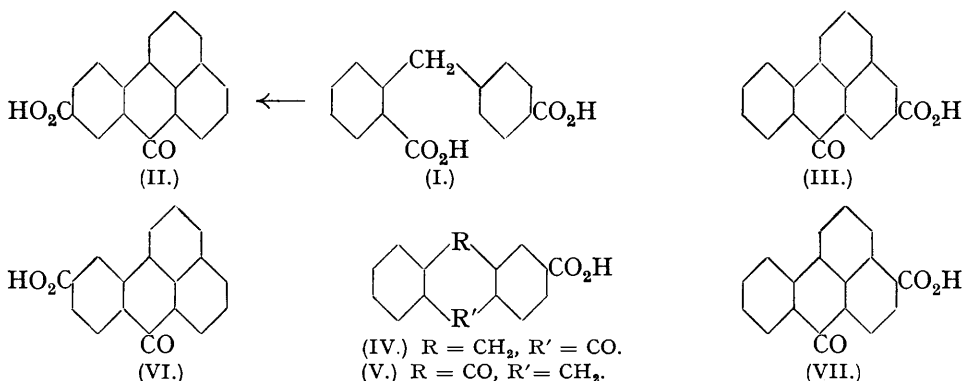


### 37. mesoBenzanthronecarboxylic Acids.

By F. C. COPP and J. L. SIMONSEN.

The mesobenzanthronecarboxylic acids prepared by the condensation of glycerol with diphenylmethane-2:4'-dicarboxylic acid and with the anthrone of anthraquinone-2-carboxylic acid have been examined. The former condensation yields mesobenzanthrone-9-carboxylic acid, and the latter gives a mixture of the 9- and the 10-acid. Attempts to condense the anthrone of anthraquinone-1-carboxylic acid with glycerol failed, but the amide can be condensed. The amide of mesobenzanthrone-11-carboxylic acid formed the main product of the reaction, together with a small quantity of the 8-acid.

Of the ten theoretically possible mesobenzanthronecarboxylic acids, five have so far been described and rigidly oriented, namely, the 1-, 2-, 3-, 4- and 11-acids. By the condensation of diphenylmethane-2:4'-dicarboxylic acid (I) with glycerol in the presence of sulphuric acid Schaarschmidt (G.P. 251,480, 254,023; Friedländer's "Fortschritte," Vol. 11, 703) prepared a mesobenzanthronecarboxylic acid stated to be the 9-acid (II) (Béilstein's "Organische Chemie," Ergänzungsband, 10, 382), although from its method of preparation it can equally well be the 5-acid (III). Schaarschmidt prepared also an isomeric acid by the condensation of the anthrone of anthraquinone-2-carboxylic acid with glycerol. This acid is assumed to be the 10-acid (VI), although the condensation can yield either the 9- (II), 5- (III) or 4- (VII) acid depending upon whether the anthrone has the structure (IV) or (V).



Reinvestigating these two glycerol condensations, we have found that the first yields a homogeneous product consisting of the 9-acid, and the second gives a mixture of the 9- and the 10-acid. The acid from the first condensation, characterised by the preparation of the *methyl* and the *ethyl* ester, has been shown to be the 9-acid by two distinct methods. By the Schmidt reaction (G.P. 307,798; von Braun, *Annalen*, 1931, 490, 125; Boyes, Grieve, and Rule, J., 1938, 1834) the acid was converted into an *aminomesobenzanthrone*, yielding on diazotisation and treatment with cuprous chloride 9-chloromesobenzanthrone. It followed, therefore, that the carboxyl and the amino-group were in the 9-position. Confirmation of the structure assigned to the acid was obtained by its preparation from 9-methylmesobenzanthrone by oxidation of the alkyl group with selenium dioxide, the aldehyde, which formed the main product of the reaction, being further oxidised to the acid by potassium permanganate in pyridine solution.

