The compound yielded a *p*-nitrophenylhydrazone melting at 201–203°, which agrees with the value given by Mauthner.[9]

Anal. Subs., 0.1011: H_2O, 0.0457; CO_2, 0.2424. Calcd. for $C_9H_8O_3$: H, 4.88; C, 65.90. Found: H, 5.05; C, 65.45.

2,4,6-Trihydroxystyryl-3,4-methylenedioxyphenyl Ketone (VIII).—Two grams of phloroglucinaldehyde and 2 g. of acetopiperone were condensed by the method described above for the other isomer. Crystallization from 75% methyl alcohol yielded an orange powder which decomposed at 265–270°. In its decomposition point, color (deep orange) and also its insolubility in dilute ammonia, this compound resembled the natural product described by Oesterle.

Anal. Subs., 0.0770; H_2O, 0.0289; CO_2, 0.1798. Calcd. for $C_{16}H_{12}O_6$: H, 4.03; C, 64.00. Found: H, 4.20; C, 63.71.

The triacetate was prepared by refluxing 1 g. of the above ketone with acetic anhydride and sodium acetate for one hour. After decomposition with and crystallization from alcohol, light yellow needles were obtained which melted at 205–206°.

Anal. Subs. 0.0876: H_2O, 0.0328; CO_2, 0.1995. Calcd. for $C_{22}H_{18}O_9$: H, 4.22; C, 61.97. Found: H, 4.18; C, 62.08.

Summary

The two isomeric chalkones, 2,4,6-trihydroxystyryl-3,4-methylenedioxyphenyl ketone and 2,4,6-trihydroxyphenyl-3,4-methylenedioxystyryl ketone, corresponding to the possible structures for the chalkone previously isolated from natural sources, have been synthesized. A comparison of the properties of the natural chalkone with those of the synthetic isomers indicates that the natural compound is 2,4,6-trihydroxystyryl-3,4-methylenedioxyphenyl ketone. The other isomer, which possesses the structure originally assigned to the natural chalkone, differs markedly from the compound found in nature.

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DIFURYLETHYLENE

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In making a study of the disappearance of furfural in alcohol fermentation, Lintner[1] found that furfural in dilute aqueous solution reacts with hydrogen sulfide to form a milky emulsion of polythiofurfuraldehyde which has a peculiar penetrating bread-like odor. The emulsion which was formed could be coagulated to a rubbery mass on the addition of a few drops of sulfuric or hydrochloric acid.

A study of this reaction has been made and an attempt to identify the product has brought about the discovery of a method whereby difurylethylene may easily be prepared. By the vacuum distillation of

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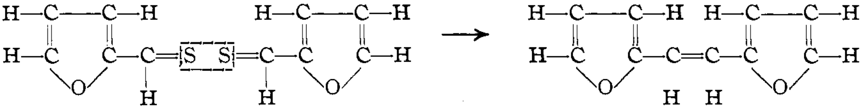
[1] Lintner, *Z. ges. Brauw.*, **15**, 189 (1910); *C. A.*, **5**, 755 (1911).

the polythiofurfuraldehyde, difurylethylene is formed and is obtained almost pure in the distillate.

The mechanism of the reaction is probably of the following order:



The product of this reaction is one which should be of considerable value in the synthesis of furfural compounds. With the remarkable increase in the production of furfural and its accompanying low cost per pound, the synthesis of compounds made from furfural becomes increasingly interesting.

Experimental

The polythiofurfuraldehyde was prepared as follows: A 3% solution of furfural in water was placed in a large absorption bottle of about 4-liters capacity. A slow stream of hydrogen sulfide gas was passed through the solution for three hours. By raising the temperature of the solution to 50°, the absorption rate may be increased. The resulting emulsion was coagulated with a small amount of hydrochloric acid and the resulting mass dried as much as possible without warming.

One hundred grams of the polythiofurfuraldehyde was placed in a 500-cc. Claisen flask and slowly warmed with a low flame, maintaining a vacuum of from 10 to 15 mm. of mercury. At about 60° a slight amount of ebullition took place but the solid crystals did not begin to condense on the walls of the receiver until 90°. The distillation was complete at 135°, leaving only a char. The product had a small amount of water with it and had a very penetrating odor due to a trace of sulfur compounds. The odor was entirely removed by petroleum ether, in which the compound which was formed was only slightly soluble.

The compound was purified by redistillation *in vacuo*. It was found that recrystallization from alcohol caused the compound to darken, indicating its rather unstable structure. It did not discolor farther on standing and the redistilled compound remained white. The yield was 18 g., or 18%.

Anal. Subs., 0.2076: CO_2, 0.5674; H_2O, 0.0960. Calcd. for C_5H_4O: C, 74.94; H, 5.09. Found: C, 74.55; H, 5.17.

The molecular weight determination using the freezing-point method with benzene as solvent was 162. The nearest theoretical weight would be 160.18, making the molecular formula $C_{10}H_8O_2$.

The compound melts at 100°. It is very soluble in acetone, soluble in benzene, ether, carbon tetrachloride, chloroform and hot alcohol, slightly soluble in petroleum ether and cold alcohol.

Summary

The vacuum distillation of polythiofurfuraldehyde, a compound prepared from furfural by treatment with hydrogen sulfide in dilute aqueous solution, yields what is believed to be difurylethylene.

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