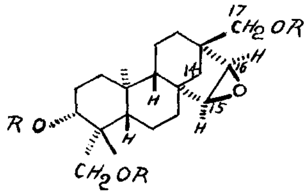
Tetrahedron Letters No. 27, pp. 1853-1855, 1963. Pergamon Press Ltd.
Printed in Great Britain.

LONG RANGE SHIELDING BY THE EPOXIDE RING

P.R. Jefferies, R.S. Rosich, and D.E. White.
Chemistry Department, University of Western Australia,
Nedlands, Western Australia.

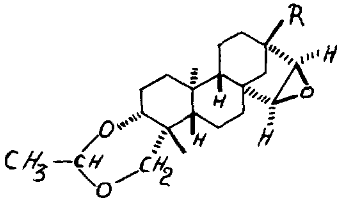
(Received 10 September 1963)

During a study of the stereochemistry of the diterpene beyerol (1,2) we have encountered some examples of N.M.R. spectra* which appear to demonstrate a long range shielding effect by the epoxide ring. A doublet arising from a single proton is found at high field when a 15β, 16β-epoxide ring is present (see Table I).



I R = -COMe

II R = -COPh



III R = $-CH_2OH$

IV R = $-CO_2Me$

TABLE I

Compound	14α-H		15α- and 16α-H			15,16-ene		
	14α-H	J	15α-H	16α-H	J	15-H	16-H	J
I	9.40	11	6.56	6.75	3	4.21	4.42	5.5
II	9.28	10.5	6.53	6.67	3	4.16	4.31	5.5
III	9.47	11	6.59	6.76	3	4.22	4.39	5.5
IV	48 c/s**		6.54	6.63	2	4.21	4.21	-

** Only one of the two peaks visible.

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* N.M.R. spectra were measured as before (2).

The coupling constant (10.5-11 c/s) is in good agreement with the value expected (3) of a geminal pair of hydrogens at an angle close to tetrahedral. The absence of any further splitting locates this hydrogen atom at C-14 and since the 14α-proton is considerably closer to the epoxide group than the 14β- proton the former is implicated as the shielded proton. Although the doublet due to the 14β- proton is not resolved, an approximate calculation based on the relative intensities of the peaks of the 14α- doublets locates the 14β- protons about 45 c/s downfield from the 14α- protons.

Whereas the positions of the 15- protons are constant within the group (see Table I), small changes in the 14α- and 16α- protons with alteration of R are expected and similar effects occur in compounds (I-IV) where the 15,16- olefin replaces the epoxide ring (see Table I).

It is well known that three membered rings show ring proton resonances abnormal to larger cyclic compounds although the reason for this effect is not fully understood. The possibility of a ring current in cyclopropane (4) has been considered recently by Wiberg and Nist (5) and the epoxide ring might be expected to show a similar effect which could explain the shielding we have observed. Alternately the shielding might be due to diamagnetic anisotropy of the carbon-carbon and carbon-oxygen single bonds. It is doubtful if the available anisotropies (6) of these bonds are valid in epoxide compounds although calculations based on this assumption indicate that much of the long range effect could arise from bond shielding.

The authors wish to record their thanks to Dr. M.W. Fuller for helpful discussions.

One of us (R.S.R.) wishes to acknowledge the financial support of a Commonwealth Postgraduate Scholarship.

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