

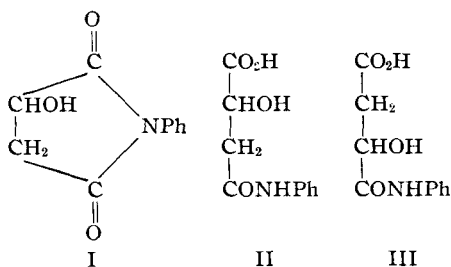
Characterization of Racemic α -Hydroxy- and β -Hydroxysuccinanic Acids

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Alkaline hydrolysis of racemic malic acid phenylimide (malanil) yielded two products corresponding to the two possible directions of cleavage. These were shown to be racemic α -hydroxy- and β -hydroxysuccinanic acid present in the ratio 5:1, the proportion being essentially as expected on the basis of the relative electrophilicities of the respective carbonyl centers.

ALKALINE HYDROLYSIS of DL-malic acid phenylimide (malanil) (I) yielded two isomeric monoanilides of malic acid which had different melting points, ultraviolet spectra, and pKa values. Characterization of these anilides was undertaken so that they could be used as model compounds in an investigation (1) of the anilides formed when aniline was added to a mixture of acetic anhydride in malic acid buffers.

The structures of the anilides were assigned from their pKa values on the basis that the stronger acid would be the one with the hydroxy substituent α to the carboxylic acid function. Thus, the isomer with m.p. 139.5–140.5°; λ_{\max} . 243 m μ , log ϵ = 4.06 (in chloroform); pKa = 3.69; was assigned the structure of the α -hydroxy isomer (II), and the isomer with m.p. 149.5–150.5°; λ_{\max} . = 243 m μ , log ϵ = 4.12 (in chloroform); pKa = 4.35; was assigned the structure of the β -isomer (III).



Other examples of the acid-strengthening effect of an α -hydroxy substituent relative to a β -hydroxy substituent include the greater acidity of lactic acid (pKa = 3.86) (2) and ethylmethylglycolic acid (pKa = 3.99) (2) compared to hydracrylic acid (pKa = 4.51) (3) and 2-hydroxy-1-methyl-butiric acid (pKa = 4.65) (2), respectively.

The relative yield of the isomeric hydroxysuccinanic acids obtained in the alkaline hydrolysis of malanil (I) was $[\beta\text{-hydroxysuccinanic acid}]/[\alpha\text{-hydroxysuccinanic acid}] = 0.2$. This is expected as the carbonyl group α to the hydroxy group in malanil is likely to be more electrophilic than the carbonyl group β to the hydroxy group, and thus be more susceptible to attack by hydroxide ions.

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EXPERIMENTAL

DL-Malic Acid Phenylimide (Malanil) (I)—Dry solid anilinium malate, prepared by slowly adding 1 mole of aniline in ethanol to 1 mole of malic acid in ethanol, was heated at 140° for 3 hr. while nitrogen was bubbled through the reaction mixture. The product was recrystallized from toluene and further purified on a silicic acid column. Upon recrystallization from chloroform white crystals were obtained, m.p. 179.5–180°.

Anal.—Calcd. C₁₀H₉NO₃: for C, 62.82; H, 4.75; N, 7.33. Found: C, 62.66; H, 4.84; N, 7.48.

α - and β -Hydroxysuccinanic Acids—Alkaline hydrolysis of malanil yielded two isomeric monoanilides of malic acid which were separated and purified by column partition chromatography. The structures of the two anilides were assigned from measurements of pKa values and the assumption that the stronger acid would be the one with the hydroxy substituent α to the carboxylic function. DL- β -Hydroxysuccinanic acid (III), m.p. 149.5–150.5° (from toluene), $\lambda_{\max}^{\text{CHCl}_3}$ = 243 m μ (log ϵ = 4.12). pKa = 4.35 \pm 0.01 at 25°, determined potentiometrically (4) with [β -hydroxysuccinanic acid] = 0.01 M.

Anal.—Calcd. for C₁₀H₁₁NO₄: C, 57.41; H, 5.30; N, 6.70. Found: C, 57.46; H, 5.42; N, 6.82.

DL- α -Hydroxysuccinanic acid (II), m.p. 139.5–140.5° (from chloroform), $\lambda_{\max}^{\text{CHCl}_3}$ = 243 m μ (log ϵ = 4.06), pKa = 3.69 \pm 0.05 at 25° with [α -hydroxysuccinanic acid] = 0.01 M. Found: C, 57.44; H, 5.25; N, 6.60.

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Keyphrases

DL-Malic acid phenylimide—alkaline hydrolysis
 α -Hydroxysuccinanic acid—hydrolysis product
 β -Hydroxysuccinanic acid—hydrolysis product pKa values
 UV spectrophotometry—structure