

TABLE IV

Chloride	Ml.	Ligroin, ml.	Carbon dioxide, lb.	Sodium, g.	Init. temp., °C.	Yields of organic acids, percentage based on			
						Sodium mono-	di-	Chloride mono-	di-
<i>n</i> -Amyl chloride	50	100	120	3.5	30	22	39	23	40
<i>n</i> -Butyl chloride	100	150	250	23	90	9	14	10	15
<i>n</i> -Propyl chloride	90	150	260	23	176				Tarry products
Ethyl chloride	30 <sup>a</sup>	100	220	8.3	110	1	4	1.3	6.5
Methyl chloride	50 <sup>a</sup>	100	200	13.3	110				Traces
2-Chloropentane	120	100	240	23	150	34	13	39	19
2-Chloro-3-methylbutane	120	100	220	2.3	30	0.5	6	1	10
<i>n</i> -Hexyl chloride	100	100	340	10.8	76	18	9	30	15
Cetyl chloride	60 <sup>a</sup>	50	200	6.3	50	4	14	9	30
Benzyl chloride <sup>b</sup>	50	100	120	10	200	1	1		

<sup>a</sup> Quantity in grams. <sup>b</sup> The autoclave should be copper plated when benzyl chloride is used. When the experiment was carried out in the presence of iron a side reaction took place which caused the pressure to rise above the reading of the gage.

chlorides in particular may be lower than the actual amount present.

### Conclusions

Further studies have been made of the preparation of organic acids by interaction of organic chlorides, sodium and carbon dioxide.

In the case of primary and secondary alkyl chlorides in ligroin as a solvent there was obtained the expected monocarboxylic acids, together with larger amounts of substituted malonic

acids. Oxalic and carbonic acids were also present. When the reaction was carried out in benzene as a solvent, iso- and terephthalic acids could be isolated from among the products.

A study of conditions with one chloride showed that a yield of 51% of butylmalonic acid, based on the amyl chloride consumed, could be had. This yield is high enough for the method to be considered as a one-step synthesis in this series.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

## The Hydrolysis of Beta-Hydroxyanthraquinone-beta-*d*-glucoside<sup>1</sup>

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In connection with our study of the ease of hydrolysis of glycosides derived from hydroxyanthraquinones, we have prepared  $\beta$ -hydroxyanthraquinone- $\beta$ -*d*-glucoside and studied its hydrolysis under conditions similar to those used in a similar study of  $\alpha$ -hydroxyanthraquinone- $\beta$ -*d*-glucoside and  $\beta$ -*d*-arabinoside.<sup>2</sup> The data obtained may be of diagnostic value in determining the structure of naturally occurring glycosides of hydroxyanthraquinones.

$\beta$ -Hydroxyanthraquinonetetraacetyl- $\beta$ -*d*-glucoside was prepared by the method of Müller.<sup>3</sup> This was hydrolyzed to the glucoside by the method of Robertson.<sup>4</sup> Hydrolyses were carried out with 0.050 *N* hydrochloric acid, 0.050 *N* po-

tassium hydroxide and approximately 10% borax solutions as was described for the experiments with  $\alpha$ -hydroxyanthraquinone derivatives.<sup>2</sup> Since in all cases, the glycosides were insoluble in the reaction medium, it is impossible to compare reaction velocity constants. However, since the samples of all compounds were ground to the same degree of fineness and were treated under identical conditions, the time required for hydrolysis gives some indication of the relative stability.

The results of this investigation are shown graphically in Fig. 1. In addition to the experiments on hydrolysis with acid, alkali and borax, a study was made of the rate of hydrolysis with emulsion. These measurements were made at 37° and so are not comparable with the others, which were made at 100°. They do, however, justify the designation of the glucoside as a  $\beta$

(1) Anthracene Series XI; No. X, THIS JOURNAL, 58, 597 (1936).

(2) Gardner, McDonnell and Wiegand, *ibid.*, 57, 1074 (1935).

(3) Müller, *Ber.*, 62, 2800 (1929).

(4) Robertson, *J. Chem. Soc.*, 1137 (1930).

type. For comparison, Table I shows the time required for 25 and 50% hydrolysis of  $\beta$ -hydroxyanthraquinone- $\beta$ -*d*-glucoside with potassium hydroxide, hydrochloric acid and borax under the conditions used, together with the same data for  $\alpha$ -hydroxyanthraquinone- $\beta$ -*d*-glucoside and  $\beta$ -*d*-arabinoside. It will be noted that both of the  $\alpha$ -hydroxyanthraquinone derivatives are much more easily hydrolyzed than is the  $\beta$ -hydroxyanthraquinone glucoside. This is as would be expected since ethers and esters of  $\alpha$ -hydroxyanthraquinone are more easily hydrolyzed than are the corresponding  $\beta$ -hydroxyanthraquinone derivatives.

