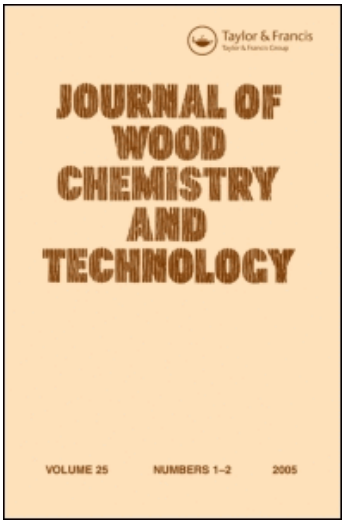

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THE MODIFICATION OF LIGNIN AT POSITIONS 2 AND 6 OF THE PHENYLPROPANOID NUCLEII - PART II[1]: HYDROXYMETHYLATION OF LIGNIN MODEL COMPOUNDS

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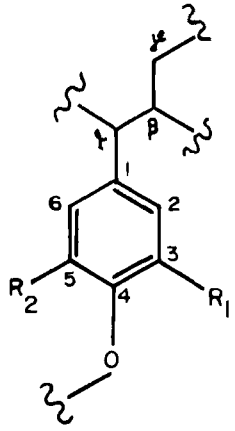
ABSTRACT

Phenolic hardwood and softwood lignin model compounds were hydroxymethylated with formaldehyde at positions *meta* to the aromatic hydroxy group. O-alkylated phenolic model compounds were hydroxymethylated at the same relative positions. The introduction of the reactive hydroxymethyl groups in high yield has tremendous potential for the utilization of lignin in polymeric products.

INTRODUCTION

Lignin is produced in large quantities as an under-utilized waste material during the chemical pulping of wood or other plant material. The utilization of this renewable material consequently received widespread attention as is attested by the extensive literature on the subject[2,3]. However, only limited success has been achieved. This may be largely attributed to the low number of reactive sites on the degraded waste lignin which limits its application particularly in polymeric applications.

Industrial by-product lignin is usually condensed extensively[4,5]. The lignin therefore does not have a high number of unsubstituted 3- and 5-positions on phenolic phenyl propanoid units (Fig. 1). This clearly prevents the utilization of lignin in applications requiring alkali catalysed electrophilic substitution reactions on the aromatic ring. Industrial by-product lignosulphonates and alkali lignin is therefore unsuitable for the preparation of phenol formaldehyde adhesives with the exception of one documented case[6]. The only positions on the lignin phenyl propanoid units available in large proportions are the 2- and 6-positions. These positions are almost always unsubstituted in natural and alkali



R_1, R_2 = H / OCH_3 / -≀

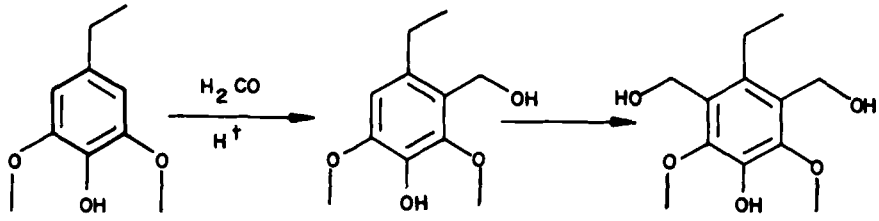
≀ = possible linkage to other phenylpropanoid units

FIGURE 1: PHENYLPROPANOID BUILDING BLOCKS OF LIGNIN

lignin[4]. In the first part of this series, these positions which are *meta* to the aromatic hydroxy group were used for the crosslinking of lignin model compounds with formaldehyde in acidic medium[1]. In this paper, the introduction of the reactive hydroxymethyl group to these *'meta'* positions is described.

DISCUSSION

The hardwood model compound 4-hydroxy-3,5-dimethoxyphenyl ethane (**1**) was used for the initial hydroxymethylation reactions. This compound (**1**) was preferred to a softwood (guaiacylic) model compound owing to its symmetry and the absence of any vacant positions *ortho* and *para* to the aromatic hydroxy group.



