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Studies on the Chemistry of Lichens

XIII.* The Structure of Pannaric Acid

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Pannaric acid, $C_{16}H_{12}O_7$, a phenolic acid from *Crocynea membranacea* (Dicks.) Zahlbr., has been shown to contain two carboxyl groups, two phenolic hydroxyl groups and two C-methyl groups. On decarboxylation, it forms a phenol $C_{14}H_{12}O_3$, identified as 3,9-dihydroxy-1,7-dimethyldibenzofuran, which was synthesised. From biogenetic considerations, the most probable structure would be (V). This structure has been confirmed by permanganate oxidation of di-O-methylpannaric acid to 1,2,6,7-tetracarboxy-3,9-dimethoxydibenzofuran, previously obtained from porphyrilic acid (I). Structure (V) is also in harmony with colour reactions and the infra-red absorption spectra of pannaric acid and its derivatives.

One of the main aims of these investigations has been the isolation of compounds illustrating the role of oxidative coupling of phenols in biosynthesis. The importance of this reaction in lichen chemistry, in the lignan field and also to an understanding of the biosynthesis of thyroxin [1] was discussed by one of us in a lecture to the Chemical Society, Stockholm, in December 1933 shortly after the structural elucidation of the depsidone salazinic acid by Asahina [2]. The depsidones were considered to be coupling products of phenol oxygen radicals and mesomeric carbon radicals.

Examples of the pairing of carbon radicals were expected and have since been found: usnic acid [3], the "depsone" picrolichenic acid [4,5] and the dibenzofurans strepsilin [6], didymic acid [7] and porphyrilic acid [8,9]. Usnic acid and picrolichenic acid are particularly interesting because one of the nuclei has not returned to the aromatic state.

The biosynthetic aspects of phenol dehydrogenation in general have been recently discussed by Barton and Cohen [10] and by Erdtman and Wachtmeister [11] and with particular reference to lichen chemistry by Wachtmeister [12].

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In this search for new oxidative coupling products attention has been focussed on lichen acids which cannot be cleaved hydrolytically into two or more components; these can easily be found by paper chromatography [13].

Hesse's pannaric acid * from *Crocynea membranacea* (Dicks.) Zahlbr. (= *Pannaria lanuginosa* Ach.) has such properties. According to Hesse [14], pannaric acid has the composition $C_9H_8O_4$ but the high melting point (Hesse reports 224°) indicates a higher molecular weight.

Exhaustive extraction of the lichen with ether afforded a crude crystalline product from which roccellic acid could be removed by extraction with hot petroleum ether. The residual crude pannaric acid (about 1.5 % of the dry lichen) was conveniently recrystallised from diacetone alcohol and further purified by filtration through alumina. The purity of the acid was checked chromatographically on phosphate-impregnated paper [13].

Pannaric acid exhibits a bluish-white fluorescence in ultra-violet light. It is readily soluble in the lower alcohols and in acetone containing about 2 % of water but only sparingly soluble in dry acetone, ether, benzene and chloroform. It dissolves with effervescence in aqueous sodium hydrogen carbonate to give a colourless solution. Like porphyrilic acid [9], pannaric acid gives a blue colour with iron(III) chloride and a blue colour with Gibb's reagent [15]; with bleaching powder it gives the green colour characteristic of all known lichen acids belonging to the dibenzofuran group.

Pannaric acid crystallises from aqueous acetone as colourless needles containing solvent of crystallisation. It melts with decomposition at 243—245° and after drying *in vacuo* gave analytical results in agreement with the composition $C_{16}H_{12}O_7$. Pannaric acid possesses two strongly acidic groups and carbon dioxide is evolved on thermal decomposition. Kuhn-Roth determination indicated the presence of two C-methyl groups.

