# Electron Spin Resonance Study of the Stereochemistry of Radicals related to Cinnamic Acid

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The e.s.r. spectra of radicals formed by the oxidation of hydroxycinnamic acid derivatives are reported and ambiguities in the assignments of coupling constants are resolved by means of graphical methods and also by using a tested theory. The time-averaged dihedral angle between the double bond and the ring seems to be of the order of 30°, and this is increased to ca. 60° by a methyl substituent on the β-carbon atom.

IN our studies of the e.s.r. spectra of radicals (I) from hydroxycoumarins [1] we were able to account for the spin distribution by considering the radicals as if there were no connection between the annular oxygen and the benzenoid ring. From the theoretical viewpoint, then,

(I)   (II)
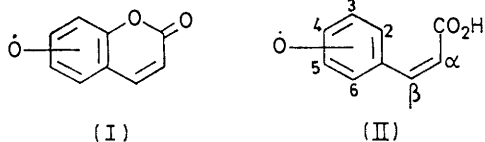
it was as if the heterocyclic ring had opened and we were dealing with radicals from hydroxycinnamic acids (II). However, in (I) we would expect the two rings to be planar whereas in cinnamic acid itself we would expect, e.g. from crystallographic data,[2] that there would be a

small angle of twist (ca. 20°) about the C(1)–C(β) bond. We decided to investigate this possibility, both for its intrinsic interest and in order to confirm that we had indeed previously observed radicals of type (I), i.e. that ring opening had not occurred in acid solution. Provided that certain technical difficulties can be overcome, e.s.r. is an ideal tool to use in this type of problem, for in radicals of type (II), the delocalisation of spin into the side chain will be very sensitive to the dihedral angle θ, i.e. the angle between the nodal plane of the benzenoid ring and that of the double bond.

RESULTS

The radicals were generated in a flow system using Ce^{IV} as oxidant as reported for phenoxyl radicals [3] except for the

[1] W. T. Dixon, M. Moghimi, and D. Murphy, *J.C.S. Perkin II*, 1975, 101.

[2] R. W. G. Wychoff, ' Crystal Structures,' Interscience, New York, 1969, 2nd edn., vol. 6, p. 39.

[3] W. T. Dixon, M. Moghimi, and D. Murphy, *J.C.S. Faraday II*, 1974, 1713.

semiquinones which were obtained by means of alkaline autoxidation of appropriate hydroxylated cinnamic acids.

The assignment of the observed coupling constants was not a trivial problem, and it was especially difficult to decide which coupling constants could be ascribed to the protons on C(α) and C(β). The first step was to differentiate between the ring protons and the others. This was easy for the radicals from *para*- and *meta*-hydroxycinnamic acids but not for the *ortho*-isomer which we shall therefore take as an example. Fortunately we were able to use the graphical techniques developed for aryloxyl radicals [3] and were therefore able to choose the assignments which best followed the general trends. The effect of the side chain on the spin distribution in the ring is similar to that of alkyl groups and contrasts with that of the cyano-group which might have been expected to resemble a C=C double bond (see Table 1).

and hence that the system must be twisted, or at least oscillating or rotating rapidly.

The question is whether the larger coupling constant must be assigned to α- or to β-H. We shall consider the radicals from *ortho*- and from *para*-hydroxycinnamic acids.

ortho-*Case*.—A negative density corresponding to -0.21 Q^{-1} means that on C(1) there must be a density of at least $0.7\ Q^{-1}$. The positive density C(α) is either 0.38 or 0.26 Q^{-1} which give sums of 2.5 and 2.41 Q^{-1} respectively. From (2) above, 0.26 Q^{-1} is the value preferred.

para-*Case*.—Density on the *para*-position is at least 0.9 Q^{-1} so the two sums are $(1.98 + 0.64)\ Q^{-1} = 2.62\ Q^{-1}$, $(1.98 + 0.31)\ Q^{-1} = 2.29\ Q^{-1}$ so the value of a_α is probably $0.31\ Q^{-1}$.

