

Shearing and Smiles : Dehydrodi-2-hydroxy-1-naphthylmethane. 1931**406. *Dehydrodi-2-hydroxy-1-naphthylmethane.***

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The structures assigned by previous investigators to dehydrodi-2-hydroxy-1-naphthylmethane are examined. It is shown that the substance has the quinolic ring structure suggested by Pummerer and Cherbuliez, the relations between it and the monoalkali derivatives of di-2-hydroxynaphthylmethane being thus elucidated. The formation of dehydro-compounds and covalent monoalkali derivatives from substituted di-2-hydroxyphenylmethanes is demonstrated and evidence is offered that the formation of these is controlled by conditions of substitution similar to those observed with the derivatives of di-2-hydroxyphenyl sulphide. Further investigation has shown the existence of dehydro-compounds of "mixed" type as required by theory.

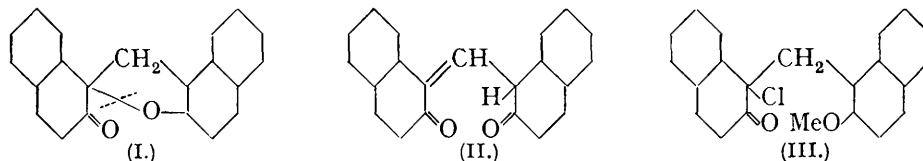
ABEL (*Ber.*, 1892, **25**, 3482) found that mild alkaline oxidation converts di-2-hydroxy-1-naphthylmethane into a dehydro-derivative by removal of two hydrogen atoms. He regarded the product as a peroxide, but Pummerer and Cherbuliez, having shown (*Ber.*, 1914, **47**, 2957) that it yields a monophenylhydrazone and recognising the analogy between it and bimolecular dehydrophenols such as dehydro-1-methyl-2-naphthol,

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assigned to it the structure (I). More recently Kohn and Ostersetzer (*Monatsh.*, 1918, 39, 299) and Kohn and Schwarz (*ibid.*, 1925, 46, 273) have advocated for this substance the structure (II) or the tautomeric form; and Dischendorfer (*Ber.*, 1926, 59, 774), regarding (II) as more probably correct than (I), has employed it as a basis for explaining the formation of dibenzacridone during the reaction of the substance with hydroxylamine and later with his colleagues has applied this type of structure (II) to other members of the group (*Monatsh.*, 1927, 48, 545). A decision between these structures was desired mainly on account of the relationship of the substance to the covalent alkali derivatives of di-2-hydroxy-1-naphthylmethane, which are converted into it by oxidation, and also because it gave promise of serving as a useful source of unsymmetrical derivatives of the series.

Dehydrodi-2-hydroxy-1-naphthyl sulphide is known (J., 1930, 959, 1740) to have a structure analogous to (I) (S instead of CH_2). In their modes of formation and in much of their chemistry the dehydro-methane and dehydro-sulphide show close similarity. For example, it is now shown that the adduct formed from bromine and the dehydro-methane yields after loss of hydrogen bromide a monobromo-derivative which evidently contains the halogen in the 3-position of the quinonoid nucleus, since it does not form a phenyl-hydrazone and on reduction yields 3-bromodi-2-hydroxy-1-naphthylmethane. Similar behaviour has been recorded with the dehydro-sulphide (J., 1932, 638). Also the two dehydro-derivatives behave similarly on nitration (J., 1914, 105, 1746).

The two series of dehydro-compounds differ notably in their behaviour on reduction and on treatment with acetyl halides. In the sulphide series reduction with zinc and acetic acid yields the "isosulphide," whilst acetic anhydride and acetyl halides lead to "iso"-dinaphthathioxins; these products are known to contain the 1:2'-dinaphthyl oxide group (J., 1930, 959; 1931, 719). On the other hand, dehydrodi-2-hydroxy-1-naphthylmethane and its derivatives are converted by zinc and acetic acid into the



