The characterisation of organic components in the calcium and magnesium effluent streams at Sappi Saiccor

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Abstract

Sappi Saiccor is one of the few pulp mills that use the acid sulphite pulping process with hardwood feedstock to produce a high-grade cellulose pulp. The major constituents identified in the calcium effluent stream and the magnesium condensate effluent stream were a mixture of lignan isomers, episyringaresinol 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.

Keywords: effluent, analysis, lignan

Introduction

Sappi Saiccor, whose factory is situated south of Durban, South Africa, is an international leader in the manufacture of dissolving pulp using the acid sulphite pulping process with calcium and magnesium bases. Hardwood feedstock, *Eucalyptus grandis* and *Acacia mearnsii* wood, are milled and passed through the sulphite process to produce a high-grade pulp. The resulting effluent waste is generally pumped out to sea but increasing environmental consciousness has prompted Sappi Saiccor to find ways of reducing their effluent. The first step has been the characterisation of the effluent.

The major findings of this project are of importance to the industry as no work on the characterisation of the organic constituents of Saiccor's waste effluent had previously been undertaken. Furthermore, Saiccor differs from other manufacturers of dissolving pulp in that they use hardwood feedstocks and this is likely to lead to different breakdown products in their pulping and bleaching effluent streams. Although much work has been published on the components which occur in Kraft effluent streams, little has been published on the constituents of acid sulphite pulping and bleaching effluent streams.

The aim of this project was to extract and identify the major organic components of Sappi Saiccor's effluent. There are four main streams of effluent, namely, the calcium spent liquor, the magnesium condensate and two bleaching stage effluent streams as shown in Fig. 1. Attempts made by Saiccor, thus far, to reduce the amount of effluent pumped out to sea have included pumping a proportion of the calcium - spent liquor to an adjacent plant, where lignosulphonates are recovered for commercial purposes (Weightman, 2000; Thubron, 2000). Furthermore, the effluent from the magnesium stream is reduced by passing it through a recovery process. This involves first evaporating the effluent down in two stages to a thin liquor and thereafter burning the concentrated liquor and recovering the magnesium oxide. The only effluent produced here is the condensate that forms during the evaporation of the thin liquor before the burning stage.

Much research was carried out on spent sulphite liquors from 1950 to 1970. However, that research has now somewhat diminished as the pulp and paper industry has moved away from sulphite pulping towards Kraft pulping processes. Studies by Kvasnicka and McLaughlin (1955) on the butyl acetate extract of spruce sulphite liquor showed three main groups of components present, namely, tannins and conidendrins and other phenols and neutral compounds such as hydrocarbons and esters. Further isolation and extraction techniques yielded, in particular, compounds such as vanillin, 3-(3-methoxy-4-hydroxyphenyl)-propanol-1 and 3,3'-dimethoxy-4,4'-dihydroxystilbene.

Studies based on laboratory sulphite pulped aspen wood using ammonia as the base showed the presence of many different types of compounds ranging from lignans to long-chain fatty acids. Pearl and Justman (1961) identified a number of saturated and unsaturated long chain fatty acids and their alcohol derivatives, such as myristic, lauric, palmitic, stearic and linoleic acids. The aromatic compounds isolated and identified were vanillin, syringaldehyde, *p*-hydroxybenzoic acid, vanillic acid and syringic acids. Isomers of the lignan lirioresinol (diasyringaresinol) were also identified as well as some flavonoids (Pearl et al., 1962).

Thereafter work was carried out on a commercial sulphite liquor sample. Studies by Pearl and Beyer (1964a, b) of an ammonia-based aspen spent sulphite liquor involved ether extraction and separation of the extract into various fractions. Some lignin-like or phenolic materials were identified, but only on hydrolysis of this fraction and it was therefore thought that these phenolic materials were complexed with carbohydrates. Some examples of the lignin precursors isolated were vanillin, syringaldehyde and *p*-hydroxybenzoic acid. The 'weak acid' fraction also contained phenolic compounds linked to carbohydrates, and on acid hydrolysis, compounds such as vanillic acid, syringic acid and *p*-hydroxybenzoic acid were identified. The 'strong acid' fraction was found to contain similar components on acid and alkaline hydrolysis. This early work was based on paper chromatographic techniques. Earlier studies on aspenwood, *Populus tremuloides*, revealed a large quantity of naringenin, which has been previously isolated from this species (Pearl and Beyer, 1963).

