

Synthesis of New Trimeric Lignin Model Compounds Containing 5-5' and β -O-4' Substructures, and their Characterization by 1D and 2D NMR Techniques

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Os trímeros-modelo de lignina contendo as subestruturas bifenila (5-5') e aril-éter (β -O-4') foram sintetizados a partir dos derivados da desidrodivanilina e da α -bromo acetovanilona pela reação de Williamson. O estudo de RMN de ¹H e de ¹³C destes trímeros foi feito utilizando as técnicas homo e heteronucleares. A atribuição dos sinais de RMN de ¹H e de ¹³C e a conformação das moléculas são também discutidas neste artigo.

Trimeric lignin model compounds containing biphenyl (5-5') and β -aryl ether (β -O-4') were synthesized from dehydrodivanillin derivatives and α -bromo acetovanillone derivatives via Williamson's reaction. The ¹H and ¹³C NMR characteristics of the resulting trimers were studied using corresponding ¹H and ¹³C NMR spectra as well as homo- and heteronuclear 2D NMR techniques. The results are discussed in terms of signal assignment and conformation of the molecules.

Keywords: trimeric lignin model compounds, biphenyl substructure, β -aryl ether substructure, synthesis, 2D NMR spectroscopy

Introduction

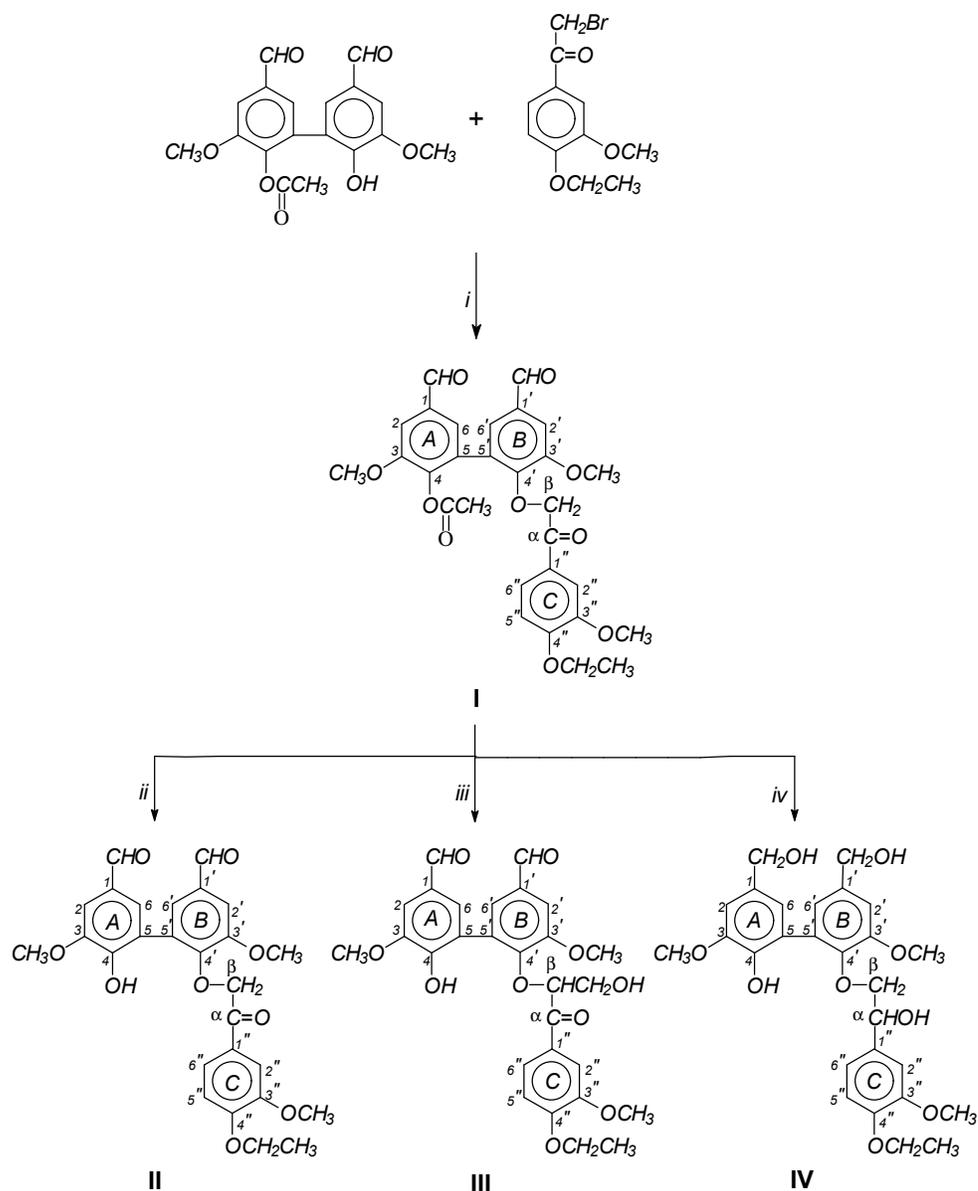
Lignin is an integral component of wood consisting approximately one-third of the woody material in vascular plants. In general, lignin is removed in wood based industries, particularly in pulping processes in the pulp and paper industry, as by-products, usually burned in the recovery furnace to produce energy for mill operation. However, there is an increasing interest in its structural study because of its potential utilization as chemical feedstock in the chemical industry^{1,2}.

