second hot water extract has been rendered soluble in the first hot water extraction, but was held in the water phase of the mass of partially gelatinized starch. The volume of the washed paste was measured and found to be 2.9 l., containing 2.57 l. of water phase. Total grams soluble at 70° is $25.59 + 6.84 + 1.85 = 34.28$ g. per 550 g. corn starch at moisture 10.66%.

gamma-Amylose from Water Extracted Starch.—Five hundred grams of corn starch, which had been twice extracted for one hour with water at 70°, in accordance with the above procedures, was taken up in 2 l. of water to which was added sufficient sodium hydroxide in solution to give a normality of 0.667 *N* sodium hydroxide. The volume was about 6 liters. It was stirred at room temperature for about an hour, during which time the paste became more or less clear. The solution was then carefully neutralized to *p*H 6.0 with hydrochloric acid over a period of several hours, and 400 cc. of barley diastase (≈ to extract from 100 g. of ground barley) added. The volume was now 7.5 liters. The mixture was allowed to be converted at 55° for twenty-four hours at *p*H 6.0 under toluene.

The insolubles were separated by centrifuging, washed twice in the centrifuge with a volume of water equal to the centrifugate removed, and then dissolved in 0.667 *N* sodium hydroxide to a total volume of one liter. After thirty minutes at room temperature, with stirring, the solution was centrifuged and the centrifugate was neutralized to *p*H 4.8 with hydrochloric acid. The insolubles were then centrifuged, washed several times in the centrifuge with water, then with increasing concentrations of alcohol until finally 100% ethanol was used. It was washed twice with ethyl ether before drying in a vacuum desiccator over sulfuric acid; yield, 23.7 g. per 500 g. of dry starch.

Summary

Procedures have been given for the isolation of a crystalline amylose from corn starch.

Some of the properties of the amylose are given which relate it to gamma-amylose and which show that it is a constituent of other corn amylose fractions recently reported.

Its configuration is given as a linear arrangement of glucopyranose units.

Corn starch is now believed to be made up of a series of components, a small percentage of which are crystallizable, relatively long in chain length and linear in constitution, others complicated with some branching, and the remainder very highly branched and quite amorphous in nature.

While no product corresponding to gamma-amylose has been obtained from potato starch, the latter yields a crystalline fraction when its pastes are precipitated with alcohols. This fraction contains a crystalline amylose which can be isolated by procedures similar to those used with corn starch.

An additional difference found between corn and potato starch is that potato starch contains a larger ratio of the more highly branched, amorphous fraction.

ARGO, ILLINOIS RECEIVED FEBRUARY 9, 1942

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Rearrangement of Phenyl Allyl Ethers. VII. The Isomeric Ethyl *p*-(α- and γ-methylallyloxy)-benzoates[1]

BY WALTER M. LAUER AND PAUL A. SANDERS[2]

The behavior upon pyrolysis of the two pairs of isomeric ethers, (1) the ethyl *p*-(α- and γ-ethylallyloxy)-benzoates and (2) the ethyl *p*-(α- and γ-propylallyloxy)-benzoates, has been described in earlier papers[3] in the present series. Rearrangement products involving an attachment of the β-carbon atom of the allyl group to the aromatic nucleus were produced along with the normal rearrangement products in the case of the γ-substituted allyloxybenzoates, while only normal inversion of the allyl group occurred in the case of the α-substituted allyloxybenzoates. The present study deals with the simplest isomeric pair in this homologous series and the charts indicate the transformations which were carried out.

Pyrolysis of ethyl *p*-(γ-methylallyloxy)-benzoate, I, gave ethyl 3-(α-methylallyl)-4-hydroxybenzoate, III. It should be noted, however, that this rearrangement product might result from either a normal or abnormal rearrangement process (or both), since attachment of the γ-carbon atom or the β-carbon atom of the allyl group to the aromatic nucleus would result in the formation of the pyrolysis product which was actually obtained.

