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FUNGUS PIGMENTS—XII*

THE STRUCTURE AND SYNTHESIS OF THELEPHORIC ACID

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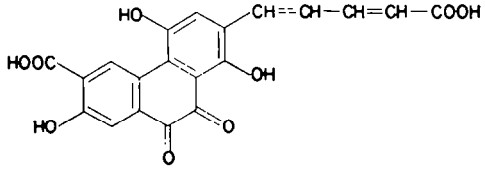
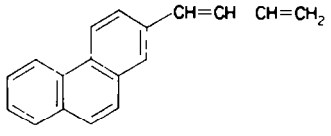
Abstract—Degradative and spectroscopical evidence, as well as biogenetic considerations led to the conclusion that thelephoric acid is 2,3,8,9-tetrahydroxybenzobis[1,2-b,4,5-b']benzofuran-6,12-quinone(VI). This view was confirmed by synthesis, involving condensation of chloranil with two molecules of 3,4-dimethoxyphenol and subsequent demethylation.

THELEPHORIC acid was investigated by Kögl *et al.*[1] and on the basis of degradation reactions formula I was proposed. Doubt concerning this formula was cast by Millward and Whiting,[2] who synthesized 1,2'-phenanthryl-1,3-butadiene(II), which Kögl *et al.*[7] claimed to have obtained from thelephoric acid acetate and record properties very different from those reported by Kögl *et al.*[1] As no authentic sample was available for direct comparison, the possibility of polymorphism and/or stereoisomerism could not be ignored, but the necessity of a more thorough study of thelephoric acid was obvious.



I



II

Thelephoric acid, first found in several species of *Thelephora*[1,3] also occurs in *Hydnum* spp.[4–7] For the present work the sporophores of *Hydnum suaveolens* collected in 1948 were used.†

Extraction of the fungus material with acetone gave thelephoric acid in a yield of about 0·6 per cent. Thelephoric acid is best recrystallized from pyridine, but the solvent can only be completely removed by prolonged heating under vacuum to 120–150°. Thelephoric acid dissolves quite readily in dimethyl sulphoxide and crystallizes upon addition of ethanol but again the dimethyl sulphoxide is very difficult to remove completely.

Thelephoric acid has an absorption maximum at 493 mμ in pyridine.[1] In alcohol

* Part XI: *Acta Chem. Scand.* **13**, 1305 (1959). A preliminary account of the present work has appeared in *Suomen Kemistilehti* **B 33**, 72 (1960).

† This material was generously placed at the author's disposal by Prof. H. Erdtman, Stockholm.

[1] F. Kögl, H. Erxleben and L. Jänecke, *Liebigs Ann.* **482**, 105 (1930).
[2] B. B. Millward and M. C. Whiting, *J. Chem. Soc.* 903 (1958).
[3] W. Zopf, *Bot. Z.* 69 (1889),
[4] J. Zellner, *Monatsh.* **36**, 615 (1915).
[5] M. Sawada, *Nippon Ringaku Kaishi* **34**, 110 (1952); *Chem. Abstr.* **47**, 4436 (1953).
[6] M. Sawada, *Nippon Ringaku Kaishi* **40**, 195 (1958); *Chem. Abstr.* **52**, 18638 (1958).
[7] J. Gripenberg, *Acta Chem. Scand.* **12**, 1411 (1958).

this maximum is shifted to 480 mμ (the complete spectrum in alcohol is reproduced in Fig. 1). In acetone the maximum is at 463 mμ and in dioxan at 450 mμ. In alkaline solution thelephoric acid has a weak maximum at 720–730 mμ.

In the I.R. spectrum (in KBr-disk the position of the carbonyl band varies in different preparations between 1635 and 1660 cm^{-1}. Read and Vining[8] report 1629 cm^{-1} for this band, which is regarded as that of a quinone carbonyl. Even in the region 1400–1100 cm^{-1} some differences can be observed. On the other hand the finger print region is very consistent

The analytical figures of Kögl *et al.*[1] favoured the composition $C_{20}H_{12}O_9$, but fit

