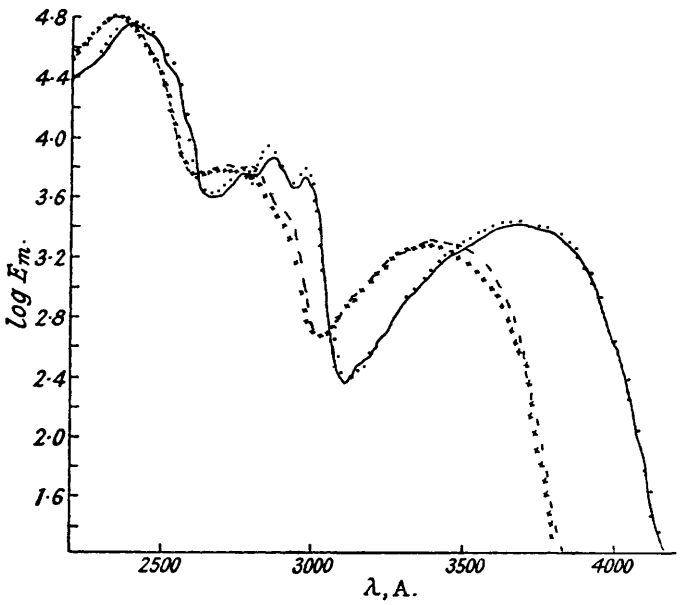
482. *Ultra-violet Spectrum and Constitution of 3-Hydroxy-2-naphthoic Acid and Related Compounds.*

By Ernst D. Bergmann, Y. Hirshberg, and S. Pinchas.

The ultra-violet absorption spectra of this acid and its methyl ester give indications of hydrogen-bonding in the acid, and this is supported by infra-red spectra. The ultra-violet spectra of the *O*-methyl derivatives of the above and of salicylic acid and its ester and also of certain acetylnaphthols are recorded.

It has long been known that 3-hydroxy-2-naphthoic acid (I) and its methyl ester are yellow (Schmidt and Burkard, *Ber.*, 1887, **20**, 2702; Strohbach, *Ber.*, 1901, **34**, 4153; H. Meyer, *Monatsh.*, 1901, **22**, 791), whilst 1-hydroxy-2- and 2-hydroxy-1-naphthoic acid and also

Fig. 1.



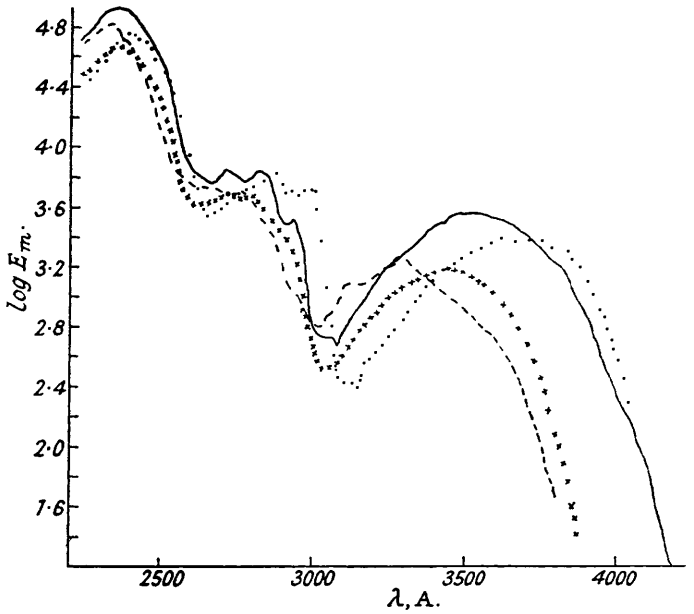
Dioxan solutions of 3-*hydroxy-2-naphthoic acid* (——); *methyl* 3-*hydroxy-2-naphthoate* (· · · ·); 3-*methoxy-2-naphthoic acid* (– – –); *methyl* 3-*methoxy-2-naphthoate* (× × ×).

3-methoxy-2-naphthoic acid (II) and its methyl ester are colourless. As no theoretical explanation of this somewhat surprising effect appears to have been attempted, an investigation was undertaken. Fig. 1 shows the absorption spectra of dioxan solutions of 3-hydroxy- and 3-methoxy-2-naphthoic acid and of their methyl esters in the ultra-violet (and the visible) region. The spectra of the respective free acids and their methyl esters are identical, but there are visible differences between the 3-hydroxy-compounds on the one hand and the 3-methoxy-derivatives on the other: especially, the maximum at 3700 A. in the spectrum of the hydroxy-acid is shifted into the ultra-violet (3400 A.) upon methylation. It is suggested that this difference is due to the occurrence of hydrogen bonding in the hydroxyl compounds (see below).

