Pergamon

Chemosphere, Vol. 28, No. 5, pp. 921-930, 1994
Elsevier Science Ltd
Printed in Great Britain.
0045-6535/94 $6.00+0.00

0045-6535(94)E0027-Q

PREPARATION OF CHLOROSYRINGOLS AND CHLOROPYROGALLOLS - COMPONENTS OF PULP BLEACHING EFFLUENTS

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(Received in Germany 4 November 1993; accepted 10 January 1994)

ABSTRACT

The preparation and properties of chlorosyringols and chloropyrogallols, components of pulp bleaching effluents, and their acetates are given. The compounds are obtained mainly by direct chlorination of both phenols or of syringol acetate with various chlorinating reagents. 5-Chloropyrogallol and 4,5-dichloropyrogallol were the products of demethylation of 5-chloro-3-methoxycatechol acetate and 4,5-dichloro-3-methoxycatechol acetate, respectively. The acetates of all ten chloro compounds were separated by gas chromatography. Electron impact mass spectra and ^{1}H and ^{13}C NMR data for the acetates are given.

INTRODUCTION

Chlorinated phenols are important components of effluents arising from the bleaching of papermaking pulps with molecular chlorine or its oxygenated derivatives, hypochlorite or chlorine dioxide. The chlorinated substances in bleaching effluents have been the source of environmental concern, which has led to extensive changes in pulping and bleaching technology aimed at minimising the use of chlorine-containing reagents.[1] The main classes of chlorinated phenols identified in effluents from bleaching of softwood pulps are chlorophenols, chlorocatechols, chloroguaiacols and chlorovanillins,[2] whereas hardwood and non-wood pulps also give chlorosyringols and chlorosyringaldehydes,[3,4] and minor amounts of other chlorinated phenols including chloro-3-methoxycatechols and chloropyrogallols.[5]

Although chlorosyringols are ubiquitous components of effluents from bleaching of hardwood and non-wood pulps, synthesis of four of the five compounds has only recently been reported,[6] and the remaining compound, 3,4,5-trichlorosyringol (**6a**), was described earlier.[7] Three chloropyrogallols have been detected in effluents from the bleaching of sulfite pulp with chlorine-containing reagents[8] and we have found a dichlorotrihydroxybenzene, probably a pyrogallol, in the filtrates from the bleaching of oxygen-delignified eucalypt kraft pulp.[9] Of the five chloropyrogallols, all except the 4,5-dichloro compound have been reported previously. Thus Friedman and Ginsburg[10] prepared 4-chloro-, 4,6-dichloro- and 4,5,6-trichloropyrogallol (**2c**, **5c** and **6c** respectively) by the direct chlorination of pyrogallol with N-chlorosuccinimide, and 5-chloropyrogallol (**3c**) was the product of demethylation of 5-chloro-3-methoxycatechol.[11]

The positive identification of chlorinated phenols in bleaching effluents requires well-characterised reference compounds. We have recently described the synthesis and properties of chloro-3-methoxycatechols,[12] and in this report we continue with a discussion of improved methods for synthesising the chlorosyringols and chloropyrogallols. The most widely-used analytical method for chlorinated phenols in pulp bleaching effluents is the *in situ* acetylation method of Voss *et al.*,[13] in which the phenols are estimated as their acetates by gas

chromatography (gc). The gc behaviour and spectral properties of the chlorosyringol acetates and the pyrogallol triacetates are thus also presented.

EXPERIMENTAL

NMR spectra were obtained at 100 MHz for protons and 25 MHz for carbons on a Bruker AM-100 spectrometer, and chemical shifts are relative to tetramethylsilane (δ 0.00 ppm). Unless otherwise specified, deuterochloroform solutions were used. Syringol (2,6-dimethoxyphenol) and pyrogallol were obtained from the Aldrich Chemical Company Inc. Silica gel for column chromatography was Bio-sil A, 200-400 mesh, purchased from Bio-Rad. Elementary analyses were carried out by the University of Otago, Dunedin, New Zealand.