Methylation of pannaric acid with a large excess of diazomethane in the presence of some methanol yielded dimethyl di-O-methylpannarate, $C_{12}H_2O(CH_3)_2(OCH_3)_2(COOCH_3)_2$ which on hydrolysis gave di-O-methyl pannaric acid, $C_{12}H_2O(CH_3)_2(OCH_3)_2(COOH)_2$. Treatment of pannaric acid at −10° with a slight excess of diazomethane for 1—2 min afforded dimethyl pannarate, $C_{12}H_2O(CH_3)_2(OH)_2(COOCH_3)_2$, which was readily acetylated to a diacetate.

Pannaric acid itself yielded a diacetate $C_{12}H_2O(CH_3)_2(OCOCH_3)_2(COOH)_2$ which decomposed above 240° without melting.

On prolonged boiling with formic acid, pannaric acid was decarboxylated with the formation of pannarol, $C_{12}H_4O(CH_3)_2(OH)_2$, m.p. 183—184°, which gave a diacetate and a dimethyl ether. As described by Hesse, pannarol was also formed on thermal decomposition of the dry acid.

The ultra-violet absorption curves of pannarol and of its diacetate were very similar to those of 3,7-dihydroxy-1,9-dimethyldibenzofuran [7] (II) and its diacetate, respectively, but pannarol was not identical with compound II.

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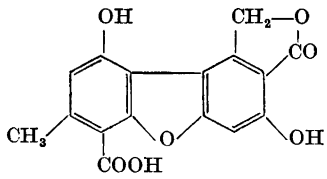
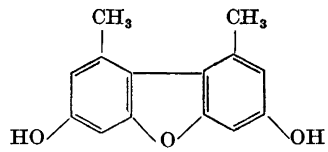
* The name pannaric acid, unfortunately, has also been given to an oxidation product obtained from pannarin, a chlorine-containing depsidone isolated from the Japanese *Pannaria lanuginosa* and some other *Pannaria* species by Yosioka. Compare Asahina, Y. and Shibata, S. *Chemistry of Lichen Substances*, Tokyo 1954.



I



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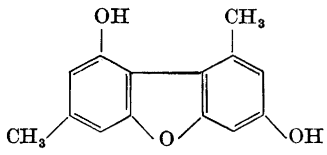

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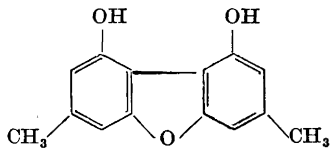

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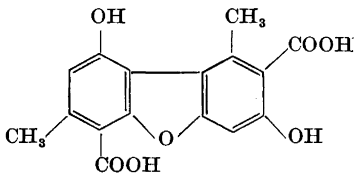

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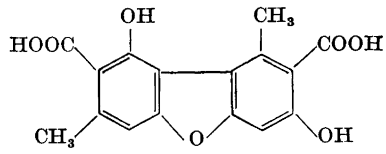

VI

For biogenetic reasons, pannarol was considered to be either 3,9-dihydroxy-1,7-dimethyldibenzofuran (III) or 1,9-dihydroxy-3,7-dimethyldibenzofuran (IV). These phenols were therefore synthesised.

Dibenzofurans of these types are readily available by Ullmann coupling of the appropriate iodides and cyclisation of the tetramethoxydiphenyl obtained. Although 2-iodo-3,5-dimethoxytoluene [5] is formed in high yield by direct iodination of orcinol dimethyl ether, the 4-iodo-analogue has so far only been prepared from 4-nitroorcinol which is obtained in very low yield on nitration of orcinol. It is known, however, that resorcinol dimethyl ether reacts with phenyl lithium forming mainly the 2-lithium derivative [17]. Orcinol dimethyl ether when metalated in the same way and treated with iodine gave 4-iodo-3,5-dimethoxytoluene in an overall yield of 50 %.

Ullmann coupling of 4-iodo-3,5-dimethoxytoluene afforded 2,6,2′,6′-tetramethoxy-4,4′-dimethyldiphenyl [16]. On boiling with hydrobromic acid this compound was demethylated and dehydrated, giving 1,9-dihydroxy-3,7-dimethyldibenzofuran (IV), m.p. 190—192°, which was different from pannarol. Like its lower homologue, 1,9-dihydroxydibenzofuran, it showed abnormally high R_F-values (*cf.* Ref.[12]).