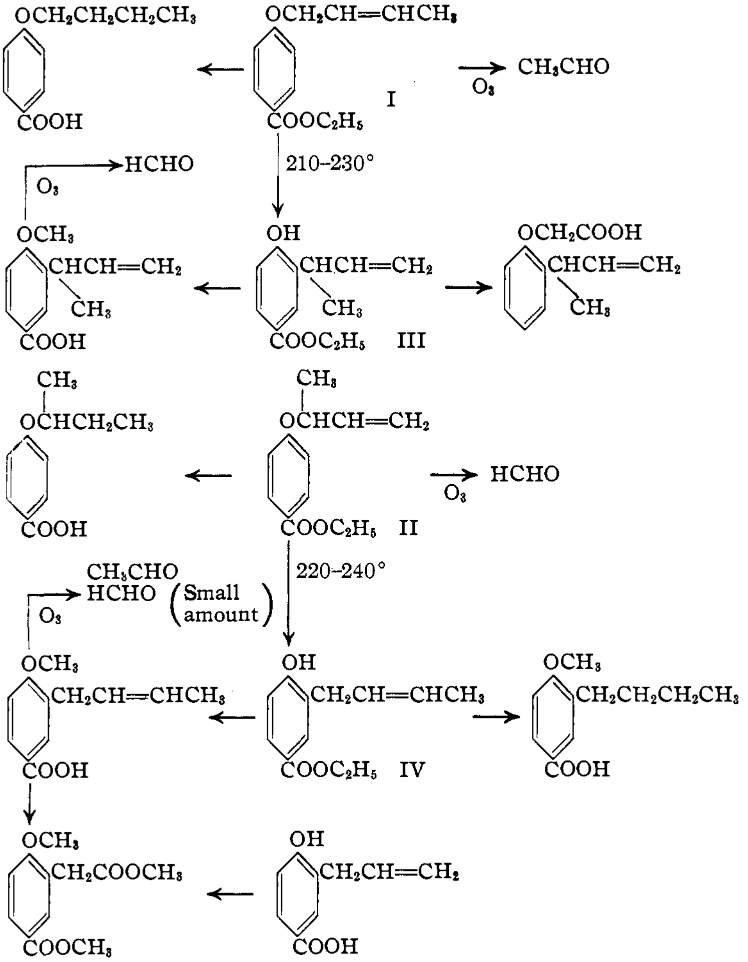
The isomeric ethyl *p*-(α-methylallyloxy)-benzoate, II, likewise, gave the pyrolysis product, IV, which would be expected on the basis of a normal

---

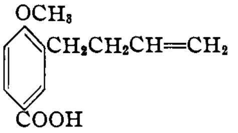
[1] Paper VI, THIS JOURNAL, 61, 3047 (1939).

[2] Abstract of Ph.D. Thesis submitted in June, 1940.

[3] Lauer, *et al.*, THIS JOURNAL, 61, 3047 and 3043 (1939).



rearrangement process. The formation of a small amount of formaldehyde upon ozonolysis of 3-(γ-methylallyl)-4-methoxybenzoic acid is somewhat disturbing. Clemo and MacDonald[4] have reported the identification of small amounts of formaldehyde produced by the ozonolysis of compounds which perhaps would not be expected to yield this aldehyde. On the other hand, there is the possibility that in spite of repeated crystallizations the 3-(γ-methylallyl)-4-methoxybenzoic acid might still have contained a small amount of an isomeric compound, such as



Experimental[5]

A. Ethyl *p*-(γ-Methylallyloxy)-benzoate.—1-Chloro-2-butene and 3-chloro-1-butene were prepared by the action of dry hydrogen chloride on methylvinylcarbinol. These halides were separated by careful fractionation. Ethyl *p*-hydroxybenzoate (105 g.) was added to a solution of sodium ethoxide (14.5 g. of sodium in 350 ml. of absolute alcohol). After complete solution of the phenol, 1-chloro-2-butene (50 g.) was added in 10-ml. portions and the reaction mixture was heated under reflux for eight hours. The major portion of the alcohol was next removed by distillation and sufficient water was added to dissolve the sodium chloride. The two layers were separated and the aqueous portion was extracted with ether. The ether extract, added to the original non-aqueous layer, was treated with aqueous sodium hydroxide (10%) to remove unchanged ethyl *p*-hydroxybenzoate. The dry ether solution yielded ethyl *p*-(γ-methylallyloxy)-benzoate (101 g.), which upon crystallization from dilute ethanol melted at 51–51.5°.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.90; H, 7.27. Found: C, 70.73; H, 7.38.

Hydrolysis of ethyl *p*-(γ-methylallyloxy)-benzoate was accomplished by means of alcoholic (methanol) potassium hydroxide. Crystallization from petroleum ether (b. p. 90–100°) or from dilute methanol yielded *p*-(γ-methylallyloxy)-benzoic acid of m. p. 176.5–178°.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.71; H, 6.29. Found: C, 68.82; H, 6.48.

