^{19}F Nuclear Magnetic Resonance Spectroscopy for the Elucidation of Carbonyl Groups in Lignins. 1. Model Compounds

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A new method for the detection of different classes of carbonyl groups in a series of carbonyl-containing lignin-like model compounds has been developed. The method is based on the selective fluoride-induced trifluoromethylation of carbonyl groups with (trifluoromethyl)trimethylsilane (TMS-CF_3) in the presence of tetramethylammonium fluoride (TMAF), followed by hydrolysis with aqueous HF or TMAF in the case of quinones. In this study a series of ketones, aldehydes, quinones, and dimeric-lignin model compounds were quantitatively trifluoromethylated followed by ^{19}F NMR spectral analyses of the resulting fluorine-containing derivatives, allowing for a thorough understanding of their structure/^{19}F chemical shift relationships. These studies have shown that the ^{19}F-NMR chemical shifts of the trifluoromethyl groups vary significantly and consistently for various classes of carbonyl groups which may be present in complex lignocellulosic materials. These studies are to form the basis for the development of a novel and sensitive method that can be used to obtain quantitative information on the various carbonyl groups present in such materials.

Keywords: *Carbonyl groups; model compounds; Ruppert's reagent; trifluoromethylation; nuclear magnetic resonance (NMR); chemical shifts*

INTRODUCTION

The carbonyl groups present in wood and pulps play an important role in determining the reactivity of lignin structures toward the yellowing of paper and the bleaching of pulp (Heitner and Schmidt, 1991; Schmidt and Heitner, 1991, 1993; Leary, 1994). The low contents of these groups in wood, in pulp, and in paper have made the elucidation of their role rather elusive. Detecting and determining these groups will pave the way toward arriving at new conclusions in relation to a variety of pressing issues as far as the yellowing of paper and the bleaching of chemical and mechanical pulps are concerned. Therefore, the necessity to obtain essential information toward understanding the reactivity of lignin structures during yellowing and inhibition initiated efforts at developing a novel method for the fine structural elucidation and quantitation of the various carbonyl groups present in lignin.

The presence of carbonyl groups in lignin was first postulated by Klason (1922) as early as 1922. However, Adler et al. (Adler, 1951; Adler and Ellmer, 1948; Adler et al., 1948) and Pew (1951) were the first to obtain reliable direct evidence for the presence of conjugated carbonyl groups, in particular coniferyl aldehyde-type structures in spruce lignin. Further investigations by Geiger and Fuggerer (1979) resulted in the detection of cinnamaldehyde-type structures of conjugated carbonyls in milled wood lignin. Additional experimentation suggested the presence of other types of conjugated and possibly nonconjugated carbonyl structures in lignin. These structures, including trace amounts of quinone ketals (Adler and Marton, 1959; Larsson and Miksche, 1972), have been recognized to be a portion of the total carbonyl content present in milled wood lignins. However, different lignin isolations may contain a variety of other possible carbonyl-containing structures. For instance, technical lignins, and, in particular, alkali lignins, contain appreciable amounts of α-carbonyl groups in addition to benzaldehydes and *o*-quinones. Investigations of carbonyl groups have continued to expand aimed at the identification of these groups and elucidation of their role in lignin reactivity. Recent studies by Panchapakesan (1990) provided evidence and new information on such groups in lignin.

These studies have shown that the presence of carbonyl groups in lignins, in particular those present as *o*- and *p*-quinonoids, quinonemethides, and other extended conjugate enone systems, are not only contributors to the color observed in lignified plant tissues (Hon and Glasser, 1979; Lebo et al., 1990) but also sensitizers in the photoyellowing of lignocellulosics (Brunow and Eriksson, 1971; Lin and Kringstad, 1970). Oxidation of lignins with reagents such as molecular oxygen, hydrogen peroxide, and chlorine may further increase their carbonyl content (Chang and Allen, 1971). The *o*- and *p*-quinone structures so generated in residual lignins of pulps may further alter the color of the pulps and promote their capacity to be photosensitized (Panchapakesan, 1990; Gierer and Lin, 1972).

Despite our advances aimed at understanding and elucidating the role of the carbonyl groups in lignins, there are still no fundamental techniques available for classifying these groups. The objective of this study is to identify and determine all distinct classes of carbonyl groups in lignin by implementing an innovative method.

The strategy followed toward the development of such a method was as follows:

Various carbonyl groups present in lignins and several model compounds were to be quantitatively derivatized with a reagent which readily reacts with carbonyls and which contains an NMR sensitive heteroatom. Next, the structure/chemical shift relations must be evaluated in order to allow for the precise qualification of the different classes of carbonyls in complex mixtures. Therefore, according to these criteria, Ruppert's reagent [(trifluoromethyl)trimethylsilane (TMS-CF_3)] was cho-

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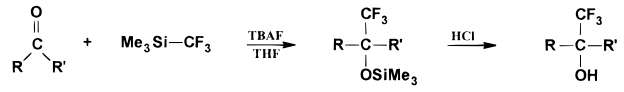
sen for the selective and quantitative fluoride-induced trifluoromethylation of carbonyl groups. This was followed by ^{19}F NMR spectroscopy aimed at probing the resulting fluorine-containing derivatives.

The introduction of trifluoromethyl groups into organic molecules and macromolecules has been the subject of significant interest by both synthetic and medicinal chemists (Liebman et al., 1988). These compounds have been examined for their potential as biologically active drugs and agrochemicals (Banks, 1979). Trifluoromethyl-substituted compounds often exhibit significant effects in their physical and chemical properties. In 1989 Prakash and co-workers (Prakash et al., 1989) reported the efficient and selective fluoride-induced trifluoromethylation of carbonyl compounds with TMS-CF_3 (Ruppert et al., 1984). The work of this group has been focused at developing new synthetic methods for introducing perfluoroalkyl groups into different classes of carbonyl compounds by using efficient nucleophilic trifluoromethylating agents. Various carbonyl containing-compounds when reacted with TMS-CF_3 in the presence of a catalytic amount of tetra-*n*-butylammonium fluoride (TBAF) have been shown to undergo the following reaction.



This reaction works equally well for different classes of carbonyl groups, such as aldehydes, ketones, enones, carboxylic acid, and even ketoesters (Prakash and Pichika, 1991) without being affected by moisture.

In this work, a series of organic compounds containing different classes of carbonyl groups were subjected to the proposed chemical reaction and their carbonyl groups were converted to their trifluoro analogues. Finally, the resulting fluorine-containing derivatives were examined by ^{19}F NMR spectroscopy. As a result, numerous signals, due to the different classes of carbonyl groups, were detected and studied.

MATERIALS AND METHODS

I. Reactions. *Acetylation of Lignin Model Compounds.* The carbonyl-containing compound (~200 mg) was acetylated with 2−4 mL of acetic anhydride/pyridine (1:1, (v/v)) at room temperature overnight in a 100 mL flask. Ethanol (50 mL) was added, and, after 30 min, the solvents were removed by film evaporation. Repeated addition and removal (film evaporation) of ethanol (5−10 times) resulted in the removal of acetic acid and pyridine from the sample. The acetate was dried in vacuo over KOH and P_2O_5 or purified as described below prior to drying.