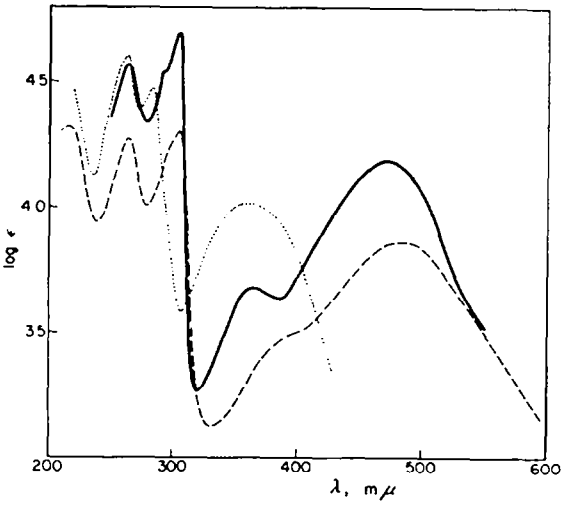


FIG. 1. Spectra of: (– – – –) thelephoric acid(VI) (ethanol); (———) thelephoric acid tetramethyl ether(VIII) (chloroform) and (.....) thelephoric acid tetra-acetate(IX) (dioxan).

equally well $C_{18}H_{10}O_8$.[9] The difficulty in removing solvent of crystallization makes the analytical results somewhat uncertain, but on an extensively dried sample figures point to $C_{18}H_8O_8$ as the correct composition.

Potentiometric titration in dimethyl sulphoxide with tetrabutylammonium hydroxide gave an equivalent weight of 176, corresponding to two ionizable hydrogens. Comparison of the titration curves with other strongly acidic phenols show thelephoric acid as a slightly weaker acid than *o*-nitrophenol.

Acetylation gave the known[1] acetate originally regarded as a triacetate, but acetyl values (33·8%) are higher than those reported earlier[1] (25·24 and 24·97%) and the analyses agree well with a tetra-acetate ($C_{26}H_{16}O_{12}$). The U.V. spectrum (Fig. 1) shows a pronounced hypsochromic shift relative to thelephoric acid. In the I.R. spectrum the band at 1780 cm^{-1} is attributed to the ester carbonyls and the band at 1680 cm^{-1} to the quinone carbonyl.

Reductive acetylation gave the leuco-acetate,[1] which is now regarded as dihydrothelephoric acid hexa-acetate ($C_{30}H_{22}O_{14}$). The U.V. spectrum (Fig. 2) has also been reported by Read and Vining,[8] and in agreement with these authors is the presence of a single strong band in the carbonyl region of the I.R. spectrum at 1760 cm^{-1}, due to ester carbonyls.

[8] G. Read and L. C. Vining, *Canad. J. Chem.* **37**, 1442 (1959).
[9] J. Gripenberg, *Svensk Kem. Tidskr.* **72**, 256 (1960).

The U.V. spectrum of the leuco-acetate cannot be that of a leuco-acetate of I, which should be similar to that of II.[2] Also the lack of any absorption in the I.R. spectrum, that could be attributed to the carboxyl groups in the leuco-acetate of I clearly shows that this formula cannot be correct.[9]

As can be seen from Fig. 2 the spectrum of thelephoric acid leuco-acetate is

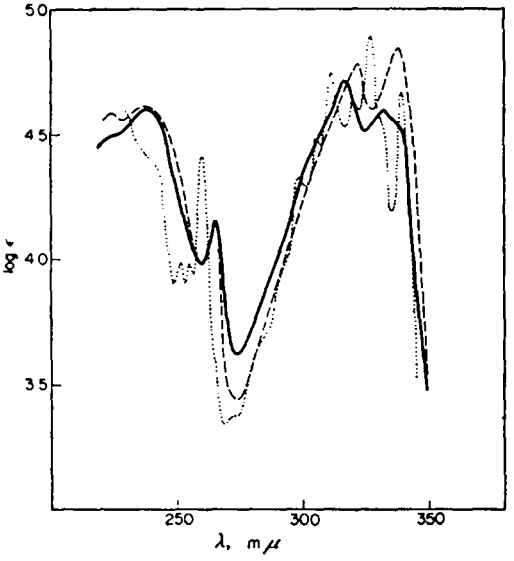
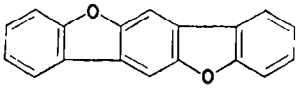


FIG. 2. Spectra of: (———) dihydrothelephoric acid hexa-acetate(XI) (dioxan), (- - - -) dihydroisothelephoric acid hexa-acetate (dioxan) and (.....) benzobis [1,2-b,4,5-b'] benzofuran(III) (cyclohexane).

similar to that of benzobis[1,2-b,4,5-b']benzofuran(III), and on the basis of the analytical evidence should be a hexa-acetoxy derivative. This has also been suggested by Read and Vining[8] based on a comparison of the spectrum of thelephoric acid leuco-acetate with the less similar spectrum of 2,11-diacetoxybenzobis[1,2-b,4,3-b']-benzofuran.

