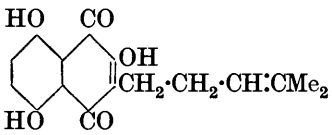
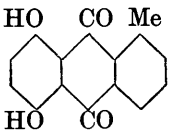
CCCXXXVI.—*A New Isomerism of Halogenohydroxybenzoyltoluic Acids.*

By MOSUKE HAYASHI.

THE roots of *Lithospermum Erythrorhizon*, commonly known as Shikon, were used in ancient Japan as an important violet dye. A few years ago the main constituent of this colouring matter was isolated by Majima and Kuroda (*Acta Phytochim.*, 1922, **1**, 43) and found to be a monoacetyl compound of a hydroxynaphthaquinone derivative. This derivative, which has been termed *shikonin* from the Japanese name of the plant, melts at 147° and has the molecular formula $C_{16}H_{16}O_5$; its constitutional formula, representing it as 2 : 5 : 8-trihydroxy-3-δ-methyl-Δ$^{\gamma}$-pentenyl-1 : 4-naphthaquinone (I), was deduced from the results of careful investigations.

(I.)



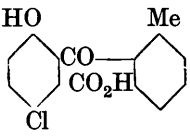


(II.)

One of the most characteristic properties of shikonin is the formation of a red sublimate on heating; this decomposition product, termed *shikizarin*, m. p. 232°, has the molecular formula $C_{15}H_{10}O_4$. Whereas shikonin itself, as a naphthaquinone derivative, is relatively unstable, shikizarin is stable enough to be regarded as an anthraquinone derivative; it gives 3-methylphthalic anhydride on oxidation with potassium permanganate. From these results, shikizarin (II) seems to be 8-methylquinizarin, formed by the extrusion of a molecule of hydrogen and of the elements of methyl alcohol from shikonin.

To decide the constitution of shikizarin, 8-methylquinizarin was synthesised by Majima by condensing 3-methylphthalic anhydride with quinol dimethyl ether and heating the dihydroxybenzoyltoluic acid thus formed with concentrated sulphuric acid.* It was identical with shikizarin, and strong support was thus obtained for the constitution of shikonin. The yield of the dihydroxybenzoyltoluic acid was, however, very poor, so the synthesis was attempted in another way by Sakurai in the same laboratory, but without much improvement in the result.* Yet another synthesis was carried out by the present author by condensing 3-methylphthalic anhydride with *p*-chloroanisole in acetylene tetrachloride solution in the presence of aluminium chloride (compare Ullmann and Schmidt, *Ber.*, 1919, **52**, 2098). Thereby chlorohydroxybenzoyltoluic acid was obtained in good yield, the methoxyl group being hydrolysed at the same time. 8-Methylquinizarin was then produced by treating this intermediate substance with concentrated sulphuric acid and heating the chlorohydroxymethylanthraquinone thus formed with a solution of boric acid in sulphuric acid. The yield was about 50% of the chlorohydroxymethylanthraquinone.

The stage of the reaction resulting in the formation of chlorohydroxymethylanthraquinone was, however, not at all simple and the action of concentrated sulphuric acid on the chlorohydroxybenzoyltoluic acid gave rise, in addition to chlorohydroxymethylanthraquinone, to an interesting isomeric change, which has been studied in some detail. The above-mentioned chlorohydroxybenzoyltoluic acid, m. p. 238—239°, may have one of the formulæ III, IV, V, and VI. Many authors (Nourrisson, *Ber.*, 1886, **19**,



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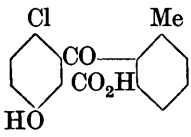

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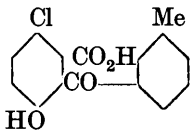

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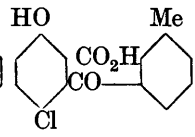


(VI.)