1 2

The hydroxymethylation of 1 was first attempted by using a 20 molar excess formaldehyde in 1,1 N HCl in 50 % aqueous dioxane. Since 1 has two reactive sites (2 and 6) this means a ten-fold excess of formaldehyde per reactive site. Samples were taken at different intervals, neutralized, extracted and acetylated for ^{1}H-NMR analyses. The ratio of the integrals of the aliphatic (δ 2,0 - 2,2) and the aromatic (δ 2,3 - 2,5) acetoxy groups of the proton NMR spectra, were taken as the yields of hydroxymethylation. The degree of dimer formation via a methylene linkage (crosslinking) (Fig. 2) was estimated by the coefficient of the integrals of the proton NMR spectra of methoxy groups situated adjacent to the newly formed bond - of which the resonances are shifted upfield[1] (δ 3,4 - 3,7) - and that of the total methoxy resonances (δ 3,4 - 4,0).

The large excess of formaldehyde resulted in the hydroxymethylation of 1 in yields of about 50 % mono-hydroxymethylation. This yield was obtained within fifteen minutes and remained constant for over six hours. The number of unsubstituted aromatic positions decreased from 0,6/model compound after 15 minutes to 0,2 after one hour reaction time. However, after only 15 minutes about one methylene linkage per model compound occurred indicating substantial methylene linkage formation.

Previously it was shown that the 2,6-methylene linkage between two model compounds can be cleaved by protonolysis in acidic aqueous dioxane solvents[1]. If such cleavages can be followed up by additional hydroxymethylation, the equilibrium of the reaction may be shifted towards high yields of hydroxymethylation (Fig. 2).

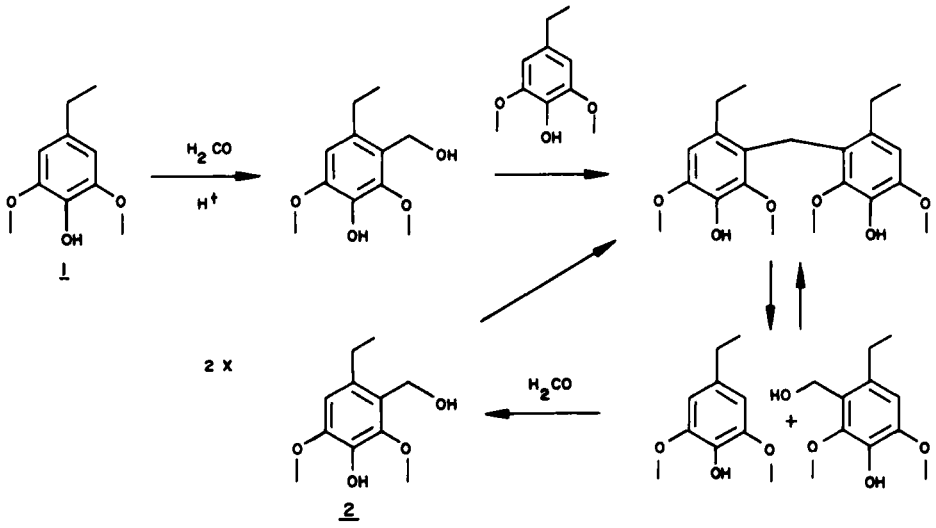


FIG. 2. PROPOSED APPROACH FOR THE META-HYDROXYMETHYLATION OF THE LIGNIN MODEL COMPOUND (1). (MONO-SUBSTITUTION IS USED FOR SIMPLICITY)

TABLE 1

Reaction of **1** with an excess of formaldehyde in 1,1 N HCl in 50 % aqueous dioxane at reflux

ENTRY	mole H_2CO/ mole **1**	REACTION TIME (h)	YIELD (mole/mole **1**) (NMR)		
			META-HYDROXYMETHYL(a) GROUPS	ARYLMETHYL SUBSTITUENTS (b)	AROMATIC PROTONS(c)
1	20:1	0,25	0,49	0,9	0,6
2	20:1	0,5	0,53	1,1	0,4
3	20:1	1	0,50	1,3	0,2
4	20:1	2	0,47	1,3	0
5	20:1	4	0,53	1,3	0
6	20:1	8	0,58	1,3	0
7	20:1	20	0,60	1,2	0
8	2:1	20	0,05	1,2	0,6