The condensation of the anthrone of anthraquinone-2-carboxylic acid proceeded much less smoothly and gave a complex mixture of acids, which was resolved by chromatographing the ethyl esters. This

resulted in the separation of (i) ethyl anthraquinone-2-carboxylate, (ii) ethyl mesobenzanthrone-9-carboxylate, and (iii) in small amount an ethyl mesobenzanthronecarboxylate, m. p. 137—139°. The last ester gave on hydrolysis an acid, m. p. 326—327°, yielding a methyl ester, m. p. 167—168°. For the purposes of comparison mesobenzanthrone-4-carboxylic acid (VII), m. p. 314—315°, was prepared from 4-methylmesobenzanthrone (I.G., B.P. 277,670) and characterised by the preparation of its methyl ester, m. p. 215—216°, and its ethyl ester, m. p. 134—135°. The melting points of the methyl esters showed that the two acids were not identical and this was confirmed by the two ethyl esters in admixture showing a marked depression in m. p. Further the 4-acid dissolved in sulphuric acid to give a deep red non-fluorescent solution in marked contrast to the pink solution of the new acid with its strong yellowish-green fluorescence. The structure of the latter acid as mesobenzanthrone-10-carboxylic acid (VI) was established by the direct comparison of the acid and its derivatives with specimens of this acid and its esters prepared by the oxidation of 10-methylmesobenzanthrone.

In view of these results it appeared of interest to investigate the condensation of anthraquinone-1-carboxylic acid or its anthrone with glycerol, since this could theoretically yield either the 6-, 8- or 11-carboxylic acid. It was found, however, that neither anthraquinone-1-carboxylic acid nor its anthrone (Barnett, Cook, and Grainger, *Ber.*, 1924, 57, 1777) would condense with glycerol. Since it appeared possible that this failure might be due to lactonisation, the amide was utilised in place of the free acid. This derivative condensed readily under the conditions given on p. 212 to yield a mixture of acid and neutral products. The acid, obtained in small yield, after purification through its methyl ester, had m. p. 254—255° and was identified as mesobenzanthrone-8-carboxylic acid by oxidation with chromic acid to anthraquinone-1:5-dicarboxylic acid.

The main product of the condensation, insoluble in aqueous sodium carbonate, crystallised from nitrobenzene in yellow needles. Analysis showed this to be the amide of a mesobenzanthronecarboxylic acid and it gave on hydrolysis an acid, m. p. 267—268°, methyl ester, m. p. 160—161°. This acid was found to be the 11-carboxylic acid by direct comparison with a specimen for which we are indebted to Dr. Rule.

Condensations with the glycerol occur in the unsubstituted anthraquinone ring, as would perhaps be expected on general theoretical grounds. In the appended table we give the melting points of the mesobenzanthronecarboxylic acids and their esters so far as they are known. Only the 5- and the 6-carboxylic acid have still to be prepared.

#### mesoBenzanthronemonocarboxylic Acids.

CO <sub>2</sub> H.	M. p.	Me ester, m. p.	Et ester, m. p.	CO <sub>2</sub> H.	M. p.	Me ester, m. p.	Et ester, m. p.
1	285° <sup>1</sup>	—	—	4	314—315°	215—216°	134—135°
2	347 <sup>2</sup>	—	172—173°	8	254—255	173·5—174·5	—
	342 <sup>3</sup>	—	—	9	352—354	188—189	172·5—173·5
3	335 <sup>4, 5</sup>	—	—	10	326—327	167—168	137—139
4	307—308 <sup>4</sup>	—	—	11	273 <sup>7</sup>	159 <sup>8</sup>	—
	295 <sup>6</sup>	—	—		267—268	160—161	—

<sup>1</sup> Boyes, Grieve, and Rule, J., 1938, 1833. <sup>2</sup> Schaarschmidt, *Ber.*, 1917, 50, 294. <sup>3</sup> Heilbron, Hislop, and Irving, J., 1936, 781. <sup>4</sup> B.P. 277,670. <sup>5</sup> U.S.P. 1,740,771. <sup>6</sup> B.P. 321,916; F.P. 671,399. <sup>7</sup> Rule, Pursell, and Bennett, J., 1935, 570. <sup>8</sup> Bigelow and Rule, *ibid.*, p. 574. M. p.'s in italics are our determinations.

#### EXPERIMENTAL.

*Diphenylmethane-2 : 4'-dicarboxylic Acid.*—The following method is more convenient than that of Limpricht (*Annalen*, 1899, 309, 98). A mixture of benzophenone-2 : 4'-dicarboxylic acid (35 g.), amalgamated zinc wool (120 g.), hydrochloric acid (200 c.c.), water (50 c.c.), and anisole (200 c.c.) was refluxed for 30 hours, further hydrochloric acid (40 c.c.) being added at eight-hourly intervals. After removal of the anisole in steam the diphenylmethane-2 : 4'-dicarboxylic acid, with a little unchanged zinc, was collected from the cooled solution, the acid dissolved in aqueous sodium carbonate, and the filtered solution acidified. The acid (32 g.), which was pure enough for further experiments, crystallised from acetic acid in needles, m. p. 219—220° (Found: *M*, 252. Calc. for C<sub>15</sub>H<sub>12</sub>O<sub>4</sub>: *M*, 256).

