We have just observed that *ethyl* phenyl sulfide with *n*-butyllithium gives *o*-ethylmercaptobenzoic acid.

DEPARTMENT OF CHEMISTRY
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Hydrogenation of Wood

BY H. P. GODARD, JOSEPH L. MCCARTHY AND HAROLD HIBBERT

Studies on hydrogenation of lignin and other plant materials at high pressures have now shown that maple and spruce wood meals readily undergo hydrogenation. The two latter products were first freed from resin, fats, etc., by the customary preliminary extraction treatment with alcohol–benzene, alcohol, and water in the order named, then dried, suspended in anhydrous dioxane, the copper–chromium oxide catalyst added and the mixture then subjected to the action of hydrogen at around 250 to 280° at a pressure of 5000–6000 pounds per square inch (333–400 atm.) for periods of twelve to sixteen hours.

The main products isolated were (a) 4-*n*-propylcyclohexanol-1, b. p. 92–95° (7 mm.), refractive index $n^{25}\text{D}$ 1.4633, and (b) 4-*n*-propylcyclohexanediol-1,2, b. p. 107–110° (1 mm.), refractive index $n^{25}\text{D}$ 1.4808; some higher boiling oils also were obtained. These substances undoubtedly originate from the lignin present in the wood, the combined yields of (a) and (b) in the preliminary work, when calculated on the total (Klason) lignin present originally, amounting to around 60 to 70% in the case of maple and about 35 to 40% in the case of the spruce meal. Similar results were obtained using wood meal previously extracted with cold 5% alkali, although in these cases the yields were somewhat lower.

Presumably other suspending media such as tetralin, decalin, cyclohexane, as well as the above solvents (a) and (b), can be used in place of dioxane, and these are being actively investigated.

It is of considerable interest that the accompanying carbohydrate–polysaccharide components also undergo simultaneous hydrogenation and hydrogenolysis as indicated by the large absorption of hydrogen (about 3.2 moles of hydrogen per 100 g. of wood meal). The nature of these reactions and of the resulting products are also under investigation.

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The Effect of Chlorine Substitution on the Fungistatic Properties of Acetic and Propionic Acids

BY CHARLES HOFFMAN, T. R. SCHWEITZER AND GASTON DALBY

In a recent paper the fungistatic properties of β-iodopropionic acid were reported in connection with a study of a series of normal, branched-chain, and substituted fatty acids.[1] It was shown that β-iodopropionic acid had remarkable fungistatic properties which apparently depended to some extent on the nature of the iodine atom itself. The effect of substituents is also of interest from the point of view of the relationship of molecular structure to fungistatic power. Monochloroacetic, α-chloropropionic, and β-chloropropionic acids are readily available and their fungistatic curves illustrate the effect of the introduction of a single chlorine atom in all possible positions.

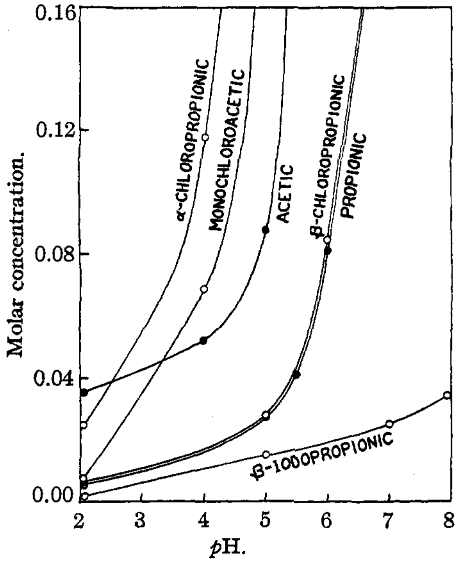

Fig. 1.—Molar concentrations of the indicated acids at various *p*H values necessary to inhibit mold for forty-eight hours at 37.5°.

The method used was as previously reported.[1] β-Chloropropionic acid has a curve practically identical with that of propionic acid itself and is markedly different from the β-iodopropionic acid curve which is indicated on the graph for comparison. The introduction of chlorine on the alpha carbon of propionic acid sharply decreases its fungistatic properties. Monochloroacetic acid is also much less effective than acetic acid except

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(1) Hoffman, Schweitzer and Dalby, *Food Research*, **4**, 539 (1939).

in the very high *p*H ranges. A chlorine atom on the carbon next to the carboxyl affects the fungistatic properties of the acid, whereas the same substituent on the beta carbon atom has no effect. Constitutional factors are therefore of considerable significance on the biological effect of fatty acids.

