



Synthesis of Vanillin from Lignin

Njiema Gitaari^{1*}, Kandie Benard¹, Joyline Gichuki¹ and Patrick Kareru¹

¹*Department of Chemistry, Jomo Kenyatta University of Agriculture and Technology,
P.O.Box 62000-00200, Nairobi, Kenya.*

Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

Vanillin (4-hydroxy-3-methoxybenzaldehyde) is the major flavour constituent of vanilla. It has a wide range of applications in food industry and in perfumery. Vanillin is also very useful in the synthesis of several pharmaceutical chemicals. Lignin is a phenolic polymer which is found in plant cell walls with a structure depending strongly on the source of lignin and the process condition, which should be adjusted for different samples. In this work, lignin was extracted from Kraft cooking liquor of wood ash. The amount of extracted lignin was 25.5%, based on oven dry weight of wood ash. The lignin obtained was then reacted with alkaline nitrobenzene and refluxed at 170°C for 3 hours to obtain vanillin. The FT-IR spectrum of vanillin was similar to standard. The yield obtained from oxidation with nitrobenzene was 3.9%.

Keywords: Vanillin; FT-IR and Lignin.

1. INTRODUCTION

Vanillin is a flavouring obtained from the vanilla orchid. It is one of the widely used expensive spice after saffron [1]. Despite being expensive,

vanillin still stands as a highly appreciated flavour. Vanillin is widely used for both commercial and domestic purposes including, aroma and food flavouring, baking, complementary flavouring in chocolate; caramel;

*Corresponding author: E-mail: gitaarijaphet@gmail.com;

custard or coffee, perfumes, and aromatherapy [2]. The major word vanillin is the *Vanilla planifolia* species, commonly known as the Bourbon or Madagascar vanilla, which originates from Madagascar and neighbouring islands in the southwestern region of the Indian Ocean and Indonesia. Combined sources of the vanilla produce about two-thirds of the world vanillin [3].

Due to scarcity and the high cost of vanillin extracted from natural sources along with its popularity, there is increasing interest in the synthesis of the predominant component vanillin from alternative greener sources [4,5]. Vanillin is one of the most popular flavours, but less than 1% of it comes from a mature vanilla orchid. Big food brands that vowed to only use natural flavours in products marked are experiencing shortages due to an emerging shortage of vanilla orchid [6].

Food and beverage flavour industries are looking forward to supplying alternative sources to curb shortage of vanillin flavour and to sustain the venture. In addition, vanillin obtained through synthesis is not considered a sustainable method of obtaining alternative flavouring [7]. Application of this method is considered greener and more sustainable.

2. MATERIALS AND METHODS

2.1 Preparation of Samples of Pulp for the Experiment

Kraft cooking process was performed. The specified conditions for the process were; 10 grams of fine wood ash weighed and white liquor prepared under the conditions of active alkali charge of 25% Sodium hydroxide and Sulphidity of 30% Sodium Sulphide by weight in the ration of 3:1, that is, the white liquor. A white liquor (NaOH and NaS₂) to wood Ratio of 6:1 at cooking temperatures of 140°C for 2 hours [8,9].

2.2 Lignin Extraction

The black liquor was characterised by the pH value of about 13. In order to extract the lignin component from the black liquor, dilute sulphuric acid (4 M, 22% by weight) was added to the black liquor and agitated using a magnetic stirrer until the pH value reduced to 2. The pH value of 2 was necessary to obtain an increased yield of extracted lignin [10]. At this point, the black liquor turned from black to brown resulting into a

precipitate. The resulting precipitate was then agitated for 1 hour. The Lignin mixture containing the lignin was filtered and washed with 100 ml warm water to wash the excess sulphuric acid. The obtained product was dried at 100°C for 30 minutes in a vacuum oven and then finely pulverized using a motor and pestle. Without additional purification procedure, the pulverised product was tightly sealed and kept at ambient temperature prior to use. A portion of the dried product was then subjected to FT-IR analysis.