A second effect becomes evident if one compares the spectra of the dioxan (Fig. 1) and of the ethyl alcoholic (Fig. 2) solutions of the four compounds. The hydroxylic solvent does not affect the spectra of the two methyl esters, while those of the free acids are somewhat influenced, probably owing to a loose addition of solvent molecules to the carbonyl double bond of the carboxyl group, as is known for aldehydes and ketones (Herold and Wolf, *Z. physikal. Chem.*, 1931, *B*, **12**, 165, 194). It is in keeping with this hypothesis that the influence of the alcohol is much more prominent with 3-hydroxy-2-naphthoic acid than with the 3-methoxy-compound; indeed, there is almost no difference in the position of the " 3500-A. band " in the alcoholic solutions of the two compounds. It is reasonable to assume that the solvent competes with the

intramolecular hydrogen bond in the former acid and, thereby, destroys the cause of the difference between the spectra of the two acids.

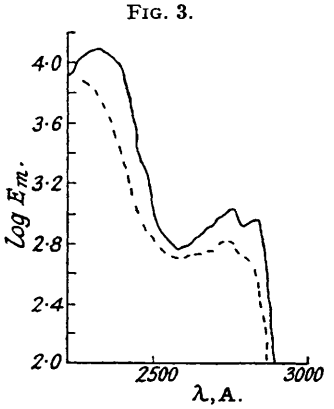
FIG. 2.



Alcoholic solutions of 3-*hydroxy*-2-*naphthoic acid* (——); *methyl* 3-*hydroxy*-2-*naphthoate* (· · ·); 3-*methoxy*-2-*naphthoic acid* (– – –); *methyl* 3-*methoxy*-2-*naphthoate* (× × ×).

This difference in the solvent-dependency of the spectra of free aromatic acids and their methyl esters seems to be fairly general. Scheibe (*Ber.*, 1926, **59**, 2617; cf. Wolf and Strasser, *Z. physikal. Chem.*, 1933, *B*, **21**, 389) has shown that ethyl benzoate has almost identical spectra in heptane and in methanol solutions, and Fig. 3 and Fig. 4 indicate the differences between the ultra-violet spectra in ethanol and in non-hydroxylic solvents for benzoic and 1- and 2-naphthoic acids. Whereas for benzoic and 2-naphthoic acid, the difference lies more in a decrease in intensity than in a shift of the maxima, on transition to ethanol, yet the effect in the case of 1-naphthoic acid is remarkable inasmuch as the longer band shifts by 140 A. to the ultra-violet in ethanol, as compared with dioxan (the spectra of the two naphthoic acids in hexane solution have been measured by de Laszlo, *Proc. Roy. Soc.*, 1926, *A*, **111**, 355).

FIG. 3.



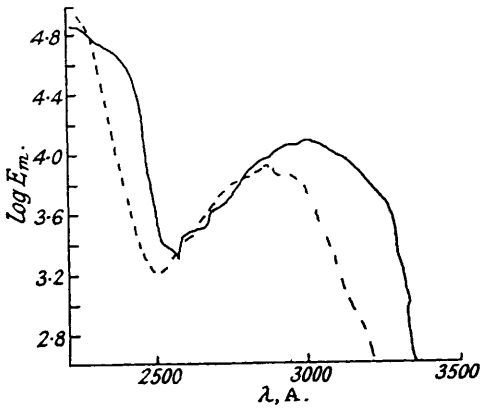
Benzoic acid in isooctane (——) *and alcohol* (– – –).

It is interesting to compare the behaviour of the corresponding phenyl compounds with that of the above naphthalene derivatives. As Fig. 5 shows, salicylic acid and methyl salicylate have the same absorption spectrum in non-hydroxylic solvents, and the same holds true for *o*-methoxybenzoic acid and its methyl ester. The longer absorption band of the hydroxy-compounds lies again nearer to the visible than that of the corresponding methoxy-derivatives. Comparison with Fig. 6, in which the analogous absorption spectra in ethyl alcohol are collated, proves that in this case also, the methyl esters are not affected by the change of solvent, whilst the free acids become more transparent in the hydroxylic solvent. However, the difference is smaller than in the naphthalene series [cf. Ley and v. Engelhardt, *Z. physikal. Chem.*, 1910, **74**, 43; Ley, *Z. wiss. Phot.*, 1919, **18**, 177 (*Centr.*, 1919, I, 947); Gibbs and Pratt, *Centr.*, 1913, II, 1045; Magini, *J. Chim. physique*, 1904, **2**, 403].