Studies on a sample of black liquor, obtained from a Kraft pulp mill using *Eucalyptus globulus*, were carried out by separating the liquor into various fractions (Neto et al., 1999). The aromatic acid

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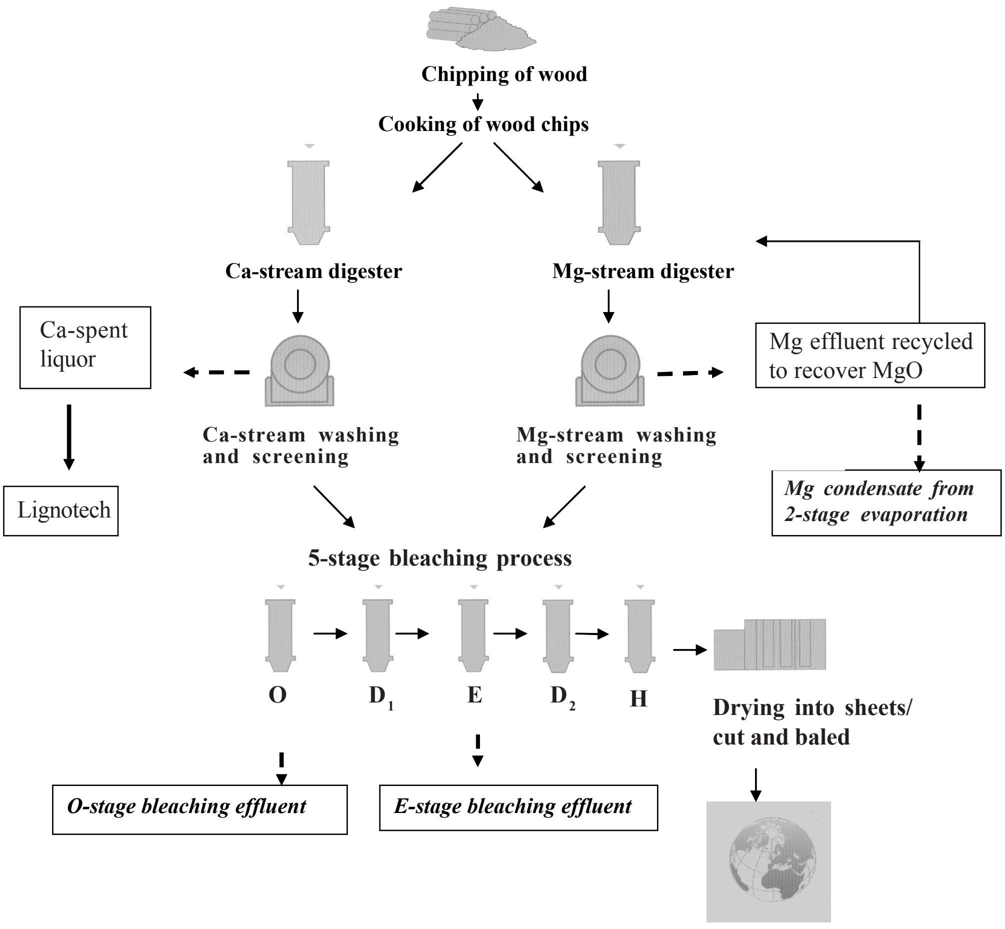

Figure 1
Simplified flowchart of Sappi Saiccor's process

fraction was found to contain syringaldehyde as the major component and other compounds isolated included syringol, acetosyringone, and aspidinol. The phenolic fraction contained similar compounds as well as syringaresinol, acetovallinone and dehydrodiguaiacol. Syringaresinol was found to be the major component of the ether extract and other compounds identified were 4,4'-dihydroxy-3,3'-dimethoxy-stilbene, 1,1'-disyringyl-ethane, 2-syringyl-ethanol and 3-vanillyl-propanol.

Experimental

Sampling and extraction of the calcium effluent

The calcium effluent stream was sampled from a sampling spigot before the washing and screening stages prior to it being pumped to the adjacent plant that extracts the lignosulphonates for commercial purposes (Fig. 1). During pumping, the sample is generally under pressure to maintain a continuous flow through the pipeline, which results in a high velocity and ensures the homogeneity of the sample. The sample container was first rinsed with the sample to be taken and thereafter filled. The temperature of the sample was approximately 90^0C and had a pH of 1.8.