2103; Logodzinski, *Ber.*, 1895, **28**, 116; *Annalen*, 1905, **342**, 90; Bistrzycki and Schepper, *Ber.*, 1898, **31**, 2790; Ullmann and Schmidt, *Ber.*, 1919, **52**, 2098; Simonsen and Rau, J., 1921, **119**, 1339; Simonsen, J., 1924, **125**, 721; Eder and his co-workers, *Helv. Chim. Acta*, 1922, **5**, 3; 1923, **6**, 419, 966; 1925, **8**, 126; Bistrzycki and Krauer, *Helv. Chim. Acta*, 1923, **6**, 750; Adams and his collaborators, *J. Amer. Chem. Soc.*, 1923, **45**, 2439, 2455; 1925, **47**, 283; compare also Bentley, Gardner, and Weizmann, J., 1907, **91**, 1626) have shown that phthalic anhydride and its derivatives condense with phenolic ethers in the *p*-position to the alkyloxy-

* The details of these experiments have not yet been published.

group, provided that position is open, and with phenols in the *o*-position to the hydroxy-group, and that no condensation in the *m*-position to the alkyloxy- or hydroxy-group can be effected. The constitutional formula of the chlorohydroxybenzoyltoluic acid may therefore be either (III) or (V). As α-substituted phthalic anhydrides usually condense with phenol and its ethers through the carbonyl group adjacent to the substituent (Bistrzycki and Schepper; Simonsen and Rau; Simonsen; Eder and his co-workers; Bistrzycki and Krauer; Adams and his collaborators; *locc. cit.*), it is highly probable that the chlorohydroxybenzoyltoluic acid is 5′-chloro-2′-hydroxy-2-benzoyl-*m*-toluic acid (III).

By the action of concentrated sulphuric acid (98·25%) on the chlorohydroxybenzoyltoluic acid, an anthraquinone derivative, m. p. 223—224°, was obtained, and this should be 5-chloro-8-hydroxy-1-methylanthraquinone.

When 5′-chloro-2′-hydroxy-2-benzoyl-*m*-toluic acid was treated with concentrated sulphuric acid on the steam-bath, the greater part of the product was soluble in aqueous sodium carbonate. Two isomeric substances, differing in solubility, crystalline form, and in the amount of water of crystallisation of their salts, were obtained by fractional crystallisation of the recovered acids from alcohol; one melted at 171—171·5° and the other at 238—239°. The latter was proved to be identical with the initial substance by the mixed melting point method. These two isomerides are designated α- and β-5′-chloro-2′-hydroxy-2-benzoyl-*m*-toluic acid, respectively.

After the isolation of the α- and β-acids from the material soluble in sodium carbonate, the residue (C) melted at about 160—165° and was difficult to purify by further fractional crystallisation.

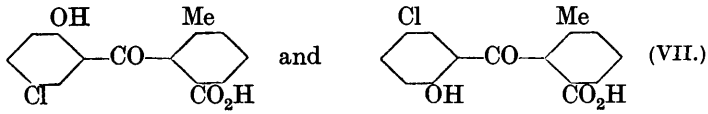
The α-acid (m. p. 171—171·5°) was treated with concentrated sulphuric acid, and the isolation of the products carried out, as in the case of the β-acid; the anthraquinone derivative, the β-acid, unchanged α-acid, and the residue (C′), from which it was difficult to separate the α- and β-acids by further fractional crystallisation, were then obtained.

When treated with concentrated sulphuric acid on the steam-bath, the residue C or C′ gave essentially the same results as those obtained from the α- or the β-acid. Therefore the residues C and C′ seem to consist of somewhat impure mixtures of the α- and β-acids, and the percentages of these acids in them can be approximately deduced from a table of melting points of mixtures of the two acids.

On treating the α-acid, the β-acid, the residue C and the residue C′ separately with concentrated sulphuric acid at room temperature, the anthraquinone derivative was not obtained, but in each case

the α- and β-acids could be isolated. Consequently the production of the anthraquinone derivative from the α- or the β-acid is preceded by a reversible change between these acids.

The α- and the β-acid, being so readily interconvertible on treatment with concentrated sulphuric acid, are probably stereoisomeric, and this view is supported by the great similarity of their ultra-violet absorption curves. This theory of the isomerism may be illustrated by the following formulæ :



(VII.)

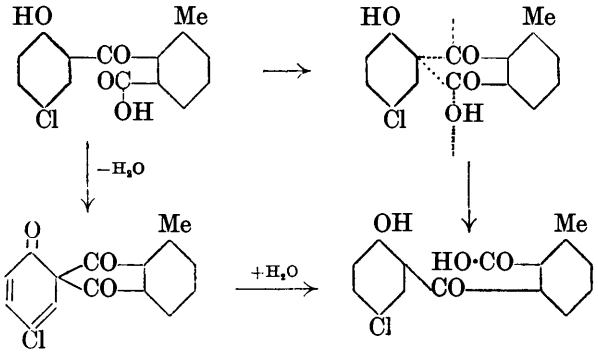
At present there is no diagnostic reaction which will enable us to apportion these configurations, but since in an equilibrium mixture of the two acids at about 100° the amount of the β-acid is very small and that of the α-acid is great, whilst the yield of the anthraquinone derivative is relatively small, it seems probable that the configuration (VII) is that of the α-acid.