*mesoBenzanthrone-9-carboxylic Acid.*—(1) *Condensation of diphenylmethane-2 : 4'-dicarboxylic acid and glycerol.* To a solution of the acid (10 g.) in sulphuric acid (90%; *d*<sub>4</sub><sup>20</sup> 1·820; 300 c.c.) at 76°, glycerol (15 c.c.) was added (mechanical stirring). The temperature rose to 94° and a green fluorescence developed. After being kept at 100—120° for 45 minutes, the mixture was cooled and poured into water (1 l.) and the solid which separated was collected. The crude acid was digested with aqueous sodium carbonate (charcoal), the filtered solution acidified, and the acid (7 g.) collected. After digestion with alcohol to remove readily soluble impurities the acid was esterified *via* the acid chloride. The ethyl ester crystallised from ethyl acetate in long yellow

needles, m. p. 172.5—173.5° (Found: C, 79.0; H, 5.1.  $C_{20}H_{14}O_3$  requires C, 79.5; H, 4.6%), and the methyl ester from methyl alcohol in yellow needles, m. p. 188—189° (Found: C, 78.7; H, 4.1.  $C_{19}H_{12}O_3$  requires C, 79.2; H, 4.1%).

mesoBenzanthrone-9-carboxylic acid, obtained by hydrolysis of the ethyl ester with methyl-alcoholic potassium hydroxide solution, crystallised from nitrobenzene in long yellow needles, m. p. 352—354° (Found: C, 78.7; H, 3.9.  $C_{18}H_{10}O_3$  requires C, 78.8; H, 3.6%). The acid dissolved in alkali to give a yellow solution with a brilliant emerald-green fluorescence; the potassium salt was somewhat sparingly soluble in water. The solution of the acid in sulphuric acid was canary-yellow with a green fluorescence.

(2) Oxidation of 9-methylmesobenzanthrone. A mixture of the benzanthrone (4.8 g.), selenium dioxide (2.2 g.), and water (20 c.c.) was heated in a rotatory autoclave at 230—240° for 2 hours. The solid was collected and digested with hot acetic acid, and the filtered solution poured into water. The precipitated solid was digested with hot aqueous sodium carbonate, and the filtered solution acidified, yielding the acid (0.5 g.). The residue (4 g.) insoluble in alkali consisted of unchanged benzanthrone and an aldehyde; the percentage of the latter, estimated as semicarbazone, was approximately 24%. For the preparation of a further quantity of the acid the crude solid (3 g.) was dissolved in pyridine (50 c.c.), and finely divided potassium permanganate (0.3 g.) added during  $\frac{1}{2}$  hour (mechanical stirring). The filtered solution was diluted with water and acidified, giving crude mesobenzanthrone-9-carboxylic acid (0.7 g.). The acid, after crystallisation from nitrobenzene, had m. p. 320—330°; the ethyl ester had m. p. 172—173°, both alone and in admixture with the ethyl ester of the acid prepared as described in section (1).

9-Amino- and 9-Chloro-mesobenzanthrones.—To a solution of mesobenzanthrone-9-carboxylic acid (3 g.) in sulphuric acid (30 c.c.) and chloroform (30 c.c.) maintained at 40—50°, sodium azide (5 g.) was added during 7 hours, chloroform (20 c.c.) being added to replace loss by evaporation (mechanical stirring). The cooled mixture was poured into water, the chloroform removed in steam, and the solid collected. After digestion with aqueous sodium carbonate the crude amine (0.7 g.) was obtained as a red powder; unchanged acid (2.1 g.) was recovered from the sodium carbonate solution. 9-Aminomesobenzanthrone crystallised from *o*-dichlorobenzene in red needles having a metallic lustre, m. p. 216—217° (Found: C, 82.9; H, 4.8.  $C_{17}H_{11}N$  requires C, 83.3; H, 4.5%). The amine is a weak base, being insoluble in dilute mineral acids; it dissolved in hot hydrochloric acid and the cooled solution deposited a sparingly soluble, yellow hydrochloride. The base dissolved in sulphuric acid to give a greenish-yellow solution having a faint green fluorescence. The acetyl derivative crystallised from acetic acid in deep yellow needles, m. p. 252—254° (Found: C, 79.1; H, 4.8.  $C_{19}H_{13}O_2N$  requires C, 79.4; H, 4.6%).