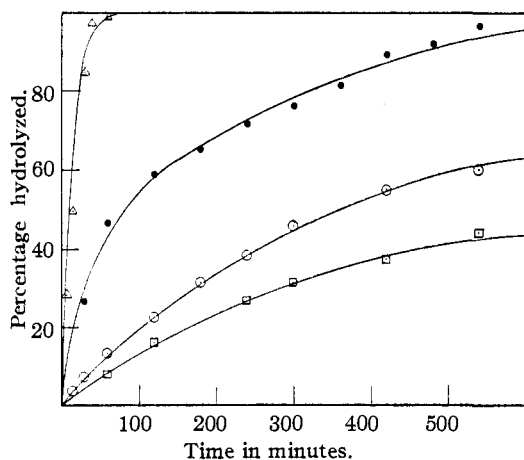


Fig. 1.—Hydrolysis of  $\beta$ -hydroxyanthraquinone- $\beta$ -*d*-glucoside:  $\Delta$ , KOH;  $\circ$ , HCl;  $\square$ , borax;  $\bullet$ , emulsin.

The difference in the rate of hydrolysis of  $\alpha$ -hydroxyanthraquinone- $\beta$ -*d*-glucoside and  $\beta$ -*d*-arabinoside indicates that the rate is also a function of the nature of the sugar residue. There is not enough evidence available to justify any conclusions on this point at present.

### Experimental

**$\beta$ -Hydroxyanthraquinonetetraacetyl- $\beta$ -*d*-glucoside.**  
—This was prepared by the method of Müller;<sup>3</sup> m. p. 170.0–170.3° (corr.). Robertson<sup>4</sup> gives m. p. 168°. Müller reports two forms, one pale yellow, m. p. 164°, one white, m. p. 132°. In agreement with Robertson, we were unable to detect the white form.

*Anal.* Calcd. for  $C_{23}H_{26}O_{12}$ : C, 60.62; H, 4.73. Found: C, 60.35; H, 4.67.

TABLE I

Reagent	$\beta$ -Hydroxyanthraquinone- $\beta$ - <i>d</i> -glucoside		$\alpha$ -Hydroxyanthraquinone- $\beta$ - <i>d</i> -glucoside		$\beta$ - <i>d</i> -arabinoside	
	Hydrolyzed, %	Time (min)	Hydrolyzed, %	Time (min)	Hydrolyzed, %	Time (min)
KOH	3	15	5	12	2	8
HCl	135	360	15	36	3	10
Borax	220	>600	110	>200	19	80

**$\beta$ -Hydroxyanthraquinone- $\beta$ -*d*-glucoside.**—This was prepared by the method of Robertson;<sup>4</sup> m. p. (anhydrous) 244.4–244.7° (corr.). Robertson gives m. p. 248–249°. For the hydrolysis experiments, the hydrated material (with one molecule of water of crystallization) was ground to pass a 100-mesh sieve.

*Anal.* Calcd. for  $C_{20}H_{18}O_8 \cdot H_2O$ : H<sub>2</sub>O, 5.43. Found: H<sub>2</sub>O, 4.50. Calcd. for  $C_{20}H_{18}O_8$ : C, 62.16; H, 4.70. Found: C, 61.95, 61.89; H, 4.71, 4.86.

**Hydrolyses with Potassium Hydroxide, Hydrochloric Acid and Borax.**—These were carried out as described for the similar experiments with the  $\alpha$ -hydroxyanthraquinone glycosides.<sup>2</sup>

**Emulsin Hydrolysis.**—Emulsin was prepared by the method described by Morrow.<sup>5</sup> The solution was made by allowing 0.6 g. of emulsin to stand in 150 cc. of distilled water for twenty-four hours, filtering and placing in a water-bath at 37° until the solution had reached that temperature. An accurately weighed 0.4000-g. sample of the glucoside was placed in a flask provided with a mechanical stirrer in a thermostat set at 37°. One hundred cc. of the emulsin solution was added. At frequent intervals, 1-cc. aliquots were withdrawn and the liberated glucose was determined by the method of Shaffer and Somogyi.<sup>6</sup>

### Summary

1. The rate of hydrolysis under empirically determined conditions of  $\beta$ -hydroxyanthraquinone- $\beta$ -*d*-glucoside with potassium hydroxide, hydrochloric acid, borax and emulsin has been determined.

2. Comparison has been made with similar measurements on  $\alpha$ -hydroxyanthraquinone- $\beta$ -*d*-glucoside and  $\beta$ -*d*-arabinoside, indicating that these reaction rates may be of value in indicating the structure of hydroxyanthraquinone glycosides.

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(5) Morrow, "Biochemical Laboratory Methods," John Wiley and Sons, Inc., New York, 1927, p. 289.

(6) Shaffer and Somogyi, *J. Biol. Chem.*, **100**, 695 (1933).