The Kaufler diphenyl configuration (*Annalen*, 1907, **351**, 151; *Ber.*, 1907, **40**, 3250) has been employed by Cain and his collaborators (J., 1914, **105**, 1437, 1442, etc.), by Turner (J., 1915, **107**, 1495), by Kenner and his co-workers (J., 1922, **121**, 614; 1923, **123**, 779, 1043, 1948), by Brady and McHugh (J., 1923, **123**, 2047), by Bullock and Wilson (*J. Amer. Chem. Soc.*, 1923, **45**, 521), and by many other chemists to account for the stereoisomerism of diphenyl derivatives.* Moreover, Kaufler and Basel (*Ber.*, 1907, **40**, 3253) and Kenner (J., 1922, **121**, 614) expected the existence of stereoisomerides of the same kind in derivatives of diphenylmethane and diphenylethane, but so far as the author is aware, their existence has not been reported. In the case of 5′-bromo-2′-hydroxy-2-benzoyl-*m*-toluic acid, the author obtained results similar to those described above in connexion with the chloro-derivatives.

When 5′-chloro-2′-hydroxy-*o*-benzoylbenzoic acid, obtained by condensing phthalic anhydride with *p*-chloroanisole or *p*-chlorophenol, was heated with concentrated sulphuric acid (98·25%) on the steam-bath, 4-chloro-1-hydroxyanthraquinone was easily obtained in 90% yield (compare Ullmann, D.R.-P. 282,493), but interaction over-night at room temperature gave only a 5% yield

* More recent investigations have shown that the conception is not even necessary for the satisfactory explanation of the chemistry of the diphenyl group, and as a result of these developments in the period following the writing of this communication the author feels that the alternative structural explanation of his results requires all the more careful consideration.

of the anthraquinone, 92% of the original substance being recovered. In these experiments, two isomerides of 5′-chloro-2′-hydroxy-*o*-benzoylbenzoic acid, anticipated from the analogy with the above-mentioned benzoyltoluic acids, were not encountered. This circumstance lends some colour to the view that the isomerism of these substituted benzoylbenzoic acids is, after all, structural in accordance with one of the schemes :



Obviously, in this case the shikizarin ultimately obtained would be a homogeneous product, whereas the chlorohydroxymethylanthraquinone might consist of two isomerides. Experience in the anthraquinone group suggests that such a mixture might simulate the behaviour of a pure substance.

The investigation of the analogous isomerism of other derivatives of benzoylbenzoic acid is in progress with the object of deciding between the two possible interpretations of the results.

Experimental.

β-5′-*Chloro*-2′-*hydroxy*-2-*benzoyl*-m-*toluic Acid.*—3-Methylphthalic anhydride (10 g., m. p. 115·5—116·5°) was dissolved in acetylene tetrachloride (50 c.c.), mixed with *p*-chloroanisole (10 g.), and finely powdered aluminium chloride (25 g.) gradually added in the course of 1—1½ hours, with frequent shaking, the temperature being maintained at 115—120° (oil-bath) during the addition and thereafter at 120—130° for 3 hours. The product was cooled, mixed with ice-water and, after the addition of an excess of hydrochloric acid, distilled in steam in order to remove *p*-chloroanisole and acetylene tetrachloride. The solid residue was extracted several times with boiling ammonia solution,* and the ammoniacal extracts

* Chlorohydroxymethylanthraquinone (7% of the theoretical) was isolated from the part insoluble in ammonia, and proved to be identical with the anthraquinone derivative, which was obtained from the α- or β-5′-chloro-2′-hydroxybenzoyltoluic acid, by the method of mixed melting points.

