Tetrahedron. Vol. 27, pp 5207 to 5216. Pergamon Press 1971. Printed in Great Britain

THE INFLUENCE OF ALLYLIC OXYGEN ON THE $\pi \rightarrow \pi^*$ CD OF CERTAIN CHROMOPHORES

A. F. BEECHAM

Division of Chemical Physics, C.S.I.R.O., P.O. Box 160, Clayton, Victoria, Australia

(*Received in the UK* 18 *May* 1971; *Accepted for publication* 18 *July* 1971)

Abstract—The CD associated with the lowest energy $\pi \rightarrow \pi^*$ transition is discussed for compounds in which the chromophore of interest is a single or conjugated olefinic double bond, with an allylic oxygen substituent. It is shown that the Cotton effect concerned is usually intense, with positive sign if the chirality of the system C=C—C—O is right-handed and negative if the chirality is left-handed. In cases where the olefinic double bond is conjugated and the conjugated system is itself skewed, the chiralities of the two systems may be opposed. When this occurs, the sign of the Cotton effect is found usually to accord with the helical sense of the system C=C—C—O. The basic phenomenon is believed to be the same as that underlying the Mills' rule for the configuration of cyclic allylic alcohols.

THE *cisoid*- and *transoid*-diene rules[1,2,3] correlate the sign of the Cotton effect associated with the lowest energy transition of the conjugated diene chromophore with the skew-sense of the diene system. The relationships between chirality and sign are indicated in Fig. 1. where the models represent the system C=C—C=C. Both rules have been successfully applied to stereochemical problems but in certain cases they have been found not to hold.[2,3,4,9] It has recently been demonstrated[4] that the presence of an allylic oxygen can profoundly modify the optical rotatory properties

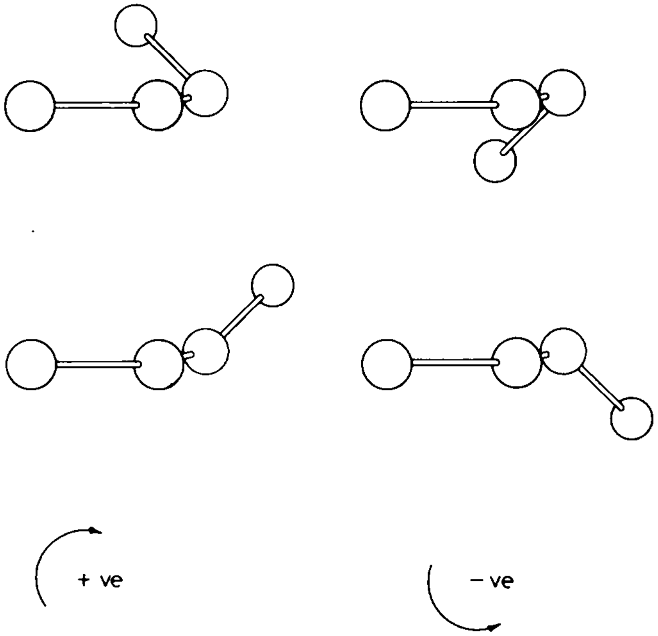


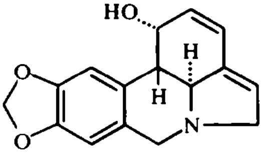
FIG 1.

of the $\pi \rightarrow \pi^*$ transition to which the rules refer. If the four atoms comprising the allylic oxygen, the carbon atom to which it is attached and the two carbon atoms of the nearer double bond of the diene are viewed as a chiral system, then the sense in which this unit influences the CD is again as indicated in Fig. 1, where the models now represent the system C=C—C—O.

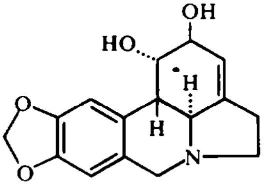
The relationship between sign and helical sense is the same in both the diene helix and the oxygen-containing helix; thus, a skew-diene with an allylic oxygen substituent may be conveniently regarded as two helices in series. In each of five cases in which the senses of these two helices were opposed, the diene rule was violated;[4] that is, the oxygen-containing helix appeared to be the dominant dissymmetric unit in that it determined the sign of the Cotton effect associated with the diene $\pi \rightarrow \pi^*$ transition.

