Lignin–carbohydrate model compounds. Formation of lignin–methyl arabinoside and lignin–methyl galactoside benzyl ethers *via* quinone methide intermediates

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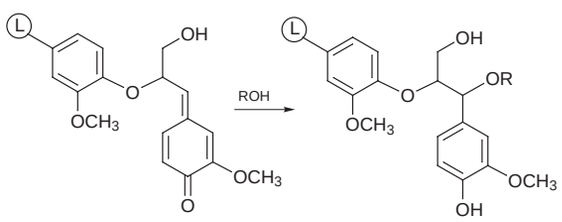
Model compounds for lignin–carbohydrate complexes (LCCs) were synthesized from β-*O*-4-type quinone methides and methyl glycosides of α-L-arabinofuranose and α-D-galactopyranose. Both monosaccharides reacted predominantly through primary hydroxy groups with the benzyl position of the dilignol but some secondary C-3 hydroxy groups of galactopyranosides also took part in ether-bond formation. Methyl α-L-arabinofuranosides were found to be more reactive than methyl α-D-galactopyranosides. LCC model-compound formation *via* quinone methides gave a mixture of four diastereomers. The diastereomers were isolated using silica gel and HPLC chromatography and all products were characterized by NMR spectroscopy.

Introduction

The high mechanical strength and resistance to biodegradation of woody cell walls is thought to stem from the interactions of wood lignin with the carbohydrates of the cell wall. One important component is the bonding of the lignin to the cell wall hemicelluloses.[1] The nature of these bonds remain an open question. Many lignin–carbohydrate complexes (LCCs) have been isolated[1] and the nature of the bonds have been inferred from their susceptibility to different cleavage reactions, such as acid or base treatment, methylation analysis or treatment with oxidants.[2–4] For the correct interpretation of such results it is necessary to make available a range of model compounds with different linkages. It has been indicated that spruce arabinoxylan and galactoglucomannan are bonded to lignin through the arabinose and the galactose branch units.[2] Also, the arabinose and the galactose branch units of arabinan and galactan have been found to be linked to pine lignin.[3] Tropical hardwood lignin has been suggested to bond straight to the backbone of hemicellulose, namely to xylopyranosyl units of glucuronoxylan.[4]

In wood it is assumed that possible covalent bonds between lignin and carbohydrates are formed during lignin biosynthesis when the three-dimensional cell-wall matrix is organized. When benzyl ether-type lignin–carbohydrate bonds are formed, coupling products of phenol free radicals called quinone methides are thought to be involved. Nucleophiles (phenols, carbohydrates, carbohydrate uronic acids or water molecules) compete for addition to quinone methides.[5] As a result hemicelluloses can attach covalently to a lignin molecule by benzyl ether bonds (Scheme 1). Quinone methides are also thought to play an important role as reactive intermediates during ageing of lignin and in pulping processes, and some lignin–carbohydrate bonds may be formed during those processes. LCC model compounds provide an essential tool for searching for these chemical bonds between lignin and carbohydrates in the native wood and in pulp.

Model compounds for LCCs have previously been formed *via* quinone methide intermediates in several reports.[6–12] In acidic buffer solution of D-glucose and vanillyl alcohol, the site of the linkage has been reported to be between the benzyl position of vanillyl alcohol and the glucose C-6 alcohol.[6] Also, in neutral buffer solutions of vanillyl alcohol and several monosaccharides, *viz.* D-glucose, D-galactose, D-mannose, L-rhamnose, L-arabinose and their methyl glycosides, etherification has been reported to favour the primary C-6 position of hexopyranoses and C-5 positions of pentofuranosides, but bond formation has also been observed at other positions of the carbohydrates, although in minor amounts.[7] The addition reactions of methyl α-D-glucoside to quinone methides of the β-*O*-4 model dilignol, guaiacylglycerol β-guaiacyl ether, in an organic solvent with acid catalyst have been reported to favour the C-6 position.[8] Reactivity of quinone methides of β-*O*-4 dilignols towards monosaccharides in organic solvents without acid catalyst have been reported to follow the order: methyl α-D-glucopyranoside ≥ methyl β-D-galactopyranoside > methyl β-D-arabinopyranoside > methyl β-D-xylopyranoside, but NMR data have been given for only the glucose adduct.[9,10] In addition there appears to be no formation of glycoside linkages between quinone methides and non-methylated D-glucose.[11] These LCC model compounds are a mixture of 4 diastereomers due to the presence of asymmetric carbon atoms of the propyl side chain of β-*O*-4 dilignol and the carbohydrate. Separation of the *erythro*- and *threo*-diastereomers of the methyl α-D-glucopyranoside LCC model compounds by HPLC has previously been reported; however, these diastereomers have not been identified by NMR spectroscopy.[12]



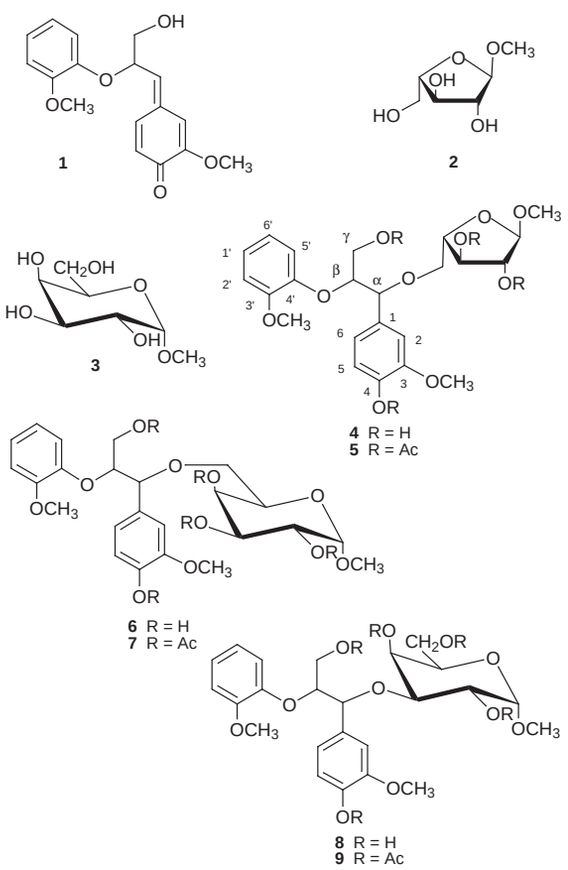
Scheme 1 The formation of benzyl ethers during lignin biosynthesis.