A litre of the cooled calcium-spent liquor sample was extracted with 3 x 1 ℓ portions of chloroform using a 6 ℓ separating flask. The organic extract was neutralised with a saturated solution of sodium bicarbonate. The neutralised organic portions were evaporated using a BUCHI Rotavapor.

Sampling and extraction of the magnesium condensate

The magnesium effluent is burnt to recover the magnesium oxide, but during the evaporation process, some of the gases condense to form a colourless magnesium condensate, which goes to the effluent drain. Some of this condensate is used as wash water during the washing and screening stage giving it a reddish-brown colour. A sample of the magnesium condensate, which had been used during washing, was collected in the same manner as described for sampling of the calcium-spent liquor. The temperature of the sample was approximately 90^0C and was acidic (pH = 2).

A 3 ℓ sample of the cooled magnesium condensate sample was extracted with 7.5 ℓ of chloroform, in portions, using a 6 ℓ separating flask. The organic extract was neutralised with a saturated solution of sodium bicarbonate. The neutralised organic portions were evaporated using a BUCHI Rotavapor.

Analytical procedures

General chromatography

All compounds from both organic extracts, were isolated using gravity column chromatography and thin-layer chromatographic techniques. Gravity columns of 1 and 2 cm in diameter were used depending on the amount of sample available and final purifications were generally carried out on open 0.75 cm pasteur-pipette columns.

All columns were packed with Merck Art. 9385 silica gel. The mobile phase for both column and thin-layer chromatography (t.l.c.) was varying ratios of dichloromethane, hexane, 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 developed with a mixture of anisaldehyde : concentrated sulphuric acid:methanol (1:2:97) spray reagent. They were first observed under UV (336 nm) and then heated to develop the plates.

Nuclear magnetic resonance spectroscopy (NMR spectroscopy)

Nuclear magnetic resonance spectroscopy was carried out on a 300 MHz Varian Gemini spectrophotometer and a 400 MHz Varian UNITY-INOVA spectrophotometer. The spectra for all compounds were recorded at room temperature in deuterated chloroform or deuterated water. The chemical shifts were all recorded in ppm relative to the tetramethylsilane (TMS) signal. The spectra were referenced against the central line of the deuterated chloroform signal at $\delta_C = 77.2$ ppm and $\delta_H = 7.24$ ppm and for the deuterated water signal at $\delta_H = 4.61$ ppm.

Infrared (IR) spectroscopy

The infrared spectra were recorded using a Nicolet Impact 400D Fourier-Transform Infrared (FT-IR) spectrometer, which was calibrated against an air background. The compounds were analysed using a sodium chloride window with dichloromethane as the solvent.

Gas chromatography/mass spectrometry (GC/MS)

All samples were introduced using a 1 μℓ auto injection system onto a HP5-MS column in the GC/MS with 1:75 split. The starting temperature was 50^0C, the sample was held for two minutes, the temperature was ramped at 20^0C per minute until it reached 300^0C and thereafter the sample was held for another two minutes. Low-resolution mass spectrometry was carried out on an Agilent 5973 mass spectrometer connected to a 6890 GC.

Preparative thin-layer chromatography (p.t.l.c.)

Some compounds were purified using preparative thin-layer chromatography. Samples dissolved in a minimum of solvent (dichloromethane) were applied to the plates with the aid of a capillary tube. The plates were developed in a chromatography tank and the compound of interest was marked under UV. The marked bands were cut off the plate, dissolved in methanol and thereafter the solvent evaporated.

Acetylation

Compound 5 (7 mg) was dissolved in pyridine (1 mℓ) and acetic anhydride (2 mℓ) and left to react over 48 hours in a round-bottom flask connected to a calcium chloride drying tube. The acetic anhydride and pyridine were removed with methanol and toluene, *in vacuo*. The acetylated mixture was spotted on a t.l.c. plate to see if the reaction had gone to completion and if it needed to be purified. The acetylated product was passed through a column to separate the product from the impurities. The pure acetylated compound was eluted with 100% dichloromethane.

Optical rotation

Optical rotations were measured at room temperature in chloroform using a Perkin Elmer 241 Polarimeter with tube 10 cm in length or Optical Activity AA-5 Polarimeter together with a series A2 stainless steel (4 x 200 mm) unjacketed flow tube, 20 cm in length.

