THE OPTICAL ROTATION OF TERTIARY ALCOHOLS

By R. M. Carman*

Abstract

Brewster's rules are modified to deal with the optical rotation of tertiary alcohols.

The optical rotation of alcohols has been tested by Brewster[1] through a consideration of the conformational asymmetry about each bond in the molecule.†
Brewster obtains an empirical value of $+50$ for the molecular rotation contribution
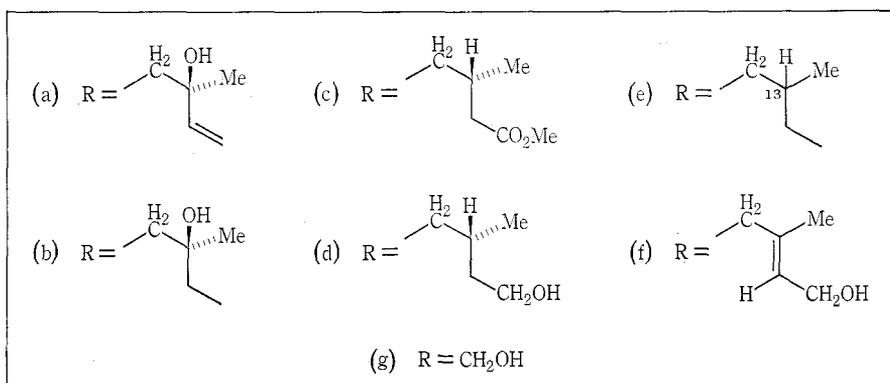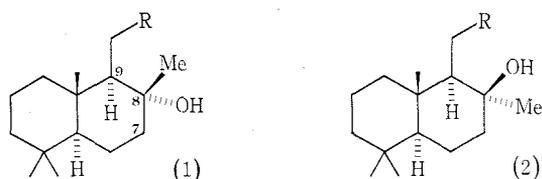
Scheme 1.—Note that (1e) and (2e) are quasiracemic at C 13 and are in the 50/50 α/β arrangement.

of the grouping $k(C-H)(O-H)$ and this value, which was derived from the rotations of compounds with secondary hydroxyl groups, gives good results[3] for secondary alcohols.

* Department of Chemistry, University of Queensland, St. Lucia, Qld. 4067.

† We find the recent approach of Yamana[2] to the rotation of hydroxyl groups to be unsatisfactory, at least insofar as the discrete values of polarization of the C–H bond and the electronic theory interpretation of these are concerned.

[1] Brewster, J. H., *J. Am. chem. Soc.,* 1959, **81**, 5475, 5483; *Tetrahedron,* 1961, **13**, 106.
[2] Yamana, S., *J. org. Chem.,* 1972, **37**, 1405.
[3] Eliel, E. L., "Stereochemistry of Carbon Compounds," p. 403 (McGraw–Hill: New York 1962).

For some time[4] we have been concerned about the rotations of tertiary labdanols with partial structures (1) and (2) (Scheme 1). The molecular rotation[4] for partial structure (1) is -3, and that for (2) is $+55$. Assuming that the conformations of these two structures are the same, the treatment of Brewster would suggest that the difference in rotation is due only to differences about the $C\,7, C\,8$ and $C\,8, C\,9$ bonds. Structure (1) about the $C\,7, C\,8$ bond gives

$$k(C.H-C.C+C.C-C.H+O.H-O.H)$$

which cancels to zero, while about the $C\,8, C\,9$ bond the epimer (1) gives $k(C.C$ $-C.O+O.H-C.H)$. Structure (2) about $C\,7, C\,8$ gives $k(C.H-C.C+C.O-O.H)$ and about $C\,8, C\,9$ gives zero. Thus the molecular rotation difference calculated for structure $(2)-$structure (1) is $2k(C.O-O.H+C.H-C.C)$ which factorizes to $2k(C-H)(O-H)-2k(C-H)^2$. If Brewster's value[1] of $+50$ for $k(C-H)(O-H)$ is accepted, then partial structure (2) should be more negatively rotating than structure (1) by a $\Delta[M]_D$ of 20 units. The reverse holds, and (2) is actually more positive than (1). This finding has caused us to examine the partial structures (1) and (2) to check that they were not in fact enantiomeric at $C\,8$. However, a large number of compounds with partial structures (1) and (2) are recorded in the literature, and p.m.r. and chemical data clearly indicate that the correct structures have been assigned.

The problem of the anomalous rotation is resolved when it is realized that the value $k(C-H)(O-H)$ of $+50$ has been derived[1] from secondary alcohols. The value for any group depends upon the polarizability of the group, and it is well known that tertiary alcohols are more polarizable than secondary alcohols. Any increase of $k(C-H)(O-H)$ above the value of $+60$ given by $k(C-H)^2$ will lead to partial structure (2) being more dextrorotary than (1), in agreement with the observed findings. Therefore, we have examined epimeric pairs of tertiary alcohols to obtain a value for $k(C-H)(O^t-H)$ for tertiary alcohols where O^t signifies a tertiary group.

Ten pairs of compounds are listed in Table 1 with each pair epimeric at the tertiary alcohol. The rotational contributions about the bonds adjacent to the tertiary hydroxyl are listed and from each pair of compounds, using differences in rotation and assuming $k(C-H)^2 = 60$, a value for the rotation of $k(C-H)(O^t-H)$ has been derived. It is clear that a value of about $+90$ for $k(C-H)(O^t-H)$ gives good results for tertiary alcohols. In all the cases listed in the table a value of > 60 is required to give the correct stereochemistry at the epimeric centre.