Trifluoromethylation Procedure. The carbonyl-containing model compound (10 mmol) was dissolved in 3 mL of high-purity tetrahydrofuran (THF). To this solution, an excess (15 mmol) of TMS-CF_3 was added. The mixture was then treated with a catalytic amount (20 mg) of tetramethylammonium fluoride (TMAF) under constant stirring at 0 °C for 0.5 h. It was then brought to room temperature, and the reaction was allowed to continue to completion (TLC). The intermediate siloxy adducts were hydrolyzed by the addition of (4 mL) of aqueous hydrofluoric acid (10% HF). Finally, the hydrolysed mixture was extracted with chloroform (3 × 15 mL) and dried over anhydrous magnesium sulfate. The hydrolysis of the quinones was accomplished by replacing HF with an equimolar excess of TMAF. The isolated products were characterized by ^{19}F and ^1H NMR and GC-MS.

II. Instrumentation. *NMR Spectroscopy. (a) ^{19}F NMR Spectroscopy.* All spectra were recorded on a Varian Unity 500 FT-NMR spectrometer at an operational frequency of 470.3 MHz. The model compound derivatives were dissolved in deuterated chloroform (10−20 mg/1.0 mL of $CDCl_3$) using fluorotrichloromethane ($CFCl_3$) as internal reference. The measurements were carried out in a 5 mm tube at room temperature. The acquisition time of 0.64 s was used followed by the relaxation delay of 2 s. The number of scans acquired was 8 per measurement. Pulse widths corresponding to a 45° flip angle and a line broadening of 1 Hz were used during acquisition and processing of the spectra.

(b) ^1H NMR Spectroscopy. The NMR spectra were recorded at a proton operating frequency of 200.1, 299.9, and 499.8 MHz on Varian XL-200 FT-NMR, Varian XL-300 FT-NMR, and Varian unity 500 spectrometers, respectively. The model compounds containing carbonyl groups and their derivatives were dissolved in deuterated chloroform (30 mg/1.0 mL $CDCl_3$) using TMS as internal reference. The measurements were carried out in a 5 mm tube at room temperature. No relaxation delay was used. The acquisition times for Varian XL-200 FT-NMR, Varian XL-300 FT-NMR, and Varian unity 500 spectrometers, were 3.752, 2.496, and 1.892 s, respectively. The number of scans for the ^1H NMR signals were 128.

(c) ^{13}C NMR Spectroscopy. The model compounds containing carbonyl groups and their derivatives were dissolved in deuterated chloroform (30 mg/1.0 mL $CDCl_3$), and quantitative ^{13}C NMR spectra were obtained on both Varian XL-300 FT-NMR and Varian unity 500 spectrometers operating at 75.4 and 125.7 MHz, respectively. The internal reference was TMS. The measurements were carried out in a 5 mm tube at room temperature with heteronuclear decoupling. No relaxation delay was used. The acquisition times on Varian XL-300 FT-NMR and Varian unity 500 spectrometers were 0.970 and 1.083 s, respectively. The number of scans ranged between 65 000 and 80 000.

(d) ^{31}P NMR Spectroscopy. The ^{31}P NMR spectra were obtained by using inverse gated decoupling on a Varian XL-300 FT-NMR spectrometer at 121.5 MHz. The internal deuterium lock was provided by the deuterium atoms present in the deuterated chloroform, used as the solvent. The external standard was 85% H_3PO_4. All downfield shifts from H_3PO_4 were considered positive. A sweep width of 10 000 Hz was observed, and spectra were accumulated with a time delay of 10 s between successive pulses. A pulse width corresponding to a 45° flip angle and a line broadening of 2 Hz were used for acquiring the processing of the spectra. For the 45° flip angle a series of experiments showed that there was no further increase in signal intensity after a 7 s pulse delay was applied. All chemical shifts reported are relative to the dimeric model compound with water, which has been observed to give a sharp ^{31}P signal at 121.1 ppm (Argyropoulos et al., 1993; Argyropoulos, 1994).

Gas Chromatography/Mass Spectrometry. GC-MS analyses were carried out on a Hewlett-Packard 5972 mass spectrometer interfaced to a Hewlett-Packard 5890A gas chromatograph with a 30 m × 0.25 mm packed silica capillary column DB-5. The injection port temperature was 280 °C and the oven temperature was varied from 100 to 250 °C, with a gradient of 5 °C/min. The CF_3-containing lignin model compounds were analyzed after silylation.

III. Characterization of Trifluoromethylated Compounds. *Compound **1**.* ^1H NMR ($CDCl_3$, TMS): δ 1.77 (s, 3H); 2.60 (s, 1H), 7.37−7.46 (m, 3H), 7.56−7.61 (m, 2H) ppm. ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ −81.35 (s) ppm. MS *m/z* 190 (M^+), 151, 127, 121, 105, 91, 77, 51. Anal. Calcd for $C_9H_9F_3O$: C, 56.84; H, 4.77; F, 29.97. Found: C, 56.92; H, 4.69; F, 29.92. 96% yield.

*Compound **2**.* ^1H NMR ($CDCl_3$, TMS): δ 1.74 (s, 3H), 2.35 (s, 1H), 5.67 (s, 1H), 6.829 (d, 2H, J = 8.78 Hz), 7.432 (d, 2H, J = 8.58 Hz) ppm. ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ −81.76 (s) ppm. MS *m/z* 206 (M^+), 188, 167, 149, 137, 119, 107, 91. Anal. Calcd for $C_9H_9F_3O_2$: C, 52.43; H, 4.40; F, 27.65. Found: C, 52.48; H, 4.49; F, 27.67. 98% yield.

*Compound **3**.* ^1H NMR ($CDCl_3$, TMS): δ 1.74 (s, 3H), 2.90 (s, 1H), 3.879 (d, 3H, J = 6.64 Hz), 5.84 (s, 1H), 6.86−7.13 (m, 3H) ppm. ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ −81.60 (s) ppm. MS *m/z* 236 (M^+), 197, 167, 151, 124. 110, 69, 51. Anal. Calcd

for $C_{10}H_{11}F_3O_3$: C, 50.85; H, 4.69; F, 24.13. Found: C, 50.91; H, 4.68; F, 24.19. 96% yield.

Compound ***4***. ^{1}H NMR ($CDCl_3$, TMS): δ 1.73 (s, 3H), 2.54 (s, 1H), 3.879 (d, 6H, J = 10.26 Hz), 6.78 (s, 2H), 7.22 (s, 1H) ppm. ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ −81.47 (s) ppm. MS m/z 266 (M^+), 227, 197, 181, 155, 123, 93, 69. Anal. Calcd for $C_{11}H_{13}F_3O_4$: C, 49.63; H, 4.92; F, 21.41. Found: C, 49.69; H, 4.85; F, 21.35. 95% yield.