Results and discussion

Calcium effluent stream

The major extractive component isolated from the calcium effluent stream was a mixture of lignan isomers, viz., *meso*-syringaresinol and episyringaresinol. The ^{1}H NMR spectrum of compound 1, *meso*-syringaresinol, showed only one half of the expected resonances, but the mass spectrum showed a molecular ion peak twice that of a lignin precursor. This suggested that the compound was a dimer with a symmetrical structure. The ^{1}H, ^{13}C, HMBC and COSY NMR spectra were used to determine the structure of the compound and the NOESY NMR spectrum was used to determine its stereochemistry. The optical rotation of compound 1 was determined as 0^0 and therefore the stereochemistry of the second half of the compound was determined as the exact opposite of the first half. Thus, compound 1 was identified as *meso*-syringaresinol.

Compound 2, episyringaresinol, was isolated as a mixture with compound 1. Its structure was determined by subtracting the peaks due to compound 1. Here again, the low-resolution mass spectrum showed a molecular ion peak at *m/z* 418, suggesting a lignan. However, the ^{1}H NMR spectrum showed more resonances than that observed for compound 1, suggesting that this lignan was not symmetrical. ^{1}H, ^{13}C and HMBC NMR spectra were used to determine the structure of compound 2 and the NOESY NMR spectrum was used to determine its relative stereochemistry. Compound 2 was identified as episyringaresinol and its data compared favourably with literature data regarding epi-structures (Pelter and Ward, 1976; Pelter and Ward, 1977). The combined mixture of compounds 1 and 2 had a concentration of 0.400 g/ℓ.

Other compounds identified were lignin type precursors, such as, 3-(4'- hydroxy-3',5'-dimethoxyphenyl)-prop-1-ene (0.020 g/ℓ) (3), 2,6-dimethoxy-1,4-benzoquinone (0.0030 g/ℓ) (4), 3-(4-’hydroxy-3',5'-dimethoxyphenyl)-1-hydroxy-propane-2-one (0.010 g/ℓ) (5) and syringaldehyde (0.010 g/ℓ) (6). Compound 5 was acetylated to confirm its structure. The structures of all the above compounds were determined using ^{1}H, ^{13}C, HMBC, HSQC, COSY and NOESY NMR spectra.

Magnesium condensate effluent stream

The major component of the magnesium condensate effluent stream was also a mixture of the syringaresinol isomers. The structures of these lignin dimers were identified as described for the calcium effluent stream. This stream of effluent also contained lignin-type precursors that were previously identified in the calcium effluent stream, such as, 3-(4'-hydroxy-3',5'-dimethoxyphenyl)-prop-1-ene (0.012 g/ℓ) (3) and 2,6-dimethoxy-1,4-benzoquinone (0.0033 g/ℓ) (4). In addition to this, a minor amount of vanillin (0.0016 g/ℓ) (7) was isolated, which had not been isolated from the calcium effluent.

The concentrations of the identified compounds may appear rather low but if one looks at them in conjunction with the average plant effluent flowrates (Table 1), they do make up a significant amount of material.

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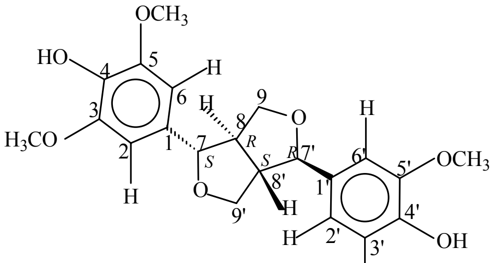

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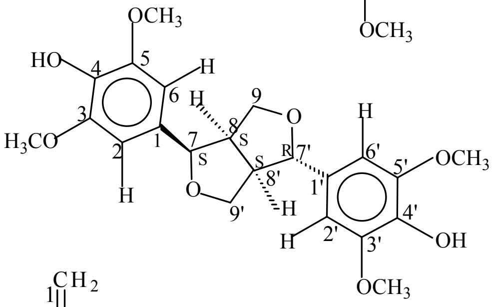

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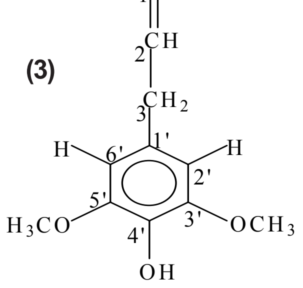