In the earlier paper on this topic[4] an attempt was made to discuss those anomalies to the diene rules which were relevant, but an important group of examples from the *Erythrina* alkaloids escaped attention. Although it was to these compounds that the transoid-diene rule was first applied[5], they were not mentioned in the later paper in which the transoid rule was enunciated.[3]

As a model compound for their studies on the *Erythrina* bases,[5] the authors used dehydrolycorine, I. At that time the absolute stereochemistry of lycorine, II, and its relatives had been assigned by application of Mills' rule.[6] X-ray structure analysis of dihydrolycorine hydrobromide[7] has since shown the assignment to be correct and as depicted in I and II. The ORD curve of I contained the first extremum of a strong negative Cotton effect attributable to the diene chromophore and appropriate in sign to the skew-sense observed in a Dreiding model. This appeared to confirm the validity of the transoid diene rule, which the authors then applied to four *Erythrina* bases, similar in structure and containing similar chromophoric groups to I.

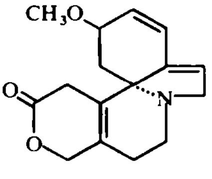


I

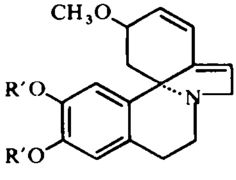


II

The compounds concerned were β-erythroidine, III, erysodine, IV, erysopine, V, and erythraline, VI, whose absolute configuration at the spiro carbon atom was unknown. Shortly afterwards, however, it became known for all the *Erythrina* bases through an X-ray structure determination of dihydro-β-erythroidine hydrobromide[8]



III

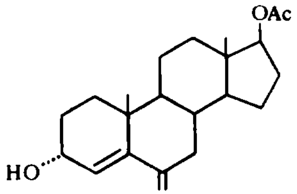


IV R^1 or R^2 = H, R^2 or R^1 = CH_3
V R^1 = H, R^2 = H
VI R^1R^2 = CH_2

and is as depicted in III, IV, V and VI. The absolute configuration at the spiro carbon atom determines the skew-sense of the diene system in these molecules. It is left-handed. From application of the transoid diene rule to their ORD data, however, Weiss and Ziffer[5] were led to conclude that the diene system had right-handed chirality and hence that the absolute configuration at the spiro carbon atom was enantiomeric to that shown in III, V and VI. Thus, the transoid diene rule is violated in these compounds. Again,[4] the reason is to be found in the disposition of the allylic oxygen with respect to the diene.

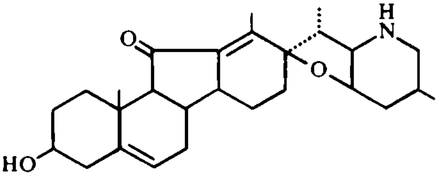
In the model compound, dehydrolycorine, I, the chirality of the diene is left-handed and so is the chirality of the system C=C—C—O. The strong negative Cotton effect observed may be thought to result from the reinforcement which this identity in skew-sense implies. In the *Erythrina* bases, on the other hand, the left-handed chirality of the diene is opposed by right-handed chirality in the system C=C—C—O and, as before,[4] it appears that the sign of the diene Cotton effect is determined by the latter.