A mixed Ullmann coupling with 4-iodo-3,5-dimethoxytoluene and an excess of 2-iodo-3,5-dimethoxytoluene furnished a mixture of diphenyls. On prolonged boiling with hydrobromic acid the crude product gave a mixture of phenols, the main component of which proved paper-chromatographically identical with 3,7-dihydroxy-1,9-dimethyldibenzofuran (II). Paper chroma-

tography also revealed a minor component of the same high R_F-value as 1,9-dihydroxy-3,7-dimethyldibenzofuran (IV). On treatment of the chromatogram with Gibbs' reagent a third component appeared as a blue spot as would be expected for 3,9-dihydroxy-1,7-dimethyldibenzofuran (III). This spot behaved in all respects like that of pannarol.

The main part of the 3,7-dihydroxy-1,9-dimethyldibenzofuran was separated from the crude phenol mixture by crystallisation from benzene. The mother liquor was evaporated and the residue was chromatographed on a column of cellulose powder impregnated with dimethyl sulphoxide, using diethyl ether as the mobile phase. The fractions eluted were analysed by paper chromatography using the same solvent system [18]. 3,9-Dihydroxy-1,7-dimethyldibenzofuran, m.p. 184—185°, was shown to be identical with pannarol by mixed melting point determination as well as by comparison of the infra-red absorption curves. Methylation gave 3,9-dimethoxy-1,7-dimethyldibenzofuran, similarly identified as pannarol dimethyl ether.

From these results, pannaric acid may be formulated as (V) or (VI), the only structures which are consistent with biosynthesis from orsellinic acid. A strong indication in favour of structure (V) was given by the negative reaction of dimethyl pannarate with Gibb's reagent [15]. Moreover, the infra-red absorption curve of dimethyl pannarate in potassium bromide showed two separate carbonyl bands at 1 660 cm^{-1} and 1 690 cm^{-1}, respectively, indicating intramolecular as well as intermolecular hydrogen bonding. The absorption curve of dimethyl di-O-methyl pannarate, as expected, showed a single carbonyl band at 1 725 cm^{-1}.

A confirmation of structure (V) was obtained by permanganate oxidation of di-O-methylpannaric acid to a tetracarboxylic acid which on heating gave a yellow di-anhydride and on methylation gave a tetramethyl ester $(CH_3O)_2C_{12}H_2O(COOCH_3)_4$, m.p. 225—226°, undepressed on admixture with 3,9-dimethoxy-1,2,6,7-tetracarbomethoxydibenzofuran [9] previously obtained from porphyrilic acid (I). The identity was confirmed by comparison of the infra-red spectra.

Porphyrilic acid (I) from *Haematomma coccineum* and pannaric acid (V) from *Crocynea membranacea* contain the same carbon skeleton and are both major phenolic compounds of the respective lichens. It is noteworthy that no lichen acid containing the carbon skeleton (VI) has so far been found. This gives some support to the proposed mechanism for oxidative coupling of orsellinic acid homologues, involving intermediate radicals, stabilised by chelation, that are formed by participation of the most acidic phenolic hydroxyl group, that *para* to the carboxyl group [12].

Fertile specimens of *Crocynea membranacea* have never been found and the classification appears somewhat questionable. Other *Crocynea* species are well defined. From a chemical point of view a relationship with the genus *Haematomma* would appear probable.

EXPERIMENTAL

All melting points were determined on a Kofler micro hot stage. Whatman No. 1 paper was used for paper chromatography. Ultra-violet absorption spectra were measured with a Beckman spectrophotometer, model DU. The infra-red spectra were recorded with

a Perkin-Elmer double beam spectrophotometer, model 21 (sodium chloride prism; potassium bromide discs).