Compound ***5***. ^{1}H NMR ($CDCl_3$, TMS): δ 1.73 (s, 3H), 2.72 (s, 1H), 3.841 (d, 6H, J = 2.16 Hz), 6.825 (d, 1H, J = 8.48 Hz), 7.03−7.11 (m, 2H) ppm. ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ −81.56 (s) ppm. MS m/z 250 (M^+), 211, 181, 139, 124, 107, 95, 77. Anal. Calcd for $C_{11}H_{13}F_3O_3$: C, 52.80; H, 5.24; F, 22.78. Found: C, 52.85; H, 5.28; F, 22.80. 95% yield.

Compound ***6***. ^{1}H NMR ($CDCl_3$, TMS): δ 2.93 (s, 1H), 7.34−7.38 (m, 6H), 7.47−7.52 (m, 4H) ppm. ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ −74.79 (s) ppm. MS m/z 252 (M^+), 233, 213, 183, 165, 127. 105, 77. Anal. Calcd for $C_{14}H_{11}F_3O$: C, 66.67; H, 4.40; F, 22.60. Found: C, 66.71; H, 4.32; F, 22.66. 94% yield.

Compound ***7***. ^{1}H NMR ($CDCl_3$, TMS): δ 3.22 (s, 1H), 3.84 (s, 6H), 6.87−7.03 (m, 4H), 7.03−7.47 (m, 4H) ppm. ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ −75.11 (s) ppm. MS m/z 312 (M^+), 273, 243, 212, 168, 135, 108, 77. Anal. Calcd for $C_{16}H_{15}F_3O_3$: C, 61.54; H, 4.84; F, 18.25. Found: C, 61.56; H, 4.88; F, 18.17. 96% yield.

Compound ***8***. ^{1}H NMR ($CDCl_3$, TMS): δ 2.60 (s, 1H), 4.989 (q, 1H, J = 6.60 Hz), 7.38−7.48 (m, 5H) ppm. ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ −78.848 (d, J_{F-H} = 6.1 Hz) ppm. MS m/z 176 (M^+), 159, 127, 107, 89, 79, 51. Anal. Calcd for $C_8H_7F_3O$: C, 54.55; H, 4.01; F, 32.36. Found: C, 54.58 H, 3.99; F, 32.40. 97% yield.

Compound ***9***. ^{1}H NMR ($CDCl_3$, TMS): δ 2.59 (s, 1H), 3.89 (s, 3H), 4.925 (q, 1H, J = 6.78 Hz), 5.72 (s, 1H), 6.947 (d, 3H, J = 13.93 Hz) ppm.^{19}F NMR ($CDCl_3$, $CFCl_3$): δ −78.981 (d, J_{F-H} = 6.1 Hz) ppm. MS m/z 222 (M^+), 205, 183, 153, 125, 93, 65, 51. Anal. Calcd for $C_9H_9F_3O_3$: C, 48.66; H, 4.08; F, 25.65. Found: C, 48.70; H, 4.11; F, 25.69. 95% yield.

Compound ***10***. ^{1}H NMR ($CDCl_3$, TMS): δ 2.18 (s, 1H), 3.85 (s, 6H), 4.924 (q, 1H, J = 6.58 Hz), 6.68 (s, 2H) ppm. ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ −78.890 (d, J_{F-H} = 6.1 Hz) ppm. MS m/z 252 (M^+), 205, 183, 167, 155, 140, 123, 95. Anal. Calcd for $C_{10}H_{11}F_3O_4$: C, 47.63; H, 4.40; F, 22.60. Found: C, 47.62; H, 4.42; F, 22.58. 98% yield.

Compound ***11***. ^{1}H NMR ($CDCl_3$, TMS): δ 2.50 (s, 1H), 3.87 (s, 6H), 4.943 (q, 1H, J = 6.64 Hz), 6.841 (t, 1H, J = 4.88 Hz), 6.976 (d, 2H, J = 3.42 Hz) ppm.^{19}F NMR ($CDCl_3$, $CFCl_3$): δ −78.916 (d, J_{F-H} = 6.1 Hz) ppm. MS m/z 236 (M^+), 219, 197, 167, 139, 124, 108, 96. Anal. Calcd for $C_{10}H_{11}F_3O_3$: C, 50.85; H, 4.69; F, 24.13. Found: C, 50.92; H, 4.66; F, 24.11. 99% yield.

Compound **12**. ^{1}H NMR ($CDCl_3$, TMS): δ 2.97 (s, 1H), 4.58−4.66 (m, 1H), 6.20 (q, 1H, J = 9.46 Hz), 6.842 (d, 1H, J = 15.93 Hz), 7.31−7.44 (m, 5H) ppm. ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ −79.458 (d, J_{F-H} = 6.1 Hz) ppm. MS m/z 202 (M^+), 184, 165, 133, 115, 91, 77, 55. Anal. Calcd for $C_{10}H_9F_3O$: C, 59.41; H, 4.49; F, 28.19. Found: C, 59.45; H, 4.52; F, 28.17. 99% yield.

Compound ***13***. ^{1}H NMR ($CDCl_3$, TMS): δ 2.25 (s, 1H), 3.84 (s, 3H), 4.531 (t, 1H, J = 13.19 Hz), 5.65 (s, 1H), 5.961 (q, 1H, J = 9.12 Hz), 6.689 (d, 1H, J = 15.73 Hz), 6.82−6.88 (m, 3H) ppm. ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ −79.607 (d, J_{F-H} = 6.1Hz) ppm. MS m/z 248 (M^+), 219, 199, 179, 161, 147, 119, 91. Anal. Calcd for $C_{11}H_{11}F_3O_3$: C, 53.23; H, 4.47; F, 22.96. Found: C, 53.28; H, 4.44; F, 22.97. 99% yield.

Compound ***14***. ^{1}H NMR ($CDCl_3$): δ 0.091 (s, 18H), 6.16 (s, 4H) ppm. ^{19}F NMR($CDCl_3$, $CFCl_3$): δ −80.51 (s) ppm. MS m/z 323 ($M^+ - CF_3$), 307, 285, 265, 254, 223, 219, 189.

Compound ***15***. ^{1}H NMR ($CDCl_3$): δ 2.42 (br, 4H), 6.19 (s, 4H), 6.27 (s, 4H) ppm. ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ −80.81 (s), −80.76 (s) ppm. MS m/z 179 ($M^+ - CF_3$), 159, 143, 110, 83, 69, 53. Anal. Calcd for $C_8H_6F_6O_2$: C, 38.73; H, 2.44; F, 45.94. Found: C, 38.75; H, 2.49; F, 45.96. 96% yield.

Compound ***16***. ^{1}H NMR ($CDCl_3$): δ 0.08−0.09 (d, 18H, J = 2.5 Hz), 1.93−1.94 (d, 3H, J = 1.26 Hz), 5.85−5.86 (d, 1H, J = 1.18 Hz), 6.16 (s, 2H) ppm. ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ −80.67 (s), −77.03 (s) ppm. MS m/z 337 ($M^+ - CF_3$), 321, 268, 229, 203, 175, 147, 127.

