An analysis of the water soluble components of Sappi Saiccor’s effluent streams

F Ismail*, DA Mulholland and JJ Marsh
School of Chemistry, University of KwaZulu-Natal, Howard College Campus, Durban 4041, South Africa

Abstract
Sappi Saiccor is a pulp mill that produces high-grade chemical cellulose (dissolving pulp) from predominantly hardwood timber and is currently the world’s largest manufacturer of this type of pulp. Attempts to isolate pure lignosulphonates were unsuccessful; however, an acid hydrolysis of the aqueous portion of the calcium effluent stream yielded a range of organic compounds. These included lignans, lignin-type precursors as well as small quantities of vanillin and syringaldehyde. The structures of these compounds were determined using NMR spectroscopic and mass spectrometric techniques.

Keywords: effluent, acid hydrolysis, lignan, lignosulphonates, dissolving pulp

Introduction
The Sappi Saiccor factory is situated at Umkomaas, 50 km south of Durban. It is the world’s single largest manufacturer of chemical cellulose with the capacity to produce up to 560 000 t of dissolving pulp per year (depending on grade mix), most of which is exported to Europe, America and Asia. It is also renowned for being the first company to produce high-grade chemical cellulose from the Eucalyptus tree (Thubron, 2002). Sappi Saiccor is one of the few pulp mills that produces chemical cellulose by the acid sulphite process, using both calcium (Ca) and magnesium (Mg) as bases. The wood chips are cooked in large digesters with liquor under high temperature (140°C) and pressure (10 bar). This process renders the lignin and hemicellulose in the wood soluble, so that it can then be washed out into the effluent streams. The four main streams of non-recovered effluent, that is, the calcium spent liquor, the magnesium pulp condensate and the two streams from the bleaching stages combine to form the main effluent stream before being pumped out to sea through a 7 km pipeline. Thus, the main effluent should contain a large proportion of lignins and lignosulphonates, as the main aim of the process is to produce a high-grade cellulose pulp free of lignin. Other components of the effluent would be hemicelluloses, resin acids, tannins and sugars.

In recent years environmental awareness has significantly increased and this has prompted Sappi Saiccor to discover ways of improving the quality of the mill’s effluent before it is disposed of into the sea. At present, a large proportion of the calcium spent liquor effluent is pumped to an adjacent plant, where the crude lignosulphonates are recovered for commercial purposes (Thubron, 2002). In addition, the effluent from the magnesium pulp section is greatly reduced during the recovery process of the magnesium oxide base material. The only waste going to the effluent stream in this section is in the form of a condensate formed during the evaporation of the liquor. Saiccor’s next step has been towards the characterisation of the effluent with the intention of identifying any commercially exploitable compounds, which can be extracted and marketed, thereby further reducing the impact of their industrial waste effluent on the environment.

The characterisation of pulping liquors has been carried out since the early 1950s. Studies have shown that the spent liquor from chemical pulping contains varying amounts of organic compounds from all wood constituents. The nature and concentrations of these compounds depend largely on the type of wood material used for pulp production, the type of pulping method employed and the composition of the cooking liquors (Sjöström and Alén, 1999).

There are two major chemical pulping processes, viz. sulphate pulping and sulphite pulping. Delignification during both sulphate and sulphite chemical pulping, using various types of bases, produces a complex mixture of products ranging from simple phenolic compounds to large macromolecules. These compounds form the major components of the total dissolved solids present in spent liquor effluents.

The importance of sulphite pulping has decreased during the recent decades, thus most of the information on the composition of sulphite spent liquors dates from the 1950s and 1960s (Sjöström and Alén, 1999). Early studies on the spent liquor of sulphite pulped aspen wood showed the presence of a large number of low-molecular mass aromatic compounds. These compounds were identified as vanillin, syringaldehyde, syringol, 4-hydroxybenzoic acid, dihydroconiferyl alcohol, syringaresinol and α-conidendrin (Pearl and Beyer, 1961; Pearl and Beyer, 1964a; Pearl and Beyer, 1964b).

Recent studies have concentrated on the isolation and characterisation of lignosulphonates from spent bisulphite liquor. A large number of sulphonated lignin-derived monomers and dimers have been isolated and identified using high-performance liquid chromatography (HPLC) (Bialski et al., 1986; Luthe, 1990). Examples of such compounds include 1-syringyl-2-propene-1-sulphonic acid, methyl-3,4-dimethoxybenzenesulphonate, 3-guaiacylpropanal-3-sulphonic acid and 1,2-disulphonomethyl-1-(3’,4’-dimethoxyphenyl)-propane (Bialski et al., 1986; Luthe, 1990).