Catalytic reduction of *p*-(γ-methylallyloxy)-benzoic acid yielded *p*-(*n*-butyloxy)-benzoic acid, which was identical with a sample prepared by the action of *n*-butyl bromide on ethyl *p*-hydroxybenzoate in the presence of alcoholic sodium ethoxide.

Ozonolysis of ethyl *p*-(γ-methylalloxy)-benzoate, dissolved in ethyl bromide, followed by decomposition of the ozonide yielded acetaldehyde, which was converted to acetaldimethone (m. p. and mixed m. p. 139–140°).

B. Pyrolysis of Ethyl *p*-(γ-Methylallyloxy)-benzoate.—The ester (4.12 g.) was heated by means of an electrically controlled metal bath under a pressure of fifty millimeters of mercury. Boiling began when the temperature (inside) reached 210° and was continued for one hour and ten minutes at which time the temperature had reached 227°. No increase in temperature was observed on further heating.

The pyrolysis product, which solidified upon cooling, was dissolved in petroleum ether and extracted with aqueous sodium hydroxide (5%). Acidification of the alkali-soluble material, followed by ether extraction, yielded ethyl 3-(α-methylallyl)-4-hydroxybenzoate (3.92 g.). After recrystallization the pyrolysis product melted at 76–78°, and did not give a precipitate with mercuric acetate.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.9; H, 7.3. Found: C, 71.0; H, 7.4.

Methylation and hydrolysis yielded 3-(α-methylallyl)-4-methoxybenzoic acid. To a solution of sodium methoxide

---

[4] Clemo and MacDonald, *J. Chem. Soc.*, 1294 (1935).

[5] All melting points are uncorrected.

(0.1 g. of sodium and 25 ml. of methanol), ethyl 3-(α-methylallyl)-4-hydroxybenzoate (0.75 g.) was added. After solution was complete dimethyl sulfate (2 ml.) was added and the solution was refluxed for forty-five minutes. Most of the methanol was then removed by distillation and aqueous sodium hydroxide (20 ml., 20%) was added and the reaction mixture was heated for about one-half hour. The aqueous solution, after extraction with ether to remove neutral impurities, was then acidified and the precipitated 3-(α-methylallyl)-4-methoxybenzoic acid was collected. Crystallization from dilute methanol yielded a product (0.36 g., m. p. 159–160°), which gave no precipitate with mercuric acetate.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.9; H, 6.75. Found: C, 69.9; H, 6.99.

Ozonolysis of 3-(α-methylallyl)-4-methoxybenzoic acid, dissolved in ethyl bromide, followed by decomposition of the ozonide yielded formaldehyde, which was identified as formaldimethone (m. p. 188–189°; yield *ca.* 80%).

3-(α-Methylallyl)-4-hydroxybenzoic acid was prepared by the hydrolysis of the corresponding ethyl ester using methyl alcoholic potassium hydroxide. This acid, crystallized from a mixture of benzene and petroleum ether, melted at 113–114° and gave no precipitate with mercuric acetate.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.8; H, 6.25. Found: C, 69.1; H, 6.45.

Decarboxylation of the above hydroxy acid was accomplished by heating in quinoline. The decarboxylated product was dissolved in petroleum ether and this solution was extracted successively with dilute sulfuric acid, sodium bicarbonate and sodium hydroxide. The sodium hydroxide extract was acidified and ether extraction yielded 2-(α-methylallyl)-phenol, which was converted to 2-(α-methylallyl)-phenoxyacetic acid by treatment of the substituted sodium phenoxide with ethyl bromoacetate, followed by hydrolysis. Crystallization from water yielded 2-(α-methylallyl)-phenoxyacetic acid, which melted at 125°. The previously reported[6] m. p. 120–120.5° is low. A mixed melting point with an authentic specimen showed no change.

C. **Ethyl *p*-(α-Methylallyloxy)-benzoate.**—*p*-(α-Methylalloxy)-benzoic acid was prepared by the action of 3-chloro-1-butene on the sodium derivative of ethyl *p*-hydroxybenzoate, followed by hydrolysis of the resulting esters and fractional crystallization of the two isomeric acids, *p*-(α-methylallyloxy)-benzoic acid and *p*-(γ-methylallyloxy)-benzoic acid.