Compound ***17***. ^{1}H NMR ($CDCl_3$): δ 2.02−2.03 (d, 3H, J = 1.16 Hz), 2.30 (br, 2H), 5.98−5.99 (d, 1H, J = 1.72 Hz), 6.24−6.25 (t, 2H, J = 2.16 Hz) ppm. ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ −81.21 (s), −77.25 (s) ppm. MS m/z 193 ($M^+ - CF_3$), 173, 145, 124, 69, 51. Anal. Calcd for $C_9H_8F_6O_2$: C, 41.24; H, 3.08; F, 43.48. Found: C, 41.27; H, 3.15; F, 43.50. 95% yield.

Compound ***18***. ^{1}H NMR ($CDCl_3$): δ −0.137 to −0.125 (d, 18H, J = 2.38 Hz), 1.36−1.39 (d, 9H, J = 5.30 Hz), 7.45−7.51 (m, 3H), 7.80−7.95 (m, 4H) ppm. ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ −78.56 (s), −78.55 (s) ppm. MS m/z 479 ($M^+ - CF_3$), 441, 410, 372, 344, 301, 267, 233.

Compound ***19***. ^{1}H NMR ($CDCl_3$): δ 1.37−1.41 (d, 9H, J = 8.60 Hz), 3.19−3.30 (d, 2H, J = 21.23 Hz), 7.52−7.60 (m, 3H), 7.89−8.03 (m, 4H) ppm. ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ −78.61 (s), −78.29 (s) ppm. MS m/z 335 ($M^+ - CF_3$), 320, 266, 251, 209, 181, 152, 112. Anal. Calcd for $C_{20}H_{18}F_6O_2$: C, 59.41; H, 4.49; F, 28.19. Found: C, 59.38; H, 4.46; F, 28.22. 94% yield.

Compound ***20***. ^{1}H NMR ($CDCl_3$): δ 0.021 (s, 18H), 1.03 (s, 9H), 1.20 (s, 9H), 5.39 (s, 1H), 6.01 (s, 1H) ppm. ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ −68.84 (s), −74.89 (s) ppm. MS m/z 504 ($M^+ - CF_3$), 489, 435, 399, 379, 327, 285, 259.

Compound ***21***. ^{1}H NMR ($CDCl_3$): δ 1.05 (s, 9H), 1.25 (s, 9H), 2.45 (s, 1H), 3.05 (s, 1H), 5.19 (s, 1H), 6.06 (s, 1H) ppm. ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ −70.13 (s), −75.90 (s) ppm. MS m/z (silylated) 504 (M^+ - CF_3), 489, 399, 379, 327, 285, 259, 239. Anal. Calcd for $C_{16}H_{22}F_6O_2$: C, 53.33; H, 6.15; F, 31.63. Found: C, 53.40; H, 6.10; F, 31.59. 89% yield.

Compound ***22***. ^{1}H NMR ($CDCl_3$): δ 0.042 (s, 18H), 7.22−7.31 (m, 3H), 7.36−7.61 (m, 4H), 7.76−7.83 (m, 3H) ppm. ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ −74.52 (s) ppm. MS m/z 247 ($M^+ - C_{11}H_{14}F_3OSi$), 213, 181, 165, 135, 105, 77, 51.

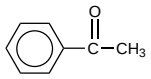
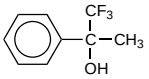
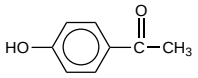
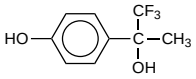
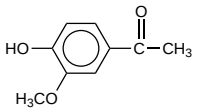
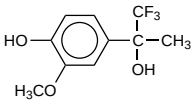
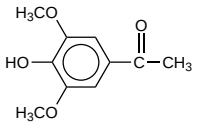
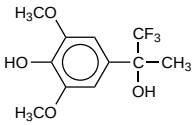
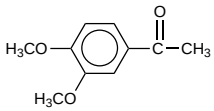
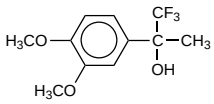
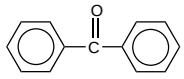
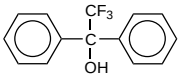
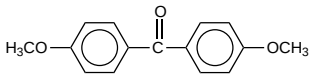
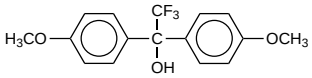
Compound ***23***. ^{1}H NMR ($CDCl_3$): δ 4.75 (s, 2H), 7.25−7.34 (m, 2H), 7.41−7.55 (m, 6H), 7.67−7.72 (t, 2H, J = 7.32 Hz) ppm. ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ −73.55 (s) ppm. MS m/z 175 ($M^+ - C_8H_6F_3O$), 152, 105, 77, 51. Anal. Calcd for $C_{16}H_{12}F_6O_2$: C, 54.87; H, 3.45; F, 32.54. Found: C, 54.91; H, 3.50; F, 32.58. 98% yield.

Compound ***25***. ^{1}H NMR ($CDCl_3$, TMS): δ 3.63 (s, 1H), 3.78 (s, 3H), 3.863 (d, 6H, J = 5.40 Hz), 4.07−4.12 (m, 2H), 4.449-(t, 1H, J = 1.80 Hz), 5.57 (s, 1H), 6.692 (q, 1H, J = 3.60 Hz), 6.77−6.83 (m, 2H), 6.865 (d, 1H, J = 5.10 Hz), 6.95−6.99 (m, 1H), 7.193 (d, 1H, J = 4.80 Hz), 7.294 (d, 1H, J = 1.2 Hz) ppm. ^{13}C NMR ($CDCl_3$, TMS): δ 55.85, 56.04, 56.17, 61.36, 79.59, 82.64, 109.87, 110.48, 112.07, 118.25, 120.72, 121.66, 123.83, 124.62, 124.97 (q, J_{C-F} = 286.59 Hz), 126.11, 128.93, 146.18, 148.56, 148.89, 151.53 ppm. ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ −75.53 (s) ppm. MS m/z (silylated) 402 (M^+), 302, 278, 248, 235, 221, 181, 165. Anal. Calcd for $C_{19}H_{21}F_3O_6$: C, 56.72; H, 5.26; F, 14.16. Found: C, 56.74; H, 5.29; F, 14.22. 95% yield.

Compound ***27***. ^{1}H NMR ($CDCl_3$, TMS): δ 3.84 (s, 3H), 3.87 (s, 3H), 3.90 (s, 3H), 3.93 (d, 1H, J = 3 Hz), 4.24 (d, 1H, J = 12 Hz), 4.640 (d, 1H, J = 12 Hz), 5.865 (d, 1H, J = 3 Hz), 6.84−7.12 (m, 6H) ppm. ^{13}C NMR ($CDCl_3$, TMS): δ 56.11, 56.19, 56.64, 79.85, 108.78, 110.06, 111.44, 113.40, 120.41, 121.80, 122.95, 124.46, 125.60 (q, J_{C-F} = 286.59 Hz), 126.74, 127.88, 147.37, 148.68, 149.16, 149.45 ppm. ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ −77.63 (s) ppm. MS m/z 372 (M^+), 303, 248, 235, 217, 189, 180. Anal. Calcd for $C_{18}H_{19}F_3O_5$: C, 58.06; H, 5.14; F, 15.31. Found: C, 58.21; H, 5.20; F, 15.29. 96% yield.