In a previous study, Drumond *et al.*³ have shown that in milled wood lignin (MWL) from spruce wood, the frequency of 5-5' is approximately 24-26 units per 100 C₉-units (phenylpropane units)¹. These 5-5' units, consist mostly in the form of etherified 5-5' units, approximately 75% of the total and the remainder in the form of nonetherified units. Recently, Karhunen *et al.*⁴⁻⁶ showed that most of the etherified 5-5' units are present in the form of dibenzo-2H,3H-1,4-dioxocin structure containing α -O-4' and β -O-4' substructures. However, Ede and Kilpeläinen⁷ determined the amounts of α -O-4' substructures in a number of soft- and hardwood MWLs by 2D NMR using inverse detection techniques. They concluded that these MWLs contain a total α -O-4' unit of less than 0.3 units per 100 C₉-units^{1,8}.

The objectives of this series of investigation are, therefore three-fold: (a) to synthesize trimeric lignin model compounds, (b) to study ¹H and ¹³C NMR spectroscopic characteristics of this class of compounds, and finally (c) to compare these NMR spectroscopic characteristics to clarify the presence of these substructures in lignin.

In this work, we will report the synthesis and the NMR spectroscopic characteristics of new trimeric lignin model compounds containing both 5-5' and β -O-4' substructures^{1,3}. These compounds include 4-O-acetyl-4'-O-[α -(3-methoxy-4-ethoxyphenyl)- α -oxoethyl]dehydrodivanillin (**I**), 4'-O-[α -(3-methoxy-4-ethoxyphenyl)- α -oxoethyl] dehydrodivanillin (**II**), 4'-O-[α -(3-methoxy-4-ethoxyphenyl)- α -oxo- β -hydroxymethylethyl]dehydrodivanillin (**III**), 4'-O-[α -(3-methoxy-4-ethoxyphenyl)- α -hydroxyethyl] dehydrodivanillyl alcohol (**IV**) (Figure 1).

Compound **I** was prepared from 4-O-acetyldehydrodivanillin and α -bromo-3-methoxy-4-ethoxyacetophenone via Williamson's reaction. Compounds **II**, **III**, and **IV** were obtained from **I** by base-catalyzed hydrolysis, hydroxy-methylation with paraformaldehyde via aldol addition, and reduction, respectively. For the NMR studies DEPT, PENDANT, nOe difference, and 2D HMBC, ¹H/¹H-COSY and ¹H/¹³C-COSY techniques were used to obtain the ¹H and ¹³C NMR spectroscopic characteristics of the compounds.



i K_2CO_3 , acetone, reflux; *ii* piperidine, EtOH, reflux; *iii* para-formaldehyde, DMF; *iv* NaBH_4 , EtOH

Figure 1. Synthetic route for trimers **I** to **IV**.

Experimental

Melting points were determined on Mettler FT 80 melting point apparatus and are uncorrected. Elemental analysis were obtained on a Perkin Elmer 2400 apparatus. All NMR spectra were recorded on Bruker DRX 400 AVANCE spectrometer. Deuterated dimethyl-sulphoxide ($\text{DMSO}-d_6$) was used as solvent, and tetramethylsilane as internal reference. The pulse and acquisition conditions employed were: for ^1H - ^1H -COSY45 - dwell time (DW) 128.800 μs (F1), acquisition time (AQ) 0.132 s, number of transient (NS) 32, recycle delay (RD) 2.000 s, time domain (TD) 1024 (F1),