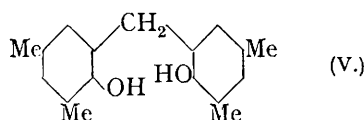
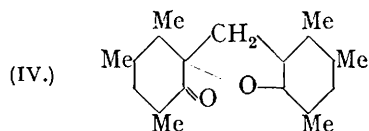
di-2-hydroxynaphthylmethanes from which they have been prepared (compare also Pummerer and Cherbuliez, *loc. cit.*) and it is also now shown that acetyl chloride and acetic anhydride are without action on the dehydro-methanes under conditions which are effective with the dehydro-sulphides, whilst acetyl iodide yields the di-2-acetoxynaphthylmethanes. This different behaviour of the two series of dehydro-compounds cannot be effectively used for the rejection of (I) and the acceptance of (II) for the dehydro-methanes. It is evident that reduction of the quinolic system of the dehydro-sulphide (I, S instead of CH_2) leads to fission of the less stable $\text{:C-S}\cdot$ linkage therein, leaving the 1:2'-oxide group intact (J., 1930, 959); on the other hand, reduction of this system in a substance of type (I) may be expected to leave the more stable $\text{:C-CH}_2\cdot$ group intact, the now less stable 1:2'-oxide group being ruptured as indicated (I). From this point of view the different results of reduction in the two series are seen to be due to different stability relations in the respective quinolic ring systems. Also it may be noted that the relative activities of the two dehydro-compounds with acetyl chloride and acetic anhydride accord with the greater stability of the quinolic ring in the dehydro-methane. In fact (I) satisfactorily expresses the known behaviour of dehydrodi-2-hydroxy-1-naphthylmethane and its relationship to the dehydro-sulphide.

The structure (II) is inadequate. Attempts to methylate or acylate the substance failed and it did not liberate methane from methylmagnesium iodide. Moreover, whilst sodium di-2-hydroxynaphthylmethane is smoothly converted into the dehydro-compound by hypochlorite, the monomethyl ether (this vol., p. 727) with this reagent yields a stable *chloro*-derivative to which the structure (III) must be assigned, since the substance is insoluble in aqueous alkali and the halogen is removed by zinc in cold acetic acid (Fries

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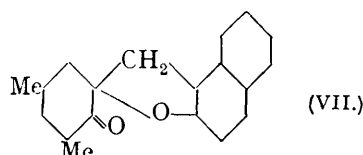
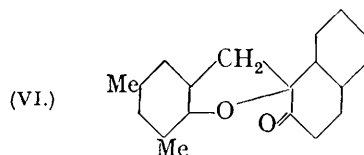
and Engel, *Annalen*, 1924, **439**, 232), the monomethyl ether being regenerated. Bromine yielded a corresponding *derivative* and the monoacetyl derivative of di-2-hydroxynaphthylmethane behaved similarly (III, $\text{CH}_3\cdot\text{CO}$ and Br instead of Me and Cl respectively), the product being converted by hydrogen chloride into the 6-bromo-derivative (compare Fries and Engel, *loc. cit.*). The monoacetyl derivative was unstable in presence of alcoholic hypochlorite, the dehydro-derivative being formed with loss of acetyl. From these results it is concluded that the conversion of the dihydroxy-methane into the dehydro-derivative involves the removal of both mobile hydrogen atoms of the naphthol nuclei and that the methylene group is not directly concerned as required by (II). In fact (I) is fully justified and (II) must be rejected on account of its incompatibility with the behaviour of the substance and with the mechanism of its formation. Bromine converts di-2-hydroxy-1-naphthylmethane into the dehydro-derivative; this circumstance together with the results of the action of the halogen with the monomethyl ether and monoacetyl derivatives suggests that the quinolic ring in the product is formed by loss of halogen from an intermediate of type (III) (OH instead of OMe).

It has been recently shown (this vol., p. 1018) that di-*o*-hydroxy-sulphides of the benzene series which have no substituent in the 6-position yield neither covalent monoalkali derivatives nor simple dehydro-compounds and are thus sharply distinguished from those containing the 6-methyl group, which yield both series of derivatives. The explanation given (*loc. cit.*) to these relations was based on a structure of type (I) (S instead of CH_2) for the dehydro-sulphides. All the dehydro-compounds and covalent monoalkali derivatives of the methane series hitherto known are derived from 2-naphthol, but it is evident that those of the benzene series should be capable of existence and their formation may be expected to be controlled by conditions of substitution similar to those observed with the sulphides. Experimental support for this conclusion has been obtained. For example, whilst the ψ -cumenol derivative (compare IV) yielded the



unimolecular dehydro-derivative (IV) and the corresponding covalent monosodium compound (this vol., p. 1018; XVI, CH_2 instead of S), the *m*-4-xenol derivative (V), which is devoid of the 6-methyl, gave neither of these characteristic products. In fact the relations between these two methane derivatives are closely similar to those existing between the corresponding sulphides.