Gas chromatography-mass spectrometry (gc-ms) conditions

Gc was carried out on a Hewlett Packard HP5890 series II chromatograph fitted with an autoinjector and an HP5971 mass selective detector. The column was a J&W bonded phase DB5 fused silica column (30 m x 0.25 mm id) with a phase thickness 0.25 μm. Purified helium was the carrier gas with a linear velocity 30 cm/sec. The injector temperature was 250°C and the transfer line was at 280°C. The column temperature program was 1 min at 50°C, 5°C/min to 250°C, 20°C/min to 280°C and 2 min at 280°C. Splitless injections of 1 μL with a 0.3 min purge delay were used and full-scan (*m/z* 30-550) electron impact (70 eV) mass spectra were collected.

Syringol acetate (1b)

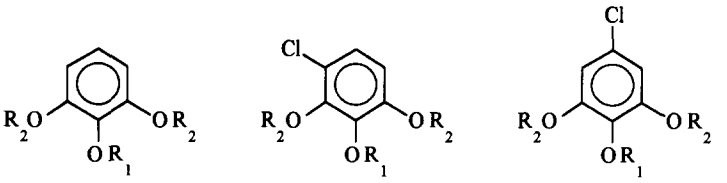
Syringol was treated with acetic anhydride in pyridine at 20°C for 18 h, and the mixture was poured over ice. The resulting solid was filtered and recrystallised from diethyl ether (ether)-hexane to give the acetate, m.p. 48-50°C (lit.[14] m.p. 53.5°C).

Pyrogallol triacetate (1d)

Pyrogallol was treated with acetic anhydride in pyridine at 20°C for 18 h, and the mixture was poured over ice. The resulting solid was filtered, and was recrystallised from ethanol to give the acetate, m.p. 163-4°C (lit.[15] m.p. 164-5°C).

Chlorination of syringol acetate (1b)

(a) Monochlorination A solution of chlorine (1 equiv) in acetic acid (15 mL) was added to a solution of syringol acetate (1.0 g) in acetic acid (10 mL) and the mixture was kept at 20°C for 1 h. The solvent was evaporated *in vacuo* and the resulting oil, after adsorption onto a column of silica gel and elution with 5:95 dichloromethane (DCM):hexane, gave *3-chlorosyringol acetate* (**2b**) (1.05 g) as a colourless oil (Found: C, 52.22, H, 4.68, Cl, 15.71. $C_{10}H_{11}ClO_4$ requires C, 52.08, H, 4.81, Cl, 15.37%) ^{1}H NMR δ 2.34 (3H, s, $COCH_3$), 3.84 (6H, s, OCH_3), 6.65 (1H, d, J=8.9 Hz, H-5) and 7.26 (1H, d, J=8.9 Hz, H-4) ^{13}C NMR, see Table 1. Ms, see Fig. 1. Analysis of the crude reaction mixture by gc-ms showed a single peak at 26.03 min assigned to **2b.** Compound **2b** (300 mg) in methanol (10 mL) containing sodium hydroxide (50 mg) was kept at 40°C for 1 h. The solution was added to water (50 mL), acidified with 1M hydrochloric acid, and the resulting mixture was extracted with DCM. After drying the extract with sodium sulfate, the



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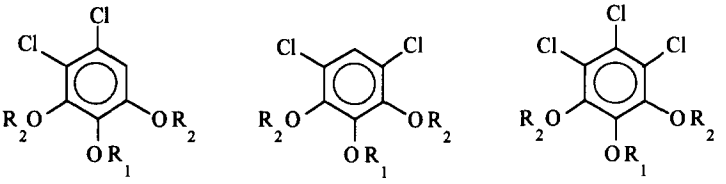

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(a) $R_1 = H$ $R_2 = CH_3$ (b) $R_1 = COCH_3$ $R_2 = CH_3$

(c) $R_1 = R_2 = H$ (d) $R_1 = R_2 = COCH_3$

solvent was evaporated and the product was recrystallised from hexane-ether to give 3-chlorosyringol (**2a**) (220 mg) m.p. 35-6°C (lit.[6] m.p. 35-6°C).

