

## Stereoselective Syntheses of Lignin Model Compounds of the $\beta$ -0-4 and $\beta$ -1 Types

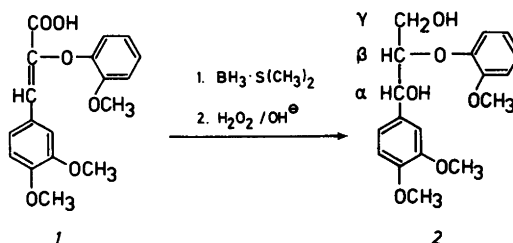
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The preparation of *erythro* forms of lignin model compounds of the  $\beta$ -0-4 type by hydroboration of  $\alpha$ -aryloxycinnamic acids, using a borane dimethyl sulfide complex as a reagent, has been studied. The *erythro* form of 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol was obtained in a yield of about 50%. Acid-catalyzed rearrangements of chalcone oxides which give 1,2-diaryl-1,3-propanediols on borohydride reduction. The synthesis of the *erythro* forms of 1,2-bis(4-hydroxy-3-methoxyphenyl)-1,3-propanediol and 1,2-bis(4-hydroxy-3,5-dimethoxyphenyl)-1,3-propanediol by this reaction route is described; both 1,2-diaryl-1,3-propanediols represent lignin model compounds for the  $\beta$ -1 type of structure.

The use of adequate lignin model compounds is often crucial in lignin research. Lignin model compounds are not commercially available and therefore have to be prepared in the laboratory. In general only small amounts of model compounds are required. Thus the obvious criteria for choosing suitable synthetic routes for such compounds would seem to be simplicity of preparation and ease of purification rather than high yield. In this paper stereoselective syntheses of some lignin model compounds of the  $\beta$ -0-4 and  $\beta$ -1 types are described.

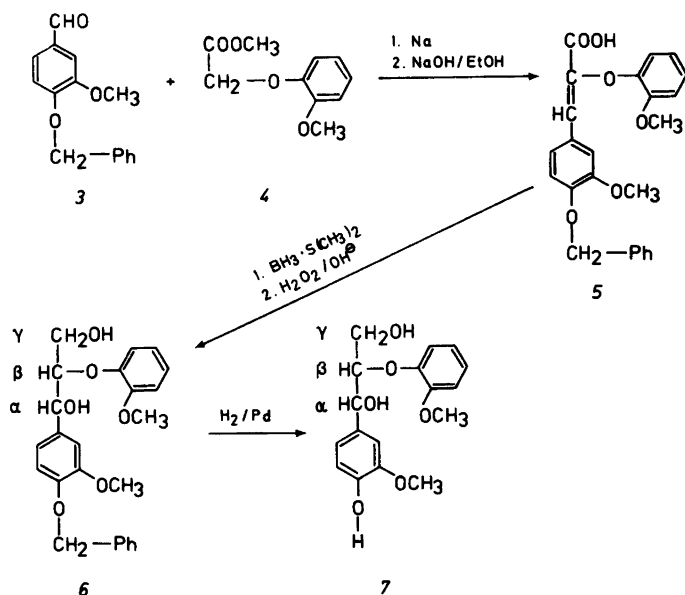
**$\beta$ -0-4 model compounds.** The synthesis of lignin model compound 2 by hydroboration of acid 1 has been described in previous studies.<sup>1,2</sup> In this paper a commercially available reagent – borane dimethyl sulfide complex – has been used



Scheme 1.

for hydroboration (Scheme 1). It was found that acid 1 reacted comparatively slowly with this reagent. However, the rate of reaction could be increased by raising the temperature. After 2 h treatment at 35 °C compound 2 (*erythro* form) could be isolated in a yield of 60%. In connection with attempts to optimize the formation of  $\beta$ -0-4 compounds, it was found that long-term treatment with the borane complex at a lower temperature (20 °C) gave a product consisting primarily of  $\alpha$ -(2-methoxyphenoxy)-3,4-dimethoxycinnamyl alcohol. This suggests that this compound is an intermediate in the synthesis of compound 2. Long-term treatment with the borane reagent also resulted in a partial isomerization which led to the occurrence of minor amounts of the *threo* form of compound 2 in the reaction mixture.