According to the type of structure now adopted (for example, I and IV) for the dehydro-derivatives of the methane series, only one of the hydroxylated nuclei in the generator is required to assume the ketonic condition during oxidation; the existence of derivatives such as (VI) is therefore to be expected. Support for this structure, assigned to the oxidation product of 1-(2'-hydroxy-3':5'-dimethylbenzyl)-2-naphthol (this vol., p. 1349; IV), is afforded by the fact that the substance readily yields a phenylhydrazone and therefore does not contain the ortho-substitution in the quinolic nucleus which is required by the alternative (VII).



Covalent monosodium derivatives have been obtained from 3-bromodi-2-hydroxy-1-naphthylmethane and from di-2-hydroxy-3:5:6-trimethylphenylmethane. These, isolated from aqueous media, contain various multiples of $2\text{H}_2\text{O}$; their stability and that of analogous hydrates is being investigated.

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EXPERIMENTAL.

Dehydrodi-2-hydroxy-1-naphthylmethane.—(a) A solution of di-2-hydroxy-1-naphthylmethane (15 g.) in warm 2*N*-sodium hydroxide (50 c.c.) was added to a cooled and stirred solution of sodium hypochlorite (300 c.c., 2%). After being washed with warm alcohol the insoluble product was purified from aqueous acetone (10 g., m. p. 172°). (b) Bromine (1.3 c.c.) was slowly added to a cooled and stirred suspension of di-2-hydroxy-1-naphthylmethane (7.5 g.) in acetic acid (150 c.c.) which contained sodium acetate (7.5 g.). The product was isolated by dilution of the solution and was purified as described (5 g.). The dehydro-compound was recovered after its solution in acetic anhydride (5 hrs.) or in a mixture of acetic anhydride and acetyl chloride (40 hrs.) had been boiled. It was also recovered after the solution in acetyl chloride had been heated (5 hrs., 120°).

Reaction with acetyl iodide. A solution of acetyl iodide (1 g.) in acetic anhydride (5 c.c.) was slowly added (0°) to a suspension of the dehydro-compound in the latter solvent. Subsequently (1 hr.) the mixture was added to water containing sulphurous acid. After purification the product was identified as di-2-acetoxy-1-naphthylmethane (m. p. 213°) in the usual manner.

Reaction with toluene-4-sulphinic acid. A suspension of the dehydro-derivative (6 g.) in acetone (20 c.c.) was added to an aqueous solution (200 c.c.) of the potassium sulphinate (6 g.) containing sulphuric acid (60%, 10 c.c.). The mixture was shaken (12 hrs.) and then set aside (3 days); the insoluble product, purified from aqueous acetone, had m. p. 139–140° (decomp.) (Found: C, 73.7; H, 4.8; S, 6.8. $C_{26}H_{22}O_4S$ requires C, 74.0; H, 4.8; S, 7.0%). The structure of this additive product is at present uncertain, but it may be noted that it is resolved into the components by 2*N*-alkali hydroxide (15°).

Nitration. Nitric acid (1.3 c.c., *d* 1.4) was added slowly to a stirred suspension of the dehydro-compound (6 g.) in acetic anhydride. After all had dissolved, the mixture was added to warm water (500 c.c.). The product was purified from acetic anhydride (charcoal) and then from aqueous acetone (4.6 g.). 4(?)-Nitrodehydrodi-2-hydroxy-1-naphthylmethane formed bright yellow plates, m. p. 166° (Found: C, 73.3; H, 4.0. $C_{21}H_{13}O_4N$ requires C, 73.5; H, 3.8%), and gave a phenylhydrazone which separated from benzene in yellow plates, m. p. 191° (decomp.) (Found: N, 9.6. $C_{27}H_{19}O_3N_3$ requires N, 9.7%).

Reaction with methylmagnesium iodide. A solution of the reagent (2 mols.) in ether was added to a solution of the dehydro-compound (1 mol.) in dry benzene. Interaction took place with rise of temperature, but the liberation of methane was not detected. The product, obtained from the benzene solution after treatment with dilute sulphuric acid, was purified from aqueous alcohol; it formed small prisms, m. p. 135° (Found: C, 83.9; H, 5.7. Calc. for $C_{22}H_{18}O_2$: C, 84.0; H, 5.8%), their composition being the same as that recorded by Kohn and Osterseizer (*loc. cit.*). It was different from the isomeric monomethyl ether of di-2-hydroxy-1-naphthylmethane, m. p. 142° (Evans and Smiles, *loc. cit.*), and was not attacked by zinc dust and acetic acid. It may be noted that the monomethyl ether in question liberated methane from methylmagnesium iodide.

