mole) of phenol. The mixture, which became hot, was heated to 70–80° for ten minutes. The reaction mixture was then cooled, and crystallization induced by scratching the wall of the flask with a glass rod. The white, solid triphenyl orthoacetate, after recrystallization from an alcohol-water mixture, weighed 12 g. (78%) and melted at 61–62°. This orthoester could be distilled; it boiled at 148–153° (0.5 mm.). *Anal.* Calcd. for $C_{20}H_{18}O_3$: C, 78.33; H, 6.02. Found: C, 78.22; H, 6.03.

Triphenyl orthoacetate is hydrolyzed by 0.1 *N* hydrochloric acid into phenol and phenylacetate. When 5 g. of the orthoester was refluxed for four hours with 10 ml. of absolute alcohol containing a drop of concentrated hydrochloric acid and the excess of alcohol then removed by distillation, sufficient phenol was extracted from the residue with alkali to yield 12 g. (81%) of tribromophenol, m. p. 94–95°.

Reactions of Ketene Diphenylacetal. (a) With Methyl and Ethyl Alcohol.—A mixture of 11 g. of the acetal and 5 g. of methyl alcohol showed no sign of reaction after standing for several days or even after refluxing for four hours. However, when the mixture was treated with 1 drop of concentrated hydrochloric acid it became quite hot. Fractionation of this reaction mixture under reduced pressure gave 1.2 g. of phenol, b. p. 80–81° (10 mm.), and a fraction that boiled 95–160° (0.1 mm.) and solidified on cooling. Recrystallization of this fraction from an alcohol-water mixture gave 7.4 g. (48%) of triphenyl orthoacetate.

When ethyl alcohol was used in the above experiment instead of methyl alcohol, 0.9 g. (18%) of phenol and 9.4 g. (61%) of triphenyl orthoacetate were obtained.

(b) **Hydrolysis.**—A 5-g. sample of ketene diphenylacetal was heated for two hours with 25 ml. of boiling water that contained one drop of concentrated hydrochloric acid. The resulting liquid mixture, after cooling, was shaken with 50 ml. of a 10% sodium hydroxide solution and extracted twice with 25 ml. of ether. The alkaline portion was acidified with 10% hydrochloric acid and the phenol precipitated as tribromophenol; 2.9 g. (38%) was obtained. Distillation of the ethereal solution gave 1.3 g. (40%) of phenyl acetate, b. p. 196°.

(c) **Reaction with Hydrogen Bromide.**—To a solution of 4 g. of hydrogen bromide in 100 ml. of ether was added 11 g. of ketene diphenylacetal. No appreciable change was observed. The resulting mixture was refluxed for fifteen minutes and then after removal of the ether, the residue was heated under reduced pressure. A distillate of 2.8 g. (58%) of phenol and a viscous, undistillable tar that remained in the flask were obtained.

(d) **Benzyl Halides.**—A mixture of 11 g. of the acetal and 6.5 g. of benzyl chloride was heated at 150° for fifteen hours. No indication of reaction was shown and upon distillation of the mixture the starting materials were recovered. When benzyl bromide was used, following the procedure of McElvain and Kundiger,[7] 8% of the theoretical quantity of hydrogen bromide was evolved and the reaction mixture turned to a red viscous liquid which was not investigated further.

Summary

Ketene diphenylacetal has been prepared by the sequence of reactions: $CH_2{=}CHOC_6H_5 \rightarrow CH_2BrCHBrOC_6H_5 \rightarrow CH_2BrCH(OC_6H_5)_2 \rightarrow CH_2{=}C(OC_6H_5)_2$.

Triphenyl orthoacetate, $CH_3C(OC_6H_5)_3$, has been prepared by the addition of phenol to this ketene acetal.

The properties now found for ketene diphenylacetal and triphenyl orthoacetate indicate that these compounds have not been described previously in the literature, and substantiate the belief that earlier workers who reported these compounds had, in reality, isolated the diphenyl ether of ethylene glycol.

Ketene diphenylacetal shows a much lower anionoid reactivity at the methylene carbon than does ketene diethylacetal.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KANSAS STATE COLLEGE]

The Isolation of Kafiroic Acid from Kafir Bran[1]

BY L. L. WOODS[1a] WITH C. W. COLVER

A critical examination of kafir bran has revealed that the material contained a pigmented acid which we have designated as kafiroic acid. The kafir brans used in these experiments were a composite of the usual commercial varieties of kafir and provided by the Department of Chemical Engineering of Kansas State College.

When kafiroic acid was first separated from the bran it was highly contaminated but methods that were devised for purifying the crude substance proved quite effective. Purified kafiroic acid was found to be a high molecular weight compound with a definite rust-brown color, and an approximate empirical formula of $C_{18}H_{30}N_2O_6$. The substance was found to be unstable in the presence of strong oxidizing agents and easily decomposed by the action of alcoholic potassium hydroxide and sulfuric and hydrochloric acids. Degradation with acids and potassium hydroxide gave 5-aminopentanoic acid. The ease with which the 5-aminopentanoic acid was produced indicated that the compound probably contained at least one piperidone structure.[2]

Experimental Part

Isolation of Kafiroic Acid.—Two hundred grams of bran were digested six hours on the hot-plate in 2 liters of 2% sulfuric acid. At the end of the period of digestion the mixture was allowed to cool and then filtered through a linen bag using pressure. The residue was washed without removing it from the bag by allowing a fine stream of water to run through the material for one-half hour. The residue was then placed in 2 liters of 1% sodium hydroxide and digested at the temperature of the boiling solution for four hours. The mixture was allowed to cool overnight and then filtered essentially as before. The filtrate which contained the kafiroic acid as the sodium salt was acidified with concentrated hydrochloric acid, and the acid pre-

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(1) This material is a part of a thesis submitted to the Graduate School of the Kansas State College by Lloyd L. Woods in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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(2) Binz and Räth, *Ann.*, **489**, 107 (1931).

cipitated out as yellow curds which rapidly darkened in color. The acid was removed from the supernatant liquid by centrifuging and decanting. The freshly precipitated acid was not removed from the centrifuge bottles, but placed in the drying oven for twenty-four hours at 90°. The acid was then removed from the bottles and finely pulverized; yield 17.06 g. or 8.53% of the dry weight of the bran used.