Hydroboration of  $\alpha$ -aryloxycinnamic acid 5 with borane dimethyl sulfide complex gave compound 6 (yield: 56%). Removal of the benzyl groups by catalytic hydrogenation of this com-

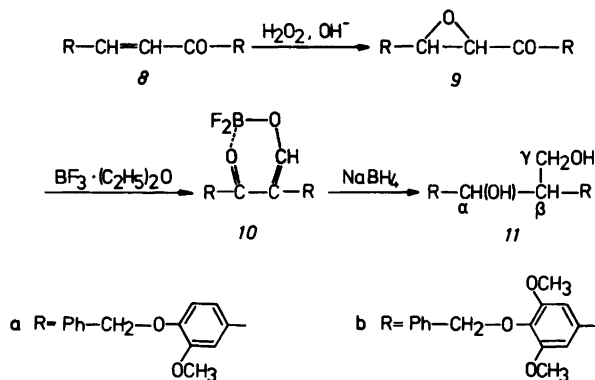


Scheme 2.

compound gave  $\beta$ -0-4 model 7 (*erythro* form). Acid 5 was prepared by the condensation of methyl (2-methoxyphenoxy)ethanoate (4) with 4-benzyloxy-3-methoxybenzaldehyde (3) (Scheme 2). It was found that the sodium salt of acid 5 could be extracted from an aqueous solution with dichloromethane. This finding was used in the work-up procedure for the isolation of acid 5. For recent work on the synthesis of  $\beta$ -0-4 model compounds, see Refs. 3, 4 and 5.

**$\beta$ -1 model compounds.** The reaction route shown in Scheme 3 has been used for the synthesis of the lignin model compounds of the  $\beta$ -1 type.<sup>5,7,8</sup> Some chalcones (e.g. chalcone 8a)

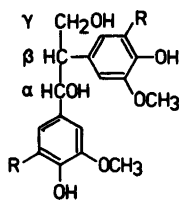
are very slightly soluble in reaction media suitable for the epoxidation step. Phase-transfer catalysis was found to be useful for the oxidation of such chalcones. Model compound 12 (*erythro* form) was prepared in a high yield.  $\beta$ -1 model compounds have been prepared by a variety of synthetic methods.<sup>9-13</sup> The reaction route in Scheme 3 has the advantage over other methods of being stereoselective. The *erythro* form of compound 13 was prepared analogously. This compound has not been synthesized previously, but has been isolated from wood hydrolysates.<sup>14,15</sup>



Scheme 3.

## EXPERIMENTAL

NMR spectra were recorded using chloroform-*d* as a solvent. Thin layer chromatography (TLC) was performed with SiO<sub>2</sub> using benzene-dioxane acetic acid (90:25:4) as eluent. Spots were made visible by first spraying with formalin



- 12 R=H  
13 R=OCH<sub>3</sub>

-H<sub>2</sub>SO<sub>4</sub> (1:9) and then heating. *R<sub>F</sub>* values: (2-methoxyphenoxy)ethanoic acid, 0.20; 7, 0.21; 2, 0.28; 1, 0.32; 6, 0.32; 5, 0.34; 4-benzyloxy-3-methoxybenzoic acid, 0.50; 3, 0.63.

Extraction of the sodium salt of acid 5 from an aqueous solution by dichloromethane. Acid 5 (100 mg) was dissolved in 12 ml 0.5 M NaOH and the solution extracted with 20 ml dichloromethane. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent removed with film evaporation. A crystalline product (75 mg, m.p. >300 °C) was obtained. The product exhibited a strong IR band at 1610 cm<sup>-1</sup> (carboxylate); the strong band found at 1680 cm<sup>-1</sup> in the spectrum of acid 5 (C=O) was absent. Sodium content: 5.45 % (determined by flame-ionization spectrometry). Calc. for the sodium salt of acid 5: 5.37 %.

