290. *New Intermediates and Dyes. Part IV.* Condensation of Thionaphthen-2 : 3-dicarboxylic Anhydride with Hydrocarbons and Phenols.*

By Arnold T. Peters and Derek Walker.

Thionaphthen-2 : 3-dicarboxylic acid anhydride (I) and its 6-chloro-4-methyl derivative were condensed with acenaphthene to give 3-(3-acenaphthenylcarbonyl)thionaphthen-2-carboxylic acids, which could not be cyclised. The anhydride (I) reacted with phenol to yield a phenolphthalein analogue, or with quinol to give 6 : 11-dihydro-7 : 10-dihydroxy-6 : 11-dioxo benzo[*b*]thiophanthrene (III). Resorcinol and the anhydride (I) afforded a fluorescein analogue and also 3-(2 : 4-dihydroxybenzoyl)thionaphthen-2-carboxylic acid; the chemistry of this acid was examined and several lactones were derived from it.

Dyes for cellulose acetate and Nylon were prepared from the dione (III), and their properties compared with those of their anthraquinone analogues; loss of tinctorial power occurs on introduction of the thionaphthen ring.

The object of the present work was to investigate the nature of intermediates and dyes derived from the anhydride (I).

Mayer [1] showed that the anhydride reacted in a similar manner to phthalic anhydride, condensation with simple aromatic hydrocarbons in the Friedel–Crafts reaction giving solely 3-aroylthionaphthen-2-carboxylic acids, cyclisation yielding the corresponding 6 : 11-dihydro-6 : 11-dioxobenzo[*b*]thiophanthrenes.

Both thionaphthen-2 : 3-dicarboxylic acid anhydride and its 6-chloro-4-methyl derivative were condensed with acenaphthene to give 3-(3-acenaphthenylcarbonyl)thionaphthen-2-carboxylic acid (II) and its 6-chloro-4-methyl derivative, respectively. Neither carboxylic acid could be cyclised, although a variety of methods was used.

We prepared 6 : 11-dihydro-7 : 10-dihydroxy-6 : 11-dioxobenzo[*b*]thiophanthrene † (III) by the method of Mayer and Zahn,[2] *i.e.*, by heating the anhydride (I) with quinol in an

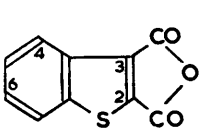
* Part III, *J.*, 1952, 1368.

† Cf. Ring Index No. 2502.

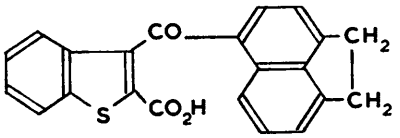
[1] Mayer (with Mombour, Lassmann, Werner, Landmann, and Schneider), *Annalen*, 1931, **488**, 259.

[2] Mayer and Zahn, G.P. 512,237/1927; B.P. 296,761/1927; U.S.P. 1,765,687/1930.

aluminium chloride–sodium chloride melt, and found it to be purified best through the crystalline diacetate. By condensing the anhydride (I) with *p*-chlorophenol, we obtained a 31% yield of 7(or 10)-chloro-10(or 7)-hydroxy-6 : 11-dioxobenzo[*b*]thiophanthrene, also purified through the acetoxy-compound.



(I)



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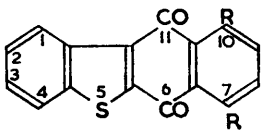
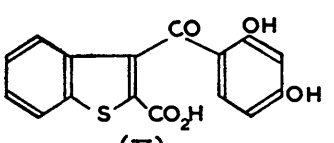


(III): R = OH
(IV): R = NHMe or NHBu^n

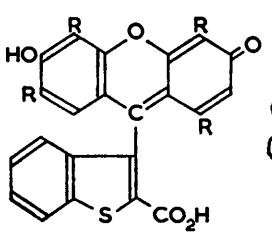
6 : 11-Dihydro-7 : 10-dihydroxy-6 : 11-dioxobenzo[*b*]thiophanthrene was only sparingly soluble in aqueous alkalis (contrast Mayer and Zahn [2]); its solution in pyridine assumed an intense royal blue colour when treated with a variety of aliphatic amines. The dione was readily converted into the 7 : 10-bismethylamino- and 7 : 10-bis-*n*-butylamino-compounds (IV) by heating it with sodium dithionite [hydrosulphite] and an alcoholic solution of the appropriate amine in a sealed tube at 140—145° and 135—140°, respectively; the dithionite assists the conversion by reducing part of the anthraquinone derivative to the corresponding *leuco*-compound.