We present the formation, diastereomeric separation, and NMR characterization of LCC model compounds which are composed of a β-*O*-4-dilignol, the most common structure type in lignin, and the monosaccharides methyl α-L-arabinofurano-

side or methyl α-D-galactopyranoside, structural units of galactoglucomannans and arabinoglucuronoxylans which are hemicelluloses in wood. These arabinofuranosides and galactopyranosides are linked to the backbone of softwood hemicelluloses by a glycosidic α-bond. For steric reasons these attached monosaccharides will probably form lignin–carbohydrate bonds more easily than will the saccharides of the hemicellulose backbone. We have studied the lignin–carbohydrate bond formation of methyl α-L-arabinofuranoside and methyl α-D-galactopyranoside model saccharides, in which hemicellulose backbones are replaced by methyl groups, with quinone methides similar to the reactive intermediates in lignin biosynthesis.

Results and discussion

For synthetic purposes we have prepared methyl α-L-arabinofuranosides from L-(+)-arabinose in dry methanol with conc. sulfuric acid in an application of the Fischer method.[13] Instead of the conventional neutralization of the reaction mixture with pyridine we have exchanged the sulfate anions with hydroxy anions using Amberlite IRA-410 resin. The mixture of methyl α,β-L-arabinofuranosides was separated on silica gel.



We have studied the chemical reactivity of β-*O*-4-type quinone methides, *e.g.* compound **1**, towards hydroxy groups of monosaccharides in an organic solvent according to the method of Sipilä and Brunow.[8] Under these conditions formation of lignin–carbohydrate benzyl ether bonds required a catalytic amount of acid catalyst, PTSA. Excess (3–5 mole equiv.) of pure methyl α-L-arabinofuranoside **2** or methyl α-D-galactopyranoside **3** yielded LCC model compounds **4**, **6** and **8** in reasonable (~50%) yield.

In the reactivity studies methyl α-L-arabinofuranoside formed ether bonds mainly through primary hydroxy groups and compounds **4** (four diastereomers) were formed in 55–60% yield. LCC models were not formed through the secondary C-2 or C-3 hydroxy groups in detectable amounts. Methyl α-D-galactopyranosides produced two LCC model products. Attachment through the primary C-6 hydroxy group was favored but the secondary C-3 hydroxy group took part in ether-bond formation to a significant degree. LCC models **6** and **8** were formed in a 4:1 ratio in 40–48% combined yield. Reaction of the secondary C-2 and C-4 hydroxy groups (if it occurred) did not produce detectable products.

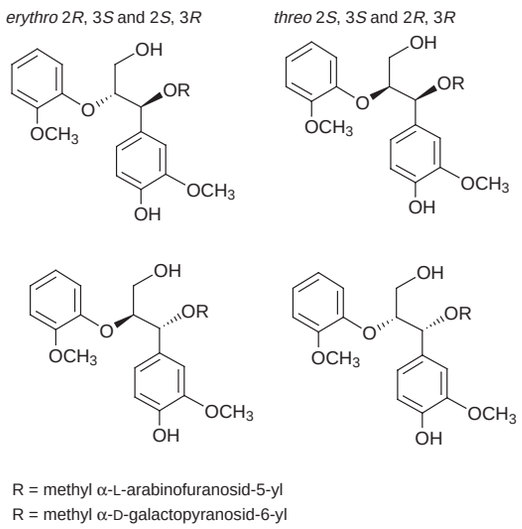


Fig. 1 *erythro*- and *threo*-diastereomers of LCC models.

Formation of lignin–carbohydrate compounds by addition of a carbohydrate to the quinone methide from a β-*O*-4-dilignol always produces a mixture of *erythro*- and *threo*-diastereomers (Fig. 1). In our studies these diastereomers were formed in equal amounts when the primary hydroxy groups of methyl α-L-arabinofuranoside and methyl α-D-galactopyranoside were attached to lignin models. There was observed an excess of *threo*-isomers over *erythro*-isomers when secondary C-3 hydroxy groups were involved in LC-bond formation.

Previously, diastereomeric LCC model-compound separation has been applied successfully to the mixture of *erythro*- and *threo*-diastereomers of lignin–methyl glucoside benzyl ether models[12] and also to the acetylated pair of *erythro*- and *threo*-diastereomers of lignin model glycosides produced by stereoselective reductions[14] and to the benzylated pair of *erythro*- and *threo*-diastereomers of lignin–methyl glucoside benzyl ether models.[15] In the present study we report that it is also possible to separate most of the individual LCC diastereomers in non-acetylated form from a mixture of diastereomers of two different LCC products (Fig. 2). To accomplish this we fractionated the crude LCC products by flash chromatography and the enriched diastereomer fractions were separated by HPLC. Combination of flash and HPLC chromatography gave better separation results than did HPLC alone due to incomplete resolution of diastereomers in HPLC. Assignments of the *erythro*- and *threo*-LCC model compounds were made from ^{1}H NMR signals of the propyl side-chain protons in analogy with previous work on β-*O*-4 lignin model compounds.[16]

Experimental

General

Methyl α-D-galactopyranoside **3** was obtained from Fluka. LCC samples were acetylated with pyridine and acetic anhydride (1:1) at RT overnight. Analytical TLC was performed on silica gel 60 F_{254} plates (Merck) and compounds were visualized by charring (9:1 H_2SO_4–formalin) and then heating. Silica gel 60, 230–400 mesh (Merck) was used for flash column chromatography. Semi-preparative HPLC experiments were carried out on a Waters liquid chromatograph consisting of a Waters 600E multisolvent delivery system and a Waters 996

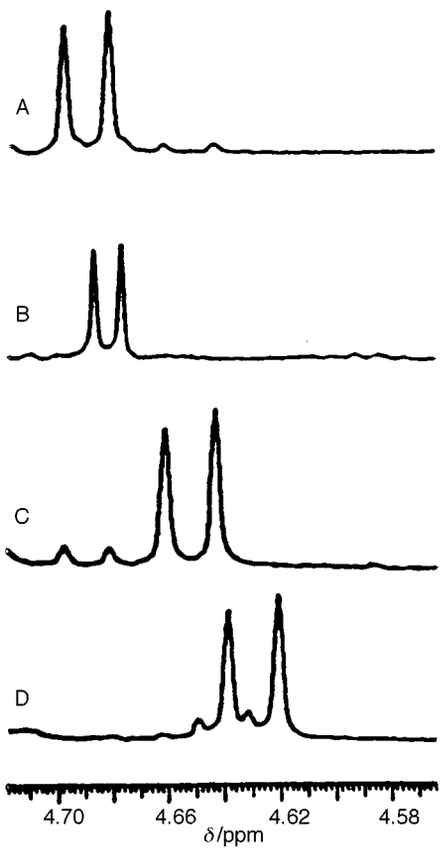


Fig. 2 ^{1}H NMR spectra of benzylic proton region of the diastereomers of LCC model **4**. A, *threo*$_2$ (300 MHz); B, *threo*$_1$ (600 MHz); C, *erythro*$_2$ (300 MHz) and D, *erythro*$_1$ (300 MHz).

