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AN ALTERNATE METHOD TO IDENTIFY PROTON(S) ON THE CARBON BEARING A HYDROXYL GROUP*

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In PMR spectroscopy, the usual method to identify the proton or protons on a carbon bearing a hydroxyl group is to acetylate or in general esterify the hydroxyl group, when the proton(s) concerned moves downfield by about 0.5 to 1.5 τ units (1). However, this procedure may not always be convenient, either due to interfering protons in the regions, or due to other reasons. We are presenting an alternate method to achieve this end.

If the hydroxyl group is methylated it is found that this proton on a secondary carbon moves upfield by about 0.6 τ units. Five examples with different types of alcohols (2) are given in Table 1. The Table shows that in the C_3-alcohols of steroids and triterpenes acetylation causes a downfield shift of about 0.8 to 1.2 τ units whereas methylation brings about an upfield shift of about 0.6 τ units (Compare columns a and b, and a and c). Thus, if both acetylation and methylation of the alcohol are done, the proton concerned undergoes a very large shift of 1.5 to 1.9 τ units (Compare columns b and c).

Under similar environments a methine proton resonates at a lower field than methylene and at much lower field than methyl protons (3). The methyl ethers in the Table can be considered as dimethyl ethers with alkyl substituents on one of the carbon atoms (the one at C_3). But in this case, interestingly, the methine protons resonate

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TABLE 1

Compound		Chemical shift of the C_3-H in the			d methoxy methyl
		a alcohol	b acetate	c methyl ether	
I	Cholesterol	6.44	5.6	7.1*	6.75
II	Cholestanol	6.45	5.33	7.05*	6.8
III	Cholestane-3α-ol	6.15	5.05	6.7	6.8
IV	4-Cholestene-3β-ol	5.8	4.88	6.4	6.78
V	Lupanol	6.82	5.6	7.46*	6.75

Spectra of the compounds were taken on a Varian A-60, high resolution spectrometer in 10% solution in carbon tetrachloride (except lupanol and its acetate, which were taken in chloroform) using TMS as internal standard and the signals are recorded in τ values.

at very high fields compared to the methyl protons (Compare columns c and d) and in the case of I, II and V (marked with asterisks), they are actually at higher fields (highest for V) than the corresponding methyls. This should be related to the diamagnetic anisotropy of the carbon-carbon single bonds in and on the ring holding the methyl ether (4). The same should be the reason for the high field shift of about 0.3 - 0.4 τ unit for the C_3-H, in lupanol, its acetate and methyl ether compared to the corresponding cholestane derivatives (Compare II and V) since in lupanol there are two additional carbon-carbon single bonds on the adjacent carbon i.e. on C_4. This latter shift may also serve to distinguish between triterpene and steroid C_3-alcohols.

REFERENCES

1 See e.g. J.N.Shoolery and M.T.Rogers, J.Amer.Chem.Soc. 80, 5121 (1958); N.S.Bhacca and D.H.Williams, Application of NMR spectroscopy in organic chemistry, p.77, Holden-Day, San Francisco (1964) etc.

2 For a recent reference for the preparation and spectral properties of these compounds, see C. R. Narayanan and K.N.Iyer, J. Org. Chem. 30, 1734(1965).

3 L.M.Jackman, Applications of NMR spectroscopy in Organic Chemistry, pp.50-57, Pergamon Press, London (1959).

4 Reference 3, pp.112-119.