by dissolving 3 g. of the ketone in alcohol and adding an excess of concentrated hydrochloric acid. The product is precipitated by the addition of ether and recrystallized from alcohol. The ketones do not readily form dihydrochlorides, evidenced by the fact that all the salts prepared in the above way were the monohydrochlorides. These salts are only very slightly soluble in water.

The physical data of these compounds are shown in the accompanying table.

Summary

1. Certain α-amino ketones and derivatives related to N-phenylpiperazine have been prepared and studied.

2. The action of various reducing agents on these ketones will form the basis of a subsequent publication.

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[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, MCGILL UNIVERSITY]

Studies on Lignin and Related Compounds. XXXII. The Guaiacyl and Syringyl Groups in Various Woods

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In two recent communications of this series[1] it was shown that treatment of spruce lignin sulfonic acid with alkali gives a 6–7% yield of vanillin, the higher percentage being obtained from the β-lignin sulfonic acid, fractionated with quinoline. This finding has been confirmed by application of the method to various other species of wood and to straw.[2] In the present investigation comparable yields of vanillin have been obtained from other soft woods (balsam and Eastern hemlock), but the hard woods, such as birch, oak, aspen and maple, have been found to yield both vanillin and syringaldehyde in approximately equal amounts (2.8% of each, Table I).

Although there was little doubt but that these aldehydes originated in the lignin, and not in some other part of the woody substance, the latter contingency has been eliminated by actual isolation of 2.3% of vanillin and 2.3% of syringaldehyde by treatment of the lignin sulfonic acid recently prepared from oak lignin[3] with alkali. Since this oak lignin, prepared by acetolysis of wood and subsequently purified by saponification, had been separated from the non-ligneous constituents it is evident that the aromatic aldehydes represent fission products of the lignin structure. The approximately equal yield of both aldehydes suggests either that they are incorporated in the same complex or, alternatively, that two closely related lignins exist in equal quantities in the same wood. These two possibilities which may have some bearing on the mode of formation of lignin in wood will be discussed in a forthcoming communication. For the present it is to be noted that the age of the woody tissue seems to have no connection with aromatic type since the heart and sap wood of maple were found to give approximately identical amounts of the mixed aldehydes. This conclusion regarding relation of age to vanillin formation is also in harmony with the production of vanillin from straw lignin sulfonic acid,[2] in other words, the synthesis of aromatic groups formed as the result of a short, seasonal plant metabolism.

Experimental

Isolation of Vanillin and Syringaldehyde from Yellow Birch Sulfite Liquors.—The liquors, obtained by cooking 13.5 kg. of yellow birch chips with 60 liters of sodium bisulfite cooking liquor (6.0% "total" and 1.1% "combined" sulfur dioxide) at a maximum temperature of 125° for eight hours, were heated in 12-liter batches with 9% sodium hydroxide solution at 160° (90 lb./sq. in. (6 atm.)) for four hours. The combined cooks were treated with carbon dioxide until barely alkaline and the solution then heated to 90°. After cooling, the supernatant liquor was decanted from solid material and extracted continuously with benzene. This extract was concentrated to 3 liters and extracted with 1.3 liters of 21% sodium bisulfite. The resulting bisulfite addition compound was decomposed with excess sulfuric acid and the aldehydes extracted with ether. This extract, upon evaporation, yielded 73.5 g. of a brown viscous oil, 4.5 g. of which was distilled at 140–145° (0.014 mm.). The crystalline distillate (3.5 g.) was fractionally crystallized from benzene–petroleum ether (b. p. 30–50°). The more soluble fraction (0.62 g.) after two recrystallizations from water melted at 111.5–112°; a mixed melting point with synthetic syringaldehyde[4] (m. p. 110–112°) was not lowered. The compound was further

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(1) Tomlinson and Hibbert, THIS JOURNAL, **58**, 345, 348 (1936).

(2) Alvfeldt and Hägglund, *Svensk Papፕers-Tidn.*, **40**, 236 (1937).

(3) Hibbert and Steeves, THIS JOURNAL, **59**, 1768 (1937).

(4) Graebe and Martz, *Ber.*, **36**, 1032 (1903).

TABLE I

ANALYSIS OF LIGNIN SULFONIC ACIDS FROM VARIOUS WOODS

(Hibbert-Tomlinson Method[1])

	Analysis of sodium lignin sulfonates, %			Yield of vanillin, %, based on					
				SO_3Na-free lignin				Solvent-extracted	
Soft woods	S	Na	OCH_3	by subl.	by pptn.			wood[a,c]	
Spruce	5.3	3.2	11.4	6.0	5.9			1.6	
Eastern hemlock	5.3	3.6	11.8	6.0	6.1			1.8	
Balsam	5.2	3.3	11.6	5.8	5.7			1.7	
				Yield, %, of					
				Vanillin based on		Syringaldehyde based on		Hydrazones by	
Hard woods				lignin	wood[c]	lignin	wood[c]	subl.[b]	pptn.[d]
Yellow birch	5.3	2.9	15.7	2.7	0.6	2.8	0.6	10.9	11.8
White oak	5.2	2.7	14.3	2.7	.6	2.9	.7	11.1	10.8
Aspen	5.2	3.1	15.6	1.5	.3	1.6	.3	6.1	9.5
Maple-sap	5.4	3.1	15.5	2.9	.6	2.9	.6	11.6	11.6
Maple-heart	5.2	3.2	15.2	2.6	.6	2.9	.6	10.9	11.6

