(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 umbelliferone. 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.

1. French, D. Advan Carbohydrate Chem. 9 (1954) 149.

Received February 13, 1965.

A New Synthesis of Thelephoric Acid

MAURI LOUNASMAA *

Department of Chemistry, Institute of Technology, Helsinki, Finland

The structure (I) of thelephoric acid has been supported by two independent syntheses. 1,2 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).

---

* Present address: Institut de Chimie des Substances Naturelles, Gif-sur-Yvette (Seine-et-Oise), France.

The starting material, 2,4,5,2',5',2"-pentamethoxy-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. 3 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. 4-9 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. 1 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-Diodohydroquinone dimethylether 8,10 (1.8 g), 5-iodohydroxyhydroquinone trimethylether 11 (10.8 g) and copper

Acta Chem. Scand. 19 (1965) No. 2
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 sub-
ject ed 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-I. M.p. 218–219° (corr.).
(Found: C 66.1; H 6.2. Calc. for C₂₈H₃₂O₂:
C 66.4; H 6.4). U.V. spectrum: (dioxane) λ_max
308 mμ (log ε 4.33); λ_min 275 mμ (log ε 3.84).
Main I.R. maxima (KBr disc): 3000 m, 2940m,
2838m, 1614m, 1534s, 1508s, 1470s, 1440m,
1406s, 1380m, 1236m, 1280m, 1212s, 1182m,
1152m, 1060m, 1034s, 960w, 804m, 828m,
814m, 768s, 728w, 716w, 708w cm⁻¹.
4,4'-Dihydroxytryquinone (III) was
prepared from 2,4,5,2',5',2',4',5'-octamethoxy-
p-terphenyl according to the method of Erdt-
man et al.² mentioned above. The yield was
50% as calculated from the methoxy
compound. When dried (dried at room tempera-
ture in vacuo) the initially yellowish brown
sample became browner. 4,4'-Dihydroxytry-
quinone has no melting point but turns dark
at about 230–280°. (Found: C 57.0; H 2.9.
Calc. for C₂₈H₃₂O₂: C 61.4; H 2.3). The sample
contained some ash.

Tryquinone (IV) was prepared from
2,4,2',5',2',4'-hexamethoxy-p-terphenyl (V) ac-
cording to Erdtmann et al.²

Telephoric acid tetra-acetate. 4,4'-Dihydroxy-
tryquinone (50 mg) was boiled for 1 h in
acetic anhydride containing 2 drops of pyri-
dine. 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 telephoric acid tetra-acetate.¹

The telephoric acid leuco-acetate. 4,4'-Dihydroxy-
tryquinone (50 mg) was boiled for 5 min in
acetic anhydride containing 2 drops of pyri-
dine. Zinc dust was added and refluxing con-
tinued for ½ h. The mixture was filtered hot,
cooled, and after standing, refiltered. The pre-
cipitate (8 mg) was recrystallised from acetic
anhydride. The U.V. and I.R. spectra were
identical with those of telephoric acid
leuco-acetate.¹

The author's thanks are due to Associate
Professor Jarl Gripenberg for his valuable
suggestions during the course of this work.

2. Wanzlick, H.-W. Angew. Chem. 76
(1964) 313.
3. Erdtmann, H., Granath, M. and Schultz, G.
(1934) 223.
5. Pummerer, R., Pfaff, A., Riegelbauer, G.
and Rosenhauer, E. Ber. 72 (1939) 1623.
6. Schulte-Frohlinde, D. and Erhardt, F.
7. Schulte-Frohlinde, D. and Klasine, L.
8. Schulte-Frohlinde, D. and Erhardt, F.
9. Shand, A. J. and Thomson, R. H. Tetra-
hedron 19 (1963) 1919.
1075.
11. Hughes, G. K., Neill, K. G. and Ritchie, E.
Australian J. Sci. Res. 3 A (1950) 497;
Chem. Abstr. 46 (1952) 4644.

Received March 8, 1965.

Acta Chem. Scand. 19 (1965) No. 2