For conversion into 9-chloromesobenzanthrone a solution of the amine (0.5 g.) in concentrated sulphuric acid (10 c.c.) at 0—5° was gradually treated with powdered sodium nitrite (0.2 g.). After remaining at 0° for 2 hours, the mixture was cooled in salt-ice and cautiously diluted with water (20 c.c.); precipitation of the sparingly soluble diazonium sulphate was completed by the addition of sodium sulphate. The diazonium salt was collected and made into a paste with hydrochloric acid (10 c.c.), and the mixture added gradually to hydrochloric acid (30 c.c.) containing cuprous chloride (1 g.), the temperature being maintained at 30—35°. After 3 hours the temperature was raised to 80°, the mixture cooled, and the crude chloromesobenzanthrone collected. The solid was digested with acetic acid to remove copper salts, with alkali to remove phenols, and sublimed in a high vacuum, giving yellow needles (0.1 g.), m. p. 182—184°, raised to 186° by crystallisation from acetic acid. This m. p. was unchanged by authentic 9-chloromesobenzanthrone.

Condensation of Anthraquinone-2-carboxylic Acid and Glycerol. mesoBenzanthrone-9- and -10-carboxylic Acids.—A mixture of the anthraquinone acid (10 g.), sulphuric acid (300 c.c.); 90%,  $d^{18}_4$  1.820, copper bronze (2 g.), a trace of zinc dust, and glycerol (10 c.c.) was heated at 110° for 1 hour and at 120° for 15 minutes (mechanical stirring). The cooled mixture was poured into water, the solid collected and digested with aqueous sodium carbonate, and the filtered alkaline solution acidified. The crude acid (8.6 g.) which separated was collected, dried, and extracted with hot nitrobenzene, which left undissolved a black solid; the nitrobenzene deposited an acid (2.9 g.) in brownish-yellow needles having an indefinite m. p. For purification the acid (6.2 g.) was converted into the silver salt and this was esterified with ethyl iodide in benzene solution.\* The resulting ester (5.5 g.), m. p. 145—172°, gave in sulphuric acid a red solution with a green fluorescence. The ester, in benzene solution, was chromatographed, an alumina tower being used which had been previously washed with phenol to diminish the alkalinity. The ester (0.5 g.) was thus readily separated into two fractions: (a) a fraction (0.3 g.), m. p. 169—171°, adsorbed by the alumina, and (b) a yellow gum (0.15 g.) which passed through. Fraction (a), after crystallisation from alcohol, had m. p. 172.5—173.5°, both alone and in admixture with ethyl mesobenzanthrone-9-carboxylate. Fraction (b) was rechromatographed and thus separated into a more soluble fraction consisting of ethyl anthraquinone-2-carboxylate and an ester crystallising from alcohol in light yellow needles, m. p. 136—138° after softening at 134°. From a concentrated alcoholic solution ethyl mesobenzanthrone-10-carboxylate crystallised in deep golden needles, but the m. p. was unchanged (Found: C, 79.1; H, 4.6.  $C_{20}H_{14}O_3$  requires C, 79.5; H, 4.6%). The acid, obtained by the hydrolysis of the ester with methyl-alcoholic potassium hydroxide solution and separated as the sparingly soluble, yellow potassium salt,

\* If the acid was esterified *via* the acid chloride, prepared by the action of thionyl chloride, chloro-esters were formed probably from the anthraquinone acid present in the mixture.

crystallised from nitrobenzene in yellow needles, m. p. 326—327°, both alone and in admixture with the acid prepared from 10-methylmesobenzanthrone (see below) (Found: C, 78.4; H, 3.7.  $C_{18}H_{10}O_3$  requires C, 78.8; H, 3.6%). The acid dissolved in alkali to give a yellow solution with a green fluorescence; its solution in concentrated sulphuric acid was pink with a brilliant yellowish-green fluorescence. The methyl ester crystallised from methyl alcohol in yellow needles, m. p. 167—168° (Found: C, 79.1; H, 4.5.  $C_{19}H_{12}O_3$  requires C, 79.2; H, 4.2%).