2.3 Preparation of Vanillin

To the 0.2 grams of the oven dried lignin, 7 ml of 2 M NaOH was added. 0.5 ml nitrobenzene was measured and added to the mixture in a 500 ml round bottom flask and refluxed at 170°C for 3 hours. The combined organic phase was then evaporated in a fume chamber. The sample was then transferred to a 50 ml volumetric flask and filled with methanol/water in the ratio 1:1. The solution was then filtered through a membrane filter of 0.45-micron pore size [11]. The lignin oxidation product was then analysed using FT-IR and compared with the standards.

3. RESULTS AND DISCUSSION

In this research the amount of extracted lignin was 25.5% based on oven dry weight of wood ash. The synthesised vanillin was 3.9% of the obtained lignin. Alkaline nitrobenzene oxidation of lignin resulted into the formation of vanillin.

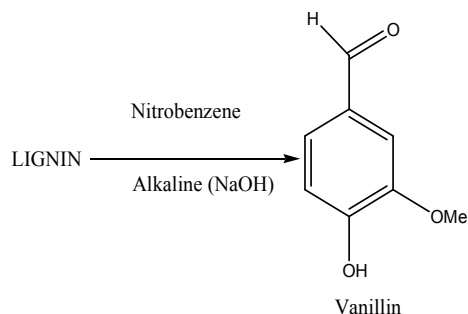


Fig. 1. Proposed chemical equation for reaction of lignin and nitrobenzene to produce vanillin

Lignin from grasses contains p-hydroxyphenyl propane unit (R₁=R₂=H). Grassy plants, therefore, contain relatively small amounts of lignin approximately 15 % of the biomass. Oxidation of this lignin leads to the formation of a

more complex aldehyde and hence it is not used for the case of oxidative production of vanillin.

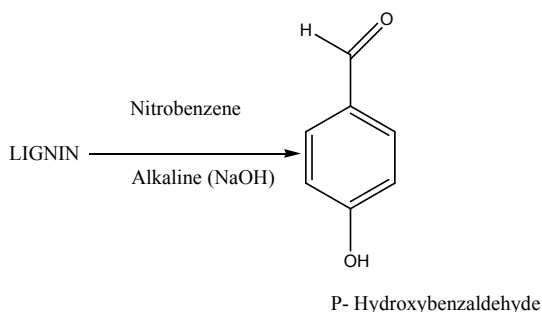


Fig. 2. Proposed chemical equation for reaction of lignin and nitrobenzene to produce p-hydroxybenzaldehyde

Fig. 3 below shows a picture of the formulated vanillin



Fig. 3. Formulated vanillin

3.1 FT-IR characterization of Obtained Lignin

The purpose of FT-IR was to determine the functional groups present in the lignin. The analytes were in powder/solid form. The obtained results were in frequency range of 4000 and 400 cm^{-1} . Usually, the percentage of lignin in softwood is 30 % and 20% hardwood. In order to enhance the industrial application of lignin the precise structure as well as the functional groups has to be known in order to develop new application. The most important chemical functional groups present in the extracted lignin included methoxyl, hydroxyl, carboxyl and carbonyl. The results obtained from the FT-IR analysis of Kraft lignin were as follows;

The lignin revealed a very close resemblance to the lignin extracted from the *Pinus eldrica* [4] as in Fig. 5.

3.2 FT-IR Characterization of Synthesised Vanillin

Figs. 6 and 7 shows the FT-IR spectra of the synthesized vanillin and the commercial standard vanillin respectively.

From the FTIR spectra in it is clear that there is a close semblance on the functional groups present in both the synthesized and the commercial vanillin.