Isolation of pannaric acid. *Crocynea membranacea* (3.14 kg) was extracted with ether for 5 days in a Soxhlet apparatus. The ether extract (10 l) deposited a crystallisate (10 g, m. p. 172—181°) which was not further investigated *. The mother liquor was evaporated to dryness and the crystalline residue was extracted repeatedly with boiling petroleum ether (b. p. 100—120°). The material extracted was crystallised from ethanol giving roccellic acid (90 g), m. p. 130.5—132.0°, $[\alpha]_D^{20}$ +18.0 (EtOH, *c* 1.94). Lit. m. p. 131°, $[\alpha]_D$ +17.4 (EtOH) [19].

The insoluble fraction (45 g, m. p. 228—234°) on crystallisation from diacetone alcohol afforded crude pannaric acid as yellowish needles (25 g, m. p. 230—235°) of sufficient purity for most of the degradative work. A solution of the crude acid (1.2 g) in acetone (20 ml), water (0.5 ml) and ether (200 ml) was filtered through a 3 cm column of alkali-free alumina (5 g) and followed by 200 ml ether-acetone (10:1). The combined filtrates on evaporation afforded pannaric acid (700 mg), which crystallised as colourless needles (300 mg) from aqueous acetone. The purity of the acid was checked by chromatography on phosphate-impregnated paper [9,13] using a *n*-butanol-water solvent system. The acid showed the R_F-values 0.05 (0.1 M Na_3PO_4); 0.10 (0.1 M Na_2HPO_4 + 0.1 M NaH_2PO_4 1:1) and 0.65 (0.1 M NaH_2PO_4). The spots were visible in ultraviolet light (bluish-white fluorescence under alkaline conditions) and gave a blue colour with Gibbs' reagent and a dark red-brown colour with *bis*-diazotised benzidine [20] under alkaline conditions.

Pannaric acid was dried for analysis *in vacuo* for 1 h at 120°; loss of weight: 9.6 %; $C_{16}H_{12}O_7$, $2H_2O$ requires 10.2 %; m. p. 243—245°. The equivalent weight was determined by potentiometric titration in 50 % methanol. (Found: C 60.6; H 4.2; equiv. wt. 160. $C_{16}H_{12}O_7$ requires C 60.8; H 3.8; equiv. wt. required for a dicarboxylic acid, 158.)

Di-O-acetylpannaric acid. Pannaric acid (75 mg) was boiled for 5 min with acetic anhydride (1 ml) containing pyridine (0.05 ml). The solution was evaporated *in vacuo* and the residue crystallised from aqueous methanol to give the diacetate, colourless needles decomposing from 240°. (Found: C 59.6; H 4.0; CH_3CO 20.5. $C_{20}H_{16}O_9$ requires C 60.0; H 4.0; $(CH_3CO)_2$ 21.5.)

Dimethyl pannarate. A solution of pannaric acid (160 mg) in acetone containing 2 % of water (20 ml) was cooled to −10° and a slight excess of ethereal diazomethane added. After 2 min, the reaction was interrupted by the addition of acetic acid. The dimethyl ester crystallised from methanol as needles m. p. 254—255°, sparingly soluble in most solvents. (Found: C 62.7; H 4.6; OCH_3 18.0. $C_{18}H_{16}O_7$ requires C 62.8; H 4.65; $(OCH_3)_2$ 18.0.) The infra-red absorption curve showed carbonyl bands at 1 690 and 1 660 cm^{-1}.

The ester gave a light brown colour with *bis*-diazotised benzidine when tested on alkaline paper (Na_3PO_4) but no colour with Gibbs' reagent. A saturated solution of the ester in 96 % ethanol did not give any colour with ferric chloride. R_F-values (*n*-butanol-water): 0.78 (Na_3PO_4); 0.84 (Na_3PO_4 + Na_2HPO_4 1:1).