Reaction with bromine. Bromine (3.2 g.) was slowly added to a cooled and stirred suspension of the dehydro-compound (6 g.) in acetic acid (40 c.c.). The colourless material which separated (30 mins.) was washed with water and purified from cold aqueous acetone. Dehydrodi-2-hydroxy-1-naphthylmethane 3:4-dibromide formed prisms, m. p. 148° (decomp.) (Found: C, 54.6; H, 3.2. $C_{21}H_{14}O_2Br_2$ requires C, 55.0; H, 3.1%).

3-Bromodehydrodi-2-hydroxy-1-naphthylmethane was obtained from the purified dibromo-additive product by treatment with warm pyridine. After the base had been removed by excess of dilute mineral acid, the insoluble product was washed with ether and purified from aqueous acetone; it formed orange prisms, m. p. 136° (Found: C, 66.8; H, 3.6. $C_{21}H_{13}O_2Br$ requires C, 66.8; H, 3.45%), which did not yield a phenylhydrazone. When zinc dust was added to its solution in hot acetic acid (5 g. in 50 c.c.) until the latter became colourless, a sparingly soluble zinc derivative separated. 3-Bromodi-2-hydroxy-1-naphthylmethane (4.5 g.) was liberated from this by dilute mineral acid; it had m. p. 201° (decomp.) (Found: C, 66.3; H, 4.1. Calc.: C, 66.6; H, 4.0%), and was identical with a sample prepared by synthesis (this vol., p. 1350). Oxidation of the latter in alkaline solution with hypochlorite gave a mixture of dehydro-derivatives which could not be effectively resolved (compare J., 1932, 637 for the behaviour of the corresponding sulphide).

Di-6-bromo-2-hydroxy-1-naphthylmethane.—Formaldehyde (4 c.c., 40%) was added to a stirred solution of 6-bromo-2-naphthol (18 g.) in acetic acid (125 c.c.) which contained

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concentrated hydrochloric acid (8 c.c.). The insoluble *product* (15 g.) was purified from amyl alcohol and formed needles, m. p. 242° (decomp.) (Found : C, 54.9; H, 3.3. $C_{21}H_{14}O_2Br_2$ requires C, 55.0; H, 3.1%). The *diacetyl* derivative had m. p. 287° (Found : C, 55.2; H, 3.4. $C_{25}H_{18}O_4Br_2$ requires C, 55.3; H, 3.5%). The covalent sodium derivative separated in an amorphous state when a solution in warm aqueous sodium hydroxide was cooled; it was soluble in ether and in hot benzene.

Dehydrodi-6-bromo-2-hydroxy-1-naphthylmethane was obtained by oxidising the corresponding hydroxy-derivative with aqueous hypochlorite in the usual manner. The crude material was washed with warm alcohol before purification from aqueous acetone. It formed yellow prisms, m. p. 209° (Found : C, 55.5; H, 2.8. $C_{21}H_{12}O_2Br_2$ requires C, 55.3; H, 2.6%), and gave a *phenylhydrazone* which separated from acetic acid as a yellow crystalline powder, m. p. 200° (Found : C, 59.1; H, 3.5. $C_{27}H_{18}ON_2Br_2$ requires C, 59.3; H, 3.3%). When submitted to the usual treatment with a cold solution of acetyl iodide in acetic anhydride, this dehydro-derivative yielded di-6-bromo-2-acetoxy-1-naphthylmethane, m. p. 287° , identical with an authentic sample.

Di-3-bromo-2-hydroxy-1-naphthylmethane was obtained from 3-bromo-2-naphthol and formaldehyde in the usual manner. It separated slowly from the reacting mixture and after purification from acetic acid formed tufts of needles, m. p. 207° (Found : C, 55.0; H, 3.3. $C_{21}H_{14}O_2Br_2$ requires C, 55.0; H, 3.1%).

