Chem. Pharm. Bull. 37(6) 1665—1666 (1989)

SOLVENT AND LANTHANIDE SHIFTS USED TO DETERMINE THE STRUCTURE OF TWO NEW NEOHOP-18,19-EPOXIDES

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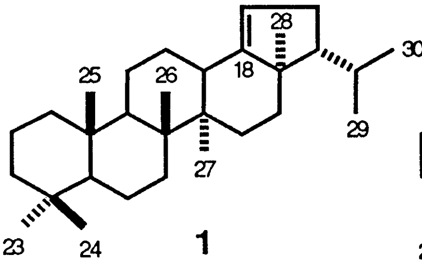
Solvent and lanthanide shift methods were applied to determine the structure of two neohop-18,19-epoxides. One of the isomers, **2**, did not show any lanthanide shifts because of the steric hindrance, while the other, **3**, caused typical lanthanide shifts.

KEYWORDS ^{1}H-NMR; solvent shift; lanthanide shift; Eu(FOD)$_3$; triterpenoid; neohop-18α,19α-epoxide; neohop-18β,19β-epoxide

During the course of the studies of the ozone-oxidation products of various kinds of triterpenoid monoenes belonging to the hopane and migrated hopane groups, we were forced to determine the stereostructures of two isomeric epoxides derived from neohop-18-ene (**1**). This paper deals with the very dramatic results of solvent$^{1)}$ and lanthanide$^{2)}$ shifts in the compounds and with the assignments of the ^{1}H-NMR signals of eight methyl groups of the compounds.

Ozone oxidation of **1** (50 mg) in n-hexane under cooling in Me$_2$CO/dry ice afforded two crystalline epoxides: less polar compound (**2**), mp 218 °C (2 mg), and more polar one (**3**), mp 173-174 °C (15 mg). Both compounds gave the molecular formula $C_{30}H_{50}O$ shown by high resolution MS and only oxide absorption appeared in their IR spectra. The ^{1}H-chemical shift values are shown in TABLE I . The chemical shifts of the three methyl signals (H-23, -24 and -25) of the three compounds are similar because the methyls are located rather far from a double bond or an oxygen function. The solvent shifts of the eight methyl groups of **2** clearly indicate that the four methyl signals (H-23, -24, -25 and -26) gave positive shifts$^{3)}$ and the other four (H-27, -28, -29 and -30) gave negative shifts (TABLE I and Fig. 1). The former methyl groups are on the side (β) opposite the epoxy ring (α) and the latter are on the same side (α). But in the case of compound **3**, only one methyl signal (H-26) gave a negative shift and the seven signals including H-27, -28, -29 and -30 show positive shifts (TABLE I and Fig. 2) to indicate the four methyl groups located the side opposite the epoxy ring (β). A dreiding model of 3 indicates that only one methyl group (C-26) is located on the same side as oxygen from the plane across C-18 and C-19 to cause a negative shift, while the other seven methyl groups are located on the side opposite the plane, causing positive shifts. These results are similar to those in the carbonyl group.$^{4)}$

Surprisingly, solutions of compound **2** and a lanthanide reagent, Eu(FOD)$_3$, in CDCl$_3$ did not cause any shifts at various concentrations. This may be because the lanthanide reagent cannot make a complex with the epoxy group of **2** because of steric hindrance by the two α-methyl groups (C-27 and -28) and an isopropyl group at C-21α. On the other hand, the solutions of compound **3** with Eu(FOD)$_3$ show typical lanthanide shifts (TABLE I and Fig. 3), the values of



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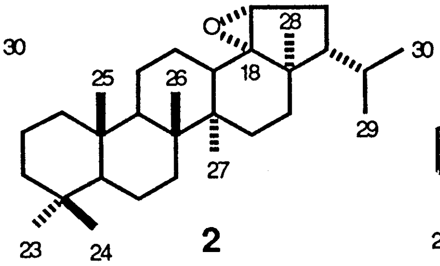

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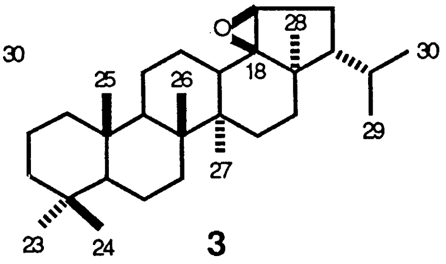

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TABLE I. ^1H-Chemical shifts (δ) on JEOL GX 270 (270 MHz) in $CDCl_3$