Studies of the black liquor obtained from a Eucalyptus globulus bleached Kraft pulp mill showed the presence of many different types of compounds. The ether-soluble fractions were found to contain aromatic acids and phenolic compounds. The major components were identified as syringaldelate, acetosyringone, syringol and syringaresinol (Neto et al., 1999). Other compounds...
isolated from these fractions included vanillin acid, acetovanil- 
one, 1,1’-disyringylethane, 2,6-dimethoxyhydroquinone, 4,4’- 
dihydroxy-3,3’-dimethoxystilbene and aspidinol (Neto et al., 
1999). A number of aliphatic carboxylic acids, such as lactic acid, 
2-hydroxy acetic acid and oxalic acid, were also isolated from the 
liquid phase of the black liquor (Neto et al., 1999). The water-
soluble fractions contained predominantly carbohydrates with 
xyllose and galactose as the major sugars (Neto et al., 1999). 
A preliminary study on Sappi Saiccor pulp mill’s effluent con-
centrated on the characterisation of the compounds contained in 
the neutral organic extracts of all four effluent streams. A number 
of known organic compounds were isolated and characterised. 
These included a mixture of lignan isomers, epi-syringaresinol and 
meso-syringaresinol and lignin-type precursors such as 3- 
(4’-hydroxy-3,5’-dimethoxyphenyl)-prop-1-one, 2,6-dimeth-
 oxy-1,4-benzoquinone, 3-(4’-hydroxy-3,5’-dimethoxyphenyl)-
1-hydroxy-propane-2-one, syringaldehyde and vanillin (Moodley 
et al., 2003a; Moodley et al., 2003b). Lignans are dimeric com-
ponds formed by the combination of two phenylpropanoid 
units.

The commercial applications of both syringaldehyde and 
vanillin are extensive, however, these compounds were not iso-
lated in commercially viable quantities from the organic com-
ponent of the effluent streams and the bulk of the effluent which 
remained in the aqueous phase was not fully characterised. 
Thus, the objective of this work was two-fold. Firstly, to extract, 
separate and identify the remaining water-soluble compounds 
present, viz: lignosulphonates, which are also of commercial 
interest and secondly to try and increase the concentrations of 
vannilin and syringaldehyde obtained by further treatment of the 
effluent.

Experimental

Sampling procedure

The calcium spent liquor effluent was sampled after the washing and screening stages as the waste spent liquor goes to the effluent drain but before it is pumped to the adjacent plant for the recovery of crude lignosulphonates. During pumping the sample is generally under high pressures to maintain a continuous flow through the pipelines, which results in a high velocity and ensures the homogeneity of the effluent sample. The sample was collected in plastic containers from a sampling spigot of a storage tank. The collected sample had a temperature of between 85 and 100°C and a pH of between 1 and 2.

Lignosulphonate extraction procedure

(Kontturi and Sundholm, 1986; Lin, 1992)

Step 1

A liquid ion exchanger was prepared by mixing 1 M HCl (150 ml) with a solution of dodecylamine in butanol for 10 min in a sepa-
rating funnel.

Step 2

Equal volumes of the liquid ion exchanger (mass = 100.37 g) and calcium spent liquor (mass = 77.36 g) were added together and the mixture was stirred continuously for 30 min at a tem-
perature of 49 to 54°C. The amount of spent liquor was calcu-
lated to give an equivalent amount of sulphonic acid groups as the 
dodecylamine in the ion exchanger (Lin, 1992). This was done 
using the method of conductometric titration (Beatson, 1992).

Thereafter, the two phases were allowed to separate for 2 h in a 
separating funnel. The temperature was maintained at 50 to 60°C 
to facilitate phase separation. The top organic layer was removed 
and used in 3.

Step 3

The organic layer was adjusted to pH 9 using a 1 M NaOH solu-
tion. The mixture was then allowed to separate for 24 h at a tem-
perature of 50 to 60°C. The bottom aqueous layer was extracted 
with 3 x 100 ml portions of butanol to remove as much of the 
amine as possible. Thereafter, the aqueous layer was evaporated 
on a BUCHI Rotavapor and a creamish-brown precipitate of mass 
0.81 g (w/w % = 1.05 %) was collected.

