

# 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 After allowing contact for 3 hrs, iodine was withdrawn by repeated butanol extraction.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 thyroxine (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 Vidensk. 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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seems to be that the individual trees were selected on the basis of their apparent vigor, health, and good stem form as compared with their associates in the various stands throughout the United States and Canada, where the collections were made. This, then, suggests that a positive correlation may exist in this genus between maleness and such desirable characters as vigor and form.

Further support of this hypothesis is revealed by a check of the old cottonwood or black poplar clones long cultivated in Europe. G. Houtzagers (*Het Geslacht Populus in Verband met zijn Beteekenis voor de Houtteelt* (The genus *Populus* and its significance in silviculture). Wageningen, Netherlands: H. Veenman and Zonin, 1937), for instance, in his description of poplar clones cultivated in Holland, notes that of the 8 most commonly planted, only 2 (25%) are females.

If the accumulation of more extensive data confirms these preliminary observations, it is needless to point out that this knowledge will be an invaluable tool to tree breeders and silviculturists interested in the genus *Populus*.

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### Weed Control—A Liquid Concentrate of the Isopropyl Ester of 2,4-D Miscible With Oil or Water in Any Proportion

A number of proprietary concentrates of various esters of 2,4-D are on the market, but few, if any, of them carry more than 40–45% of the parent ester. When added to the diluting water, many of these concentrates produce a smooth white emulsion which remains in stable suspension for only a very limited time. Thus, in about an hour, two distinct layers may begin to form, the upper water-like and the lower a dense white flocculation. A casual examination of the white flocculent material would suggest that this substance consisted of a precipitate of 2,4-D acid in fine division. A consideration of the chemical reaction which occurs upon the preparation of the ester would appear to support the suggestion that 2,4-D acid was depositing at the bottom of the container by virtue of a reversal of the acid-alcohol to ester-water reaction.

An associate in this laboratory has shown that the so-called hydrolysis of the ester in the diluting water does not take place, except at a very slow rate. A difference in density between the ester, its coupling agent, and the diluting water accounts for the precipitate of dispersed globules of oily material settling out by gravity. Obviously, the spraying of such a dispersion in the field or glass house, without frequent agitation, introduces errors not only in the uniformity of the application of the active constituent of the herbicide, but also in the subsequent evaluation of the treatment.

An effort was made in this laboratory to develop a concentrate of 2,4-D which would carry about double the amount of 2,4-D to be found in proprietary preparations of this character. A simple process, involving dilution with water, was also recommended to plantation workers in which the precipitation of oily globules could be inhibited for a sufficient length of time to assist materially in a more even application of the spray components. With fuel oil, Diesel oil, and other petroleum oils, this concentrate forms a clear solution.

The formula follows:

#### Concentrate No. 1

Dissolve, in the cold, 15 lbs of conditioning agent<sup>1</sup> in 85 lbs of clear isopropyl ester of 2,4-D (weight approximately 10 lbs/gal). This carries 70.4% of 2,4-D (calculated to acid) or about 7 lbs of 2,4-D acid/gal.

To inhibit rapid settling of heavy oily globules in the water dispersion of Concentrate No. 1, add from 8 to 10 pints of Stoddard solvent to each gallon of concentrate before incorporating the diluting water.

Observations made in current pre-emergence field studies indicate that 1½ pints of Concentrate No. 1, diluted to 25 gals with Diesel oil and applied evenly upon the bare soil surface over 1 acre of planted sugar-cane seedpieces, will arrest the germination and growth of weed and grass seeds and seedlings for 7 weeks. This treatment has not shown as yet any abortive effect upon the germination and growth of the planted seedpieces.

Concentrate No. 1, diluted with Diesel oil at from 2 to 4% equivalent of 2,4-D acid, shows promise of controlling the growth of woody pests such as guava, lantana, Java plum, etc. Application should be made to the basal portion of the plant, not the foliage. From 50 to 100 ml of the diluted concentrate may be used. No primary treatment of the tree or shrub is required. A slight cupping out of the soil where the plant emerges from the ground may be helpful. The effect of the treatment may show progressive action for 5 or 6 months. The conditioning agent, it is believed, renders the diluted concentrate miscible with plant moisture after the treatment permeates the bark.

Concentrate No. 1 has one outstanding disadvantage. It employs the isopropyl ester of 2,4-D, the latter exerting an appreciable vapor tension. Even when diluted to 160 times its original volume with Diesel oil, the "vapor drift" of the ester may carry to nearby sensitive vegetation.

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<sup>1</sup> There are several conditioning agents which may be used. Good results were obtained in Hawaii in which we employed an oleate of polyoxyethylene hexahydric alcohol (Atlas G-1096).