

**682. Tocopherols. Part VII.\* The Condensation of Toluquinol with Phytol.**

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The condensation of toluquinol with phytol leads to a 1 : 2 : 1 mixture of 5-, 7-, and 8-methyltolcol.

A RECENT paper by Pendse and Karrer<sup>1</sup> on the nature of the products of condensation of toluquinol and phytol, a reaction first examined by Karrer and Fritzsche,<sup>2</sup> prompts us to record our observations on this reaction.

When examined by the paper-chromatographic technique<sup>3</sup> and by the differential nitroso-assay,<sup>4</sup> the initial product proved to be a 71% concentrate containing 5-, 7-, and 8-methyltolcol in an approximate ratio of 1 : 2 : 1. An attempt to prepare a *p*-nitrophenylurethane from this concentrate gave only a gum.

It was possible to separate the 8-methyltolcol from the 5- and 7-methyltolcol by chromatography. The two fractions obtained were further purified by molecular distillation, pure 8-methyltolcol and a concentrate containing 32% of 5-methyltolcol and 56% of 7-methyltolcol being obtained. This concentrate gave a *p*-nitrophenylurethane, m. p. 109—111°, which did not depress the m. p. of the *p*-nitrophenylurethane, m. p. 112°, prepared from an authentic specimen of 7-methyltolcol.<sup>5</sup> Pendse and Karrer reported m. p. 86—87° for a *p*-nitrophenylurethane prepared from their purified 7-methyltolcol. The difference in m. p. between authentic 7-methyltolcol *p*-nitrophenylurethane and Pendse and Karrer's derivative indicates that the latter's 7-methyltolcol was not pure and was probably contaminated with 5- and 8-methyltolcol.

## EXPERIMENTAL

*Condensation of Toluquinol with Phytol.*—Toluquinol (6.2 g.), phytol (14 g.), dry benzene (50 ml.), and anhydrous formic acid (50 ml.) were heated under reflux for 4 hr. The benzene layer was separated, washed with *N*-sodium hydroxide and water, and concentrated to a straw-coloured oil (18.6 g.) which contained 8-methyltolcol (21%), 5-methyltolcol (18%), and 7-methyltolcol (32%). A portion (3 g.) of this oil was adsorbed from light petroleum (b. p. 40—60°) on to alumina (Peter Spence type "H"; 100 g.), which contained a small quantity of alumina previously treated with sodium fluorescein in methanol and activated at 150° for 1 hr. After development with light petroleum, the dense mixed methyltolcol band, which could be detected by the quenching of the fluorescence under ultraviolet light, was cut from the column, extracted with ether-ethanol (3 : 1) and combined with the extract of a second portion of oil similarly treated. The combined extract was rechromatographed on alumina (100 g.) and, after development with light petroleum, gave two bands which were extracted separately from the column with ether-ethanol. Evaporation of the extract of the leading band gave an oil (1.48 g.), which contained 56% of 5- and 7-methyltolcol. Since the extract of the following band when run on paper treated with zinc carbonate<sup>3</sup> gave two bands, this material was rechromatographed on alumina and the front portion of the band discarded. Extraction, after cutting the column, gave an oil containing 71% of 8-methyltolcol. Distillation at 150° (bath)/10<sup>-3</sup> mm. gave pure 8-methyltolcol (130 mg.).

Distillation [150° (bath)/10<sup>-3</sup> mm.] of the mixture of 5- and 7-methyltolcol gave an 88% concentrate containing 32% of 5-methyltolcol and 56% of 7-methyltolcol.

*p*-Nitrobenzazide.—A stirred solution of *p*-nitrobenzoyl chloride (10 g.) in acetic acid (30 ml.) was treated with sodium azide (3.5 g.), and the precipitated solid collected. Dilution of the filtrate with water gave *p*-nitrobenzazide (7.1 g.), m. p. 71—74° (after drying *in vacuo* over

\* Part VI, preceding paper.

<sup>1</sup> Pendse and Karrer, *Helv. Chim. Acta*, 1958, **41**, 396.

<sup>2</sup> Karrer and Fritzsche, *ibid.*, 1939, **22**, 260.

<sup>3</sup> Green, Marcinkiewicz, and Watt, *J. Sci. Food Agric.*, 1955, **6**, 274.

<sup>4</sup> Marcinkiewicz and Green, *Analyst*, 1959, **84**, 304.

<sup>5</sup> McHale, Mamalis, Green, and Marcinkiewicz, *J.*, 1958, 1600.

calcium chloride). Though not pure (Sah and Chiao <sup>6</sup> gave m. p. 77—78°) this material was suitable for the preparation of nitrophenylurethanes.

*p*-Nitrophenylurethane from the Concentrate of 5- and 7-Methyltolcol.—88% Concentrate (0.3 g.), *p*-nitrobenzazide (0.6 g.), and toluene (10 ml.) were refluxed for 2 hr. The solid was filtered off and washed with benzene. The filtrate and benzene washings were combined and evaporated, and the product hydrolysed by aqueous acetone for 1 hr. The mixture was diluted with benzene, washed free from acetone, filtered, and concentrated. Crystallisation of the oil from methanol gave a solid (50 mg.), m. p. 109—111°, which was not depressed on admixture with authentic 7-methyltolcol *p*-nitrophenylurethane.

7-Methyltolcol *p*-Nitrophenylurethane.—7-Methyltolcol <sup>6</sup> (0.3 g.) when treated as above gave 7-methyltolcol *p*-nitrophenylurethane (0.15 g.), m. p. 112° (from methanol) (Found: C, 72.3; H, 8.5; N, 4.7.  $C_{34}H_{50}O_5N_2$  requires C, 72.1; H, 8.9; N, 4.9%).

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<sup>6</sup> Sah and Chiao, *Rec. Trav. chim.*, 1939, **58**, 595.

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