photodiode array detector. Components were monitored by measuring the absorption at 260 nm. A Merck LiChrospher Si60 (5 μm) column was used for HPLC separation. Mass spectra were run on a JEOL JMS-SX102 instrument. Optical rotations were recorded on a JASCO DIP-1000 polarimeter, with $[a]_D$-values given in units of 10^{-1} deg cm^2 g^{-1}. NMR spectra were recorded in [$^2H_6$]acetone with the central solvent peak serving as the internal reference (δ_H 2.04, δ_C 29.8) with Varian Inova 300 MHz or Varian Unity 600 MHz instruments; *J*-values are given in Hz. The spectra were measured at 27 °C, non-spinning. Samples for which multiplicity problems with OH–OD exchange were encountered were exchanged with D_2O prior to measurements. Inverse-detected ^{1}H–^{13}C correlation HMQC† spectra were measured according to the method of Summers *et al.*[17] The delay for polarization transfer between ^{13}C and ^{1}H was set for an assumed $^1J_{C-H}$ = 140 Hz and a relaxation delay of 0.9 s was used between scans. The spectral width in F2 was set to 3 kHz (4.5 kHz at 600 MHz) and to 18 kHz (20 kHz at 151 MHz) in F1. GARP-1 decoupling was used in the ^{13}C channel during acquisition. 128 or 160 Time increments and 32 scans per increment were collected by the hypercomplex method. The spectra were processed using 90°-shifted squared sinebell functions in both domains prior to Fourier transformation. Homonuclear Hartman–Hahn spectra, HOHAHA, were recorded using the method of Griesinger *et al.*[18] The spectral width was 3 kHz (4.5 kHz at 600 MHz) (F1 = F2). A relaxation delay of 2.0 s was used between scans. Spin-lock periods were 40–120 ms (MLEV-17). 160 Time increments and 16 or 32 scans per increment were collected by the hypercomplex method. The spectra were processed using 90°-shifted squared sinebell functions in both domains prior to Fourier transformation. Homonuclear nuclear Overhauser enhancement (NOESY) spectra were recorded using the standard NOESY pulse sequence on the Varian spectrometer. The spectral width was 2 kHz (4.5 kHz at 600 MHz) (F1 = F2). A relaxation delay of 2.0 s was used between scans. Mixing time was 1.0 s. 128 Time increments and 32 scans per increment were collected by the hypercomplex method. The spectra were processed using 90°-shifted squared sinebell functions in both domains prior to Fourier transformation.

† 2D Heteronuclear multiple quantum-filtered coherence.

1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol

1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-propane-1,3-diol was prepared by the Adler method.[19] Benzylation of acetovanillone, bromination, coupling with guaiacol, hydroxymethylation, reduction and debenzylation gave the title product (62% overall).

Methyl α-L-arabinofuranoside 2

A solution of L-(+)-arabinose (2 mmol) and conc. sulfuric acid (0.2 ml) in dry methanol (45 ml) was stirred at RT until the solution was clear (24 h). The reaction mixture was made neutral by filtration through Amberlite IRA-410 resin, dried with Na_2SO_4 and evaporated to dryness. Methyl α-L-arabinofuranoside was separated from methyl β-L-arabinofuranoside on silica gel with 20 : 1 methylene dichloride–methanol.

β-*O*-4-Type quinone methide 1

Quinone methide was prepared from 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol using the TMSBr method of Brunow *et al.*[20]

Formation of LCC models[8]

Quinone methides of 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol (1.5 mol equiv.), monosaccharides (7.5 mol equiv.) and PTSA (0.1 mol equiv.) were dissolved in dry DMF (5 ml) and stirred in argon for 4 h. The reaction mixture was poured into distilled water. LCC and unchanged lignin model were extracted with chloroform, and the extract was dried over Na_2SO_4 and evaporated to dryness. TLC indicated that water phases contained monosaccharides only. The yield of methyl arabinoside LCC models was 55–60% and that of methyl galactoside LCC models 40–48%.

Purification

Methyl arabinoside LCC models were separated on silica gel, using 20 : 1 methylene dichloride–methanol. From 4 diastereomers both *threo*-isomers eluted before the *erythro*-isomers. The first *threo*-isomer, t_1, eluted as a pure fraction by flash separation. Secondary flash purification with 22 : 1 methylene dichloride–methanol gave the other *threo*-isomer, t_2. Finally the mixture of *erythro*-isomers was separated by HPLC with a silica column, using methylene dichloride–propan-2-ol (88 : 12 v/v) as eluent.

Methyl galactoside LCC models were pre-purified on silica gel with 12 : 1 methylene dichloride–methanol. The pure pair of *threo*-isomers of the C-3 adduct eluted first on silica gel. Next to elute were the pair of *erythro*-isomers of the C-3 adduct, but they were not separated from *threo*-isomers. Both *threo*-isomers of the C-6-bonded galactoside eluted faster than the *erythro*-isomers. Flash fractions of the C-6 adduct were enriched to afford a pair of *erythro*- or *threo*-isomers and they were separated to give the individual diastereomers by HPLC with methylene dichloride–propan-2-ol (81 : 19 v/v).

Compound 4. *erythro*$_1$: 83% purity by ^{1}H NMR spectroscopy, $[a]_D^{22}$ −11.4 (*c* 0.3, acetone); δ_H(300 MHz) 3.29 (3 H, s, OCH_3, Ara), 3.51 (1 H, dd, *J* 5.8 and 10.6, Ara-5), 3.61 (1 H, dd, *J* 3.9

and 10.5, Ara-5), 3.74 (1 H, d, *J* 3.8, H_γ), 3.76 (3 H, s, OCH_3, Ar), 3.80 (1 H, overlapped with OCH_3, H_γ), 3.82 (3 H, s, OCH_3, Ar), 3.86 (1 H, m, Ara-3), 3.93 (1 H, m, Ara-2), 4.01 (1 H, dt, *J* 5.9 and 4.0, Ara-4), 4.33 (1 H, dt, *J* 4.2 and 6.4, H_β), 4.63 (1 H, d, *J* 6.4, H_α), 4.73 (1 H, d, *J* 1.4, Ara-1) and 6.74–7.10 (7 H, Ar); δ_C(75 MHz) 54.8 (OCH_3, Ara), 56.2 (OCH_3, Ar), 61.9 (C_γ), 70.3 (Ara-5), 79.6 (Ara-3), 82.4 (C_α), 83.1 (Ara-2), 83.9 (Ara-4), 85.3 (C_β), 110.4 (Ara-1) and 112.1, 113.6, 115.2, 119.1, 121.7, 123.0, 131.1, 147.0, 148.0, 148.8 and 151.6 (Ar).