Dehydrodi-3-bromo-2-hydroxy-1-naphthylmethane was prepared from this hydroxy-derivative by treatment with alkaline hypochlorite in the usual manner. It separated from benzene in yellow prisms, m. p. 232° (Found : C, 55.5; H, 2.6. $C_{21}H_{12}O_2Br_2$ requires C, 55.3; H, 2.6%), which did not yield a phenylhydrazone.

1'-Chloro-2'-keto-2-methoxy-1' : 2'-dihydrodi-1-naphthylmethane (III).—Aqueous sodium hypochlorite (30 c.c., 6%) was added to a stirred solution of the monomethyl ether of di-2-hydroxy-1-naphthylmethane (6 g.) in warm alcohol (50 c.c.) and aqueous sodium hydroxide (20 c.c., 2N). The insoluble *product*, after purification from cold aqueous acetone and subsequently from alcohol, formed yellow prisms (4 g.), which had m. p. 147° and became red on exposure to light (Found : C, 75.5; H, 4.8; Cl, 10.3; *M*, 343. $C_{22}H_{17}O_2Cl$ requires C, 75.7; H, 4.8; Cl, 10.2%; *M*, 348.5). When zinc dust was added to a cold solution of the substance in acetic acid which contained a little hydrochloric acid, the colour was rapidly discharged; dilution then yielded the monomethyl ether of di-2-hydroxy-1-naphthylmethane, m. p. 142° , which was identified as usual.

1'-Bromo-2'-keto-2-methoxy-1' : 2'-dihydrodi-1-naphthylmethane (III, Cl replaced by Br).—Bromine (1.3 c.c.) was slowly added to a cooled and stirred suspension of the monomethyl ether (7.8 g.) in acetic acid (100 c.c.) which contained sodium acetate (7 g.). The *product* separated as an amorphous yellow mass; it was dried, and after purification from benzene or from cold aqueous acetone formed yellow needles (5.5 g.), m. p. 155° , which were decomposed by light (Found : C, 67.0; H, 4.3. $C_{22}H_{17}O_2Br$ requires C, 67.2; H, 4.3%). Reduction with zinc dust in a cold mixture of acetic and hydrochloric acids yielded the monomethyl ether of di-2-hydroxy-1-naphthylmethane.

The *monoacetyl* derivative of di-2-hydroxy-1-naphthylmethane, required for the preparation of the following keto-bromide, was obtained by slowly adding finely divided monosodium di-2-hydroxy-1-naphthylmethane tetrahydrate (20 g.; this vol., p. 729) to cooled (0°) and stirred acetic anhydride (70 c.c.). It separated (15 g.) from the reacting mixture in the crystalline state and, purified from acetone, formed needles, m. p. 195° (Found : C, 80.5; H, 5.4. $C_{23}H_{18}O_3$ requires C, 80.7; H, 5.3%).

1'-Bromo-2'-keto-2-acetoxy-1' : 2'-dihydrodi-1-naphthylmethane.—Bromine (1.1 c.c.) was slowly added to a cooled and stirred suspension of the above acetyl derivative (6.8 g.) in acetic acid (120 c.c.) which contained sodium acetate (5.6 g.). After continued stirring (15 mins.) the insoluble matter was removed, the solution diluted with water (120 c.c.), and the impure product which separated washed with alcohol and purified from cold aqueous acetone (yield, 3 g.). It formed yellow prisms, m. p. 127° (decomp.) (Found : C, 65.6; H, 4.0. $C_{23}H_{17}O_3Br$ requires C, 65.5; H, 4.0%), which after reduction with zinc dust in cold acetic acid yielded the monoacetyl derivative of di-2-hydroxy-1-naphthylmethane.

Reaction with hydrogen chloride. After a solution of the keto-bromide (5 g.) in acetic acid (50 c.c.) saturated with hydrogen chloride had been kept (3 days), it was diluted (50 c.c. of water). The impure red material which separated was submitted to alkaline hydrolysis, the deacetylated product being liberated from the solution thus obtained. This, after repeated purification from aqueous alcohol (charcoal), was identified as 6-bromodi-2-hydroxy-1-

naphthylmethane (1.5 g.), m. p. 207°, by comparison with a synthetic specimen (this vol., p. 1350). Attempts to obtain a corresponding keto-chloride were made by adding aqueous alkaline hypochlorite to a cold suspension of the monoacetyl derivative in alcohol. In all cases dehydrodi-2-hydroxy-1-naphthylmethane was obtained in high yield.