The spectrographic data are summarized in Table I.

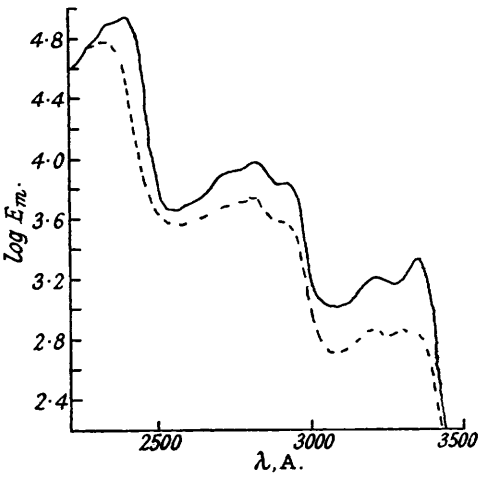
In order to verify the hypothesis offered, the infra-red absorption of methyl salicylate and methyl 3-hydroxy-2-naphthoate was studied. In carbon tetrachloride solution, and at a concentration of about 0·1 g./c.c., they showed an absorption at 3192 and 3245 cm.$^{-1}$, respectively, and with approximately the same intensity. This indicates strong hydrogen bonding. Buswell,

FIG. 4a.



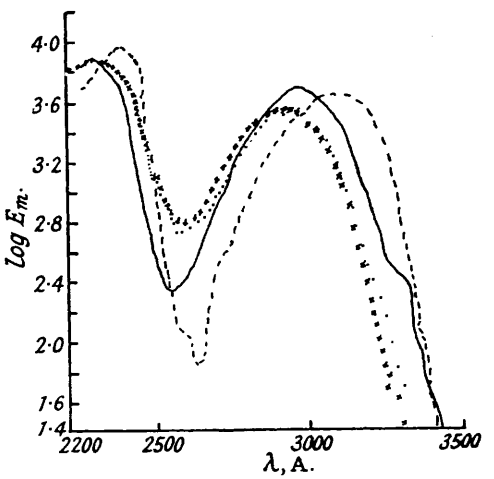
1-*Naphthoic acid in dioxan* (——) *and alcohol* (– – –).

FIG. 4b.



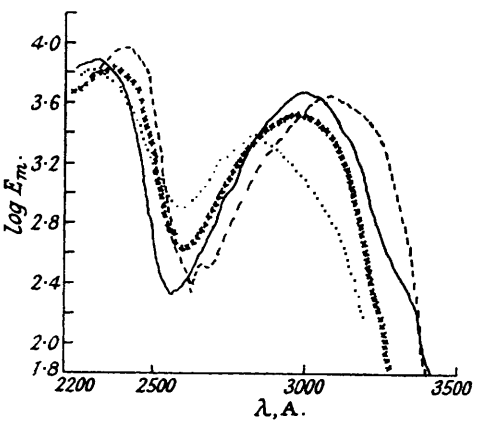
2-*Naphthoic acid in dioxan* (——) *and alcohol* (– – –).

FIG. 5.



Dioxan solutions of salicylic acid (——); *methyl salicylate* (– – –); o-*methoxybenzoic acid* (· · · ·); *methyl* o-*methoxybenzoate* (× × ×).

FIG. 6.



Alcoholic solutions of salicylic acid (——); *methyl salicylate* (– – –); o-*methoxybenzoic acid* (· · · ·) *methyl* o-*methoxybenzoate* (× × ×).

Deitz, and Rodebush (*J. Chem. Physics*, 1937, **5**, 501) found the hydroxyl absorption in methyl salicylate shifted to about 3350 cm.$^{-1}$ (cf. also Davies and Sutherland, *ibid.*, 1938, **6**, 755. For the modified carbonyl frequency, see Gordy, *J. Chem. Physics*, 1940, **8**, 516). The hydrogen bonding in salicylic acid expresses itself equally in the unusually high dissociation constant of that acid (Dippy *et al.*, *J.*, 1937, 1421; Branch and Yabroff, *J. Amer. Chem. Soc.*, 1934, **56**, 2568).