Compound ***29***. ^{1}H NMR ($CDCl_3$, TMS): δ 2.25 (s, 3H), 3.75 (s, 1H), 3.79 (s, 3H), 3.88 (s, 3H), 3.935 (d, 1H, J = 9 Hz), 4.12 (d, 1H, J = 5.99 Hz), 4.33 (s, 1H), 5.60 (s, 1H), 5.70 (s, 1H), 6.55−6.64 (m, 3H), 6.94 (d, 1H, J = 5.40 Hz), 7.10 (d, 1H, J = 4.80 Hz), 7.311 (d, 1H, J = 1 Hz) ppm. ^{13}C NMR ($CDCl_3$, TMS): δ 21.19, 55.88, 55.93, 61.31, 79.52, 82.64, 109.59, 112.95, 113.93, 118.43, 121.01, 122.19, 123.93, 125.07 (q, J_{C-F} = 286.59 Hz), 126.21, 128.71, 134.83, 143.81, 145.62, 146.35, 151.36 ppm.^{19}F NMR ($CDCl_3$, $CFCl_3$): δ −75.48 (s) ppm. MS m/z (silylated) 618 (M^+), 480, 451, 411. 365, 343, 323, 271. Anal. Calcd for $C_{19}H_{21}F_3O_6$: C, 56.72; H, 5.26; F, 14.16. Found: C, 56.78; H, 5.19; F, 14.18. 93% yield.

Table 1. Fluoride Ion Induced Trifluoromethylation of Ketones with Trifluoromethyltrimethylsilane

entry	precursor	product	reacn conditions	overall % yield	^{19}F NMR (ppm)	GC-MS *m/e*
1			0 °C, 30 min 25 °C, 16 h hydrolysis, 8 h	96	−81.35	MS *m/z* 190 (M^+), 151, 127, 121, 105, 91
2			0 °C, 30 min 25 °C, 6 h hydrolysis, 2 h	98	−81.76	MS *m/z* 206 (M^+), 188, 167, 149, 137, 119
3			0 °C, 30 min 25 °C, 14 h hydrolysis, 5 h	96	−81.60	MS *m/z* 236 (M^+) 197, 167, 151, 124, 110
4			0 °C, 30 min 25 °C, 18 h hydrolysis, 2 h	95	−81.47	MS *m/z* 266 (M^+), 227, 197, 181, 155, 123
5			0 °C, 30 min 25 °C, 14 h hydrolysis, 5 h	95	−81.56	MS *m/z* 250 (M^+) 211, 181, 139, 124, 107
6			0 °C, 30 min 25 °C, 16 h hydrolysis, 5 h	94	−74.79	MS *m/z* 252 (M^+), 233, 213, 183, 165, 127
7			0 °C, 30 min 25 °C, 16 h hydrolysis, 5 h	96	−75.11	MS *m/z* 312 (M^+), 273, 243, 212, 135, 108

RESULTS AND DISCUSSION

Initially a series of model compounds containing carbonyl groups, including various quinones, were trifluoromethylated, and their ^{19}F NMR spectra were examined . This was done in order to understand the relationships between the chemical environment of CF_3-containing derivatives and their ^{19}F NMR chemical shifts. Detailed work with carbonyl-containing arylglycerol β-O-4 ether model compounds followed, aimed at understanding the trifluoromethylation reaction so that it can eventually be applied to lignins, solid wood, and paper samples.

Aromatic Compounds Containing Carbonyl Groups. Various organic compounds containing carbonyl groups in different chemical environments were subjected to the described trifluoromethylation reaction. This eventually allowed for the correlation of trifluoromethylated structures to their ^{19}F resonance for carbonyl environments that may be present in lignins. These studies indicated that the ^{19}F NMR chemical shifts vary significantly for several classes of carbonyl groups. For example, the ^{19}F NMR signal of various trifluoromethylated ketones, such as acetophenone **(1)** was observed at −81.35 ppm, distinguishing it from that of *p*-hydroxyacetophenone **(2)** recorded at −81.76 ppm upfield from $CFCl_3$. Such variations of ^{19}F chemical shifts were also apparent for different aldehydes.

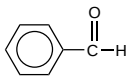
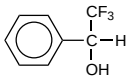
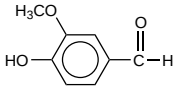
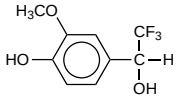
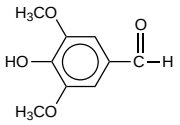
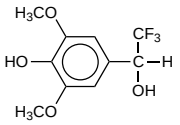
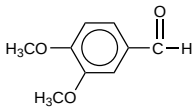
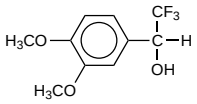
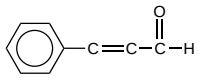
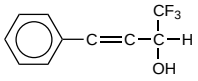
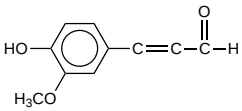
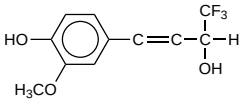
The ^{19}F NMR chemical shift of trifluoromethylated benzaldehyde **(8)** was recorded (doublet) at −78.848 ppm, while the ^{19}F NMR signals moved progressively downfield with the addition of different substituents on the benzene ring. This demonstrates that the chemical shift of ^{19}F is quite sensitive to the environment (Gerig, 1978), and therefore ^{19}F spectroscopy would be a useful tool for measuring and probing different classes of compounds containing fluorine and fluorine derivatives.

It is well-known that the fluorine (^{19}F) nucleus has similar magnetic properties to those of the proton and may be coupled not only with each other but also with protons. Absorption by fluorine does not appear in the proton NMR spectrum since it appears far off the proton observation scale, but fluorine splitting of proton signals can be seen. This was evident for all the trifluoromethylated aldehyde derivatives examined during this work (Tables 1 and 2).

Salient Features of the Reaction. The trifluoromethylation of most of the examined organic compounds was first carried out in the presence of catalytic amounts of tetra-*n*-butylammonium fluoride (TBAF) acting as an initiator for the reaction. Although this salt was effective, other catalysts were investigated since the reaction yields were consistently low. Potassium *tert*-butoxide and tetra-*n*-butylammonium iodide (TBAI) have been used with success as initiators for the trifluoromethylation of acetophenone (Prakash et al., 1989). In comparison to TBAF, both were found to be equally effective. In fact the final yields of the reaction increased to about 88% when potassium *tert*-butoxide was employed. However, there are some drawbacks associated with the use of such initiators, restricting their use in trifluoromethylating lignins.

In general the treatment of carbonyl-containing compounds with Ruppert's reagent in the presence of TBAF only resulted in qualitatively converting these compounds to their siloxy intermediates. The hydrolysis of trimethylsiloxytrifluoromethylated intermediates was found to be inefficient when dilute HCl was used, particularly for the case of benzophenone (**5**). Such problems were also observed by another group in their attempt to trifluoromethylate hindered steroidal ketones (Wang and Ruan, 1994). Both of these issues were found to be responsible for the low overall yields of the reaction. Such yields could not qualify this reaction as an analytical tool. Wang and Ruan succeeded in improving the yields of this reaction to quantitative levels, by using the more effective tetramethylammonium fluoride (TMAF) as an initiator.

