In order to get a better estimation of the relative amounts of the acids present in the fat, the saponification equivalents of all the fractions were determined. Assuming the intermediate fractions to be composed solely of the pure higher and lower boiling main fractions, the mixed esters were found to consist of 0.9% methyl caprylate, 37.5% methyl caprate[3] and 61.6% methyl laurate. Fractionation of a 1630-g. lot of fat gave almost identically the same results.

Although the iodine value would indicate the presence of about 6% of oleic acid, the saponification equivalents of the highest fractions of the methyl esters gave no indication of any acids of higher molecular weight than lauric. The presence of caprylic acid and absence of lower acids were shown by fractionating at atmospheric pressure all the fractions below methyl caprate from the total 2160 g. of fat. A pure methyl caprate fraction was isolated but no lower boiling ester.

The three acids were positively identified by saponifying the esters and converting the free fatty acids into the amides. These showed no depression in melting point when mixed with the amides prepared from specimens of caprylic, capric and lauric acids obtained from coconut oil.

Summary

The chemical constants of the seed fat of the California bay tree have been determined and the composition of the free fatty acids studied by fractionating their methyl esters. This showed that the fat is an excellent source of capric acid since the free fatty acids consist of approximately 1% caprylic, 37% capric and 62% lauric acids.

(3) This is by far the best source of capric acid. For other sources see Taylor and Clarke, THIS JOURNAL, **49**, 2829 (1927); Marvel and Hager, *ibid.*, **46**, 726 (1924); Kao and Ma, *J. Chem. Soc.*, 2047 (1931).

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The Preparation of Furil

BY W. W. HARTMAN AND J. B. DICKEY

In recent years furil dioxime has found favor as an analytical reagent. A new method for the preparation of furil from inexpensive materials should prove to be of interest.

Furil can be prepared by the oxidation of furoin in alkaline alcoholic solution with oxygen,[1] iodine[2] and nitrobenzene.[3] The method described in the Experimental Part is an application of a method for the preparation of benzil.[4]

Experimental

Furoin.—The furoin used was prepared in slightly improved yields[5] by a modification of the method of Fischer.[6] In a 22-liter flask fitted with a mechanical stirrer, an

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(1) Fischer, *Ber.*, **13**, 1337 (1880); *Ann.*, **211**, 218 (1882).

(2) Corson and McAllister, THIS JOURNAL, **51**, 2822 (1929).

(3) Nisbet, *J. Chem. Soc.*, 3121 (1928).

(4) Clarke and Dreger, *Org. Syn. Coll.*, 1, 80 (1932); Fischer, *Ann.*, **211**, 214 (1932).

(5) The best yield reported previous to this is 25%.

(6) Fischer, *Ann.*, **211**, 218 (1882).

S-tube with dropping funnel, and an inverted Liebig condenser, were placed 8 liters of water, 4 kg. (41.65 moles) of freshly distilled furfural,[7] and 3 liters of 95% of ethyl alcohol. The reaction mixture was then heated to boiling and the flame was removed. When the liquid had just ceased to boil, a solution containing 200 g. (3.07 moles) of potassium cyanide dissolved in 600 cc. of water was added with stirring as rapidly as the vigor of the reaction would permit. The reaction mixture boiled for twenty minutes (heat of reaction) and was then heated to boiling for an additional five minutes. The alkaline solution was made acid to litmus with glacial acetic acid and placed in a cool place to crystallize overnight. The resulting mass of dark-colored tarry crystals was filtered on a large Büchner funnel and washed with cold water followed by cold methyl alcohol to remove as much of the tar as possible. Then the brown-colored residue was crystallized from methyl alcohol using 200 g. of "Norit" decolorizing carbon. The furil separated as light-brown needles melting at 134–135°. The yield of purified material is 1500 g., which is 37.5%.

Furil.—In a 1-liter round-bottomed flask fitted with a mechanical stirrer was placed 158 g. (0.63 mole) of powdered copper sulfate ($CuSO_4 \cdot 5H_2O$), 210 g. of pyridine (b. p. 109–118°) and 90 g. of water. The stirrer was started and the mixture was heated on a water-bath until solution was effected. To the solution was added 57.6 g. (0.3 mole) of furoin (m. p. 134–135°). After a short time the color of the reaction mixture changed from a deep blue color to a deep green with a brownish tinge. Stirring and heating were continued for two hours and the reaction mixture[8] was poured into 1 liter of cold water, filtered on a Büchner funnel, and washed with water until the wash water was colorless. The black residue was then washed with 500 cc. of cold methyl alcohol and recrystallized from methyl alcohol,[9] using 25 g. of "Norit" decolorizing carbon. Yellow needles were obtained melting at 165–166°. The yield of purified material was 35.9 g., or 63%. A yield of 64% was obtained from a run ten times that described above.

Summary

An improved method for the preparation of furoin has been described. Furoin can be oxidized to furil by means of copper sulfate in excellent yields.

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[7] The furfural was distilled from a water bath under reduced pressure (20–30 mm.).

[8] If desired, the reaction mixture can be cooled and the furil removed by filtration. The solution is reactivated by passing oxygen into it.

[9] Furil can be crystallized satisfactorily from benzene.