Compound 4. *erythro*$_2$: 86% purity by ^{1}H NMR spectroscopy, $[\alpha]_D^{23}$ −27.8 (*c* 0.3, acetone); δ_H(300 MHz) 3.30 (3 H, s, OCH_3, Ara), 3.57 (1 H, d, *J* 4.6, Ara-5), 3.71–3.76 (1 H, dd, overlapped with OCH_3, *J* 4.0, H_γ), 3.77 (3 H, s, OCH_3, Ar), 3.83 (1 H, dd, *J* 4.6 and 11.7, H_γ), 3.83 (3 H, s, OCH_3, Ar), 3.90 (1 H, m, Ara-3), 3.93 (1 H, m, Ara-2), 4.00 (1 H, dt, *J* 4.3 and 5.9, Ara-4), 4.30 (1 H, dt, *J* 4.3 and 6.4, H_β), 4.65 (1 H, d, *J* 6.6, H_α), 4.73 (1 H, d, *J* 1.3, Ara-1) and 6.74–7.11 (7 H, Ar); δ_C(75 MHz) 54.8 (OCH_3, Ara), 56.2 (OCH_3, Ar), 61.8 (C_γ), 69.8 (Ara-5), 79.7 (Ara-3), 82.3 (C_α), 83.3 (Ara-2), 83.6 (Ara-4), 85.4 (C_β), 110.4 (Ara-1) and 112.1, 113.6, 115.2, 119.2, 121.7, 123.1, 131.1, 147.2, 148.2, 149.0 and 151.8 (Ar).

Compound 4. *threo*$_1$: 98% purity by ^{1}H NMR spectroscopy, $[\alpha]_D^{23}$ −46.5 (*c* 0.5, acetone); δ_H(600 MHz) 3.29 (3 H, s, OCH_3, Ara), 3.43 (1 H, dt, *J* 5.8, 5.8 and 11.5, H_γ), 3.57 (2 H, d, *J* 4.2, Ara-5), 3.60 (1 H, ddd, *J* 4.3, 6.7 and 11.5, H_γ), 3.82 (3 H, s, OCH_3, Ar), 3.83 (3 H, s, OCH_3, Ar), 3.91 (1 H, m, Ara-3), 3.92 (1 H, m, Ara-2), 4.00 (1 H, dt, *J* 4.2 and 5.3, Ara-4), 4.30 (1 H, dt, *J* 5.8 and 4.3, H_β), 4.68 (1 H, d, *J* 5.8, H_α), 4.73 (1 H, dd, *J* 1.0 and 1.0, Ara-1), 6.81 (1 H, d, *J* 8.0, H-5), 6.83 (1 H, ddd, *J* 1.6, 7.4 and 7.9, H-6′), 6.89 (1 H, dd, *J* 1.8 and 8.0, H-6), 6.91 (1 H, ddd, *J* 1.6, 7.9 and 8.0, H-1′), 6.95 (1 H, dd, *J* 1.6 and 8.0, H-2′), 7.10 (1 H, d, *J* 1.8, H-2) and 7.14 (1 H, dd, *J* 1.6 and 7.9, H-5′); δ_C(151 MHz) 54.8 (OCH_3, Ara), 56.3, 56.4 (OCH_3, Ar), 61.9 (C_γ), 70.0 (Ara-5), 79.6 (Ara-3), 82.7 (C_α), 83.1 (Ara-2), 84.4 (Ara-4), 86.3 (C_β), 110.5 (Ara-1), 112.0 (C-2), 113.6 (C-2′), 115.5 (C-5), 119.7 (C-5′), 121.5 (C-6), 122.0 (C-6′), 123.2 (C-1′), 130.8 (C-1), 147.4 (C-4), 148.4 (C-3), 149.9 (C-4′) and 151.9 (C-3′).

Compound 4. *threo*$_2$: 93% purity by ^{1}H NMR spectroscopy, $[\alpha]_D^{23}$ −12.3 (*c* 0.7, acetone); δ_H(300 MHz) 3.29 (3 H, s, OCH_3, Ara), 3.44 (1 H, dd, *J* 5.8 and 11.5, H_γ), 3.54 (2 H, dd, *J* 5.3 and 10.5, Ara-5), 3.62 (1 H, dd, *J* 3.9 and 10.4, H_γ), 3.83 (6 H, s, OCH_3, Ar), 3.86 (1 H, m, Ara-3), 3.91 (1 H, m, Ara-2), 4.03 (1 H, dt, *J* 5.5 and 3.9, Ara-4), 4.31 (1 H, dt, *J* 5.8 and 4.4, H_β), 4.69 (1 H, d, *J* 5.7, H_α), 4.73 (1 H, d, *J* 1.0, Ara-1) and 6.78–7.16 (7 H, Ar); δ_C(75 MHz) 54.8 (OCH_3, Ara), 56.2, 56.3 (OCH_3, Ar), 61.8 (C_γ), 70.3 (Ara-5), 79.7 (Ara-3), 82.3 (C_α), 83.0 (Ara-2), 84.2 (Ara-4), 86.2 (C_β), 110.5 (Ara-1) and 111.9, 113.5, 115.4, 119.3, 121.4, 121.9, 123.0, 130.7, 147.2, 148.3, 149.8 and 151.6 (Ar).

Compound 6. *erythro*$_1$: 87% purity by ^{1}H NMR spectroscopy, $[\alpha]_D^{22}$ 36.5 (*c* 1.1, acetone); δ_H(300 MHz) 3.34 (3 H, s, OCH_3, Gal), 3.50 (2 H, dd, *J* 7.1 and 10.0, Gal-6), 3.65 (1 H, m, Gal-5), 3.69 (2 H, m, Gal-3 and -2), 3.76 (3 H, s, OCH_3, Ar), 3.79 (2 H, d, *J* 5.0, H_γ), 3.82 (3 H, s, OCH_3, Ar), 3.87 (1 H, m, Gal-4), 4.33 (1 H, dt, *J* 5.9 and 4.6, H_β), 4.61 (1 H, d, *J* 6.0, H_α), 4.65 (1 H, d, *J* 1.5, Gal-1) and 6.74–7.10 (7 H, Ar); δ_C(75 MHz) 55.4 (OCH_3, Gal), 56.3 (OCH_3, Ar), 62.0 (C_γ), 69.6 (Gal-6), 70.1 (Gal-5), 70.3 (Gal-3, -4), 71.2 (Gal-2), 82.9 (C_α), 85.3 (C_β), 101.2 (Gal-1) and 112.2, 113.6, 115.2, 119.0, 121.7, 123.0, 131.2, 147.1, 148.2, 149.2 and 151.8 (Ar).

