Comments and Communications

Starch Blue

Blue color has long been associated with the presence together of starch and iodine. This empirical fact has been without satisfactory explanation. Theories of a starch-iodide compound, a starch-iodide complex, and, more recently, a theory of adsorption have been advanced.

With the use of radioactive iodine it has been possible to show that the change leading to blue color is a change induced in the starch molecule by iodine acting catalytically in the presence of oxygen and that the blue color is not dependent on the presence of iodine.

To 2 ml of 1% corn starch solution, 2 ml of iodine solution (10 mg of KI, 4 mg of I_2) and 10 microcuries of I^{131} (radioactive iodine) were added. After allowing contact for 3 hrs, iodine was withdrawn by repeated butanol extraction. (An analytical reagent grade of butanol is necessary to prevent loss of blue color by contaminants. It has long been known that so-called "starch-iodine blue" loses its color in the presence of NaOH.) After complete extraction of the iodine, the butanol was found to contain the radioactive iodine, while no radioactivity was found in the starch blue. (If on dehydration the precipitate becomes red, the blue color is returned by washing with water.)

This finding is comprehensible when one recalls that the dye stuff, indigo, prior to its synthetic preparation, was obtained from the East Indian plant, indican, and occurs as an indoxyl-glucoside which goes onto the cloth in a colorless vat form and is then air-oxidized to the indigo color form.

The test reported above confirms earlier work in which it was possible to demonstrate the absence of iodine in starch blue by the following method:

To 50 ml of 2% starch (1 gm of corn starch to 50 ml of H_2O) 50 ml of H_2O_2 was added. To this, 5 ml of 1% KI was added. Formation of dark blue color was followed by extraction with 800 ml of butanol in 50-ml lots over a period of time. For some time the butanol extracted showed brownish and yellow coloration. When the butanol was completely white and the ppt. a blue-black, the ppt. was examined for iodine by the following method: The sample was decomposed in a Parr peroxide bomb using sodium peroxide and accelerating agents. The fusion was dissolved in dilute HNO_3, and the halogens precipitated as silver salts which were filtered out on an asbestos Gooch crucible. From here analysis was by Scott's Standard Method of Analysis (5th ed., Vol. 1, p. 276). There was no evidence of iodine by this method.

While this method had demonstrated no iodine, it is a cumbersome procedure. The method employing radioactive iodine is simple and direct and would appear to be a conclusive demonstration.

This finding is interesting in connection with the action of thyroxin (the catalytic activity of the iodine of diiodotyrosine) in carbohydrate metabolism.

We are indebted to Lorraine Kirschner, of the Massachusetts General Hospital, for the Geiger determinations.

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Preparation of Succindialdehyde and Its Derivatives From Furan

The investigations of Clauson-Kaas and co-workers (N. Clauson-Kaas. *Kgl. danske Videnskab Selsk., Math.-Fys. Medd.*, 1947, 22, 6; *Chem. Abstr.*, 1948, 42, 1930; N. Clauson-Kaas, F. Limborg, and J. Fakstorp. *Acta Chem. Scand.*, 1948, 2, in press) have resulted in the development of a convenient method for the synthesis of 2,5-dialkoxy-2,5-dihydrofurans. Attempts to hydrogenate these compounds, using Pt or Pd catalysts, resulted in mixtures of hydrogenation and hydrogenolysis products. It has now been found that catalytic hydrogenation of one of these products over a Raney-Ni catalyst offers a simple and direct route for the preparation of succindialdehyde. Hydrogenation of 2,5-diethoxy-2,5-dihydrofuran in absolute ethanol with a catalyst prepared according to Pavlic and Adkins (*J. Amer. chem. Soc.*, 1946, 68, 1471) proceeds fairly rapidly at room temperature under a hydrogen pressure of about 50 p.s.i. to give a 79% yield of 2,5-diethoxy-tetrahydrofuran (I). This product, which is an acetal of succindialdehyde, boils at 30°–31°/1 mm and is readily converted to the *bis*-phenylhydrazone (m.p., 123°), dioxime (m.p., 169°), and *bis*-semicarbazone (m.p., 192°) of succindialdehyde. Hydrolysis of (I), following the procedure described by Harries (*Chem. Cbl.*, 1901, II, 307), gives the free aldehyde in a 30% yield.

A detailed account of the hydrogenation of 2,5-dialkoxy-dihydrofurans will be published elsewhere.

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Sex and Vigor in *Populus*

A point of some interest to geneticists and tree breeders is suggested by the preliminary analysis of data on the sex of a number of poplar clones selected in the fall of 1947. The material assembled represents the initial collection of a project sponsored by the Maria Moors Cabot Foundation and designed to assess the degree of wild variability prevailing within various species of the genus. Out of 76 clones (including *tremuloides, grandidentata, Tacamahaca, trichocarpa,* and *deltoides*) bearing flower buds, only 18 (23.7%) proved to be females. Several factors were involved which would tend to destroy the true randomness of the sample. The most important of these

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