Caridiene: A New Sesquiterpene from *Pseudoterogorgia americana*

R. Baluja Rivero, A. Rosado Pérez*, H. Vélez Castro

National Center for Scientific Research, Apdo. 6990, Havana, Cuba

C. Sedeño Argilagos, R. D. Henríquez

Faculty of Pharmacy, University of Havana, Vedado, Cuba

*Z. Naturforsch. 45b, 1571–1572 (1990); received January 5 / February 26, 1990

**Pseudoterogorgia americana.** Sesquiterpene Hydrocarbon, 1,1-Dimethyl-7-isopropylidene-1,2,3,4,5,6,7,8-octahydronaphthalene

Research on the chemical composition of gorgonian *Pseudoterogorgia americana,* which grows in the coasts of Havana, has led to the isolation of a new sesquiterpene hydrocarbon, 1,1-dimethyl-7-isopropylidene-1,2,3,4,5,6,7,8-octahydronaphthalene, named caridiene. This compound not previously reported, was found to be a major constituent of the volatile fraction. The proposed structure was confirmed by spectroscopical data (UV, IR, Raman, MS, '*H and '*C NMR techniques).

During our search for constituents from gorgonians, volatiles obtained by steam distillation from *n*-hexane extracts of powdered air dried *Pseudoterogorgia americana* collected off Havana, Cuba, were subjected to repeated silica gel column chromatography, yielding a variety of sesquiterpene compounds. Weinheimer *et al.* [1] isolated and identified the following four sesquiterpene hydrocarbons from the volatile fraction of the same specimen: \( \beta \)-gorgonene (as major constituent), \( \gamma \)-maaline, 9-, and \( l\)(10)-aristolene. However, \( \beta \)-gorgonene could not be curiously identified by us. We found by means of GC-MS measurements \( \alpha \)-chamigrene and a new sesquiterpene hydrocarbon as major constituent (5% of the total volatile fraction). Other known sesquiterpenes identified as minor constituents were \( \gamma \)-maaline, \( \beta \)-epibourbonene, \( l\)(10)-aristolene, and calame-nene, the latter suspected to be an artifact formed during the distillation of the hydrocarbon fraction [2, 3].

The present communication is concerned with the elucidation of structure 1 for the new compound, 1,1-dimethyl-7-isopropylidene-1,2,3,4,5,6,7,8-octahydronaphthalene, named by us caridiene.

Compound 1 was isolated by preparative gas chromatography and analyzed by means of several spectroscopical techniques. In the mass spectrum an intense molecular ion (67%) was observed at \( m/z \) 204 (molecular formula \( C_{15}H_{24} \) was determined by HR-MS). The compound exhibits mass spectral characteristics, strong peaks at \( m/z \) 91, 105, 119, and 133, very similar to those of bicyclic or tricyclic sesquiterpene hydrocarbons. Moreover, a very strong peak at \( m/z \) 189 (100%) support that the elimination of a methyl group is a very favourable process, indicating the presence of such groups in allylic position to a double bond.

The IR spectrum showed sharp medium bands at 995, 1060, 1120 (doublet), 1170, and 1195 cm\(^{-1}\). The very sharp symmetric \( CH_2 \) deformation at 1380 cm\(^{-1}\) indicates that these groups are very similarly attached. The weak band at 1650 cm\(^{-1}\) indicates tri- or tetrasubstituted double bonds.

Much more valuable for this purpose was the Raman spectrum; when conjugated double bonds exist, the symmetric stretching band intensifies strongly [4, 5]. It has been also recognized that ring compounds and among them the terpenes [6] show as the strongest band in Raman the ring breathing which generally lies between 300–800 cm\(^{-1}\). For...
determining whether the conjugation is present or not we have used the fact that the intensity relation between the C= C stretching band, in this case at 1655 cm⁻¹, and the breathing band at 580 cm⁻¹, was only 1.1 and for terpenes with conjugated double bonds this relation was found to be 2–8 [7]. Besides, there is only one band in the double bond region so we can finally conclude that the two existing double bonds in this molecule are not conjugated and must have same or similar structure, namely both tri- or tetrasubstitution.

The ¹H NMR spectrum (90 MHz, CDCl₃) showed four 3 proton singlets at 0.9, 1.45, 1.48 and 1.7 ppm, a 9 proton multiplet between 1.3–1.9 ppm, a 2 proton multiplet at 1.91 ppm and a 1 proton multiplet at 2.64 ppm. No olefinic proton signals were detected in this spectrum. Its complete decoupled ¹³C spectrum (22.53 MHz, CDCl₃) showed 4 olefinic quaternary carbon atoms (the substitution of each carbon atom was determined by the INEPT technique [8]), 6 aliphatic methylene groups, 4 methyl groups, and a quaternary aliphatic carbon (see Table I). The absence of methynic carbon atoms and the presence of only one quaternary aliphatic carbon atom corroborate that the joining ring carbons are of olefinic nature.

A comparison of this spectrum with that of terpinolene [9] permitted the assignment of several signals. The geminal position of two methyl groups (21.7 and 24.4 ppm) is also confirmed by the existence of a unique quaternary aliphatic carbon atom.

Table I. ¹³C NMR chemical shifts of caridienea.

<table>
<thead>
<tr>
<th>C</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>4a</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>8a</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ</td>
<td>39.8</td>
<td>19.3</td>
<td>43.2</td>
<td>37.4</td>
<td>138.2</td>
<td>32.2</td>
<td>125.7</td>
<td>23.8</td>
<td>31.9</td>
<td>132.0</td>
</tr>
<tr>
<td>C#</td>
<td>9</td>
<td>10</td>
<td>11</td>
<td>12</td>
<td>13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>δ</td>
<td>124.0</td>
<td>20.6</td>
<td>19.2</td>
<td>24.4</td>
<td>21.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Measured in CDCl₃ and TMS as internal standard at 22.53 MHz, 8 K memory size, pulse width of 45 degrees; 2.5 s pulse repetition.