Compound 6. *erythro*$_2$: 88% purity by ^{1}H NMR spectroscopy, $[\alpha]_D^{24}$ 26.2 (*c* 0.8, acetone); δ_H(300 MHz) 3.34 (3 H, s, OCH_3, Gal), 3.50 (2 H, dd, *J* 7.1 and 10.1, Gal-6), 3.65 (1 H, m, Gal-5), 3.69 (2 H, m, Gal-2 and -3), 3.76 (3 H, s, OCH_3, Ar), 3.77–3.83 (2 H, m, H_γ), 3.81 (3 H, s, OCH_3, Ar), 3.86 (1 H, m, Gal-4), 4.34 (1 H, dt, *J* 5.9 and 4.6, H_β), 4.61 (1 H, d, *J* 6.1, H_α), 4.65 (1 H, d, *J* 3.0, Gal-1) and 6.73–7.64 (7 H, Ar); δ_C(75 MHz) 55.4 (OCH_3, Gal), 56.2 (OCH_3, Ar), 62.1 (C_γ), 69.6 (Gal-6), 70.3 (Gal-5), 71.2 (Gal-2, -3, -4), 82.8 (C_α), 85.2 (C_β), 101.2 (Gal-1) and 112.1, 113.5, 115.2, 118.9, 121.7, 122.9, 131.1, 147.1, 148.1, 149.2 and 151.7 (Ar).

Compound 6. *threo*$_1$: 95% purity by ^{1}H NMR spectroscopy, $[\alpha]_D^{24}$ 33.7 (*c* 1.0, acetone); δ_H(300 MHz) 3.31 (3 H, s, OCH_3, Gal), 3.42 (1 H, dd, *J* 6.2 and 11.7, H_γ), 3.47 (2 H, dd, *J* 6.5 and 10.0, Gal-6), 3.56 (1 H, dd, *J* 3.9 and 11.9, H_γ), 3.67 (3 H, m, Gal-2, -3 and -5), 3.83 (6 H, s, OCH_3, Ar), 3.88 (1 H, m, Gal-4), 4.32 (1 H, dt, *J* 6.2 and 3.8, H_β), 4.62 (1 H, d, *J* 1.8, Gal-1), 4.66 (1 H, d, *J* 6.1, H_α) and 6.79–7.18 (7 H, Ar); δ_C(75 MHz) 55.4 (OCH_3, Gal), 56.2 (OCH_3, Ar), 62.0 (C_γ), 69.4 (Gal-6), 70.1 (Gal-2), 70.3 (Gal-5 and -4), 71.2 (Gal-3), 82.9 (C_α), 86.2 (C_β), 101.2 (Gal-1) and 111.8, 113.5, 115.3, 119.1, 121.4, 121.8, 122.8, 130.9, 147.1, 148.2, 150.1 and 151.6 (Ar).

Compound 6. *threo*$_2$: 92% purity by ^{1}H NMR spectroscopy, $[\alpha]_D^{24}$ 9.1 (*c* 0.2, acetone); δ_H(300 MHz) 3.31 (3 H, s, OCH_3, Gal), 3.42 (1 H, dd, *J* 6.1 and 11.4, H_γ), 3.47 (2 H, dd, *J* 6.6 and 10.1, Gal-6), 3.56 (1 H, dd, *J* 3.7 and 12.1, H_γ), 3.67 (3 H, m, Gal-2, -3 and -5), 3.83 (6 H, s, OCH_3, Ar), 3.87 (1 H, m, Gal-4), 4.32 (1 H, dt, *J* 6.2 and 3.8, H_β), 4.61 (1 H, d, *J* 1.8, Gal-1), 4.66 (1 H, d, *J* 6.1, H_α) and 6.79–7.18 (7 H, Ar); δ_C(75 MHz) 55.4 (OCH_3, Gal), 56.3 (OCH_3, Ar), 62.0 (C_γ), 69.4 (Gal-6), 70.1 (Gal-2), 70.3 (Gal-4 and -5), 71.2 (Gal-3), 83.0 (C_α), 86.3 (C_β), 101.2 (Gal-1) and 111.8, 113.5, 115.3, 119.2, 121.4, 121.8, 122.8, 130.8, 147.1, 148.3, 150.2 and 151.7 (Ar).

Compound 8. *erythro*: 61% purity by ^{1}H NMR spectroscopy, $[\alpha]_D^{25}$ 52.6 (*c* 0.2, acetone); δ_H(300 MHz) 3.24 (3 H, s, OCH_3, Gal), 3.47 (1 H, dd, *J* 3.2 and 9.7, Gal-3), 3.62 (1 H, m, Gal-5), 3.74 (2 H, d, *J* 6.0, Gal-6), 3.77 (3 H, s, OCH_3, Ar), 3.81 (3 H, s, OCH_3, Ar), 3.85 (1 H, dd, *J* 2.5 and 9.3, H_γ), 3.92 (1 H, dd, *J* 3.6 and 9.9, Gal-2), 4.00 (1 H, dd, *J* 3.5 and 12.3, H_γ), 4.27–4.33 (2 H, m, H_β, Gal-4), 4.65 (1 H, d, *J* 3.6, Gal-1), 4.94 (1 H, d, *J* 6.8, H_α) and 6.73–7.32 (7 H, Ar); δ_C(75 MHz) 55.0 (OCH_3, Gal), 56.1 (OCH_3, Ar), 61.0 (C_γ), 62.7 (Gal-6), 65.7 (Gal-4), 68.7 (Gal-2), 71.3 (Gal-5), 75.9 (Gal-3), 76.3 (C_α), 85.3 (C_β), 101.0 (Gal-1) and 111.9, 113.4, 115.1, 118.2, 121.6, 121.7, 122.9, 131.4, 146.9, 148.5, 149.4 and 151.6.

Compound 8. *threo*: 99% purity by ^{1}H NMR spectroscopy, $[\alpha]_D^{26}$ 110.1 (*c* 0.7, acetone); δ_H(300 MHz) 3.23 (3 H, s, OCH_3, Gal), 3.43 (1 H, dd, *J* 4.7 and 12.1, H_γ), 3.48 (1 H, dd, *J* 3.2 and 9.8, Gal-3), 3.62 (1 H, m, Gal-5), 3.71–3.77 (3 H, m, H_γ and Gal-6), 3.82 (3 H, s, OCH_3, Ar), 3.83 (3 H, s, OCH_3, Ar), 3.84 (1 H, m, Gal-2), 4.27–4.32 (2 H, m, H_β and Gal-4), 4.60 (1 H, d, *J* 4.0, Gal-1), 4.94 (1 H, d, *J* 7.6, H_α) and 6.77–7.51 (7 H, Ar); δ_C(75 MHz) 55.0 (OCH_3, Gal), 56.1 (OCH_3, Ar), 61.1 (C_γ), 62.6 (Gal-6), 65.6 (Gal-4), 68.5 (Gal-2), 71.4 (Gal-5), 76.2 (Gal-3), 77.1 (C_α), 85.8 (C_β), 101.0 (Gal-1) and 112.3, 113.0, 115.2, 117.8, 121.7, 122.0, 122.7, 130.5, 147.3, 148.4, 149.5 and 151.2.