These further examples strengthen the conclusions already reached[4] regarding the effect that allylic oxygen may exert on the CD of the lowest energy diene transition. The compounds in which the effect has so far been observed have been either *transoid* or homoannular *cisoid* dienes, the two diene classes for which the diene rules were generally found to hold.[2, 3] It was stated[2] that the small number of heteroannular *cisoid* dienes examined were found not to obey the *cisoid* rule and Burgstahler and Barkhurst[9] have proposed an explanation for this in terms of interaction between the diene chromophore and axial or pseudo-axial bonds to allylic hydrogens or methyls. In homoannular *cisoid* dienes such as 1,3-cyclohexadiene the helical sense of the allylic axial bond—adjacent double bond systems is necessarily the same as the helical sense of the diene itself, whereas in heteroannular *cisoid* dienes the helicities may be opposed. A compound prepared by Ziffer and Robinson[10] is of particular interest since it is a conjugated *cisoid* diene with an allylic OH group, in which the diene system is not homoannular. These authors reduced the 3-keto function of 6-methylene testosterone with borohydride and obtained crystalline one of the two possible product epimeric alcohols to which they assigned the 3β-ol structure. The diene Cotton effect found for the compound was positive, $\Delta\varepsilon_{222\text{nm}} = +15$. With any of the possible conformations of ring A and with the allylic OH group β-orientated, both the diene helix and the C=C—C—O helix would possess left-hand chirality from which a negative Cotton effect would be expected. On the other hand, the allylic axial hydrogens would form right-handed helical systems with their adjacent double bonds, from which, according to Burgstahler and Barkhurst,[9] the observed positive Cotton effect might be expected. However, it is not easy to see why the effect of the allylic axial hydrogens should outweigh that of the allylic OH in this case, whereas in other cases, discussed here and earlier,[4] the allylic oxygen helix determines the Cotton effect sign although it is opposed by the helicities of both the diene itself and the systems allylic axial bond—double bond. There appear to be two possible alternatives; either the allylic oxygen effect does not extend to *cisoid* skew-dienes of this type, or the C3 configuration of Ziffer and Robinson's product has been wrongly assigned. If the compound were, in fact, 6-methylene, 17-acetylandrost-4-ene, 3α, 17β diol, VII, the positive Cotton effect observed would be explicable in terms of the influence of allylic oxygen. While the 3β-ol structure is the more probable, it would evidently be desirable for the configuration at C3 to be established beyond doubt.



VII

The nature of the interaction between a skew-diene and an allylic oxygen substituent is not yet known, but it is evident that the influence of such a substituent on the CD of $\pi \rightarrow \pi^*$ transitions in other chromophores should be considered. A chirality rule for the lowest energy $\pi \rightarrow \pi^*$ transition (K-band) of $\alpha\beta$-unsaturated ketones has been proposed[11, 12] based on similar considerations to those on which the diene rules were formulated. The sign-chirality relationship is again that of Fig. 1, where the models now represent the system $O{=}C{-}C{=}C$. The ORD curves through the K-band region were obtained originally from eight compounds,[11] the only one containing allylic oxygen being the alkaloid, jervine, VIII. A strong and well-defined Cotton effect



VIII

centred near 250nm was observed for VIII and this was stated to identify the absolute conformation of the system $O{=}C{-}C{=}C$ as that of a left-handed helix. However, no helical sense for the system can be deduced from a Dreiding model of the compound since the two double bonds of the enone appear to be co-planar. If the enone is, in fact, planar, the chromophore is not dissymmetric and no strong K-band Cotton effect would be observed unless some other influence were intervening. Obviously, the influence of allylic oxygen is a possibility.

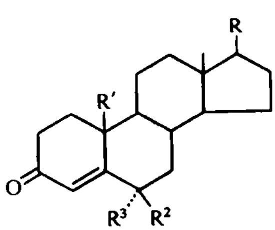
At that time the absolute configuration at the spiro carbon atom of VIII had not been rigorously established but, on the basis of biogenetic analogy to normal steroids, the α-oxide configuration was accepted.[13] With this configuration the four-atom helix containing allylic oxygen, $C{=}C{-}C{-}O$, is right-handed and, if it were to operate in the same sense as in the dienes, would impose positive CD on the K-band of the enone chromophore, contrary to what is observed. However, it is now known[14] that jervine has the β-oxide configuration at the spiro carbon atom, as shown in VIII and, hence, that the allylic oxygen helix has the left-handed chirality from which, by analogy with the diene situation, the observed negative $\pi \rightarrow \pi^*$ Cotton effect would be predicted.

