pound obtained was practically the same when either γ-phenylbutyric acid or its methyl ester was cyclized, the yields being 70 and 72%, respectively. Methyl δ-phenylvalerate has been used to give benzosuberone in 90% yield as compared to that of 85% from the corresponding acid.[2]

Experimental[4]

Esterifications.—In all cases the esters were produced by refluxing the acid in 4% methanolic hydrochloric acid and isolating the neutral fraction in the usual manner. Although only methyl esters have been used in the present reported investigation, ethyl esters have been employed with equal success.

Ring Closures.—The preparation of the phosphorus pentoxide–85% orthophosphoric acid slurry and the isolation of the neutral ketonic material were carried out in a manner already described in detail.[2] To ensure homogeneity of the neutral compound from each cyclization, the compound was refluxed for 1 hour in 50 ml. of aqueous ethanol containing 2 g. of sodium hydroxide. The neutral material isolated from this procedure was used for determining the yield of compound and for preparing the reported derivatives. Fifty-four grams of slurry per gram of ester or acid was employed in all instances. The mixture of compound and slurry was heated in a flask protected from moisture by a calcium chloride tube for two hours on a steam-cone, although a shortened working time resulted in no decrease in yield of ketone in one instance.[5]

Derivatives.—The oxime and semicarbazone were prepared by refluxing the neutral compound from each cyclization in absolute ethanol and anhydrous pyridine containing either hydroxylamine hydrochloride or semicarbazide hydrochloride. Mixed melting points of these derivatives were not depressed when prepared from material obtained by cyclizing either the ester or its corresponding acid.

α-Hydrindone.—To 2 g. of methyl β-phenylpropionate was added the commensurate quantity of polyphosphoric acid slurry and the mixture heated. There was obtained 1.5 g. (93%) of neutral compound; oxime, m.p. 143–144°, reported,[6] 143–144°; semicarbazone, m.p. 237° (dec.), reported,[7] 239° (dec.).

α-Tetralone.—One gram of methyl γ-phenylbutyrate and 54 g. of slurry yielded, after the usual procedure, 0.59 g. (72%) of neutral compound; oxime, m.p. 101–102°, reported,[8] 102.5–103.5°; semicarbazone, m.p. 213–215°, reported,[8] 217°.

Benzosuberone.—A sufficient amount of polyphosphoric acid slurry was poured into a flask containing 1.8 g. of methyl δ-phenylvalerate and the usual procedure carried out to give 1.3 g. (90%) of neutral product; oxime, m.p. 107–108°, reported,[9] 108–109°; semicarbazone, m.p. 206–207°, reported,[9] 206–207°.

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[4] Melting points are uncorrected.

[5] Methyl γ-phenylbutyrate was cyclized to α-tetralone by heating for only 15 minutes.

[6] F. S. Kipping, *J. Chem. Soc.*, **65**, 490 (1894).

[7] C. Revis and F. S. Kipping, *ibid.*, **71**, 241 (1897).

[8] F. S. Kipping and A. Hill, *ibid.*, **75**, 151 (1899).

[9] F. S. Kipping and A. E. Hunter, *ibid.*, **79**, 607 (1901).

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Occurrence of *d*-Pinitol in Red Spruce (*Picea rubra*)

BY SIDNEY GOTTLIEB AND F. E. BRAUNS

d-Pinitol, the monomethyl ether of *d*-inositol, occurs in many species of plants, having been reported in *Pinus lambertiana*,[1] senna leaves,[2] *Mateza roritina*,[3] *Sequoia sempervirens*,[4] *Pinus strobus*,[5] *Astragulus wootoni*,[6] *Astragulus earliei*,[7] *Oxytropis lambertii*,[7] *Lotononis laxi*[8] and *Lupinus caudatus*.[9]

In the course of the preparation of "native lignin" from red spruce (*Picea rubra*), a crystalline compound was isolated in small yield from the dioxane–ether filtrate obtained in the precipitation of dioxane solutions of crude native lignin into ether. This compound was identified as *d*-pinitol. The yield was 2.5 g. of *d*-pinitol from 100 pounds of sawdust.

Freshly cut logs of 12 year-old red spruce were stripped of bark and reduced to sawdust. The sawdust was thrice extracted in copper percolators with 95% alcohol and worked up according to the method of Brauns.[10] Instead of separating the water-soluble fraction of the initial alcohol extract by decantation from the insoluble solids, dioxane was added and the water and alcohol were removed by azeotropic distillation resulting in a dioxane solution containing the total alcohol extract (except volatile materials). The precipitation of this dioxane solution (adjusted to a concentration of 10% solids) into 20 volumes of diethyl ether and subsequent centrifugation resulted in a clear yellow solution which, when concentrated to a small volume of dioxane, deposited small white prismatic crystals of *d*-pinitol which, after several recrystallizations from hot butanol, melted at 185–186° (cor.). $[\alpha]^{20}\text{D}$ −65.8° (previous values reported −67.7,[5] −62.5,[6] −65.3,[11] −65[7]).

Anal. Calcd. for $C_7H_{14}O_6$: C, 43.27; H, 7.27; OCH_3, 15.9; mol. wt., 194. Found: C, 43.55; H, 7.50; OCH_3, 16.0; mol. wt. (Rast), 189 and 197.

A mixture of the compound with an authentic sample of *d*-pinitol melted at 185–185.5°.

The pentacetyl and pentabenzoyl derivatives were prepared according to the procedure of Griffin and Nelson[11]; the crystalline pentacetate, m.p. 97.5–98°, $[\alpha]^{20}\text{D}$ −9.3°; the amorphous pentabenzoate, m.p. 96–97° $[\alpha]^{20}\text{D}$ −31.5°, in good agreement with the values reported in the literature.

A small amount of *d*-pinitol (0.5 g. per 100 g. sawdust) could be isolated by the direct extraction of ground red sprucewood (60 mesh) with cold water.

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The Diffusion Coefficient of Magnesium Sulfate in Dilute Aqueous Solution at 25°

BY HERBERT S. HARNED AND ROBERT M. HUDSON

Recently, the diffusion coefficient of zinc sulfate[1] at high dilutions in water was determined by the conductance method. The present measurements of the diffusion coefficient of magnesium sulfate, extended to somewhat lower concentrations, were carried out to supplement our knowledge of the diffusion behaviors of 2-2 electrolytes.

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