The brown-coloured precipitate was found to be insoluble 
in dichloromethane (MeCl₂) and methanol (MeOH) but solu-
ble in water. A solution of the sample dissolved in water was 
left to air evaporate producing white square-shaped crystals 
resembling sugar granules. The precipitate was subjected to an 
ignition test by heating a sample on a crucible lid. The sample 
melted easily forming a black residue. No smoke was given off 
but a characteristic odour of burnt sugar was produced. How-
ever, a Lassaigne sodium fusion test performed on the precipi-
tate gave a positive result for the presence of sulphur. The ¹H and 
¹³C NMR spectra indicated that the precipitate contained a 
mixture of aromatic compounds and sugar molecules with the 
proportion of sugars being much greater. Poor separation was 
obtained on thin layer chromatography plates and preparative

Figure 1

Simplified flowchart of Sappi Saiccor’s process (Moodley et al., 2003a)
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Hydrolysis of the calcium spent liquor effluent

The aqueous phase of the calcium spent liquor was then subjected to an acid hydrolysis using concentrated hydrochloric acid in an attempt to hydrolyse the sugars. Calcium spent liquor (25 l) was extracted with chloroform to remove any organic components. The large volume was extracted in batches of 5 l using 3 x 1.5 l portions of chloroform for each batch. The organic portions were evaporated using a BUCHI Rotavapor to recover the chloroform. The aqueous portions were acidified with concentrated HCl to a pH of below 1 and boiled on a hotplate for approximately 4 h. The cooled solution was re-extracted with the recycled chloroform as described above and the organic portions were, once again, evaporated using the BUCHI Rotavapor.

Methylation of crude lignosulphonate mixture (Luthe and Lewis, 1986; Luthe, 1990)

To a suspension of the lignosulphonate-sugar mixture (250 mg) in MeOH (10 ml) was added Amberlite 120 (H–) resin (7 g). The solution was stirred at room temperature until the mixture was completely soluble in the MeOH (approximately 10 min). The resin was filtered off and the filtrate was cooled in ice. The freshly prepared solution of ethereal diazomethane was added in portions to the cooled filtrate until gas evolution ceased. After evaporation of the solvent, a dark brown precipitate of mass 205 mg was obtained.

The dark brown precipitate was found to be partially soluble in water but completely soluble in methanol. The 1H NMR spectrum, run in deuterated methanol (CD2OD), appeared different from the original spectrum, however, the spectrum did not show any methyl ester resonances, which usually appear as strong peaks in the region of δ 4.0 ppm. Previous researchers have reported that derivatisation using diazomethane was unsuccessful (King et al., 1935).

Separation techniques

All compounds that were isolated from the organic extract of the hydrolysed spent liquor were separated using gravity column chromatography and thin layer chromatography (t.l.c.). Different sized columns were used ranging from 1 to 5 cm in diameter depending on the amount of sample available and the purification stage. Final purifications were generally carried out on an open 0.75 cm diameter Pasteur pipette column. The columns were packed with silica gel (Merck Art. 9385) as the stationary phase and separations were carried out under gravity. The mobile phase for both column and thin layer chromatography consisted of varying ratios of hexane, dichloromethane, ethyl acetate and methanol. Thin layer chromatography was carried out on 0.2 mm silica gel, aluminium-backed plates (Merck Art. 5554). The plates were first viewed under UV light (336 nm and 254 nm). The plates were then developed using anisaldehyde: concentrated H2SO4 : methanol (1:2:97) spray reagent and then heated.

Some compounds, which were visible under UV light, were purified using preparative thin layer chromatography. The aluminium-backed t.l.c plates (Merck Art. 5554) were lined with the extract sample 15 mm from the bottom edge. The plates were lined by dipping a capillary tube into the extract sample dissolved in a minimum volume of dichloromethane and allowing it to run onto the silica gel by touching the tip of the tube to the plate. The plates were dried and then developed in a chromatography tank. Compounds of interest were marked as bands under the UV light. The marked bands were then cut into small pieces, dissolved in 50% methanol in dichloromethane, filtered through cotton wool to remove the silica gel and thereafter the solvent was evaporated.

Structural elucidation techniques

All nuclear magnetic resonance (NMR) spectra were recorded at room temperature on a 300 MHz Varian Gemini spectrophotometer or a 400 MHz Varian UNITY-INOVA spectrophotometer. The solvents used were deuterated chloroform (CDCl3), deuterated methanol (CD2OD) or deuterated water (D2O). The chemical shift values were all recorded in ppm relative to TMS (tetramethylsilane). The spectra were referenced according to the central line of the CDCl3 signal at δH = 7.24 ppm and δD = 77.2 ppm, the CD2OD signal at δH = 3.34 ppm and δD = 49.0 ppm and for the D2O signal at δH = 4.61 ppm.