TD 128 (F2); for PENDANT⁹ - DW 15.700 μs , AQ 1.029 s, NS 10240, RD 1.000 s, power level for composite pulse decoupling (PL-CPD) 28 dB, 1/4JXH (D4) 1.850 ms, 1/8JXH (D7) 4.620 ms; for DEPT-135 - DW 15.700 μs , AQ 1.029 s, NS 2048, RD 1.500 s, delay for antiphase magnetization (D2) 3.571 ms; for nOe differential - DW 60.800 μs , AQ 3.985 s, NS 180, RD 2.000 s, TD 65.536, power level for nOe buildup (PL14) 80.00 dB; HMBC - 83.400 μs , AQ 0.342 s, NS 16, RD 2.000 s, delay for long range coupling (D6) 0.070 s, TD 4096 (F2) and 1024 (F1). 4-*O*-acetyldehydrodivanillin was prepared as described in the literature¹⁰, and so was α -bromo-3-methoxy-4-ethoxyacetophenone¹¹.

4-O-acetyl-4'-O-[α -(3-methoxy-4-ethoxyphenyl)- α -oxoethyl] dehydrodivanillin (I)

To a solution of α -bromo-3-methoxy-4-ethoxyacetophenone (0.19 g, 0.71 mmol) and 4-*O*-acetyldehydrodivanillin (0.29 g, 0.84 mmol) in 12 mL of dried acetone, anhydrous potassium carbonate (0.18 g, 1.3 mmol) was added. The mixture was refluxed under magnetic stirring for 1 hr. The insolubles were filtered off and the solvent was reduced under vacuum to give a residue that was dissolved in chloroform and washed with 0.5 mol L⁻¹ NaOH solution. The organic layer was dried over anhydrous Na₂SO₄, and the solvent was removed under reduced pressure. The product was precipitated by addition of tetrahydrofuran-hexane mixture to the resulting solution to give a yellow solid (0.28 g, 73%), mp. 75-78 °C. Anal. Calcd for C₂₉H₂₈O₁₀, C: 64.93, H: 5.22. Found: C: 64.80, H: 5.20. ¹H NMR [(400 MHz, DMSO-*d*₆) δ 1.36 (t, *J* 6.95 Hz, 3 H), 2.10 (s, 3 H), 3.92 (s, 3 H), 3.82 (s, 3 H), 3.79 (s, 3 H), 4.10 (q, *J* 6.95 Hz, 2 H), 5.34 (s, 2 H), 7.57 (d, *J* 1.65 Hz, 1 H), 7.60 (d, *J* 1.75 Hz, 1 H), 7.33 (d, *J* 1.93 Hz, 1 H), 6.97 (d, *J* 8.45 Hz, 1 H), 7.55 (d, *J* 1.65 Hz, 1 H), 7.38 (d, *J* 1.75 Hz, 1 H), 7.47 (dd, *J* 1.93 and 8.45 Hz, 1 H), 9.94 (s, 1 H), 9.92 (s, 1 H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 15.6, 21.0, 56.3, 57.0, 57.1, 64.8, 75.0, 111.1, 111.6, 113.3, 112.4, 123.3, 126.3, 126.6, 127.8, 130.0, 132.3, 132.9, 135.1, 143.0, 149.4, 150.0, 152.6, 153.4, 192.4, 192.7, 193.1.

4'-O-[α -(3-methoxy-4-ethoxyphenyl)- α -oxoethyl] dehydrodivanillin (II)

A mixture of **I** (0.076 g, 0.14 mmol), toluene (0.2 mL), piperidine (0.1 mL) and 95% EtOH (1 mL) was refluxed under magnetic stirring for 30 min. The mixture was neutralized with AcOH, and 5 mL H₂O was added to the solution. The resulting aqueous solution was extracted with CHCl₃. The organic layer was dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The product was precipitated by addition of petroleum ether to the resulting solution to give a yellow solid (0.039 g, 55%), mp. 133.6-136.8 °C. Anal. Calcd for C₂₇H₂₆O₉, C: 65.59, H: 5.26. Found: C: 65.39, H: 5.24. ¹H NMR [(400 MHz, DMSO-*d*₆) δ 1.34 (t, *J* 6.90 Hz, 3 H), 3.88 (s, 3 H), 3.82 (s, 3 H), 3.76 (s, 3 H), 4.10 (q, *J* 6.90 Hz, 2 H), 5.29 (s, 2 H), 7.39 (d, *J* 1.88 Hz, 1 H), 7.54 (d, *J* 1.92 Hz, 1 H), 7.30 (d, *J* 1.99 Hz, 1 H), 6.95 (d, *J* 8.28 Hz, 1 H), 7.36 (d, *J* 1.88 Hz, 1 H), 7.45 (d, *J* 1.92 Hz, 1 H), 7.44 (dd, *J* 1.99 and 8.28 Hz, 1 H), 9.74 (s, 1 H), 9.92 (s, 1 H), 9.98 (1H, exchange with D₂O). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 14.5, 55.4, 55.9, 56.0, 63.9, 74.2, 109.2, 110.1, 111.3, 111.4, 122.5, 124.4, 125.4, 126.6, 127.8, 128.0, 131.0, 131.6, 147.7, 148.0, 148.5, 150.2, 150.3, 152.5, 191.0, 191.7, 192.4.