Methyl (2-methoxyphenoxy) ethanoate (4) was prepared according to a procedure described previously.<sup>2</sup> This compound was obtained in a modification melting at 47 °C.

$\alpha$ -(2-Methoxyphenoxy)-4-benzyloxy-3-methoxycinnamic acid (5) (cf. Freudenberg and Müller<sup>16</sup>). A mixture of benzylvanillin (9.1 g) and methyl (2-methoxyphenoxy) ethanoate (4) (7.4 g) were melted together in a 100 ml flask equipped with a cooler. Ether (25 ml) and 50 % sodium in paraffin (1.7 g) were added. As indicated by the evolution of hydrogen, the sodium dissolved fairly rapidly (the temperature was kept below 30 °C to avoid a too vigorous reaction). When the evolution of hydrogen ceased, the reaction mixture was refluxed for 5.5 h (oil bath). Five ml of ethanol were added, whereupon the ether was evaporated. NaOH (1.25 g) in 25 ml ethanol was added and the mixture set aside overnight. The reaction product

was transferred to a separatory funnel with the help of 200 ml 0.1 M NaOH and 150 ml ether. The aqueous layer was separated and washed with 75 ml ether. One half of the aqueous layer was extracted with 2 × 100 ml dichloromethane. The extract was dried over Na<sub>2</sub>SO<sub>4</sub>, treated with 60 ml 0.7 M hydrochloric acid, washed with H<sub>2</sub>O (40 ml), and again dried over Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvents gave a product weighing 5.0 g. [On acidification of the dichloromethane-treated aqueous layer, crystals precipitated (m.p. ≈ 160 °C) which were identified as 4-benzyloxy-3-methoxybenzoic acid (IR, m.p.; lit.<sup>17</sup> m.p. 168–169 °C). Subsequent extraction with trichloromethane gave a product identified as (2-methoxyphenoxy)ethanoic acid (IR, TLC).] The product was chromatographed on silica gel (100 g) with dichloromethane-ethyl acetate (9:1) as eluent. Eluate 200–500 ml gave crystals (3.46 g) of m.p. 142 °C. Recrystallization from methanol-water (9:1) gave 2.6 g acid 5 of m.p. 147 °C (yield: 34 %). <sup>1</sup>H NMR (270 MHz):  $\delta$  3.71 (3 H, s; OCH<sub>3</sub>), 3.90 (3 H, s; OCH<sub>3</sub>), 5.13 (2 H, s; CH<sub>2</sub>),  $\approx$ 7 (13 H, m; aromatic protons and vinyl proton). The IR spectrum exhibited a strong band at 1680 cm<sup>-1</sup> (C=O). The second half of the original aqueous layer was acidified to pH 2 with hydrochloric acid and extracted with 2 × 100 ml ether. Evaporation of the solvents gave a residue weighing 5.9 g. Chromatographic purification (see above) gave acid 5.

$\alpha$ -(2-Methoxyphenoxy)-3,4-dimethoxycinnamic acid (1) was prepared according to the procedure for the synthesis of acid 5 described above. For the isolation of acid 1 from the reaction mixture, the work-up procedure from a previous study<sup>2</sup> was used. Yields were about the same as in the synthesis of acid 1 described in that study.<sup>2</sup>

erythro-1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol. Acid 1 (2.98 g) was dissolved in 36 ml tetrahydrofuran in a 100-ml three-necked flask (nitrogen atmosphere). Borane dimethyl sulfide complex (4.5 ml) was injected over a 15 min period (magnetic stirring). The reaction mixture was kept at 35 °C for 2 h (oil bath). Excess reagent was decomposed by the addition of 13.5 ml H<sub>2</sub>O. H<sub>2</sub>O<sub>2</sub> (1.8 ml 30 % H<sub>2</sub>O<sub>2</sub>) was added and then 18 ml 3 M NaOH was added over a 15 min period. The reaction mixture was stirred vigorously at 35 °C for a 1 h period and transferred to a separatory funnel with 90 ml H<sub>2</sub>O and 180 ml CHCl<sub>3</sub>. The layers were separated and the aqueous layer extracted with 2 × 50 ml CHCl<sub>3</sub>. The organic layers were combined, dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed by film evaporation. A residue weighing 3.2 g was obtained. The crude product was chromatographed on SiO<sub>2</sub> (150 g)

