# NOTES

## Aromatic Aldehydes from Spruce and Maple Woods

By R. H. J. Creighton, Joseph L. McCarthy and Harold Hibbert

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.

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[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

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[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).

advantages over that of Reichstein and Grüssner[2] and over the two step procedure of Köhn and Neustädter[3] as modified by Stiller, *et al.*,[4] it seemed desirable to publish the details.

## Experimental

**α,α-Dimethyl-β-hydroxypropionaldehyde.**—This compound was prepared by the method of Wesseley,[5] with the exception that the reaction flask was cooled in an ice-bath during the initial vigorous stage of the reaction.

**α-Hydroxy-β,β-dimethyl-γ-butyrolactone.**—Crude α,α-dimethyl-β-hydroxypropionaldehyde (102 g., 1 mole) was dissolved in 1 liter of water at 60–70°. The solution was cooled under the tap and a cold solution of 133 g. of calcium chloride and 98 g. of potassium cyanide was added rapidly. The flask was stoppered (to exclude carbon dioxide) and was allowed to stand at room temperature with occasional shaking for eighteen hours. The solution was then heated on the steam cone to 70–80° and 151 g. of oxalic acid dihydrate was added. The calcium oxalate was removed by filtration and the filtrate was concentrated to a gum under reduced pressure. It is essential that as much water as possible be removed at this point. The residue was extracted with 1 liter of dry acetone and the insoluble material was removed by filtration. The filtrate was concentrated to a viscous oil under reduced pressure. The oil was taken up in dry acetone and the solution was filtered. The acetone was removed and the residue was fractionated under reduced pressure. The lactone distilled at 125–130° (18 mm.) as an oil which immediately solidified to a glass in the receiver. The yield of lactone, melting at 75–80°, was 100–105 g. (77–81% of the theoretical amount). The *p*-nitrobenzoate of the lactone melted at 137–138° as reported by Stiller, *et al.*[4]

The unusual ease of hydrolysis of the nitrile is interesting in view of the lability of the amide group in pantothenic acid.

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[3] Köhn and Neustädter, *Monatsh.*, **25**, 46 (1904).

[4] Stiller, *et al.*, This Journal, **62**, 1785 (1940).

[5] Wesseley, *Monatsh.*, **21**, 231 (1930).

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## Note on the Absorption Spectra of Some Alkyl Chrysenes

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The absorption spectra of 5-methyl,[1] 4,5-dimethyl,[1] 5,6-dimethyl[1] and 4,5-methylenechrysene[2] recently have been determined in these laboratories. The wave lengths and intensities of the various maxima are summarized in Table I and the curves are given in Figs. 1, 2. The experimental technique has been described previously.[3]

The spectra of 5-methyl and 5,6-dimethylchrysene resemble that of the unsubstituted hydrocarbon[4] apart from the usual shift to longer wave lengths and some loss of fine structure. 4,5-Dimethylchrysene differs somewhat from the other two methyl derivatives, the most intense maximum showing some resolution while at longer wave lengths the intensity of absorption is greater and the resolution less.

TABLE I

Wave Lengths (Å.) of the Maxima and Corresponding Intensities (Log $E_{\text{molar}}$) of the Spectra of Some Alkyl and Alkylene-Chrysene Derivatives (Solvent Ethanol)

| | Max. | Intensity |
|---|---|---|
| 5-Methylchrysene | 2705 | 4.98 |
| | 2865 | 3.99 |
| | 3005 | 3.98 |
| | 3125 | 4.06 |
| | 3265 | 4.06 |
| | 3505 | 2.89 |
| | 3680 | 2.90 |
| 5,6-Dimethylchrysene | 2740 | 4.95 |
| | 3040 | 3.96 |
| | 3225 | 4.08 |
| | 3330 | 4.05 |
| | 3550 | 2.94 |
| | 3745 | 2.84 |
| 4,5-Dimethylchrysene | 2740 | 5.10 |
| | 2815 | 5.05 |
| | 3120 | 4.15 |
| | 3300 | 4.34 |
| | 3450 | 4.34 |
| | 3800 | 2.87 |
| 4,5-Methylenechrysene | (2590) | 4.83 |
| | 2655 | 4.99 |
| | 2690 | 5.04 |
| | 3010 | 4.09 |
| | 3130 | 4.07 |
| | 3265 | 4.09 |
| | 3420 | 2.98 |
| | 3465 | 2.82 |
| | 3525 | 2.65 |
| | 3606 | 2.89 |

The spectrum of 4,5-methylenechrysene (1) is particularly interesting as in the 1,2-benzanthracene series such a bridge methylene group has been observed to produce a considerable change in the spectrum including an increase in the amount of fine structure resolved.[5] The spectrum of 4,5-methylenechrysene also shows an increase in the amount of fine structure, particularly if comparison is made with 4,5-dimethylchrysene, substituted at the same position (Fig. 2). A corresponding comparison between the dimethyl and the methylene derivative is not possible in the

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[1] Compounds kindly supplied by Dr. M. S. Newman: see This Journal, **62**, 870 (1940); **62**, 2295 (1940).

[2] Fieser and Cason, *ibid.*, **62**, 1293 (1940).

[3] Jones, *ibid.*, **62**, 148 (1940).

[4] Mayneord and Roe, *Proc. Roy. Soc.* (London), **A152**, 299 (1935).

[5] Jones, This Journal, **63**,151 (1941).