Most studies of the optical rotatory properties of $\alpha\beta$-unsaturated ketones have been concerned only with the $n \rightarrow \pi^*$ transition. It was suggested[11] that the sign of the strong background rotatory dispersion on which the $n \rightarrow \pi^*$ Cotton effect is usually superimposed could be taken as reflecting the sign of the $\pi \rightarrow \pi^*$ Cotton effect and thus, as indicative of the O=C—C=C chirality, provided the complicating effect of conformational flexibility could be assessed. However, a second complicating factor has since become known. Contiguous to the $\pi \rightarrow \pi^*$ transition at 240–260nm is a transition at 205–220nm, often not observable in the UV spectrum, but strongly optically active.[10, 15, 16, 17] It has been shown[10] that in some instances the sign of the dispersion below 300nm is determined by this transition rather than by the $\pi \rightarrow \pi^*$ transition near 250nm. Consequently, evidence for the influence of allylic oxygen on the $\pi \rightarrow \pi^*$ Cotton effect is best sought in CD data encompassing the region 200–300nm. Results due to Kuriyama *et al.*[17] from some Δ^4-3-ketosteroids, IX-XVI, are collected in the Table.

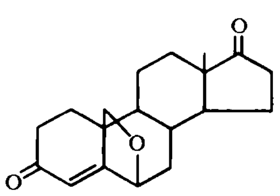
TABLE 1. THE $\pi \rightarrow \pi^*$ COTTON EFFECT OF Δ^4-3-KETOSTEROIDS

Compound	Substituents			CD Maxima		Handedness of Helices	
	R^1	R^2	R^3	$\Delta\varepsilon$	λ(nm)	O=C—C=C	C=C—C—O—
IX	H	H	H	+7·9	225·231	right	
X	H	OH	H	−5·2	242	right	left
XI	H	OAc	H	−3·5	242	right	left
XII	Me	H	H	+7·8	235sh.	right	
XIII	Me	OAc	H	−2·9	246	right	left
XIV	Me	H	OAc	+3·7	230sh.	right	right (almost planar)
XV	OH	H	H	+6·8	235infl.	right	right
XVI	CH_2—O		H	−15·5	236	right	left

In IX–XVI the Cotton effect signs for both the $n \rightarrow \pi^*$ transition at 320–330nm ($\Delta\varepsilon = -1{\cdot}3$ to $-1{\cdot}8$) and the unassigned transition at 205–220nm ($\Delta\varepsilon = +4{\cdot}7$ to $+13{\cdot}4$) are invariant. A negatively signed $n \rightarrow \pi^*$ Cotton effect has been correlated[12, 18] with right-handed helicity in the O=C—C=C chromophore and this is the geometry



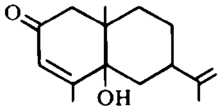
IX—XV



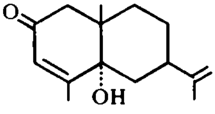
XVI

obtaining in the normal steroid conformation, which the unsubstituted Δ^4-3-ketosteroids, at least, would be expected to adopt. Right-handed helicity would also accord with the positive $\pi \rightarrow \pi^*$ Cotton effect observed in all except XVI and the 6β-OH or 6β-OAc compounds, X, XI and XIII. It is in these compounds, however, particularly XIII, that 1,3-diaxial interaction across ring B might force a conformation change, despite evidence to the contrary from the sign of the $n \rightarrow \pi^*$ Cotton effect. However, the results of a NMR study[19] support the view that the conformation of the O=C—C=C system in 6β-OH or 6β-OAc derivatives of IX or XII is not significantly different from that in the parent compounds. Thus, right-handed enone chirality is indicated throughout the series IX–XVI. The negative π → π* Cotton effects of X, XI, XIII and XVI accord with the postulated influence of allylic oxygen on this transition, since the chirality of the system C=C—C—O is left-handed only in these compounds. Kuriyama *et al.*[17] have reached similar conclusions and have also observed the analogy to the case of the *Erythrina* bases.[5]

A recent communication[20] contains reference to two further examples, also recognised as such by Kuriyama. The π → π* CD maximum at 236nm for β-rotunol, XVII, is large and positive ($\Delta\varepsilon = +15{\cdot}5$). This is opposite in sign to the π → π* Cotton effect of the reference compound, 5α-spirost-3-en-2-one, although the n → π* CD bands of the two compounds are almost identical. The chirality of the double bond—allylic oxygen helix in XVII is right-handed. Similarly in α-rotunol, XVIII, whereas the n → π* CD is essentially superimposable on that of reference substance 17β-acetoxy-5α-androst-3-en-2-one, the π → π* bands of the two compounds are opposite in sign.