(b) Dichlorination

A solution of chlorine (2 equiv) in acetic acid (30 mL) was added to a solution of syringol acetate (1.0 g) in acetic acid (10 mL) and the mixture was kept at 20°C for 1 h. The mixture was concentrated *in vacuo* to *ca.* 5 mL and was added to water. The resulting precipitate was collected (1.40 g) and recrystallised from ethanol to give *3,5-dichlorosyringol acetate* (**5b**) m.p. 65-6°C (Found: C, 45.58, H, 3.88, Cl, 27.00. $C_{10}H_{10}Cl_2O_4$ requires C, 45.31, H, 3.80, Cl, 26.75%) ^1H NMR δ 2.39 (3H, s, $COCH_3$), 3.84 (6H, s, OCH_3) and 7.31 (1H, s, H-4) ^{13}C NMR, see Table 1. Ms, see Fig. 1. Inspection of the crude mixture by gc-ms showed a single peak at 27.78 min due to the dichloro compound **5b**. Treatment of the acetate **5b** (1.0 g) with sodium methoxide as above gave, after recrystallisation from hexane, 3,5-dichlorosyringol (720 mg) m.p. 109-110°C (lit.[6] m.p. 105-6°C).

(c) Attempted trichlorination

Syringol acetate was treated with chlorine (3.5 equiv) in acetic acid at 20°C for 4 days, and the mixture was concentrated *in vacuo* and the product isolated with DCM. Gc-ms examination of the product mixture gave a single peak at 27.78 min, due to the dichloro compound **5b** as above.

Chlorination of syringol (1a)

(a) Monochlorination

(i) A solution of sodium hypochlorite (4%, 25 mL) was added to a stirred solution of syringol (3.85 g) in methanol (150 mL) at 10°C over a 20 min period. After a further 20 min water (100 mL) was added and the resulting precipitate was removed by filtration. The filtrate was adjusted to pH 2 by addition of 1M sulfuric

acid and the solution was extracted with DCM (3 x 50 mL). The combined extracts were washed with water, dried and the solvent was removed *in vacuo* to give an oil. After acetylation with acetic anhydride-pyridine, the oil was adsorbed onto a column of silica gel. Elution with 1:19 DCM:hexane gave a solid (580 mg) which after recrystallisation from hexane-ether yielded *4-chlorosyringol acetate* (**3b**) m.p. 60-1°C (Found: C, 52.13, H, 4.66, Cl, 15.50. $C_{10}H_{11}Cl_1O_4$ requires C, 52.08, H, 4.81, Cl, 15.37%) ^{1}H NMR δ 2.31 (3H, s, $COCH_3$), 3.78 (6H, s, OCH_3) and 7.15 (2H, s, H-3,5) ^{13}C NMR, see Table 1. Ms, see Fig. 1. Elution with 1:9 DCM:hexane and crystallisation from ether-hexane afforded syringol acetate (1.14 g) m.p. 48-50°C. An aliquot of a solution of the crude reaction product (0.1 mL) was added to water (2 mL), the solution was adjusted to pH 11.5 with 0.1M sodium carbonate (*ca.* 2 mL), and acetic anhydride (50 μL) was added. After mixing on a vortex mixer for 1 min, the solution was extracted into hexane and analysed by gc-ms. The crude reaction product was a 7:3 mixture of the starting material and 4-chlorosyringol (**3a**).

(ii) A solution of chlorine (1.1 equiv) in acetic acid (15 mL) was added to a solution of syringol (1.0 g) in acetic acid (10 mL) and the mixture was kept at 20°C for 1 h. Examination of the acetylated product by gc-ms showed it to be a 82:18 mixture of the 3- and 4-chloro isomers (**2a** and **3a**) respectively, with small amounts of the dichloro isomer **5a**. No purification of the mixture was attempted.

(iii) Sulfuryl chloride (50 μL, 1.05 equiv) was added to a solution of syringol (100 mg) in dry ether (10 mL). After standing for 1 h at 20°C, an aliquot of the solution was acetylated and the product analysed by gc-ms was shown to be a mixture of **1a**:**2a**:**3a**:**5a** in the ratio 10:78:2:10. The mixture was not examined further.