were freed from ammonia and cooled; the resinous substance that separated was removed. On acidification of the filtrate, impure β-5′-chloro-2′-hydroxy-2-benzoyl-*m*-toluic acid, m. p. about 210—220°, separated in 75% yield. The acid was redissolved in caustic alkali or in ammonia and the solution was boiled with animal charcoal, filtered, and acidified with hydrochloric acid; the almost colourless material thus precipitated was washed with water and crystallised from alcohol or glacial acetic acid (Found: C, 61·7; H, 4·0; Cl, 12·4; *M*, in camphor by Rast's method, 285. $C_{15}H_{11}O_4Cl$ requires C, 62·0; H, 3·8; Cl, 12·2%; *M*, 291). This acid melts at 238—239°, and dissolves readily in hot alcohol or glacial acetic acid, but is sparingly soluble in the cold solvents. It is easily soluble in acetone, slightly soluble in benzene, carbon tetrachloride, carbon disulphide or chloroform, and very sparingly soluble in light petroleum or water. The yellow solution in concentrated sulphuric acid develops a deep red colour. The crystalline form: rhombic system, *a* : *c* P (from alcohol). The ultra-violet absorption curve of this acid, determined with a Hilger quartz spectrograph, shows two bands with heads at λ 3350 and 2860 Å.U.

In an experiment similar to that described above but starting from 3-methylphthalic anhydride (10 parts) and *p*-chlorophenol (9 parts), a substance, m. p. 215—225°, was isolated in 70% yield. (Chlorohydroxymethylanthraquinone, 7% of the theoretical quantity, was also isolated from the part insoluble in ammonia.) This was purified and identified as β-5′-chloro-2′-hydroxy-2-benzoyl-*m*-toluic acid, since its m. p. was not depressed on admixture with the β-acid.

The *sodium* and *barium* salts were prepared by neutralising hot alcoholic solutions of the acid with solutions of the corresponding bases, and recrystallised from water by cooling their solutions with ice. The specimens were kept in a balance room until the weight was constant for a few hours [Found for the sodium salt (temperature of the room, 12°; relative humidity, 85%): loss at 105°/10 mm., 25·6; Na, 5·4. $C_{15}H_{10}O_4ClNa,6H_2O$ requires H_2O, 25·7; Na, 5·5%. Found for the barium salt (temperature of the room, 11°; relative humidity, 84%): loss at 105°/10 mm., 16·6; Ba, 15·7. $(C_{15}H_{10}O_4Cl)_2Ba,8H_2O$ requires H_2O, 16·7; Ba, 16·0%]. On standing in the atmosphere, the water of crystallisation was gradually lost, the more quickly the higher the room temperature. The sodium salt is readily soluble and the barium salt moderately easily soluble in water.

α-5′-*Chloro*-2′-*hydroxy*-2-*benzoyl*-m-*toluic Acid.*—The β-acid (1 g.) was heated with sulphuric acid (6 c.c.; 98·25%) in a boiling water-bath for about 1 hour. On pouring the product into ice-water, a

dirty green, sticky precipitate separated and after warming for a few minutes this was collected, washed with water by decantation, and stirred with an excess of dilute aqueous sodium carbonate; a yellow substance (20—25% yield), m. p. 220—222°, remained undissolved. This substance was recrystallised several times from glacial acetic acid and proved to be chlorohydroxymethylanthraquinone (see p. 2524). From the yellow filtrate, acidified with hydrochloric acid, a sticky substance was precipitated which crystallised on being warmed for a few minutes or kept at the ordinary temperature for several days. The solid was collected, washed with water, and dried over sulphuric acid in a vacuum desiccator, a faintly yellow, crystalline mass being obtained (yield, 55—75%). It sintered at about 160° and melted to a clear liquid at about 170°. On fractional crystallisation from alcohol, two forms were separated. The residue (C), from which nothing definite could be isolated by further recrystallisation, melted at 160—165° (yield, 10—30% of the β-acid). The less soluble fraction (yield, about 1%), m. p. 220—235°, was recrystallised from alcohol and proved to be identical with the β-acid by the mixed melting point method. The more soluble fraction (yield, 35—50%) melted at 169—171° and was recrystallised several times from aqueous alcohol (Found: C, 61·8; H, 3·8; Cl, by Nomura and Murai's method, 11·9; *M*, in camphor by Rast's method, 287. $C_{15}H_{11}O_4Cl$ requires C, 62·0; H, 3·8; Cl, 12·2%; *M*, 291). The substance is moderately easily soluble in benzene, dissolves to some extent in water, and is readily soluble in alcohol or glacial acetic acid. It dissolves in concentrated sulphuric acid to a deep red solution, a little heat being developed. Like the β-isomeride, it is soluble in dilute aqueous caustic alkali to a yellow solution. Crystalline form: rhombic system, ∞ P, P (from a mixture of alcohol and water). This acid has two absorption bands with heads at λ 3390 and 2860.