The hitherto unknown 1 : 4-di-*n*-butylaminoanthraquinone was also prepared by a similar method from quinizarin, for comparison. The new dyes (IV) were best purified by chromatography. Both dye cellulose acetate and Nylon a pale greenish-blue, weaker than the royal blues produced by 1 : 4-bismethylamino- and 1 : 4-bis-*n*-butylamino-anthraquinone. Thus the introduction of the thiophen ring in the above manner caused loss in tinctorial power.

By condensing the anhydride (I) with resorcinol, Mayer [1] obtained a fluorescein derivative, which was not purified. We have studied the interaction of the anhydride (I) and resorcinol in the presence of zinc chloride at 150—210°, and two pure compounds, one red and one yellow, were isolated from the resinous reaction mass; a summary of the results is given in the Table on p. 1434. At the lower temperatures, the products were contaminated with much starting material, and the best separation of the products was obtained after reaction at 165—175°; at 210°, relatively high yields of the red fluorescein analogue were formed. Chemical evidence and analysis of the yellow compound, and also of its dibromo-derivative, suggested that it was a benzoyldihydroxythionaphthencarboxylic acid. As Mayer [1] had shown that the anhydride (I) condensed with aromatic compounds to yield solely 3-aroylthionaphthen-2-carboxylic acids, and as the condensation of phthalic anhydride with resorcinol was proved by Heller [3] to give 2-(2 : 4-dihydroxybenzoyl)benzoic acid, the above yellow compound was probably 3-(2 : 4-dihydroxybenzoyl)thionaphthen-2-carboxylic acid (V), convertible into its dibromo-derivative. In the view of Orndorff and



(V)



(VI): R = H
(VII): R = Br

Kline,[4] 2-(2 : 4-dihydroxybenzoyl)benzoic acid is an intermediate in the formation of fluorescein. If formula (V) is correct, then the derived fluorescein and eosin derivative can be designated as (VI) and (VII) respectively.

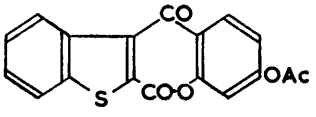
[3] Heller, *Ber.*, 1895, **28**, 312.
[4] Orndorff and Kline, *J. Amer. Chem. Soc.*, 1924, **46**, 2276.

The ultraviolet absorption spectra of the red fluorescein analogue and of fluorescein itself are very similar, and quite different from that of 3-(2 : 4-dihydroxybenzoyl)thionaphthen-2-carboxylic acid.

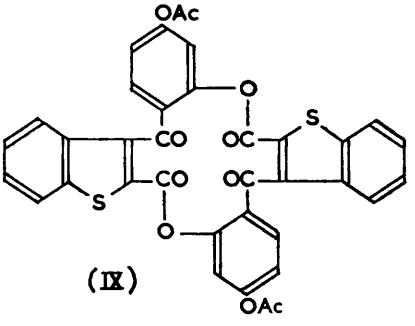
Further investigation of the last-named acid and of its dibromo-derivative led to interesting results. Neither acid could be cyclised by standard procedures; both formed insoluble lead, silver, and mercuric salts, and the copper and barium salts were soluble in hot but insoluble in cold water. 3-(2 : 4-Dihydroxybenzoyl)thionaphthen-2-carboxylic acid behaved as a monobasic acid towards methyl-red (titrated in aqueous alcohol with 0·1N-alkali) but as a dibasic acid towards phenolphthalein: we found 2:4-dihydroxybenzoyl-*o*-benzoic acid to behave similarly.

When 3-(2 : 4-dihydroxybenzoyl)thionaphthen-2-carboxylic acid was refluxed with acetic anhydride alone, or with acetyl chloride in an inert solvent, a yellow compound, $C_{18}H_{10}O_5S$, insoluble in sodium hydrogen carbonate solution and in cold aqueous sodium hydroxide, was obtained. This acetylation product dissolved rapidly in warm aqueous sodium hydroxide, and acidification then gave the above carboxylic acid. The yellow compound crystallised unchanged from benzene: in addition to acetylation, anhydride formation had occurred, to yield probably one of the two compounds (VIII) and (IX). Both such types have been recorded: Orndorff and Kline [4] claimed that, when 2-(2 : 4-dihydroxybenzoyl)benzoic acid was refluxed in acetic anhydride alone, the lactone (X) was formed, whereas the lactide resulted when the pure acid was refluxed in acetyl chloride.

