The Sesquiterpene Hydrocarbons of the Gorgonian, *Pseudopterogorgia americana*, the Nonisoprenoid β-Gorgonene.

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THE sesquiterpene hydrocarbon mixture occurring[1] in the gorgonian *Pseudopterogorgia americana* (Gmelin) (taken in shallow waters at Bermuda and the Florida Keys) has been examined in more detail, and found to consist primarily (96%) of four components. Two of the components are the well known pair 9-aristolene (I; 8%) and 1(10)-aristolene (II; 25%). They are accompanied by (+)-γ-maaliene (III; 8%) which has not been encountered previously in Nature, and (+)-β-gorgonene (IV; 55%) which possesses a new isoprenoid skeleton having a "misplaced" isopropenyl residue. β-Gorgonene constitutes the first observation of a sesquiterpene analogue of the biogenetically enigmatic monoterpene, sylvestrene.

The hydrocarbon mixture† was isolated by chromatography (Florisil) of the nonsaponifiable fraction of the cold hexane extract of the total organism. The mixture consisted primarily of four components present in the same relative proportions and having identical g.l.c. retention times (Carbowax 20M) as found for the crude extract prior to saponification. Chromatography in hexane on 25% $AgNO_3$–silicic acid[2] afforded first (I), n_D^{25}1·4975, d_4^{25}0·9249, $[\alpha]_D^{25}$80·9° (neat), M^+ 204 (mass spectrum), n.m.r. (neat): δ 5·07m (C=CH), 2·12m (four allylic protons), 1·09s, 1·04s (three quat. methyls), 0·94d (*J* 6Hz.) (sec. methyl) and 0·65m (two cyclopropyl protons), and then (II), n_D^{25}1·5005, d_4^{25}0·9198, $[\alpha]_D^{25}$ − 78·5° (neat), M^+ 204, n.m.r. (neat): δ 5·22dd (*J* 3·6, 2·2Hz.) (C=CH), 1·04s, 1·00s, 0·96s (three quat. methyls), 0·96d (*J* 7Hz.) (sec. methyl) and 0·59m (two cyclopropyl protons). Their identities followed from comparisons with reported properties,[3,4] particularly their n.m.r. spectra.[4,5]

(+)-γ-Maaliene (III), n_D^{25}1·4992, d_4^{25}0·9230, $[\alpha]_D^{25}$10·9° (*c* 1·15, hexane), M^+ 204 n.m.r. (neat): δ 4·79m ($C=CH_2$), 1·02s, 0·90s, 0·73s (three quat. methyls) and 0·67m (two cyclopropyl protons), was eluted by hexane–benzene (3 : 1), and was identified by conversion into the diol (OsO_4),[6] m.p. 141—142° (sublimed), $[\alpha]_D^{25}$ − 24·8° (*c* 6·3, $CHCl_3$). A precisely 1 : 1 mixture with its enantiomer[6] melted at 126—128° (sublimed).

Elution with ethyl acetate afforded a mixture of β-gorgonene (IV) and its crystalline $AgNO_3$ complex (V; 4%), m.p. 132·5—133·5° (recryst. acetone–hexane).

The crystal structure of (V) was determined using single-crystal *X*-ray diffraction. The crystals are orthorhombic, space group $P2_12_12_1$, with $a = 9{\cdot}036$, $b = 21{\cdot}79$, and $c = 8{\cdot}008$ Å, $Z = 4$. The structure was determined using a Patterson synthesis and the heavy-atom technique. The final *R* index for 1181 reflections after least-squares refinement is 0·066. The absolute configuration of (IV) in the crystal structure of (V) was determined using 21 pairs of reflections. Complete details of the structure determination will appear in a separate paper.[7]

Re-chromatography of the hydrocarbon on Florisil afforded pure (IV; 51%) n_D^{25}1·5010, d_4^{25} 0·9108, $[\alpha]_D^{25}$13·9° (neat), M^+ 204, ν_{max} 878 and 888 cm.$^{-1}$ (two $C=CH_2$), n.m.r. (neat): δ 4·66m (two $C=CH_2$), 1·55d (*J* 1Hz.) (vinyl methyl) and 0·79s (angular methyl). The β-gorgonene thus isolated and that recovered by decomposition of

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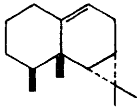
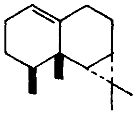
† Kindly provided by Professor L. S. Ciereszko.

the $AgNO_3$ complex with alcohol showed identical i.r. spectra, g.l.c. retention times, and R_F values on $AgNO_3$/silicic acid t.l.c., all corresponding to one of the components in the original hydrocarbon mixture.


(I)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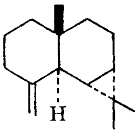
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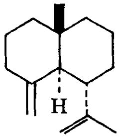
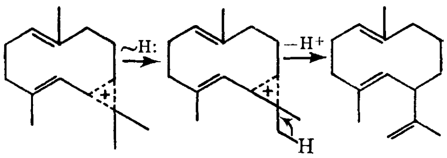

(IV)



(VI) (VII) (VIII)

It is worthy of note that (I) and (II) are enantiomeric, with one exception,[3] with the forms commonly encountered in terrestrial plants. The same relationship obtains for the skeleton of (III).

A biogenetic process similar to that proposed[8] for sylvestrene can account for the novel β-gorgonene skeleton. "Migration" of the isopropenyl residue would result from hydride migration within the farnesyl-derived cyclic ion (VI), leading to (VII), from which proton loss would lead to the monocyclic intermediate (VIII). Normal cyclization would then lead to β-gorgonene.

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