

# THE USE OF CREN TO IMPROVE $^{13}\text{C}$ -NMR SPECTRA OF COMPOUNDS CONTAINING CARBON ATOMS REPRESENTATIVE OF ORGANICS DISSOLVED IN KRAFT BLACK LIQUOR

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## ABSTRACT

Tris(ethylenediamine)chromium(III) chloride (CREN) was added as a relaxation agent for  $^{13}\text{C}$ -NMR spectra of cellobiose, ferulic acid [3-(4-hydroxy-3-methoxyphenyl)-2-*trans*-propenoic acid], and vanillin (4-hydroxy-3-methoxybenzaldehyde) in aqueous alkaline solutions. The three compounds contain carbon atoms representative of those in kraft black liquor dissolved organics. CREN improved the  $^{13}\text{C}$ -NMR spectra of the compounds by increasing the chemical shift dispersion in several cases, and by elucidating peaks that were not identifiable in  $^{13}\text{C}$ -NMR spectra without CREN.

**Keywords:** Kraft black liquor, CREN,  $^{13}\text{C}$ -NMR, cellobiose, ferulic acid, vanillin.

## INTRODUCTION

Kraft pulping of wood involves heating wood chips in an aqueous solution of sodium hydroxide and sodium sulfide to solubilize the lignin, leaving the bulk of the carbohydrate fibers behind as pulp. In addition to the pulping chemicals and dissolved lignin compounds, other chemicals end up in solution (kraft black liquor) after pulping. Cellulose and other wood carbohydrates are degraded by the harsh chemicals and also are dissolved in the kraft black liquor. A knowledge of these dissolved organics, particularly their function-

al groups, is important to studies of certain processes in kraft pulp mills.

The wood-chip raw material is a major source of nonprocess elements that contaminate the kraft black liquor. Nonprocess elements are those elements that are not essential to the chemical process. They are neither active pulping chemicals nor compounds present as a result of incomplete conversion of make-up chemicals to active pulping chemicals (Streisel 1987). Many of these elements (aluminum, calcium, iron, potassium, magnesium, manganese, and vanadium) are metals that ex-

ist as cations in several pulping stages. They can cause problems in the process chemical recovery cycle when they accumulate to certain levels in the system. These problems include scaling in the black liquor evaporators, and fouling and corrosion of heat-transfer surfaces.

Wood organics that dissolve in the kraft black liquor contain chemical functional groups that interact with the nonprocess metal cations. For example, carboxylic acids form salts and catechol groups chelate with bivalent cations (Marton 1971; Frederick and Grace 1981; Westervelt 1981; Westervelt et al. 1982). To avoid scaling and other problems, nonprocess elements must be removed. The most promising method is through natural purges (Streisel 1987), which requires an understanding of the complexes formed between dissolved wood organics and nonprocess elements.

The overall aim of the present work was to study the functional groups of the kraft black liquor organics in the same state as when they were generated in the kraft pulp mill, without alteration or derivatization. Toward this end, we determined the  $^{13}\text{C}$ -NMR spectra of the authentic compounds cellobiose, ferulic acid [3-(4-hydroxy-3-methoxyphenyl)-2-*trans*-propenoic acid], and vanillin (4-hydroxy-3-methoxybenzaldehyde) to ascertain the position assignments of carbon atoms in functional groups that are representative of those in kraft black liquor dissolved wood organics.

A major concern in developing analytical techniques for the functional groups was to minimize changes to those chemicals that are dissolved in the kraft black liquor. Other investigators (Nimz et al. 1981; Obst and Landucci 1986) have generally used acid precipitation and/or organic solvent extraction techniques to fractionate the dissolved liquor components, and acetylation plus organic solvents for  $^{13}\text{C}$ -NMR analyses. We found that by  $^{13}\text{C}$ -NMR analyses, the functional groups could be detected without precipitation or derivatization as they existed in the kraft black liquor, but that method required aqueous solutions at high

pH. Therefore we approximated the condition of kraft black liquor by using 0.1 N aqueous sodium hydroxide as the solvent for  $^{13}\text{C}$ -NMR of the authentic compounds. A relaxation agent, tris(ethylenediamine)chromium(III) chloride (CREN) was used to aid structure determination in aqueous solution (Bose et al. 1977). The use of CREN in this manner has been reported (Antonucci and Smith 1983), but has not been applied extensively in pulping research.