*Oxidation of 10-Methylmesobenzanthrone.*—The benzanthrone (10 g.) in nitrobenzene (100 c.c.) was refluxed with selenium dioxide (10 g.) for 12 hours. The nitrobenzene was removed from the filtered solution in steam and the aqueous solution, after being made alkaline with sodium carbonate, was filtered, the filtrate (A) being reserved. The dried residue (9 g.) was extracted with chloroform and the soluble fraction (4 g.), containing 32% of aldehyde (estimated as the semicarbazone), was oxidised with potassium permanganate in pyridine solution as described in the case of the 9-methyl derivative (p. 211). The acid so obtained, together with that isolated from the alkaline solution (A) (in all 2.1 g.), was converted into the ethyl ester, which after being chromatographed, crystallised from alcohol in yellow needles, m. p. 133—136°. The acid, regenerated from the ester by hydrolysis with methyl-alcoholic potassium hydroxide solution, was esterified by diazomethane in dioxan solution. The methyl ester, after crystallisation from methyl alcohol, had m. p. 166—168°, both alone and in admixture with the methyl ester described above (Found: C, 79.1; H, 4.1%). Hydrolysis of the pure methyl ester gave the acid, which crystallised from acetic acid or nitrobenzene in yellow needles, m. p. 324—326° (Found: C, 79.1; H, 3.8%). This acid also resulted in very poor yield by the oxidation of 10-methylmesobenzanthrone with nitrobenzene and alkali.

*mesoBenzanthrone-4-carboxylic Acid.*—A mixture of 4-methylmesobenzanthrone (7 g.), nitrobenzene (50 c.c.), and potassium hydroxide (7 g.) was heated at 140—150° for 30 minutes (mechanical stirring). On cooling, a sparingly soluble potassium salt separated; this was collected, washed with nitrobenzene, and dissolved in hot water (charcoal), and the acid (5.6 g.) separated from the acidified solution. After crystallisation from nitrobenzene the acid was esterified through the acid chloride, and the ester chromatographed on alumina from a benzene solution and eluted with alcohol. Ethyl mesobenzanthrone-4-carboxylate crystallised from alcohol in fine yellow needles, m. p. 134—135° (Found: C, 79.3; H, 4.8%), largely depressed by the ethyl ester, m. p. 137—139°, of the 9-carboxylic acid. The 4-carboxylic acid, obtained by hydrolysis of the ethyl ester, crystallised from nitrobenzene in yellow needles, m. p. 314—315° (Found: C, 78.8; H, 3.4%). Its deep red solution in sulphuric acid was not fluorescent, but the yellow alkaline solution showed a yellowish-green fluorescence. The methyl ester crystallised from methyl alcohol in yellow needles, m. p. 215—216° (Found: C, 79.2; H, 4.4%).

*Condensation of Anthraquinone-1-carboxamide and Glycerol.* mesoBenzanthrone-8- and -11-carboxylic Acids.—A mixture of the amide (15 g.), glycerol (40 c.c.), aniline (10 c.c.), and copper bronze (6 g.) in sulphuric acid (750 c.c.; 90%;  $d_{15}^{20}$  1.820) was heated at 95—100° for 30 minutes (mechanical stirring). The solution became deep red and had a green fluorescence. The cooled solution was poured into water, and the precipitated solid collected and extracted with hot aqueous sodium carbonate. The insoluble residue (X) was reserved. The alkaline solution after digestion with charcoal was acidified, a black tar being precipitated. The supernatant liquor was decanted, and the residue extracted with boiling acetic acid (100 c.c.), the insoluble fraction being discarded. The filtrate (charcoal) deposited, on cooling, brownish-yellow needles (1.3 g.); a further quantity (1.1 g.) of less pure material was obtained after concentration of the solution. The acid in dioxan solution was esterified with diazomethane, and the methyl ester purified by passage through an alumina tower with benzene as the solvent. The pure ester remained as a lemon-yellow zone and was eluted by benzene containing a little methyl acetate. Methyl mesobenzanthrone-8-carboxylate crystallised from methyl alcohol containing methyl acetate (10%) in brilliant yellow needles, m. p. 173.5—174.5° (Found: C, 79.1; H, 4.4.  $C_{19}H_{12}O_3$  requires C, 79.2; H, 4.1%). Its solution in sulphuric acid was canary-yellow with a yellowish-green fluorescence.