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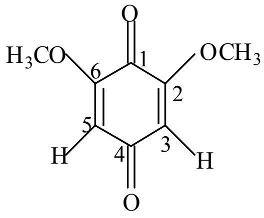

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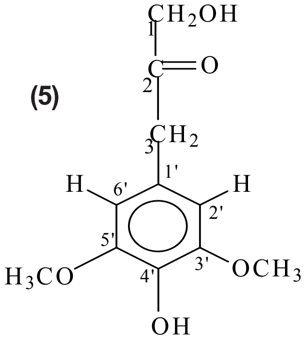

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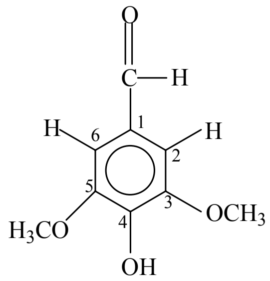

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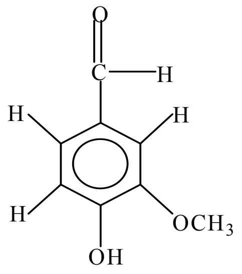

Conclusion

The major organic compound identified in both the calcium and magnesium condensate effluent streams was a mixture of lignan isomers, viz., meso-syringaresinol and episyringaresinol. This result agrees with previous work done on *Eucalyptus globulus*, which showed syringaresinol as the major component (Neto et al., 1999). Other compounds identified from both effluent streams include lignin precursors. These are 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.

TABLE 1
Calculated quantities (based on the stated flow rates) of the identified compounds from both effluent streams that pass out to the effluent holding site

Compound identified	Calcium - spent liquor ($75\ m^3/h$)	Magnesium condensate ($170\ m^3/h$)
Syringaresinol mixture	30 kg/h	2.83 kg/h
3-(4'-hydroxy-3',5'-dimethoxyphenyl)-prop-1-ene	1.50 kg/h	1.98 kg/h
2,6-dimethoxy-1,4-benzoquinone	0.23 kg/h	0.567 kg/h
3-(4'-hydroxy-3',5'-dimethoxyphenyl)-1-hydroxy-propane-2-one	0.75 kg/h	
Syringaldehyde	0.75 kg/h	
Vanillin		0.283 kg/h

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References

KVASNICKA EA and McLAUGHLIN RR (1955) Identification of spruce sulphite liquor components. *Can. J Chem.* **33** 637-645.

NETO CP, BELINO E, EVTUGUIN D and SILVESTRE AJD (1999) Total fractionation and analysis of organic components of industrial *Eucalyptus globulus* kraft black liquor. *Appita* **52** 213-217.

PEARL IA and BEYER DL (1963) Studies on the chemistry of aspenwood XVI. Further studies on the ether extractives of spent sulphite liquor from authentic quaking aspenwood. *Tappi* **46** 502-505.

PEARL IA and BEYER DL (1964a) Studies on the chemistry of aspenwood XVII. The ether-insoluble, water-soluble components of aspen spent sulphite liquor. *Tappi* **47** 458-462.

PEARL IA and BEYER DL (1964b) The ether-insoluble, water-soluble components of several spent sulphite liquors. *Tappi* **47** 779-782.

PEARL IA, BEYER DL and JUSTMAN O (1962) Studies on the chemistry of aspenwood XIV. The ether-soluble portion of spent sulphite liquor from authentic quaking aspenwood. *Tappi* **45** 107-113.

PEARL IA and JUSTMAN O (1961) Studies on the chemistry of aspenwood XIII. Further studies on the neutral extractives of commercial aspen spent sulphite liquor. *J. Org. Chem.* **26** 3563-3564.

PELTER A and WARD RS (1976) General methods for the assignment of stereochemistry to 2,6-diaryl-3,7-dioxabicyclo[3.3.0]octane lignans. *Tetrahedron* **32** 2783-2788.

PELTER A and WARD RS (1977) Revised structures for epiaschantin and epimagnolin. *Tetrahedron Letters* **47** 4137-4140.

THUBRON J (2000) Personal communication. Technical Process Manager at Sappi Saiccor.

WEIGHTMAN D (2000) Personal communication. Technical Director at Sappi Saiccor.