(b) Dichlorination

(i) A solution of chlorine (2 equiv) in acetic acid (35 mL) was added to a solution of syringol (1.0 g) in acetic acid (10 mL) and the mixture was kept at 20°C for 1 h. The solution was concentrated *in vacuo* to *ca.* 5 mL, and the product was isolated with DCM to give an oil (1.49 g). The oil was acetylated with 1:1 acetic anhydride:pyridine (2 mL) at 20°C for 18 h, and the acetylated mixture was adsorbed on silica gel. Elution with 1:39 DCM:hexane gave successively 3,4,5-trichlorosyringol acetate (**6b**), and 3,5-dichlorosyringol acetate (**5b**) (gc-ms examination). Elution with 1:19 DCM:hexane gave a solid (430 mg) which after recrystallisation from hexane-ether yielded *3,4-dichlorosyringol acetate* (**4b**) m.p. 94-5°C (Found: C, 45.22, H, 3.72, Cl, 27.05. $C_{10}H_{10}Cl_2O_4$ requires C, 45.31, H, 3.80, Cl, 26.75%) ^{1}H NMR δ 2.34 (3H, s, $COCH_3$), 3.79 (3H, s, OCH_3), 3.85 (3H, s, OCH_3) and 6.85 (1H, s, H-5) ^{13}C NMR, see Table 1. Ms, see Fig. 1. Further elution afforded 3-chlorosyringol acetate (**2b**) (gc-ms examination). Analysis of the crude product by gc-ms showed the mixture to comprise **2a**:**4a**:**5a**:**6a** in the ratio 10:36:43:11. Treatment of the acetate **4b** (200 mg) with sodium methoxide as above gave, after recrystallisation from hexane, 3,5-dichlorosyringol (130 mg) m.p. 65-6°C (lit.[6] m.p. 69-70°C).

(ii) Sulfuryl chloride (100 μL, 2.1 equiv) was added to a solution of syringol (100 mg) in dry ether (10 mL) and the mixture was kept at 20°C for 1 h. Examination of the crude mixture (acetylated as above) by gc-ms showed the presence of three peaks at 27.78, 30.21 and 32.38 min in the ratio 66:27:7, assigned to the dichloro compounds **5b** and **4b**, and the trichloro compound **6b**, respectively.

(c) Trichlorination

A solution of chlorine (3.5 equiv) in acetic acid (60 mL) was added to a solution of syringol (1.0 g) in acetic acid (10 mL) and the mixture was kept at 20°C for 1 h. The solution was concentrated *in vacuo* to *ca.* 5 mL, and added to water. The resulting solid was collected and recrystallised from hexane to give 3,4,5-trichlorosyringol (**6a**) (750 mg) m.p. 123-4°C (lit.[11] 121.5°C). Compound **6a** acetylated with 1:1 acetic