4'-O-[α -(3-methoxy-4-ethoxyphenyl)- α -oxo- β -hydroxymethylethyl] dehydrodivanillin (III)

A solution of **I** (0.10 g, 0.18 mmol), paraformaldehyde (0.026 g, 0.3 mmol) and NaOH (0.0076 g) in 5.5 mL of DMF was stirred on an oil bath at 60 °C under a N₂ atmosphere for 12 h. The reaction mixture was then poured into 10 mL of ice-cooled water. The precipitate was filtered off, and the aqueous layer was extracted with CHCl₃, and the solvent was removed under reduced pressure. The product was precipitated by addition of ice-cooled water into the resulting solution to give a beige solid (0.010g, 10%), mp. 91-94 °C. Anal. Calcd for C₂₈H₂₈O₁₀, C: 64.12, H: 5.34. Found: C: 63.91, H: 5.33. ¹H NMR [(400 MHz, DMSO-*d*₆) δ 1.36 (t, *J* 7.00 Hz, 3 H), 3.88 (s, 3 H), 3.61 (s, 3 H), 3.75 (s, 3 H), 4.10 (q, *J* 7.00 Hz, 2 H), 4.81 (d, *J* 5.80 Hz, 2 H), 4.87 (s, 1 H, exchange with D₂O), 5.54 (t, *J* 5.80 Hz, 2 H), 7.43 (d, *J* 2.00 Hz, 1 H), 7.46 (d, *J* 2.00 Hz, 1 H), 7.58 (d, *J* 1.90 Hz, 1 H), 7.30 (d, *J* 1.80 Hz, 1 H), 6.97 (d, *J* 8.20 Hz, 1 H), 7.33 (d, *J* 1.90 Hz, 1 H), 7.50 (dd, *J* 1.80 and 8.20 Hz, 1 H), 9.73 (s, 1 H), 9.89 (s, 1 H), 9.96 (1H, exchange with D₂O). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 15.6, 21.0, 56.3, 57.0, 57.1, 64.8, 75.0, 109.2, 110.1, 111.3, 123.2, 124.0, 127.0, 127.6, 127.8, 128.6, 130.3, 131.0, 140.8, 148.3, 150.1, 150.2, 151.4, 152.3, 192.4, 192.7, 193.1.

4'-O-[α -(3-methoxy-4-ethoxyphenyl)- α -hydroxyethyl] dehydrodivanillyl alcohol (IV)

To a solution of **I** (0.10g, 0.18 mmol) in 2 mL CHCl₃ and 3 mL 95% EtOH, NaBH₄ (0.051 g, 1.35 mmol) was added. The solution was stirred at room temp. for 24 h. The reaction mixture was then acidified and extracted with CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄, and the solvent was removed under reduced pressure. The product was precipitated by addition of hexane to the resulting mixture to give a beige solid (0.047 g, 51%, mp. 70-74.1 °C). Anal. Calcd for C₂₇H₃₂O₉, C: 64.80, H: 6.40. Found: C: 64.59, H: 6.42. ¹H NMR [(400 MHz, DMSO-*d*₆) δ 1.26 (t, *J* 7.00 Hz, 3 H), 3.81 (s, 3 H), 3.82 (s, 3 H), 3.68 (s, 3 H), 3.89-3.95 (m, 4 H), 4.38-4.43 (m, 3 H), 4.90-5.30 (m, 3 H, exchange with D₂O), 6.64-7.74 (m, 7 H), 9.60 (1H, exchange with D₂O). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 14.7, 55.3, 55.7, 55.8, 62.6, 62.7, 63.7, 71.3, 78.0, 109.4, 110.1, 110.3, 113.1, 118.6, 121.0, 121.1, 125.5, 132.2, 132.5, 134.8, 137.3, 142.4, 144.5, 146.9, 147.5, 149.0, 151.8.