(a) = ROAc / ArOAc

(b) = OCH_3 (δ 3,4 - 3,7) /[OCH_3 (δ 3,4 - 4,0)/2]

(c) = ArH / [OCH_3/6]

TABLE 2

Reaction of **1** with formaldehyde for 4 hours in sealed glass tubes

ENTRY	REACTION TEMPERATURE (°C)	ACID CONCENTRATION (mole/ℓ)	SOLVENT	MOLE H_2CO/ MOLE **1**	YIELD (mole/mole **1**) (NMR)		
					META-HYDROXYMETHYL GROUPS	ARYLMETHYL SUBSTITUENTS	AROMATIC PROTONS
1	150	1,1	50 % aq. Dioxane	20 : 1	a	-	-
2	"	0,2	"	20 : 1	a	-	-
3	"	1,1	"	2 : 1	0	-	-
4	"	1,1	H_2O	20 : 1	0,24	1,5	0,2
5	"	0,2	H_2O	"	0,12	1,2	0,5
6	100	1,1	50 % aq. Dioxane	"	0,46	1,5	0
7	"	0,2	"	"	0,19	1,4	0,2
8	"	1,1	H_2O	"	0,09	$\pm$2	0
9	"	0,2	H_2O	"	0,05	$\pm$2	0

a = Products obscured by by-products resulting from dioxane

TABLE 3

Reaction of **1** with excess formaldehyde (20 mole/mole **1**) in 1,1 N HCl in 50 % aqueous dioxane for 4 hours

ENTRY	TEMPERATURE (°C)	YIELD (mole/mole **1**) (NMR)	
		META-HYDROXYMETHYL GROUPS	ARYLMETHYL SUBSTITUENTS
1	105	0,61	1,2
2		0,50	1,3
3	70	0,70	1,2
4	50	0,76	1,3
5	25 (14 days)	0,58	-

The syringyl model **1** was subsequently reacted with excess formaldehyde at higher temperatures. The acid concentration and solvent composition was also varied. None of these variations (Table 2), however, resulted in an increase in hydroxymethylation yield.

The reactions were subsequently repeated at lower temperatures using an acid concentration of 1,1 N and 50 % aqueous dioxane as solvent. The results listed in Table 3 show no significant increase in hydroxy-

methylation versus methylene linkage formation at lower temperatures indicating that the equilibrium of the reaction (Fig. 2) is not affected by temperature or acid concentration.

For the *meta* hydroxymethylation of lignin for its use in polymeric applications, the yields of 0,5 to 0,7 mono-hydroxymethyl groups obtained for the model compound **1** can be considered acceptable. Furthermore higher hydroxymethylation yields can be expected for lignin since methylene linkage formation should be decreased by steric effects created by the sterically more demanding lignin substituents at position 1 in comparison with **1**. The process would nevertheless be much more attractive from an industrial point of view if the reagent requirements could be decreased.

The hydroxymethylation of **1** was subsequently attempted via varying solvent composition. Model compound **1** was reacted for one hour with excess formaldehyde in 10 % aqueous dioxane containing 5 % concentrated hydrochloric acid (Table 4, entry 1). Under these conditions crosslinking was almost completely eliminated. Longer reaction times of up to 48 hours did not result in the formation of any more methylene linkages. At the same time, mono-hydroxymethylation of **1** occurred in high yield.

Various other solvent combinations were subsequently used in order to find a more suitable industrial solvent. At the same time a smaller excess of formaldehyde of 4 moles per 1 mole **1** was employed. In 31 or 40 % aqueous dioxane containing 1 N hydrochloric acid, mono-hydroxymethylation occurred quantitatively whilst 20 % methylene linkage formation occurred (Table 4, entries 6 and 7). An increase in acid concentration (entries 8 and 9), however, decreased hydroxymethylation in preference to methylene linkage formation.