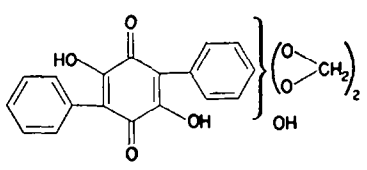


III

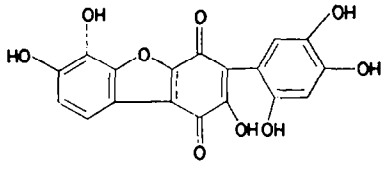
Further proof of the presence of the benzobis[1,2-b,4,5-b']benzofuran ring system in thelephoric acid was obtained from zinc dust distillation of thelephoric acid acetate. Kögl *et al.*[1] obtained in this reaction what they believed to be 1,2'-phenanthryl-1,3-butadiene(II), but the crystalline sublimate described by Kögl *et al.* proved to be a mixture of at least five components. By a combination of chromatography and recrystallization one component was isolated in a pure state and identified as *p*-terphenyl. A second component is most probably biphenyl, although it was not obtained pure. Three further components were characterized only by their U.V. spectra, and one had maxima at exactly the same positions, and with the same relative intensities as benzobis[1,2-b,4,5-b]benzofuran(III), whose presence in the mixture is thus strongly indicated.

Aghoramurthy *et al.*[10] have also reported the formation of *p*-terphenyl from the zinc dust distillation of thelephoric acid acetate, but their conclusion that thelephoric acid is a simple 2,5-diphenyl-*p*-benzoquinone derivative, such as IV cannot, however, be correct.

It has been shown[11] that 2,5-diphenyl-*p*-benzoquinones with hydroxyl or methoxyl groups in the *p*-positions of the aromatic rings have a long-wave maximum at 380–405 mμ. This should not be changed by the introduction of more hydroxyl groups and a compound of structure IV should therefore be expected to absorb in the same region or only at a slightly longer wave-length, whereas thelephoric acid, absorbs at 450 mμ in dioxan, the same solvent in which the other measurements were made. The U.V. spectrum of thelephoric acid leuco-acetate differs completely from the spectrum one would expect for the leuco-acetate of a compound with structure IV. This should be similar to the spectrum of 2′,5′-diacetoxy-4,4″-dimethoxy-*p*-terphenyl (see experimental, with a maximum at 280–290 mμ, and not above 300 mμ. As we have been unable to get a positive test[12] for a methylenedioxy group in thelephoric acid or any of its derivatives, it is possible that the Indian workers had a different substance.*



IV



V

On the assumption that thelephoric acid leuco-acetate is a hexa-acetoxybenzobis-[1,2-b,4,5-b′]benzofuran thelephoric acid may be formulated as a tetrahydroxy-benzobis[1,2-b,4,5-b′]benzofuranquinone.

Read and Vining[8], proposed formula V for thelephoric acid, assuming that ring closure to the benzobis[1,2-b,4,5-b′]benzofuran system occurred on acetylation and reductive acetylation. Formula V does not agree with analytical figures now reported, and cannot explain that thelephoric acid acetate and leuco-acetate are readily hydrolysed to thelephoric acid (in the case of the leuco-acetate the primarily formed dihydro-thelephoric acid is spontaneously oxidized in air to thelephoric acid). The opening of only one furan ring under the conditions of the hydrolysis is extremely improbable.

Further evidence against formula V is obtained from the methylation of thelephoric acid. The product corresponds to a tetramethyl ether of thelephoric acid, the U.V. spectrum (Fig. 1) indicating that no fundamental change in the chromophore had taken place during methylation. A compound with structure V should give a hexa-methyl ether, or possibly an anhydrotetramethylether, with the spectrum very different from that of thelephoric acid.

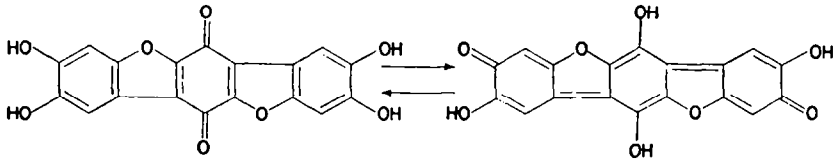
The position of the quinone group in the benzobis[1,2-b,4,5-b′]benzofuran ring system, cannot be in one of the terminal aromatic rings, as *p*-terphenyl is formed during zinc dust distillation. The other end of the molecule should contain a preformed

* See "Note added in proof", p. 143.