Baker and his co-workers [5] have shown that both 2-carboxy-2'-hydroxybenzophenone and its 5'-methyl derivative yielded simple lactones with acetic anhydride, but gave lactides with phosphoric oxide, phosphorus oxychloride, or trifluoroacetic anhydride; the lactones were much more readily hydrolysed than the lactides. The use of acetic anhydride in the present work probably gave the lactone (VIII), which shows properties similar to



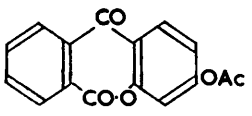
(VIII)



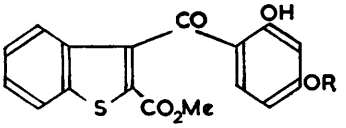
(IX)

those of other lactones.[4, 5] The lactone (VIII) is very readily hydrolysed, even by boiling water; when crystallised from methyl alcohol it afforded the methyl ester (XI), thus resembling the lactone (X).

When 3-(2 : 4-dihydroxybenzoyl)thionaphthen-2-carboxylic acid was refluxed with acetyl chloride in an inert solvent, the lactone (VIII) and a product sparingly soluble in

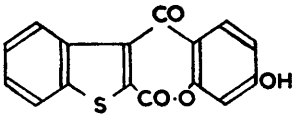


(X)



(XI): R = Ac

(XIII): R = H



(XII)

benzene resulted; the latter was not isolated when a large excess of acetyl chloride was used and is probably an intermediate in the formation of the lactone (VIII), into which it can be converted by acetyl chloride. The new product is insoluble in aqueous sodium hydrogen carbonate but soluble in aqueous sodium hydroxide, and is the lactone (XII) of

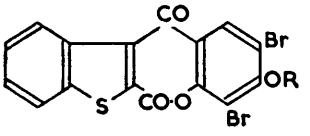
[5] Baker, Clark, Ollis, and Zealley, *J.*, 1952, 1452.

3-(2 : 4-dihydroxybenzoyl)thionaphthen-2-carboxylic acid; it was prepared in 93% yield by refluxing the acid with thionyl chloride in an inert solvent and is readily hydrolysed by aqueous alkalis.

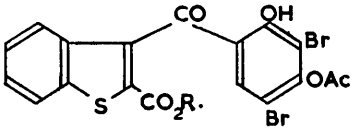
Crystallisation of the lactone (XII) from methyl alcohol gave the methyl ester (XIII), also prepared by the Fischer–Speier method from 3-(2 : 4-dihydroxybenzoyl)thionaphthen-2-carboxylic acid.

Benzoyl chloride in an inert solvent converted 3-(2 : 4-dihydroxybenzoyl)thionaphthen-2-carboxylic acid into the benzoylated lactone, analogous to the lactone (VIII).

3-(3 : 5-Dibromo-2 : 4-dihydroxybenzoyl)thionaphthen-2-carboxylic acid behaved in identical manner to the unbrominated acid. Thus, acetyl chloride in an inert solvent converted it into the easily hydrolysable lactone (XIV), which on crystallisation from aqueous acetic acid gave the acetate (XV) or from methanol afforded the methyl ester (XVI).



(XIV): R = Ac
(XVII): R = H



(XV): R = H
(XVI): R = Me

When the dibromo-acid was refluxed with thionyl chloride in an inert solvent, the simple lactone (XVII) resulted.

Experimental

Thionaphthen-2 : 3-dicarboxylic Anhydride (I) (cf. Friedländer and his co-workers [6]).—Sodium 3-hydroxythionaphthen-2-carboxylate (80 g.) was converted through 3-hydroxythionaphthen into 2 : 3-dihydro-2 : 3-dioxothionaphthen (31·7 g.), golden-yellow prisms (from ethanol), m. p. 119°, and thence into thionaphthen-2 : 3-dicarboxylic acid (30·3 g.) and into its anhydride (I), which crystallised from acetic anhydride in stout, colourless needles, m. p. 171° (overall yield, 25 g., 33%).

6-*Chloro*-4-*methylthionaphthen*-2 : 3-*dicarboxylic Anhydride*.—6-Chloro-3-hydroxy-4-methylthionaphthen (7·9 g.) gave, through the dione, yellow needles (from methanol), m. p. 129—130°, the dicarboxylic acid (7·6 g.), m. p. 259—260° (from acetic acid), and thence the anhydride (6·8 g.), light brown needles (from acetic anhydride), m. p. 188—189°.