#### MATERIALS AND METHODS

##### *Tris(ethylenediamine)Chromium(III) Chloride (CREN)*

The CREN complex as purchased (ICN Biochemicals, Incorporated, K&K Labs, Plainview, New York) was not thermally stable and degraded at temperatures of 60°C or higher; it was refrigerated at 5°C. Purification was necessary because the purchased material had a slight brown color, especially on exposed surfaces. The CREN complex was dissolved in water, and 95% ethanol was added to precipitate the pure CREN complex (Gillard and Mitchell 1972). The pure CREN complex, recovered by filtration, was bright yellow. It was dissolved in deuterium oxide at ambient temperatures (22°C) when used.

##### *Authentic compounds*

The authentic compounds were purchased: cellobiose and vanillin from J. T. Baker Company, Philipsburg, New Jersey, and ferulic acid from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin. Cellobiose was used as a compound that contained carbon atoms representative of those in the dissolved carbohydrates in kraft black liquors. The dissolved lignin fragments, which are composed of the basic phenylpropane carbon arrangement known to be the fundamental building units of lignin (Sarkanen and Ludwig 1971), were represented by the phenylpropane carbon atoms in ferulic acid. Vanillin was used as a compound to represent the lignin fragments

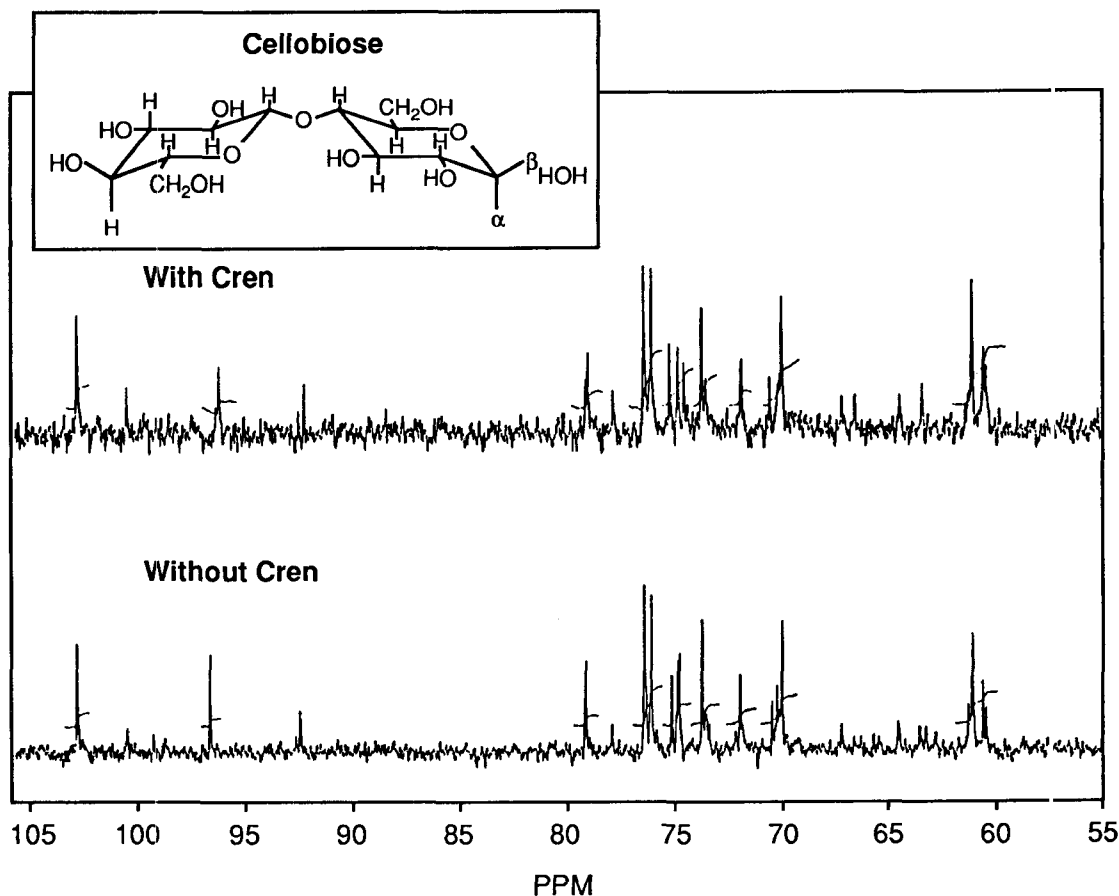


FIG. 1.  $^{13}\text{C}$ -NMR spectra of cellobiose with CREN and without CREN.

that are benzylic in nature and contain carbonyl groups.

#### $^{13}\text{C}$ -NMR spectroscopy

The spectrometer was a Bruker Model AM400 FT (Bruker Instruments, Inc., Manning Park, Billerica, Massachusetts) that used a pulsed signal and fourier transformation of the raw data. The spectrometer was set for 100.6 MHz  $^{13}\text{C}$ -NMR. The pulse width was 8.3  $\mu\text{sec}$ , and the sweep width was 250 ppm. A 5-mm NMR tube was used for all spectra.

