Structure of the Ethanolysis Products from Spruce and Maple Wood

BY LEO BRICKMAN, J. J. PYLE, W. L. HAWKINS AND HAROLD HIBBERT

A re-investigation of the "aldehyde fraction" obtained in the ethanolysis of maple and spruce wood[1] has shown that two of the constituents previously identified (incorrectly) as syringoyl- and vanilloyl-acetaldehydes are, in reality, 1,2-diketones, namely, the benzil derivatives, methyl-4-hydroxy-3,5-dimethoxyphenyl diketone (C_6H_3-$(OH)(OCH_3)_2$-CO-CO-CH_3) (A) and methyl guaiacyl diketone ($C_6H_2(OH)(OCH_3)$-CO-CO-CH_3) (B), respectively. Proof of this has been found in the synthesis of the benzils by oxidation of the corresponding benzoins, namely, α-hydroxypropiovanillone and α-hydroxypropiosyringone, by means of copper sulfate and pyridine. The monosemicarbazone of (A) melts at 213° and its disemicarbazone at 240°, while the mono-2,4-dinitrophenylhydrazone of (B) melts at 226–227° and its monosemicarbazone at 214–215°. No depression in melting point was found on admixture with the corresponding products isolated from the ethanolysis products.

The mistake in identity arose as a result of the aldehyde-like properties possessed by these 1,2-diketones.

A full account of the supporting chemical evidence is to be given in a forthcoming publication.

(1) Pyle, Brickman and Hibbert, THIS JOURNAL, **61**, 2198 (1939).

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Purification of High Molecular Weight Fatty Esters

BY LORAN O. BUXTON AND ROLAND KAPP

In the course of our research it became necessary to prepare relatively large quantities of substantially acid-free high molecular weight fatty esters. We have found that the following process is more satisfactory for removing substantially all of the unreacted fatty acids than the usual methods.

The procedure most suitable is as follows. The unreacted alcohol is distilled from the esterification mass, and the residual mixture of free fatty acids, crude ester, and catalyst is dissolved in 2 to 5 parts by weight of a solvent such as ethylene dichloride to 1 part of ester. A convenient sample (10 to 20 g.) of the solvent solution of the crude ester is dissolved in an alcohol–ether mixture, and titrated with standard 0.5 *N* alcoholic potassium hydroxide. On the basis of this titration value an equivalent weight of concentrated aqueous potassium hydroxide, preferably of 38% strength, is added slowly with constant stirring to the solvent solution of the ester mixture. In a relatively short time the potassium soap of the unreacted fatty acids will rise to the surface as a flocculent aggregate, and any mineral acid present as catalyst will also precipitate out as the potassium salt. The solvent solution is filtered without suction, and the soap mass is washed with a small amount of fresh ethylene dichloride to remove traces of neutral ester, and the filtrate distilled. It is not necessary to dry the filtrate.

By this process we have been able to obtain quantitatively the yields of methyl and ethyl esters of lauric, oleic, linoleic, stearic and ricinoleic acids, from the original esterified mass prepared with the respective crude acids. The process also has been applied successfully to the preparation of relatively pure mono- and di-naphthenates of diethylene glycol. The esters obtained in this manner have acid values from 0.5 to 1.0 and can be purified further by vacuum distillation. Relatively large amounts of ester can be purified in this manner without the formation of troublesome emulsions and without the hazards hitherto inherent in the use of ether.

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Lupine Studies. XVI.[1] The Isolation of Nonalupine from *Lupinus andersonii* Wats

BY JAMES FITTON COUCH

The isolation of nonalupine from *Lupinus sericeus* has been reported recently.[1] In that species this alkaloid is associated with spathulatine first isolated from *L. marianus*.[2] Nonalupine has now been isolated from *L. andersonii*, a perennial, Pacific States lupine, which has not previously been examined chemically. Spathulatine was not found in the last named species.

Experimental

Material.—The plant used in this investigation was collected by the writer on the south road, Crater Lake Mt.,

(1) Previous paper, No. XV, THIS JOURNAL, **62**, 554 (1940).
(2) J. F. Couch, *ibid.*, **46**, 2507 (1924).