3-(3-*Acenaphthenylcarbonyl*)*thionaphthen*-2-*carboxylic Acid* (II).—Aluminium chloride (10 g., 2·2 mols.), acenaphthene (5·25 g., 1 mol.), and thionaphthen-2 : 3-dicarboxylic anhydride (7 g., 1 mol.) in dry nitrobenzene (50 ml.) were stirred at room temperature for 2 days. After decomposition of the mixture with ice and hydrochloric acid, the nitrobenzene was distilled with steam; the residue was extracted with boiling 7% aqueous sodium carbonate and then with boiling water (the sodium salt is only sparingly soluble). The extracts were treated with charcoal, filtered, and allowed to cool; the *sodium salt* of the acid (II) then crystallised in colourless leaflets, m. p. 320° (decomp.) (Found: C, 69·4; H, 3·4; Na, 6·1. $C_{22}H_{13}O_3SNa$ requires C, 69·5; H, 3·4; Na, 6·0%). The *acid* (II) (10·5 g., 82·3%) was obtained by refluxing the sodium salt in aqueous ethanol containing hydrochloric acid, or by refluxing it with acetic acid, and crystallisation from acetic acid gave colourless needles, m. p. 274—275° (decomp.) (Found: C, 73·2; H, 4·2; S, 8·9. $C_{22}H_{14}O_3S$ requires C, 73·7; H, 3·9; S, 8·9%). The acid dissolves in 20% oleum with a deep blue colour, changing to reddish-brown at room temperature in 30 min. The *methyl ester*, prepared by the Fischer–Speier method, crystallised from methanol in colourless needles, m. p. 157° (Found: S, 8·5. $C_{23}H_{16}O_3S$ requires S, 8·6%).

3-(3-*Acenaphthenylcarbonyl*)-6-*chloro*-4-*methylthionaphthen*-2-*carboxylic Acid*.—By the above procedure, acenaphthene (3·0 g., 1 mol.) and 6-chloro-4-methylthionaphthen-2 : 3-dicarboxylic anhydride (5·0 g., 1 mol.) gave the *sodium salt* (Found: Cl, 8·5; S, 7·7; Na, 5·4. $C_{23}H_{14}O_3ClSNa$ requires Cl, 8·3; S, 7·5; Na, 5·4%), converted into the *acid* (6·2 g., 77%), which crystallised from ethanol in colourless needles, m. p. 289—290° (Found: Cl, 8·3; S, 7·4. $C_{23}H_{15}O_3ClS$ requires Cl, 8·7; S, 7·9%).

[6] Friedländer, Bezdrick, and Koeniger, *Ber.*, 1908, **41**, 237.

Attempted Cyclisation of 3-(3-*Acenaphthenylcarbonyl*)*thionaphthen*-2-*carboxylic Acid and its* 6-*Chloro*-4-*methyl Derivative*.—The following reagents were tried on both carboxylic acids: sulphuric acid and 20% oleum at room temperature, phosphoric oxide at 120°, aluminium chloride on the acid chloride in carbon disulphide at room temperature or in nitrobenzene at 120—130°, and molten aluminium chloride–sodium chloride at 150—180°. Further methods tried with the acid (II) included benzoyl chloride in chloronaphthalene at 200° (Beyer and Richter [7]), boiling benzoyl chloride for 1 hr., and boiling acetic anhydride for 10—24 hr. In no case was a cyclised product isolated; water-soluble products resulted from the sulphuric acid experiments and the only other products isolated were unchanged material or intractable resins.

Condensation of the Anhydride (I) *with Phenol : Phenolphthalein Analogue*.—Thionaphthen-2 : 3-dicarboxylic anhydride (2 g., 1 mol.), phenol (3·7 g., 4 mols.), and anhydrous zinc chloride (5·4 g., 4 mols.) were heated together at 120° for 2 hr.; the temperature was raised to 160° during 1 hr. and kept thereat for a further 3 hr. The dark red product was extracted with ethanol, and the solution treated with cold water; a black tar was deposited; the liquor was decanted, water added to it, and phenol distilled off with steam. A yellow solid, m. p. 220—225°, was deposited from the residual solution during several days (the filtrate from it was shown to contain some thionaphthen-2 : 3-dicarboxylic acid). The solid was purified by boiling its ethanol solution with charcoal and adding it to water, collecting the solid, and then boiling this in 10% aqueous sodium hydroxide solution, filtering the mixture, and acidifying the alkaline filtrate with hydrochloric acid. Both processes were repeated; the final yellow amorphous solid had m. p. 228—231° (Found: S, 8·6. $C_{22}H_{16}O_5S$ requires S, 8·2%). The *phenolphthalein analogue* dissolves in aqueous sodium hydroxide to a deep and permanent bluish-red solution.