Results and Discussion

The chemical shift assignments and coupling constants for **I** and **II** (Table 1) were deduced from 1D NMR spectra,

Table 1. ^1H Chemical Shifts (δ) of trimers **I** and **II**

Trimer		I		II		
Group	δ	Multip.	J (Hz)	δ	Multip.	J (Hz)
OCH_2CH_3	1.36	t	6.95	1.34	t	6.90
CH_3COO	2.10	s				
OCH_3 - A	3.92	s		3.88	s	
OCH_3 - B	3.82	s		3.82	s	
OCH_3 - C	3.79	s		3.76	s	
OCH_2CH_3	4.10	q	6.95	4.10	q	6.90
OCH_2CO	5.34	s		5.29	s	
H-2 - A	7.57	d	1.65	7.39	d	1.88
H-2 - B	7.60	d	1.75	7.54	d	1.92
H-2 - C	7.33	d	1.93	7.30	d	1.99
H-5 - C	6.97	d	8.45	6.95	d	8.28
H-6 - A	7.55	d	1.65	7.36	d	1.88
H-6 - B	7.38	d	1.75	7.45	d	1.92
H-6 - C	7.47	dd	1.93 and 8.45	7.44	dd	1.99 and 8.28
CHO -A	9.94	s		9.74	s	
CHO -B	9.92	s		9.92	s	

Multip.= Multiplicities (400 MHz, $\text{DMSO}-d_6$)

Table 2. H/C correlations ($^3J_{\text{CH}}$) for model compound **I** using HMBC technique

δ ^1H	H	Ring	C ($\delta^{13}\text{C}$)
9.94	CHO	A	C-2 (111.6) and C-6 (126.6)
7.57	H-2	A	C-4 (143.0), C-6 (126.6) and CHO (192.7)
7.55	H-6	A	C-2 (111.6) and C-4 (143.0)
9.92	CHO	B	C-2 (113.3) and C-6 (126.3)
7.60	H-2	B	C-6 (126.3), C-4 (152.6) and CHO (192.4)
7.38	H-6	B	C-2 (113.3), C-4 (152.6) and CHO (192.4)
7.33	H-2	C	C-4 (153.4), C-6 (123.3) and CO (193.1)
6.97	H-5	C	C-3 (149.5) and C-1 (130.0)
7.47	H-6	C	C-2 (111.1) and C-4 (153.4)
5.34	CH_2 - β	B/C	C-4/B (152.6) and C-1/C (130.0)

and confirmed by $^1\text{H}/^1\text{H}$ -COSY, HMBC and nOe difference spectra. For example, for compound **I**: the ^1H resonances at δ 7.33 (doublet, J 1.93Hz), 6.97 (doublet, J 8.45Hz) and 7.47 (double doublet J 1.93 and 8.45 Hz) indicate the three spin system of ring C and were confirmed by HMBC technique (Table 2) and nOe difference spectra (Table 3).

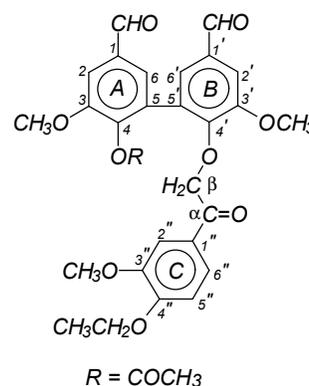
The HMBC data confirmed the aromatic and formyl hydrogen chemical shifts for rings A and B. Hence, Table 2 data show that methylene at δ 5.34 (β to B and C) as well as both H-2 at δ 7.60 and H-6 at δ 7.38 are correlated with C-4 at δ 152.6. These correlations confirm ring B hydrogen assignments. H-2 at δ 7.60 also correlates with formyl carbon at δ 192.4 and C-6 at δ 126.3. Once the hydrogen chemical shifts for rings B and C were assigned, the remaining ones were attributed to ring A. Finally, H-2 at δ 7.57 shows correlation with formyl group of ring A at δ 192.7.

The nOe difference spectra are useful in establishing molecular conformation and steric arrangement of substituents. Therefore, spectra obtained by using these techniques were used to verify the conformation of **I** (Table 3).