Per-acetates

Compound 5. *erythro*$_1$: δ_H(300 MHz) 1.92, 2.02, 2.04 and 2.22 ($COCH_3$), 3.32 (3 H, s, OCH_3, Ara), 3.70 (2 H, d, *J* 3.8, Ara-5), 3.77 (3 H, s, OCH_3, Ar), 3.82 (3 H, s, OCH_3, Ar), 4.16 (1 H, dt, *J* 4.1 and 5.3, Ara-4), 4.43 (2 H, dd, *J* 5.5 and 11.9, H_γ), 4.62 (1 H, dt, *J* 5.6 and 3.5, H_β), 4.79 (1 H, d, *J* 5.8, H_α), 4.91 (1 H, s, Ara-1), 5.0 (1 H, dd, *J* 0.5 and 1.7, Ara-2), 5.17 (1 H, ddd, *J* 0.6, 1.7 and 5.4, Ara-3) and 6.77–7.24 (7 H, Ar); δ_C(75 MHz) 20.5 and 20.7 ($CO\mathit{C}H_3$), 54.7 (OCH_3, Ara), 56.2 (OCH_3, Ar), 63.5 (C_γ), 69.6 (Ara-5), 78.2 (Ara-3), 81.9 (C_α), 82.0 (C_β), 82.3 (Ara-4), 82.4 (Ara-2), 107.5 (Ara-1), 112.5, 113.8, 119.7, 120.6, 121.6, 123.2, 123.6, 138.3, 140.5, 148.4, 152.0 and 152.1 (Ar)

and 168.9, 170.2, 170.5 and 170.8 (*C*OCH$_3$); HRMS: $C_{31}H_{38}O_{14}$ requires *M*, 634.2262. Found: M$^+$, 634.2270.

Compound 5. *erythro*$_2$: δ_H(300 MHz) 1.93, 2.02, 2.03 and 2.21 (COCH$_3$), 3.33 (3 H, s, OCH$_3$, Ara), 3.70 (2 H, d, *J* 4.0, Ara-5), 3.76 (3 H, s, OCH$_3$, Ar), 3.81 (3 H, s, OCH$_3$, Ar), 4.16 (1 H, dt, *J* 4.1 and 5.6, Ara-4), 4.34 (1 H, dd, *J* 3.4 and 11.7, H$_\gamma$), 4.45 (1 H, dd, *J* 5.7 and 11.7, H$_\gamma$), 4.62 (1 H, dt, *J* 5.8 and 3.5, H$_\beta$), 4.76 (1 H, d, *J* 5.9, H$_\alpha$), 4.89 (1 H, s, Ara-1), 4.98 (1 H, dd, *J* 0.5 and 1.7, Ara-2), 5.13 (1 H, ddd, *J* 0.6, 1.7 and 5.7, Ara-3) and 6.76–7.24 (7 H, Ar); δ_C(75 MHz) 20.5 and 20.7 (CO*C*H$_3$), 54.7 (OCH$_3$, Ara), 56.2 (OCH$_3$, Ar), 63.7 (C$_\gamma$), 69.8 (Ara-5), 77.9 (Ara-3), 82.0 (C$_\alpha$ and C$_\beta$), 82.1 (Ara-4), 82.6 (Ara-2), 107.5 (Ara-1), 112.6, 113.7, 119.5, 120.7, 121.6, 123.2, 123.6, 138.3, 140.5, 148.6, 151.9 and 152.1 (Ar) and 168.9, 170.1, 170.6 and 170.9 (*C*OCH$_3$); HRMS: Found: M$^+$, 634.2270.

Compound 5. *threo*$_1$: δ_H(300 MHz) 1.92, 2.01, 2.02 and 2.22 (COCH$_3$), 3.31 (3 H, s, OCH$_3$, Ara), 3.72 (2 H, dd, *J* 3.9 and 11.7, Ara-5), 3.81 (3 H, s, OCH$_3$, Ar), 3.82 (3 H, s, OCH$_3$, Ar), 4.06 (1 H, dd, *J* 6.6 and 11.6, H$_\gamma$), 4.14 (1 H, dt, *J* 5.1 and 3.8, Ara-4), 4.28 (1 H, dd, *J* 4.1 and 11.6, H$_\gamma$), 4.66 (1 H, dt, *J* 4.6 and 6.6, H$_\beta$), 4.84 (1 H, d, *J* 5.0, H$_\alpha$), 4.87 (1 H, s, Ara-1), 4.97 (1 H, dd, *J* 0.6 and 1.7, Ara-2), 5.12 (1 H, ddd, *J* 0.6, 1.7 and 5.6, Ara-3) and 6.80–7.27 (7 H, Ar); δ_C(75 MHz) 20.5, 20.6 (CO*C*H$_3$), 54.7 (OCH$_3$, Ara), 56.2 (OCH$_3$, Ar), 64.1 (C), 69.7 (Ara-5), 78.0 (Ara-3), 81.5 (C$_\beta$), 82.3 (Ara-4 and C$_\alpha$), 82.5 (Ara-2), 107.5 (Ara-1), 112.7, 113.7, 118.7, 120.4, 121.6, 123.3, 137.7, 140.6, 149.4, 151.7 and 152.1 (Ar) and 168.9, 170.2, 170.5 and 170.8 (*C*OCH$_3$); HRMS: Found: M$^+$, 634.2247.

Compound 5. *threo*$_2$: δ_H(300 MHz) 1.91, 1.97, 2.01 and 2.22 (COCH$_3$), 3.31 (3 H, s, OCH$_3$, Ara), 3.70 (2 H, dd, *J* 2.8 and 4.5, Ara-5), 3.81 (3 H, s, OCH$_3$, Ar), 3.82 (3 H, s, OCH$_3$, Ar), 4.03 (1 H, dd, *J* 6.4 and 11.6, H$_\gamma$), 4.14 (1 H, m, Ara-4), 4.28 (1 H, dd, *J* 4.0 and 11.7, H$_\gamma$), 4.63 (1 H, dt, *J* 4.6 and 6.6, H$_\beta$), 4.84 (1 H, d, *J* 5.2, H$_\alpha$), 4.87 (1 H, s, Ara-1), 4.96 (1 H, dd, *J* 0.6 and 1.7, Ara-2), 5.09 (1 H, ddd, *J* 0.6, 1.7 and 5.4, Ara-3) and 6.80–7.28 (7 H, Ar); δ_C(75 MHz) 20.5 and 20.7 (CO*C*H$_3$), 54.7 (OCH$_3$, Ara), 56.2 (OCH$_3$, Ar), 64.1 (C$_\gamma$), 69.8 (Ara-5), 78.2 (Ara-3), 81.6 (C$_\beta$), 82.2 (Ara-4 and C$_\alpha$), 82.3 (Ara-2), 107.5 (Ara-1), 112.7, 113.7, 118.8, 120.6, 121.6, 123.2, 137.7, 140.6, 149.4, 151.7 and 152.2 (Ar) and 168.9, 170.1, 170.5 and 170.7 (*C*OCH$_3$); HRMS: Found: M$^+$, 634.2247.