An aliquot of 2.1 ml of 0.1 N sodium hydroxide solution containing 10% of each model compound was mixed with 0.6 ml of 0.1 M CREN in deuterium oxide. Pure deuterium oxide (0.3 ml) was added for lock, resulting in a

final sample that was 0.02 M in CREN (Antonucci and Smith 1983). Aliquots of the samples were filtered through a 0.100- $\mu\text{m}$  microfilter as they were added to the NMR tubes. Samples were prepared at room temperature (22°C) and kept refrigerated under argon gas until analyzed to prevent degradation of the CREN complex. A capillary tube with tetramethylsilane (TMS) was added to each sample as a coaxial sample tube to provide a reference TMS peak in the spectrum. Chemical shifts are recorded as ppm downfield from TMS.

#### RESULTS AND DISCUSSION

Figure 1 includes the structure of cellobiose with its reducing and nonreducing end groups. Because the hydroxyl group on the anomeric

TABLE 1.  $^{13}\text{C}$ -NMR chemical shifts<sup>a</sup> of cellobiose in aqueous alkaline solution with and without CREN<sup>b</sup>.

		C-1	C-2	C-3	C-4	C-5	C-6
Cellobiose with CREN							
Reducing end-unit	$\alpha$	92.6	72.0	73.6	79.4	70.5	60.7
	$\beta$	96.7	74.8	75.2	79.1	75.5	60.8
Nonreducing end-unit	$\beta$	103.2	73.9	76.4	70.1	76.8	61.3
Cellobiose without CREN							
Reducing end-unit	$\alpha$	92.9	72.0	72.2	79.6	70.6	60.8
	$\beta$	96.9	74.9	75.0	79.5	75.3	61.3
Nonreducing end-unit	$\beta$	103.2	73.9	76.2	70.1	76.7	61.5

<sup>a</sup> Chemical shifts in ppm downfield from external tetramethylsilane.<sup>b</sup> Spectra shown in Fig. 1.