Dimethyl di-O-acetylpannarate. Dimethyl pannarate was warmed for a few minutes with acetic anhydride containing pyridine. The dimethyl di-O-acetylpannarate was crystallised from ethanol as needles, m. p. 162—164°. (Found: C 61.7; H 4.7; OCH_3 14.5; CH_3CO 21.1. $C_{22}H_{20}O_9$ requires C 61.7; H 4.7; $(OCH_3)_2$ 14.5; $(CH_3CO)_2$ 20.1.)

Dimethyl di-O-methylpannarate. Pannaric acid suspended in acetone containing methanol was treated for two days with an excess of ethereal diazomethane; the acid gradually dissolved. The reaction product crystallised from methanol to give dimethyl di-O-methylpannarate, needles, m. p. 166—168°. (Found: C 64.2; H 5.8; OCH_3 32.6; C—CH_3 (Kuhn-Roth) 7.55. $C_{20}H_{20}O_7$ requires C 64.5; H 5.4; $(OCH_3)_4$ 33.3; $(C-CH_3)_2$ 8.06.) The infra-red absorption curve showed carbonyl band at 1 725 cm^{-1}.

Di-O-methylpannaric acid. Dimethyl di-O-methylpannarate (2.25 g) was heated for 1 h on a boiling water bath with ethanol (25 ml) and 2 N aqueous sodium hydroxide (25 ml). Acidification with hydrochloric acid afforded a precipitate which was collected (1.9 g) and crystallised from ethanol to give di-O-methylpannaric acid, m. p. 240—246°

* It is not certain that these products are constituents of *Crocynea* since the material collected is always contaminated with small amounts of other lichens. It is, however, easy to prove by paper chromatography that the pure *Crocynea* contains pannaric acid.

(decomp.). R_F-values (*n*-butanol-water): 0.05 (Na_3PO_4); 0.10 (NaH_2PO_4, Na_2HPO_4 1:1); 0.75 (NaH_2PO_4). The spots were detected by their bluish-white fluorescence in ultraviolet light. (Found: C 62.3; H 4.8; OCH_3 16.8. $C_{18}H_{16}O_7$ requires C 62.8; H 4.65; $(OCH_3)_2$ 18.0.)

Pannarol (III). *a*) Pannaric acid (400 mg) was boiled for 12 h under reflux in an atmosphere of carbon dioxide with 88 % formic acid (10 ml). The dark solution was evaporated to dryness under reduced pressure and the residue dissolved in ether. The ether solution was extracted with aqueous sodium bicarbonate, dried and filtered through a small column of alkalifree alumina. Evaporation of the filtrate afforded pannarol (230 mg) which crystallised from aqueous ethanol as needles, m. p. 184—185°, undepressed on admixture with 3,9-dihydroxy-1,7-dimethyldibenzofuran, m. p. 184—185°, described below. The identity was confirmed by comparison of the infra-red absorption curves. (Found: C 74.0; H 5.6. $C_{14}H_{12}O_3$ requires C 73.7; H 5.3.) U.V. absorption (in 96 % ethanol): λ_{max} 233 mμ (log ε 4.74); 267 mμ (4.46); 287 mμ (4.40); 300 mμ (4.21); 312 mμ (4.39).

b) Pannaric acid (50 mg) placed in a small test tube was heated cautiously over a free flame under reduced pressure. It decomposed and sublimed. Loss of weight, 28.5 %. $C_{16}H_{12}O_7$ — 2 CO_2 requires a loss of weight of 27.8 %. The sublimate was identical with the pannarol obtained in the previous experiment.

Pannarol gave a red-brown colour with *bis*-diazotised benzidine, a blue colour with Gibbs' reagent, a red colour with bleaching powder but no colour with ferric chloride in ethanol. Paper chromatography (benzene-water): R_F 0.33. The spot was fairly elongated. A more convenient solvent system is described below (see 3,9-dihydroxy-1,7-dimethyldibenzofuran).