Compound 7. *erythro*$_1$: δ_H(300 MHz) 1.90, 1.92, 1.95, 2.00 and 2.21 (COCH$_3$), 3.38 (3 H, s, OCH$_3$, Gal), 3.49 (2 H, d, *J* 6.8, Gal-6), 3.74 (3 H, s, OCH$_3$, Ar), 3.78 (3 H, s, OCH$_3$, Ar), 4.23 (1 H, m, Gal-5), 4.36 (1 H, d, *J* 3.3, H$_\gamma$), 4.38 (1 H, dd, *J* 1.7 and 3.3, H$_\gamma$), 4.62–4.67 (2 H, m, H$_\alpha$ and H$_\beta$), 4.93 (1 H, d, *J* 3.7, Gal-1), 5.02 (1 H, dd, *J* 3.7 and 11.0, Gal-2), 5.29 (1 H, dd, *J* 3.4 and 10.9, Gal-3), 5.46 (1 H, dd, *J* 1.4 and 3.5, Gal-4) and 6.75–7.25 (7 H, Ar); δ_C(75 MHz) 20.5, 20.6 and 20.7 (CO*C*H$_3$), 55.7 (OCH$_3$, Gal), 56.1 (OCH$_3$, Ar), 63.7 (C$_\gamma$), 67.7 (Gal-6), 67.8 (Gal-5), 68.4 (Gal-3), 68.9 (Gal-2), 69.0 (Gal-4), 81.6 (C$_\beta$), 82.2 (C$_\alpha$), 98.0 (Gal-1), 112.9, 113.6, 119.4, 121.0, 121.5, 123.1, 123.5, 137.9, 140.7, 148.6, 151.8 and 152.1 (Ar) and 168.9, 170.2, 170.6 and 170.8 (*C*OCH$_3$); HRMS: $C_{34}H_{42}O_{16}$ requires *M*, 706.2473. Found: M$^+$, 706.2457.

Compound 7. *erythro*$_2$: δ_H(300 MHz) 1.90, 1.92, 1.95, 2.00 and 2.21 (COCH$_3$), 3.38 (3 H, s, OCH$_3$, Gal), 3.49 (2 H, d, *J* 6.6, Gal-6), 3.74 (3 H, s, OCH$_3$, Ar), 3.78 (3 H, s, OCH$_3$, Ar), 4.23 (1 H, m, Gal-5), 4.36 (1 H, d, *J* 3.4, H$_\gamma$), 4.37 (1 H, dd, *J* 1.5 and 3.4, H$_\gamma$), 4.60–4.70 (2 H, m, H$_\alpha$ and H$_\beta$), 4.93 (1 H, d, *J* 3.6, Gal-1), 5.02 (1 H, dd, *J* 3.6 and 10.8, Gal-2), 5.29 (1 H, dd, *J* 3.5 and 10.9, Gal-3), 5.46 (1 H, dd, *J* 1.4 and 3.4, Gal-4) and 6.75–7.25 (7 H, Ar); δ_C(75 MHz) 20.5, 20.6 and 20.7 (CO*C*H$_3$) 55.7 (OCH$_3$, Gal), 56.1 and 56.2 (OCH$_3$, Ar), 63.7 (C$_\gamma$), 67.7 (Gal-6), 67.8 (Gal-5), 68.4 (Gal-3), 68.9 (Gal-2), 69.0 (Gal-4), 81.5 (C$_\beta$), 82.1 (C$_\alpha$), 98.0 (Gal-1), 112.9, 113.6, 119.4, 121.0, 121.5, 123.1, 123.5, 137.9, 140.7, 148.6, 151.8 and 152.1 (Ar) and 168.9, 170.3, 170.6 and 170.8 (*C*OCH$_3$); HRMS: Found: M$^+$, 706.2457.

Compound 7. *threo*$_1$: δ_H(300 MHz) 1.90, 1.91, 1.99 and 2.22 (COCH$_3$), 3.36 (3 H, s, OCH$_3$, Gal), 3.44 (2 H, dd, *J* 1.9 and 6.7, Gal-6), 3.82 (3 H, s, OCH$_3$, Ar), 3.83 (3 H, s, OCH$_3$, Ar), 3.94 (1 H, dd, *J* 4.8 and 11.8, H$_\gamma$), 4.03 (1 H, m, Gal-5), 4.15 (1 H, dd, *J* 3.2 and 12.0, H$_\gamma$), 4.70 (2 H, m, H$_\alpha$ and H$_\beta$), 4.90 (1 H, d, *J* 3.5, Gal-1), 4.98 (1 H, dd, *J* 3.6 and 10.9, Gal-2), 5.22 (1 H, dd, *J* 3.4 and 10.9, Gal-3), 5.36 (1 H, dd, *J* 1.4 and 3.4, Gal-4) and 6.83–7.13 (7 H, Ar); δ_C(75 MHz) 20.5 and 20.6 (CO*C*H$_3$), 55.7 (OCH$_3$, Gal), 56.2 (OCH$_3$, Ar), 64.0 (C$_\gamma$), 67.7 (Gal-6), 67.8 (Gal-5), 68.3 (Gal-3), 68.8 (Gal-2), 69.0 (Gal-4), 81.3 (C$_\beta$), 83.4 (C$_\alpha$), 98.0 (Gal-1), 112.8, 113.7, 119.0, 120.6, 121.6, 123.3, 123.4, 137.4, 140.8, 149.5, 151.8 and 152.3 (Ar) and 168.9, 170.2, 170.6, 170.7 and 170.7 (*C*OCH$_3$); HRMS: Found: M$^+$, 706.2490.

Compound 7. *threo*$_2$: δ_H(300 MHz) 1.90, 1.91, 2.00 and 2.22 (COCH$_3$), 3.31 (3 H, s, OCH$_3$, Gal), 3.58 (2 H, m, Gal-6), 3.81 (6 H, s, OCH$_3$, Ar), 3.99 (1 H, dd, *J* 6.4 and 11.7, H$_\gamma$), 4.17 (1 H, m, Gal-5), 4.22 (1 H, dd, *J* 4.0 and 11.8, H$_\gamma$), 4.61 (1 H, m, H$_\beta$), 4.74 (1 H, d, *J* 5.1, H$_\alpha$), 4.92 (1 H, d, *J* 3.6, Gal-1), 5.04 (1 H, dd, *J* 3.6 and 10.9, Gal-2), 5.28 (1 H, dd, *J* 3.5 and 11.0, Gal-3), 5.49 (1 H, dd, *J* 1.4 and 3.5, Gal-4) and 6.81–7.24 (7 H, Ar); δ_C(75 MHz) 20.5 and 20.6 (CO*C*H$_3$), 55.5 (OCH$_3$, Gal), 56.2 (OCH$_3$, Ar), 63.9 (C$_\gamma$), 68.3 (Gal-5), 68.9 (Gal-3), 69.1 (Gal-2 and -6), 69.6 (Gal-4), 81.2 (C$_\beta$), 82.1 (C$_\alpha$), 97.9 (Gal-1), 112.7, 113.7, 118.6, 120.4, 121.6, 123.3, 137.6, 140.6, 149.2, 151.7 and 152.1 (Ar) and 168.9, 170.2, 170.6, 170.7 and 170.8 (*C*OCH$_3$); HRMS: Found: M$^+$, 706.2490.