Ethyl *p*-hydroxybenzoate (154 g.), added to a solution of sodium ethoxide (20 g. sodium and 500 ml. ethanol), was treated with 3-chloro-1-butene (72 g.). The portion-wise addition of the halide was followed by a ten-hour heating period. The major portion of the alcohol was then removed by distillation, sufficient water was added to dissolve the precipitated sodium chloride and the solution was extracted with ether. The ether extract, after having been shaken with aqueous sodium hydroxide (10%), yielded a mixture (110 g.) of ethyl *p*-(α-methylallyloxy)-benzoate and ethyl *p*-(γ-methylallyloxy)-benzoate. Distillation from a Hickman still at low pressures brought about a partial separation; ethyl *p*-(α-methylallyloxy)-benzoate was the main constituent of the lower boiling fractions. Hydrolysis of the lower boiling fractions with alcoholic (methyl) potassium hydroxide, acidification and repeated fractional crystallizations from petroleum ether-benzene mixtures and dilute methanol yielded *p*-(α-methylallyloxy)-benzoic acid (m. p. 155–156°; 40 g.).

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.7; H, 6.29. Found: C, 68.9; H, 6.67.

This acid was esterified by treating the silver salt with ethyl iodide. *p*-(α-Methylallyloxy)-benzoic acid (39 g.), suspended in distilled water (200 ml.), was treated with small portions of ammonium hydroxide using care to prevent an excess. The solution of the ammonium salt was then treated with an aqueous silver nitrate solution containing forty-five grams of the salt. The silver salt of the organic acid was collected, washed with water, acetone and ether and finally dried at 60°. The silver *p*-(α-methylallyloxy)-benzoate (56 g.), placed in a flask containing dry ether (1000 ml.) and ethyl iodide (60 g.) was heated under reflux for five hours and then allowed to stand overnight. The precipitated silver iodide was removed and the ether solution was shaken with aqueous sodium hydroxide. The dry ether solution yielded ethyl *p*-(α-methylallyloxy)-benzoate (35 g., $n^{20}\text{D}$ 1.5200).

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.9; H, 7.32. Found: C, 70.6; H, 7.54.

Ozonolysis of an ethyl bromide solution, followed by decomposition of the ozonide yielded formaldehyde, which was identified as formaldimethone (m. p. and mixed m. p. 188–189°).

Catalytic reduction of *p*-(α-methylallyloxy)-benzoic acid using a palladium (on calcium carbonate) catalyst yielded *p*-(*s*-butyloxy)-benzoic acid (m. p. 118–120°). *p*-(*s*-Butyloxy)-benzoic acid was synthesized by treatment of ethyl *p*-hydroxybenzoate with *s*-butyl bromide in the presence of alcoholic sodium ethoxide. A mixed melting point of the synthetic *p*-(*s*-butyloxy)-benzoic acid (m. p. 119–120°) with the sample prepared by catalytic reduction was 118–120°.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.0; H, 7.27. Found: C, 68.2; H, 7.22.

D. **Pyrolysis of Ethyl *p*-(α-Methylallyloxy)-benzoate.**—Pyrolysis was carried out in a manner similar to that described above for ethyl *p*-(γ-methylallyloxy)-benzoate. In this case the initial and final temperatures were 222 and 240°. The time was one hour and thirty minutes, and the ester (30 g.) yielded a very small amount of butadiene (identified as 1,2,3,4-tetrabromobutane, m. p. and mixed m. p. 115–117°) and crude ethyl 3-(γ-methylallyl)-4-hydroxybenzoate (27 g., m. p. 69–75°).

The crude rearrangement product (5.5 g.) was hydrolyzed with aqueous sodium hydroxide. the solution was acidified and then extracted with ether. The ether solution was next extracted with aqueous sodium bicarbonate and acidification of the aqueous portion yielded 3-(γ-methylallyl)-4-hydroxybenzoic acid (4.0 g.; m. p. 108–113°; after repeated crystallization from petroleum ether the m. p. was 115–116°; mixed m. p. with the isomeric 3-(α-methylallyl-4-hydroxybenzoic acid (m. p. 113–114°) was 97–104°).

---

(6) Lauer and Ungnade, THIS JOURNAL, **58**, 1393 (1936).

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.7; H, 6.29. Found: C, 68.4; H, 5.93.

