5. Hydroxy-benzoylacrylic acid can be prepared from maleic anhydride, phenol and aluminum chloride, in benzene solution.

6. Pyrogallol condenses with maleic anhydride, in the presence of fused zinc chloride, to the *sym*-di(trihydroxybenzoyl ethylene), which is a poor and weak dye.

7. α-Methyl-β-benzoylacrylic acid can be prepared from citraconic anhydride, benzene and aluminum chloride.

8. Naphthalene, maleic anhydride and aluminum chloride yield a mixture of naphthoylacrylic acids consisting of approximately 40% β-(α-naphthoyl) and 60% of β-(β-naphthoyl) derivative.

9. The following new compounds have been synthesized and studied: *iso*-benzoylacrylic acid dibromide, monobromo-β-benzoylacrylic acid, monosulfo-β-benzoylpropionic acid, β-(*m*-nitrobenzoyl)acrylic acid, β-(hydroxybenzoyl)acrylic acid, α-methyl-β-benzoylacrylic acid and β-(α-naphthoyl)acrylic acid.

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[CONTRIBUTION FROM THE HAVEMEYER LABORATORY OF COLUMBIA UNIVERSITY]

# ESTERS OF FURFURYL ALCOHOL

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The esters of furfuryl alcohol have been little investigated. Wissell and Tollens[1] obtained the acetate and benzoate, but so far no others have been prepared. As remarked by these authors, the ordinary methods of esterification cannot be employed with furfuryl alcohol, as mineral acids quickly decompose it. Resort must be had to the action of acid anhydrides or to reactions like the Schotten-Baumann.

The first of these methods was employed in this work. To one mole of furfuryl alcohol, a little over one mole of anhydride was added and the the mixture heated in an oil-bath to 130–150° for two hours. After cooling, the reaction mixture was neutralized with sodium carbonate solution, washed with cold water to remove as much as possible of the unconverted alcohol, dried with calcium chloride and fractionated. It was found that when the fractionation was conducted under reduced pressure, the esters, although boiling constantly, quickly became colored on standing. This, it is thought, was due to traces of furfuryl alcohol which could not readily be removed by fractionation under reduced pressure, owing to the fact that the boiling points of the alcohol and the esters were too close together under reduced pressure. When, however, the separation was conducted at ordinary atmospheric pressure, the boiling points of the two were far enough apart to insure a satisfactory separation. Some decomposition always

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[1] Wissell and Tollens, *Ann.*, **272**, 303 (1893).

ensued on distilling under atmospheric pressure owing to the high boiling points of the esters. To be obtained pure, these esters should be redistilled under reduced pressure. Thus prepared they will remain colorless for a considerable time and color only very slightly on long exposure to the light.

The propionate, butyrate and valerate esters of furfuryl alcohol were prepared by the method described above. Their boiling points form a series showing a regular increase of sixteen degrees for a homolog, except between the acetate and propionate, where the increase seems to be about 19°. The acetate was prepared by Wissell and Tollens and as it boiled fairly closely to furfuryl alcohol, the separation was probably not so complete as in the case of the others which boil from 28° to 60° above furfuryl alcohol. The specific gravities show the usual decrease as the molecular weights of the acids in this series increase.

These esters are not readily hydrolyzed by water and will remain in contact with it for weeks without apparent decomposition. They are, however, readily hydrolyzed by potassium and sodium hydroxide, producing the corresponding acids and furfuryl alcohol. The amounts of these bases used should be as nearly as possible those calculated, in order to avoid the action of these hydroxides on furfuryl alcohol. The hydrolysis of the propionate was the only one undertaken with the view of recovering both the acid and the alcohol, yielding furfuryl alcohol, b. p. 168–170°, and propionic acid, b. p. 140°. It was not thought necessary, owing to the similarity of preparation of the other two esters, to recover the acid and alcohol obtained by hydrolysis.

The esters are all water-white, oily liquids with pleasant odors. The results are given below in tabular form.

TABLE I

PROPERTIES AND ANALYSES

| Ester | Formula | Boiling Point (corr.) 764 mm. °C. | Boiling Point (corr.) 1 mm. °C. | Densities 20° | Carbon Calcd. | Carbon Found | Hydrogen Calcd. | Hydrogen Found |
|---|---|---|---|---|---|---|---|---|
| Acetate[1] | $C_7H_6O_3$ | 175–177 | ... | 1.1175 | ... | ... | ... | .. |
| Propionate | $C_8H_{10}O_3$ | 195–196[a] | 59–60 | 1.1085 | 62.40 | 62.35 | 6.49 | 6.52 |
| Butyrate | $C_9H_{12}O_3$ | 212–213 | 69–70 | 1.0530 | 64.29 | 64.11 | 7.14 | 7.27 |
| Valerate | $C_{10}H_{14}O_3$ | 228–229 | 82–83 | 1.0284 | 65.93 | 65.78 | 7.69 | 7.51 |

[a] Barometer, 762 mm.

## Summary

The propionate, butyrate and valerate of furfuryl alcohol have been prepared and their properties reported.

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