Tetrahedron Letters Vol. 21, pp 2249 - 2252
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0040-4039/80/0601-2249$02.00/0

NEW DITERPENOIDS OF THE BROWN SEAWEED STOECHOSPERMUM MARGINATUM : STRUCTURE OF STOECHOSPERMOL

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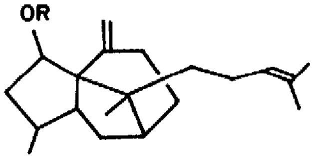
Summary: A new diterpene alcohol, stoechospermol has been isolated from Stoechospermum marginatum (Dictyotaceae) and shown to possess structure(1) containing a novel carbon skeleton related to isopatchoulane. The structure assignment rests heavily on spectroscopic data and biogenetic considerations, but is consistent with chemical transformations.

In search of drugs from marine sources, several genera such as Stypopodium[1], Pachydictyon[2], Dictyota[3,4] Dilophus[5], Glossophora[6], Dictyopteria[7], Taonia[8] (Fam: Dictyotaceae) belonging to the natural order Dictyotales (Pheophyta) have been subjected to critical chemical examination. As a result of these studies, several sesqui and diterpenoids having new skeletal types have been fully characterised. We herein wish to report the isolation and characterisation of yet another new diterpene alcohol, stoechospermol (1), possessing a new carbon framework from Stoechospermum marginatum (Ag.) Kutz (Dictyotaceae).

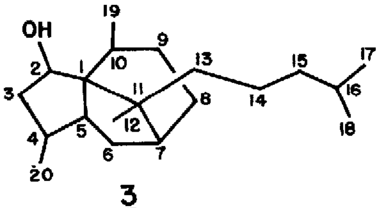
The neutral portion of the methylene chloride extract of S. marginatum on extensive column chromatography (alumina, silica gel,/AgNo$_3$) yielded stoechospermol (1), mp. 64-65°, $(\alpha)_D^{27}$ + 21.8° (EtOH). The mass spectrum of (1) showed a parent ion at m/e = 288 corresponding to the elemental composition, $C_{20}H_{32}O$; ν_{max} 3325 (-OH), 3090, 1669, 1635, 880, 828 ($>C = CH_2$, $-\underset{|}{C} = \underset{|}{C}H$) cm^{-1}. Treatment of (1) with Ac_2O/pyridine gave its acetate (2).

The ^1H-NMR spectrum ($CDCl_3$,100 MHz) displayed signals at 'δ'

0.87(3H,d,J = 6Hz), 0.99(3H,s), 1.61(3H), 1.69(3H), 2.25, (1H, ddd, J = 4,13,13), 2.98(2H, bm), 3.73 (1H,d,J = 4Hz), 4.74 (1H), 4.84 (1H), 5.11 (1H,bt). The -C<u>H</u>OH signal appeared as a doublet at 5.02 (J=4Hz) when the ^{1}H-NMR was measured after addition of trichloroacetyl isocyanate. Its ^{13}C-NMR spectrum ($CDCl_3$, Me_4Si, Brucker, B-22 C at 22.63 MHz) showed the signals : quartets at 12.9, 14.1, 17.1 and 25.5; triplets at 26.3, 27.7, 34.9, 36.3, 36.5, 37.4 and 108.1; doublets at 42.9, 43.0, 45.4, 80.2 and 124.1; singlets at 44.4(?), 46.5, 131.3 and 148.3.



<u>1</u>, R = H
<u>2</u>, R = AC



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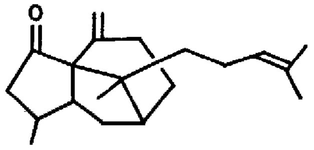

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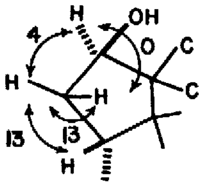

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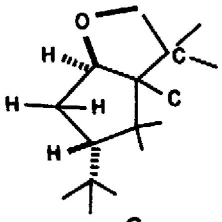

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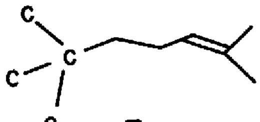
Catalytic hydrogenation of (<u>1</u>) using PtO_2/ethanol afforded two tetrahydroderivatives (<u>3</u>), (M^+292), tetrahydro-stoechospermol-I, mp.122°(less polar) and tetrahydrostoechospermol-II, mp. 97°, indicating the presence of two double bonds. Stoechospermol must therefore be tricyclic. Oxidation of (<u>1</u>) with Sarett's reagent afforded ketone (<u>4</u>), $C_{20}H_{30}O$, (M^+286) whose IR spectrum (bands at 1730, 1410 cm^{-1}) showed a saturated ketone on a five membered ring and a $O=\underset{|}{C}-CH_2-$ grouping. The bands due to terminal methylene group were also present. The ketone (<u>4</u>) was recovered unchanged on treatment with NaOMe/MeOH[9], thus eliminating the location of $>C=CH_2$ grouping between C-4 and C-20.