XVII



XVIII

As far as has been ascertained, the foregoing examples, together with those of the earlier paper,[4] provide the only recorded instances in which the influence of allylic oxygen on the CD of dissymmetric chromophores is clearly revealed. It will be as well to note, here, those pieces of experimental evidence which might be interpreted as contrary to the general conclusion. The first of these, concerning VII or its C3 epimer, has already been discussed. The second relates to XV (Table 1). In this compound both the enone and allylic oxygen helices are right-handed. The sign of the π → π* Cotton effect is positive, as expected, but its magnitude is very similar to those observed for IX and XII, in which the allylic OH is replaced, respectively, by H and Me. Thus the reinforcement to the enone π → π* Cotton effect which might be expected from allylic oxygen is not evident. The tabulated data are, perhaps, less informative in this regard than the CD curves would be but, while Kuriyama *et al.* do not reproduce these, they state that the curves of IX and XV are similar.[17] The apparent inactivity of the 10β-OH group in XV as compared, for instance, to the 6β-OH group of X they attribute to the different spatial directions of these substituents from the chromophore.[17] Further evidence seems essential before useful comment can be made.

The third body of data that requires noting comes from a study by Bloch and Wallis[21] who recorded the ORD to about 210nm of B-nor-4-en-3-one steroids, with and without an α-OH group allylic to the 4,5 double bond. For the unsubstituted compound they list extrema at 260 and 230nm, a = −750 and for the α-OH derivative, extrema at 236 and 208nm, a = −730. In the α-OH compound the allylic oxygen helix is right-handed and, by analogy, would be expected to produce a positive π → π*

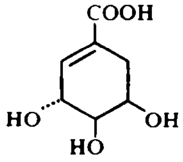
Cotton effect. This was evidently not observed. Similar compounds with 4-Br substituents, with and without allylic α-OH or α-OAc substituents, gave similar apparent negative Cotton effects of comparable magnitudes in the same region. In the absence of CD studies it is impossible to be certain that in these compounds the $\pi \rightarrow \pi^*$ Cotton effect is not influenced by allylic oxygen, particularly since a second strongly optically active transition is known to occur near the $\pi \rightarrow \pi^*$ region in enones, as discussed above. But it is necessary to note these results.

It is possible, then, that an oxygen disposed with respect to a conjugated diene as in VII, or to an enone as in XV, or allylic to a 4-en-3-one grouping in a B-norsteroid does not markedly modify the $\pi \rightarrow \pi^*$ CD. Further CD studies on such systems would be welcome.

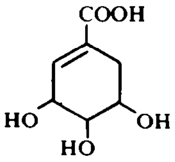
The influence of 6β-oxygen substituents on the $\pi \rightarrow \pi^*$ CD of Δ^4-3-ketosteroids is clear from the work of Kuriyama[17] discussed above. It is natural to enquire into the effect on the chromophore of oxygen substituents at C2. There appear to be no CD data from such systems for the $\pi \rightarrow \pi^*$ region and such indications as exist come from ORD "background" rotations obtained incidentally in studies of the $n \rightarrow \pi^*$ Cotton effect.[22, 23, 24, 25] There is no evidence that oxygen at C2 has an effect similar to that of oxygen allylic to the olefinic double bond; it may, in fact, operate in the inverse sense. Here, too, appropriate CD studies would be welcome.

Little further information in regard to allylic oxygen and dissymmetric chromophores is, as yet, available. Snatzke[26] mentions the possibility of a strong contribution from an allylic OH group to the CD of a homoconjugated triene. The same author has recorded the CD through the $\pi \rightarrow \pi^*$ region of some αβ-epoxy enones with allylic OH groups[27] and of jurineolide[28] in which a lactonised OH group is allylic to a diene conjugated across a ten-membered ring. The evidence is not clear in any of these cases but in none it is incompatible with the postulated general effect. Compounds containing oxygen substituents allylic to the styrene chromophore have also been examined[13,29] but in these cases the configuration at the carbon atom bearing the allylic oxygen and, thus, the chiral sense of the C=C—C—O grouping are unknown. It would be interesting to determine what effect, if any, the allylic substituent has on such systems, since the skewed styrene chromophore, contrary to the original assumption,[27] is now stated[30] to obey the sign-chirality relationship of twisted biaryls rather than that of dienes.