Di-O-methylpannarol. Pannarol (90 mg) in dry acetone (10 ml) was boiled under reflux with potassium carbonate (1.10 g) and dimethyl sulphate (0.38 g). After 6 h, excess dimethyl sulphate was destroyed by the addition of water and heating for 1 h. The solution was filtered and evaporated to dryness, the residue was dissolved in benzene and the solution was filtered through a small column of alumina. The filtrate was evaporated and the residue crystallised from aqueous methanol and finally distilled under reduced pressure to give di-O-methylpannarol, m. p. 94.5—95.5°, undepressed on admixture with the 3,9-dimethoxy-1,7-dimethyldibenzofuran, m. p. 94—95°, described below. The identity of the two compounds was confirmed by comparison of the I.R. absorption curves. (Found: C 74.7; H 6.0; OCH_3 24.2. $C_{16}H_{16}O_3$ requires C 75.0; H 6.3; $(OCH_3)_2$ 24.0.)

Di-O-acetylpannarol. Pannarol was acetylated at room temperature with acetic anhydride containing pyridine to give di-O-acetylpannarol which was crystallised from methanol, needles, m. p. 136.5—137.5°. (Found: C 68.6; H 5.1; CH_3CO 27.3. $C_{18}H_{16}O_5$ requires C 69.2; H 5.1; $(CH_3CO)_2$ 26.9). U.V. absorption (in 96 % ethanol) λ_{max} 226 mμ (log ε 4.38), 258 mμ (4.15), 285 mμ (4.28).

Permanganate oxidation of di-O-methylpannaric acid. Pannaric acid dimethyl ether (400 mg) in water (60 ml) containing potassium carbonate (700 mg) was heated on a boiling water bath and a solution of potassium permanganate (4 g) in water (100 ml) was added dropwise with stirring over 3 h. After heating for another 12 h, the excess permanganate was destroyed and the manganese sludge was filtered off and washed with water. The combined filtrates were concentrated to a volume of 40 ml and acidified with concentrated hydrochloric acid (2 ml). On standing in the refrigerator, the solution deposited a crystalline acid (A) which was collected, washed and dried at room temperature. Yield, 250 mg. It showed no definite melting point but readily formed a yellow anhydride. (Found: Equiv. wt. 94. $C_{18}H_{12}O_{11}$ requires equiv. wt. as a tetracarboxylic acid, 102.)

Dianhydride of the acid A. The acid (A) (80 mg) was dried *in vacuo* at 150° (loss of weight, 9.5 %. $C_{18}H_{12}O_{11}$ requires a loss of weight of 9.6 %) and the anhydride was purified by sublimation. M. p. 320—325°. (Found: C 58.5; H 2.1; OCH_3 16.1. $C_{18}H_8O_9$ requires C 58.7; H 2.2; $(OCH_3)_2$ 16.8.) The I.R. absorption curve showed carbonyl bands at 1 850 and 1 785 cm^{-1}.

Tetramethyl ester of the acid A. The acid (A) (80 mg) in methanol suspension was methylated with an excess of ethereal diazomethane. The ester crystallised from acetone as prisms, m. p. 225—226°, undepressed on admixture with 3,9-dimethoxy-1,2,6,7-tetracarbomethoxydibenzofuran [9], m. p. 225—226.5°. (Found: C 57.0; H 4.3; OCH_3 38.0.

$C_{22}H_{20}O_{11}$ requires C 57.4; H 4.3; $(OCH_3)_6$ 40.4.) The identity was confirmed by comparison of the I.R. absorption curves.