α-5′-Chloro-2′-hydroxy-2-benzoyl-*m*-toluic acid was treated with sulphuric acid (98·25%) under the same conditions as in the case of the β-acid, and the separation and identification of the reaction products were carried out as before. In this separation the chlorohydroxymethylanthraquinone and the β-acid, together with the initial substance, were isolated. Nothing definite could be isolated, by further recrystallisation, from the residue (C′).

However, the α- and β-acids and the chlorohydroxymethylanthraquinone were isolated from the residue (C or C′) by applying the same method as in the preceding cases, after treatment with concentrated sulphuric acid (98·25%).

In the latter three cases, the percentages of the α- and β-acids

and of the chlorohydroxymethylanthraquinone thus formed were almost the same as in the case of the β-acid. The details are given below in tabular form.

TABLE I.

Action of 98·25% Sulphuric Acid at about 95°.

Initial substance.	Insoluble in dil. Na_2CO_3 soln. (crude anthraquinone derivative).		Soluble in dilute sodium carbonate solution.				
	M. p.	%.	M. p.	%.		M. p.	%.
β-Acid	220—222°	20—25	160—170°	55—75	Crude α-acid	169—171°	35—50
					Crude β-acid	220—235	1
					Residue (C)	160—165	10—30
α-Acid	219—222	20—25	158—170	60—70	Crude α-acid	168—170	30—50
					Crude β-acid	220—230	trace
					Residue (C′)	160—165	20—30
Residue C or C′	210—220	20—25	158—170	60—70	Crude α-acid	169—170	30—50
					Crude β-acid	220—235	
					Residue	160—165	10—30

The anthraquinone derivative was not obtained when a solution of the α- or the β-acid or of the residue (C or C′) in concentrated sulphuric acid (98·25%) was kept over-night at room temperature (see Table II). This method is preferable for the preparation of the α-acid from the β-acid.

TABLE II.

Action of 98·25% Sulphuric Acid at Room Temperature.

Initial substance.	Soluble in dilute sodium carbonate solution.				
	M. p.	%.		M. p.	%.
β-Acid	168—170·5°	95—98	Crude α-acid	170—171°	70—80
			Crude β-acid	could not be separated	
			Residue (D)	163—168	15—25
α-Acid	,,	,,	Crude α-acid	169—171°	70—80
			Crude β-acid	could not be separated	
			Residue (D′)	163—168	20—25
Residue C or C′	,,	,,	Crude α-acid	169—171°	60—80
			Crude β-acid	could not be separated	
			Residue	160—166	15—20

It is clear from the data in Table III that the velocity of the reaction by which the β-acid changes to the α-acid is extremely rapid.

TABLE III.

The β-acid (0·1 g.) was treated with 98·25% sulphuric acid (1 c.c.) at 24° for the times stated.

Time (mins.).	Reaction product, m. p.	% α-Acid (from Table IV).	Time (mins.).	Reaction product, m. p.	% α-Acid (from Table IV).
5	162·5—169°	75—80	21	165·5—168·5°	*ca.* 93
10	162·5—165	*ca.* 80	30	165·5—169	*ca.* 95
16	162 —166	*ca.* 85	60	168·5—170·5	*ca.* 98

TABLE IV.

Melting Points of Mixtures of the α- and β-Acids.

β-Acid %.	α-Acid %.	M. p.	β-Acid %.	α-Acid %.	M. p.
0·0	100·0	171—171·5°	18·7	81·3	162—165°
1·3	98·7	169—171	19·2	80·8	162—166
2·4	97·6	168—170	24·2	75·8	162—200
3·6	96·4	166—170	29·2	70·8	162—205
9·5	90·5	163—167	40·4	59·6	162—215
13·4	86·6	163—167	49·5	50·5	162—220

The *sodium* and *barium* salts of the α-acid were prepared and analysed under conditions similar to those described for the sodium and barium salts of the β-acid. The *sodium* salt is readily soluble in water and closely resembles the sodium salt of the β-acid (Found: loss at 105°/10 mm., 19·0; Na, 5·9. $C_{15}H_{10}O_4ClNa,4H_2O$ requires H_2O, 18·7; Na, 6·0%). The *barium* salt is moderately easily soluble in water and does not effloresce at about 12° [Found: loss at 105°/10 mm., 4·7; Ba, 18·4. $(C_{15}H_{10}O_4Cl)_2Ba,2H_2O$ requires H_2O, 4·8; Ba, 18·3%]. The solubility of the α-acid and its salts is generally greater than that of the β-acid and its salts.