The infrared spectra were recorded using a Nicolet Impact 400D Fourier-Transform Infrared (FT-IR) spectrometer, which

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**Scheme 1**

The chemical reactions occurring during the amine extraction of lignosulphonates (Kontturi and Sundholm, 1986; Lin, 1992)

<table>
<thead>
<tr>
<th>Reaction Number</th>
<th>Reaction Details</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>STEP 1</strong></td>
<td>Preparation of liquid ion exchanger, amine hydrochloride</td>
</tr>
<tr>
<td>R1R2R3N + HCl</td>
<td>→ R1R2R3NHCl</td>
</tr>
<tr>
<td><strong>STEP 2</strong></td>
<td>Formation and extraction of the lignosulphonate - amine complex</td>
</tr>
<tr>
<td>Lignin-SO3 H+ + R1R2R3NHCl</td>
<td>→ Lignin-SO3 N+HR1R2R3 + HCl (complex)</td>
</tr>
<tr>
<td><strong>STEP 3</strong></td>
<td>Regeneration of the lignosulphonate with an alkali</td>
</tr>
<tr>
<td>Lignin-SO3 N+HR1R2R3 + NaOH</td>
<td>→ Lignin-SO3Na + NR1R2R3 + H2O (Na-salt) (creamish-brown ppt)</td>
</tr>
</tbody>
</table>

where R1, R2 & R3 are hydrogen or alkyl groups

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thin layer chromatography plates.

The isolation of pure lignosulphonates has been known to be difficult mainly due to the hydrophilic nature of these compounds. All structural analysis and manipulations have to be performed in aqueous media. Therefore, an attempt was made to try and derivatise the precipitate containing the mixture of lignosulphonates and sugars using diazomethane to form the corresponding sulphonic acid methyl esters thus rendering them organic soluble.

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Structural elucidation techniques

All nuclear magnetic resonance (NMR) spectra were recorded at room temperature on a 300 MHz Varian Gemini spectrophotometer or a 400 MHz Varian UNITY-INOVA spectrophotometer. The solvents used were deuterated chloroform (CDCl3), deuterated methanol (CD2OD) or deuterated water (D2O). The chemical shift values were all recorded in ppm relative to TMS (tetramethylsilane). The spectra were referenced according to the central line of the CDCl3 signal at δH = 7.24 ppm and δD = 77.2 ppm, the CD2OD signal at δH = 3.34 ppm and δD = 49.0 ppm and for the D2O signal at δH = 4.61 ppm.

The infrared spectra were recorded using a Nicolet Impact 400D Fourier-Transform Infrared (FT-IR) spectrometer, which
The samples were recorded at 20.0 °C with a tube length of 100 mm and a volume of 1.0 mℓ was used. using a Perkin Elmer Model 341 Polarimeter. A quartz Microcell apparatus and are uncorrected. Optical rotations were measured were determined using a Kofler micro-hot stage melting point 6890 GC.

Acid hydrolysis of the calcium spent liquor resulted in the depolymerisation of the lignin molecule releasing more lignin monomers and dimers into the organic phase.

The major component isolated from the organic portion of the hydrolysed calcium spent liquor was a creamish-white crystalline solid, identified as the lignan epi-syringaresinol. The mass spectrum of compound 1 showed a molecular ion [M+] peak at m/z 418, which corresponded to a molecular formula of C_{34}H_{44}O_{6}. The number of carbon atoms corresponded to twice those of a phenylpropanoid monomer suggesting that compound 1 was a dimeric structure, as in a lignan molecule. The ¹H, ¹³C, HSQC, HMBC and COSY NMR spectra were used to determine the structure of this compound and the relative stereochemistry of the molecule was determined from the 2D-NOESY NMR spectrum. The approximate concentration of epi-syringaresinol in the hydrolysed aqueous phase of the calcium spent liquor effluent was 0.014 g/ℓ.

Compound 2 was isolated as an inseparable mixture with compound 1 (epi-syringaresinol). It was identified as a stereoisomer of compound 1 in that it had the same molecular structure and formula but the stereochemistry at the chiral centres of the two tetrahydrofuran rings was different. The structure of
compound 2 was fully elucidated by subtracting the peaks of the known compound, epi-syringaresinol. The 1H and 13C NMR spectra of compound 2 (with epi-syringaresinol impurity peaks subtracted) showed fewer peaks than those seen for compound 1, which indicated that this compound was symmetrical. The intensity of the carbon resonances for compound 2 was twice that of compound 1, which suggested that the ratio of compound 2 to compound 1 in the mixture was 2:1. Compound 2 was identified as the stereoisomer of compound 1 known as meso-syringaresinol. It is the second major compound isolated from the hydrolysed aqueous phase of the calcium spent liquor effluent stream. The mixture of the two isomers had a combined approximate concentration of 0.142 g/l. Taking into consideration that the ratio of compound 2 to compound 1 in the mixture was 2:1, the approximate concentration of compound 2 was, therefore, estimated to be 0.095 g/l.

