

NMR SPECTRA OF SOME 2-OXYGENATED PINANES

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The stereochemistry of 2,3-oxygenated pinanes has been the subject of much debate¹⁻⁵. Zschunke *et al*⁶ have noted that for 10 α -pinane-2 β ,3-diols (2b and 2c) the 9-CH₃ signal (ca. δ 1.05 ppm) occurred significantly downfield from that signal (ca. δ 0.93 ppm) for 10 β -pinane-2 α ,3-diols (1b and 1c).

We now wish to report NMR data (Table I) for some 2 α - and 2 β - oxygenated pinanes. The values for diols (1b and 1c) are consistent with those reported earlier⁶. The notable feature of these data is that for the compounds containing

Table I - NMR Spectra* (δ in ppm)

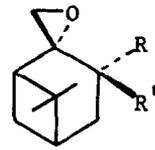
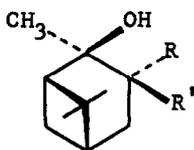
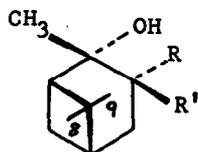
Compound	Configuration of C ² -O bond	8-CH ₃	9-CH ₃	10-CH ₃
1a	α -	1.24	0.95	1.24
2a	β -	1.22	1.09	1.22
1b	α -	1.23	0.93	1.26
1c	α -	1.25	0.95	1.35
3	β -	1.22	1.03	-
4a	α -	1.23	0.92	-
4b	α -	1.29	0.87	-
4c	α -	1.25	0.92	-

* Determined at 60Mc for CCl₄ solutions with CHCl₃ and TMS as internal standards.

a 2 β - oxygen function the 9-CH₃ signal lies in the range δ 1.03 - 1.09 ppm while for compounds with a 2 α - oxygen function the range for the signal due to the 9-CH₃ group is δ 0.87 - 0.95 ppm. The marked deshielding of the 9-CH₃ group by a 2 β - oxygen function is analogous to the 1,3-syn-axial deshielding effect⁷

found for the angular methyl groups in the steroid series.

Since the above Table incorporated data for cis-2-pinanol (1a) and trans-2-pinanol (2a), for which unambiguous chemical proof of stereochemistry is available⁸, the C-2 stereochemistry of the remaining compounds would appear secure.



- (1) (a) R, R' H
 (b) R OH; R' H
 (c) R H; R' OH

- (2) (a) R, R' H
 (b) R OH; R' H
 (c) R H; R' OH

(3)

- (4) (a) R, R' H
 (b) R OH; R' H
 (c) R H; R' OH

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