Langmuir[2] pointed out that halogen substitution had an appreciable effect on the dissociation constant of a fatty acid. The theory[3] is rather widely held that the biological activity of an acid is dependent on the dissociation constant; that is, the less ionized the acid, the more powerful its biological effect. The relative fungistatic properties of acetic and monochloroacetic, and of propionic and α-chloropropionic acids, when compared with their respective dissociation constants are in agreement with this theory. In the case of propionic and β-chloropropionic acids, however, the fungistatic properties are not so closely related to the dissociation constants. Propionic acid has a dissociation constant of 1.33×10^{-5}, and β-chloropropionic acid 8.59×10^{-5},[2] but the two acids have essentially identical fungistatic properties.

(2) Langmuir, *Chem. Rev.*, **6**, 465 (1929).

(3) (a) Tekelenburg, *Nederland. Tijdschr. Hyg. Microbiol. Serol.*, **2**, 176 (1927); (b) Bach, *Bull. sci. pharmacol.*, **39**, 7 (1932).

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The Preparation of Aurin Tricarboxylic Acid*

By Duncan A. Holaday

Recent work in this Laboratory required the use of pure aurin tricarboxylic acid. Several methods of preparing this compound were tried, including those of Scherrer and Smith,[1] Heisig and Lauer,[2] and Caro.[3] A product satisfactory for use in the determination of aluminum was obtained by each of these methods, but in no instance did the product contain more than 70% aurin tricarboxylic acid based on the air-dried material. The content of dye was determined by titration with titanium trichloride solution.[4]

In the course of the work it was observed that the material prepared by Caro's method would undergo a further reaction on treatment with a second portion of the oxidizing mixture (sodium nitrite–sulfuric acid solution). A study of this reaction developed the following modification of Caro's procedure which has several advantages over previously described preparations and yields a product of high purity. The methods of Heisig and Lauer, and of Scherrer and Smith, require that the temperature be kept below 5°. In the following procedure the reaction is not highly exothermic, and therefore no rigid temperature control is necessary. Caro recommends a purification with sodium bisulfite, which is difficult to perform and in the author's hands does not yield a pure product. In the modified procedure no purification of the reaction product is necessary except the removal of inorganic salts.

Experimental Part

Five grams of finely powdered sodium nitrite was added slowly and with vigorous stirring to 36 cc. of sulfuric acid, avoiding evolution of oxides of nitrogen. To this solution an intimate mixture of 10 g. of methylene-disalicylic acid[5] and 5 g. of salicylic acid was added in small portions with vigorous stirring. After addition of all of the solid material, the mixture was allowed to stand for an hour with occasional stirring. It was then poured into a solution of 5 g. of sodium nitrite in 36 cc. of sulfuric acid, stirred, and allowed to stand overnight. The reaction mixture was added slowly to one liter of cold water, allowed to stand for an hour, and filtered on a Büchner funnel. The precipitate was suspended in one liter of warm water (50°) and filtered. This suspension and filtration was repeated, the free water removed by drawing air through the funnel, and drying was completed in a vacuum oven at 70°. The yield of dry product was 10.5 g. It titrated 97% aurin tricarboxylic acid.

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* Not copyrighted.

(1) Scherrer and Smith, Bureau of Standards Res. Paper RP1118.

(2) Heisig and Lauer, *Org. Syntheses*, **9**, 8 (1929).

(3) Caro, *Ber.*, **25**, 941 (1892).

(4) Evenson and Nagel, *J. Ind. Eng. Chem.*, *Anal. Ed.*, **3**, 167 (1931).

(5) Vanino, "Präparative Chemie," Vol. II, 1937, p. 585.

Food Division
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Type III Surface Tension Curves with Minimum in Dilute Solution in Pure Hydrocarbons

By M. E. L. McBain and L. H. Perry

Many properties of colloid systems in water are usually explained in terms of free ions, so that it becomes interesting to examine non-ionizing solvents to see in how far similar behavior is to be found where free ions are almost or quite lacking. One very striking property of many colloidal electrolytes in water is that in very dilute solution they lower the surface tension to about one-third that of water. The surface tension is then at a minimum and thereupon rises to a flat maximum in slightly less dilution. Some non-electrolytic detergents likewise similarly lower the surface