with  $\text{CH}_2\text{Cl}_2$ —ethyl acetate (1:1) as eluent. Compound 2 (1.80 g) was obtained from eluate 525–1000 ml. Yield: 60%.  $^1\text{H}$  NMR (270 MHz) of the acetate derivative:  $\delta$  2.02 (3 H, s;  $\text{CH}_3\text{-C}$ ), 2.07 (3 H, s;  $\text{CH}_3\text{-C}$ ), 3.79 (3 H, s;  $\text{CH}_3\text{-O}$ ), 3.86 (3 H, s;  $\text{CH}_3\text{-O}$ ), 3.87 (3 H, s;  $\text{CH}_3\text{-O}$ ), 4.23 (1 H, dd,  $J=4$  and 12 Hz;  $\text{H}_\gamma$ ), 4.42 (1 H, dd,  $J=6$  and 12 Hz;  $\text{H}_\gamma$ ), 4.70 (1 H, m;  $\text{H}_\beta$ ), 6.02 (1 H, d,  $J=5$  Hz;  $\text{H}_\alpha$ ),  $\approx 7$  (6 H, m; aromatic protons).

*erythro-1-(4-Benzyloxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol* (6). Acid 5 (1.22 g) was dissolved in 12 ml tetrahydrofuran under magnetic stirring (nitrogen atmosphere). Borane dimethyl sulfide complex (1.5 ml) was injected over a 10 min period. The reaction mixture was kept at 35 °C (oil bath) for 3 h. Excess reagent was decomposed by the addition of 4 ml  $\text{H}_2\text{O}$ . First hydrogen peroxide (0.6 ml 30%  $\text{H}_2\text{O}_2$ ), and then 6 ml 3 M NaOH were added over a 15 min period. The reaction mixture was then stirred vigorously for 1 h (35 °C). The reaction mixture was transferred with water (30 ml) and chloroform (60 ml) to a separatory funnel. The layers were separated and the aqueous layer extracted with  $2 \times 20$  ml  $\text{CHCl}_3$ . The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$  and the solvents removed by film evaporation. A residual oil (1.25 g) was obtained. The product was chromatographed on  $\text{SiO}_2$  (58 g) with  $\text{CH}_2\text{Cl}_2$ —ethyl acetate (9:1) as eluent. Compound 6 was found in eluate 500–700 ml (TLC). Removal of the solvents gave 0.69 g of an oil. Yield: 56%.  $^1\text{H}$  NMR (270 MHz) of the acetate derivative:  $\delta$  2.00 (3 H, s;  $\text{CH}_3\text{-C}$ ), 2.06 (3 H, s;  $\text{CH}_3\text{-C}$ ), 3.76 (3 H, s;  $\text{CH}_3\text{-O}$ ), 3.86 (3 H, s;  $\text{CH}_3\text{-O}$ ), 4.23 (1 H, dd,  $J = 4$  and 12 Hz;  $\text{H}_\gamma$ ), 4.41 (1 H, dd,  $J = 6$  and 12 Hz;  $\text{H}_\gamma$ ), 4.68 (1 H, m;  $\text{H}_\beta$ ), 5.12 (2 H, s;  $\text{CH}_2$ ), 6.02 (1 H, d,  $J = 5$  Hz;  $\text{H}_\alpha$ ),  $\approx 7$  (11 H, m; aromatic protons).