In 23 % aqueous dioxane (1 N HCl), mono-hydroxymethylation of **1** was achieved in high yield, even when it was reacted with an equimolar quantity of formaldehyde. Methylene linkage formation was, however, still in the region of 20 % (Table 4, entries 10 to 12).

The small quantity of formaldehyde required (Table 4) is clearly more attractive when compared with the large excess required previously (Table 3). Although it would be preferable to carry out the hydroxymethylation of lignin in water in order to eliminate costly organic solvents, this problem

TABLE 4

Reaction of 1 with formaldehyde at 80 °C

ENTRY	MOLES 1/ MOLE PARAFORMALDEHYDE	SOLVENT (% aqueous dioxane)	ACID CONCENTRATION (mole/ℓ)	TIME (h)	YIELD (mole/mole 1) (NMR)	
					META-HYDROXY-METHYL GROUPS	ARYLMETHYL SUBSTITUENTS
1	1 : 20	10	0,4	1	0,74	0,06
2	1 : 20	10	0,4	4	0,98	0,00
3	1 : 20	10	0,4	8	1,02	0,00
4	1 : 20	10	0,4	48	0,98	0,00
5	1 : 4	23	1,0	6	1,05	0,20
6	1 : 4	31	1,0	6	0,93	0,16
7	1 : 4	40	1,0	6	1,10	0,22
8	1 : 4	31	1,8	6	0,31	0,36
9	1 : 4	40	2,7	6	0,00	0,40
10	1 : 2	23	1,0	6	1,03	0,19
11	1 : 1	23	1,0	6	0,68	0,20
12	1 : 0,7	23	1,0	6	0,52	0,18
13	1 : 4	23[a]	1,0	6	0,32	0,26
14	1 : 4	23[b]	1,0	6	0,00	0,00
15	1 : 4	23[c]	1,0	6	0,00	0,00

a = 23 % aqueous acetone, temperature 50 °C

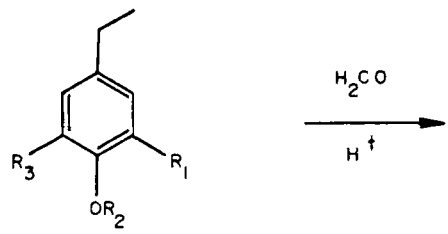
b = 23 % aqueous methanol, temperature 50 °C

c = 23 % aqueous ethylacetate, temperature 50 °C

is not insurmountable since organic solvent recovery by evaporation and condensation is frequently practised in phenol formaldehyde resin preparation procedures[7].

Various other solvents were also evaluated. These included acetone, methanol and ethylacetate. Methanol resulted in no reaction. This is probably due to a decrease in the reactivity of the formaldehyde due to acetylisation. The reaction done in ethyl acetate resulted in almost quantitative recovery of starting material. The reaction done in acetone resulted in a 32 % hydroxymethylation of 1. Crosslinking was, however, not excluded and resulted in the linkage of 26 % of the model compounds.

The conditions used for the hydroxymethylation of the hardwood model 1 was subsequently used to hydroxymethylate other model compounds. These were 4-hydroxy-3-methoxyphenyl ethane (**3**), 3,4-dimethoxyphenyl ethane (**4**)



3 $R_1 = OCH_3$, $R_2 = R_3 = H$
4 $R_1 = OCH_3$, $R_2 = CH_3$, $R_3 = H$
5 $R_1 = R_3 = OCH_3$, $R_2 = CH_3$

6 $R_1 = OCH_3$, $R_2 = R_3 = H$
7 $R_1 = OCH_3$, $R_2 = CH_3$, $R_3 = H$
8 $R_1 = R_3 = OCH_3$, $R_2 = CH_3$

FIGURE 3: MODEL COMPOUNDS USED IN THE INVESTIGATION

and 3,4,5-trimethoxyphenyl ethane (**5**). These model compounds simulate respectively phenolic softwood lignin fragments or etherified softwood and hardwood lignin fragments (Fig. 3).