carbon atom of the reducing-end unit can be in the axial position ( $\alpha$  end-unit) or in the equatorial position ( $\beta$  end-unit), there are in reality 2 reducing end-units, each with its own

environment as far as  $^{13}\text{C}$ -NMR is concerned. Thus, there are 6 carbons in the NMR environment for the  $\alpha$  end-unit and 6 different carbons in the NMR environment for the  $\beta$  end-

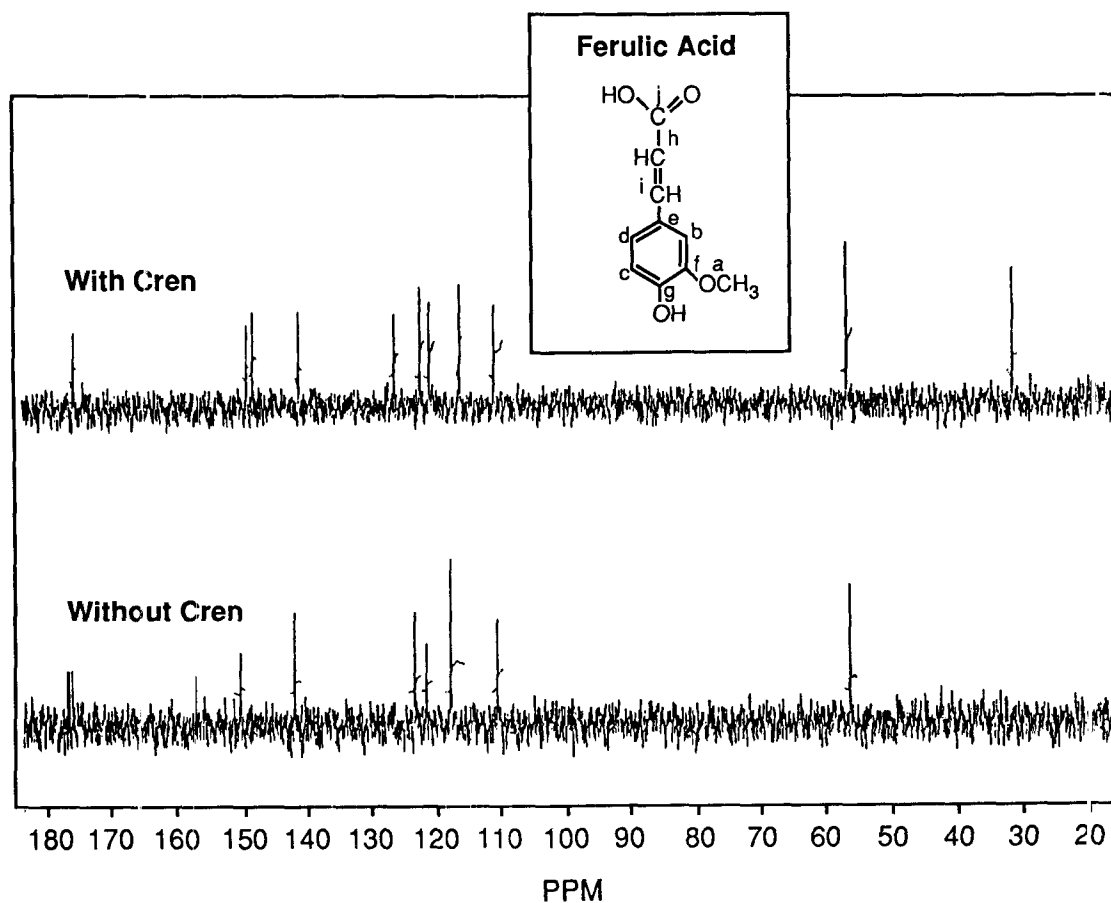
FIG. 2.  $^{13}\text{C}$ -NMR spectra of ferulic acid with CREN and without CREN.

TABLE 2.  $^{13}\text{C}$ -NMR chemical shifts<sup>a</sup> of ferulic acid in aqueous alkaline solution with and without CREN<sup>b</sup>.