In these cases, and by extrapolation to the other cases too, it seems that $|a_\alpha| < |a_\beta|$ and that since a_β must therefore arise largely due to hyperconjugation the time-averaged

TABLE 1

(A) E.s.r. parameters (a/mT) for radicals obtained from hydroxycinnamic acids * (calculated values for dihedral angle of 30° in parentheses)

Substituents	a_2	a_3	a_4	a_5	a_6	a_α	a_β
2-OH	a	0.54 (−0.55)	0.16 (0.14)	0.91 (−0.91)	0.21 (0.23)	0.26 (−0.20)	0.38 (0.36)
3-OH	0.64 (−0.61)ᵃ		0.74 (−0.70)	0.20 (0.20)	1.04 (−1.04)	0.06 (0.0)	0.085 (−0.08)
4-OH	0.17 (0.15)ᵃ	0.54 (−0.585)		0.54 (−0.585)	0.17 (0.15)	0.31 (−0.26)	0.64 (0.47)
3,4-(OH)₂	0.175ᵃ			0.35	0.015	0.245	0.48
	0.015 (−0.03)ᶜ			0.135 (−0.063)	0.275 (−0.36)	0.12 (−0.08)	0.245 (0.19)
3-OH-4-OCH₃	0.32 (−0.33)ᵃ		a_{OCH_3} 0.19	0.19 (−0.26)	0.80 (−0.83)	0.0 (−0.03)	0.0 (0.0)
2,4-(OH)₂	b, †	0.35 (−0.37)		0.90 (−0.85)	0.20 (0.23)	0.325 (−0.26)	0.475 (0.48)
2,3,4-(OH)₃-β-CH₃	c			0.08	0.54	0.0	a_{CH_3} 0.0
2,4,5-(OH)₃	c	0.045(0.135)			0.135 (−0.08)	0.19 (−0.11)	0.29 (0.34)
2,5-(OH)₂-β-CH₃	c	0.225 (−0.25)	0.26 (−0.25)		0.185 (−0.24)	0.15 (−0.02)	a_{CH_3} 0.0

(B) E.s.r. parameters (a/mT) for radicals obtained from cyanophenols

	$-a_2$	a_3	$-a_4$	a_5	$-a_6$
2-CN	a_N 0.07ᵃ	0.14	1.01	0.21	0.71
3-CN	0.725ᵃ	a_N 0.02	0.99	0.205	0.68
4-CN	0.675ᵃ	0.225	a_N 0.145	0.225	0.675

* Radicals produced in acid solution are assumed to have the stable *trans*-cinnamic acid structure. Primary radicals (produced from the corresponding lactones) in alkaline solution are assumed to have the *cis*-configuration. † Average values, assuming rapid proton exchange.

ᵃ Oxidation by Ce^{IV} in acid solution. ᵇ Oxidation by Fe^{III} in alkaline solution. ᶜ Autoxidation in aqueous alkali.

The same procedure was applied to radicals from di- and tri-hydroxycinnamic acid derivatives, where there were doubts about the ring proton assignments.

In each case, the larger of these two coupling constants is approximately half that of the methyl proton splitting in the radical in which the double bond system is replaced by a methyl group. This suggests that the coupling constants of α- and β-H are roughly of the same relative order in all of the radicals.

To help us establish an empirical assignment for the two protons not attached to the ring we use two general observations. (1) The negative spin density on a position is related to the sum of the positive densities on either side. Thus from the results in Table 1 we get a *meta*-splitting of *ca.* $+0.2$ mT which corresponds to a sum of the adjacent *ortho*- and *para*-splittings of *ca.* -1.6 mT. When the spin density is unity on a carbon π orbital, the coupling constant of a proton attached to it is Q. (2) The sum of positive spin densities leaving out the C–O group is *ca.* $2.35 \pm 0.05\ Q^{-1}$ in many phenoxyl radicals.