Oxidation of tetrahydrostoechospermol (<u>3</u>), mp. 122°, gave a saturated five ring ketone having a $O=\underset{|}{C}-CH_2-$ grouping (IR bands at 1728 & 1410 cm^{-1}). The hydroxyl group of (<u>1</u>) is, therefore, located on a five membered ring. The appearance of methine hydrogen of -C<u>H</u>OH as a doublet at 3.73(J=4Hz) and the signal at 'δ' 2.25(ddd, J=4, 13, 13) could be best explained by considering the part structure (<u>5</u>) in stoechospermol. The high field signal (doublet at 80.2 ppm) in the ^{13}C-NMR spectrum is indicative of the carbon bearing hydroxyl group adjacent to a quaternary carbon atom. The part structure (5) including the relative stereochemistry of the functional groups as shown looked certain on the basis of comparison of the chemical shifts and coupling constants reported for a similar part structure (6) present in ginkolide'A'-ether[10].



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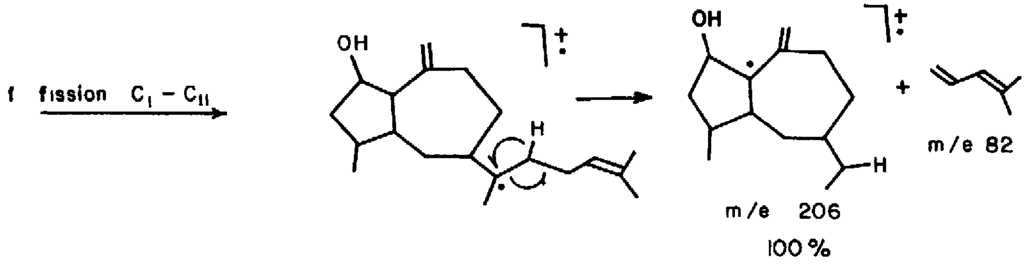
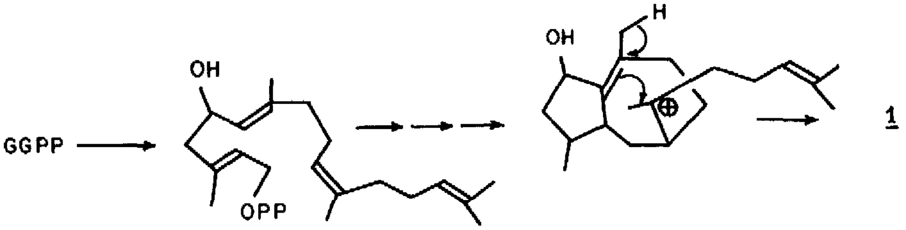
The mass spectral fragmentation of (1) reflects the presence of a six carbon side chain having part structure (7). Thus, the net loss of side chain (M^{+}-82)[11] results in the observed base peak at m/e 206. The fission of the allylic C-1-C-11 bond in (1) appears to be favoured mode of fragmentation as shown (scheme I). The mass spectrum of (1) also showed prominent ions at m/e 145, 137, 135, 123, 121, 119, 109, 107, 105, 95, 93, 91, 55, 43, 41 and 28. Presence of part structure (7) is also supported by comparison of ^{1}H & ^{13}C-NMR chemical shifts with those of appropriate model compounds[12].



Scheme – I

Assuming its biogenetic origin from geranyl-geranyl pyrophosphate (Scheme II) and considering the presence of part structures (5) and (7), the structures of other diterpenoids from Dictyotaceae[2,3], we propose structure (1) for stoechospermol.

Finally, it is of interest to note that the carbon skeleton of (1) can be considered as isoprenologue of the C_{15} isopatchoulane skeleton.



Scheme – II

We wish to thank Prof. R.B. Bates (for ^{13}C-NMR) and Dr. O. Motl and Prof. V. Herout (for ^{1}H-NMR & Mass spectral data) and valuable comments. We also thank Dr. K. Subbramaiah for identification of S. marginatum (Ag) Kutz. and Dr. S.Z. Qasim, Director, NIO, and Mr. C.V.G. Reddy, for their keen interest in the work.

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(Received in UK 7 February 1980)