Tetrahedron Letters No. 29, pp. 2729-2732, 1971. Pergamon Press. Printed in Great Britain.

TAONDIOL, A NEW COMPONENT FROM TAONIA ATOMARIA

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(Received in UK 7 June 1971; accepted in UK for publication 16 June 1971)

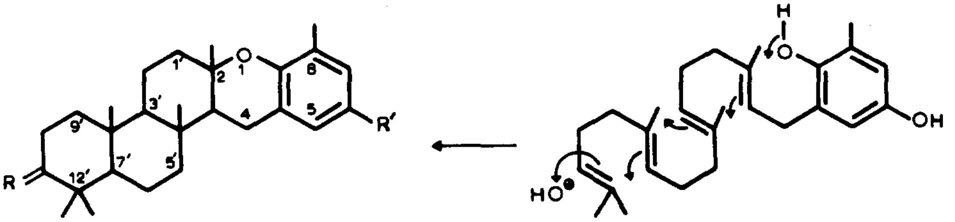
In our search for constituents of marine algae, we have isolated, in 0·05 % yield, a crystalline phenolic compound from Taonia atomaria, designated as taondiol for which, on the basis of the data shown below, we propose formula (I) as the most probable structure.

Taondiol (I), $C_{27}H_{40}O_3$, M^+ 412·292 (required 412·292), m.p. 283-284°, $[\alpha]_D$ - 76° (c, 0·30; $CHCl_3$), was isolated by chromatographic purification of the neutral fraction from the ether extracts of the dried seaweed. The IR spectrum (ν_{max}^{KBr} 3540, 3340, 1620, 1500, 860 and 800 cm^{-1}) indicates that (I) has phenolic structure. Upon methylation with diazomethane the compound affords the methoxy derivative (II).

The 6-chromanol nature of the chromophore in taondiol was evident from its UV spectrum (λ_{max}^{EtOH} 298 nm; ϵ 3860) which is very similar to that of δ-tocopherol.[1] Examination of the mass spectrum of (I) lends support to this hypothesis: the base peak at m/e 137·0599 ($C_8H_9O_2$ requires 137·0602) occurs by cleavage, with hydrogen transfer, of the fragment (VII).[2] Further peaks are found at m/e 275·2369 ($C_{19}H_{31}O$ requires 275·2374), m^* 183·5 ($M^+ - C_8H_9O_2$); and m/e 257·2290 ($C_{19}H_{29}$ requires 257·2269), m^* 240·2 ($M^+ - C_8H_9O_2 - H_2O$).

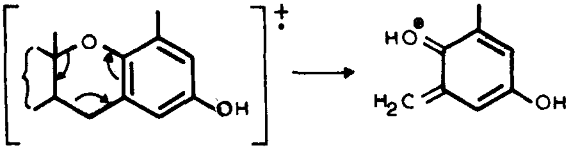
The NMR spectrum (100 MHz, $CDCl_3$, τ-scale) shows two meta-coupled protons at 3·56 and 3·62 (2d, 1H each, J = 2·3 Hz); a peak at 5·76 (1H, exchangeable with D_2O) assigned to the phenolic hydroxyl proton; a broad signal at 6·8 (1H, m, $W_{\frac{1}{2}}$ = 14 Hz, H-C-OH), two benzylic protons at 7·4 (d, broad, J = 8 Hz), one aromatic methyl group at 7•89 (3H, s), and a singlet at 8•86 (3H, CH_3-C-O-). In the upfield region appear signals for four tertiary methyl groups at 9•00, 9•10, 9•12, and 9•18 (3H each, s).

The presence of three additional rings in (I) was demonstrated from the absence of further unsaturation beside the chromanol moiety, and from the clarification of the chemical nature of the remaining oxygen atom. Taondiol gave the monoacetyl derivative (III) by acetic acid treatment, and the diacetyl derivative (IV) by refluxing with acetic anhydride. Upon oxidation at 0° with Jones' reagent the methoxy derivative (II) yielded the ketone (V), which is indicative of a secondary OH. The NMR spectra of I and III (or IV) reveal that the alcoholic group is equatorial.



VI

	R	R'
I	OH H	OH
II	OH H	OMe
III	OAc H	OH
IV	OAc H	OAc
V	=O	OMe



m/e 412

m/e 137

VII

Examination of the NMR spectra of (I) and derivatives in the methyl region, and critical comparison with literature data on the methyl groups in ring A of 3(equatorial)-hydroxy-4,4-dimethyl terpenoids,[3] indicate the presence of this same cyclic system in taondiol, and lead to the assignment of the methyl peaks (see Table).

Table: τ-Values in $CDCl_3$ (100 MHz)

Compound	C_8-Me	C_2-Me	$C_{4'}$-Me	$C_{8'}$-Me	$C_{12'}$-βMe	$C_{12'}$-αMe
I	7·89	8·86	9·12	9·10	9·18	9·00
II	7·88	8·86	9·13	9·11	9·19	9·01
III	7·89	8·88	9·12	9·12	9·12	9·12
IV	7·89	8·85	9·12	9·12	9·12	9·12
V	7·86	8·83	9·05	9·02	8·92	8·88

All these results indicate that taondiol is represented most favourably by formula (I), which is also well explained from the standpoint of biogenesis. In fact, we may imagine that (VI) undergoes an essentially synchronous process for the ring formation if some oxidizing agent furnishes $HO^{\oplus}$ at $C_{11'}$. To our knowledge, this is the first time that cyclic side-chain derivatives of tocopherols are shown to occur naturally.

Further studies, in order to solve the remaining ambiguities and to determine the stereochemistry of this new class of compounds, are in progress.

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

Acknowledgements. We thank Dr. C. Pascual, Physikal.-chem. Institut, Universität Basel, for realizing some of the NMR and mass spectra. We are also indebted to Dr. J.L. Bretón for the interest shown. J.D.M. thanks the Foundation "Juan March" for a fellowship, and J.D. for a grant "Formación de Personal Investigador" from the Ministerio de Educación y Ciencia.

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