

in good yield into any one of the following reduction products: the keto form of the hydroquinone, the anthrone, a di-anthranyl ether, the dihydroanthranol, naphthacene or dihydronaphthacene. Naphthacenehydroquinone, known only in solution or in the form of derivatives, is a remarkably unstable substance. It may be reduced with great ease, it ketonizes readily and it also undergoes a disproportionation.

All of the naphthacene derivatives which have a completely aromatic structure show a marked tendency to pass into derivatives of dihydronaphthacene. This is interpreted in terms of the ortho quinonoid structure for anthracene. The theory of bivalent radical formation is also discussed.

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THE PREPARATION AND SOME PROPERTIES OF THE CHLOROMANDELIC ACIDS, THEIR METHYL ESTERS AND AMIDES

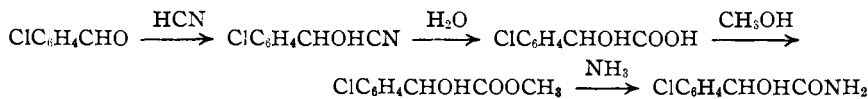
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In connection with another research² some derivatives of the chloromandelic acids were desired. Apparently only the ortho³ and para⁴ acids and the para⁵ amide have been described heretofore. It was thus decided to prepare the three acids with the corresponding methyl esters and amides.

The method of Karrer,³ in which *o*-chloromandelic acid was obtained from the aldehyde through the cyanohydrin, was employed. Certain modifications described in the experimental part, however, greatly increased the yield. For the esterification the method of Fischer and Speier⁶ was employed. The amides were obtained by treating alcoholic ether solutions of the esters with anhydrous ammonia. The reactions are



Experimental

Preparation of the Chloromandelic Acids.—Into a 500-cc. Claisen flask standing in an ice-bath were placed 100 g. of the chlorobenzaldehyde, 48 g. of 96–98% potassium

¹ Graffin Scholar, 1930–1931.

² To be published.

³ Karrer, *Helv. Chim. Acta*, **4**, 144 (1921).

⁴ Collet, *Bull. soc. chim.*, [3] **21**, 70 (1899); Straus, *Ann.*, **393**, 320 (1912).

⁵ Rule, *J. Chem. Soc.*, **113**, 17 (1918).

⁶ Fischer and Speier, *Ber.*, **28**, 3252 (1895).

TABLE I
 PROPERTIES OF THE CHLOROMANDELIC ACIDS, METHYL ESTERS AND AMIDES

	Best solvent for crystallization	M. p., °C. (corr.)	Appearance	Soly. in 100 cc. of ben- zene at 22°, g.
Ortho acid	Bz-pet. ether (10:1)	85-85.5 ^a	Needles	0.877
Meta acid	Benzene	115-115.5	Rosets of short needles	.271
Para acid	Benzene	120.5-121 ^b	Short needles	.470
Ortho methyl ester		B. p. 134-136° (6 mm.)	Colorless viscous liquid	
Meta methyl ester	Bz-pet. ether (4:1)	84	Tufts of small needles	
Para methyl ester	Bz-pet. ether (2:1)	55.6	Tufts of small short needles	
Ortho amide	Benzene	87.5	Plates	.244
Meta amide	Benzene	126.5	Scales	.021
Para amide	Benzene	125.5°	Plates	.044

^a Karrer, ³ 84-85°. ^b Collet, ⁴ 112-113°; Straus, ⁴ 119-120°. ^c Rule, ⁵ 122-123°.

cyanide, finely powdered, and 150 cc. of ether. Seventy-five cc. of concentrated hydrochloric acid was added from a dropping funnel during forty-five minutes, while the solution was being rapidly stirred mechanically. The ice-bath was removed after thirty minutes more and the stirring continued for two hours longer at room temperature. Since cyanohydrins, in general, are unstable, no attempt was made to isolate them. The ether solution containing the nitrile was decanted from the potassium chloride directly into 500 cc. of concentrated hydrochloric acid. The acid mixture was heated on a boiling water-bath for five hours with vigorous mechanical stirring. The cooled solution was made slightly alkaline with 30% sodium hydroxide and extracted twice with 150-cc. portions of ether to remove unchanged material. The purified solution of sodium chloromandelate was then treated with 75 cc. of concentrated hydrochloric acid and again extracted twice with 150-cc. portions of ether. The ether solution was dried over anhydrous sodium sulfate after which the ether was distilled and the crude chloromandelic acid recrystallized from benzene. (See Table II for yields and analytical data.)

The ortho and para chlorobenzaldehydes used in this work were purchased from the Eastman Kodak Company, the former being the practical grade. The *m*-chlorobenzaldehyde was prepared from *m*-nitrobenzaldehyde according to the method of Erdmann and Schwechten.⁷

Preparation of the Methyl Esters.⁶—Fifty grams of acid, 300 cc. of absolute methyl alcohol and 15 cc. of concentrated sulfuric acid were refluxed for five hours, after which 225 cc. of the alcohol was distilled off. The remaining liquid was made slightly alkaline with 10% sodium carbonate solution and extracted twice with 100-cc. portions of ether. The ether solution was dried over anhydrous sodium sulfate and the ester obtained by distilling off the ether.

The ortho ester was purified by fractionation *in vacuo* since it could not be induced to crystallize. The meta and para esters were obtained pure by crystallization from benzene-petroleum ether (b. p. 30-60°) solution.

Preparation of the Chloromandelamides.—The amides were prepared by dissolving 25 g. of the esters in 50 cc. each of anhydrous ether and absolute alcohol. The solution

⁷ Erdmann und Schwechten, *Ann.*, 260, 53 (1890).

was cooled to 0° and treated with anhydrous ammonia for ten hours. At the expiration of this time most of the amide had crystallized out. The alcohol and ether were evaporated under reduced pressure, after which the amide was pulverized and washed with ether. This treatment gave a product sufficiently pure for most purposes. The pure amides were obtained by recrystallization from benzene.

TABLE II
YIELDS AND ANALYTICAL DATA

Chloromandelic acid	Yield, %	Analysis	
		Calcd. Cl, 19.01% Found (Parr bomb), Cl	Calcd. neut. equiv., 186.5 Found
Ortho	41 ^a	19.03	186.3
Meta	67	19.30	184.9
Para	82	19.28	187.6
		Calcd. Cl, 17.68% Found (Parr bomb), Cl	
Ester			Calcd. ester no., 279.7 Found
Ortho	85	17.83	280.9
Meta	95	17.49	279.5
Para	83	17.87	280.9
		Calcd. Cl, 19.11% Found (Parr bomb), Cl	
Amide			Calcd. N, 7.55%
Ortho	90	19.06	7.56
Meta	90	19.19	7.64
Para	90	19.21	7.69

^a Karrer reported 18 g. of this acid from 50 g. of *o*-chlorobenzaldehyde or 28%.

In conclusion the writer wishes to thank Dr. E. Emmet Reid for his interest and valuable suggestions.

Summary

1. A convenient method for the preparation of the monochloromandelic acids has been described.
2. The complete series of acids, methyl esters and amides was obtained and some properties of these compounds are given. Six new compounds were prepared in the course of this work.

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