The first thing to note here, from (1), is that in every case, the extranuclear proton coupling constants are both too large to arise from negative spin density on C(β). This implies a significant contribution from hyperconjugation

dihedral angle is close to 30°. This could arise either from the system being relatively fixed at that angle or from relatively large oscillations between two enantiomeric twisted conformations.
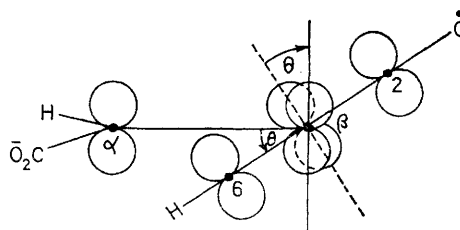
Radicals (II) observed along C(β)—C(1) bond

McLachlan-type Calculations.—We have previously found that a straightforward application of McLachlan's simplified SCF theory [4] accounted well for the coupling constants in a wide variety of phenoxyl radicals if we used as oxygen parameters $\alpha_O = \alpha_C + 1.6\beta$, $\beta_{CO} = 1.3\beta$. This theory also gave some good results for oxygen heterocyclic systems [1]

[4] A. D. McLachlan, *Mol. Phys.*, 1960, **2**, 233.

so we expect it could be applied successfully to these radicals too.

Since the double bond is significantly shorter than the bond length in benzene we took a resonance integral of 1.2β for it, and the π-resonance integral for the $C(1)-C(\beta)$ bond was varied, which is, in effect equivalent to varying the angle of twist. Table 2 gives the results for one radical, and

TABLE 2

Theoretical results for the radical from 2-hydroxycinnamic acid (coupling constants in mT)

$C(6)-C(\beta)$ resonance integral	$-a_2$	a_3	$-a_4$	a_5	a_β *	$-a_\alpha$
0.3β	0.62	0.17	0.97	0.21	0.33	0.072
0.5β	0.55	0.14	0.91	0.23	0.37	0.20
0.7β	0.46	0.09	0.82	0.24	0.40	0.40
Expt.	0.54	(−)0.16	0.91	(−)0.21	(−)0.38	0.26

* Calculated in each case for dihedral angle of 30° using $Q_{CH_3} = 3.0$ mT; $Q_H = -3.0$ mT; $\beta_{C=C} = 1.2\beta$ (45° average).

similar calculations were carried out for all the other radicals. No account was taken of the carboxy-group. The best overall fit was obtained with a value of 0.5β for the variable integral. No significant change in the results came from including the effects of hyperconjugation with the vinyl σ-bond system. Taking Q values of 3.0, i.e. $Q_H = -3.0$ mT, $Q_{CH_3} = +3.0$ mT the calculations also gave an angle of ca. 30°. This calculation applies to a fixed conformation and the agreement with experiment does not imply that the actual radicals have fixed conformations or even that they oscillate about this dihedral angle. However, since free rotation would give an average of θ 45° the results do show that rotation is restricted.

⁵ W. T. Dixon, W. E. J. Foster, and D. Murphy, J.C.S. Perkin II, 1973, 2124.

A rather low value, 0.6β, is obtained for the maximum resonance integral of the long bond, but it has to be remembered that as with all such parameters it has to include a number of implicit effects (e.g. hyperconjugation).

DISCUSSION

The theory does help confirm our empirical assignments of the hyperfine splittings in the radicals considered. However we feel that it is not fine enough for us to be able to calculate small differences in dihedral angle with any degree of confidence. As far as we can tell the average dihedral angle is not significantly affected by an adjacent oxygen atom. However, a methyl group attached to the β-carbon atom does have a very large effect and we deduce that there must be a time-averaged dihedral angle of something like 60° in these cases.

EXPERIMENTAL

E.s.r. Spectra.—Most radicals were produced by flowing 10^{-2}M solutions of phenols against 10^{-2}M-Ce^{IV} solutions in 0.5M-sulphuric acid in the flow system described previously.⁵ 2,4-Dihydroxycinnamic acid (10^{-2}M) was flowed against 10^{-2}M-potassium ferricyanide in 0.1M-sodium hydroxide solution. Spectra from o- and p-semiquinone anions were obtained in a static system which gave better line widths.

Materials.—2,4-Dihydroxycinnamic acid, 2,3,4-trihydroxy-β-methylcinnamic acid, and 2,4,5-trihydroxycinnamic acid were obtained by the spontaneous alkaline hydrolysis of resublimed umbelliferone, 4-methyldaphnetin, and aesculetin respectively. The other phenols were commercial materials which were purified by the usual methods. Their physical constants agreed well with those of the literature.