

by the spontaneous rearrangement of tetraphenyl-di-*tert.*-butylethynyl-ethane has the diindene structure which was recently suggested for it.

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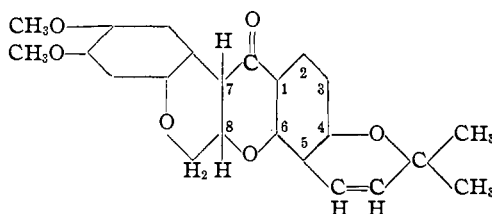
## TEPHROSIN. II. ISOTEPHROSIN

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In a recent communication<sup>1</sup> formula I was proposed as representing the structure of deguelin, and it was also indicated that tephrosin is an hydroxydeguelin in which the hydroxyl group replaces one of the hydrogen atoms attached to either carbon atom 7 or 8.



I. Deguelin

In the course of the preparation of tephrosin from a recent shipment of Peruvian cubé root a white crystalline material separated which after purification melted at 252°. The substance was an isomer of tephrosin, as shown by its molecular composition, its methoxyl content, and the ease with which it was converted to dehydrodeguelin by the loss of a molecule of water. The material has been designated as isotephrosin.

Isotephrosin is a colorless crystalline material which like tephrosin is optically inactive. It is considerably less soluble in ordinary solvents than is tephrosin, and it is oxidized by potassium permanganate to a dicarboxylic acid isomeric with tephrosindicarboxylic acid.

While the ready conversion of isotephrosin into dehydrodeguelin, through the loss of a molecule of water, leaves no doubt that the difference between tephrosin and isotephrosin consists in the orientation of the hydrogen and hydroxyl groups on carbon atoms 7 and 8, no definite information is available as to the exact configurations existing at these carbon atoms. The most plausible assumption is that if in tephrosin the hydroxyl group is on carbon atom 7, then in isotephrosin the hydroxyl group would be on carbon atom 8 or *vice versa*.

Although there appears to be no immediate prospect of reaching a definite decision concerning these configurations, it is, nevertheless, an interesting fact that the two isomeric forms of this compound exist.

<sup>1</sup> Clark, *THIS JOURNAL*, 54, 3000 (1932).

## Experimental

**Preparation of Isotephrosin.**—Two kilograms of ground cubé root was extracted with ether. After separating the rotenone and removing the solvent from the mother liquors as completely as possible by vacuum distillation, 250 g. of non-crystalline extractives was obtained. This material was dissolved in 3 liters of methanol, and 180 cc. of 10% sodium hydroxide was added. After standing for a day, 12.8 g. of practically pure deguelin (m. p. 166°) separated. Upon removing this material further crystallization of the filtrate soon occurred, yielding three different fractions. The first, 19.6 g., consisted of somewhat impure deguelin, m. p. 164–174°. The second fraction, 17.5 g., was a mixture of deguelin and tephrosin, m. p. 187°. The third fraction, 10.5 g., was composed essentially of isotephrosin, m. p. 250°. This was recrystallized first from its solution in chloroform by the addition of methanol, and finally it was purified to a constant melting point of 252° by recrystallization from boiling *n*-butanol.

The material consisted of plate-like rhombs many of which extinguished sharply in parallel polarized light (crossed nicols); others, however, were only partly extinguished and in convergent polarized light showed biaxial interference figures;  $\alpha$ , 1.547 (common);  $\beta$ , indeterminate, apparently perpendicular to the broad face of the plates;  $\gamma$ , 1.582 (common); both  $\pm 0.003$ .<sup>2</sup>

*Anal.* Calcd. for  $C_{23}H_{22}O_7$ : C, 67.30; H, 5.41;  $OCH_3$  (2), 15.1. Found: C, 67.31; H, 5.61;  $OCH_3$ , 15.2.

**Dehydrodeguelin from Isotephrosin.**—A mixture of 0.5 g. of isotephrosin, 0.25 g. of sodium acetate and 4 cc. of acetic anhydride was boiled for ten minutes. The condenser was then disconnected, and two-thirds of the anhydride was removed by distillation. The remainder of the anhydride was then decomposed with methanol, after which 10 volumes more of methanol was added. Crystallization of dehydrodeguelin began at once and was soon completed. The material was recrystallized from its solution in chloroform by the addition of methanol. Thus obtained it melted at 233° and was proved by comparison with an authentic sample to be dehydrodeguelin.

