

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

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## 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 000t 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.

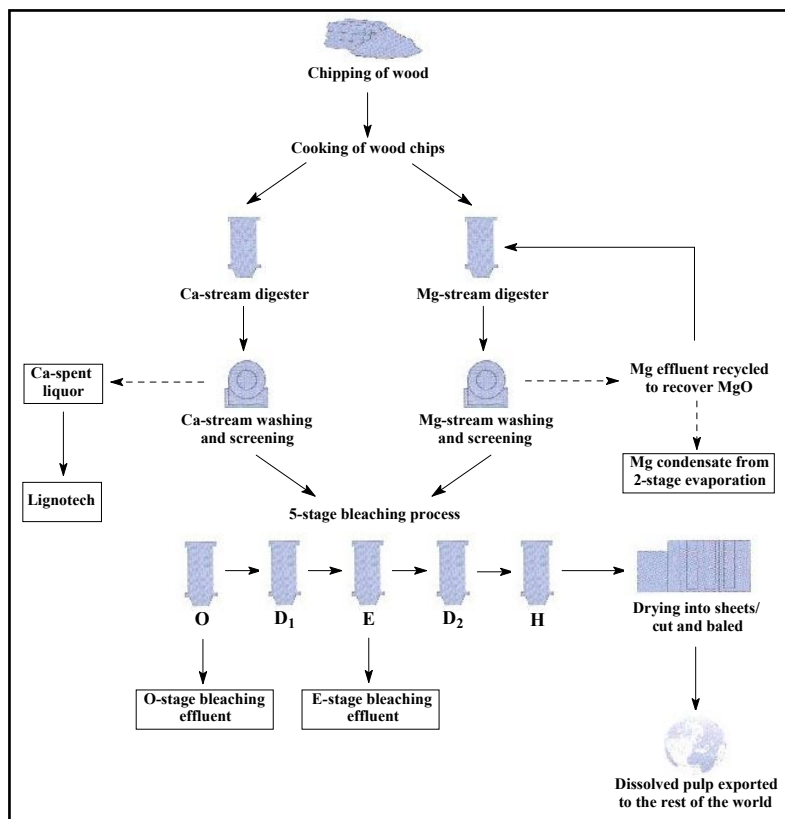
The importance of sulphite pulping has decreased during the recent decades, thus most of the information on the composition of sulphite spent liquors dates from the 1950s and 1960s (Sjöström and Alén, 1999). Early studies on the spent liquor of sulphite pulped aspen wood showed the presence of a large number of low-molecular mass aromatic compounds. These compounds were identified as vanillin, syringaldehyde, syringol, 4-hydroxybenzoic acid, dihydroconiferyl alcohol, syringaresinol and  $\alpha$ -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 syringaldehyde, acetosyringone, syringol and syringaresinol (Neto et al., 1999). Other compounds

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**Figure 1**  
Simplified flowchart of Sappi Saiccor's process (Moodley et al., 2003a)

isolated from these fractions included vanillic acid, acetovanilone, 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 xylose and galactose as the major sugars (Neto et al., 1999).

A preliminary study on Sappi Saiccor pulp mill's effluent concentrated 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-ene, 2,6-dimethoxy-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 compounds formed by the combination of two phenylpropanoid units.

The commercial applications of both syringaldehyde and vanillin are extensive, however, these compounds were not isolated in commercially viable quantities from the organic component 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 vanillin 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 separating funnel.

#### Step 2

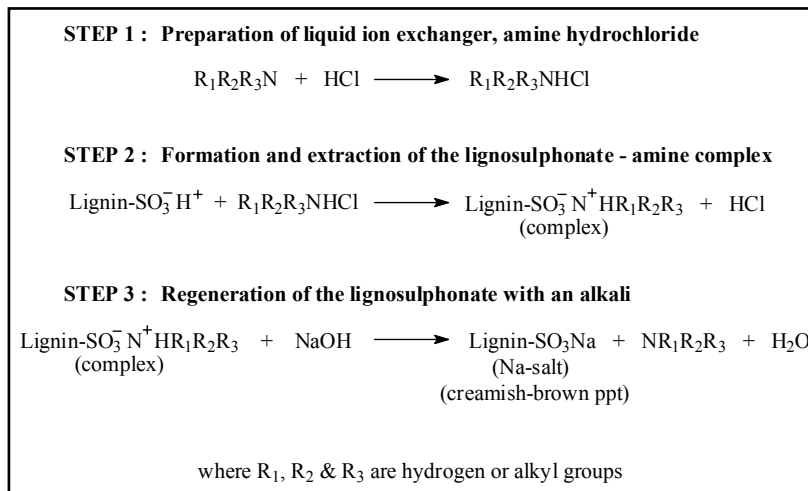
Equal volumes of the liquid ion exchanger (mass = 100.37 g) and calcium spent liquor (mass = 77.36 g) were added together and the mixture was stirred continuously for 30 min at a temperature of 49 to 54°C. The amount of spent liquor was calculated to give an equivalent amount of sulphonic acid groups 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 solution. The mixture was again allowed to separate for 24 h at a temperature 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 (MeCl<sub>2</sub>) and methanol (MeOH) but soluble 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. However, a Lassaigne sodium fusion test performed on the precipitate gave a positive result for the presence of sulphur. The <sup>1</sup>H and <sup>13</sup>C 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