	Protons signal							
	H-23	H-24	H-25	H-26	H-27	H-28	H-29, 30	
1	0.837 (0.074)	0.782 (0.056)	0.843 (0.068)	0.923 (0.057)	1.083 (0.006)	1.106 (0.151)	0.882d (0.032)	0.914d (0.055)
2	0.840 (0.084) [0.002]	0.788 (0.062) [0.002]	0.840 (0.108) [0.002]	1.235 (0.277) [0.000]	1.175 (-0.011) [0.001]	0.874 (-0.142) [-0.002]	0.839d (-0.028) [0.000]	0.852d (-0.028) [0.000]
3	0.849 (0.057) [0.043]	0.793 (0.060) [0.040]	0.849 (0.018) [0.072]	1.180 (-0.070) [0.224]	1.087 (0.003) [0.545]	1.006 (0.084) [0.999]	0.816d (0.044) [0.336]	0.838d (0.058) [0.363]

Solvent shift values, δ (C_6D_6) - δ ($CDCl_3$), are shown in parentheses.

Lanthanide shift values, δ ($CDCl_3$ with molar ratio 0.5 of $Eu(FOD)_3$) - δ ($CDCl_3$), are shown in square brackets.

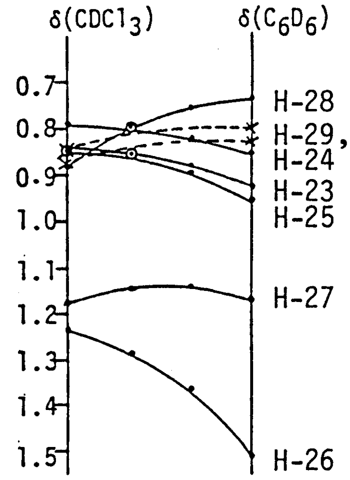

Fig. 1

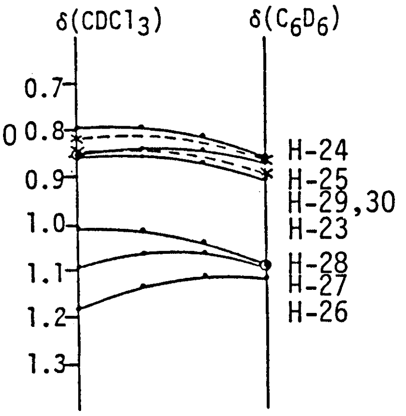

Fig. 2

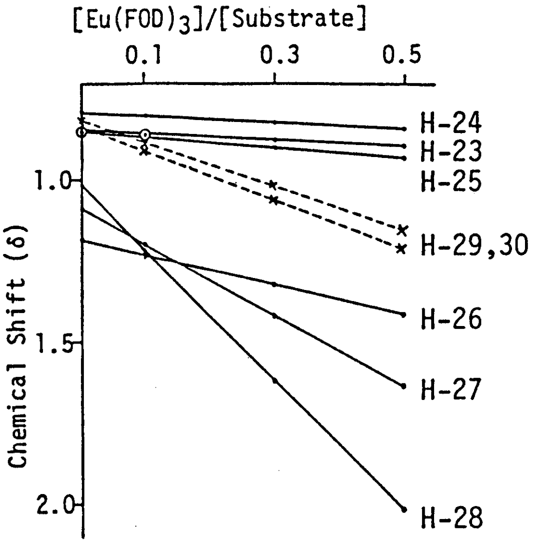

Fig. 3

which decrease with the distances of the epoxy group and the methyl groups such as C-28 > -27 > -29, -30 > -26 > -25 > -23 > -24.

We believe these two compounds, 18α,19α-epoxyneohopane (**2**) and 18β,19β-epoxyneohopane (**3**) are typical examples explaining the effect of solvent and lanthanide shifts on triterpenoid epoxide. The signals of the eight methyl groups of the three compounds can also be assigned as shown in TABLE I.

REFERENCES AND NOTES

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2) A. F. Cockerill, G. L. O. Davies, R. C. Harden, D. M. Rackham, *Chem. Rev.*, **73**, 553 (1973).
3) The solvent shift values were first shown as τ (arom. solv.) - τ (CCl_4) or δ (CCl_4) - δ (arom. solv.) until the 1960s, so down field shifts were shown with negative signs. After 1970 many authors indicated solvent shift values as δ (arom. solv.) - δ ($CDCl_3$) and down field shifts with lanthanide were shown with positive signs. We also indicate solvent shifts as well as lanthanide shifts down field with positive signs using δ values.
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(Received April 21, 1989)