cose is partly changed into fructose, recently made by H. Koenigsfeld,[1] is apparently without foundation.

5. Decomposition of Glucose by Acids at Ordinary Temperatures.

The results of the preceding section show that glucose decomposes far less rapidly than fructose, and since it was found that even the rate of fructose decomposition is not rapid enough to vitiate the final polarimetric reading in ordinary sugar hydrolysis, it was to be expected that danger from the decomposition of glucose was to be feared even less. Nevertheless, a few experiments were instituted to test the point directly.

A solution containing 0.179 mol HCl per liter and no less than 52% of glucose showed no change in rotation in 12 days; in 25 days the rotation was found to have changed only slightly over 0.3%. Even a solution nearly 0.9-normal with respect to hydrochloric acid and containing 27% of glucose was found to have changed its rotation only 0.25% in 25 days. A solution similarly strong in hydrochloric acid and containing no less than 43% of glucose showed no change of rotation in 7 days, and only 0.2% change in 12 days. Similarly, a solution containing 28% of glucose and two mols of formic acid per liter showed a change in rotation of only little over 0.2% in 76 days. Finally, a 24% solution of invert sugar containing two mols of formic acid per liter did not show the slightest change of rotation in 76 days. It is thus plain that under all ordinary circumstances the observed "final" rotation of an inverting sugar solution is entirely reliable and needs no correction.

In conclusion, I wish to thank Professor M. A. Rosanoff, of Clark University, for invaluable help in preparing this paper. It is further a pleasure to express my appreciation to Dr. W. G. Lyle and Mr. P. A. Kober of this laboratory for their kindly interest in the work.

WORCESTER, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF COLORADO.]

THE ACTION OF ACETIC ANHYDRIDE ON SOME BENZYLIDENE ANTHRANILIC ACIDS. III.

BY JOHN B. EKELEY AND L. CECIL SLATER.

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Ekeley and Dean[2] and Ekeley and Clinton[3] have shown that acetic anhydride reacts with benzylidene anthranilic acids with the formation of acetylketodihydrobenzmetoxazines, according to the following reactions:

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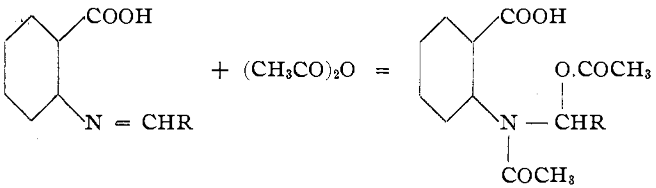
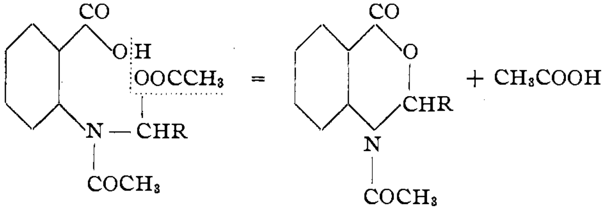
[1] *Biochem. Z.*, **38**, 310 (1912).

[2] THIS JOURNAL, **34**, 161.

[3] *Ibid.*, **35**, 282.





This paper will describe the benzylidene anthranilic acids obtained from *o*-chlorobenzaldehyde, *m*-chlorobenzaldehyde, *p*-chlorobenzaldehyde, *m*-toluylaldehyde, *p*-toluylaldehyde, and *m*-oxybenzaldehyde, and the benzmetoxazines obtained from them by means of acetic anhydride.

o-Chlorobenzylideneanthranilic Acid.—This benzylidene product separates out in solid form, when molecular proportions of anthranilic acid and *o*-chlorobenzaldehyde are brought together in cold alcohol solution. Recrystallized from alcohol, it yields colorless crystals. M. p. 130°.

Calc. for $C_{14}H_{10}O_2NCl$: N, 5.39; found: N, 5.0.

o-Chlorophenylacetketodihydrobenzmetoxazine.— *o*-Chlorobenzylideneanthranilic acid was heated with a slight excess of acetic anhydride on the water bath for several hours. On cooling the solution, the oxazine crystallized out in colorless crystals, which, after being pressed out on a porous plate, were recrystallized from benzene. M. p. 154°.

Calc. for $C_{16}H_{12}O_3NCl$: N, 4.64; found: N, 4.62.

m-Chlorobenzylideneanthranilic Acid.—The aldehyde and acid react in cold alcohol solution, so that in a few minutes the solid acid may be filtered off, pressed out on a porous plate, and recrystallized from toluene. Colorless crystals. M. p. 174°.

Calc. for $C_{14}H_{10}O_2NCl$: N, 5.39; found: N, 5.39.

m-Chlorophenylacetketodihydrobenzmetoxazine.—The above benzylidene anthranilic acid was heated several hours on the water bath with an excess of acetic anhydride. The excess anhydride was driven off by heating the reaction mixture with methyl alcohol, after which, on cooling the product, the oxazine crystallized out. Recrystallized from methyl alcohol, it yielded colorless crystals. M. p. 171°.

