Chemical studies of marine invertebrates. XXVII[1]. On the absolute configuration of aromadendrane sesquiterpenes from the soft coral Cespitularia aff. subviridis[2]

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Summary. Allo-aromadendrene, (–)viridiflorol and (+)ledol have been identified as minor constituents of the soft coral Cespitularia aff. subviridis.

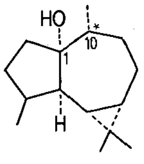
The xeniid alcyonarian Cespitularia aff. subviridis Q. and G., 1833, was collected at Albatross Rock, near La Digue, Seychelles Islands, where it colonizes dead hermatypic corals in shallow waters. The peculiar odor of freshly collected specimens suggested a high terpene content and, indeed, (+)palustrol (**I**) has been found to constitute 46% of the hexane extract of the sun-dried animal[5]. We wish to report here on the identification of 3 of its minor companions: allo-aromadendrene (**II**), (–)viridiflorol (**III**) and (+)ledol (**IV**).

Allo-aromadendrene was isolated only in trace amounts. Its NMR and mass spectra agree with the proposed structure and furthermore, the published IR spectrum of **II**[6,7] is identical with that of our sample. The small quantity that was isolated and the instability of the compound did not allow us to measure its optical rotation. Silicagel column chromatography yielded a mixture of 2 sesquiterpenes, that was separated by preparative GLC into pure (–)viridiflorol and (+)ledol. Here again, the published IR spectra of (+)viridiflorol[8] and (+)ledol[8] are identical with those of our samples, and NMR and mass spectra completely support the structure assignments. While the structure and the stereochemistry of allo-aromadendrene, viridiflorol and ledol have been entirely determined[8,9], the stereochemistry at C-10 of palustrol is not yet unambiguously established[10].

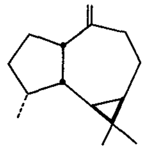
On dehydration, (+)palustrol yields 3 isomeric hydrocarbons[5], the major one being compound (**V**) which results from a preferential elimination of water between positions C-1 and C-10. This suggests a cis relationship between the methyl group at C-10 and the OH at C-1. In order to test the validity of this, we have determined the molecular geometry of the 2 C-10 epimers of **I**, using a Westheimer-Allinger program. From these geometric values, we have estimated the pseudo-contact terms associated with the different orientations of the C-10 methyl group[11]. These were compared with the experimental values obtained by measuring the evolution of the methyl chemical shift of palustrol in presence of increasing concentration of Eu $(DPM)_3$. Unfortunately, none of the possible combinations gives figures that group well around a single value for the angle of rotation of the europium atom around the C–O bond. 2 hypotheses could explain this failure: either the assumed molecular geometries are incorrect, or palustrol exists as a mixture of 2 or more conformers.

Allo-aromadendrene, (–)palustrol, (+)viridiflorol and (+)ledol are well-known aromadendrane sesquiterpenes which have been found in several terrestrial plants[12]. It is interesting to notice that while the rotatory power of palustrol and viridiflorol has opposite signs according to their terrestrial or marine origin, that of ledol is always positive (table). As far as we know, this constitutes the first exception to the intriguing antipodal relationship existing between sesquiterpenes from marine coelenterates and their corresponding terrestrial forms[13].

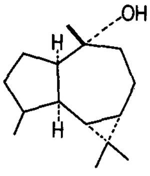
$(\alpha)_D^{CHCl_3}$	Terrestrial plant origin	Marine origin
Palustrol	– 17°[12]	+ 14°[5]
Ledol	+ 5°[12]	+ 5°
Viridiflorol	+ 4°[12]	– 5°



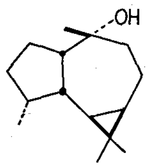
I (+)Palustrol



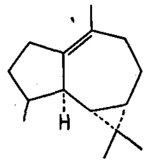
II (–)Alloaromadendrene



III (–)Viridiflorol



IV (+)Ledol



V

* Tentative stereochemistry at C-10.

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[1] For part XXVI, see Y. M. Sheikh, C. Djerassi, J. C. Braekman, D. Daloze, M. Kaisin, B. Tursch an R. Karlsson, Tetrahedron (in press).

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[4] Service de Chimie Organique E. P.

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