**Scheme 1**  
The chemical reactions occurring during the amine extraction of lignosulphonates (Kontturi and Sundholm, 1986; Lin, 1992)



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.

#### 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<sup>+</sup>) 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 <sup>1</sup>H NMR spectrum, run in deuterated methanol (CD<sub>3</sub>OD), 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  $\delta$  4.0 ppm. Previous researchers have reported that derivatisation using diazomethane was unsuccessful (King et al., 1935).

#### 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.

#### 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 H<sub>2</sub>SO<sub>4</sub>: 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 (CDCl<sub>3</sub>), deuterated methanol (CD<sub>3</sub>OD) or deuterated water (D<sub>2</sub>O). The chemical shift values were all recorded in ppm relative to TMS (tetramethylsilane). The spectra were referenced according to the central line of the CDCl<sub>3</sub> signal at  $\delta_H = 7.24$  ppm and  $\delta_C = 77.2$  ppm, the CD<sub>3</sub>OD signal at  $\delta_H = 3.34$  ppm and  $\delta_C = 49.0$  ppm and for the D<sub>2</sub>O signal at  $\delta_H = 4.61$  ppm.

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

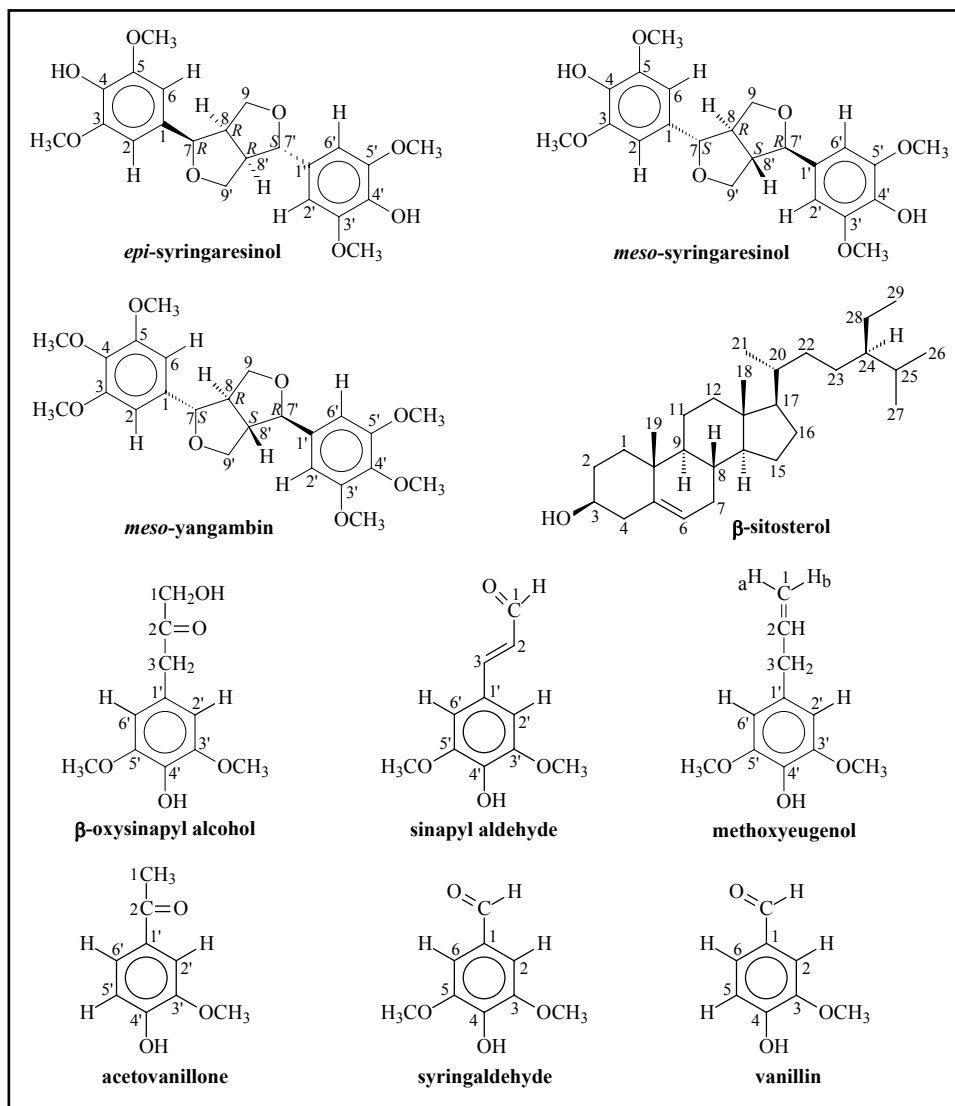


Figure 2  
Structures of com-  
pounds isolated

was calibrated against an air background. The compounds were analysed using a NaCl window with dichloromethane as the solvent. All data were acquired using the OMNIC software. Ultraviolet absorption spectra were obtained on a Varian Cary 1E double beam UV-visible spectrophotometer. The UV spectra of the isolated organic compounds were run in dichloromethane using matched quartz cuvettes and the instrument was calibrated against dichloromethane.

All samples were injected manually, using a 1  $\mu$ l syringe, onto a HP5-MS column in the gas chromatography-mass spectrometer (GC-MS) with a 1:50 split ratio. The starting temperature was 50°C and the sample was held at this temperature for 2 min. The temperature was then ramped at 20°C/min until a temperature of 300°C was reached. Thereafter, the sample was held for a further 15 min at this maximum temperature. A solvent delay of 2 min was set. Low-resolution mass spectrometry was carried out on an Agilent 5973 mass spectrometer connected to a 6890 GC.

