NOTES

Aromatic Aldehydes from Spruce and Maple Woods

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It has recently been reported[1] that a yield of 25% of vanillin based on Klason lignin can be obtained by treatment of spruce wood with alkali in the presence of nitrobenzene. Employing the same technique,[1] we have confirmed this result by digesting spruce woodmeal (35.0 g., 28.6% Klason lignin), sodium hydroxide solution (400 cc., 2 *N*), and nitrobenzene (24 cc.) in a stainless steel bomb with good agitation at 160° for three hours. In duplicate experiments, 4.73 and 5.12 g. of crude vanillin *m*-nitrobenzoylhydrazones (m. p. 204–206°) were finally isolated; after recrystallization, m. p. 210–211°; mixed m. p. 210–211°. Yields were 22.8 and 24.7%, respectively, calculated on the Klason lignin.

Application of this method to maple wood (38.5 g., 22.0% Klason lignin) left 13.7 g. of insoluble woody residue containing 0.2% Klason lignin. Neutralization of the alkaline reaction liquors and continuous extraction with benzene removed 4.23 g., of which 3.63 g. was extractable with sodium bisulfite solution. Acidification of the neutralized aqueous liquor to *p*H 3, and benzene extraction, yielded additional benzene-soluble substances (1.21 g.). The benzene-insoluble material precipitated by acidification of the alkaline aqueous reaction liquor weighed 4.1 g.

Vanillin and syringaldehyde were isolated from the bisulfite solution by acidification and benzene extraction. Their separation was effected by solution of the crude extract in 250 cc. of ethanol and fractional precipitation by gradual addition of increasing amounts of ammonia. In this way, by precipitation of the much more insoluble syringaldehyde addition product, crude syringaldehyde (2.7 g.) was isolated; m. p. 105–112°; after recrystallization, m. p. 110.5–112°; mixed m. p. gave no depression. The ammoniacal ethanol solution remaining after removal of the syringaldehyde component was evaporated to remove the ammonia and ethanol and the residue dissolved in about 125 cc. of dry ether. Addition of ammonia precipitated the crude addition product from which 0.55 g. of crude vanillin-containing material was isolated. A preliminary purification by sublimation[2] at 61° (1 mm.) yielded 0.29 g. crude vanillin (m. p. 75–80°), recrystallized m. p. 80–82°, mixed m. p. no depression. Vanillin was also isolated by direct fractional sublimation[2] of the bisulfite soluble material (3.56 g.) to yield 0.60 g. of crude vanillin (m. p. 77–81°). Precipitation of the total aldehydes in 3.63 g. of the bisulfite soluble extract yielded 7.01 g. of mixed *m*-nitrobenzoylhydrazones.

Based on the Klason lignin content of maple wood, the yield of syringaldehyde isolated by treatment with ammoniacal ethanol amounted to 31.8%; that of vanillin 3.4%. By sublimation 7.1% vanillin was obtained. By weight, the total yield of bisulfite soluble material was 42.9%, while the yield of total carbonyl-containing constituents of the bisulfite soluble fraction was 43.0% (calculated from the mixed *m*-nitrobenzoylhydrazones on the assumption of a syringaldehyde–vanillin ratio of 3:1). A duplicate experiment gave very similar yields.

(1) Freudenberg, Lautsch and Engler, *Ber.*, **73**, 167 (1940).

(2) Hawkins, Wright and Hibbert, This Journal, **59**, 2447 (1937).

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α-Hydroxy-β,β-dimethyl-γ-butyrolactone

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In the course of work on analogs of pantothenic acid, it was discovered that α-hydroxy-β,β-dimethyl-γ-butyrolactone is obtained readily in a single step by treating an aqueous solution of α,α-dimethyl-β-hydroxypropionaldehyde with potassium cyanide and calcium chloride. The intermediate cyanohydrin is smoothly hydrolyzed at room temperature by the calcium hydroxide produced in the reaction.[1] Shortly after the completion of this work, Reichstein and Grüssner[2] reported a somewhat similar procedure for preparing the lactone. Since our method has certain

(1) This method has been used in the sugar field by Haworth, *et al.* [*J. Chem. Soc.*, 1419 (1933)] and by Hudson, *et al.* [This Journal, **56**, 1248 (1934)].

(2) Reichstein and Grüssner, *Helv. Chim. Acta*, **23**, 650 (1940).