	Carbon atoms as designated by the letters in Fig. 2									
	a	b	c	d	e	f	g	h	i	j
With CREN	56.8	111.8	117.0	121.9	123.0	142.0	148.9	127.1	150.5	177.5
Without CREN	56.6	111.6	118.8	118.8	122.7	143.1	151.5	124.6	158.8	177.8

<sup>a</sup> Chemical shifts in ppm downfield from external tetramethylsilane.<sup>b</sup> Spectra shown in Fig. 2.

unit, for a total of 12 environmentally different carbon atoms in the reducing end-units. Whether the reducing end-unit is in the  $\alpha$  configuration or the  $\beta$  configuration has no effect on the NMR environment of the nonreducing end-unit; there are only 6 environmentally different carbon atoms in the nonreducing end-unit. The net result is a total of 18  $^{13}\text{C}$ -NMR environmentally different and unique carbon

atoms in an aqueous solution of cellobiose at equilibrium.

The spectrum of cellobiose with CREN showed the 18 carbon atoms (Fig. 1). The assignments are given in Table 1. The unidentified peaks were due to impurities in the CREN compound. The assignments of the carbon atoms without CREN (Table 1) were close to the literature assignments given by Bock et

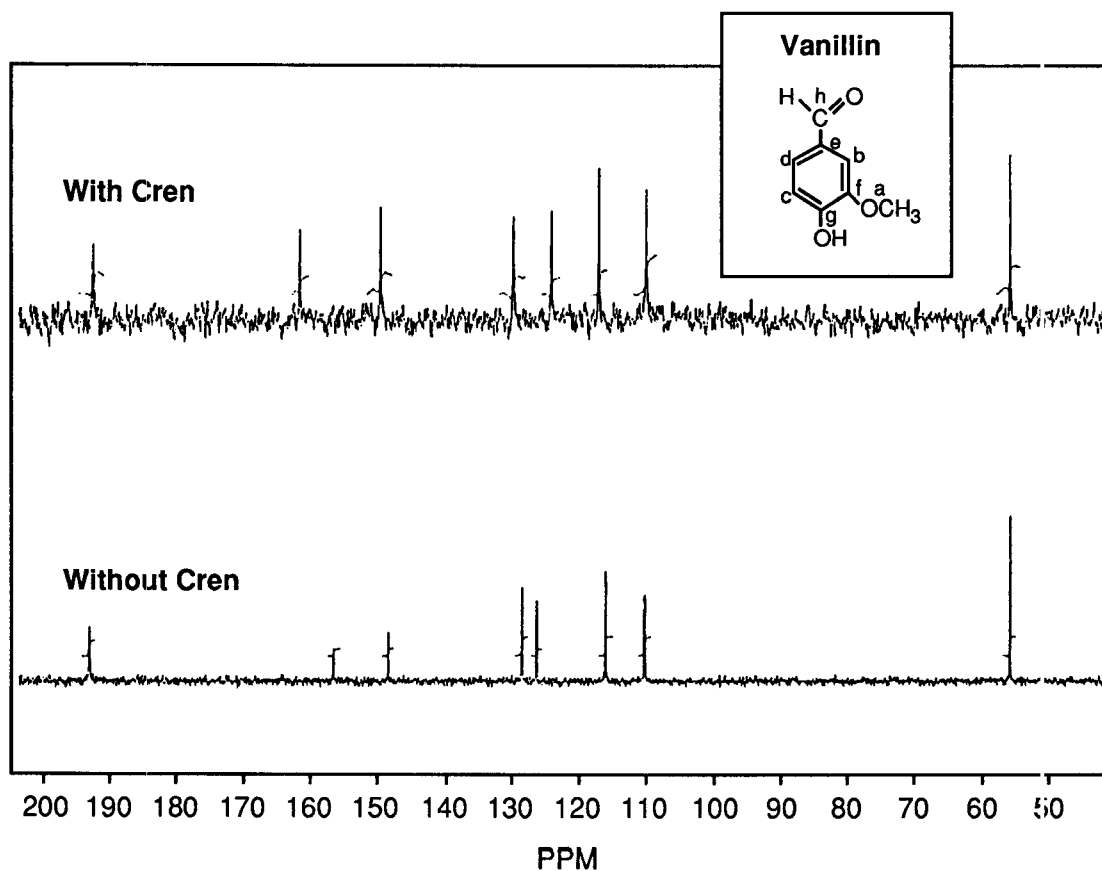
FIG. 3.  $^{13}\text{C}$ -NMR spectra of vanillin with CREN and without CREN.