The phenolic softwood model compound **3** was reacted with formaldehyde (4 moles/mole **3**) in 23 % aqueous dioxane containing 1,0 N hydrochloric acid. Part of the crude product was acetylated. ^{1}H NMR analysis showed a 60 % yield of hydroxymethyl groups per model compound. Thin layer chromatography (tlc) indicated a variety of products. Flash chromatography afforded the mono-hydroxymethylated product **6** only in a yield of 30 % together with various other products. The structure of **6** was established by comparison by tlc and of its ^{1}H-NMR, IR and mass spectra with that of the authentic compound[1].

The guaiacyl model **3** was subsequently reacted with formaldehyde (4 : 1 as before) in 10 % aqueous dioxane containing 0,4 N hydrochloric acid. After 6 hours a sample was acetylated for ^{1}H-NMR analysis which showed 100 % mono-hydroxymethylation. Flash chromatography of the remaining product offered pure **6** in 56 % yield. The milder conditions clearly led to less side reactions and a higher degree of *meta*-hydroxymethylation.

The non-phenolic softwood lignin model compound (**4**) was reacted with formaldehyde (2 moles/mole **4**) in 1,0 N hydrochloric acid in 23 % aqueous dioxane to give the mono-hydroxymethylated product **7** in high yield

TABLE 5

Reaction of **4** with formaldehyde (2 moles/mole **4**) in 1,0 N hydrochloric acid in 23 % aqueous dioxane at 80 °C

ENTRY	REACTION TIME (h)	YIELD OF META-HYDROXYMETHYL GROUPS (mole/mole 4) (NMR)	ARYLMETHANE SUBSTITUENTS
1	2	1,04	0,0
2	4	1,03	0,0
3	8	0,92	0,0
4	12	0,92	0,0

TABLE 6

Reaction of **5** with formaldehyde (2 moles/mole **5**) in 1,0 N hydrochloric acid in 23 % aqueous dioxane at 80 °C

ENTRY	REACTION TIME (h)	YIELD (mole/mole **5**) (NMR)	
		META-HYDROXYMETHYL GROUPS	ARYLMETHANE SUBSTITUENTS
1	2	0,92	0,00
2	4	0,96	0,00
3	8	0,97	0,04
4	24	0,94	0,03

(Table 5). The crude product was purified by flash chromatography and analysed by ^{1}H-NMR and IR and these spectra compared with those of an authentic compound[1].

The non-phenolic syringyl model compound **5** was reacted with a two molar equivalent of formaldehyde under the same conditions as above. Again only mono-hydroxymethylation occurred and **8** was isolated in high yield. The structure of **8** was proved by comparison with an authentic specimen. Hydroxymethylation was complete in less than two hours (see Table 6) whilst almost no methylene linkage formation was detected even after 24 hours.

CONCLUSION

Hardwood and softwood model compounds were hydroxymethylated on positions *meta* to the aromatic hydroxy groups. The hydroxymethylations

were achieved in high yield with a small excess of formaldehyde in 10 to 23 % aqueous dioxane as solvent and acid concentrations of 0,4 to 1,0 N. Both phenolic and non-phenolic softwood and hardwood lignin model compounds were hydroxymethylated in high yield. This indicates that all the lignin phenylpropanoid units, represented by the above model, could be hydroxymethylated under the optimized conditions. The *meta* hydroxymethylation of lignin will result in the realization of a versatile raw material useful for various polymeric applications, since aromatic hydroxymethyl groups can be very reactive towards nucleophiles.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer spectrophotometer (710B) in chloroform as solvent. ^{1}H-NMR spectra were determined with a Varian spectrometer in deuterochloroform with tetramethylsilane as internal standard. Mass spectra, including accurate mass determination, were obtained on a Varian MAT-212 double focussing spectrometer with direct probe insertion, operated with an ionization potential of 70 eV. Qualitative thin layer chromatography was done on Merk (Kieselgel $60F_{254}$) plates and column chromatography on Merk Kieselgel 60(0,063 - 0,2 mm).

The model compounds **1**, **3**, **4** and **5** were prepared as before[1].