The 1H and 13C NMR spectra of compound 3 were similar to that of compound 2, meso-syringaresinol. Only half of the expected proton and carbon resonances were seen, which suggested that compound 3 must also be a lignan with a symmetrical structure. The mass spectrum of compound 3 showed a molecular ion [M]+ peak at m/z 446, corresponding to a molecular formula of C36H40O6. The 13C NMR spectrum of compound 3 was compared to that of meso-syringaresinol. It showed an extra peak at δ 60.8 ppm, which confirmed the presence of an extra methoxy group in the structure. The HSQC and HMBC NMR spectra were used to confirm the proposed structure of compound 3. Once again, the NOESY NMR spectrum was used to determine the relative stereochemistry of the molecule. Compound 3 was identified as the dimethyl ether of meso-syringaresinol and was hence named meso-syringambin. The optical rotation was measured to be zero, which confirmed that this was a meso compound. Its approximate concentration in the hydrolysed aqueous phase of the calcium spent liquor effluent was 6.000 x 10-3 g/l.

Lignin precursors such as methoxylcyanogen (~ 1.440 x 10-3 g/l), β-oxysinapyl alcohol (~ 1.164 x 10-3 g/l), sinapyl aldehyde (~ 7.440 x 10-4 g/l), acetovanillone (~ 3.840 x 10-4 g/l), vanillin (~ 1.800 x 10-3 g/l) and syringaldehyde (~ 2.160 x 10-3 g/l) were also identified along with the common plant triterpenoid, α-sitosterol (~ 4.400 x 10-4 g/l).

Using the average plant effluent flow rates of the calcium spent liquor effluent, the quantity of the organic compounds being passed to the main effluent holding was estimated (Table 1) (Thubron, 2002; Moodley, 2001).

### Conclusion

The extraction and isolation of pure lignosulphonates proved to be very difficult, mainly due to the hydrophilic nature of these compounds. The extraction procedure employed yielded a mixture of lignosulphonates with a large proportion of sugars. Attempts to separate and derivatise these mixtures were also unsuccessful. Hydrolysis of the aqueous phase of the calcium spent liquor led to the isolation of a number of commercially viable organic compounds. The major compounds were identified as the lignans meso-syringaresinol, epi-syringaresinol and meso-yangambin. Vanillin and syringaldehyde were also isolated from the hydrolysed spent liquor but in low yields. Further work needs to be done to study selective oxidation of the effluent using various different oxidising agents as well as electrochemical methods of oxidation in an attempt to improve the yields of these compounds.

### References


### Acknowledgements

The authors wish to express their sincere gratitude to Mr Derek Weightman from Sappi Saiccor for the generous funding of this project. We would also like to acknowledge John Thubron and Tracy Wessels from Sappi Saiccor for their assistance in collecting the required samples during this study and for providing the necessary information regarding the plant’s processes. We thank Mr Dilip Jagjivan for running the NMR spectra, Mr Bret Parel for his technical assistance as well as Dr Phil Coombes and Miss Brenda Moodley for their laboratory assistance.

### TABLE 1

<table>
<thead>
<tr>
<th>Compounds isolated</th>
<th>Ca – spent liquor Flow rate ~ 75 m³/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>epi-syringaresinol</td>
<td>~ 1.050 kg/h</td>
</tr>
<tr>
<td>meso-syringaresinol</td>
<td>~ 7.125 kg/h</td>
</tr>
<tr>
<td>meso-yangambin</td>
<td>~ 0.045 kg/h</td>
</tr>
<tr>
<td>methoxylcyanogen</td>
<td>~ 0.108 kg/h</td>
</tr>
<tr>
<td>β-oxysinapyl alcohol</td>
<td>~ 0.087 kg/h</td>
</tr>
<tr>
<td>sinapyl aldehyde</td>
<td>~ 0.056 kg/h</td>
</tr>
<tr>
<td>acetovanillone</td>
<td>~ 0.029 kg/h</td>
</tr>
<tr>
<td>vanillin</td>
<td>~ 0.135 kg/h</td>
</tr>
<tr>
<td>syringaldehyde</td>
<td>~ 0.162 kg/h</td>
</tr>
<tr>
<td>β-sitosterol</td>
<td>~ 0.033 kg/h</td>
</tr>
</tbody>
</table>