TABLE 3.  $^{13}\text{C}$ -NMR chemical shifts<sup>a</sup> of vanillin in aqueous alkaline solution with and without CREN<sup>b</sup>.

	Carbon atoms as designated by the letters in Fig. 3							
	a	b	c	d	e	f	g	h
With CREN	56.5	111.0	117.8	125.2	130.5	150.8	163.2	194.0
Without CREN	56.0	111.0	116.5	127.1	129.5	149.6	157.8	194.3

<sup>a</sup> Chemical shifts in ppm downfield from external tetramethylsilane.<sup>b</sup> Spectra shown in Fig. 3.

al. (1984). There were some shifts in the positions of the peaks with CREN (Fig. 1 and Table 1). The addition of CREN improved the spectrum in the 74–76 ppm region.

Figure 2 includes the structure of ferulic acid, with individual carbon atoms labeled "a" through "j." The assignments in ppm (Table 2) were based primarily on the *trans*-cinnamaldehyde spectrum of Johnson and Jankowski (1972; Spectrum No. 336) and the vanillin spectrum of Johnson and Jankowski (1972; Spectrum No. 292).

The spectrum with CREN was demonstrably better than that without CREN (Fig. 2). There are 10 different carbon atoms in ferulic acid; the spectrum with CREN showed all 10 carbon atoms well separated, whereas the spectrum without CREN showed only 9 peaks. The peak at 118.8 ppm accounted for 2 carbon atoms. The spectrum with CREN showed well-separated peaks for these carbon atoms at 117.0 ppm and 121.9 ppm (Table 2). The spurious peak at 31.2 ppm in the spectrum with CREN (Fig. 2) was an impurity in the CREN compound. CREN did shift some of the positions of the peaks, but they were all present and clearly resolved. Thus, CREN provided an improved spectrum for the lignin-like fragments in kraft black liquor.

Figure 3 shows the structure of vanillin, with individual carbon atoms labeled "a" through "h"; the spectra of vanillin with and without CREN also is included. The peak assignments in ppm (Table 3) were assigned on the basis of the vanillin spectrum of Johnson and Jankowski (1972; Spectrum No. 292).

The spectrum with CREN (Fig. 3) showed more intense peaks than did the spectrum without CREN (Fig. 3) and had some shifting of peak positions. The spectrum without

CREN showed peaks that were almost identical in position to those shown by Johnson and Jankowski (1972; Spectrum No. 292).

#### CONCLUSIONS

The addition of CREN better separated several of the  $^{13}\text{C}$ -NMR peaks of the compounds used to represent the major functional groups present in the dissolved organics of kraft black liquor. The cellobiose spectrum with CREN showed all 18 different carbon atoms more clearly than did the spectrum without CREN. The spectrum of ferulic acid showed all 10 carbon atoms with CREN, but only 9 carbon atoms without CREN. The spectrum of vanillin showed more intense peaks with CREN than without CREN. The use of CREN to help assign the carbons in these lignin model compounds can aid in identifying similar carbons, without isolation or derivatization, in the dissolved organics in kraft black liquor obtained directly from kraft pulp mills. This will provide a better understanding of the buildup of nonprocess elements in kraft pulp mills.

#### ACKNOWLEDGMENT

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