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THE SYNTHESIS OF A TAONDIOL DERIVATIVE [1]

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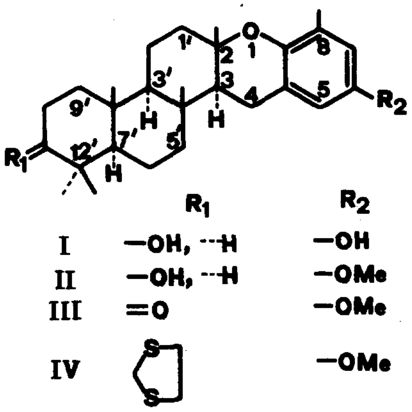
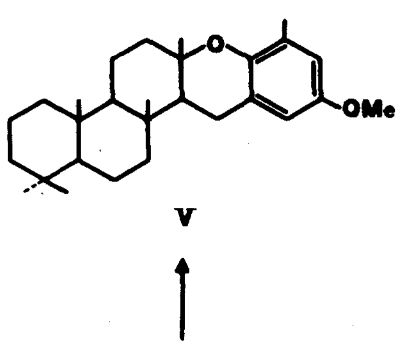
Previously we reported [2] the isolation from the marine alga Taonia atomaria of the tocopherol-like compound taondiol, for which we proposed structure I based on spectroscopic analyses, chemical transformation and biogenetic considerations. The stereo-structure has now been established as I by X-ray analysis of methoxytaondiol iodoacetate.[3] The present communication describes the two-steps synthesis of desoxytaondiol methyl ether (V), obtained from taondiol in which the OH group is removed by conversion of methoxytaondiol (II) to the thioketal IV, via the ketone III, followed by Raney nickel desulfurization.[2,4]

Condensation of commercial manool (VI) with toluquinol 4-methyl ether (VII) at room temperature in dry dioxane with the aid of boron trifluoride [5] afforded a mixture of products from which, after chromatographic purification on silica gel, the desired prenyl phenol VIII was isolated, in 62% yield, as an oil.

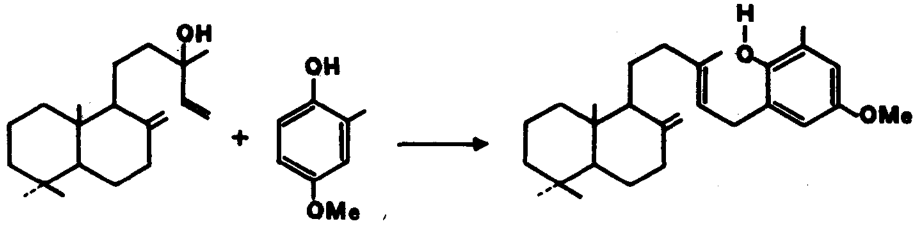
The NMR spectrum of VIII (60 MHz, $CDCl_3$, τ-scale) in the lowfield region shows signals for five protons: a two-protons singlet at 3.33 (aromatic H), a one-proton triplet centred at 4.63 (J = 8 Hz, H-C_3), and two broad singlets at 5.10 and 5.40 (1H each, exocyclic =CH_2). Further appear one three-protons singlet at 6.24 (Me-O-Ø), two benzyl protons at 6.65 (d, broad, J = 8 Hz), one aromatic Me group at 7.77 (3H, s), and a three-protons singlet at 8.23 (Me-C_2). In the upfield region appear signals for three tertiary Me groups at 9.13, 9.20, and 9.32 (3H each, s).

Treatment of VIII with 98% formic acid at 70° gave, in 85% yield, the crystalline compound V, m.p. 158-159°, $[\alpha]_D$ -69° (c, 0.8; $CHCl_3$). Its NMR spectrum shows two meta-coupled protons at 3.32 and 3.43 (2d, 1H each, J = 3 Hz), one three-protons singlet at 6.20 (OMe), two benzyl protons at 7.39 (d, broad, J =





V



VI VII VIII

8 Hz), one aromatic Me group at 7.85 (3H, s), and a singlet at 8,86 (3H, Me-C-O-). A signal for four tertiary methyl groups appears at 9.13 (12H, s, broad). By direct comparison with an authentic sample, compound V was shown to be identical with the taondiol degradation product.

The elemental analyses, mass spectrometric and spectral data of all the compounds reported were in agreement with the structures shown.

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