

(0.01 N sulphuric acid, 40 min in a boiling water bath). The results obtained are shown in Fig. 1.

*Hydrolysis of raffinose by yeast invertase in the presence of umbelliferose.* The experimental procedure given above was followed and the total volume of the assay mixture reduced to 2 ml. Results and further information are given in Fig. 2.

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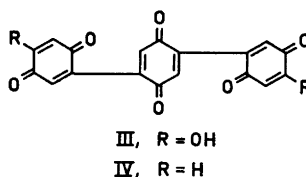
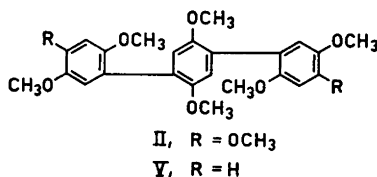
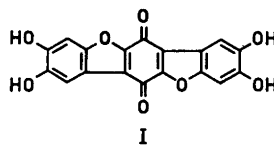
## A New Synthesis of Thelephoric Acid

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The structure (I) of thelephoric acid has been supported by two independent syntheses.<sup>1,2</sup> However, neither of them can be regarded as completely unambiguous and a third synthesis is described here, which finally removes any doubts that might be cast on the correctness of formula (I).

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The starting material, 2,4,5,2',5',2'',4'',5''-octamethoxy-*p*-terphenyl (II), was prepared by standard Ullmann coupling. Its conversion into the triquinone (III) is analogous to the synthesis of (IV) described by Erdtman *et al.*<sup>3</sup> The triquinone (III) is rather unstable and its complete purification has not been possible to achieve.

That diquinones can undergo photochemical and/or thermal rearrangement to dibenzofuranquinones is known.<sup>4-9</sup> A triquinone such as (III) should in the same way give a benzobisbenzofuranquinone. In fact, when (III) was boiled with acetic anhydride it gave thelephoric acid tetra-acetate and in the presence of zinc dust thelephoric acid leuco-acetate, both of which have earlier been converted into thelephoric acid.<sup>1</sup> The triquinone (IV), on the other hand, failed to undergo any conversion to a benzobisbenzofuranquinone.

*Experimental.* U. V. spectra were measured with a Beckman DK-2 spectrophotometer, and I.R. spectra with a Perkin-Elmer 125 spectrophotometer. Microanalyses were done by Dr. A. Bernhardt, Mülheim, Germany. 2, 4, 5, 2', 5', 2'', 4'', 5''-Octamethoxy-*p*-terphenyl (II). 2,5-Diiodohydroquinone dimethylether<sup>3,10</sup> (1.8 g), 5-iodohydroxyhydroquinone trimethylether<sup>11</sup> (10.8 g) and copper

bronze (25 g) were thoroughly mixed in a 250-ml flask and heated on an oil bath to about 240°, at which the reaction started. The temperature was raised during 20 min to 270°. The reaction mixture was allowed to cool and the combined organic products from two runs were extracted with chloroform. The solvent was evaporated and the residue subjected to distillation *in vacuo*. This yielded 2,4,5,2',4',5'-hexamethoxydiphenyl (7.8 g) and an orange-yellow oil (2.2 g), (b.p. 270–300°/1 mm), which crystallised on cooling. The terphenyl was recrystallised three times from butanol-1. M.p. 218–219° (corr.). (Found: C 66.1; H 6.2. Calc. for C<sub>26</sub>H<sub>30</sub>O<sub>8</sub>: C 66.4; H 6.4). U. V. spectrum: (dioxane)  $\lambda_{\max}$  308 m $\mu$  (log  $\epsilon$  4.33);  $\lambda_{\min}$  275 m $\mu$  (log  $\epsilon$  3.84). Main I.R. maxima (KBr disc): 3000 m, 2940s, 2838m, 1614m, 1534s, 1508s, 1470s, 1440m, 1406s, 1380m, 1326m, 1280m, 1212s, 1182m, 1152m, 1060m, 1034s, 960w, 864m, 828m, 814m, 766s, 728w, 716w, 708w cm<sup>-1</sup>.

4,4'-Dihydroxytriquinone (III) was prepared from 2,4,5,2',5',2'',4'',5''-octamethoxy-*p*-terphenyl according to the method of Erdtman *et al.*<sup>3</sup> mentioned above. The yield was 80 % as calculated from the methoxy compound. When dry (dried at room temperature *in vacuo*) the initially yellowish brown sample became browner. 4,4'-Dihydroxytriquinone has no melting point but turns dark at about 230–280°. (Found: C 57.0; H 2.9. Calc. for C<sub>18</sub>H<sub>8</sub>O<sub>8</sub>: C 61.4; H 2.3). The sample contained some ash.

Triquinone (IV) was prepared from 2,4,2',5',2'',4''-hexamethoxy-*p*-terphenyl (V) according to Erdtman *et al.*<sup>3</sup>

Thelephoric acid tetra-acetate. 4,4'-Dihydroxytriquinone (50 mg) was boiled for ½ h in acetic anhydride containing 2 drops of pyridine. The mixture was filtered hot, cooled, and after standing, refiltered. The precipitate

(7 mg) was recrystallised from nitrobenzene. The U.V. and I.R. spectra were identical with those of thelephoric acid tetra-acetate.<sup>1</sup>

Thelephoric acid leuco-acetate. 4,4'-Dihydroxytriquinone (50 mg) was boiled for 5 min in acetic anhydride containing 2 drops of pyridine. Zinc dust was added and refluxing continued for ½ h. The mixture was filtered hot, cooled, and after standing, refiltered. The precipitate (8 mg) was recrystallised from acetic anhydride. The U.V. and I.R. spectra were identical with those of thelephoric acid leuco-acetate.<sup>1</sup>

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