Table 2. Fluoride Ion Induced Trifluoromethylation of Aldehydes with Trifluoromethyltrimethylsilane

entry	precursor	product	reacn conditions	overall % yield	^{19}F NMR (ppm)	GC-MS *m/e*
8			0 °C, 30 min 25 °C, 20 h hydrolysis, 5 h	97	−78.848 (d, J_{F-H} = 6.1 Hz)	MS *m/z* 176 (M^+), 159, 127, 107, 89, 79
9			0 °C, 30 min 25 °C, 20 h hydrolysis, 5 h	95	−78.981 (d, J_{F-H} = 6.1 Hz)	MS *m/z* 222 (M^+), 205, 183, 153, 125, 93
10			0 °C, 30 min 25 °C, 24 h hydrolysis, 5 h	98	−78.890 (d, J_{F-H} = 6.1 Hz)	MS *m/z* 252 (M^+), 205, 183, 167, 155, 140
11			0 °C, 30 min 25 °C, 24 h hydrolysis, 5 h	99	−78.916 (d, J_{F-H} = 6.1 Hz)	MS *m/z* 236 (M^+), 219, 197, 167, 139, 124
12			0 °C, 30 min 25 °C, 16 h hydrolysis, 5 h	99	−79.458 (d, J_{F-H} = 6.1 Hz)	MS *m/z* 202 (M^+), 184, 165, 133, 115, 91
13			0 °C, 30 min 25 °C, 18 h hydrolysis, 5 h	99	−79.607 (d, J_{F-H} = 6.1 Hz)	MS *m/z* 248 (M^+), 219, 199, 179, 161, 147

In our work we addressed the issue of efficiently cleaving the silyl ethers by using 40% aqueous HF solution in acetonitrile (CH_3CN) (Greene and Wuts, 1991). After careful isolation of the products, their yield was calculated and compared to those with TBAF. The combination of TMAF and aqueous HF was therefore used in all subsequent efforts of trifluoromethylating the various sets of compounds discussed in this report (quinones were hydrolyzed with TMAF).

Quinones. A number of studies have shown that quinones are present, in small amounts, in wood and high-yield mechanical pulps (Lebo et al., 1990; Argyropoulos et al., 1995; Argyropoulos and Heitner, 1994). Despite their low abundance, they have been held responsible as one of the significant factors for the yellowing of paper (Lin and Kringstad, 1971; Kringstad, 1973; Forsskåhal and Janson, 1991; Castellan et al., 1993; Gellersted and Pattersson, 1977; Lebo et al., 1990).

The trifluoromethylation of quinones by adding only to one of the carbonyl carbon atoms has been studied by Stahly and Bell (1989). In an effort to evaluate the reactivity of quinones (on both carbonyl carbon atoms) with Ruppert's reagent, a number of different compounds were selected and trifluoromethylated. The isolated products at each step of the reaction were thoroughly examined by ^{19}F and ^{1}H NMR and GC-MS.

Initially *p*-benzoquinone was trifluoromethylated. The CF_3-containing trimethylsiloxy intermediate (**14**) was isolated and later examined by ^{1}H and ^{19}F NMR spectroscopies. The resulting spectra confirmed the trifluoromethylation of both carbonyl groups.

The subsequent hydrolysis of the CF_3-containing siloxy intermediates with 40% HF solution was limited since such concentrations would result in the cleavage of several arylglycerol β-O-4 ether bonds when applied to lignins. However, lower concentrations of HF (i.e. 10%) failed to cleave silyl ether bonds completely due to the low solubility of quinones in acetonitrile. This problem was resolved by the addition of TMAF in THF at room temperature. Such a combination was able to cleave the trimethylsiloxy intermediates effectively to their corresponding alcohols, resulting in the development of an improved method for cleaving silyl ethers. After hydrolysis, the isolated compound **(15)** was subjected to ^{19}F and ^{1}H NMR investigations in order to assign the signals for the corresponding fluorine and alcohol groups of the derivative. The ^{19}F NMR spectrum showed two signals with equal intensity and 0.05 ppm difference in their chemical shifts. The ^{1}H NMR spectrum confirmed the complete hydrolysis of the silyl ethers since a new signal due to the hydroxyl group appeared at 2.42 ppm. In addition, two other signals corresponding to the four unsaturated protons of each stereoisomer were observed.

These data, in conjunction with its GC-MS spectrum, confirmed the purity of the products. As such, the formation of two stereoisomers (*syn* and *anti*) as a result of trifluoromethylation and hydrolysis became evident. The absence of these geometric isomers prior to hydrolysis can only be explained by the presence of the bulky trimethylsiloxy groups which considerably hinders the formation of the "*syn*" isomer, therefore giving rise to only one signal in the ^{19}F NMR spectrum at −80.51ppm.

The isolated trifluoromethyltrimethylsiloxy intermediate of methyl-*p*-benzoquinone (**16**), an unsymmetric derivative of *p*-benzoquinone, displayed two well-resolved signals at −77.03 and −80.67 ppm. These signals were assigned to both CF_3 substituted on the former carbonyl carbons adjacent and nonadjacent to the methyl group, respectively.

When 2-*tert*-butyl anthraquinone was subjected to trifluoromethylation, the ^{1}H NMR spectrum of the isolated intermediate **(18)** showed the presence of trimethylsiloxy groups, and its ^{19}F NMR spectrum displayed two overlapping signals separated by 0.007 ppm. Such evidence supported the observation of two stereoisomers of derivatized *p*-benzoquinones. This was concluded since the *tert*-butyl group, though far removed from the carbonyl groups is, less sterically hindering than the neighboring methyl group in methyl-*p*-benzoquinone (Figure 1).