Reaction of Anhydride (I) *with Quinol:* 6 : 11-*Dihydro*-7 : 10-*dihydroxy*-6 : 11-*dioxobenzo*[b]-*thiophanthrene* (III).—To a stirred melt of aluminium chloride (50 g.) and sodium chloride (10 g.) at 160° was added a powdered mixture of thionaphthen-2 : 3-dicarboxylic anhydride (10 g.) and quinol (10 g.); the temperature was raised to 190° and kept there for 6 hr. After decomposition of the dark red mass with dilute hydrochloric acid and filtration, the solid was treated with boiling acetic anhydride (450 ml.) and a few drops of concentrated sulphuric acid, to give 7 : 10-*diacetoxy*-6 : 11-*dihydro*-6 : 11-*dioxobenzo*[b]*thiophanthrene*, which crystallised from acetic acid in bright yellow needles, m. p. 241—242° (Found: C, 63·4; H, 3·2; S, 8·4. $C_{20}H_{12}O_6S$ requires C, 63·2; H, 3·2; S, 8·4%). The dihydroxy-diketone was obtained by warming the diacetate with concentrated sulphuric acid on the water-bath until the solution was bright blue and pouring it into water; the dione crystallised from pyridine in red laminæ, m. p. 254—256° (8·1 g., 55·8%). The analytical specimen was prepared by sublimation *in vacuo* at 220°, in dark red needles, m. p. 257—258° (Found: C, 65·0; H, 2·9; S, 10·6. Calc. for $C_{16}H_8O_4S$: C, 64·9; H, 2·7; S, 10·8%). The same product was obtained in only low yield from the anhydride (I), quinol, and zinc chloride at 185°, much unchanged anhydride being recovered. The brownish-yellow alkaline dithionite vat of the dione afforded, in air, a blue suspension, probably of the sodium salt of the dione. Reaction of the dione in pyridine with alcoholic potassium hydroxide gave a royal-blue precipitate, and deep royal-blue solutions resulted on interaction with primary aliphatic amines, but not aromatic amines.

7(or 10)-*Chloro*-6 : 11-*dihydro*-10(or 7)-*hydroxy*-6 : 11-*dioxobenzo*[b]*thiophanthrene*.—Replacement of quinol by *p*-chlorophenol (10 g.) in the above experiment gave yellow needles (from acetic anhydride) of the *acetoxy-diketone*, m. p. 249—250° (Found: C, 60·3; H, 2·5. $C_{18}H_9O_4ClS$ requires C, 60·6; H, 2·5%). This was warmed with concentrated sulphuric acid to give the *hydroxy-compound* (4·8 g., 31%), which sublimed *in vacuo* at 200°/3 mm. in orange-red needles, m. p. 260—261° (Found: C, 61·5; H, 2·3; Cl, 10·9; S, 10·2. $C_{16}H_7O_3ClS$ requires C, 61·0; H, 2·2; Cl, 11·3; S, 10·2%). It gave a reddish-blue solution in cold concentrated sulphuric acid.

6 : 11-*Dihydro*-7 : 10-*bismethylamino*-6 : 11-*dioxobenzo*[b]*thiophanthrene* (IV).—The dihydroxy-diketone (2 g.), sodium dithionite (2 g.), and 33% ethanolic methylamine (12 ml.) were heated in a sealed tube at 140—145° for 8 hr. The crude product was washed with warm water, dried (2 g.), extracted with toluene, and chromatographed on alumina, with toluene as eluant. 6 : 11-*Dihydro*-7 : 10-*bismethylamino*-6 : 11-*dioxobenzo*[b]*thiophanthrene* separated from impurities as an intense bluish-green band, eluted to a deep blue solution; crystallisation from toluene gave blue needles, m. p. 260° (1·44 g., 66·2%) (Found: C, 67·2; H, 4·6; N, 8·3; S, 10·2. $C_{18}H_{14}O_2N_2S$ requires C, 67·1; H, 4·4; N, 8·7; S, 10·0%). A small royal-blue band which

[7] Beyer and Richter, *Ber.*, 1940, **73**, 1325.

remained on the alumina column was extracted with acetic acid to give a blue solid, m. p. 170—184°, not investigated further.

7 : 10-*Bis*-n-*butylaminobenzo*[*b*]*thiophanthrene*-6 : 11-*dione* (IV).—The dihydroxy-diketone (2 g.), sodium dithionite (2 g.) and 33% ethanolic *n*-butylamine (14 ml.) were heated at 135—140° for 8 hr. The crude product was frequently obtained as a tar, and its acetone solution was dried (K_2CO_3); removal of acetone, followed by extraction with benzene and chromatography on alumina, gave a bluish-green band and thence bluish-violet needles (1·34 g., 49%). Crystallisation from light petroleum (b. p. 60—80°) gave the *bis*-n-*butylamino-derivative* as bluish-violet needles with a coppery lustre, m. p. 151° (Found : C, 71·0; H, 6·2; N, 6·8; S, 8·1. $C_{24}H_{26}O_2N_2S$ requires C, 70·9; H, 6·5; N, 6·9; S, 7·9%). A brown band remaining on the column was not examined.