Chlorohydroxymethylanthraquinone.—A mixture of α- or β-5′-chloro-2′-hydroxy-2-benzoyl-*m*-toluic acid (1 g.) and sulphuric acid (6 c.c.; 98·25%) was heated at 115—120° for about an hour, cooled, and added to ice-water, and the green precipitate that separated was collected and treated with an excess of dilute sodium carbonate solution. A yellow substance (yield, 65%), m. p. 220—222°, remained undissolved; after several recrystallisations from glacial acetic acid it melted at 223—224° (Found: C, 65·8; H, 3·6; Cl, 13·3. $C_{15}H_9O_3Cl$ requires C, 66·1; H, 3·3; Cl, 13·0%). This substance is easily soluble in hot benzene, appreciably soluble in hot glacial acetic acid, and sparingly soluble in hot alcohol. It dissolves with difficulty in caustic alkalis and easily in concentrated sulphuric acid, giving a red solution in each case.

5 : 8-*Dihydroxy*-1-*methylanthraquinone* (8-*Methylquinizarin*).—Chlorohydroxymethylanthraquinone (1 g.) was gradually added to a solution of boric acid (2·4 g.) in concentrated sulphuric acid (10 c.c.) at 140—150°, and the whole was heated at 150—160° until the evolution of hydrogen chloride ceased. After cooling, the product was poured into ice-water, and the reddish-black precipitate was collected, and well washed with hot water. The substance was purified by dissolution in caustic soda and reprecipitation (yield, about 50%) and then by crystallisation several times from *iso*butyl alcohol or glacial acetic acid (Found: C, 70·6; H, 4·0. Calc., C, 70·9; H, 4·0%). The dark red crystals melted at 233—234° and at the same temperature when mixed with a specimen of

8-methylquinizarin (m. p. 232—233°) obtained from shikonin by Majima and Kuroda (*loc. cit.*).

β-5′-*Bromo*-2′-*hydroxy*-2-*benzoyl*-m-*toluic Acid.*—Aluminium chloride (12·5 g.) was gradually added to a solution of 3-methylphthalic anhydride (5 g.) and *p*-bromophenol (7·5 g.) in acetylene tetrachloride (20 c.c.), and the subsequent treatment and the separation of the reaction products were carried out as in the case of the chloro-derivative. Impure β-5′-*bromo*-2′-*hydroxy*-2-*benzoyl*-m-*toluic acid*, m. p. about 220—230°, was obtained in 75% yield from the part soluble in ammonia, and bromohydroxymethylanthraquinone in about 6% yield from the insoluble part. The former, after several crystallisations from alcohol, had m. p. 246—246·5° (Found : C, 53·8; H, 3·5; Br, by Nomura and Murai's method, 23·8. $C_{15}H_{11}O_4Br$ requires C, 53·7; H, 3·3; Br, 23·8%). It is easily soluble in hot alcohol, hot glacial acetic acid or hot acetone, and sparingly soluble in carbon disulphide, carbon tetrachloride or benzene. It is very sparingly soluble in water or light petroleum. The solution of this acid in concentrated sulphuric acid is at first yellow, but soon becomes deep red. The acid is also soluble in dilute caustic alkali to a yellow solution. It exhibits an absorption band with a head at λ 3335.

The bromohydroxymethylanthraquinone mentioned above was proved to be identical with bromohydroxymethylanthraquinone, which was obtained from α- or β-5′-bromo-2′-hydroxy-2-benzoyl-*m*-toluic acid, by the mixed melting point method.