The postulated allylic oxygen effect is clearly compatible with the $\pi \rightarrow \pi^*$ CD of those αβ unsaturated acids which have been examined and which incorporate such a substituent. While the carboxyl group in αβ unsaturated acids is formally freely-rotating, its minimum energy conformations are found to be those in which it is antiplanar or synplanar to the olefinic double bond.[31] Thus, the chromophore



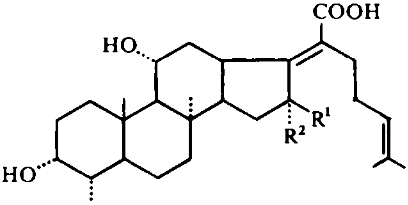
XIX



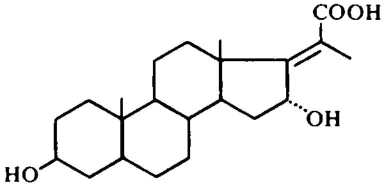
XX

can be classed as dissymmetric only when further conformational restrictions force a skew disposition. No such restrictions can be postulated for shikimic acid, XIX, nevertheless this compound exhibits a well-defined negative Cotton effect, $\Delta\varepsilon_{218\text{nm}} = -12{\cdot}9$, associated with the $\pi \rightarrow \pi^*$ absorption band at 211nm. The sign of the Cotton effect is in accord with the left-handed chirality of the allylic OH–double bond helix. The ORD and CD of XIX and of epishikimic acid, XX, have been recorded by Weiss and Ziffer.[32] Epishikimic acid was not available for study here but the ORD curves of XIX and XX[32] are tending strongly negative and positive respectively at the limit of observation (240nm), indicating oppositely signed Cotton effects in the $\pi \rightarrow \pi^*$ region in accord with their respective allylic oxygen configurations.

The CD to 215nm has been determined for XXI, XXII and XXIII, three further αβ unsaturated acids bearing allylic OH groups.[33] In addition to the $n \rightarrow \pi^*$ band near 260nm, each exhibits a strong Cotton effect at about 230nm, positive in sign in the case of XXI in which the chirality of the allylic OH–double bond helix is right-handed and negative in XXII and XXIII in which it is left-handed.

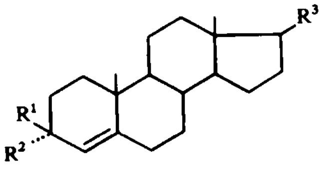


XXI $R^1 = OH, R^2 = H$
XXII $R^1 = H, R^2 = OH$



XXIII

The evidence from skew-dienes discussed earlier[4] and the evidence surveyed above together show that the $\pi \rightarrow \pi^*$ CD of certain conjugated chromophores may be strongly influenced by allylic oxygen substituents. Each of the systems considered may be regarded as an allylic alcohol, extended by conjugation and sometimes modified by substitution on oxygen. One of the more useful generalisations in stereochemistry has proved to be that advanced by Mills in 1952,[6] relating the absolute configuration at the carbon atom bearing the OH group in a cyclic allylic alcohol to the optical rotation at the sodium D line. The rule states that such an alcohol with the allylic OH α-oriented, as in XIX, is always more laevorotatory than its epimer, XX. The general validity of Mills' rule is indicative of strong CD induced in one or more electronic transitions of the olefin chromophore by the allylic oxygen. This was clearly shown to be the case by Legrand and Viennet[34] who found that the CD spectra of three steroids, XXIV, XXV and XXVI, each exhibited a strong Cotton effect associated with the first observable ethylenic transition near 200nm. That from XXIV, $\Delta\varepsilon = -10$.