Compound 9. *erythro*: δ_H(300 MHz) 1.70, 1.83, 2.00, 2.13 and 2.22 (COCH$_3$), 3.28 (3 H, s, OCH$_3$, Gal), 3.80 (3 H, s, OCH$_3$, Ar), 3.81 (3 H, s, OCH$_3$, Ar), 3.87 (1 H, d, *J* 3.6, Gal-6), 3.98 (1 H, d, *J* 3.4, Gal-6), 4.01 (1 H, m, Gal-5), 4.19 (2 H, d, *J* 5.8, H$_\gamma$), 4.19–4.25 (1 H, m, overlapped with H$_\gamma$, Gal-3), 4.62 (1 H, m, H$_\beta$), 4.84 (1 H, d, *J* 3.6, Gal-1), 5.00 (1 H, d, *J* 4.3, H$_\alpha$), 5.05 (1 H, dd, *J* 3.7 and 10.6, Gal-2), 5.81 (1 H, d, *J* 3.3, Gal-4) and 6.80–7.25 (7 H, Ar); δ_C(75 MHz) 20.5, 20.6, 20.7 and 20.8 (CO*C*H$_3$), 55.3 (OCH$_3$, Gal), 56.2 and 56.3 (OCH$_3$, Ar), 62.9 (Gal-6), 63.1 (C$_\gamma$), 67.8 (Gal-5), 69.3 (Gal-4), 71.0 (Gal-2), 74.1 (Gal-3), 81.1 (C$_\alpha$), 81.9 (C$_\beta$), 98.1 (Gal-1), 112.8, 113.6, 118.4, 120.5, 121.6, 123.2, 123.3, 137.8, 140.4, 148.9, 151.6 and 151.9 (Ar) and 169.0, 170.7, 170.8 and 170.9 (*C*OCH$_3$); HRMS: Found: M$^+$, 706.2466.

Compound 9. *threo*: δ_H(300 MHz) 1.86, 1.94, 1.98, 2.08 and 2.22 (COCH$_3$), 3.30 (3 H, s, OCH$_3$, Gal), 3.81 (6 H, s, OCH$_3$, Ar), 3.92 (1 H, dd, *J* 6.4 and 11.7, H$_\gamma$), 3.97 (1 H, d, *J* 3.5, Gal-6), 4.07 (1 H, m, Gal-5), 4.09 (1 H, d, *J* 4.5, Gal-6), 4.17 (1 H, dd, *J* 4.0 and 11.7, H$_\gamma$), 4.22 (1 H, dd, *J* 3.3 and 10.6, Gal-3), 4.62 (1 H, m, H$_\beta$), 4.88 (1 H, d, *J* 3.8, Gal-1), 5.02 (1 H, d, *J* 5.6, H$_\alpha$), 5.05 (1 H, dd, *J* 3.7 and 10.6, Gal-2), 5.63 (1 H, d, *J* 3.1, Gal-4) and 6.82–7.20 (7 H, Ar); δ_C(75 MHz) 20.5, 20.6, 20.7 and 20.8 (CO*C*H$_3$), 55.3 (OCH$_3$, Gal), 56.2 and 56.3 (OCH$_3$, Ar), 63.0 (Gal-6), 63.6 (C$_\gamma$), 67.6 (Gal-5), 68.7 (Gal-4), 71.0 (Gal-2), 73.1 (Gal-3), 79.8 (C$_\alpha$), 80.6 (C$_\beta$), 98.1 (Gal-1), 113.4, 113.5, 117.8, 120.8, 121.7, 122.0, 123.2, 137.2, 140.7, 148.9, 151.4 and 151.9 (Ar) and 169.0, 170.6, 170.7 and 170.9 (*C*OCH$_3$); HRMS: Found: M$^+$, 706.2468.

References

1 D. Fengel and G. Wegener, *Wood – Chemistry, Ultrastructure, Reactions*, Walter de Gruyter, Berlin, 1984, pp. 167–174.
2 Ö. Eriksson and B. O. Lindgren, *Svensk Papperstidn.*, 1977, **79**, 59.
3 J. Minor, *J. Wood Chem. Technol.*, 1982, **2**, 1.

4 T. Watanabe, M. Karina, Y. Sudiyani, T. Koshijima and M. Kuwahara, *Wood Res.*, 1993, **79**, 13.
5 K. Freudenberg, in *Constitution and Biosynthesis of Lignin*, ed. K. Freudenberg and A. C. Neish, Springer-Verlag, Berlin, 1968, pp. 47–116.
6 J. Hemmingson, G. Leary, I. J. Miller, W. Thomas and A. Woodhouse, *J. Chem. Soc.*, *Chem. Commun.*, 1978, 92.
7 G. Leary, D. A. Sawtell and H. Wong, *Holzforschung*, 1983, **37**, 11.
8 J. Sipilä and G. Brunow, *Holzforschung*, 1991, **45**, Suppl. 3.
9 S. Hosoya, H. Taneda and H.-M. Chang, *Wood Pulping Chem.*, 1989, 698.
10 H. Taneda and A. Ishizu, *Mokuzai Gakkaishi*, 1989, **35**, 996.
11 K. Tanaka, F. Nakatsubo and T. Higuchi, *Mokuzai Gakkaishi*, 1979, **25**, 653.
12 H. Taneda, J. Nakano, S. Hosoya and H.-M. Chang, *J. Wood Chem. Technol.*, 1987, **7**, 485.
13 K. Mizutani, R. Kasai, M. Nakamura and O. Tanaka, *Carbohydr. Res.*, 1989, **185**, 27.
14 R. Helm, M. Toikka, K. Li and G. Brunow, *J. Chem. Soc.*, *Perkin Trans. 1*, 1997, 553.
15 T. Tokimatsu, T. Umezawa and M. Shimada, *Holzforschung*, 1996, **50**, 156.
16 M. Hauteville, K. Lundquist and S. von Unge, *Acta Chem. Scand.*, *Sect. B*, 1986, **40**, 31.
17 M. F. Summers, L. G. Marzilli and A. Bax, *J. Am. Chem. Soc.*, 1986, **108**, 4285.
18 C. Griesinger, G. Otting, K. Wüthrich and R. R. Ernst, *J. Am. Chem. Soc.*, 1988, **110**, 7870.
19 E. Alder and E. Eriksoo, *Acta Chem. Scand.*, 1955, **9**, 341.
20 G. Brunow, J. Sipilä and T. Mäkelä, *Holzforschung*, 1989, **43**, 55.

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