Table 3. Interpretation of nOe difference spectra* of trimer **I**

δ Irradiation (H/Ring)	δ Observed Nuclear Overhauser Enhancements (H/Ring)
9.92 (CHO/B)	7.38 and 7.60 (H-6 and H-2/B)
7.38 (H-6/B)	9.92 (CHO)
9.94 (CHO/A)	7.55 and 7.57 (H-6 and H-2/A)
3.92 (OCH_3 /A)	7.57 (H-2/A)
7.33 (H-2/C)	3.79 (OCH_3 /C) and 5.34 (OCH_2CO)
4.10 (CH_2CH_3)	6.97 (H-5/C) and 1.36 (CH_2CH_3)
3.82 (OCH_3 /B)	7.60 (H-2/B)
5.34 (OCH_2CO)	7.33 (H-2/C) and 7.47 (H-6/C)

*at 400 MHz in $\text{DMSO}-d_6$



Irradiation of OCH_2CO hydrogens at δ 5.34 enhances the signals of H-2'' at δ 7.33 and H-6'' at δ 7.47, both aromatic hydrogens in the ring C of compound **I**, while the intensity of the signal at δ 3.82, corresponding to hydrogens of methoxy group in ring B, was not affected. This last observation shows that the C_4 -O bond is not free to rotate. On the other hand, irradiation of the methoxyl group resonance at δ 3.82 only enhances the signal at δ 7.60 corresponding to H-2' of ring B.

These results show that the 3-methoxy-4-ethoxyphenacyl group is *syn* to ring A and also that ring C is rotating about C_α-C₁, bond. In addition, the analysis of nOe difference spectra has allowed to assign unambiguously the chemical shifts of hydrogens and methoxy groups of each aromatic ring (Table 3).

From broadband decoupled ¹³C NMR and DEPT spectra of compound **I**, the signals for aliphatic carbons at δ 15.6 (OCH₂CH₃), 21.0 (CH₃COO), 56.3, 57.0 and 57.1 (OCH₃), 64.8 (OCH₂CH₃), 75.0 (CH₂-β), 192.4 and 192.7 (CHO), and 193.1 (CO) were assigned.

In ¹³C NMR spectrum of trimer **II**, obtained by PENDANT pulse sequence⁹ methyl carbons (CH₃ and OCH₃), aromatic CH and CHO show normally phase positive signals while secondary (>CH₂) and quaternary (>C<) carbons show phase inverted signals. On the basis of these results and the signal assignments of **I**, signals for aliphatic carbons were assigned at δ 14.5 (CH₃), 55.4, 55.9, and 56.0 (OCH₃), 63.9 (OCH₂), 74.2 (CH₂-β), 191.0 and 191.7 (CHO), and 192.4 (CO).

By combining the data obtained from ¹³C NMR, DEPT, and PENDANT spectra with those of 2D ¹H/¹³C - COSY contour plot it was possible to assign the aromatic hydrogenated carbons for each A, B, and C rings of trimers **I** and **II**. ¹H/¹³C - COSY data are summarized in Table 4.

¹H NMR spectra of trimers **III** and **IV** were analyzed using the ¹H NMR spectra of both compounds **I** and **II** as a reference. This leads to assignments of hydrogens in trimers **III** and **IV**. The results are summarized in Table 5.

In addition, the presence of a hydroxymethyl group in trimer **III** was verified by comparing chemical shifts of trimer **II** (Table 1) with those of trimer **III** (Table 5). This group was characterized by signals at δ 4.87 (CH₂OH) and δ 4.81 (CH₂OH). As for trimers **I** and **II**, the ¹³C chemical shift assignments for compounds **III** and **IV** were deduced from ¹³C NMR spectra with help of the corresponding DEPT spectra and ¹H/¹³C - COSY.

The ¹³C spectrum of trimer **III** exhibited signals for aliphatic carbons at δ 14.6 (CH₃CH₂), 55.3, 55.7, and 55.9 (OCH₃), 64.0 (CH₃CH₂O), 62.5 (OCHCH₂OH), 83.8

Table 4. Heteronuclear correlation (¹H/¹³C-COSY)* for trimers **I** and **II**

Trimer	Ring	C-2 / H-2	C-5 / H-5	C-6 / H-6	CHO
I	A	111.6 / 7.57		126.6 / 7.55	192.7 / 9.94
	B	113.3 / 7.60		126.3 / 7.38	192.3 / 9.92
	C	111.1 / 7.33	112.4 / 6.97	123.3 / 7.47	
II	A	109.2 / 7.39		128.0 / 7.36	191.0 / 9.74
	B	111.3 / 7.54		126.6 / 7.45	191.7 / 9.92
	C	110.1 / 7.30	111.4 / 6.95	122.5 / 7.44	