Dehydrodi-2-hydroxy-3 : 5 : 6-trimethylphenylmethane (IV).—Alcohol was added to a mixture of the relevant hydroxy-compound (3 g.; Zincke and Hohorst, *Annalen*, 1907, 353, 363) and 2N-sodium hydroxide until the insoluble monosodium derivative of the phenol had dissolved. A slight excess of aqueous sodium hypochlorite (3%) was added to the stirred solution; the yellow mass which had separated was then removed and purified from aqueous acetone. The product (2.7 g.) formed small yellow prisms, m. p. 137° (Found: C, 80.6; H, 7.7; M, 272. $C_{19}H_{22}O_2$ requires C, 80.8; H, 7.8%; M, 282).

Dehydro-1-(2'-hydroxy-3' : 5'-dimethylbenzyl)-2-naphthol (VI).—A solution of the relevant hydroxy-derivative (this vol., p. 1351; 6 g.) in 2N-sodium hydroxide (20 c.c.) was added to stirred aqueous sodium hypochlorite (240 c.c.; 1%). The insoluble yellow product was washed with warm aqueous sodium hydroxide and the dry residue was treated with boiling light petroleum. The residue obtained after removal of the solvent was submitted to repeated fractionation by the same process; the required product separated in yellow prisms, m. p. 107°, when the solvent was allowed to evaporate spontaneously (Found: C, 82.3; H, 5.6. $C_{18}H_{16}O_2$ requires C, 82.6; H, 5.8%). The sparingly soluble phenylhydrazone was readily obtained from the crude product of the foregoing preparation by reaction with phenylhydrazine in hot acetic acid; it formed orange prisms, m. p. 167°, from aqueous acetone (Found: N, 7.6. $C_{26}H_{22}ON_2$ requires N, 7.6%).

Monosodium di-2-hydroxy-3 : 5 : 6-trimethylphenylmethane separated when a mixture of the hydroxy-compound (1 mol.) and 2N-sodium hydroxide (2 mols.) was warmed (90°). Exactly sufficient alcohol was added to effect solution; when the liquid cooled, the pure material separated in needles; these lost some water at 100° and finally melted at 175° (approx.). It was readily soluble in ether and in warm benzene, the latter solvent effecting partial dehydration. This covalent derivative was dried at 25° before analysis (Found: Na, 6.1. $C_{19}H_{23}O_2Na, 4H_2O$ requires Na, 6.1%). Water was removed from it in a vacuum at 118° (P_{2O_5}) (Found: Na, 7.6. $C_{19}H_{23}O_2Na$ requires Na, 7.5%). Di-2-hydroxy-3 : 5-dimethylphenylmethane (V) (Fries and Kann, *Annalen*, 1907, 353, 352) was completely soluble in N-alkali hydroxide; no covalent monosodium derivative could be obtained from it under the usual conditions or others. Addition of hypochlorite to the alkaline solution yielded an amorphous, unstable, green material; this was insoluble in the usual solvents and no simple dehydro-derivative could be isolated from it.

Monosodium 6-bromodi-2-hydroxy-1-naphthylmethane separated in the crystalline state when a solution of the hydroxy-compound (1 mol.) in warm N-sodium hydroxide (2 mols.) was cooled. After being dried (18°), it showed the usual solubility in ether, benzene or chloroform; it melted at 215° (approx.) after losing water at about 100° (Found: Na, 4.5. $C_{21}H_{14}O_2BrNa, 6H_2O$ requires Na, 4.5%).

Monosodium Phenyl-di-2-hydroxy-1-naphthylmethane.—When alcohol was added to a hot (90°) mixture of the hydroxy-compound (1 mol.) (Hewitt and Turner, *Ber.*, 1901, 34, 302) and N-sodium hydroxide (2 mols.), the sodium derivative, which had separated, dissolved. This crystallised from the cooled solution in plates, which were dried in air (15°) (Found: Na, 4.9. $C_{27}H_{19}O_2Na, 4H_2O$ requires Na, 4.9%). Part of the water was lost when the substance was dried at 35° (Found: Na, 5.5. $C_{27}H_{19}O_2Na, 2H_2O$ requires Na, 5.3%). The tetrahydrate was readily soluble in ether and in warm benzene; the dihydrate was less soluble and separated when the benzene solution of the tetrahydrate was boiled.

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