1 : 4-*Bis*-n-*butylaminoanthraquinone*.—Recrystallised quinizarin (2 g.), sodium dithionite (2 g.), and 33% ethanolic *n*-butylamine (20 ml.) were heated at 140° for 8 hr. The product was dried in a vacuum, extracted with toluene, and purified by chromatography; toluene eluted a faint orange band (not examined), followed by the main intense blue band. Removal of solvent and crystallisation from light petroleum (b. p. 60—80°) afforded purple needles with a coppery lustre, m. p. 122°, of 1 : 4-*bis*-n-*butylaminoanthraquinone* (1·1 g., 38%) (Found : C, 75·2; H, 7·3; N, 8·4. $C_{22}H_{26}O_2N_2$ requires C, 75·4; H, 7·5; N, 8·0%). This compound dyes cellulose acetate and Nylon a deep blue shade.

Condensation of the Anhydride (I) *with Resorcinol, to give a Fluorescein Analogue* (VI) *and* 3-(2 : 4-*Dihydroxybenzoyl*)*thionaphthen*-2-*carboxylic Acid* (V).—The anhydride (I) (8·2 g., 1 mol.) and resorcinol (8·8 g., 2 mols.) were melted together at 170° (internal temp.), and fused zinc chloride (3·4 g., 0·63 mol.) was added. After about 10 min., the mixture was too viscous to stir. It was then cooled to 90°, concentrated hydrochloric acid (2 ml.) in water (38 ml.) added, and the suspension boiled for 20 min. When cold, the plastic solid and crystals were filtered off. The plastic mass was dispersed to a yellow solid when ground with water; the total solid was then extracted with boiling 5% sodium carbonate solution (300 ml.) (charcoal) and the alkaline extract was filtered and acidified with hydrochloric acid; the resulting solid was dissolved in boiling acetic acid, and hot water added dropwise. First, the red granular fluorescein analogue was deposited; when the volume of the suspension was *ca.* 500 ml., the red solid was filtered off hot, and the filtrate allowed to cool, whereupon yellow needles separated. The *fluorescein analogue* (VI) was purified by repeating the above process and was a red granular solid, m. p. 287—289° (decomp.) (3·2 g., 20·5%) (Found : C, 68·4; H, 3·3; S, 8·5. $C_{22}H_{12}O_5S$ requires C, 68·0; H, 3·1; S, 8·3%). It is insoluble in ether, carbon tetrachloride, benzene, and *o*-dichlorobenzene, sparingly soluble in acetone and alcohols and moderately soluble in acetic acid. Its orange-red alkaline solution shows a strong green fluorescence. The above yellow needles of 3-(2 : 4-*dihydroxybenzoyl*)*thionaphthen*-2-*carboxylic acid* (V) were crystallised several times from dilute acetic acid; they then had m. p. 254—255° (3·6 g., 28·6%) (Found : C, 61·3; H, 3·5; S, 10·6. $C_{16}H_{10}O_5S$ requires C, 61·1; H, 3·2; S, 10·2%). Although the yellow colour could not be removed by crystallisation from alcohol or acetic acid, a colourless sample was obtained by hydrolysis of the lactone (VIII) (see below). Aqueous-alcoholic solutions of the acid became reddish-brown on addition of ferric chloride solution. The acid is insoluble in carbon tetrachloride, sparingly soluble in benzene and cold water, soluble in *o*-dichlorobenzene and hot water, and very soluble in alcohols, acetone, ether, and acetic acid.

Interaction of the anhydride (I) (4·1 g., 1 mol.) and resorcinol (4·4 g., 2 mols.) at the temperatures shown (initial and final internal temperatures) gave the results tabulated.

Temp.	Time (min.)	Compound (VI) (g.)	Acid (V) (g.)	Temp.	Time (min.)	Compound (VI) (g.)	Acid (V) (g.)
150—155°	25	0·6	2·8	160—170°	25	1·3	2·0
150—155	40	0·5	2·4	165—175	25	1·7	2·2
150—160	15	1·8	1·9	180—195	5	1·6	1·9
160—167	15	0·8	1·5	210—225	1	2·6	1·3

Eosin Analogue (VII).—Excess of bromine (4·0 g.) was added slowly to the above red fluorescein analogue (2 g.) in absolute alcohol (10 ml.), and the mixture shaken for 1 hr.; the precipitate was filtered off and the *eosin analogue* (VII) crystallised from absolute alcohol in maroon needles, m. p. 295—297° (2·1 g., 57·8%) (Found : C, 37·7; H, 1·4; Br, 44·9; S, 4·7. $C_{22}H_8O_5Br_4S$ requires C, 37·5; H, 1·2; Br, 45·4; S, 4·6%).