The acid, prepared by hydrolysis of the ester with acetic-hydrochloric acids, alkaline hydrolysis yielding impure material, crystallised from chlorobenzene or acetic acid in yellow needles, m. p. 254—255° (Found: C, 78.9; H, 3.9.  $C_{18}H_{10}O_3$  requires C, 78.8; H, 3.6%). Its solution in sulphuric acid was golden-yellow with a yellow fluorescence markedly different from that shown by the methyl ester; its solution in alkali was yellow with a green fluorescence.

For its oxidation to anthraquinone-1:5-dicarboxylic acid, chromic acid (1 g.) in acetic acid (5 c.c.) was added gradually to a boiling solution of the acid (0.5 g.) in acetic acid (35 c.c.). On completion of the oxidation sulphuric acid (1.5 g.) was added, the solution evaporated to dryness, the chromium sulphate dissolved in water, the oxidation acid collected and dissolved in concentrated sulphuric acid, and the solution poured into water; the precipitated acid was collected, dissolved in aqueous ammonia, and reprecipitated from the filtered solution. The anthraquinone acid (0.3 g.), which now separated as a crystalline solid, was esterified through the acid chloride, and the ethyl ester passed through an alumina tower, chloroform being used as the solvent. The chromatogram was colourless apart from a small ring at the top which showed a bright green fluorescence in the mercury lamp. The purified ester crystallised from alcohol in long needles, m. p. 153—154°, after slight softening (Found: C, 67.6; H, 4.8. Calc. for  $C_{20}H_{14}O_6$ : C, 68.1; H, 4.5%). Ethyl anthraquinone-1:5-dicarboxylate prepared from 1:5-dichloroanthraquinone (Coulson, J., 1930, 1931) crystallised from ethyl

alcohol or acetic acid in needles, m. p. 149—151°, not raised by further crystallisation. In admixture with the ester from the oxidation acid the m. p. was 150—153°.

The condensation product (X) (p. 212) (10 g.), insoluble in alkali, crystallised from nitrobenzene (180 c.c.) (charcoal) in yellow needles, m. p. 312—314° on fairly rapid heating; on slow heating, decomposition much below this temperature was observed (Found: C, 78.9; H, 4.1. Calc. for  $C_{18}H_{11}O_2N$ : C, 79.1; H, 4.0%). This m. p. is somewhat lower than that recorded by Boyes, Grieve, and Rule (*loc. cit.*), but, as they observed, the melting is accompanied by decomposition and is not very characteristic. For hydrolysis the amide (5 g.) was dissolved in sulphuric acid (100 c.c.) and treated at 0° with sodium nitrite (1.4 g.), added during 1 hour (mechanical stirring). After a further hour the mixture was poured on ice and the solid was collected and digested with aqueous sodium carbonate; the residue (4.2 g.) consisted of the unchanged amide, m. p. 312—314° (Found: C, 79.3; H, 4.1; N, 5.3%). The red alkaline solution was cautiously acidified till the red colour was just discharged; the small yellow precipitate obtained dissolved in alkali to give a purple solution with a red fluorescence and was obviously the lactone of 1-hydroxymesobenzanthrone-11-carboxylic acid (Boyes, Grieve, and Rule, *loc. cit.*). The yellow filtrate was made acid to Congo-paper; the acid which separated was esterified in dioxan solution with diazomethane. Methyl mesobenzanthrone-11-carboxylate, after passage through an alumina tower with benzene as the solvent, crystallised from methyl alcohol in yellow needles, m. p. 160—161°, both alone and in admixture with a specimen of the ester prepared from an authentic sample of the 11-carboxylic acid by the action of methyl alcohol on the acid chloride (Found: C, 78.9; H, 4.4. Calc. for  $C_{19}H_{12}O_3$ : C, 79.2; H, 4.1%). *meso*Benzanthrone-11-carboxylic acid, prepared from the ester by alkaline hydrolysis, crystallised from chlorobenzene or acetic acid in slender yellow needles, m. p. 267—268°, both alone and in admixture with the 11-carboxylic acid (Found: C, 79.0; H, 3.9. Calc. for  $C_{18}H_{10}O_3$ : C, 78.8; H, 3.6%). When the acid was moistened with sulphuric acid, a red colour developed, but a solution of the acid was deep yellow with a very intense golden fluorescence (cf. Rule, Pursell, and Barnett, *loc. cit.*); the alkaline solution of the acid was yellow with a brilliant greenish-yellow fluorescence.

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UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

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