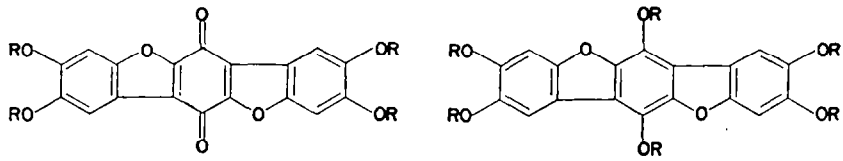
[10] K. Aghoramurthy, K. G. Sarma and T. R. Seshadri, *Tetrahedron Letters* No. 8, 20 (1959).
[11] J. Gripenberg, *Acta Chem. Scand.* **12**, 1762 (1958).
[12] O. A. Stamm, H. Schmid and J. Büchi, *Helv. Chim. Acta* **41**, 2006 (1958).

dibenzofuran ring system which should not loose its oxygen in the zinc dust distillation.[13,14] If the quinone group is in the central ring or extended over the whole ring system the oxygen bridges would terminate in a quinone double bond and the removal of these oxygen atoms appears more likely. Such a loss of an oxygen between an aromatic ring and a quinonoid system was observed in the zinc dust distillation of cinnabarin.[15]

The positions of the four hydroxyl groups could not be established analytically. Formula VI which is closely related to the structure of other fungus pigments of the diphenyl-*p*-benzoquinone type, is likely on biogenetic considerations and was established by synthesis. Acharya *et al.*[16] synthesized 3,9-dimethoxybenzobis-



VI VII



VIII, R=CH_3 X, R=CH_3

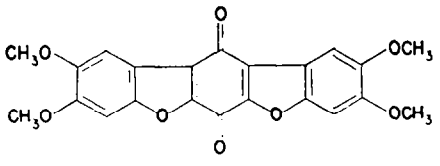
IX, R=CH_3CO XI, R=CH_3CO

[1,2-b,4,5-b']benzofuran-6,12-quinone by condensation of chloranil with two molecules of 3-methoxyphenol. By substituting 3,4-dimethoxyphenol for 3-methoxyphenol 2,3,8,9-tetramethoxybenzobis[1,2-b,4,5-b']benzofuran-6,12-quinone(VIII) should be formed. The reaction, gave a very difficultly soluble compound, whose U.V. and I.R. spectra were completely identical with those of thelephoric acid tetramethyl ether. Demethylation gave thelephoric acid, identified by its I.R. spectrum.

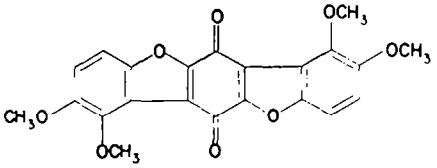
This synthesis of thelephoric acid does not, constitute unequivocal proof of the structure of thelephoric acid. The condensation of chloranil with 3,4-dimethoxyphenol could also lead to 2,3,9,10-tetramethoxybenzobis[1,2-b,5,4-b']benzofuran-6,12-quinone(XII). Acharya *et al.*[16] have, however, shown that the analogous condensation of chloranil with β-naphthol proceeds through 2,5-dichloro-3,6-di-β-naphthoxy-*p*-benzoquinone and it is therefore reasonable to assume that in the present case the reaction cannot give XII. Furthermore XII is a derivative of *m*-terphenyl, whereas thelephoric acid is definitely a derivative of *p*-terphenyl. That the condensation should occur in the 2-position of the 3,4-dimethoxyphenol giving 1,2,7,8-tetramethoxybenzobis[1,2-b,4,5-b']benzofuran-6,12-quinone(XIII) is highly unlikely in view of

[13] W. Hoffmeister, *Leibigs Ann.* **159**, 191 (1871).
[14] H. Erdtman and N. E. Stjernström, *Acta Chem. Scand.* **13**, 653 (1959).
[15] J. Gripenberg, E. Honkanen and O. Patoharju, *Acta Chem. Scand.* **11**, 1485 (1957).
[16] R. V. Acharya, B. D. Tilak and M. R. Venkiteswaran, *J. Sci. Ind. Res. India* **16B**, 400 (1957).

the demonstrated unreactivity of this position in ethers of hydroxyhydroquinone.[17] Thelephoric acid tetramethyl ether must therefore have structure VIII and thelephoric acid on this basis is either VI or its tautomere VII. The similarity of the U.V. spectra of thelephoric acid and its methyl ether clearly indicate that they have the same



XII



XIII

chromophore. A compound with structure VII would be expected to have a different spectrum and VI must be the correct structure of thelephoric acid.