The melting points of all the organic compounds isolated were determined using a Kofler micro-hot stage melting point apparatus and are uncorrected. Optical rotations were measured using a Perkin Elmer Model 341 Polarimeter. A quartz Microcell with a tube length of 100 mm and a volume of 1.0 ml was used. The samples were recorded at 20.0°C in chloroform.

## Results and discussion

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  $C_{22}H_{26}O_8$ . The number of carbon atoms corresponded to twice those of a phenylpropanoid monomer suggesting that compound **1** had a dimeric structure, as in a lignan molecule. The  $^1H$ ,  $^{13}C$ , 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  $^1\text{H}$  and  $^{13}\text{C}$  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  $^1\text{H}$  and  $^{13}\text{C}$  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  $[\text{M}^+]$  peak at  $m/z$  446, corresponding to a molecular formula of  $\text{C}_{24}\text{H}_{30}\text{O}_8$ . The  $^{13}\text{C}$  NMR spectrum of compound **3** was compared to that of *meso*-syringaresinol. It showed an extra peak at  $\delta$  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*-yangambin. 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  $6.000 \times 10^{-4}$  g/l.

Lignin precursors such as methoxyeugenol ( $\sim 1.440 \times 10^{-3}$  g/l),  $\beta$ -oxysinapyl alcohol ( $\sim 1.164 \times 10^{-3}$  g/l), sinapyl aldehyde ( $\sim 7.440 \times 10^{-4}$  g/l), acetovanillone ( $\sim 3.840 \times 10^{-4}$  g/l), vanillin ( $\sim 1.800 \times 10^{-3}$  g/l) and syringaldehyde ( $\sim 2.160 \times 10^{-3}$  g/l) were also identified along with the common plant triterpenoid,  $\beta$ -sitosterol ( $\sim 4.400 \times 10^{-4}$  g/l).

Using the average plant effluent flow rates of the calcium stream, 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.

Compounds isolated	Ca – spent liquor Flow rate $\sim 75 \text{ m}^3/\text{h}$
<i>epi</i> -syringaresinol	$\sim 1.050 \text{ kg/h}$
<i>meso</i> -syringaresinol	$\sim 7.125 \text{ kg/h}$
<i>meso</i> -yangambin	$\sim 0.045 \text{ kg/h}$
methoxyeugenol	$\sim 0.108 \text{ kg/h}$
$\beta$ -oxysinapyl alcohol	$\sim 0.087 \text{ kg/h}$
sinapyl aldehyde	$\sim 0.056 \text{ kg/h}$
acetovanillone	$\sim 0.029 \text{ kg/h}$
vanillin	$\sim 0.135 \text{ kg/h}$
syringaldehyde	$\sim 0.162 \text{ kg/h}$
$\beta$ -sitosterol	$\sim 0.033 \text{ kg/h}$

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