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The Qualitative Detection of Methanol*

By Walter C. Gakenheimer† and Walter H. Hartung‡

An attempt was made to adapt, as a general laboratory exercise, the qualitative U. S. P. test for methanol in whisky (1) as a general method for detecting methyl alcohol in the presence of ethyl alcohol. In the class assignment, every student reported a positive reaction when no methanol was present. This is not surprising when it is realized that fuchsin-sulfurous acid T.S. is a general reagent for identifying aldehydes as a class (2). Under the U. S. P. conditions of the test, it is obvious that ethanol must be oxidized, at least in part, to acetaldehyde.

Eegriwe has reported (3) that chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid) is a sensitive, specific and characteristic reagent for formaldehyde. His procedure has been adopted by Feigl (4) to apply to methyl alcohol. In Feigl's discussion, he says that "with chromotropic acid in a concentrated sulfuric acid solution, a violet-red color appears" and "the following give no reaction: acetaldehyde, propionic aldehyde, butyric aldehyde, isobutyric aldehyde, isovaleric aldehyde, oenanthol, crotonaldehyde, chloral hydrate, glyoxal and aromatic aldehydes. Glyceryl aldehyde, furfural, arabinose, fructose and sucrose give yellow colors. Other sugars, acetone and carboxylic acids do not react. High concentrations of furfural give a red color."

* From the Department of Chemistry, School of Pharmacy, University of Maryland.

† Alumni Fellow, 1939–1940.

‡ Professor of Pharmaceutical Chemistry.

Accordingly, several series of experiments were designed to show:

(*a*) the sensitivity of fuchsin-sulfurous acid T.S. to acetaldehyde;

(*b*) the sensitivity of fuchsin-sulfurous acid T.S. to ethanol (after oxidation according to the U. S. P. procedure);

(*c*) the sensitivity of chromotropic acid to methanol in ethanol;

(*d*) the sensitivity of chromotropic acid to methanol in whisky.

EXPERIMENTAL

Fuchsin-Sulfurous Acid T.S. and Acetaldehyde.—Five cc. of fuchsin-sulfurous acid T.S. was added to 10 cc. quantities of aqueous acetaldehyde solutions of the following concentrations: 1%, 0.1%, 0.01% and 0.001%. A positive reaction was obtained with concentrations of 0.01% or higher, and negative results with the 0.001% solution, showing a sensitivity of at least 1:10,000.

Fuchsin-Sulfurous Acid T.S. and Ethanol.—The U. S. P. procedure for detecting methanol was applied to aqueous solutions of ethanol varying in concentration from 50% to 0.01% and in every case a positive reaction was obtained. By using a blank, it was determined that the oxalic acid-sulfuric acid solution of the Pharmacopœia was sufficient in itself to restore the color to the fuchsin-sulfurous acid T.S.

Chromotropic Acid and Methanol in Ethanol.—The above facts indicate the necessity for an improved test for the presence of methyl alcohol in ethyl alcohol. Consequently, the procedure of Eegriwe, as outlined by Feigl, was applied to a series of solutions of methanol in 50% (by volume) ethanol. The concentrations of methanol used were: 1%, 0.75%, 0.50%, 0.25%, 0.10%, 0.075%, 0.050%, 0.025% and 0.01%. All concentrations as low as 0.1% gave a positive reaction to the naked eye. Those of 0.075% and less gave a negative reaction. It is noteworthy that this test is carried out with 0.02 cc. of the sample and is sensitive to 16γ (0.016 milligram) of methanol.

The procedure consists in mixing drop quantities of 5% phosphoric acid, 5% potassium permanganate solution and the sample. The mixture is allowed to stand a minute and is then decolorized with a little solid sodium bisulfite, after which 4 cc. of 72% sulfuric acid and a little finely powdered chromotropic acid are added. The mixture is well shaken and heated to 60° for 10 minutes. A violet color, intensifying on cooling, indicates the presence of methyl alcohol.

This test is as simple to carry out as is the U. S. P. method using fuchsin-sulfurous acid T.S. and, in addition, eliminates the need for freshly prepared solutions. Furthermore, chromotropic acid is readily available and at a price which makes the cost per test almost negligible.

Chromotropic Acid and Methanol in Whisky.—In order to determine whether whisky contains interfering substances, the tests above were repeated, using whisky in the place of 50% ethanol. The same order of sensitivity was observed, again detecting 0.016 milligrams of methanol. Pure whisky gave negative results.

CONCLUSIONS

1. The U. S. P. test for methanol in whisky gives a positive reaction with ethanol even though no methanol is present.
2. Chromotropic acid is specific and extremely sensitive to formaldehyde and may be employed in detecting methanol in amounts as little as 0.016 milligrams. Ethanol and whisky do not interfere with this test.
3. The chromotropic acid method is dependable as a specific test for methanol, it is easily carried out and it may be applied to samples as small as 0.02 cc. of a 1:1000 solution of methanol.

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The following scientists have been honored by France by portrayal on postage stamps: Marcelin Berthelot, pioneer in organic synthesis; Claude Bernard, physiologist; Louis Pasteur, Pierre Curie and Marie Curie, discoverers of polonium and radium; Leon Calmette, research worker in tuberculosis.

Determination of Unsaturates in Cyclopropane*

By Frederick K. Bell and John C. Krantz, Jr.†

The quantitative determination of the amount of unsaturated hydrocarbons present in cyclopropane as impurity presents an interesting and difficult problem. In the preparation of cyclopropane the formation of some unsaturated hydrocarbons is to be expected especially since the chemical procedure involves the transition from a straight chain to a closed ring structure.

There is evidence to indicate that certain of these unsaturated compounds predispose the patient to pulmonary edema, therefore, it is important both to the manufacturer and to the patient that suitable methods be available for determining the efficiency of purification methods employed before this anesthetic gas is used.

Cyclopropane or trimethylene, is the simplest possible cyclic hydrocarbon and it is the least stable of the cyclic hydrocarbons, the stability increasing markedly in passing to the tetra or the pentamethylene ring. It is not surprising then that cyclopropane displays in its chemical reactivity many of the properties ascribed to straight chain unsaturated hydrocarbons, for with simple rupture of the cyclopropane ring the unsaturated hydrocarbon, propene, results.

There are three unsaturated hydrocarbons which are most likely to occur in the preparation of cyclopropane: (1) propene, or methylethene, which is the straight chain isomer of cyclopropane; (2) propadiene, C_3H_4, which contains two double bonds and has a boiling point very near to that of cyclopropane; (3) propyne, or methyl acetylene, which is isomeric with propadiene and contains one triple bond. Reactions typical of these compounds such as the ease of hydrogenation and halogenation, oxidation by potassium permanganate and addition of hydriodic acid are all displayed to some extent by cyclopropane and at the present time no specific reaction has been discovered

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† Department of Pharmacology, School of Medicine, University of Maryland Baltimore, Maryland.