The resonance stabilization of the anion common to VI and VII explains the relatively strong acidity of thelephoric acid. That thelephoric acid absorbs at longer wavelengths than similarily substituted diphenyl-*p*-benzoquinones is certainly due to the fact that the benzene rings in thelephoric acid are forced into the same plane as the quinone ring.

Two further reactions of thelephoric acid are of interest.

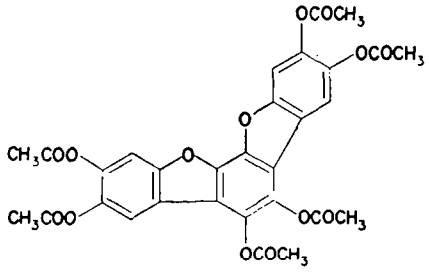
When the methylation of thelephoric acid was carried out for a longer period with excess of dimethyl sulphate, the initially formed difficultly soluble tetramethyl ether dissolved and a colourless compound was obtained in good yield. This had a higher methoxyl-content, showed no carbonyl band in the I.R. spectrum and when heated with hydrobromic acid gave thelephoric acid. It was thought to be formed by methylation of an enolic form of thelephoric acid and therefore called isothelephoric acid hexamethyl ether[9] but later was proved identical with dihydrothelephoric acid hexamethyl ether(X), described earlier by Kögl *et al.*[1] and Aghoramurthy *et al.*[10] The reducing agent in the reaction was found to be pyridine present when the thelephoric acid had not been thoroughly dried after recrystallization.

Decker[18] has shown that methylpyridinium hydroxide is oxidized to N-methyl-α-pyridone by potassium ferricyanide and although no report has been found that quinones can effect this reaction, it is believed that the reaction is analogous to the Decker-oxidation, the quinone being reduced to the hydroquinone, which is instantly methylated. Preliminary experiments with other quinones have shown that they also can be reductively methylated in the presence of pyridine and a more thorough study of this reaction is in hand.

On the assumption that thelephoric acid was enolizable the preparation of the enol acetate by boiling with acetic anhydride and sodium acetate was attempted. This reaction gave a colourless compound termed isothelephoric acid acetate.[9] Both the U.V. (Fig. 2) and I.R. spectra are similar to those of thelephoric acid leuco-acetate, but definitely not identical. The compound is readily hydrolysed but no pure product has as yet been obtained. It is isomeric with thelephoric acid leuco-acetate and it is thought that some kind of rearrangement as well as reduction has taken place during the acetylation. The compound is, therefore, called dihydroiso-thelephoric acid hexa-acetate. One possible structure would be XIV. A reduction

[17] W. Baker and C Evans, *J. Chem. Soc.* 372 (1938).
[18] H. Decker, *J. Prakt. Chem.* [2] **47**, 28 (1893).

of a quinone to the corresponding hydroquinone acetate under the conditions used is known, *p* benzoquinone can be converted in low yield to hydroquinone diacetate



XIV

upon boiling with acetic anhydride and sodium acetate.[19,20] The formation of this compound and its structure will be the subject of further work.

EXPERIMENTAL

Analyses were by Dr. A. Bernhardt, Mülheim, Germany. The I.R. spectra were measured as KBr-disks with a Beckman IR-5 instrument and the U.V. spectra with a Beckman DK-2 instrument.