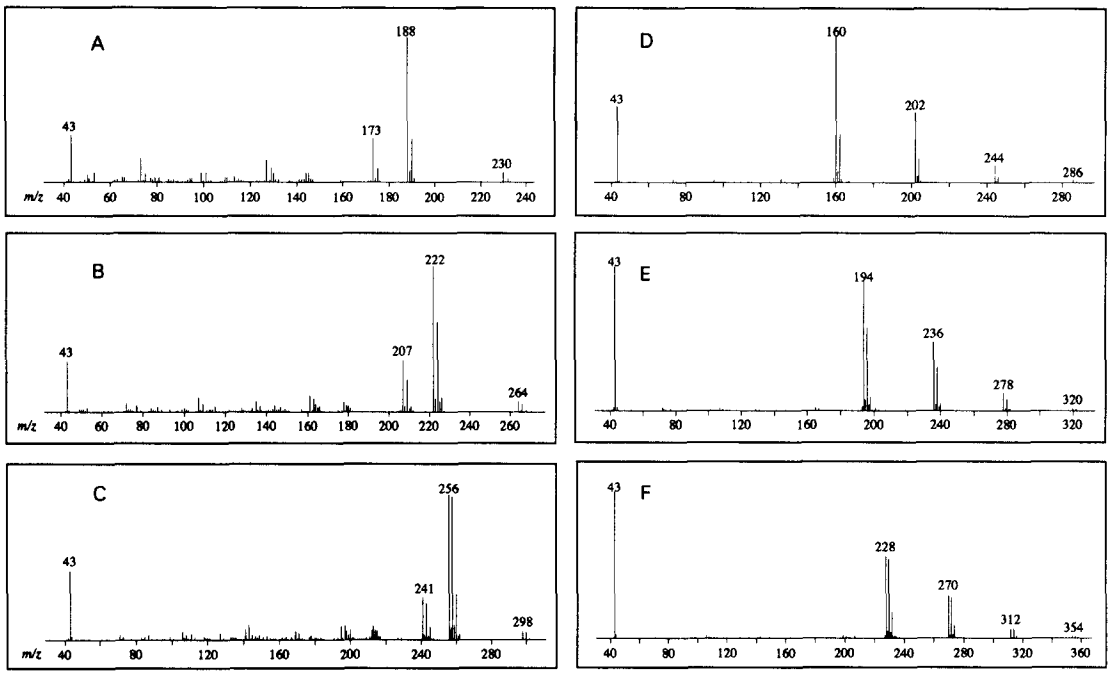

Figure 1. Mass spectra of chlorosyringol acetates: A, monochloro; B, dichloro; C, trichloro; and chloropyrogallol triacetates: D, monochloro, E, dichloro; F, trichloro.

anhydride:pyridine (2 mL) at 20°C for 18 h yielded after recrystallisation from hexane-ether 3,4,5-trichloro-syringol acetate (**6b**) m.p. 105-6°C (lit.[11] m.p. 102-3°C) ^{13}C NMR, see Table 1. Ms, see Fig. 1.

Attempted chlorination of pyrogallol triacetate (1d)

(a) With molecular chlorine

A solution of chlorine (2 equiv) in acetic acid (15 mL) was added to a solution of the the triacetate **1d** (500 mg) in acetic acid (5 mL), and the mixture was kept at 20°C for 4 days. Examination of the reaction mixture by gc-ms revealed only unreacted starting material **1d**.

(b) With sulfuryl chloride

Sulfuryl chloride (100 μL, 2 equiv) was added to a solution of pyrogallol triacetate (120 mg) in dry ether (10 mL) and the mixture was kept at 20°C for 4 days. Examination of the reaction product by gc-ms showed unreacted starting material as the sole component.

Chlorination of pyrogallol (1c)

(a) Monochlorination

A solution of pyrogallol (500 mg) and N-chlorosuccinimide (495 mg, 1.05 equiv) in ether (150 mL) was kept at 20°C for 48 h. The solvent was removed *in vacuo*, and the resulting solid was extracted in boiling chloroform (50 mL). The chloroform solution on cooling yielded crystals of 4-chloropyrogallol (**2c**) ^{1}H NMR (acetone-d_6) δ 6.69 (1H, d, J=8.7 Hz, H-5), 6.42 (1H, d, J=8.7 Hz, H-6) and 7.96 (3H, br s, OH) ^{13}C NMR (acetone-d_6) δ 108.4, 110.6, 122.4, 131.7, 141.9 and 143.6. Examination of the acetylated crude reaction

product by gc-ms showed the monochloro compound **2c** to be the sole reaction product. Compound **2c** when acetylated with acetic anhydride-pyridine gave, after recrystallisation from chloroform, the *triacetate* **2d** m.p. 115-7°C (Found: C, 50.42, H, 3.92, Cl, 12.63. $C_{12}H_{11}ClO_6$ requires C, 50.28, H, 3.87, Cl, 12.37%) ^{1}H NMR δ 2.26 (3H, s, $COCH_3$), 2.28 (3H, s, $COCH_3$), 2.33 (3H, s, $COCH_3$), 7.35 (1H, d, J=8.9 Hz, H-5) and 7.10 (1H, d, J=8.9 Hz, H-6) ^{13}C NMR, see Table 2. Ms, see Fig. 1.

