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REVISED STRUCTURE OF CAESPITOL AND ITS CORRELATION WITH ISOCAESPITOL[1]

A.G. González, J. Darias, J.D. Martín, and C. Pérez

Departamento de Química Orgánica, Universidad de La Laguna,
Instituto de Investigaciones Químicas, C.S.I.C., Tenerife, Spain.

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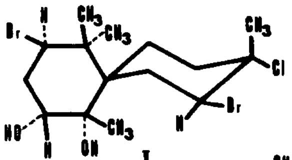
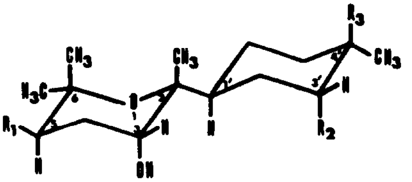
Caespitol is an halogenated sesquiterpene, $C_{15}H_{25}O_2Br_2Cl$, isolated from the marine alga Laurencia caespitosa Lamx, for which structure I has been advanced on the basis of its chemical and spectral properties[2]. From the results of X-ray studies and chemical experiments structure II was established for isocaespitol, a co-existing sesquiterpene in the same seaweed[3]. Chemical correlation between caespitol and isocaespitol has now proved that the former possesses a 2-(4′-methylcyclohexyl)-2,6,6-trimethyltetrahydropyrane skeleton, so that formula I had to be revised to III. Caespitol crystallizes with one molecule of water very tightly bound; this had led us to believe that it held a tert OH, which in turn brought out the assumption of a spirane skeleton[2].

Chemical correlation between the two isomers was attained as follows. Reduction of caespitol with excess LAH in refluxing ether yielded a complex mixture from which the partially dehalogenated compounds (IV,V,VII), the tri-dehalo derivatives (VI,VIII), and the unsaturated glycols (IX,X) were isolated[4]. Reduction of isocaespitol (II) in the same conditions afforded three major products which proved to be identical with authentic samples of VII, VIII, and X, derived from caespitol.

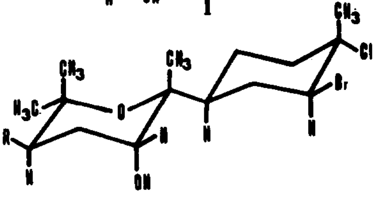
These results show that the structure of caespitol is represented by the formula III, in which the configurations at C-2, C-3, C-5 and C-1′ were confirmed from those of II, and the others at C-3′ and C-4′ are established on the basis of spectroscopic and chemical evidence as follows. Nmr analysis of II and III, along with comparison with the spectra of the LAH reduction derivatives, lead to the assignments shown in the Table. The trans-diequatorial dihalide conformation in III was deduced from the methine signal at τ5.61 (dd,J=12 and 4Hz) attributed to the axial C-3′ proton. Comparison of the chemical shift of



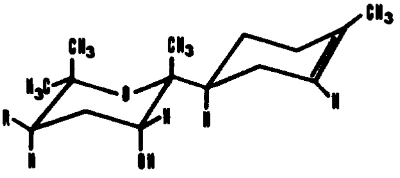
I



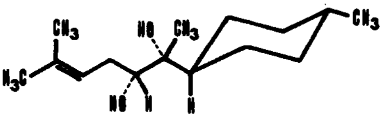
II, $R_1 = R_3 = Br$, $R_2 = Cl$
V, $R_1 = Br$, $R_2 = R_3 = H$
VI, $R_1 = R_2 = R_3 = H$



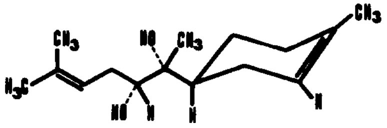
III, R = Br
IV, R = H



VII, R = Br
VIII, R = H



IX



X

Table: NMR Data (τ,60MHz,$CDCl_3$)

Comp.	C-2	C-3	C-5	C-6	C-3′	C-4′
II	8.84(3H,s)	6.33(1H,t, J=3Hz)	5.70(1H,dd, J=12,5Hz)	8.62(3H,s) 8.69(3H,s)	5.54(bs, W1/2=5Hz)	8.08(3H,s)
III	8.83(3H,s)	6.43(1H,t, J=2.5Hz)	5.69(1H,dd, J=12,5Hz)	8.63(3H,s) 8.69(3H,s)	5.61(1H,dd, J=12,4Hz)	8.33(3H,s)

the Me-C4′ in III (τ8.33) with that of trans-2-bromo-1-chloro-1,4,4-trimethylcyclohexane (τ8.35), in which the halogens exist exclusively in the diequatorial conformation[5], indicated that the Cl atom is located at the tert position. This configuration was confirmed by the fact that on melting II rearranges to III, which occurs by a known intramolecular mechanism[6]. When an extraction procedure from the alga was devised which rigorously excluded the conditions predicting rearrangement, II and III were isolated in a ratio 2:1 from the original extract.

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