai, C.-L. Chen, and J.S. Gratzl, J. Wood Chem. Technol. 7(4), 555 (1987).

14. D. Robert and C.-L. Chen, Holzforschung, 43, 325 (1989).

15. M. Erickson, S. Larsson, and G. Miksche, Acta Chem. Scand., 27, 903 (1973).

16. M. Bardet, D. Gagnaire, R. Nardin, D. Robert and M. Vincendon, Holzforschung, 40 Suppl., 17 (1986).