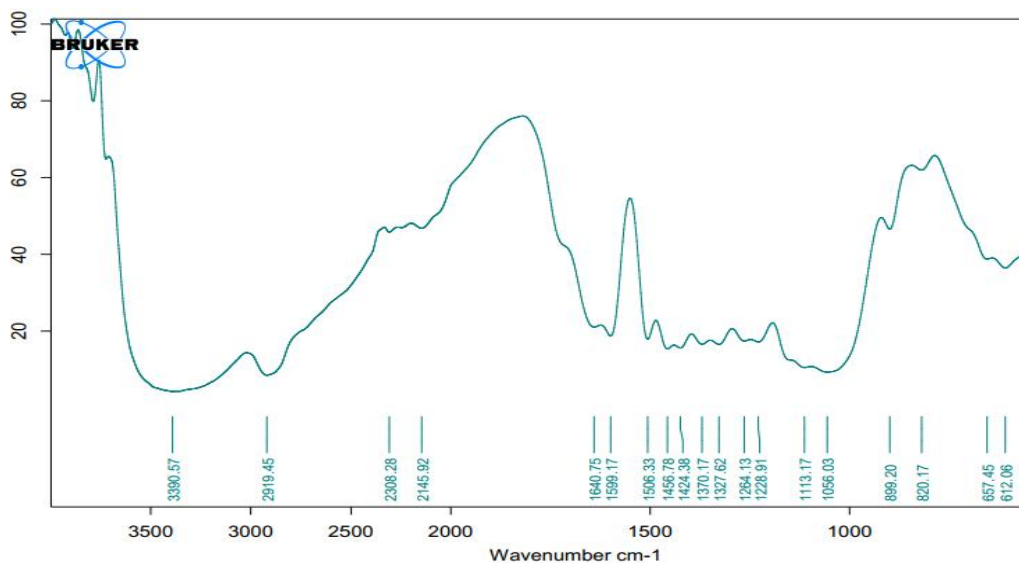


Fig. 4. FT-IR results for the Kraft Lignin

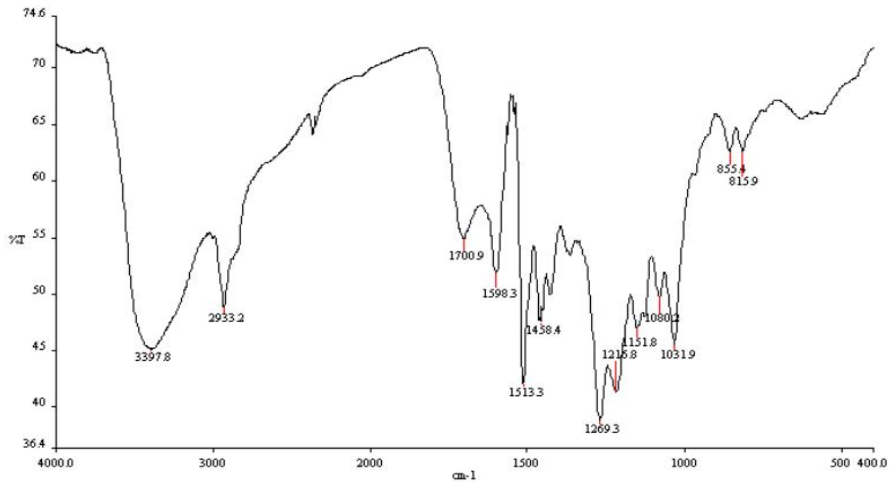


Fig. 5. FT-IR spectra of *Pinus eldarica* Kraft Lignin [4]