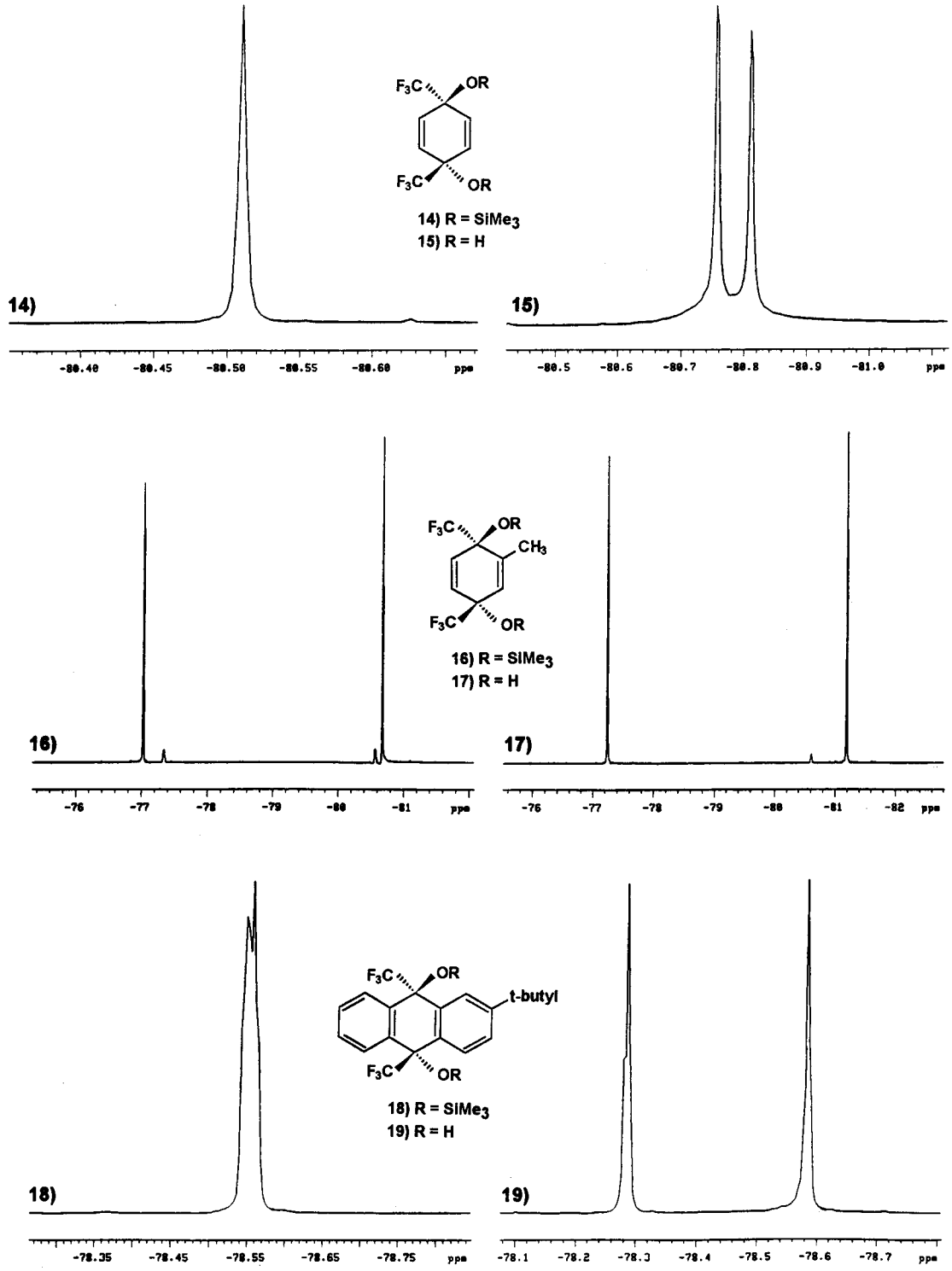


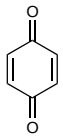
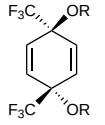
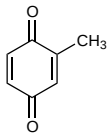
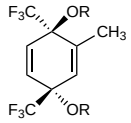
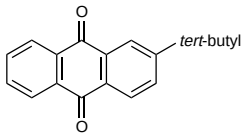
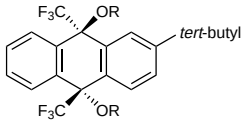
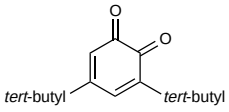
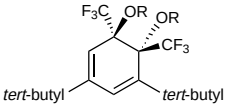
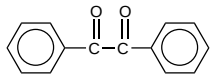
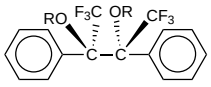
Figure 1. ^{19}F NMR spectra of trifluoromethylated quinones before (left) and after (right) hydrolysis.

The ^{1}H NMR spectrum of **19** showed a broad signal due to the hydroxyl groups at 3.19 ppm, while its trifluoromethylated ^{19}F NMR spectrum showed two distinct signals at −78.29 and −78.61 ppm due to the desilylation of CF_3 intermediates during hydrolysis with TMAF. In addition to *p*-quinones, *o*-quinones are another important class of dicarbonyl-containing compounds that may be found in lignin. *o*-Quinones may be formed during demethylation and/or deprotonation of several syringyl- and guaiacyl-lignin structures as a result of various chemical reactions.

To evaluate the reactivity of *o*-quinones with Ruppert's reagent, 3′,5′-di-*tert*-butyl-1,2-benzoquinone was trifluoromethylated (**20**) and hydrolyzed (**21**). According to the obtained data, *o*-quinones were found to undergo this process quite efficiently, as shown in Table 3. Furthermore, the same procedure was carried out for benzil, and the chemistries of the trifluoromethylated intermediates (**22**) and alcohols (**23**) were studied. The ^{19}F NMR spectra of the both **22** and **23** depicted only one signal due to the symmetric structure of benzil.

Lignin Model Compounds. Our efforts toward examining the potential of Ruppert's reagent for the elucidation of carbonyl groups in lignins were then focused on dimeric model compounds containing carbonyl groups, resembling those present in lignins. Dimer-

Table 3. Fluoride Ion Induced Trifluoromethylation of Quinones with Trifluoromethyltrimethylsilane

entry	precursor	product	reacn conditions	overall % yield	[19]F NMR (ppm)	GC-MS *m/e*
14, 15		 **14**, R = $SiMe_3$; **15**, R = H	0 °C, 30 min 25 °C, 6 h hydrolysis, 5 h	96	**14** {−80.51	MS *m/z* 323 ($M^+ - CF_3$), 307, 285, 265, 254, 223
					15 {−80.75, −81.80	MS *m/z* 179 ($M^+ - CF_3$), 159, 143, 110, 83, 69
16, 17		 **16**, R = $SiMe_3$; **17**, R = H	0 °C, 30 min 25 °C, 7 h hydrolysis, 5 h	95	**16** {−77.03, −80.67	MS *m/z* 337 ($M^+ - CF_3$), 321, 268, 229, 203, 175
					17 {−77.25, −81.21	MS *m/z* 193 ($M^+ - CF_3$), 173, 145, 124, 69, 51
18, 19		 **18**, R = $SiMe_3$; **19**, R = H	0 °C, 30 min 25 °C, 8 h hydrolysis, 6 h	94	**18** {−78.55, −78.56	MS *m/z* 479 ($M^+ - CF_3$), 410, 372, 344, 301, 267
					19 {−78.29, −78.61	MS *m/z* 335 ($M^+ - CF_3$), 320, 266, 251, 209, 181
20, 21		 **20**, R = $SiMe_3$; **21**, R = H	0 °C, 30 min 25 °C, 4 h hydrolysis, 5 h	89	**20** {−68.84, −78.89	MS *m/z* 504 ($M^+ - CF_3$), 489, 435, 399, 379, 327
					21 {−69.59, −75.87	MS *m/z* 504 (silylated), ($M^+ - CF_3$), 489, 399, 379, 327, 285
22, 23		 **22**, R = $SiMe_3$; **23**, R = H	0 °C, 30 min 25 °C, 5 h hydrolysis, 4 h	98	**22** {−74.52	MS *m/z* 247 ($M^+ - C_{11}H_{14}F_3OSi$), 213, 181, 165, 135, 105
					23 {−73.55	MS *m/z* 175 ($M^+ - C_8H_6F_3O$), 152, 105, 77, 51

ic model compounds have often been used in NMR studies aimed at the structural elucidation of lignins (Adler et al., 1987; Lundquist, 1980; Lundquist and Olsson, 1977; Brunow and Lundquist, 1980; Lundquist, 1981). ^{31}P, ^{1}H, and ^{13}C NMR spectroscopies and GC/MS analyses were used in a manner similar to that described so far in each step of the trifluoromethylation reaction, and the obtained spectra were compared to those of the starting materials aimed at monitoring all changes that took place during the course of the reaction.

