

# Vanillin from Saw Dust

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## SUMMARY

Experiments on the preparation of vanillin were carried out utilizing saw dust of gymnosperm species as a source for lignin. The saw dust was given mild oxidation treatment under alkaline condition at temperatures 160–170°C. Vanillin was isolated from the reaction aliquot. Vanillin to the extent of 1.43% yield based on the dry weight of saw dust was obtained.

## INTRODUCTION

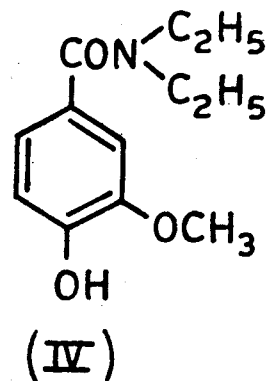
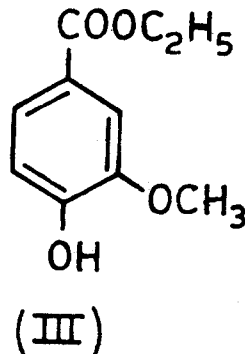
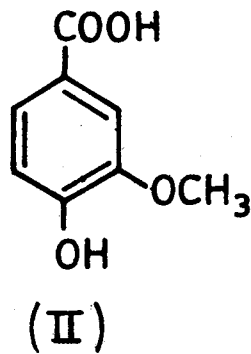
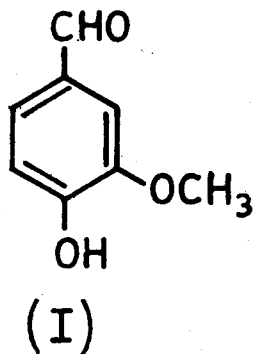
The importance of agro industrial ligno cellulosic wastes as a renewable organic reservoir of raw material, for the commercial production of variety of industrial products, requires no emphasis. There are number of possibilities of exploiting these valuable resources for useful products. It is not only necessary to reduce the cost of production, but also provides an array of useful economic products. In addition, it will solve the disposal problem and minimize the environmental pollution hazard. The present investigation deals with the potential value of saw dust available as a waste from lumber industry for the preparation of vanillin.

Vanillin (I) is an important pleasant smelling crystalline aromatic organic compound and is most extensively used for flavouring of confectionery baked food, ice cream, candies, chocolates etc. It is also used in perfumes and fancy scents. Even simple conversion of vanillin to vanillic acid (II) had been a laboratory curiosity. Its ester of ethenol was found to be useful as preservative in food stuffs<sup>1</sup> and specific treatment of progressive disseminated form of two mycotic diseases, histoplasmosis and coccidiomycosis (valley fever)<sup>3</sup>. The ultraviolet absorption characteristics of ethyl vanillate (III) also make it useful in sunburn preparations<sup>2</sup> and for the topical

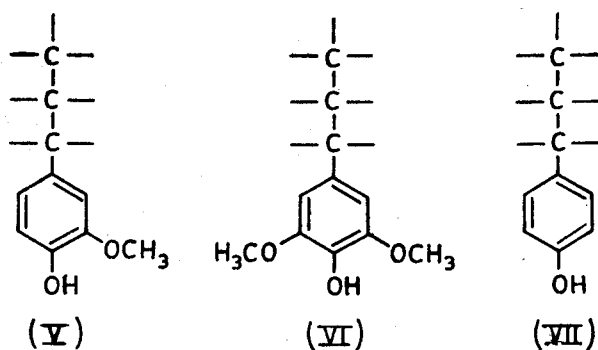
treatment of skin fungal infections<sup>3</sup>. In Europe the diethylamide of vanillic acid (IV) has found<sup>4-6</sup> wide use as an analgetic agent.

Vanillin in nature is found in vanilla beans, gum benzoin, and perubalsam. The utilisation of lignin for production of vanillin is well known. Lignin is a highly polymerised three-dimensional network, containing predominately aromatic compounds. Plant lignin is divided into three classes which are commonly called soft wood (gymnosperm), hard wood (dicotyledonous, angiosperm) and grasses or annual plant (monocotyledonous angiosperm) which include bamboo and palm lignin. The soft wood or coniferous lignin is generally derived from coniferyl alcohol or similar guaiacyl propane (4-hydroxy-3-methoxy phenyl propane) (V) monomer. While the hard wood lignin contains syringyl propane (3,5-dimethoxy -4-4 hydroxy phenylpropane (VI) monomer in addition to guaiacylpropane monomers generally in equal proportions. Similarly the monocotyledonous angiosperm lignin contain polymer of syringyl propane and 4-hydroxy phenyl propane (VII) monomere along with guaiacylpropane polymers.

For the manufacture of vanillin from lignin and ligno sulphonates quite a number of patent are available. Vanillin from groundnut shells has been re-



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ported<sup>12-13</sup> in an Indian Patent. Vanillin in U.S.A. and Canada is mostly obtained<sup>7-11</sup> by Marthon and Howard process using lignosulphonates of liquor of sulfite pulping process in paper and pulp industries.

In India sulphite liquor of coniferous wood species is not available. Indian Paper Mills are mainly using bamboo and other hard wood species adopting alkaline sulphate pulping process. Even alkaline sulphate black liquor is not freely available for any commercial exploitation as the paper mills are burning to recover the inorganic chemicals for reuse in pulping. The lignin in the liquor also differs in chemical composition from that obtained from pure coniferous wood species. There are only one or two pulp mills which are adopting sulphite process for pulping mainly using bamboos as the raw material, therefore, ligno-sulphonates of bamboo and hard wood are not suitable for vanillin due to various technical reasons. The oxidation products of ligno-sulphonates contain p-hydroxybenzaldehyde and syringaldehyde in addition to vanillin and thus causes separation problems, thus not economical.