Purification of Kafiroic Acid.—The powdered crude acid was extracted with five successive portions of 200 ml. each of petroleum ether. Each extraction was allowed to continue for twenty-four hours. The acid was then similarly extracted with five successive portions of diethyl ether. The acid now freed from fats and ether soluble impurities was washed with boiling water and filtered. The final drying was done in the vacuum desiccator over sulfuric acid. Seventy-five grams of crude kafiroic acid produced 66 g. of the pure material with a melting point of 244.8° dec. (cor.); neutral equivalent, 366 (av. of 5 detns.). Calcd. for $C_{18}H_{30}N_2O_6$: C, 58.97; H, 8.25; N, 7.65. Found: C, 58.37; H, 8.33; N, 7.57.

The color of the purified acid was rust-brown. The compound was found to be fairly soluble in ethyl alcohol and slightly soluble in methyl alcohol, and insoluble in ether, ligroin, acetone, benzene, or water.

5-Aminopentanoic Acid.—Twenty-five grams of purified finely powdered kafiroic acid was digested on the hot-plate with 80 ml. of 30% sulfuric acid for four to six hours. During the digestion the volume of the mixture was not allowed to decrease more than one-half before the volume was restored with water. This process was watched carefully as too great a decrease in volume caused losses due to carbonization. After the digestion the volume was made up to 200 ml. and filtered. The filtrate was made up to 500 ml. and the theoretical amount of barium hydroxide (octahydrate) was added to convert all the sulfate to the insoluble barium sulfate. The mixture was filtered and decolorized with charcoal. The filtrate was slowly evaporated on the steam cone, and then extracted with ethyl alcohol. The alcoholic solution was then evaporated on the steam cone. The last traces of alcohol were removed in the vacuum desiccator over sulfuric acid; yield, 6.31 g., m. p. 149–154° (dec.). The acid produced was 5-aminopentanoic acid. Calcd. for $C_5H_{11}NO_2$: C, 51.28; H, 9.40; N, 11.96. Found: C, 51.03; H, 9.00; N, 11.45. The identity of the acid was confirmed by the fact that when heated above its melting point the compound was converted into 2-piperidone, m. p. 200°.

Action of Alcoholic Potassium Hydroxide on Kafiroic Acid.—Twenty grams of finely powdered and purified kafiroic acid was mixed with 50 ml. of absolute ethyl alcohol and 10 g. of potassium hydroxide. This mixture was evaporated on the steam cone until a viscous brown mass was obtained. This process required about three to four hours. The mass was then placed in the drying oven at 110°, for twenty-four hours. After this treatment the residue was dissolved in 300 ml. of water and made acid with concentrated hydrochloric acid. The solution was then filtered, and clarified with norite. The clarified solution was now placed back into the drying oven for another twenty-four hours but at 90°. The resulting dried mass was extracted with alcohol and again decolorized with norite. The alcoholic solution was treated with 2 volumes of ether and chilled. The amino acid hydrogen chloride separated out. The alcohol–ether mixture was decanted. The residue was placed in a high vacuum in the desiccator over sulfuric acid; yield 5.6 g., m. p. 92°. Nitrogen (calcd.) for $C_5H_{11}NO_2 \cdot HCl$: N, 9.12. Found: N, 9.00 (Dumas).

When the acid hydrogen chloride was heated above its melting point, 2-piperidone hydrogen chloride was formed, m. p. 182°.

The preparation of the ureido derivative of the acid hydrogen chloride by the method of Schniepp and Marvel[3] gave a compound m. p. 177–178 (dec.) which agreed fairly well with their value of 178°.

Action of Concentrated Hydrochloric Acid on Kafiroic Acid.—Ten grams of finely powdered and purified kafiroic acid was intimately mixed with 100 ml. of concentrated hydrochloric acid in a 400-ml. beaker and covered with a watch glass. The mixture was heated on the hot-plate in the hood at the lowest heat level until the liquid was concentrated to a thick paste. Finally, 200 ml. of water were added and the material filtered. The residue was discarded and the filtrate decolorized with norite. The filtrate was then placed in the drying oven at 90°, for twenty-four hours. The final purification was effected in the same manner as the preceding experiment; yield 2.2 g.; m. p. 89–98°. Nitrogen calcd. from $C_5H_{11}NO_2 \cdot HCl$: N, 9.12. Found: N, 8.26.

The 5-aminopentanoic acid produced in this manner was always more highly colored than in the foregoing experiment and repeated attempts to remove the color were of no avail.

Summary

1. A new acid, which has been named kafiroic acid, was found in kafir bran.

2. Kafiroic acid, which is a brown nitrogenous acid, was found to be present to the extent of 8.53% of the dry weight of the bran used. The acid was easily attacked by alcoholic potassium hydroxide and strong acids which produced 5-aminopentanoic acid or one of its salts.

MANHATTAN, KANSAS RECEIVED SEPTEMBER 18, 1944

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[3] Schniepp and Marvel, THIS JOURNAL, 57, 1557 (1935).