The same reaction involving the loss of a molecule of water was obtained by boiling 0.2 g. of isotephrosin with 10 cc. of 5% absolute ethanolic hydrochloric acid. The yield of dehydrodeguelin was 80% and after recrystallization as described before the material had the same melting point, mixed melting point and optical properties as recorded for dehydrodeguelin.

**Isotephrosindicarboxylic Acid.**—A constantly stirred solution of 2 g. of isotephrosin in 300 cc. of acetone, maintained at a temperature between 15 and 20°, was treated with 4 g. of potassium permanganate until the solution became colorless. The resulting manganese dioxide was extracted with boiling water and the solution filtered from the residue. The aqueous extract was acidified to Congo red with sulfuric acid and the acid allowed to crystallize. There was obtained 0.9 g. of material which melted at 185°. The crude substance was dissolved in the necessary quantity of alkali, the solution was diluted to 75 cc., then acidified with acetic acid and filtered through norit. The filtrate was heated to boiling and made acid to Congo red with sulfuric acid. The isotephrosindicarboxylic acid separated as thin colorless irregular-shaped plates which when air-dried melted at 185°. When dried in a high vacuum it melted at 187°. The plates invariably extinguished sharply with crossed nicols, precluding distinct interference figures (convergent polarized light), but the substance appears to be biaxial;  $\alpha$ , 1.485;  $\beta$ , not determined but apparently shown when the plates are tipped on edge;  $\gamma$ , 1.660; both  $\pm 0.003$ .

<sup>2</sup> The optical data here recorded were determined by George L. Keenan of the Food and Drug Administration, U. S. Department of Agriculture.

*Anal.* Calcd. for  $C_{23}H_{22}O_{11} \cdot 0.5 H_2O$ : mol. wt., 492.6; C, 57.13; H, 4.80;  $OCH_3$  (2), 12.8. Found: mol. wt. (titration, 482); C, 57.29; H, 4.93;  $OCH_3$ , 12.9.

**Tephrosinmonocarboxylic Acid.**—When isotephrosindicarboxylic acid was boiled for one-half minute with diphenyl ether, tephrosinmonocarboxylic acid was formed in essentially the same yield as recorded for tephrosindicarboxylic acid.<sup>1</sup>

As obtained from the cooled diphenyl ether solution upon the addition of methanol the acid melted at 266–268°, and when it was mixed with an authentic sample of tephrosinmonocarboxylic acid no depression of the melting point occurred. It also gave the characteristic scarlet color with ferric chloride that is obtained with tephrosinmonocarboxylic acid.

### Summary

A crystalline material, shown by its composition and certain of its derivatives to be an isomer of tephrosin, has been obtained from a sample of Peruvian cubé root. This substance has been designated as isotephrosin. The structural difference between tephrosin and isotephrosin exists in the orientation of the hydrogen and hydroxyl groups on carbons 7 and 8 in the structure given in the text.

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### NOTES

#### The Nitration of 4,4'-Dichlorodiphenyl

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Shaw and Turner have recently published an article<sup>1</sup> which concerns in part the exhaustive nitration of 4,4'-dichlorodiphenyl. In it they have shown that the three nitro groups entered the 2,3',5' positions.

Without knowledge that the problem was being investigated elsewhere, this study has been in progress in this Laboratory for the past two years. The results attained are in agreement with those of Shaw and Turner, as the following brief account shows. Direct nitration of 4,4'-dichlorodiphenyl at 100°, using a mixture of fuming nitric and fuming sulfuric acids, resulted in the formation of a trinitro derivative with a melting point which corresponded to that of the 4,4'-dichloro-2,3',5'-trinitrodiphenyl reported by Shaw and Turner. The yield was lower than that secured by them, but the product, precipitated by pouring the filtered reaction mixture over cracked ice, melted at 164–165° without further purification. Nitration of 4,4'-dichloro-2,3'-dinitrodiphenyl under these conditions resulted in the formation of the same compound, as was shown by the melting point of a mixture of the two.

The lability of the chlorine atoms was determined by hydrolysis with dilute sodium hydroxide solutions in the presence of metallic copper, and under quantitative conditions.<sup>2</sup> Only one chlorine atom was found to be

<sup>1</sup> Shaw and Turner, *J. Chem. Soc.*, 285–297 (1932).

<sup>2</sup> Hale and Britton, *Ind. Eng. Chem.*, 20, 114 (1928).