*erythro-1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol* (7). Compound 6 (0.28 g) was hydrogenated in 15 ml dioxane with 0.1 g 10% Pd/C as a catalyst. When the calculated amount of hydrogen had been consumed, the catalyst was filtered off and the dioxane removed by film evaporation. A residue (0.20 g) was obtained which crystallized on inoculation with authentic 7 (m.p. 87–89 °C, lit.<sup>18</sup> 90–92 °C).  $^1\text{H}$  NMR (270 MHz) of the acetate derivative (cf. Ref. 3):  $\delta$  2.02 (3 H, s;  $\text{CH}_3\text{-C}$ ), 2.09 (3 H, s;  $\text{CH}_3\text{-C}$ ), 2.30 (3 H, s;  $\text{CH}_3\text{-C}$ ), 3.77 (3 H, s;  $\text{CH}_3\text{-O}$ ), 3.81 (3 H, s;  $\text{CH}_3\text{-O}$ ), 4.25 (1 H, dd,  $J = 4$  and 12 Hz;  $\text{H}_\gamma$ ), 4.46 (1 H, dd,  $J = 6$  and 12 Hz;  $\text{H}_\gamma$ ), 4.67 (1 H, m;  $\text{H}_\beta$ ), 6.08 (1 H, d,  $J = 5.5$  Hz;  $\text{H}_\alpha$ ),  $\approx 7$  (6 H, m; aromatic protons).

*1,3-Bis(4-benzyloxy-3-methoxyphenyl)-2-propene-1-one* (8a). A solution of 20 g potassium hydroxide in 20 ml water was dropped into a

stirred solution of the benzyl ethers of 4-hydroxy-3-methoxybenzaldehyde (2.42 g) and 1-(4-hydroxy-3-methoxyphenyl) ethanone (2.56 g) in 80 ml ethanol. After 2 h the yellow precipitate was filtered off and washed with ethanol and water. Recrystallization from chloroform—ethanol gave 4.2 g (87%) crystals of m.p. 145–147 °C.  $^1\text{H}$  NMR (60 MHz):  $\delta$  3.96 (3 H, s;  $\text{CH}_3\text{O}$ ), 3.98 (3 H, s;  $\text{CH}_3\text{O}$ ), 5.20 (2 H, s;  $\text{CH}_2$ ), 5.25 (2 H, s;  $\text{CH}_2$ ), 6.8–7.7 (18 H, m; aromatic and vinylic protons).

*1,3-Bis(4-benzyloxy-3,5-dimethoxyphenyl)-2-propene-1-one* (8b) was prepared from the benzyl ethers of 4-hydroxy-3,5-dimethoxybenzaldehyde and 1-(4-hydroxy-3,5-dimethoxy) ethanone analogously with the preparation of chalcone 8a, m.p. 147–150 °C (from dioxane-ethanol).

*1,3-Bis(4-benzyloxy-3-methoxyphenyl)-2,3-epoxy-1-propanone* (9a). Chalcone 8a (3.4 g, 7.1 mmol) was dissolved in 18 ml dichloromethane. To this a mixture of 3.5 ml hydrogen peroxide (35% aqueous solution) and 11 ml 3 M sodium hydroxide was added while stirring at 4 °C. At a constant temperature of 4 °C, 0.72 g (2.1 mmol) of tetrabutylammonium hydrogen sulfate was added in small portions for 10 min. The rapid stirring was continued for 6 h, during which time the temperature of the mixture was allowed to rise to 16 °C. The organic phase was separated and washed with water containing a few crystals of ammonium chloride until the aqueous phase was neutral. The organic phase was dried ( $\text{MgSO}_4$ ) and the solvent evaporated. Recrystallization from ethyl acetate—light petroleum yielded pale yellow crystals (2.8 g, 79%) that melted at 144.5–146 °C.  $^1\text{H}$  NMR (60 MHz):  $\delta$  3.87 (3 H, s;  $\text{CH}_3\text{O}$ ), 3.92 (3 H, s;  $\text{CH}_3\text{O}$ ), 4.16 (1 H, d,  $J = 2.0$  Hz;  $-\text{CH}<$ ), 4.20 (1 H, d,  $J = 2.0$  Hz;  $-\text{CH}<$ ), 5.13 (2 H, s;  $\text{CH}_2$ ), 5.20 (2 H, s;  $\text{CH}_2$ ), 6.8–7.5 (16 H, m; aromatic protons).