Isolation of thelephoric acid

The finely powdered fungus material (750 g) was extracted in a Soxhlet-apparatus with acetone. The almost black precipitate formed was thoroughly washed with water and the insoluble residue recrystallized from pyridine, giving very dark violet crystals (8 g). This material still containing pyridine on heating at 140°/0·1 mm lost 41% of its weight, corresponding to a total yield of pure solvent-free thelephoric acid of 4·7 g. (Found: C, 60·79, 61·42; H, 2·30, 2·41. $C_{18}H_8O_8$ requires: C, 61·37; H, 2·29%). U.V. spectra: (ethanol) λ_{max} 217 (log ε 4·33), 264 (log ε 4·27), 305 (log ε 4·30), 390 (infl) (log ε 3·48) and 483 mμ (log ε 3·86), λ_{min} 241 (log ε 3·94), 280 (log ε 4·01) and 330 mμ (log ε 3·13). Owing to the very low solubility of thelephoric acid in ethanol these extinction values are probably too low; (pyridine) λ_{max} 311 (log ε 4·51), 395 (infl) (log ε 3·59) and 493 mμ (log ε 4·05), λ_{min} 340 mμ (log ε 3·11); (dioxan) λ_{max} 450 mμ; (acetone) λ_{max} 463 mμ. Main I.R. maxima: 3550 (m), 3260 (s), 1645 (s), 1610 (m), 1530 (s), 1480 (m), 1430 (w), 1385 (m), 1365 (m), 1332 (w), 1267 (s), 1175 (s), 1128 (m), 1085 (m), 1038 (s), 863 (m), 840 (w), 798 (s), 749 (w), 713 (w) and 698 (w) cm^{-1}.

Thelephoric acid tetra-acetate(IX). This was obtained as described by Kögl *et al.*[1] m.p. 330–335°. (Found: C, 59·79; H, 3·36; CH_3CO, 33·8, $C_{26}H_{16}O_{12}$ requires: C, 60·01; H, 3·10; $(CH_3CO)_4$, 33·1%). U.V. spectrum: (dioxan) λ_{max} 263 (log ε 4·60), 283 (log ε 4·47) and 360 mμ (log ε 4·01), λ_{min} 236 (log ε 4·12), 273 (log ε 4·39) and 307 mμ (log ε 3·59). Main I.R. maxima: 1780 (s), 1680 (s) 1625 (w), 1585 (w), 1535 (s), 1478 (m), 1448 (m), 1370 (s), 1318 (m), 1262 (s), 1205 (vs), 1159 (s), 1125 (s), 1076 (m), 1033 (vs), 1015 (m), 919 (m), 907 (m), 882 (m), 832 (m), 807 (m), 753 (w), 728 (w) and 709 (w) cm^{-1}.

Thelephoric acid leuco-acetate(XI). This was prepared according to Kögl *et al.*[1] m.p. 380–390°. (Found: C, 58·69; H, 3·57; CH_3CO, 41·3, $C_{30}H_{22}O_{14}$ requires: C, 59·41; H, 3·66; $(CH_3CO)_6$, 42·5%). Main I.R. maxima: 1760 (s), 1635 (w), 1600 (w), 1538 (m), 1462 (s), 1428 (m), 1412 (m), 1377 (s), 1347 (m), 1320 (m), 1292 (m), 1263 (m), 1205 (vs), 1161 (s), 1130 (s), 1074 (s), 1023 (s), 991 (m), 920 (m), 879 (m), 802 (m), 742 (w), 727 (w), 706 (w), 674 (w) and 658 (w) cm^{-1}.

Methylation of thelephoric acid

(a) Thelephoric acid (air dried material, 150 mg) was methylated with dimethyl sulphate (2 g) and potassium carbonate (2 g) in acetone by boiling on a water bath for 3 hr. The insoluble residue was washed with water, dilute sodium hydroxide, acetone and ether leaving a dark violet crystalline

[19] E. Sarauw, *Liebigs Ann.* **209**, 93 (1881).
[20] K. Buschka, *Ber. Dtsch. Chem. Ges.* **14**, 1326 (1881).

mass (95 mg). This was recrystallized from anisol giving *thelephoric acid tetramethyl ether*(VIII) as brown-violet crystals, which decompose without melting at 360°. (Found: C, 64·25; H, 3·99; OCH_3, 26·5. $C_{22}H_{16}O_8$ requires: C, 64·70; H, 3·95; $(OCH_3)_4$, 30·4%). U.V. spectrum: (chloroform) λ_{max} 264 (log ε 4·57), 293 (infl) (log ε 4·54), 303 (log ε 4·70), 364 (log ε 3·68) and 472 mμ (log ε 4·18), λ_{min} 280 (log ε 4·34), 320 (log ε 3·27) and 386 mμ (log ε 3·64). Main I.R. maxima: 1661 (s), 1618 (w), 1588 (w), 1528 (s), 1500 (m), 1481 (s), 1460 (m), 1435 (s), 1378 (w), 1363 (w), 1325 (m), 1253 (s), 1217 (s), 1194 (w), 1186 (w), 1148 (m), 1092 (s), 1040 (s), 1000 (m), 858 (m), 846 (m), 783 (s), 765 (w), 751 (w), 723 (w), 711 (w) and 700 (w) cm^{-1}.