The entire India's industrial demand for vanillin is met with from imports. Very recently a small unit has been set in Bombay. It is understood that this unit uses 0.anisidine as the starting material for vanillin. Vanillin can also be prepared from eugenol which is abundantly present in clove oil and cinnamon oil. Cinnamon tamala commonly known as Tajpata grown wild in forest of North Eastern India mainly in Khasi, Jaintia and Mikria Hills. The leaves and steam on distillation yield 2% oil which contains 90% eugenol. Eugenol can be converted into isoeugenol and further to vanillin. It is estimated that an investment for production of 15 tonnes per annum is about 35 lakhs. The source of eugenol and clove oil and cinnamon oil is not enough and unreliable to last long. The price of vanillin fluctuates between Rs. 250/- and Rs. 300/- per kg.

#### MATERIAL AND METHOD

The species taken<sup>12</sup> for present study were *Cedrus deodara* (deodar). The saw dust of *Cedrus deodara* both distilled for essential oil and undistilled was subjected to oxidation. The oxidation of the saw dust was carried out in an alkaline medium using both

nitrobenzene and cupric oxide as oxidants. The saw dust was heated with reagents for 4 hours at 160-170°C in a pressure autoclave keeping solid liquid ratio 1:6 including one hour to raise the temperature to maximum. The alkaline reaction mixture after the separation of excess of oxidising agent was acidified with H<sub>2</sub>SO<sub>4</sub> and filtered. The light brown filtrate was then extracted counter currently with benzene. The benzene extract was distilled to remove benzene under vacuum, and the dark reddish brown residue was treated with hot water. The hot water extract was subjected to extraction with petroleum ether which on concentration gave light yellow crystalline needles of vanillin. This was recrystallised with petroleum ether. The vanillin thus obtained was chemically pure melting point 81-82°C. Further purity of the compound was checked by TLC and GLC techniques.

#### RESULTS AND DISCUSSIONS

The yield of the vanillin in the most of gymnosperm is reported to be as high as 25-30% based on lignin content. The total lignin in conifers varies from 25-32% and thus the recovery of vanillin should be 6-8% based on saw dust. The results are recorded in the Table-I & II. Under the conditions of oxidation, the maximum yield of vanillin obtained in our experiment was 1.43% based on saw dust. The yield is calculated from the weight of vanillin obtained as pure crystalline vanillin. The yield of vanillin obtained from saw dust and other material under different patents is given in Table-11.

TABLE I

#### REACTION CONDITION

Saw dust 300 gm (oven dry)

Cupric oxide = 150 gms

Water = 1.8 litres

No.	Reaction time	NaOH based on	Vanillin
		oven dry saw dust	
		w.r.t.	
	Minutes	%	%
1.	30	20	0.3
	60	"	0.4
	90	"	0.43
2.	30	30	0.95
	60	"	1.20
	90	"	1.43
3.	30	38	0.38
	60	"	0.30
	90	"	0.41
	120	"	0.43
4.	30	40	0.56
	60	"	0.70
	90	"	0.73
	120	"	0.70

TABLE—II  
APPROXIMATE YIELDS OF VANILLIN AS REPORTED IN PATENTED LITERATURE

Year	Source (Lignocellulosic material or lignin)	% Yield of vanillin (on lignin basis or on saw dust basis)	References
1940	Sulphite waste liquor	25% on lignin basis	13
1942	Sulphite waste liquor	21.9% on lignin basis	14
1942	Sulphite waste liquor	15.6% on lignin basis	15
1944	Gymnosperms like white spruce, hemlock, white pine, western red cedar and red wood etc.	15.0% on Klason lignin basis	16
1950	Wood Powder	14.4% on lignin basis	17
1952	Wood powder	16.8% on lignin basis	18
1952	Wood powder	8.0% on wood basis	19
1952	Sulphite waste liquor	21.0% on lignin basis	20
1954	Wood powder	21.0% on lignin basis	21
1955	Saw dust	2.04% on saw dust basis	22
1955	Spruce wood	7.31% on saw dust basis	23
1956	Saw dust ) $C_6H_5NO_2$ or ) + Lignin ) buffer solution of ) NaOH-Na <sub>2</sub> S (pH 14)	9.0% on saw dust basis & 32.4% on lignin basis	24
1958	Romanian coniferous saw dust	5.12% on saw dust basis & 19.0% on lignin basis	25
1958	Waste sulphite liquor	17.0% on lignin basis	26
1960	Spent sulphite liquor	10.0-13.0% on lignin basis	27
1962	Spruce saw dust	1.9-2.5% on saw dust basis	28
Summary of literature reported yields of Vanillin		Approximate Range (%)	
I (On saw dust basis)		2.0- 9.0	
II (On lignin basis)		10.0-32.0	

In the present investigation both nitrobenzene and cupric oxide were used as oxidants. The other oxidant such  $\text{CuSO}_4$  and  $\text{V}_2\text{O}_5$  have also been used<sup>10</sup>. In alkaline nitrobenzene oxidation the reaction poses some difficulties during the process of isolation of vanillin. After the reaction the excess nitrobenzene have to removed either by steam distillation or continuous extraction with benzene. During the extraction with benzene large amount of emulsion was formed which created isolation problems. The alkaline cupric oxide oxidation was, therefore, preferred. This saves chemicals, labour and time. Therefore this process was more convenient than that of nitrobenzene oxidation. The  $\text{Cu}_2\text{O}$  formed as reaction by product can be fully recovered. The residual saw dust could be used as a semi-chemical pulp for blending purposes specially in straw boards.

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### Unpublished Results

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