3-(3 : 5-*Dibromo*-2 : 4-*dihydroxybenzoyl*)*thionaphthen*-2-*carboxylic Acid*.—3-(2 : 4-Dihydroxybenzoyl)thionaphthen-2-carboxylic acid (2 g.) in absolute alcohol (10 ml.) was treated with

bromine (4·0 g.), and the orange mixture shaken for 1 hr. The precipitated *dibromo-acid* was washed, and crystallised from acetic acid in orange prisms, m. p. 256—257°, containing 1 mol. of acetic acid of crystallisation (Found : C, 40·4; H, 2·1; Br, 30·2; S, 6·1. $C_{18}H_{12}O_7Br_2S$ requires C, 40·6; H, 2·3; Br, 30·0; S, 6·0%). The solvent was removed at 130° in 12 hr., with a change in colour from orange to a dull pink (2·2 g., 80·9%) (Found : C, 40·7; H, 2·1; Br, 34·0; S, 6·6. $C_{16}H_8O_5Br_2S$ requires C, 40·7; H, 1·7; Br, 33·9; S, 6·8%). Almost colourless specimens could be obtained by hydrolysing the lactone (XIV) (see below later).

3-(4-*Acetoxy*-2-*hydroxybenzoyl*)*thionaphthen*-2-*carboxylic Lactone* (VIII).—(a) *Use of acetyl chloride.* 3-(2 : 4-Dihydroxybenzoyl)thionaphthen-2-carboxylic acid (1·5 g., 1 mol.), xylene (50 ml.), and acetyl chloride (1·5 ml., 4 mols.) were refluxed for 12 hr. Yellow needles, m. p. 194—197°, were deposited on cooling. Recrystallisation from light petroleum (b. p. 60—80°)–benzene (1 : 1) afforded yellow needles, m. p. 199—200° (1·45 g., 90%) (Found : C, 63·7; H, 2·7; S, 9·6. $C_{18}H_{10}O_5S$ requires C, 63·9; H, 3·0; S, 9·5%), of the *lactone* (VIII). A small amount of crystals, insoluble in the light petroleum–benzene, was obtained unless larger quantities (4 ml.) of acetyl chloride were used. Crystallisation of this by-product from acetic acid yielded yellow needles, m. p. 289°, of the unacetylated lactone (XII).

(b) *Use of acetic anhydride.* The carboxylic acid (V) (1 g.) was refluxed with acetic anhydride (50 ml.) for 12 hr. and gave 91% (0·96 g.) of the lactone (VIII), m. p. and mixed m. p. 199—200°.

The acetylated lactone (VIII) was completely hydrolysed by refluxing 1% aqueous sodium hydroxide in 5 min., aqueous sodium hydrogen carbonate in 2 hr., or dilute hydrochloric acid (1 : 10) in 6 hr., to yield almost colourless needles, m. p. 254—255°, of 3-(2 : 4-dihydroxybenzoyl)thionaphthen-2-carboxylic acid. When the lactone (VIII) was refluxed in distilled water for 18 hr., 43% was hydrolysed.

Methyl 3-(4-*Acetoxy*-2-*hydroxybenzoyl*)*thionaphthen*-2-*carboxylate* (XI).—The acetylated lactone (VIII) (1 g.) was refluxed with methyl alcohol for 12 hr. and, on cooling, colourless needles, m. p. 175—176°, of the *methyl ester* (XI) (0·95 g.) were obtained (Found : C, 61·6; H, 3·8; S, 9·0. $C_{19}H_{14}O_6S$ requires C, 61·6; H, 3·8; S, 8·7%).

3-(2 : 4-*Dihydroxybenzoyl*)*thionaphthen*-2-*carboxylic Lactone* (XII).—Freshly distilled thionyl chloride (1·4 g.) was refluxed with 3-(2 : 4-dihydroxybenzoyl)thionaphthen-2-carboxylic acid (1·5 g.) in dry toluene (100 ml.) for 24 hr. On cooling, the crystals, m. p. 284—286°, were collected and recrystallised from acetic acid in bright yellow needles of the *lactone* (XII), m. p. 289° (decomp.) (1·32 g., 93·6%) (Found : C, 64·8; H, 2·3; S, 11·0. $C_{16}H_8O_4S$ requires C, 64·9; H, 2·7; S, 10·8%). Hydrolysis with boiling dilute aqueous sodium hydrogen carbonate afforded colourless needles, m. p. 254—255°, of 3-(2 : 4-dihydroxybenzoyl)thionaphthen-2-carboxylic acid.