(b) Dichlorination

Sulfuryl chloride (1.4 mL, 2.1 equiv) was added over 5 min to a rapidly stirred solution of pyrogallol (1.0 g) in ether (25 mL), and the mixture was kept at 20°C for 1 h. The solvent was removed *in vacuo*, and the resulting solid after recrystallisation from chloroform gave 4,6-dichloropyrogallol (**5c**) (1.30 g) ^{1}H NMR (acetone-d_6) δ 6.87 (1H, s, H-5) and 8.24 (3H, br s, OH) ^{13}C NMR (acetone-d_6) δ 112.6, 119.8, 136.3 and 142.1. Examination of the acetylated crude reaction product by gc-ms showed the dichloro compound **5c** to be the sole reaction product. Compound **5c** when acetylated with acetic anhydride-pyridine gave a solid which was recrystallised from chloroform to give the *triacetate* **5d** m.p. 137-8°C (Found: C, 44.63, H, 3.36, Cl, 21.74. $C_{12}H_{10}Cl_2O_6$ requires C, 44.89, H, 3.14, Cl, 22.08%), ^{1}H NMR δ 2.32 (9H, s, $COCH_3$) and 7.10 (1H, s, H-5) ^{13}C NMR, see Table 2. Ms, see Fig. 1.

(c) Trichlorination

Sulfuryl chloride (2.1 mL, 3.3 equiv) was added over 5 min to a rapidly stirred solution of pyrogallol (1.0 g) in ether (25 mL), and the mixture was kept at 20°C for 1 h. The solvent was removed *in vacuo*, and the resulting solid after recrystallisation from chloroform gave 4,5,6-trichloropyrogallol (**6c**) (1.30 g) ^{1}H NMR (acetone-d_6) δ 6.33 (3H, br s, OH) ^{13}C NMR (acetone-d_6) δ 112.6, 121.7, 134.7 and 143.1. Compound **6c** when acetylated with acetic anhydride-pyridine gave the *triacetate* **6d** which was recrystallised from hexane-ether m.p. 126-7°C, (Found: C, 40.83, H, 2.30, Cl, 29.97. $C_{12}H_9Cl_3O_6$ requires C, 40.54, H, 2.55, Cl, 29.91%) ^{1}H NMR δ 2.30 (3H, s, $COCH_3$), 2.34 (6H, s, $COCH_3$) ^{13}C NMR, see Table 2. Ms, see Fig. 1.

5-Chloropyrogallol triacetate (3d)

A solution of 1M boron tribromide in DCM (4 mL) was added to a solution of 5-chloro-3-methoxycatechol[12] (150 mg) in DCM (10 mL), and the mixture was kept at 20°C for 16 h. Water (10 mL) was added to the solution and the mixture was extracted with DCM (3 x 50 mL). The combined extracts were dried and the solvent was removed to give an oil, which was reacetylated with 1:1 acetic anhydride:pyridine (2 mL) for 18 h at 20°C. Evaporation of the mixture *in vacuo* yielded an oil, which was recrystallised from hexane-ether to give 5-chloropyrogallol triacetate (110 mg) (**3d**) m.p. 124-5°C (lit.[11] m.p. 123-4°C) (Found: C, 50.37, H, 3.56, Cl, 12.45. $C_{12}H_{11}ClO_6$ requires C, 50.28, H, 3.87, Cl, 12.37%) ^{1}H NMR δ 2.27 (9H, s, $COCH_3$) and 7.15 (2H, s, H-4,6) ^{13}C NMR, see Table 2. Ms, see Fig. 1.

4,5-Dichloropyrogallol triacetate (4d)

A 1M solution of boron tribromide in DCM (12 mL) was added to a solution of 4,5-dichloro-3-methoxy-catechol[12] (500 mg) in DCM (30 mL), and the mixture was kept at 20°C for 4 days. Water (50 mL) was added to the solution and the mixture was extracted with DCM (3 x 50 mL). The combined extracts were dried and the solvent was removed to give an oil, which was reacetylated with 1:1 acetic anhydride:pyridine (2 mL) for 18 h at 20°C. Evaporation of the mixture *in vacuo* yielded an oil, which was recrystallised from hexane-ether give *4,5-dichloropyrogallol triacetate* (**4d**) m.p. 113-4°C (Found: C, 45.07, H, 2.87, Cl, 22.46.

$C_{12}H_{10}Cl_2O_6$ requires C, 44.89, H, 3.14, Cl, 22.08%) ^1H NMR δ 2.25 (3H, s, $COCH_3$), 2.27 (3H, s, $COCH_3$), 2.33 (3H, s, $COCH_3$) and 7.34 (1H, s, H-6) ^{13}C NMR, see Table 2. Ms, see Fig. 1.