[a] Average of the precipitation and sublimation values. [b] Calculated yield of *m*-nitrobenzoylhydrazones based on the yields of vanillin and syringaldehyde from the sublimation run. [c] Calculated on the lignin content of the extracted wood as determined by the method of Ritter, Seborg and Mitchell [*J. Ind. Eng. Chem., Anal. Ed.*, **4**, 202 (1932)]. [d] Comparison of these alternative procedures shows a maximum error of ±5%.

characterized by the olive-green ferric chloride test and by preparation of the semicarbazone (m. p. 184–185°).

Anal. Calcd. for $C_9H_{10}O_4$: C, 59.3; H, 5.5; OCH_3, 34.0; mol. wt., 182. Found: C, 59.4; H, 5.7; OCH_3, 33.8; mol. wt. (Rast), 166.

The less soluble fraction (0.85 g.) was recrystallized from water and identified as vanillin (m. p. 79–81°), mixed m. p. not lowered.

Preparation of the Sodium Lignin Sulfonates.—Sixty-six grams of yellow birch woodmeal (previously extracted successively with 1:1 ethanol–benzene, with ethanol and with water, equivalent to 60 g. on a dry basis) was cooked in an Allegheny metal bomb with 600 cc. of sodium bisulfite liquor, containing 6.0% "total" and 1.2% "combined" sulfur dioxide. The temperature was increased to 125° over a period of one hundred and fifty minutes and maintained at that temperature for twelve hours. After cooling, the liquor was filtered off, dialyzed through cellophane against flowing distilled water for three days, and then concentrated (22 mm.) using a foam-breaking flask. The residual liquid (50 cc.) was evaporated to complete dryness in a vacuum oven (50°, 14 mm.). The sodium lignin sulfonate, left as a glassy moisture-free residue, was pulverized and analyzed for sodium, sulfur[5] and methoxyl.

Alkaline Cleavage of the Sodium Lignin Sulfonates.—A solution of 1 g. of the sodium lignin sulfonate in 24% sodium hydroxide solution (50 cc.) was heated for twelve hours and extracted as described previously.[1] Two procedures were employed for determination of the aldehydes. (1) Total aldehydes were evaluated by treating the acidified bisulfite solution (obtained from the trichloroethylene extract) with an excess of aqueous *m*-nitrobenzoylhydrazine. With soft woods only vanillin *m*-nitrobenzoylhydrazone was found (mixed m. p.). With hard woods a mixture of syringaldehyde and vanillin *m*-nitrobenzoylhydrazone was obtained which was weighed for total aldehyde content. (2) The aldehydes were separated quantitatively as follows: the acidified bisulfite solution (obtained from the trichloroethylene extract, and corresponding to 1 g. of sodium lignin sulfonate) was extracted continuously with ether. The evaporated extract (20 mm., wt. *ca.* 0.1 g.) was a brown oil, which was sublimed at 80–100° (2 mm.) for twelve hours to remove about 0.05 g. of non-volatile material. The sublimate was transferred quantitatively with absolute ether into a small tared flask and the residue, after evaporation of the solvent, was sublimed at exactly 61° (chloroform vapor-bath) for sixty minutes at 2 mm. This more volatile vanillin fraction was then removed from the condenser and the sublimation continued at 80° (2 mm.) for one hour to ensure complete sublimation of the less volatile syringaldehyde. The vanillin fraction was resublimed under identical conditions, the residue being combined with the syringaldehyde fraction and likewise resublimed. Both fractions were transferred with dry ether to tared weighing bottles, evaporated, dried, weighed and melting points and mixed melting points determined (Table I). The reliability of this separation was checked by fractionally subliming a mixture of 0.0436 g. of vanillin and 0.0095 g. of syringaldehyde under the same conditions to yield 0.0433 g. of vanillin (m. p. 79–80°) and 0.0097 g. of syringaldehyde (m. p. 105–110°).

Vanillin and Syringaldehyde from Oak Lignin.—The lignin sulfonic acid prepared by complete solution of the chloroform-insoluble fraction (OCH_3, 23.4%) of *extracted* oak lignin[3] in sodium bisulfite liquor (6.0% "total" and 1.4% "combined" sulfur dioxide) at 100–120°, was refluxed for twelve hours with 24% alkali. Application of the identical procedure outlined above gave a mixture of 2.3% each of vanillin and of syringaldehyde.

Summary

1. It has been shown that whereas lignin sulfonic acids from soft woods, on treatment with hot aqueous alkali, yield only vanillin, those from hard woods give approximately equal quantities of vanillin and syringaldehyde (2.8% of each calculated on the weight of lignin).

2. Definite evidence is provided in the case of oak wood that these aromatic aldehydes are derived from isolated oak lignin.

MONTREAL, CANADA RECEIVED OCTOBER 6, 1937

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(5) Wolensky, *Ind. Eng. Chem., Anal. Ed.*, **20**, 1236 (1928).