The lactone (XII) (0·5 g.), acetyl chloride (1 ml.), and toluene (80 ml.), refluxed for 13 hr., and then treated with light petroleum (b. p. 60—80°) (80 ml.) when cold, afforded yellow needles, m. p. 199—200°, of the acetylated lactone (VIII) (0·56 g., 98%).

Methyl 3-(2 : 4-*Dihydroxybenzoyl*)*thionaphthen*-2-*carboxylate* (XIII).—The lactone (XII) (1 g.) was refluxed in methyl alcohol (50 ml.) to give, after crystallisation from acetic acid, colourless plates, m. p. 206—207°, of the *methyl ester* (XIII) (1 g., 96%) (Found : C, 62·2; H, 3·8; S, 9·4. $C_{17}H_{12}O_5S$ requires C, 62·2; H, 3·7; S, 9·8%). It was also obtained by refluxing 3-(2 : 4-dihydroxybenzoyl)thionaphthen-2-carboxylic acid (1 g.) in methanol (100 ml.) saturated with hydrogen chloride, for 18 hr. (0·8 g., 77%).

Benzoylated Lactone of 3-(2 : 4-*Dihydroxybenzoyl*)*thionaphthen*-2-*carboxylic Acid.*—The carboxylic acid (1 g.) was refluxed with benzoyl chloride (1·4 g.) in toluene (60 ml.) for 10 hr.; an equal volume of light petroleum (b. p. 100—120°) was added; the *benzoylated lactone* separated; crystallisation from toluene–light petroleum gave pale yellow needles, m. p. 209—210° (1·1 g., 86%) (Found : C, 69·1; H, 2·9; S, 7·9. $C_{23}H_{12}O_5S$ requires C, 69·0; H, 3·0; S, 8·0%).

Acetylated Lactone of 3-(3 : 5-*Dibromo*-2 : 4-*dihydroxybenzoyl*)*thionaphthen*-2-*carboxylic Acid* (XIV).—(*a*) The carboxylic acid (1·5 g.) was refluxed with acetyl chloride (1 g.) in xylene (50 ml.) for 15 hr. Crystallisation of the product from benzene–light petroleum (b. p. 60—80°) afforded pale yellow needles of the *lactone* (XIV), m. p. 214—215° (1·47 g., 93%) (Found : C, 43·4; H, 1·3; Br, 32·1; S, 6·6. $C_{18}H_8O_5Br_2S$ requires C, 43·6; H, 1·6; Br, 32·2; S, 6·5%).

(*b*) The carboxylic acid (1 g.), refluxed with acetic anhydride (50 ml.) for 12 hr., yielded the lactone (XIV) (0·9 g., 85·6%). This lactone was readily hydrolysed by boiling aqueous sodium hydrogen carbonate to the colourless acid, which after heating at 130° gave m. p. and mixed m. p. with the pink sample obtained as above, 256—257° (Found : Br, 33·8; S, 6·8%).

3-(4-*Acetoxy*-3 : 5-*dibromo*-2-*hydroxybenzoyl*)*thionaphthen*-2-*carboxylic Acid* (XV).—The above

lactone (XIV) was crystallised from acetic acid containing a little water, to give colourless, hexagonal plates, m. p. 209—210°, of the *acid* (XV) (Found : C, 42·4; H, 2·2; Br, 31·0; S, 6·4. $C_{18}H_{10}O_6Br_2S$ requires C, 42·0; H, 2·0; Br, 31·1; S, 6·2%), soluble in aqueous sodium hydrogen carbonate with a yellow colour.

Methyl 3-(4-*Acetoxy*-3 : 5-*dibromo*-2-*hydroxybenzoyl*)*thionaphthen*-2-*carboxylate* (XVI).—The dibrominated acetyl lactone (XIV) (1 g.) was refluxed with methanol (60 ml.) for 12 hr., to give yellow plates, m. p. 194—195°, of the *methyl ester* (XVI) (1·96 g.) (Found : C, 42·7; H, 2·3; Br, 30·3; S, 6·4. $C_{19}H_{12}O_6Br_2S$ requires C, 43·2; H, 2·3; Br, 30·3; S, 6·1%).

3-(3 : 5-*Dibromo*-2 : 4-*dihydroxybenzoyl*)*thionaphthen*-2-*carboxylic Lactone* (XVII).—The carboxylic acid (1 g.) in chlorobenzene (100 ml.) was refluxed with thionyl chloride (1·5 ml.) for 6 hr. Buff-coloured needles were deposited; they crystallised from benzene containing a little light petroleum in yellow needles, m. p. 264—265° (0·72 g., 75%), of the *lactone* (XVII) (Found : Br, 35·3; S, 7·1. $C_{16}H_6O_4Br_2S$ requires Br, 35·2; S, 7·1%).

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