

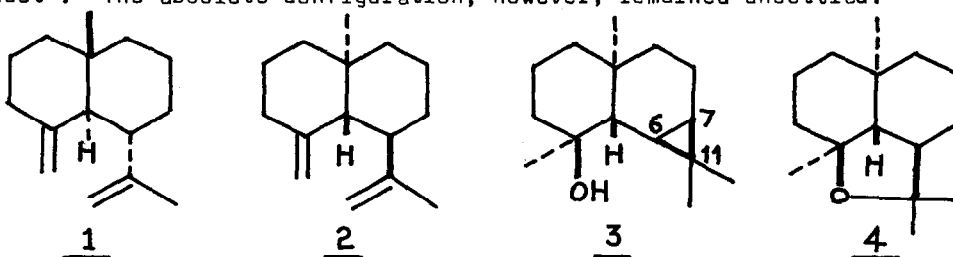
BIOGENETIC-LIKE SINGLE STEP SYNTHESIS OF (-)  $\beta$ -GORGONENE FROM MAALIOL

S.K. Paknikar and V.K. Sood<sup>1</sup>

Centre of Post-graduate Instruction and Research,  
University of Bombay, Panaji, Goa, India.

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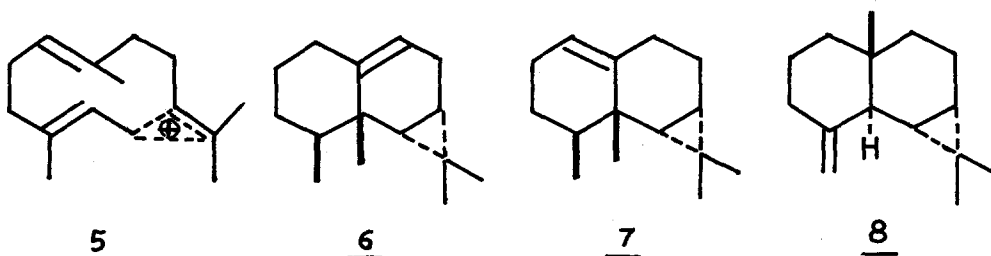
$\beta$ -Gorgonene 1, a constituent of marine organism *Pseudopteroqorgia americana*, is the only member sharing the novel nonisoprenoid sesquiterpene skeleton, gorgonane<sup>2</sup>. Its stereo-structure was established by Weinheimer and co-workers<sup>3</sup> and further confirmed by X-ray analysis of silver nitrate adduct<sup>4</sup>. The absolute configuration, however, remained unsettled.



The very recent communication by Boeckman and Silver<sup>5</sup> on the synthesis of (+)  $\beta$ -gorgonene prompted us to disclose our single step biogenetic-like synthesis of (-) gorgonene 2, from maaliol 3. Since the absolute configuration of 3 has been established beyond doubt<sup>6</sup>, the present synthesis not only confirms the assigned structure, but also defines the absolute configurations of (+) and (-)  $\beta$ -gorgonenes as in 1 and 2.

It has been proposed<sup>3</sup> that  $\beta$ -gorgonene originates from a  $\pi$ -complex intermediate 5 obtainable from all trans farnesol. The natural occurrence of (+) 9-aristolene 6, (-)1(10)-aristolene 7, (+)  $\gamma$ -maaliene 8, all containing a cyclopropane ring, in the same source as  $\beta$ -gorgonene points to the genesis of 1, from an immediate hypothetical precursor having a tricyclic maaliene skeleton.

On the basis of reported cleavage<sup>6</sup> of C<sub>7</sub>-C<sub>11</sub> bond of maaliene to give



an equatorial  $C_6$  isopropenyl substituent, it was anticipated that treatment of 3 or (-) 8 with dry HCl, followed by dehydrochlorination would yield (-)  $\beta$ -gorgonene 2. This proved to be the case: treatment of 3 in anhydrous ether with dry HCl at ice bath temperature for 1 hr, usual work up after standing at room temperature for 24 hr, followed by dehydrochlorination in situ gave a liquid mixture consisting of two major and two minor components (GLC). The major components were obtained in analytically pure form by a careful combination of chromatography on alumina (neutral, activity I) and 25%  $AgNO_3-SiO_2$ , and identified as 4 (m.p. and mixed m.p.  $65^\circ$ , IR, NMR) and (-)  $\beta$ -gorgonene 2,  $[\alpha]_D^{20} - 20^\circ$  ( $CHCl_3$ ,  $C=2.4\%$ ), by direct comparison of infrared and NMR spectra of authentic 1, kindly supplied by Professor Weinheimer.

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