CHEMISTRY LETTERS, pp. 1045-1047, 1973. Published by the Chemical Society of Japan

CYCLIZATION OF POLYENES X[1].

BIOGENETIC TYPE SYNTHESIS OF dl-TAONDIOL

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Based on biogenetical consideration taondiol (III) was synthesized upon treatments of epoxide (II) with picric acid, followed by hydrochloric acid. From the cyclized mixture, III was isolated in 2% yield.

During the course of our investigation on the components of a marine plant, *Sargassum tortile L.*, we have characterized δ-tocotrienol (I) and its epoxide (II)[2] from the plant. On the meanwhile, Martin et al.[3] reported recently the isolation of taondiol (III) from a kind of marine plant, presumably biosynthesized from the epoxide (II) or its equivalents. These findings prompted us to synthesize III based on biogenetical consideration[4].

Bromotoluquinol (IV), prepared from o-cresol by the sequences of reactions of bromination with bromine, chromic anhydride oxidation to the bromotoluquinone and then sodium hydrosulfite reduction, was chosen for the position specific introduction[5] of geranylgeranyl moiety into the toluquinol nucleus. Compound IV was converted to the di-methoxymethyl ether (V) in 95% yield by treatment with $NaOCH_2CH_2OCH_3$ and then with $ClCH_2OCH_3$ under nitrogen atmosphere.

Substitution of the bromine atom of V with all-trans geranylgeranyl group was performed as follows in 45% overall yield. The yield seems not optimum since the reaction conditions were not fully examined. Bromotoluquinol ether (V) (9.1g) was treated with BuLi (1.25 mol equivalents) in ether at -40°C to obtain ether solution of lithio derivative, to which CuI powder (0.5 mol equivalent) was added at -40°C to convert it to the corresponding copper complex. All-trans geranylgeranyl bromide (1 mol equivalent), prepared from geranyl-linalool and hydrogen bromide in isooctane, was added at -40°C and the reaction mixture was kept for 2 hr at the same temperature. The above operations were carried out under nitrogen atmosphere. The reaction mixture was worked up as usual and purified with silica gel column chromatography to afford VI. The substitution did not occur at all when addition of CuI was omitted in the above operation.

Reaction of VI with NBS in aqueous monoglyme and then with methanolic KOH gave epoxide (VII) in 31% yield after purification of the intermediate, bromohydrin, with silica gel column chromatography.

Treatment of the epoxide with 2 mol equivalents of picric acid[6] overnight at room temperature and then with methanolic HCl afforded dl-taondiol (III)[7], mp 280-282° (d) in 2% yield after repeats of silica gel column and plate chromatographies. Cyclization of the epoxide with other Lewis acids such as BF_3-ether or $SnCl_4$ gave no satisfactory results under various conditions.

Acknowledgment

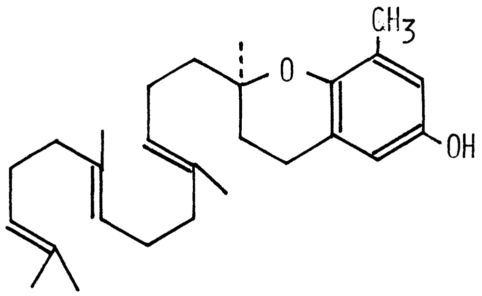
The authors express their sincere thanks to professor J. D. Martin for his generous gifts of natural taondiol and its diacetate.

References

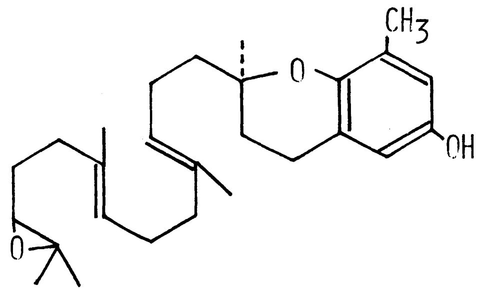
* To whom all correspondences should be addressed.

1. Part IX of this series, S. Kumazawa, T. Kato, and Y. Kitahara, Chem. Letters, 633 (1973).
2. Structure of II is tentative at present and characterization of components of the marine plant will be described elsewhere.
3. A. G. González, J. Darias, J. D. Martin, and C. Pascual, Tetrahedron, 29, 1605 (1973).
4. We were informed by professor J. D. Martin that he has synthesized taondiol monomethyl ether. We were deeply indebted to him for his sending the copy prior to publication.
5. By the reaction of toluquinol and geranylgeranyl moiety under acidic conditions, δ-tocotrienol and its related compound were synthesized, and will be reported elsewhere.
6. K. B. Sharpless, J. Am. Chem. Soc., 92, 6999 (1970).

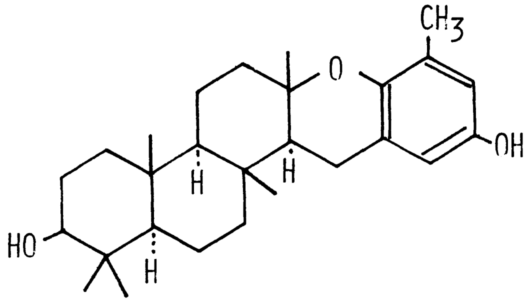
7. Due to the poor solubility of both natural and synthetic taondiols in $CHCl_3$, and hence difficulties to obtain the clear IR spectra, the synthetic specimen was converted into diacetate, the physical evidence of which was not distinguishable with that of natural one.



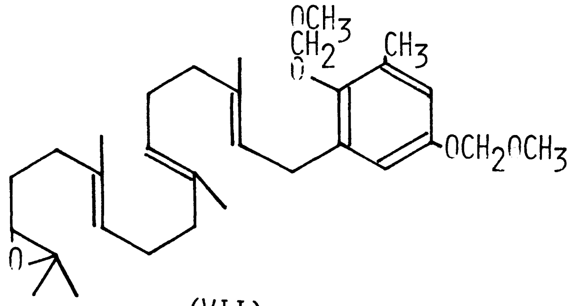
(I)



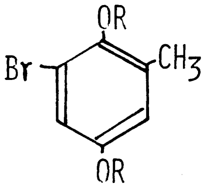
(II)



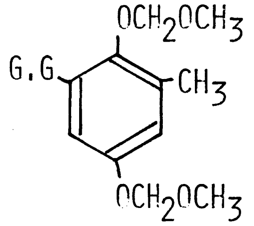
(III)



(VII)



(IV) R = H
(V) R = CH_2OCH_3



(VI) G.G = GERANYLGERANYL

(Received August 13, 1973)