*at 100 MHz and DMSO-d₆

Table 5. ¹H Chemical Shifts (δ) of trimers **III** and **IV**

Trimer	III			IV			
	Group	δ	Multip.	J (Hz)	δ	Multip.	J (Hz)
	OCH ₂ CH ₃	1.36	t	7.0	1.26	t	7.0
	OCH ₃ -A	3.88	s		3.81	s	
	OCH ₃ -B	3.61	s		3.82	s	
	OCH ₃ -C	3.75	s		3.68	s	
	OCH ₂ CH ₃	4.10	q	7.0	3.89-3.95	m	
	OCH ₂ CHOH				3.89-3.95	m	
	OCH ₂ CHOH				4.38-4.43	m	
	CHCH ₂ OH	4.81	d	5.8		s	
	CHCH ₂ OH	4.87	s				
	CHCH ₂ OH	5.54	t	5.8			
	H-2 - A	7.43/7.46	d	2.0			
	H-2 - B	7.58	d	1.9			
	H-2 - C	7.30	d	1.8			
	H-5 - C	6.97	d	8.2			
	H-6 - A	7.43/7.46	d	2.0			
	H-6 - B	7.33	d	1.9			
	H-6 - C	7.50	dd	1.8 and 8.2			
	CHO-A	9.73	s				
	CHO-B	9.89	s				
	ArCH ₂ OH				4.38-4.43	m	
	OH				4.90-5.30	m	
	ArH				6.64-7.74	m	

Multip.= Multiplicities (400 MHz, DMSO-d₆)

(OCHCH₂OH), 191.0 and 191.7 (CHO), and 194.1 (CO). The ¹³C spectrum of trimer **IV** presented signals for aliphatic carbons at δ14.7 (CH₃CH₂O), 55.3, 55.7 and 55.8 (OCH₃), 62.6 and 62.7 (CH₂OH), 63.7 (CH₃CH₂O), 71.3 (OCH₂CHOH), and 78.0 (OCH₂CHOH).

Table 6 summarizes the ¹³C NMR chemical shifts of aromatic carbons in trimers **I** to **IV**. The chemical shifts of aromatic carbons for compound **III** were assigned by comparison with those of compound **II**, while those of aromatic carbons in trimer **IV** were determined by comparison with model compounds **1** and **2** (Figure 2)^{10,11}. The chemical shift assignments for compound **IV** were also deduced from the ¹³C NMR spectrum with help of the corresponding DEPT spectra.

Table 7 shows the ¹³C NMR chemical shifts for these three compounds. From these data it may be verified that aromatic carbons of rings A and B of trimer **IV** as well as those of parent compound **1** present very close chemical shifts. Similarly, the chemical shifts assigned to aromatic carbons of ring C are closely related to those of compound **2**.

Conclusions

Trimeric lignin model compounds containing 5-5' and β-O-4' substructures were synthesized, successfully, by way of acetyldehydrodivanillin and α-bromo-3-methoxy-4-ethoxyacetophenone. This paves the way for the synthesis of oligomeric lignin model compounds containing

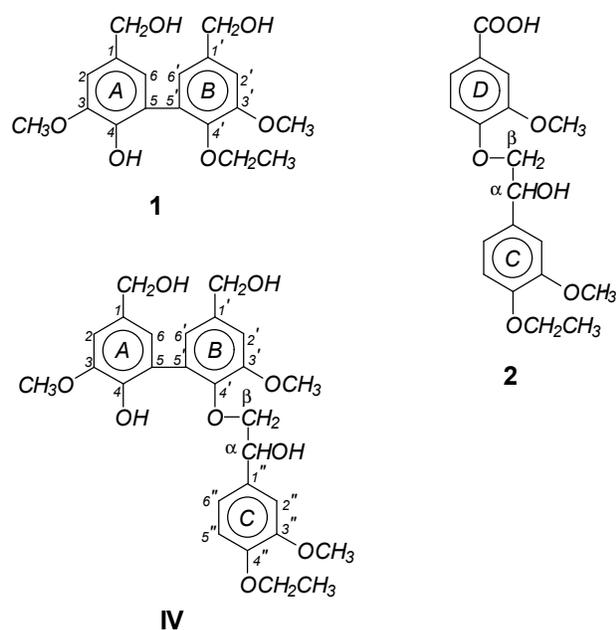


Figure 2. Model compounds related to **IV**.

biphenyl (5-5') and β-aryl ether (β-O-4') substructures through Williamson's reaction.

The chemical shifts and coupling constants for **I** and **II** were deduced from 1D NMR spectra, and confirmed by HMBC, ¹H/¹H-COSY and nOe difference spectra.

