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THE CONFORMATION OF SHYOBUNOL, AN ELEMENE-TYPE SESQUITERPENE

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From a biogenetic point of view, many elemene-type sesquiterpenes are considered to be produced from the corresponding germacrenes or germacrones. Recently, extensive studies on the relationships between the conformation of the germacranolides and the stereochemistry of their Cope rearrangement products have been made by Takeda and his co-workers.[1,2] On the basis of the CD spectra of several elemene-type sesquiterpenes, furthermore, Tanaka has suggested that an isopropenyl group and a vinyl group must interact with each other.[3] In the present paper, we wish to describe the conformation of shyobunol (1), an elemene-type compound, whose absolute configuration has been already established in connection with α-santonin.[4] Particularly, shyobunol (1), whose CD spectrum has a positive value ($\Delta\varepsilon$ = +2.4) at 202 nm (in MeOH, at 25°),[3] seems suitable for our NMR studies using a lanthanide shift reagent, because only one hydroxyl group is present in 1 and close to two isolated double bonds.

The induced shift ratios of eight protons[5] were obtained by incremental addition of weighed $Eu(fod)_3$ to substrate (1) in $CDCl_3$ containing TMS, as shown in Table 1. The coordinate system was given to 1 according to Armitage's method (see Figure 1).[6] Each ΔH value was calculated according to the following equation: $\Delta H = k(3\cos^2\theta - 1)\cdot r^{-3}$.

In the first step, ΔH values were calculated for five protons (a - e) except for the three protons (f - h) attached to the vinyl group, and the results best fitted to the observed values were shown in Table 1. At this stage, the positions of the metal and the isopropenyl group are as follows: d = 4.4 Å, Ω = 115°, ϕ = 240° and α = 15°. In consideration of these data, ΔH values of the eight protons (a - h) were further calculated and the results, in which the minimum agreement factor was 0.044, were also summarized in Table 1. At the final stage, the positions of the metal, the isopropenyl group and the vinyl group are as follows: d = 4.3-4.4 Å, Ω = 117-119°, ϕ = 228-238°, α = 15-19° and β = 210-280°. In this case, the distance between the metal and the oxygen atom is slightly longer than usual. Probably, this may be due to some steric effects, which interrupt the easy formation of the metal-substrate complex.

As a surprising result, Takeda has reported that the vinyl group of the CH_2=C(CH_2OH)-grouping is located at the 1,3-diaxial-like position with the tertiary Me group in the diol conformation (2).[1] However, further details on this point have not yet been published. In addition, the conformation of the remaining vinyl group remains unsettled. In the above results, clearly, rotation of the isopropenyl group in 1 must be restricted (α = 17 ± 2°). In connection with the CD spectrum of 1, furthermore, the remaining vinyl group is present in the region of β = 245 ± 35°, in a high probability. Accordingly, the more favorable conformation of 1 must be depicted as [A] rather than [B].[7] From a structural point of view, the more favorable conformation [A] is not related directly to the structure of the corresponding 1,5-cyclodecadiene which is produced on a

retro-Cope rearrangement. Furthermore, these two cases in 1 and 2 are not special, because deoxysaussurea lactone (3) derived from L-santonin has the CD curve similar to that of shyobunol (1),[3] suggesting that the former also adopts the same conformation as 1. In connection with the CD spectra of many elemene-type sesquiterpenes, further studies on these problems are in progress.

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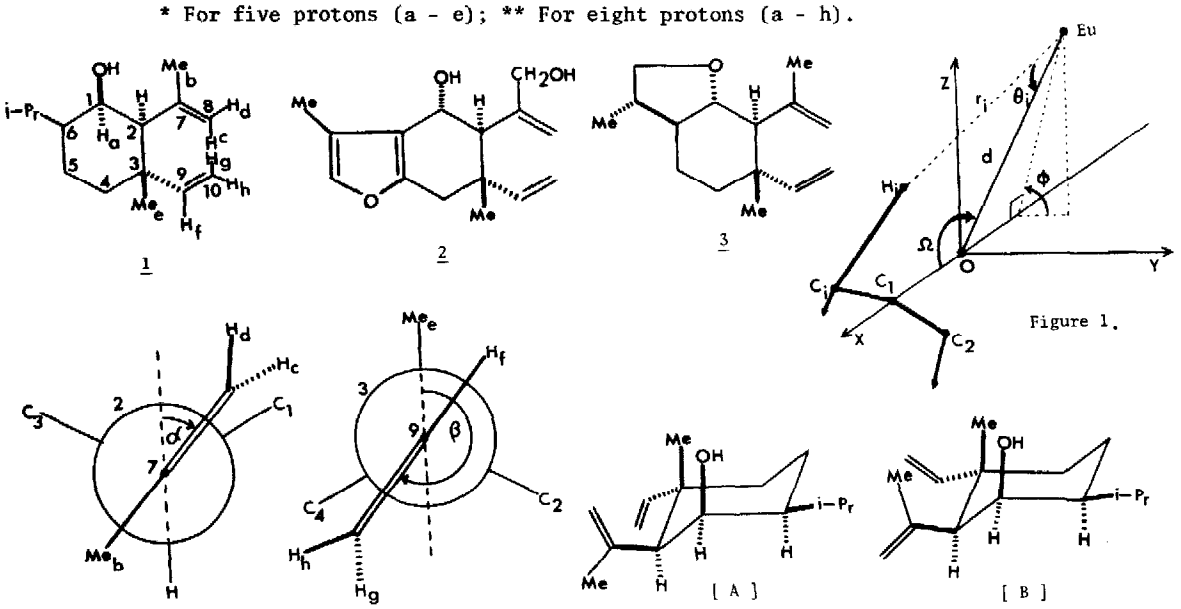
Table 1.

	H^a	H^b	H^c	H^d	H^e	H^f	H^g	H^h
◂H (obsd)	6.26	0.85	8.01	2.02	3.00	1.64	1.19	0.89
▲H (calcd)*	6.18	0.88	8.08	2.08	2.94			
▲H (calcd)**	6.28	1.02	8.04	2.02	3.15	1.28	1.00	0.75

* For five protons (a - e); ** For eight protons (a - h).



References and Footnotes

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5. Proton assignments were based on observed splitting and confirmed by decoupling at 100 MHz.
6. I.M. Armitage, L.D. Hall, A.G. Marshall and L.G. Werbelow, J. Amer. Chem. Soc. 95, 1437 (1973).
7. The induced shift ratios of eight protons are constant regardless of the concentration of added Eu(fod)3, and the NMR spectrum with a small amount of Eu(fod)3 is quite similar to that of the original compound (1) in respect of the coupling constant and shape of each signal (see F. Inagaki, M. Tasumi and T. Miyazawa, J. Chem. Soc. Perkin II 167 (1976), and references cited therein).