Methylation and Hydrolysis of the Rearrangement Product.—The crude rearrangement product (15 g.) was dissolved in methyl alcohol (75 ml.) containing sodium methoxide (1.7 g. of sodium). Dimethyl sulfate (15 g.) was then added and the solution was heated under reflux for two hours. Most of the alcohol was removed by distillation and the residue was dissolved in ether. The ether solution was then shaken with aqueous sodium hydroxide. The ether was removed by distillation and the ethyl 3-(γ-methylallyl)-4-methoxybenzoate was heated under reflux with a solution (25%) of potassium hydroxide in methanol. After the major portion of the alcohol had been removed by distillation, water was added and the solution was extracted with ether. The impure acid (10.2 g., m. p. 140–145°) was precipitated from the aqueous solution by the addition of sulfuric acid. Two recrystallizations from aqueous methanol raised the melting point of the material to 147–149°, and after fourteen recrystallizations using aqueous methanol and benzene–petroleum ether mixtures alternatively, the melting point was 150–151.5°. (The last three recrystallizations had no effect on the m. p. Mixed with the isomeric 3-(α-methylallyl)-4-methoxybenzoic acid (m. p. 159–160°), the m. p. was 130–152°.) An effort was made to isolate a second pure substance from the lower melting fractions, but all attempts were unsuccessful. A sample of 3-(γ-methylallyl)-4-methoxybenzoic acid did not yield a precipitate with mercuric acetate.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.9; H, 6.79. Found: C, 70.1; H, 6.84.

Ozonolysis of 3-(γ-methylallyl)-4-methoxybenzoic acid (m. p. 150–151.5°) produced acetaldehyde together with a small amount of formaldehyde. It is difficult to account for the occurrence of the formaldehyde since it is thought that the compound subjected to ozonolysis was a pure compound. The ozonolysis was conducted in an ethyl bromide solution at the temperature of an ice-salt bath. The mixture of dimethone derivatives which was isolated melted at 130–140°. Crystallization from methanol yielded a small amount of formaldimethone (m. p. 180–184°) and the filtrate upon dilution with water to produce turbidity yielded acetaldimethone (m. p. 133–136°). Purification of the acetaldimethone by recrystallization raised the melting point to 135–137°.

Catalytic reduction of 3-(γ-methylallyl)-4-methoxybenzoic acid produced 3-n-butyl-4-methoxybenzoic acid (m. p. 131.5–132.5°) in a practically quantitative amount.

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.3; H, 7.69. Found: C, 69.2; H, 7.71.

Methyl 2-methoxy-5-carbomethoxyphenylacetate was prepared in two ways: (1) Methylation of the oxidation product obtained from 3-(γ-methylallyl)-4-methoxybenzoic acid, and (2) methylation of the oxidation product obtained from 3-allyl-4-methoxybenzoic acid. The substituted benzoic acid dissolved in the minimum amount of acetone, was added with cooling to an aqueous potassium permanganate solution and the reaction mixture was then allowed to stand for several hours at room temperature. After the precipitated manganese dioxide was removed, the filtrate was treated with charcoal and again filtered. Distillation removed the acetone and a considerable portion of the water, and the resultant solution was then acidified and allowed to stand overnight. Crude 2-methoxy-5-carboxyphenylacetic acid separated in the case of the oxidation of 3-(γ-methylallyl)-4-methoxybenzoic acid and of 3-allyl-4-methoxybenzoic acid. The crude oxidation products were not purified or analyzed, but were converted to their dimethyl esters by treating the silver salts with methyl iodide in ether. After the removal of precipitated silver iodide, the ether solutions were extracted with aqueous sodium hydroxide (5%), and the dimethyl esters were then isolated from the ether solution. Crystallization from aqueous methanol yielded methyl 2-methoxy-5-carbomethoxyphenylacetate (m. p. 78–79° in case 1; m. p. 79–80° in case 2; mixed m. p. 78–79°).

Anal. Calcd. for $C_{12}H_{14}O_5$: C, 60.5; H, 5.88. Found: C, 60.6; H, 6.17.

Summary

The isomeric ethyl p-(α- and γ-methylallyloxy)-benzoates have been prepared and their rearrangement has been studied. Ethyl p-(α-methylallyloxy)-benzoate, on pyrolysis, is converted to ethyl 3-(γ-methylallyl)-4-hydroxybenzoate, the product expected on the basis of the general pattern suggested by Claisen. Likewise, ethyl p-(γ-methylallyloxy)-benzoate rearranged to produce ethyl 3-(α-methylallyl)-4-hydroxybenzoate. Earlier work has shown that in the case of γ-alkylallyl phenyl ethers, the normal rearrangement products are accompanied by pyrolysis products, which involve an attachment of the β-carbon atom of the allyl group to the aromatic nucleus, the so-called abnormal rearrangement products. Both of these types of rearrangement lead to ethyl 3-(α-methylallyl)-4-hydroxybenzoate, the product obtained.

MINNEAPOLIS, MINN. RECEIVED OCTOBER 8, 1942