This last one was useful in establishing the conformation of 4-O-acetyl-4'-O-[α-(3-methoxy-4-ethoxyphenyl)-

Table 6. ¹³C chemical shifts (δ) for aromatic carbons of trimers **I** - **IV**

Trimers	ring	C-1	C-2	C-3	C-4	C-5	C-6
I	A	135.1	111.6	152.6	143.0	132.3	126.6
	B	132.9	113.3	150.0	152.6	127.8	126.3
	C	130.0	111.1	149.4	153.4	112.4	123.3
II	A	127.8	109.2	147.7	148.0	124.4	128.0
	B	131.6*	111.3	150.2	150.3	125.4	126.6
	C	131.0*	110.1	148.5	152.5	111.4	122.5
III	A	127.8	109.2	140.8	148.3	124.0	128.6
	B	131.0	111.3	150.2	151.4	127.6	127.0
	C	130.3	110.1	150.1	152.3	111.3	123.2
IV	A	132.2	109.4	146.9	142.4	125.5	121.0
	B	137.3	110.1	151.8	144.5	132.5	121.1
	C	134.8	110.3	149.0	147.5	113.1	118.6

100MHz, DMSO-*d*₆, *these values may be exchangeable.

Table 7. ¹³C NMR chemical shifts (δ) of trimer **IV** and dimers **1**¹⁰ and **2**¹¹

Compound	Ring	C-1	C-2	C-3	C-4	C-5	C-6
IV	A	132.2	109.4	146.9	142.4	125.5	121.0
1	A	132.4	109.6	147.3	142.5	125.7	121.2
IV	B	137.3	110.1	151.8	144.5	132.5	121.0
1	B	137.3	110.2	152.5	144.4	133.0	121.2
IV	C	134.8	110.3	148.5	147.5	112.6	118.2
2	C	135.1	110.9	149.0	147.5	113.1	118.6

100MHz, DMSO-*d*₆

α -oxoethyl]dehydrodivanillin (**I**). The results obtained show that the 3-methoxy-4-ethoxyphenacyl group is *syn* to ring A and also that ring C is rotating about C $_{\alpha}$ -C $_1$ bond with no restriction. In addition, the analysis of nOe difference spectra has allowed to assign unambiguously the chemical shifts of hydrogens and methoxyl groups of each aromatic ring.

^1H NMR spectra of trimers **III** and **IV** were analyzed using the ^1H NMR spectra of both compounds **I** and **II** as a reference. As for trimers **I** and **II**, the ^{13}C chemical shift assignments for compounds **III** and **IV** were deduced from ^{13}C NMR spectra with help of the corresponding DEPT, $^1\text{H}/^{13}\text{C}$ COSY and HMBC spectra. While the chemical shifts of aromatic carbons for compound **III** were assigned by comparison with those of compound **II**, those of aromatic carbons in trimer **IV** were determined by comparison with dimeric model compounds.

From the 1D and 2D ^1H , ^{13}C -NMR spectroscopic studies of trimers **I-IV**, it is evident that the acetoxy group in trimer **I** undergoes base-catalyzed hydrolysis to give trimer **II** (Table 6). The later compound has a hydroxyl group at C-4 of ring A. This resulted in shielding ($\Delta\delta$ - 2.9 to $\Delta\delta$ - 7.9) of C-1, C-2, C-3 and C-5 and deshielding of $\Delta\delta$ + 5.0 and $\Delta\delta$ + 1.4 for C-4 and C-6 in ring A, respectively. For ring B, all aromatic carbons are shielded ($\Delta\delta$ - 0.2 to 2.4). For ring C, C-1, C-2, C-4, and C-5 are shielded ($\Delta\delta$ - 0.9 to $\Delta\delta$ - 1.0).

Furthermore, chemical structures of trimers **II** and **IV**, differ in the substituents at C-1 of rings A/B and at C- α of side chain in ring C. As compared to trimer **II**, C-4 and C-6 of ring A of trimer **IV** are shielded by $\Delta\delta$ - 5.6 to - 7.0, while C-1 and C-5 are deshielded by $\Delta\delta$ + 4.4 and + 1.1, respectively. For ring B of **IV**, C-2 and C-4 are shielded by $\Delta\delta$ - 1.2 and - 5.8, respectively, in addition to deshielding

of C-1, C-3 and C-5 ($\Delta\delta$ + 1.6-5.7). For ring C of **IV**, C-4 and C-6 undergo shielding of $\Delta\delta$ - 5.0 and - 3.9, respectively, and C-1 deshielding of $\Delta\delta$ + 3.8.

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