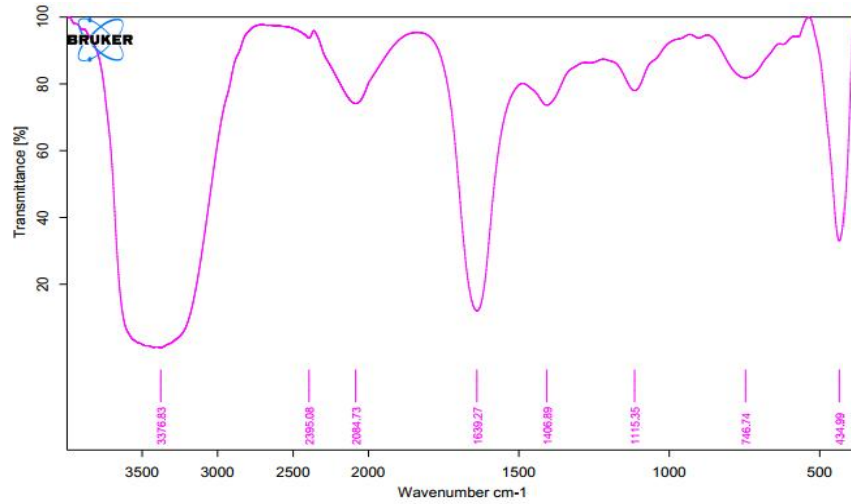


Fig. 6. FT-IR spectra of synthesized Vanillin

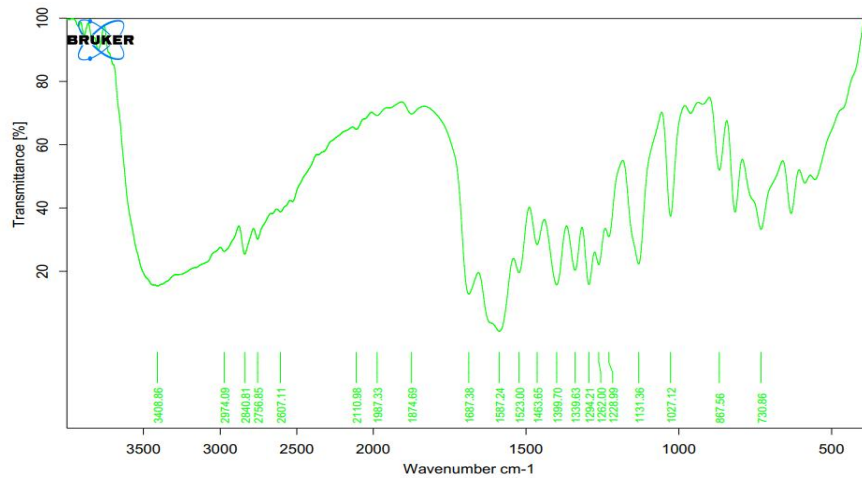


Fig. 7. FT-IR Standard/ commercial vanillin

4. CONCLUSION

From this study Lignin was isolated from black liquor of wood ash and the lignin was then oxidised in a controlled reflux heating system with nitrobenzene. The reaction system involved a step where vanillin was formed from lignin and because of the similarity of coniferyl alcohol groups to the vanillin structure; this monomer was oxidized to vanillin. Other monomers were also oxidized but recognition of the vanillin was important in this research. The yield of vanillin obtained from this study was significant.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Hocking, Martin B. Vanillin synthetic flavouring from spent sulphite liquor (PDF). Journal of Chemical Education. 1997; 74(9):1055-1059.
2. Borges Da Silva EA, Zabkova M, Araujo JD, Cateto CA, Barreiro MF, Belgacem MN, Rodrigues AE. An integrated process to produce vanillin and lignin-based polyurethanes from Kraft lignin, Chemical Engineering Research and Design. 2009; 87:1276–1292.
3. Mussato SI, Fernandes M, Roberto IC. Lignin recovery from brewer's spent grain black liquor; 2007.
4. Araujo JDP, Grande Carlos A, Rodrigues Alirio E. Vanillin production from lignin oxidation in a batch reactor, Chemical Engineering Research and Design. 2010; 88:1024-1032.
5. Boeriu CG, Bravo D, Gosselink RJA, Van Dam JEG. Characterization of structure dependent functional properties of lignin with infrared spectroscopy. Ind. Crops Prod. 2004;20:205-218.
6. Gunasekeran S, Ponusammy S. Vibrational spectra and normal coordinate analysis on organic non-linear opticacrysal 3- methoxy-4-Hydroxy benzaldehyde. Indian Journal of Pure and Applied physics. 2005;43:838-843.
7. Shamsuri A, Abdullah DK. A preliminary study of oxidation of lignin from rubber wood to vanillin in ionic liquid medium. Oxidation Communications. 2013;34(3): 767-775.
8. Baptista C, Robert A, Duarte AP. Effects of pulping conditions on lignin structure and delignification degree in Pinus Pinaster Kraft pulps, Bioresource Technology. 2006;121:153-158.
9. Glidewell C, Low JN, Melguizo M, Quesda A. 4-Amino-2, 6-Dimethoxypyrimidine: hydrogen-bonded sheets of R22 (8) and R66 (28) rings, reinforced by an aromatic Pi-Pi stacking.
10. Rose C, Kennedy. The flavour rundown: Natural vs artificial flavours. Harvard University; 2018.
11. Shakeri A, Sepideh M, Ghasemian. Oxidative production of vanillin from industrial lignin using oxygen and nitrobenzene: A comparative study. International Journal of farming. 2013; 1166-1170.

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