Calc. for $C_{16}H_{12}O_3NCl$: N, 4.64; found: N, 4.4.

p-Chlorobenzylideneanthranilic Acid.—Molecular proportions of *p*-chlorobenzaldehyde and anthranilic acid were allowed to react by pouring the molten aldehyde into a concentrated alcohol solution of the acid. Recrystallized from alcohol, the reaction product gave colorless crystals. M. p. 136°.

Calc. for $C_{14}H_{10}O_2NCl$: N, 5.39; found: N, 5.4.

p-Chlorophenylacetketodihydrobenzmetoxazine.—This was obtained in the same manner as the corresponding *o-* and *m*-compounds. The crude product was recrystallized from benzene. Colorless crystals. M. p. 187°.

Calc. for $C_{16}H_{12}O_3NCl$: N, 4.64; found: N, 4.8.

m-Toluylideneanthranilic Acid.—*m*-Toluylaldehyde reacts with anthranilic acid in concentrated alcohol solution in the cold. On allowing a small quantity of the solution to evaporate on a watch glass, crystals are obtained which, on being added to the original solution, caused it to solidify. The crude acid after being pressed out on a porous plate and recrystallized from alcohol yielded colorless crystals. M. p. 149°.

Calc. for $C_{15}H_{13}O_2N$: N, 5.57; found: N, 5.5.

m-Methylphenylacetketodihydrobenzmetoxazine.— *m*-Toluyleneanthranilic acid was heated with an excess of acetic anhydride at a temperature just below the boiling point of the anhydride for four hours. At the end of that time the vapor of the anhydride was drawn off by suction until the solution was concentrated enough to yield crystals, when a small amount was removed and treated with a drop of methyl alcohol on a watch glass. On seeding the original solution with these, the oxazine crystallized out. It was recrystallized from benzene, yielding colorless crystals. M. p. 145°.

Calc. for $C_{17}H_{15}O_3N$: N, 4.98; found: N, 4.62.

p-Toluylideneanthranilic Acid.—*p*-Toluylaldehyde reacts with anthranilic acid in cold alcohol solution. A small amount of the solution was placed on a watch glass and allowed to evaporate. The original solution was seeded with the crystals thus obtained, whereupon the *p*-toluylideneanthranilic acid crystallized out. Yellowish crystals from alcohol. M. p. 131°.

Calc. for $C_{15}H_{13}O_2N$: N, 5.57; found: N, 5.5.

p-Methylphenylacetketodihydrobenzmetoxazine.—This compound was prepared in a manner analogous to that used in the case of the corresponding *m*-compound. The crude product, recrystallized from methyl alcohol, gave colorless crystals. M. p. 121°.

Calc. for $C_{17}H_{15}O_3N$: N, 4.98; found: N, 4.76.

m-Oxybenzylideneanthranilic Acid.—This compound was prepared from *m*-oxybenzaldehyde and anthranilic acid in a manner analogous to the methods used in the preceding cases. Yellow crystals from alcohol. M. p. 175°, with decomposition.

Calc. for $C_{14}H_{11}O_3N$: N, 5.80; found: N, 5.6.

Acetyl-m-oxyphenylacetketodihydrobenzmetoxazine.—This was prepared as in the other cases by treating the above benzylideneanthranilic acid on the water bath with an excess of acetic anhydride. In this case, as in the case of the corresponding *o*- and *p*- compounds described by Ekeley and Dean,[1] the hydrogen of the phenol group has been replaced by acetyl. The crude compound was recrystallized from benzene, yielding colorless crystals. M. p. 124°.

Calc. for $C_{18}H_{15}O_5N$: N, 4.31; found: N, 3.99.

Repeated attempts to obtain oxazines using anisylaldehyde, piperonal, and furfuryl aldehyde have failed. It is not clear wherein the difficulty lies.

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NOTE.

A Case of Potassium Cyanide Poisoning.—Certain data recently obtained in a toxicological investigation seem worth putting on record. A man died from drinking whisky containing an unknown amount of potassium cyanide. The autopsy was performed about six hours after death, and the stomach and intestine placed in glass jars, where they remained unopened until four days after death, when the analysis was commenced.

Potassium cyanide was determined by the well-known method of acidifying with tartaric acid and distilling with steam, adding borax to the distillate and distilling again, and then treating this distillate with silver nitrate to precipitate silver cyanide, which was filtered out, dried, and weighed.

The stomach measured nine and one-half inches along the lesser curvature, and twenty-five and one-half inches along the greater. There were dark areas along the greater curvature, and the wall in places was abnormally red. The rugae were well obliterated. The contents were acid to litmus, and consisted of an undigested meal. The weight of the stomach wall was 288 grams, and of the stomach contents 1014 grams.

A portion of the stomach contents weighing 349 grams, in which hydrocyanic acid was determined five days after death, showed that for the whole stomach contents 0.953 gram potassium cyanide would have been necessary to produce the amount of hydrocyanic acid present. A portion of the intestine analyzed at the same time gave no cyanide. To test the rate of decay of the hydrocyanic acid in the stomach contents, the unused material was placed in a glass stoppered bottle and allowed to stand for several weeks. A portion weighing 143 grams, analyzed 23 days after death, gave 0.039 gram potassium cyanide for the whole stomach contents. A third portion, weighing 310 grams, analyzed 76 days after

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[1] THIS JOURNAL, 34, 164.