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Z-E CONFORMATIONAL ISOMERISM OF NEROL, GERANIOL AND THEIR ACETATES.

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Introduction.

Z-E conformational isomerism of the title compounds has been a long-standing problem in terpene chemistry. In most literature the Z-("cis")-conformation is assigned to nerol, the E-("trans")-conformation to geraniol.

In 1965, Rummens[1)] reversed these assignments, based mainly on IR-arguments and also on a comparison of other physical properties like boiling points, refraction indices and densities.

Relationships between NMR coupling constants (vicinal, olefinic, allylic and homoallylic) and conformation in tri- and tetrasubstituted ethylenes are not unambiguous[2)]. It has been stated[3)] that methyl substituents on olefinic double bonds have a lower δ -value when cis to an alkyl substituent. Opposite trends seem to hold for methylene and methine protons. Application of these rules would yield the Z-conformation for nerol and the E-conformation for geraniol, apparently in contradiction with the conclusions reached by Rummens. Obviously, further information concerning the problem is needed.

Quite recently, it has been shown[4)] that addition of tris(dipivalomethanato)europium-III introduces large downfield chemical shifts in compounds containing suitable functional groups like hydroxyl-, carbonyl- or amino groups. The observed chemical shifts can be correlated to the internuclear vector distance between the functional group and the protons under consideration[5)]. It was felt that application of these effects to nerol, geraniol and the corresponding acetates could yield valuable conformational information.

Experimental and Results.

Increasing amounts of the europium complex were added to solutions

(approximately 2.5% w/w) of the title compounds* in carbon tetrachloride contained in NMR sample tubes. Spectra (100 MHz) were measured at 5-7 different molar ratios of solute and complex; the maximum concentration of the complex corresponded to a molar ratio solute: complex of about 2:1. Assignments of the various signals were substantiated by a series of decoupling experiments, assuming that the methylene protons at C_1 have $\delta \simeq 4.0-4.5$. Chemical shifts were measured in the usual way.
In figures 1 and 2, some δ -values have been plotted versus molar ratios of solute and complex. The straight lines in these figures are least-sqares plots. The slopes of these lines, together with the original chemical shifts of the various signals are summarised in the table.

Table Chemical shifts in δ -units and slopes*).

	Nerol		Geraniol		Neryl acetate		Geranyl acetate	
	δ (ppm)	Slope	δ (ppm)	Slope	δ (ppm)	Slope	δ (ppm)	Slope
C_1	3.97	28.40	4.02	28.16	4.48	20.55	4.51	16.32
C_2	5.37	16.87	5.34	16.91	5.31	7.31	5.30	7.73
C_4	2.07	7.83	2.02	4.52	2.11	3.30	2.05	1.53
C_5	2.04	4.81	2.02	3.97	2.10	1.73	2.06	1.51
C_6	5.06	3.72	5.05	2.74	5.09	1.54	5.05	0.89
C_8	1.67	1.08	1.65	0.99	1.69	0.59	1.68	0.32
C_9	1.59	1.79	1.59	1.39	1.62	0.80	1.61	0.51
C_{10}	1.72	4.29	1.65	7.12	1.76	1.46	1.72	2.87

* Defined as: $\dfrac{\text{observed downfield shift (ppm)}}{\text{molar ratio complex/solute}}$

Discussion.

Information pertinent to the present problem is to be expected mainly from shift values of protons at C_4, C_5 and C_{10} and to a lesser extent

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*Physical properties and IR spectra as in ref 1.

also from the behaviour of the signals of the protons at C_6, C_8 and C_9. From the table it is evident that in geraniolderivatives protons at C_4 and C_5 experience similar downfield shifts while the methyl group at C_{10}shows a slope which is nearly twice as high. On the other hand, in nerol derivatives the C_4 protons shift nearly twice as far as the C_{10} and C_5 signals for the same relative concentration of the complex. This can be reconciled only with an E-conformation for geraniol and a Z-conformation for nerol. It is also evident that the C_6-C_9 signals in nerol derivatives shift considerably further than in geraniol compounds. Relationships between observed chemical shifts for these signals after addition of the complex and detailed molecular conformation are somewhat hard to establish due to possible internal rotation of the molecule. However, the observed effects support the idea of a smaller overall distance between the C_6-C_9 protons and the functional groups in nerol derivatives as compared with geraniol derivatives. This is in agreement with the proposed structures.

References

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Fig. 1 Some chemical shifts in nerol for different concentrations of Eu(DPM)$_3$

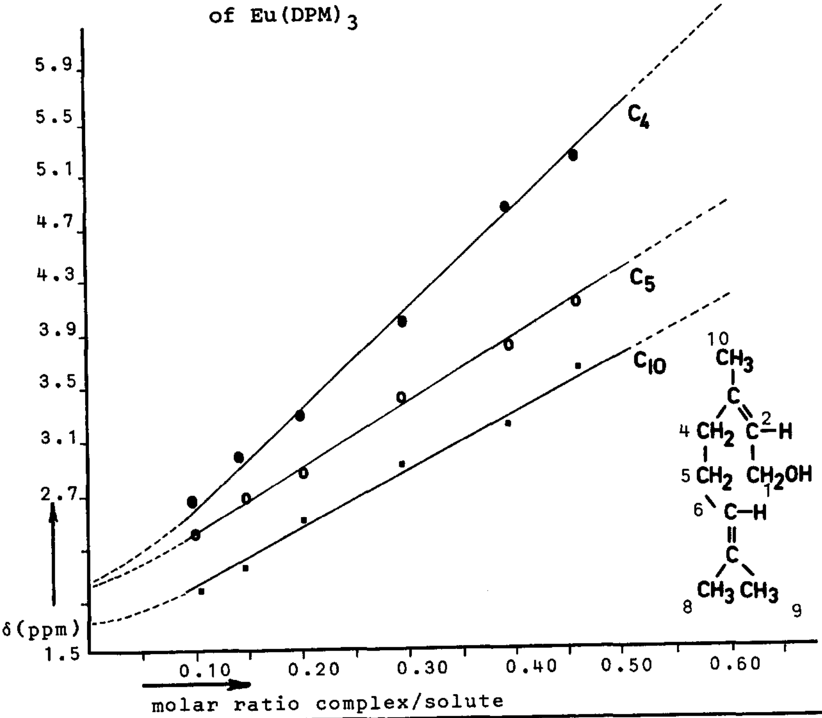

Fig. 2 Some chemical shifts in geraniol for different concentrations of Eu(DPM)$_3$