(b) Thelephoric acid (air dried material, 150 mg) was methylated as described under (a) except that the reaction time was 40 hr. The insoluble part was treated as above giving thelephoric acid tetramethyl ether (13 mg). The dark green acetone solution was evaporated to dryness under vacuum and the residue treated with water yielding a yellow crystalline precipitate. This was recrystallized from chloroform/alcohol giving colourless crystals of dihydrothelephoric acid hexamethyl ether (X, 85 mg), m.p. 260–261°. (Found: C, 66·04; H, 5·11; OCH_3, 41·2. $C_{24}H_{22}O_8$ requires: C, 65·74; H, 5·06; $(OCH_3)_6$, 42·4%). U.V. spectrum: (dioxan) λ_{max} 228 (log ε 4·64), 252 (log ε 4·55), 275 (log ε 4·11), 306 (infl) (log ε 4·40), 318 (log ε 4·66), 341 (log ε 4·57) and 357 mμ (log ε 4·81), λ_{min} 240 (log ε 4·51), 270 (log ε 4·08), 284 (log ε 3·86), 331 (log ε 4·30) and 346 mμ (log ε 4·51). Main I.R. maxima: 1631 (w), 1605 (w), 1536 (s), 1483 (s), 1463 (s), 1441 (s), 1385 (s), 1343 (w), 1300 (s), 1270 (s), 1238 (m), 1212 (s), 1191 (s), 1184 (s), 1148 (s), 1085 (m), 1060 (s), 1038 (m), 1004 (m), 913 (w), 858 (m), 808 (m), 781 (m), 753 (m), 688 (w) and 664 (w) cm^{-1}. This compound was identical with one prepared from thelephoric acid according to Kögl *et al.*[1], for which they report m.p. 246°. Aghoramurthy *et al.*[10] report m.p. 254–256°. The identification was based on a mixed m.p. and on completely superimposable I.R. spectra.

(c) Thelephoric acid (dried over phosphorus pentoxide under vacuum, 100 mg) was methylated as described under (b). The insoluble portion gave thelephoric acid tetramethyl ether (95 mg), and no crystalline material could be obtained from the almost colourless filtrate.

Reductive methylation of thelephoric acid tetramethyl ether. Thelephoric acid tetramethyl ether (50 mg) was methylated with dimethylsulphate (2 g) and potassium carbonate (2 g) in boiling acetone containing 0·1 ml pyridine for 20 hr. The solution gave as described for the methylation of thelephoric acid, under (b), dihydrothelephoric acid hexamethyl ether (40 mg).

Demethylation of dihydrothelephoric acid hexamethyl ether. Dihydrothelephoric acid hexamethyl ether (20 mg) was boiled with a mixture of acetic acid and hydrobromic acid. The solution gradually turned almost black with formation of a dark precipitate. This (10 mg) was recrystallized from pyridine and identified by I.R. spectrum as thelephoric acid.

Zinc dust distillation of thelephoric acid. The reaction was carried out as described by Kögl *et al.*[1] The light petroleum solution of the crystalline sublimate was chromatographed on a column of alumina, and the chromatogram eluted with the same solvent. The chromatogram was inspected in ultra-violet light which revealed several fluorescent zones and treated as separate fractions. The first fraction with only a very weak fluorescence gave a few crystals m.p. 65-70° and a single maximum in the U.V. spectrum at 247 mμ (cyclohexane). This substance is very probably biphenyl.

The second fraction with a strong blue fluorescence contained the bulk of the material. Recrystallization of the residue gave colourless crystals with m.p. 209–210°, λ_{max} (cyclohexane) 274 mμ. The compound was identified as *p*-terphenyl by its I.R. spectrum. The mother liquor from the crystallization of *p*-terphenyl contained a substance with λ_{max} 264 and 296 mμ which has not been obtained completely free from *p*-terphenyl and has not yet been identified.

The third fraction had a whitish blue fluorescence and contained only a very small amount of material whose U.V. spectrum had maxima at 260, 298, 305, 311, 320, 327 and 339 mμ. These maxima coincide exactly with those of benzobis[1,2-b,4,5-b']benzofuran. The rather high absorption between 265 and 280 mμ indicates that some *p*-terphenyl is still present in this fraction.