*1,2-Bis(4-benzyloxy-3-methoxyphenyl)-1,3-propanediol* (11a). Chalcone oxide 9a (2.0 g) was dissolved in 200 ml dry ether and 17.2 g freshly distilled  $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$  was gradually added to the solution. The mixture was refluxed for 30 min, washed with water and dried over  $\text{Na}_2\text{SO}_4$ . The residue was reduced with sodium borohydride (0.35 g) in 5 ml tetrahydrofuran. The mixture was stirred for 4 h and set aside for 48 h. It was then acidified with dilute hydrochloric acid and extracted with ether. The ether was dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated. The crystalline residue was recrystallized from ethyl acetate—light petroleum to yield 1.55 g (77.5%) white crystals that melted at 105–109 °C (lit.<sup>11</sup> 106–108 °C).  $^1\text{H}$  NMR (270 MHz) of the acetylated product:  $\delta$  1.92 (3 H, s;  $\text{CH}_3\text{-C}$ ), 1.94 (3 H, s;  $\text{CH}_3\text{-C}$ ), 3.32 (1 H, m;  $\text{H}_\beta$ ), 3.82 (6 H, s;  $\text{CH}_3\text{-O}$ ), 4.09 (1 H,

dd,  $J = 6.8$  and  $11.2$  Hz;  $H\gamma$ ),  $4.27$  (1 H, dd,  $J = 6.4$  and  $11.2$  Hz;  $H\gamma$ ),  $5.12$  (2 H, s;  $CH_2$ ),  $5.13$  (2 H, s;  $CH_2$ )  $6.02$  (1 H, d,  $J = 7.3$ ;  $H_a$ ),  $\approx 7$  (16 H, m; aromatic protons).

erythro-1,2-Bis(4-hydroxy-3-methoxyphenyl)-1,3-propanediol (12). The protecting benzyl groups were removed by catalytic hydrogenation in an ethanol solution using 5% Pd/C as a catalyst. Filtration of the catalyst and evaporation of the solvent gave a quantitative yield, m.p.  $151$ – $154$  °C (lit.<sup>12</sup>  $158$ – $159$  °C). The  $^1H$  NMR spectrum of the acetate derivative agreed with published  $^1H$  NMR data<sup>12</sup> for this compound.

1,3-Bis(4-benzyloxy-3,5-dimethoxyphenyl)-2,3-epoxy-1-propanone (9b). Chalcone 8b (1.2 g, 2.3 mmol) was dissolved in 6 ml dichloromethane. To this was added 1.2 ml hydrogen peroxide (35% aqueous solution) and 3.5 ml 3 M sodium hydroxide while stirring at 4 °C. After the addition of 0.23 g tetrabutylammonium hydrogen sulfate and a reaction time of 5 h, the work-up was performed as for epoxide 9a. A chromatographically homogeneous oil, 1.17 g, was obtained.  $^1H$  NMR (60 MHz):  $\delta$  3.83 (12 H, s;  $CH_3O$ ), 4.00 (1 H, d,  $J = 2.0$  Hz,  $-CH<$ ), 4.10 (1 H, d,  $J = 2.0$  Hz;  $-CH<$ ), 5.02 (2 H, s;  $CH_2O$ ), 5.12 (2 H, s;  $CH_2O$ ), 6.5–7.5 (14 H, m; aromatic protons).