RESULTS AND DISCUSSION

Treatment of syringol (**1a**) with sodium hypochlorite according to McKague[6] gave 4-chlorosyringol (**3a**) as the only chlorinated product (gc-ms examination). However, chlorination of syringol acetate (**1b**) with 1 equivalent chlorine in acetic acid yielded 3-chlorosyringol acetate (**2b**) as the sole product. Hydrolysis of the acetate **2b** gave 3-chlorosyringol (**2a**) in 80% overall yield from **1b**. Monochlorination of syringol with sulfuryl chloride in ether[6] yielded a mixture of both 3- and 4-chloro isomers **2a** and **3a** in the ratio 78:2, together with 10% unreacted starting material and 10% 3,5-dichlorosyringol (**5a**). The mixture of products provides an explanation for the relatively low yield (29%) obtained earlier for the preparation of 3-chlorosyringol by direct chlorination of syringol.[6] When chlorine in acetic acid was used to chlorinate syringol, the product was enriched with the 4-chloro isomer, having a ratio of **2a**:**3a** in the proportion 82:18, together with a small amount of the dichlorosyringol **5a**.

Table 1. ^{13}C NMR spectra of chlorosyringol acetates in deuterochloroform

	1b	**2b**	**3b**	**4b**	**5b**	**6b**
Cl-substitution	--	3	4	3,4	3,5	3,4,5
C-1	128.6	134.1	127.4 or 131.6	130.2 or 132.9	139.4	137.9
C-2	152.1	149.0 or 151.2	152.4	150.1 or 150.9	148.4	149.0
C-3	104.6	126.5	105.6	119.1	127.4	124.3
C-4	125.9	119.5	127.4 or 131.6	130.2 or 132.9	123.3	130.1
C-5	104.6	107.7	105.6	109.0	127.4	124.3
C-6	152.1	149.0 or 151.2	152.4	150.2 or 150.9	148.4	149.0
CH_3O-2	55.8	60.9	56.1	61.1	61.1	61.4
CH_3O-6	55.8	56.0	56.1	56.3	61.1	61.4
$\underline{C}H_3CO$	20.1	20.1	20.1	20.1	20.2	20.3
$CH_3\underline{C}O$	168.4	166.2	168.3	168.1	168.1	166.1

Reaction of syringol acetate with 2 equivalents of chlorine in acetic acid gave 3,5-dichlorosyringol acetate (**5b**) as the sole product. After hydrolysis of **5b**, 3,5-dichlorosyringol (**5a**) was formed in 80% overall yield from **1b**. Dichlorination of syringol with sulfuryl chloride in ether[6] yielded the dichloro isomers **4a** and **5a** and the trichloro compound **6a** in the ratio 27:66:7. Reaction of syringol with 2 equivalents of chlorine in acetic acid gave relatively more 3,4-dichloro compound **4a**; the product mixture was **2a**:**4a**:**5a**:**6a** in the ratio 10:36:43:11. The isomers were separated as their acetates on silica gel. McKague[6] isolated both dichloro isomers **4a** and **5a** from the direct chlorination of syringol. Preparation of the 3,5-dichloro isomer **5a** by chlorination of syringol acetate is clearly a more specific route to that compound.

Prolonged chlorination of **1b** with 3.5 equivalents of chlorine in acetic acid did not give rise to the trichloro compound **6b**; after 4 days at 20°C the dichloro compound (**5b**) was the sole product. Chlorination of syringol with 3.5 equivalents chlorine in acetic acid proceeds under ambient conditions to give 3,4,5-trichlorosyringol.[7]

The products obtained on chlorination of syringol or its acetate are a consequence of the reaction conditions or of the different substituents. Formation of 4-chlorosyringol by chlorination in an alkaline medium compared to an acid medium in which 3-chlorosyringol is the major product is due to the stronger activating effect of the oxy anion than the hydroxyl group. Acetylation of the phenolic hydroxyl group has the effect of deactivating the 4-position towards attack by the chlorinating species. The order of activation of various substituents for electrophilic substitution is $O^- > OH > OCH_3 > OCOCH_3$.[16]