Reactions of **1** with formaldehyde

Pure **1** was reacted with formaldehyde in the molar ratio's stated in aqueous dioxane (10 ml / 50 mg **1**) containing different quantities of concentrated hydrochloric acid in order to achieve the acid concentrations stated in Tables 1 to 4. The 50 % aqueous dioxane mixtures were obtained by mixing 5 g dioxane and 5 g H_2O, 23 % aqueous dioxane by mixing 10 g dioxane and 3 g H_2O and 10 % aqueous dioxane by mixing 10 g dioxane and 1,0 g H_2O. After the indicated reaction times, a sample (2 ml) of the reaction mixture was neutralized with sodium bicarbonate diluted with H_2O (20 ml), extracted with chloroform (3 x 10 ml), dried ($MgSO_4$), filtered and the solvent evaporated. Each sample was subsequently acetylated with acetic anhydride (3 ml) and pyridine (3 ml) at ambient temperature overnight. Azeotroping with toluene (3 x 30 ml) and chloroform (3 x 20 ml) afforded pure acetylated samples which were analysed by ^{1}H-NMR. The results are listed in Tables 1 to 4.

The reaction conditions presented in Table 4 led to the mono-hydroxymethylation of **1** in high yield. The product 2 was subsequently prepared in high yield by the reaction of **1** (200 mg) with formaldehyde (150 mg) in dioxane

(10 ml) containing H_2O (1,5 g) and concentrated hydrochloric acid (1,5 g) at 80 °C for three hours. The crude product was purified by flash chromatography (120 g silica) with ethylacetate hexane 1:1 as eluent to afford pure 6-ethyl-3-hydroxy-2,4-dimethoxybenzyl alcohol **2** in an 85 % yield with υ maxs($CHCl_3$) 3500, 2900, 1610, 1480, 1310 and 1130 cm^{-1}; δ ($CDCl_3$) 1,20 (t, 3H, J = 7,5 Hz, $CH_2\underline{CH_3}$), 2,3 (broad singlet, 1H, D_2O exchangeable, CH_2OH), 2,68 (q, 2H, J = 7,5 Hz, $\underline{CH_2}CH_3$), 3,82 - 3,95 (2 x d, 6H, 2 x OCH_3), 4,65 (s, 2H, $\underline{CH_2}OH$), 5,55 (broad singlet, 1H, D_2O exchangeable, Ar$\underline{O}$H), 6,52 (s, 1H, Ar$\underline{H}$); The acetylated product showed δ ($CDCl_3$) 1,18 (t, 3H, J = 7,5 Hz, $-CH_2\underline{CH_3}$), 2,05 (s, 3H, $-CH_2OCO\underline{CH_3}$), 2,35 (s, 3H, $ArOCO\underline{CH_3}$), 2,65 (q, 2H, J = 7,5 Hz, $-\underline{CH_2}CH_3$), 3,82 and 3,87 (singlets, 6H, 2 x $-OCH_3$), 5,15 (s, 2H, $-CH_2\underline{CH_3}$), 6,6 (s, 1H, Ar-$\underline{H}$). m/e (73 °C), 212 (M^+, 44 %), 194 (52), 179 (100), 151 (41), 91 (48), 79 (42), 77 (47), 57 (67); [Found M+ 212,105 $C_{11}H_{16}O_4$ requires 212,105].

The reaction of **3** with formaldehyde in acid:

4-Hydroxy-3-methoxyphenyl ethane (**3**) (200 mg) was reacted with paraformaldehyde (220 mg) in dioxane (10 g) containing water (0,5 g) and concentrated hydrochloric acid (0,5 g) at 80 °C. After four hours, the reaction mixture was neutralized ($NaHCO_3$) and extracted with chloroform (3 x 20 ml). Drying ($MgSO_4$) and evaporation of the solvent afforded a crude product which was purified by flash chromatography on silica (100 g) with ethyl acetate hexane (2:1) to afford 6-ethyl-3-hydroxy-4-methoxy benzyl alcohol (6) in a yield of 56 %. Tlc, IR spectra and 'H-NMR analysis was identical to those of an authentic compound prepared previously[1]. Acetylation of **6** (acetic anhydride/pyridine) afforded the acetate which showed upon 'H-NMR analysis the following: δ ($CDCl_3$) 1,24 (t, 3H, J = 7,5 H z, $-CH_2\underline{CH_3}$), 2,07 (s, 3H, $-CH_2OCO\underline{CH_3}$), 2,30 (s, 3H, $ArOCO\underline{CH_3}$), 2,70 (q, 2H, J = 7,5 Hz, $-\underline{CH_2}CH_3$), 3,83 (s, 3H, $-O\underline{CH_3}$), 5,04 (s, 2H, $-\underline{CH_2}OCOCH_3$), 6,80 and 7,0 (singlets, 2H, 2 x Ar$\underline{H}$).