erythro-1,3-Bis(4-hydroxy-3,5-dimethoxyphenyl)-1,3-propanediol (13). Crude chalcone oxide 9b (1.25 g) in 110 ml dry diethyl ether was treated with boron trifluoride diethyl etherate (9.4 g) and refluxed for 30 min. Work-up, reduction with sodium borohydride and catalytic hydrogenation as in the previous synthesis gave 1.09 g crude compound 13. Acetylation gave an acetate derivative which after purification melted at  $165$ – $167$  °C (lit.<sup>14</sup>  $169$ – $170$  °C).  $^1H$  NMR (270 MHz) of the acetate derivative:  $\delta$  1.99 (3 H, s;  $CO$   $CH_3$ ), 2.01 (3 H, s;  $CO$   $CH_3$ ), 2.30 (3 H, s;  $CO$   $CH_3$ ), 2.31 (3 H, s;  $CO$   $CH_3$ ), 3.36 (1 H, m;  $H_\beta$ ), 3.81 (3 H, s;  $OCH_3$ ), 3.82 (3 H, s;  $OCH_3$ ), 4.21 (1 H, dd,  $J = 6.5$  and  $11.4$  Hz;  $H\gamma$ ), 4.43 (1 H, dd,  $J = 7.0$  and  $11.4$  Hz;  $H\gamma$ ), 6.06 (1 H, d,  $J = 7.3$  Hz;  $H_a$ ), 6.34 (2 H, s; aromatic protons), 6.35 (2 H, s; aromatic protons).  $^{13}C$  NMR:  $\delta$  20.4, 20.8, 21.0 (acetyl  $CH_3$ ), 50.4 ( $C_\beta$ ), 56.2 ( $CH_3O$ ), 63.9 ( $C\gamma$ ), 75.2 ( $C_a$ ), 103.7, 105.7 (C-2, C-6), 135.1, 136.2 (C-1), 151.8, 151.9 (C-3, C-5), 128.0, 128.4 (C-4), 168.5 (C=O, aromatic acetyl), 169.6 (C=O, secondary acetyl), 170.8 (C=O, primary acetyl).

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## REFERENCES

1. Lundquist, K. and Remmerth, S. *Acta Chem. Scand. B* 29 (1975) 276.
2. Berndtsson, I. and Lundquist, K. *Acta Chem. Scand. B* 31 (1977) 725.
3. Nakatsubo, F., Sato, K. and Higuchi, T. *Holzforchung* 29 (1975) 165.
4. Ralph, J. and Young, R. A. *Holzforchung* 35 (1981) 39.
5. Landucci, L. L., Geddes, S. A. and Kirk, T. K. *Holzforchung* 35 (1981) 67.
6. Kristersson, P. and Lundquist, K. *Acta Chem. Scand. B* 34 (1980) 213.
7. Brunow, G., Koskinen, L. and Urpilainen, P. *Acta Chem. Scand. B* 35 (1981) 53.
8. Brunow, G. and Lundquist, K. *Kemia* 8 (1981) 9.
9. Lundquist, K. and Miksche, G. E. *Tetrahedron Lett.* 25 (1965) 2131.
10. Nakatsubo, F. and Higuchi, T. *Holzforchung* 29 (1975) 193.
11. Brezny, R. and Pufflerova, A. *Collect Czech. Chem. Commun.* 43 (1978) 3263.
12. Berndtsson, I., Khanna, B. L. and Lundquist, K. *Acta Chem. Scand. B* 34 (1980) 453.
13. Nonni, A. J. and Dence, C. W. *J. Wood Chem. Technol.* 2 (1982) 161.
14. Nimz, H. *Chem. Ber.* 98 (1965) 3160.
15. Omori, S. and Sakakibara, A. *Mokuzai Gakkaishi* 18 (1972) 355.
16. Freudenberg, K. and Müller, H. G. *Justus Liebigs Ann. Chem.* 584 (1953) 40.
17. Lovecy, A., Robinson, R. and Sugawara, S. *J. Chem. Soc.* (1930) 817.
18. Miksche, G. E., Gratzl, J. and Fried-Matzka, M. *Acta Chem. Scand.* 20 (1966) 1038.

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