Pyrogallol triacetate (**1d**) was unreactive to prolonged treatment with chlorine in acetic acid or sulfuryl chloride in ether. Chlorination of pyrogallol with 1 equivalent N-chlorosuccinimide in ether yielded 4-chloropyrogallol (**2c**) as the only product.[10] With 2 and 3 equivalents sulfuryl chloride in ether the sole products were 4,6-dichloro and 4,5,6-trichloropyrogallol (**5c** and **6c**) respectively. 5-Chloropyrogallol (**3c**) and 4,5-dichloro-pyrogallol (**4c**) were prepared by demethylation of 5-chloro-3-methoxycatechol acetate and 4,5-dichloro-3-methoxycatechol acetate respectively with boron tribromide.[17]

Table 2. ^{13}C NMR spectra of chloropyrogallol triacetates in deuterochloroform

	1d	**2d**	**3d**	**4d**	**5d**	**6d**
Cl substitution	--	4	5	4,5	4,6	4,5,6
C-1	143.5	142.1	143.7	141.7	143.1	140.3
C-2	134.6	136.3	133.6	135.0	135.3	136.5
C-3	143.5	140.8	143.7	141.7	143.1	140.3
C-4	120.7	126.5	121.2	124.7	125.3	126.4
C-5	125.9	125.3	130.9	130.1	120.7	130.4
C-6	120.7	121.1	121.2	122.0	125.3	126.4
$\underline{C}H_3CO$-1	20.6	20.5	20.5	20.3	20.2	20.0
$\underline{C}H_3CO$-2	20.1	20.1	20.0	19.7 or 19.8	20.2	20.1
$\underline{C}H_3CO$-3	20.6	20.1	20.5	19.7 or 19.8	20.2	20.0
$CH_3\underline{C}O$-1	167.8	167.5	167.3	167.1	166.3	166.2
$CH_3\underline{C}O$-2	166.9	166.5 or 166.6	167.6	166.4	166.3	166.4
$CH_3\underline{C}O$-3	167.8	166.5 or 166.6	167.3	166.4	166.3	166.2

The ^{13}C NMR spectral signals of syringol acetate and its chloro derivatives were assigned on the basis of the rules for substituent increments for substituted benzenes[18] (Table 1), taking into account the higher intensity of the secondary carbon signals than those of the tertiary carbons, and the deshielding effect of chlorine on the carbon signals, particularly when the chlorine is directly attached to the carbon atom. The C-3 and C-5 signals are more affected by chlorine substitution than the C-4 signal. The deshielding effect of an adjacent chlorine substituent on the chemical shift of the methoxyl carbons[19] is clearly shown by comparison of the data in Table 1. Using similar reasoning, the ^{13}C NMR signals for pyrogallol triacetate and its chloro derivatives were assigned (Table 2). There are indications of a subtle shielding effect of an adjacent chlorine on the methyl and carbonyl carbon signals of the acetate groups at C-1 and C-3.

Table 3. Gc characteristics of chlorosyringol acetates and chloropyrogallol triacetates

Compound	Cl-substitution	Retention time (min)	Rel. retention time*
2b	3	26.03	1.103
3b	4	27.04	1.146
4b	3,4	30.21	1.280
5b	3,5	27.78	1.177
6b	3,4,5	32.38	1.372
2d	4	31.11	1.318
3d	5	31.40	1.331
4d	4,5	34.24	1.451
5d	4,6	33.00	1.398
6d	4,5,6	36.71	1.556

* relative to 2,3,6-trichlorophenol acetate (23.6 min)

The five chlorosyringol acetates and five chloropyrogallol triacetates were separated by gc on a column with a phenylmethyl silicone mobile phase (J&W DB5) (Table 3). The retention times relative to 2,3,6-trichlorophenol acetate, a widely-used internal standard in chlorinated phenol analyses, are also given. The electron impact mass spectra of acetates of chlorosyringols and chloropyrogallols are given in Fig. 1. Although the spectra of isomers were similar and were thus not useful for differentiating between isomers, the spectra do give an indication of the level of chlorination. Knuutinen and Korhonen have noted that the spectra of positional isomers of chlorinated guaiacols are very similar,[20] although the mass spectra of chlorinated catechols can generally be distinguished from each other.[21]

ACKNOWLEDGEMENTS

The authors thank Ms M. J. Reilly for expert help with the NMR spectra. The study was funded as part of the National Pulp Mills Research Program.

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