α-5′-*Bromo*-2′-*hydroxy*-2-*benzoyl*-m-*toluic Acid.*—After a solution of β-5′-bromo-2′-hydroxy-2-benzoyl-*m*-toluic acid in sulphuric acid (6 c.c.; 98·25%) had been heated in the boiling water-bath for ½ hour, the reaction products were treated with an excess of dilute sodium carbonate solution, bromohydroxymethylanthraquinone, a yellow substance, m. p. 187—195°, remaining undissolved (yield, 8—10%); a crystalline mass, m. p. 157—162° (yield, 70—85%) was obtained from the yellow filtrate on acidification with hydrochloric acid. On repeated crystallisation from alcohol, two fractions were isolated. The less soluble crystals (about 1%) melted at 240—243°, and the more soluble ones (50—70%) at 161—164°. The former fraction was recrystallised from alcohol and proved to be identical with β-5′-bromo-2′-hydroxy-2-benzoyl-*m*-toluic acid by the mixed melting point method. The latter was recrystallised from aqueous alcohol (Found: C, 53·7; H, 3·5; Br, by Nomura and Murai's method, 24·1. $C_{15}H_{11}O_4Br$ requires C, 53·7; H, 3·3; Br, 23·8%). This isomeride melts at 163·5—164°, and is readily soluble in alcohol, glacial acetic acid, or acetone, moderately readily soluble in benzene, carbon disulphide, or carbon tetrachloride, and

very sparingly soluble in light petroleum or water. Its solubility is generally greater than that of the β-acid. It dissolves in concentrated sulphuric acid and in dilute aqueous caustic alkali, giving a red and a yellow solution, respectively. This acid has an absorption band with a head at λ 3345.

The α-acid was treated with sulphuric acid (98·25%) at 100°, and bromohydroxymethylanthraquinone and the α- and β-acids were then separated by applying the method used in the case of the β-acid. The same results were obtained from the residue (R or R′) (see Table V).

TABLE V.

Initial substance.	Insoluble in dil. Na_2CO_3 soln. (crude anthraquinone derivative).		Soluble in dilute sodium carbonate solution.				
	M. p.	%.	M. p.	%.		M. p.	%.
β-Acid	187—195°	8—10	157—162°	70—85	Crude α-acid	161—164°	50—70
					Crude β-acid	240—243	1
					Residue (R)	158—161	10—25
α-Acid	188—194	5—10	159—162	70—85	Crude α-acid	163—164	50—70
					Crude β-acid	very small	
					Residue (R′)	158—161	10—25
Residue R or R′	187—195	5—10	158—161	70—85	Crude α-acid	163—164	40—70
					Crude β-acid	240—245	1
					Residue	158—161	10—30

*The Sodium and Potassium Salts of α- and β-5′-Bromo-2′-hydroxy-2-benzoyl-*m*-toluic Acids.*—These salts were prepared by neutralising hot alcoholic solutions of the acids with solutions of the corresponding alkali hydroxides, and recrystallised from water by cooling in ice. After standing in a balance room until the weight was constant for a few hours, they were analysed (Temp. of room, 6°; relative humidity, 87%. Found for sodium salts of α-acid and of β-acid, respectively: loss at 105°/10 mm., 17·0 and 23·5; Na, 5·4 and 5·0. $C_{15}H_{10}O_4BrNa,4H_2O$ and $C_{15}H_{10}O_4BrNa,6H_2O$ respectively require H_2O, 16·8 and 23·2; Na, 5·4 and 4·9%. Temp. of room, 11°; relative humidity, 83%. Found for potassium salts of α-acid and of β-acid, respectively: loss at 105°/10 mm., 4·3 and 12·4; K, 9·8 and 9·1. $C_{15}H_{10}O_4BrK,H_2O$ and $C_{15}H_{10}O_4BrK,3H_2O$ respectively require H_2O, 4·6 and 12·7; K, 10·0 and 9·2%). The two sodium salts and the β-potassium salt gradually lost their water of crystallisation in the air.

Bromohydroxymethylanthraquinone.—The above-mentioned anthraquinone derivatives obtained from α- and β-5′-bromo-2′-hydroxy-2-benzoyl-*m*-toluic acids and the residues (R and R′) crystallised separately from *iso*butyl alcohol in yellow crystals, m. p. 198—198·5°, and were proved to be identical with each other by the mixed melting point method (Found: C, 56·7; H, 3·0; Br, by Nomura and Murai's method, 25·15. $C_{15}H_9O_3Br$ requires C, 56·8; H, 2·9; Br, 25·2%). This bromohydroxymethylanthraquinone is

easily soluble in benzene, glacial acetic acid, *iso*butyl alcohol, carbon disulphide, carbon tetrachloride, and acetone when the solvents are hot. It is moderately readily soluble in alcohol and sparingly soluble in light petroleum. It dissolves to a slight extent in dilute aqueous caustic alkali and easily in concentrated sulphuric acid, giving red solutions.

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