3,5-Dimethoxy-4-iodotoluene. Phenyllithium (20 mmole) in ether (10 ml) was added to a solution of orcinol dimethyl ether (10 mmole) in ether (10 ml) in an atmosphere of oxygen-free nitrogen. The orcinol-lithium compound started to crystallise after 24 h at room temperature. After another 5 days at 0° no further crystallisation was observed. The ethereal solution was decanted and the crystals were dissolved in dry tetrahydrofuran (10 ml). Iodine (8 mmole) was added and the solution was refluxed for 15 min. Excess iodine was destroyed with aqueous sodium thiosulphate and the solution was extracted with ether. Evaporation of the ether extract afforded a crystalline product which was crystallised from ethanol to give 3,5-dimethoxy-4-iodotoluene (1.4 g, 5 mmole), m. p. 96—97°, undepressed on admixture with an authentic specimen synthesised according to Posternak *et al.*[16]

1,9-Dihydroxy-3,7-dimethyldibenzofuran. 2,6,2′,6′-tetramethoxy-4,4′-dimethyldiphenyl was synthesised by Ullmann coupling of 3,5-dimethoxy-4-iodotoluene as described by Posternak *et al.*[16] The crude diphenyl (300 mg, m. p. 139—145°) was boiled with hydrobromic acid (10 ml; d, 1.54) for 6 h in an atmosphere of carbon dioxide. The reaction product was collected, washed with water, dried and dissolved in benzene. The solution was filtered through a short column of alumina, evaporated and the product was crystallised from dimethyl sulphoxide-water (1:4) giving 1,9-dihydroxy-3,7-dimethyldibenzofuran (100 mg), m. p. 190—192°. (Found: C 73.9; H 5.4. $C_{14}H_{12}O_3$ requires C 73.7 H 5.3.)

This phenol gave a blue colour with ferric chloride in ethanol and a blue colour with Gibbs' reagent.

3,9-Dihydroxy-1,7-dimethyldibenzofuran. Ullmann coupling of 3,5-dimethoxy-2-iodotoluene (7.5 g) and 3,5-dimethoxy-4-iodotoluene (0.8 g) with copper powder (25 g) followed by extraction of the reaction product with light petroleum afforded a crude mixture of diphenyls (3.2 g, 71 %) which was boiled for 16 h with hydrobromic acid (50 ml; *d*, 1.54) to effect demethylation and ring closure. The crude phenol mixture (2.2 g) was analysed by paper chromatography, using dimethyl sulphoxide as stationary phase [18] and either (A) diethyl ether or (B) toluene-petroleum ether b. p. 60—80° 3:1 as mobile phase. It was extracted with benzene overnight in a Soxhlet apparatus; the larger part of the main component (1.8 g), 3.7-dihydroxy-1,9-dimethyldibenzofuran, (R_F = (A) 0.68; (B) 0.18) crystallised in a fairly pure state (m. p. 239—242°; Shibata [7] gives m. p. 243°).

The mother liquor was evaporated to dryness and chromatographed on a column of cellulose powder (15 g) impregnated with 4 % dimethyl sulphoxide in ether, using 1 % dimethyl sulphoxide in ether as an eluant. The separation was followed by paper chromatography. The first fractions contained a small amount of 1,9-dihydroxy-3,7-dimethyldibenzofuran, described above (R_F = (A) 0.92; (B) 0.75.) The last fractions gave further amounts (150 mg) of 3,7-dihydroxy-1,9-dimethyldibenzofuran. The middle fractions gave 3,9-dihydroxy-1,7-dimethyldibenzofuran (250 mg) (R_F = (A) 0.79; (B) 0.21), characterised by a blue colour with Gibbs' reagent. It was crystallised from aqueous ethanol, needles, m. p. 184—185°. (Found: C 73.7; H 5.4. $C_{14}H_{12}O_3$ requires C 73.7; H 5.3.) U.V. absorption (96 % ethanol): λ_{max} 233 mμ (log ε 4.74); 267 mμ (4.46); 287 mμ (4.40); 300 mμ (4.21); 312 mμ (4.39).

3,9-Dimethoxy-1,7-dimethyldibenzofuran The phenol was methylated in boiling acetone with dimethyl sulphate and potassium carbonate giving the dimethyl ether, needles, m. p. 94.5—95.5°, from aqueous methanol. (Found: C 75.5; H 6.2. $C_{16}H_{16}O_3$ requires C 75.0; H 6.3.)

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