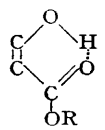
Now, a stable hydrogen-bonded ring implies the presence of a six-membered structure (III) with two conjugated double bonds (Sidgwick and Callow, *J.*, 1924, **125**, 527; W. Baker, *J.*, 1934,

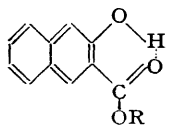
TABLE I.

Ultra-violet absorption maxima of aromatic o-hydroxy-acids and derivatives.

	Solvent.	λ, A.	log E_m.	λ, A.	log E_m.	λ, A.	log E_m.	λ, A.	log E_m.	λ, A.	log E_m.
3-Hydroxy-2-naphthoic acid	Dioxan	3680	3·41	2980	3·71	2860	3·87	2760	3·75	2390	4·74
	Alcohol	3280	3·28	—	—	2760	3·74	2660	3·78	2320	4·80
3-Hydroxy-2-naphthoic acid, methyl ester	Dioxan	3660	3·43	2980	3·76	2860	3·92	2760	3·78	2400	4·76
	Alcohol	3640	3·39	2980	3·73	2860	3·87	2760	3·74	2380	4·75
3-Methoxy-2-naphthoic acid	Dioxan	3410	3·28	—	—	2780	3·77	2700	3·78	2350	4·78
	Alcohol	3280	3·28	—	—	2760	3·74	2660	3·75	2320	4·80
3-Methoxy-2-naphthoic acid, methyl ester	Dioxan	3380	3·24	—	—	2690	3·74	—	—	2340	4·76
	Alcohol	3400	3·17	—	—	2780	3·67	2710	3·67	2340	4·65
Salicylic acid	Dioxan	3060	3·63	2370	3·89						
	Alcohol	2980	3·68	2310	3·88						
Salicylic acid, methyl ester	*iso*Octane	3080	3·63	2380	3·98						
	Alcohol	3060	3·64	2380	3·97						
o-Methoxybenzoic acid	Dioxan	2930	3·50	2320	3·84						
	Alcohol	2800	3·40	2260	3·82						
o-Methoxybenzoic acid, methyl ester	Dioxan	2920	3·54	2310	3·84						
	Alcohol	2940	3·54	2340	3·82						

1684; 1935, 628; 1936, 274, 346; *Nature*, 1936, **137**, 236; Hathway and Flett, *Trans. Faraday Soc.*, 1949, **45**, 818) and therefore, in the case of 3-hydroxy-2-naphthoic acid and its methyl

(III.) 

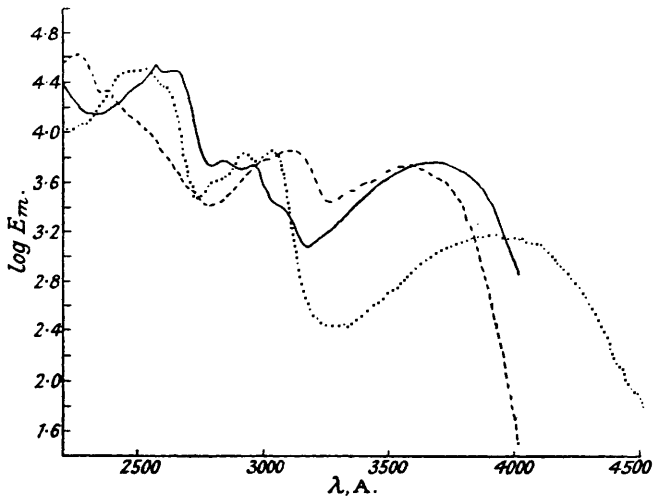
 (IV.)