Initial attempts to trifluoromethylate 3,4-dimethoxy-α-(2-methoxyphenoxy)-γ-hydroxypropiophenone (**24**) posed some difficulties since low yields were obtained when stoichiometric amounts of TMS-CF_3 in the presence of TBAF were employed; the presence of the primary γ-OH was suspected as interfering. In an effort to understand the role of the γ-OH in this reaction, two avenues were followed. The compound was acetylated prior to trifluoromethylation, thus protecting the primary γ-hydroxyl groups. Following acetylation, the model compound was trifluoromethylated and hydrolyzed with 1 N HCl. The yield of the purified products was calculated to be 46%. Although this procedure improved the final yield to a small extent, the reaction yield was still too low for the quantification of the carbonyls in lignins. Trifluoromethylation of 3,4-dimethoxy-α-(2-methoxyphenoxy)acetophenone (**26**) was the other approach. The overall trifluoromethylation of the α-carbonyl of **26** took place with somewhat more facility than that of **24**. Although the spectral analysis of product **27** showed only one ^{19}F NMR signal at −77.63 ppm due to the trifluoromethyl group, the yield of the product never exceeded 46%.

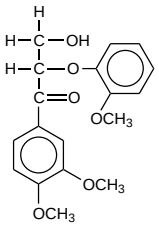
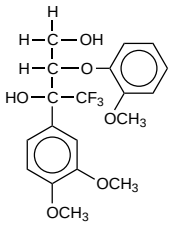
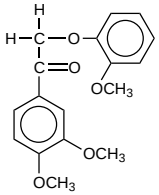
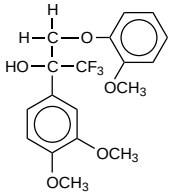
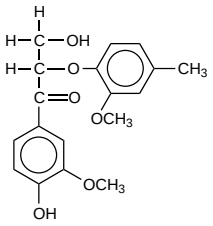
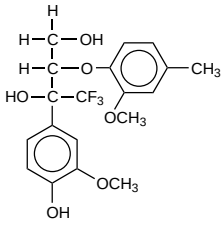
Finally the yields of these reactions were considerably improved by using TMAF as the initiator and 20% aqueous HF in acetonitrile as the hydrolysis medium. These modifications not only increased the reaction yields by more than 2-fold, they also gave clean trifluoromethylated products. The ^{19}F NMR spectrum of **25** showed a single signal at −75.53 ppm due to substituted CF_3, and the ^{31}P NMR spectra featured a signal at 127.4 ppm due to the formation of tertiary α-OH as a result of the hydrolysis. The ^{13}C NMR contained a new quartet due to the CF_3 group, while the complete elimination of the carbonyl signal signified the trifluoromethylation of the carbonyls. This was verified by examining the ^{1}H NMR spectrum of the compound, where a new signal at 5.57 ppm signified the formation of α-OH.

To further confirm our findings, 3-methoxy-4-hydroxy-α-(2-methoxy-4-methyl)-γ-hydroxypropiophenone (**28**) was triflurometylated under the same conditions. The resulting CF_3-containing compound (**29**) was then examined by GC-MS and ^{19}F, ^{13}C, and ^{1}H NMR spectroscopies. Consequently, it was demonstrated that trifluoromethylation of the dimeric lignin model compounds can be quantitatively achieved with the more effective TMAF as an initiator.

The next issue was whether or not the trifluoromethylation procedure could result in the scission of arylglycerol β-O-4 ether bonds. This is a very important issue as far as the primary objectives of this work are concerned, since more than 40% of the structural units in lignins are known to be linked together by β-ether bonds (Lai and Sarkanen, 1972; Erickson et al., 1973; Matsumoto et al., 1980).

Such an event may take place due to the presence of trimethylsilyl fluoride, formed as a side product in conjunction with trifluoromethyltrimethylsilane during the reaction. In a series of publications that address the selective cleavage of ether bonds in lignin, there is

Table 4. Fluoide Ion Induced Trifluoromethylation of the Carbonyl Group for Lignin Model Compounds with Trifluoromethyltrimethylsilane

entry	precursor	product	reacn conditions	overall % yield	^{19}F NMR (ppm)	GC-MS *m/e*
24		 **25**	0 °C, 30 min 25 °C, 24 h hydrolysis, 24 h	95	−75.53	Ms *m/z* (silylated) 402, (M+), 302, 278, 248, 235, 221
26		 **27**	0 °C, 30 min 25 °C, 24 h hydrolysis, 24 h	96	−77.63	Ms *m/z* 372, (M^+), 303, 248, 235, 217, 189
28		 **29**	0 °C, 30 min 25 °C, 24 h hydrolysis, 24 h	93	−75.48	Ms *m/z* (silylated) 618, (M^+), 480, 451, 411, 365, 343

substantial evidence that trimethylsilyl iodide is capable of cleaving β-O-4 ether bonds. In fact several studies have shown that this is an effective method of cleaving the ether bonds between lignin side chains and aromatic nuclei (Matsumoto et al., 1982; Makino et al., 1989, 1990; Fujino et al., 1992; Ho and Olah, 1976).

Although the reaction was carried out in the absence of trimethylsilyl iodide (TMSiI), the formation of trimethylsilyl fluoride (TMSiF) during the course of the reaction was a possibility to consider since it could behave similarly to TMSiI. For this reason, gas chromatography was employed to evaluate the integrity of alkyl−aryl ether bonds of the lignin model compounds (**24** and **26**) before and after the reaction. It was confirmed that, under the conditions employed in this work, the formation of TMSiF did not cleave the β-ether bonds of the models used. Tetrabutylammonium iodide cannot be used as an initiator for the reaction, since it would result in the formation of TMSiI, which will in return cleave the alkyl−aryl ether bonds in dimeric model compounds and lignin. Potassium *tert*-butoxide was found to be a very effective initiator of trifluoromethylation for a series of monomeric model compounds. Its strongly basic character, however, poses the danger of structural alterations to the delicate and complex nature of lignin. The trifluoromethylation reaction in the presence of TBAF resulted in low yields, precluding this procedure from becoming a tool for the quantitative analysis of carbonyl groups in lignins.

CONCLUSIONS

The quantitative trifluoromethylation of carbonyl groups for a series of carbonyl-containing lignin-like model compounds has been accomplished. This was achieved by using (trifluoromethyl)trimethylsilane (Ruppert's reagent) in the presence of TMAF. This reagent was found to be an efficient nucleophilic trifluoromethylating agent for derivatizing a variety of carbonyl-containing compounds. Although their ^{19}F NMR signals were well-resolved, allowing differentiation among the various classes of carbonyl groups, the chemical shifts of trifluoromethylated quinones occupied a wide range, overlapping with those of ketones.

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