The reaction of **4** with formaldehyde in acid

Model compound **4** (210 mg) was reacted with formaldehyde (74,0 mg) in dioxane (10 ml), H_2O (1,5 ml) and concentrated hydrochloric acid (1,5 ml). Samples were taken at different intervals and worked up and analysed by 'H NMR as before. These results are listed in Table 5. The remainder of the reaction mixture was flash chromatographed with ethylacetate hexane 1:2 to afford 6-ethyl-3,4-dimethoxybenzyl alcohol (**7**) in high yield. Purified **7** was compared with an authentic compound[1] by tlc, IR and 'H-NMR. 'H-NMR analysis of 6-ethyl-3,4-dimethoxybenzyl acetate (acetic anhydride/pyridine) showed δ ($CDCl_3$) 1,2 (t, 3H, J = 7,5 Hz, $CH_2\underline{CH_3}$), 2,1 (s, 3H, $CH_2OCO\underline{CH_3}$),

2,65 (q, 2H, J = 7,5 Hz, $C\underline{H}_2CH_3$), 3,85 - 3,90 (s, 6H, 2 x $OC\underline{H}_3$), 5,05 (s, 2H, $C\underline{H}_2OCOCH_3$), 6,72 and 6,85 (singlets, 2H, 2 x Ar$\underline{H}$).

The reaction of **5** with formaldehyde in acid

Compound **5** (186 mg) was reacted with formaldehyde (63 mg) in aqueous dioxane as above. The reaction was monitored by ^1H NMR and the crude product worked up as before to give the novel compound 6-ethyl-3,4,5-trimethoxybenzyl alcohol **8** in a yield of 82 % with υ maxs 3450, 2900, 1595, 1400 - 1480, 1180 - 1280, 1120, 1000 cm^{-1}; δ ($CDCl_3$) 1,23 (t, 3H, J = 7,5 Hz, $-CH_2-C\underline{H}_3$), 2,2 (s, 1H, D_2O exchangeable, $CH_2O\underline{H}$), 2,71 (q, 2H, J = 7,5 Hz, $-C\underline{H}_2-CH_3$), 3,86 (s, 6H, 2 x $OC\underline{H}_3$), 3,95 (s, 3H, $OC\underline{H}_3$), 4,68 (s, 2H, $-C\underline{H}_2OH$), 6,55 (s, 1H, Ar$\underline{H}$). m/e 226 (M^+, 8 %), 208 (18,6), 193 (11), 149 (12), 92 (10), 71 (17), 69 (16), 57 (32), 43 (100); [Found M^+ 226,120, $C_{12}H_8O_4$ requires 226,121].

Compound **8** was acetylated (acetic anhydride/pyridine) to afford 6-ethyl-3,4,5-trimethoxybenzyl alcohol acetate in high yield with υ ($CDCl_3$) 1,16 (t, 3H, J = 7,5 Hz, $-CH_2C\underline{H}_3$), 2,05 (s, 3H, $-CH_2OCOC\underline{H}_3$), 2,64 (q, 2H, J = 7,5 Hz, $-C\underline{H}_2CH_3$), 3,88 - 3,90 (multiplet, 9H, 3 x $OC\underline{H}_3$), 5,15 (s, 2H, $-C\underline{H}_2OCOCH_3$), 6,55 (s, 1H, Ar$\underline{H}$).

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