ester, unusually large double-bond character of the 2 : 3-bond. The constitution at which one thus arrives, *viz.*, (IV), contains an *ortho*-quinoid ring system and may well account for the yellow colour of these compounds. It has already been emphasized by Bergmann and Berlin (*J. Org. Chem.*, 1939, **3**, 246; cf. E. Bergmann and Hirshberg, *J.*, 1936, 331) that the ability of 2-hydroxy-3-acetylnaphthalene oxime to form a complex copper derivative, points in the same direction. In this connection, it is noteworthy that the general belief that the 3-position is not a real " *ortho*-position " relative to the $C_{(2)}$ atom of the naphthalene nucleus, is based on an oversimplification of the facts. Huisgen (*Annalen*, 1949, **564**, 16; cf. *ibid.*, 1948, **559**, 101) has shown that in Combes's quinoline synthesis (*Compt. rend.*, 1888, **106**, 142, 1536; *Bull. Soc. chim.*, 1888, **49**, 89) 2-naphthylamine readily gives linear, not angular, annellation if the 1-position is suitably substituted. On the other hand, no hydrogen bonding was detected in 3-nitro-2-naphthylamine by infra-red absorption measurements or determination of the basic strength (Bryson, *Trans. Faraday Soc.*, 1949, **45**, 257; Hathway and Flett, *ibid.*, p. 818; cf. also Nolan, Slavin, and Wheeler, *J.*, 1950, 340; Ketelaar and van Dranen, *Rec. Trav. chim.*, 1950, **69**, 477).

In order to complete this study, the infra-red and ultra-violet absorption spectra of 1-acetyl-2-naphthol, 2-acetyl-1-naphthol, and 3-acetyl-2-naphthol were investigated. These measurements supplement the recent observations of Melchior (*J. Amer. Chem. Soc.*, 1949, **71**, 3647, 3651) on the isomeric *ortho*-hydroxynaphthaldehydes. In *iso*octane solution, each of the three hydroxy-ketones shows three absorption bands; the longest one distinguishes the 2 : 3-compound from its isomers; its maximum lies at 3900 A. (as against about 3600 A. for the isomers) (Fig. 7; Table II). In alcoholic solution, too (Fig. 8), there are pronounced differences: the spectrum of the 2 : 3-compound is practically unaffected, that of 1-acetyl-2-naphthol loses its structure without material change in location or intensity of the bands, and that of 2-acetyl-1-naphthol also shows less fine-structure, but a certain increase in the intensity of the longest band. In the infra-red region, 1-acetyl-2-naphthol shows very clearly the shift characteristic of the hydrogen-bonded hydroxyl (at 3360 $cm.^{-1}$), and in both 2-acetyl-1-naphthol and 3-acetyl-2-naphthol the hydroxyl band has merged into the C–H absorption between 3100 and 2900 $cm.^{-1}$. The effect is marked, but it seems that the carbonyl group in these ketones is less responsive to hydrogen bonding than the carbomethoxy-group in the corresponding esters. It may be added that in

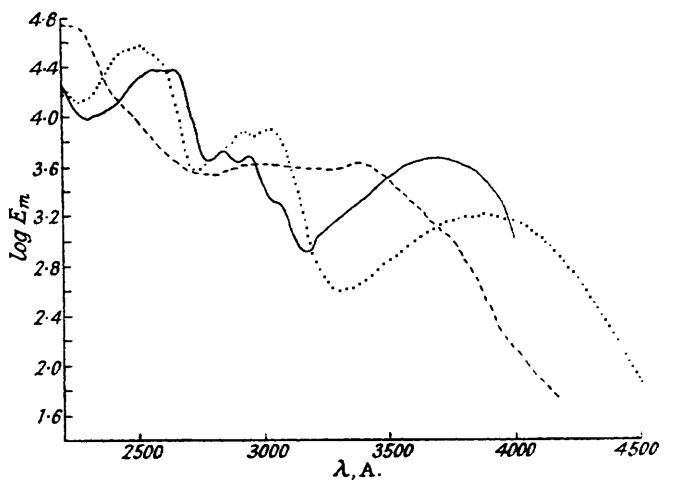
2-hydroxy-1-naphthaldehyde, too, which was studied for comparison, hydrogen bonding is indicated by the shift of the hydroxyl absorption to 3240 cm.$^{-1}$.

FIG. 7.



iso*Octane solutions of* 2-*acetyl*-1-*naphthol* (——); 1-*acetyl*-2-*naphthol* (– – –); 3-*acetyl*-2-*naphthol* (· · · ·).

FIG. 8.



Alcoholic solutions of 2-*acetyl*-1-*naphthol* (——); 1-*acetyl*-2-*naphthol* (– – –); 3-*acetyl*-2-*naphthol* (• • • •).

TABLE II.

