Experimental

Acylation of Kojic Acid (I).—Twenty grams (0.142 mole) of kojic acid was mixed with 125 g. (1.22 moles) of acetic anhydride and 10 g. of zinc chloride. The mixture was heated over a water-bath under reflux and protected from moisture with a calcium chloride tube until the first vigorous reaction had subsided. The water-bath was then removed and replaced with an oil-bath. The heating was continued by gradually increasing the temperature to 145°, and then maintaining the temperature between 135–145° for one and one-half hours. Upon completion of the heating of the mixture, the excess acetic anhydride and acetic acid were removed under reduced pressure.

The residue was then treated with 200 ml. of boiling water and set aside to cool. After cooling, the crystals were filtered off. The filtrate was extracted with three successive 100-ml. portions of benzene. The combined benzene fractions were added to the crystals, which immediately dissolved. The mixture was washed once with cold water, dried with anhydrous magnesium sulfate, and decolorized with Norite.

The benzene was allowed to evaporate and 24.8 g. of a pale yellow compound were obtained. The substance was recrystallized by dissolving it in the smallest quantity of boiling water necessary to obtain complete solution (500–600 ml.). The white compound thus obtained was air dried. The analytical sample was dried in the vacuum desiccator over sulfuric acid for three weeks, m. p. 106°. The compound was quite soluble in ether, alcohol, benzene and ethyl acetate as well as hot water.

Anal. Calcd. for $C_{10}H_{13}O_7$: C, 48.98; H, 5.30; mol. wt., 245. Found: C, 49.06, 49.28, 49.10; H, 5.39, 5.72, 5.62; mol. wt. 248. (Each of the three carbon–hydrogen analyses was on a sample from a different run.[2])

Impure samples of the compound always gave a faint red color with dilute ferric chloride solutions; however, the pure samples failed to give the test. The compound did not react with dilute sodium bicarbonate solution. When 1.6137 g. of the ketone was heated ten hours in the electric drying oven at a temperature of 100–102° it lost 0.0376 g. (2.31%) of its weight, one molecule of water would require a loss of 7.34%. This loss of weight, perhaps, cannot be entirely attributed to the loss of moisture because the material developed a faint odor at this temperature.

The 2,4-dinitrophenylhydrazine derivative of compound (I) had a melting point of 114°.

Anal. Calcd. for $C_{10}H_{13}O_3$ $(C_6H_4N_4O_4)_4$: N, 23.21. Found: N, 23.18, 23.40.

Hydrolysis of Compound (I) to Form Compound (II).—A small portion (1 g.) of purified compound (I) dissolved in 50 ml. of hot water was refluxed for fifteen hours. The solution was cooled, decolorized with a little Norite, and filtered. After the water was evaporated and the solid dissolved in absolute ethanol, the solvent was removed under reduced pressure; and the compound was completely dried in the vacuum desiccator. The compound was a colorless glassy material which had a m. p. of 55–57°. Its semicarbazide had a m. p. of 247°. The compound was very soluble in water and in alcohol, but insoluble in acetone and ether. The material was not acidic and did not give any color with dilute ferric chloride solution.

Anal. Calcd. for $C_8H_{11}O_6$: C, 47.29; H, 5.41. Found: C, 47.50; H, 5.84.

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[2] Analyses by Dr. Carl Tiedcke.

NEW COMPOUNDS

Esters of Mucic Acid

The new compounds[1] listed in Table I were prepared by refluxing and stirring mechanically a mixture of 50 g. of mucic acid and 500 g. of the corresponding alcohol in the presence of 2 g. of *p*-toluenesulfonic acid. The esters all crystallized directly from the cooled reaction mixtures, after removal of unreacted mucic acid by filtration, and were recrystallized from 95% ethanol.

TABLE I

ESTERS OF MUCIC ACID

				Analyses					
				Carbon, %		Hydrogen, %		Sapon. equiv.	
Di-esters	M. p., °C.	Yield, %	Formula	Calcd.	Found	Calcd.	Found	Calcd.	Found
n-Propyl	149–150	48	$C_{12}H_{22}O_8$	48.98	48.9	7.54	7.64	147.1	146.8
n-Butyl	142.5–143.5	93	$C_{14}H_{26}O_8$	52.16	52.2	8.13	8.17	161.2	160
n-Amyl	147–147.5	74	$C_{16}H_{30}O_8$	54.84	54.9	8.63	8.68	175.2	174.2
n-Hexyl	143–144	55	$C_{18}H_{34}O_8$	57.12	57.0	9.06	8.94	189.2	189.1
Allyl	156.5–158	78	$C_{12}H_{18}O_8$	49.65	49.6	6.25	6.35	145.1	145.6

The *n*-propyl and *n*-butyl mucates were prepared by refluxing the reaction mixtures for thirty and ten hours, respectively. The *n*-amyl and *n*-hexyl esters were prepared in essentially the same manner except that 200 g. of xylene was added to the mixture, which was refluxed under a Bidwell–Sterling water trap for twenty and forty hours, respectively. In the preparation of allyl mucate, 250 g. of benzene was added, and refluxing and stirring continued for thirty hours, after which benzene, allyl alcohol and water were slowly distilled through a fractionating column until the final reaction solution was approximately 150 ml.

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[1] Dimethyl and diethyl mucates were prepared by Fischer and Speir (*Ber.*, **28**, 3252 (1895)), the former by reaction of mucic acid and methanol–hydrochloric acid in a sealed tube at 100° and the diethyl ester by refluxing mucic acid with ethanol and hydrochloric acid.

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N-(Acetylsalicyloyl)-piperidine

Fifty grams of acetylsalicylic acid and 250 ml. of thionyl chloride were refluxed for two hours. Excess thionyl chloride was removed on a steam-bath and with vacuum. The residue was taken up in dry benzene and a solution of 55 ml. (100% excess) of piperidine in dry benzene was added cautiously and with cooling. After filtering off the piperidine hydrochloride, the combined liquors and