XXIV $R^1 = OH, R^2 = H, R^3 = OH$
XXV $R^1 = OMe, R^2 = H, R^3 = OAc$
XXVI $R^1 = H, R^2 = OMe, R^3 = OAc$

is little affected by conversion of the 3β-OH group to the Me ether or by acetylation of the 17β-OH, XXV, $\Delta\varepsilon = -11{\cdot}5$. Inversion of configuration at C3 in XXV, however, inverts the sign of the Cotton effect, XXVI, $\Delta\varepsilon = +6{\cdot}5$. The authors remark that the phenomenon underlying Mills' rule is better observed by direct CD measurement of the transition of interest. Snatzke[26] and Scott and Wrixon[35] have also suggested that the basis of Mills' rule resides in CD associated with olefinic absorption. The results discussed here and earlier[4] indicate that the phenomenon underlying Mills' rule is also operative in olefins extended by conjugation and that in many cases its effect is sufficiently strong to over-ride the effect of any dissymmetry in the conjugated system itself.

Moscowitz[36] first distinguished between chromophores which are optically active by virtue of intrinsic dissymmetry and those which are intrinsically symmetrical but are optically active through the influence of an asymmetric molecular environment. The olefin chromophore in an allylic alcohol must surely be regarded as a member of the latter class. In dienes and similar systems the shift in wavelength of the lowest energy $\pi \rightarrow \pi^*$ transition, predicted by the Woodward-Fieser rules and experimentally observed,[37] is no greater for an allylic OH substituent than for a OH substituent elsewhere in the molecule. There is, thus, no evidence from isotropic absorption that either the ground or excited state orbital concerned in this transition is especially affected by the allylic substituent—although the observation could conceivably mean that both orbitals are affected but the energy difference between them remains the same. Again, if the chromophore included the OH group, this would imply some form of electron delocalisation over the four atomic centres, C=C—C—O, which might result in detectable reduction of the carbon–oxygen bond length as compared with ordinary C—OH bonds. We have found no evidence of this in data from relevant X-ray structure analyses. Nevertheless, the CD associated with the lowest energy $\pi \rightarrow \pi^*$ transition of a double bond—allylic oxygen grouping is comparable in magnitude to that of a dissymmetric conjugated diene or enone. It has been stated[2] that the effect of an inherently dissymmetric chromophore, such as a skew-diene, would be stronger by about an order of magnitude than that produced by a symmetric chromophore asymmetrically perturbed but, if the allylic alcohol system is to be so classified, it is evident that this is too broad a generalisation. It has already been pointed out that the ranges of rotational strength of the two classes overlap.[38]

The underlying reason for the intensity of the allylic oxygen effect is a matter for future consideration. It is to be noted, meanwhile, that Mills' rule is generally valid because the $\pi \rightarrow \pi^*$ CD in which it has its origin is strong. It is further to be noted that the phenomenon on which Mills' rule is based, persists when the π-electron system of the allylic double bond is extended by conjugation and must be taken into account when the optical rotatory properties of any such system are considered.

EXPERIMENTAL

The CD of shikimic acid, $\varepsilon_{206\text{nm}} = 8.300$ (4×10^{-4}M in water), $\varepsilon_{211\text{nm}} = 8.300$ (4×10^{-4}M in EtOH), [lit.[39] $\varepsilon_{213\text{nm}} = 8.900$ (solvent not stated)] was measured on a Roussel–Jouan Dichrograph, Model A, 1961.

$\Delta\varepsilon$ (4×10^{-4}M in water): 0 (290nm), +0·15 (258nm), 0 (250nm), −10·5 (214nm).

$\Delta\varepsilon$ (4×10^{-4}M in EtOH): 0(290nm), +0·56(256nm), 0(246nm), −12·9(218nm). Lit.[30] (EtOH): 0(290nm), c. +0·5 (c. 256nm).