Not all tertiary alcohols can be employed in observing the tertiary alcohol effect because their partial rotations need not include a term in O^t. One example are the 3-methylcholestanols. The treatment of Brewster gives no term in O^t and predicts that the 3β-hydroxy-3α-methyl compound and the 3α-hydroxy-3β-methyl compound will have equal rotations in agreement with the experimental observations ($[\alpha]_D$ $+34°$ and $28°$ respectively[5]).

It is possible that some of the compounds in Table 1 suffer hydrogen bonding to the side chain. However, the diverse nature of the side chains and the consistent values for $k(C-H)(O^t-H)$ suggest that hydrogen bonding cannot contribute greatly to the rotation of most of the molecules listed.

[4] Carman, R. M., *Aust. J. Chem.*, 1966, **19**, 629.

[5] Barton, D. H. R., Campos-Neves, A. da S., and Cookson, R. C., *J. chem. Soc.*, 1956, 3500.

In this paper we have ignored 1,2-diols. It seems very likely that the polarizability of the C–O bond in 1,2-diols may vary considerably from that observed in isolated hydroxyl groups, in the same way that 1,2-dibromides have been shown[6] to have much less polarizable bonds than monohalides. It is also probable that the conformational rotary powers for groups other than hydroxyl (e.g. the halogens)

TABLE 1

$k(C-H)(O^t-H)$ CALCULATED FROM TEN PAIRS OF EPIMERS

Compound	$[M_D]$ obs.	Ref.	Rotation about bonds adjacent to the OH	Calc. value for $k(C-H)(O^t-H)$
Partial structure (1) (av. from 23 compounds)	−3	4	$-k(C-H)(O^t-H)+k(C-H)^2$	+88
Partial structure (2) (av. from 5 compounds)	+55	4	$k(C-H)(O^t-H)-k(C-H)^2$	
Labd-14-ene-8,13-diol[a] (1a) (sclareol)	−15	4	$-k(C-H)(O^t-H)+k(C-H)^2$	+86
8β-Labd-14-ene-8,13-diol (2a)	+37	4	$k(C-H)(O^t-H)-k(C-H)^2$	
Labdane-8,13-diol (1b) (dihydrosclareol)	−4	4	$-k(C-H)(O^t-H)+k(C-H)^2$	+82
8β-Labdane-8,13-diol (2b)	+40	4	$k(C-H)(O^t-H)-k(C-H)^2$	
Methyl 8-hydroxylabdan-15-oate (1c)	−29	4	$-k(C-H)(O^t-H)+k(C-H)^2$	+83
Methyl 8β-hydroxylabdan-15-oate (2c)	+17	b	$k(C-H)(O^t-H)-k(C-H)^2$	
Labdane-8,15-diol (1d)	−28	4	$-k(C-H)(O^t-H)+k(C-H)^2$	+82
8β-Labdane-8,15-diol (2d)	+16	b	$k(C-H)(O^t-H)-k(C-H)^2$	
13aβ-Labdan-8-ol (tetrahydroabienol) (1e)	−9	c	$-k(C-H)(O^t-H)+k(C-H)^2$	+86
8β,13aβ-Labdan-8-ol (2e)	+43	d	$k(C-H)(O^t-H)-k(C-H)^2$	
(E)-Labd-13-ene-8,15-diol (1f)	−2	4	$-k(C-H)(O^t-H)+k(C-H)^2$	+110
(E)-8β-Labd-13-ene-8,15-diol (2f)	+99	b	$k(C-H)(O^t-H)-k(C-H)^2$	
13,14,15,16-Tetranorlabdane-8,12-diol (1g)	−44	4	$-k(C-H)(O^t-H)+k(C-H)^2$	+96
13,14,15,16-Tetranor-8β-labdane-8,12-diol (2g)	+29	4	$k(C-H)(O^t-H)-k(C-H)^2$	
12β-Hydroxy-12α-methyltigogenin	−178	e	zero	+91
12α-Hydroxy-12β-methyltigogenin	−147	e	$k(C-H)(O^t-H)-k(C-H)^2$	
19-Norabieta-8,11,13-trien-4α-ol	+122	f	$-k(C-H)(O^t-H)+k(C-H)^2$	+67
19-Norabieta-8,11,13-trien-4β-ol	+136	f	$k(C-H)(O^t-H)-k(C-H)^2$	

[a] Nomenclature is after the convention of Rowe [Rowe, J. W., "The Common and Systematic Nomenclature of Cyclic Diterpenes," 3rd Revision (Forest Products Laboratory, U.S.D.A., Madison, Wis., 1968)].

[b] Hugel, G., Oehlschlager, A. C., and Ourisson, G., *Tetrahedron*, 1966, Suppl. 8 (Part 1), 203.

[c] Carman, R. M., and Deeth, H. C., *Aust. J. Chem.*, 1969, 22, 2161.

[d] Carman, R. M., and Zerner, G. W. D., unpublished data.

[e] Coxon, J. M., Hartshorn, M. P., and Kirk, D. N., *Tetrahedron*, 1967, 23, 3511.

[f] Rowe, J. W., Nagasampagi, B. A., Burgstahler, A. W., and Fitzsimmons, J. W., *Phytochemistry*, 1971, 10, 1647.

will also vary depending upon whether the group is primary, secondary, or tertiary. However, this variation may be most significant for hydroxyl groups, where a small increase in the polarity of the C–O bond can take the value of $k(C-H)(O-H)$ from below to above that of $k(C-H)^2$ and so change the sense of the rotation about the hydroxyl group.

[6] Carman, R. M., *Aust. J. Chem.*, 1971, **24**, 1733.