Ultra-violet absorption maxima of the o-*acetylnaphthols.*

	Solvent.	λ, A.	log E_m.	λ, A.	log E_m.	λ, A.	log E_m.	λ, A.	log E_m.
2-Hydroxy-3-acetyl-	*iso*Octane	2500	4·54	2920	3·86	3020	3·88	3860	3·20
	Alcohol	2500	4·46	2940	3·80	3040	3·82	3900	3·18
2-Hydroxy-1-acetyl-	*iso*Octane	2250	4·60	—	—	3120	3·85	3580	3·73
	Alcohol	2270	4·71	—	—	2990	3·60	3370	3·58
1-Hydroxy-2-acetyl-	*iso*Octane	2560	4·58	2840	3·78[a]	2950	3·75	3660	3·76
	Alcohol	2560	4·39	2840	3·71[b]	2940	3·68	3660	3·66

[a] This maximum is accompanied by two less developed ones [2640 A. (4·50) and 2950 A. (3·75)].
[b] Slight maximum at 2640 A. (4·38).

Experimental.

The ultra-violet absorption spectra were measured by means of a Beckman spectrophotometer, the infra-red spectra by means of a Perkin–Elmer instrument (Model 12 C). In the latter case, carbon tetrachloride was used as solvent, and the following experimental data were recorded, a lithium fluoride prism and a 0·1-mm. cell being used: Methyl 3-hydroxy-2-naphthoate, 0·1 g./c.c.; absorption at 3245 cm.$^{-1}$, optical density, 0·50. Methyl salicylate, 0·12 g./c.c; absorption at 3192 cm.$^{-1}$, optical density 0·57. 2-Hydroxy-3-acetylnaphthalene, 0·04 g./c.c.; absorption in the 3100—3400 A. region (near the C–H band). 2-Hydroxy-1-acetylnaphthalene, 0·1 g./c.c.; absorption at 3360 cm.$^{-1}$, optical density 0·18. 1-Hydroxy-2-acetylnaphthalene, 0·03 g./c.c.; absorption at 3330 cm.$^{-1}$, optical density 0·07. 2-Hydroxy-1-naphthaldehyde, 0·1 g./c.c.; absorption at 3240 cm.$^{-1}$ (approx.), optical density 0·03.

Materials.—Benzoic acid, salicylic acid, methyl salicylate, *o*-methoxybenzoic acid, 3-hydroxy-2-naphthoic acid, and 2-hydroxy-1-naphthaldehyde were commercial samples; they were purified by the customary methods. Methyl *o*-methoxybenzoate was prepared by methylation of salicylic acid with an excess (3 mols.) of diazomethane; b. p. 127°/11 mm. (v. Auwers, *Annalen*, 1915, **408**, 252). Methyl 3-hydroxy-2-naphthoate was prepared according to Cohen and Dudley (*J.*, 1910, **97**, 1748; cf. Beilstein, 1st Suppl. Vol. X, p. 148); from methanol; m. p. 94°. Methyl 3-methoxy-2-naphthoate was also obtained by methylation of 3-hydroxy-2-naphthoic acid with diazomethane (3 mols.); it boiled at 217°/30 mm. and was recrystallized from light petroleum; m. p. 49° (Werner and Seybold, *Ber.*, 1904, **37**, 3661). Alkaline hydrolysis, according to Cohen and Dudley (*loc. cit.*), gave 3-methoxy-2-naphthoic acid; m. p. 133°, from dilute alcohol.

1-Acetyl-2-naphthol was prepared (Fries, *Ber.*, 1921, **54**, 711; Fries and Ehlers, *Ber.*, 1923, **56**, 1305) by Fries arrangement of 2-naphthyl acetate (Miller, *Ber.*, 1881, **14**, 1602); it boiled at 183—185°/26 mm. and crystallized from light petroleum in diamond-shaped crystals, m. p. 65°. 2-Acetyl-1-naphthol (Witt and Braun, *Ber.*, 1914, **47**, 3219) was obtained by acetylation of 1-naphthol in presence of zinc chloride as catalyst. Repeated crystallization from *iso*propanol and methanol gave well-defined crystals of m. p. 101°.

For the synthesis of 3-acetyl-2-naphthol the method of Fries and Schimmelschmidt was employed (*Ber.*, 1925, **58**, 2838; cf. E. Bergmann and Berlin, *loc. cit.*).

For the synthesis of the naphthoic acids, the Grignard reaction was used (*Org. Synth.*, Coll. Vol. II, p. 425; Gilman and St. John, *Rec. Trav. chim.*, 1929, **48**, 744); both acids were recrystallized from dibutyl ether; m. p. 161° and 185°, respectively.

In the determination of the ultra-violet spectra, the authors were assisted by Mrs. H. Hartstein.

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