The fourth fraction which did not clearly separate from the preceding fraction showed in the U.V. spectrum in addition to the maxima of benzobis[1,2-b,4,5-b']benzofuran two strong maxima at 288 and 302 mμ.

2,3,8,9-*Tetramethoxybenzobis*[1,2-b, 4,5-b']*benzofuran*-6,12-*quinone*(VIII). Sodium (0·45 g) was dissolved in abs alcohol (15 ml) and 3,4-dimethoxyphenol[21] (3 g) added. This solution was added to a suspension of chloranil (2·4 g) in abs alcohol (40 ml) and the mixture boiled for 10 min. Abs alcohol

[21] R. I. Meltzer and J. Doczi, *J. Amer. Chem. Soc.* 72, 4986 (1950).

(15 ml) in which sodium (0·45 g) had been dissolved was then added and the boiling continued for 45 min. After cooling the precipitate was thoroughly washed first with alcohol and then with water. The remaining crude product (1·0 g) was once extracted with boiling anisol and the insoluble residue extracted with chloroform in a Soxhlet. 2,3,8,9-Tetramethoxybenzobis[1,2-b,4,5-b']benzofuran-6,12-quinone precipitated from the solution as brown violet crystals (700 mg). A sample for analysis was recrystallized from bromocymene (Found: C, 64·25; H, 3·95. $C_{22}H_{16}O_8$ requires: C, 64·70; H, 3·95%). The U.V. and I.R. spectra were identical with those of thelephoric acid tetramethylether.

2,3,7,8-*Tetrahydroxybenzobis*[1,2-b,4,5-b']*benzofuran*-6,12-*quinone* (VI). 2,3,8,9-Tetramethoxybenzobis[1,2-b,4,5-b']benzofuran-6,12-quinone (40 mg) and pyridine hydrochloride (4 g) were heated in an oil bath at 205–210° for ½ hr resulting in a clear dark melt. After cooling this was treated with water and the blue precipitate recrystallized from pyridine giving dark violet crystals (15 mg) after drying over phosphorus pentoxide under vacuum. The U.V. and I.R. spectra were identical with those of thelephoric acid.

Dihydroisothelephoric acid hexa-acetate. Thelephoric acid (100 mg) was boiled with acetic anhydride and anhydrous sodium acetate for 16 hr. A clear light brown solution resulted. The precipitate, formed upon cooling was recrystallized from acetic acid, giving colourless needles (130 mg), which decomposed at 300°. (Found: C, 59·70; H, 3·72; CH_2CO, 41·4. $C_{30}H_{22}O_{14}$ requires: C, 59·41; H, 3·66; $(CH_3CO)_6$, 42·5%). U.V. spectrum: (dioxan) λ_{max} 224 (log ε 4·58), 237 (log ε 4·62), 265 (log ε 4·17), 321 (log ε 4·78) and 338 mμ (log ε 4·84), λ_{min} 228 (log ε 4·56), 260 (log ε 3·97), 274 (log ε 3·44) and 328 mμ (log ε 4·59). Main I.R. maxima: 1780 (s), 1748 (s), 1631 (w), 1534 (w), 1462 (s), 1433 (w), 1408 (w), 1372 (s), 1338 (w), 1321 (m), 1280 (w), 1261 (m), 1197 (vs), 1157 (s), 1129 (s), 1082 (m), 1012 (m), 986 (w), 951 (w), 943 (m), 872 (m), 854 (w), 818 (w), 803 (w), 777 (w), 728 (w), 709 (w), 683 (w), 671 (w) and 657 (w) cm^{-1}.

2′,5′-*Diacetoxy*-4,4″-*dimethoxy*-p-*terphenyl.* 2,5-bis(*p*-methoxyphenyl)-*p*-benzoquinone[23] was heated to boiling with acetic anhydride, zinc dust and a drop of pyridine. The hot yellow solution was filtered and the filtrate treated with water. The colourless precipitate was recrystallized from dioxan, m.p. 204–205°. (Found: C, 71·07; H, 5·47. $C_{24}H_{22}O_6$ requires: C, 70·92; H, 5·46%). U.V. spectrum: (ethanol) λ_{max} 276 mμ (log ε 4·50), λ_{min} 241 mμ (log ε 3·90).

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Note added in proof. An exchange of samples with the Indian workers has now been arranged and comparisons carried out in both laboratories have established the identity of the preparations.

[23] R. Pummerer and E. Prell, *Ber. Dtsch. Chem. Ges.* **55**, 3105 (1922).