REFERENCES

[1] A. Moscowitz. E. Charney. U. Weiss and H. Ziffer. *J. Am. Chem. Soc.* **83**. 4661 (1961)

[2] U. Weiss. H. Ziffer and E. Charney. *Tetrahedron* **21**. 3105 (1965)

[3] E. Charney. H. Ziffer and U. Weiss. *Ibid.* **21**. 3121 (1965)

[4] A. F. Beecham. A.McL. Mathieson. S. R. Johns. J. A. Lamberton. A. A. Sioumis. T. J. Batterham and I. G. Young. *Ibid.* **27**, 3725 (1971)

[5] U. Weiss and H. Ziffer. *Experimentia* **19**. 660 (1963)

[6] J. A. Mills. *J. Chem. Soc.* 4976 (1952)

[7] M. Shiro. T. Sato and H. Koyama. *Ibid.* (B). 1544 (1968)

[8] A. W. Hanson. *Acta Cryst.* **16**. 939 (1963)

[9] A. W. Burgstahler and R. C. Barkhurst. *J. Am. Chem. Soc.* **92**. 7601 (1970)

[10] H. Ziffer and C. H. Robinson. *Tetrahedron* **24**. 5803 (1968)

[11] C. Djerassi. R. Records. E. Bunnenberg. K. Mislow and A. Moscowitz. *J. Am. Chem. Soc.* **84**. 870 (1962)

[12] W. B. Whalley. *Chem. and Ind.* 1024 (1962)

[13] See. for instance. Pierre Crabbé. *Applications de la dispersion rotatoire optique et du dichroisme circulaire optique en chimie organique.* p. 440. Gauthier-Villars. Paris (1968)

[14] S. M. Kupchan and M. I. Suffness. *J. Am. Chem. Soc.* **90**. 2730 (1968)

[15] L. Velluz and M. Legrand. *Angew. Chem.* **77**. 842 (1965)

[16] M. Legrand and R. Viennet. *Compt. Rend.* **261**. 1687 (1965)

[17] K. Kuriyama. M. Moriyama. T. Iwata. K. Tori. *Tetrahedron Letters* 1661 (1968)

[18] G. Snatzke. *Tetrahedron* **21**. 413. 421. 439 (1965)

[19] K. Tori. Y. Terui. M. Moriyama and K. Kuriyama. *Tetrahedron Letters* 1657 (1968)

[20] H. Hikino. K. Aota. D. Kuwaro and T. Takemoto. *Ibid.* 2741 (1969)

[21] J. C. Bloch and S. R. Wallis. *J. Chem. Soc.* (B). 1177 (1966)

[22] K. Kuriyama. E. Kondo and K. Tori. *Tetrahedron Letters* 1485 (1963)

[23] Y. Yamato and H. Kaneko. *Tetrahedron* **21**. 2501 (1965)

[24] T. Kawasaki and K. Miyahara. *Ibid.* **21**. 3633 (1965)

[25] Ref. 13. p. 445 *et seq.*

[26] G. Snatzke. A. J. Thomas and G. Ohloff. *Helv. Chim. Acta.* **32**. 1253 (1969)

[27] Z. Kis. A. Closse. H. P. Sigg. L. Hubran and G. Snatzke. *Ibid.* **53**. 1577 (1970)

[28] M. Suchý. L. Dolejo. V. Herout. F. Sŏrm. G. Snatzke and J. Himmelreich. *Coll. Czech. Chem. Comm.* **34**. 229 (1969)

[29] P. Crabbé and W. Klyne. *Tetrahedron* **23**. 3449 (1967)

[30] P. Crabbé. *Chem. and Ind.* 917 (1969)

[31] J. D. Dunitz and P. Strickler. *Structural Chemistry and Molecular Biology* (ed. A. Rich and N. Davidson). p. 595. Freeman. San Francisco and London (1968)

[32] U. Weiss and H. Ziffer. *J. Org. Chem.* **28**. 1288 (1963)

[33] L. Velluz. M. Legrand and M. Grosjean. *Optical Circular Dichroism.* p. 140 Academic Press. New York and London (1965)

[34] M. Legrand and R. Viennet. *Compt. Rend.* **262**. 1290 (1966)

[35] A. I. Scott and A. D. Wrixon, *Tetrahedron* **26**. 3695 (1970)

[36] A. Moscowitz. *Ibid.* **13**. 48 (1961)

[37] H. H. Jaffé and M. Orchin. *Theory and Applications of Ultraviolet Spectroscopy* John Wiley and Sons. London and New York. (1962)

[38] A. F. Beecham and A. McL. Mathieson. *Tetrahedron Letters* 3139 (1966)

[39] R. McCrindle. K. H. Overton and R. A. Raphael. *J. Chem. Soc.* 1560 (1960)