Methyl 7,7-Dimethyl-5-oxo-5,6,7,8-tetrahydro-1-naphthoate (7b). A mixture of the pyran **6b**[16] (4.3 g) and methyl propiolate (10 g) was treated as above for **7a**. The ester **7b** was obtained: bp 118–121 °C (0.05 mm) (60%); NMR ($CDCl_3$) δ 1.08 (6 H, s, C7 methyls), 2.53 (2 H, s, C8), 3.22 (2 H, s, C6), 3.92 (3 H, s, CO_2CH_3), 7.36 (1 H, apparent t, $J_{2,3} = J_{3,4} = 8$ Hz, C3), 8.09 (1 H, dd, $J = 8$, $J_{2,4} = 1.5$ Hz), 8.16 (1 H, dd, $J = 8$, $J_{2,4} = 1.5$ Hz).

Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.23; H, 7.05.

Dimethyl 4-Acetyl-3-methylphthalate (10). An equilibrium mixture of the pyran **8** and the dienedione **9**[16] (0.91 g, 6 mmol) and dimethyl acetylenedicarboxylate (0.84 g, 6 mmol) was combined and heated under a reflux condenser under nitrogen at 110 °C for 10 h. The crude product was dissolved in CCl_4 (3 ml). The solution deposited white crystals at 0 °C which were collected by filtration at 0 °C with pressure: mp 75–76 °C (69%); NMR ($CDCl_3$) δ 2.39 (3 H, s), 2.56 (3 H, s), 3.90 (3 H, s, CO_2CH_3), 3.95 (3 H, s, CO_2CH_3), 7.57 (1 H, d, $J_{5,6}$ = 8.5 Hz), 7.91 (1 H, d, $J_{5,6}$ = 8.5 Hz); (CCl_4) δ 2.30 (3 H, s,), 2.50 (3 H, s), 3.86 (6 H, s, CO_2CH_3), 7.55 (1 H, d, $J_{5,6}$ = 8 Hz), 7.77 (1 H, d, $J_{5,6}$ = 8 Hz).

Anal. Calcd for $C_{13}H_{14}O_5$: C, 62.39; H, 5.64. Found: C, 62.20; H, 5.63.

Methyl 3-Acetyl-2-methylbenzoate (11). An equilibrium mixture of the pyran **8** and the dienedione **9**[16] (2.7 g, 18 mmol) and methyl propiolate (10 g) were treated as above for **7a**. The ester **11** was obtained: bp 117–119 °C (0.1 mm) (65%); NMR ($CDCl_3$) δ 2.54 (3 H, s, CH_3), 2.58 (3 H, s, CH_3), 3.90 (3 H, s, CO_2CH_3), 7.0–8.0 (3 H, multiplets, C4,5,6).

Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.31; H, 6.27.

Isomerization of 13c in the Presence of Methyl Propiolate. A mixture of the dienal **13c**[18] (0.38 g, 1.8 mmol) and methyl propiolate (1 g, 12 mmol) was boiled under reflux under nitrogen for 60 h. Excess methyl propiolate was distilled into a cold trap (−78 °C) under reduced pressure (0.1 mm). The NMR spectrum of the residual oil (CCl_4) was identical with that reported[18] for the trans isomer(**13t**).

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Registry No.—**1**, 675-09-2; **4**, 5526-16-9; **6a**, 58133-98-5; **6b**, 58134-01-3; **7a**, 59599-49-4; **7b**, 59599-50-7; **8**, 58134-11-5; **9**, 17448-92-9; **10**, 59599-51-8; **11**, 59599-52-9; **13c**, 21451-41-2; methyl propiolate, 922-67-8; dimethyl acetylenedicarboxylate, 762-42-5.

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Electron Spin Resonance Studies of Structure and Conformation in Anion Radicals Formed during the Autoxidation of Hydroxylated Coumarins

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Coumarins containing hydroxyl groups in the aromatic ring are autoxidized in alkaline solution with the formation of semiquinone radicals, which have been studied by means of ESR spectroscopy. The hyperfine splitting data are consistent with some of these radicals possessing a closed pyrone ring, and others being cinnamic acid semiquinones formed as a result of pyrone ring opening. The cinnamic acid semiquinones are apparently observed in the trans configuration, and the effect of the side chain on the aromatic ring splittings is similar to those of alkyl and aryl groups. A qualitative model, considering delocalization of spin density from the aromatic nucleus into the side chain by both π overlap and hyperconjugation, is successful in relating conformational changes resulting from substitution, and the resultant extranuclear hyperfine splittings.

The coumarins form a group of natural products of considerable importance, being widely distributed throughout the plant kingdom.[1] Much of the interest in the chemistry of this group has arisen from their physiological activity, which manifests itself particularly in the hydroxylated derivatives.

One of the most valuable methods of structure determination for coumarins[1] is furnished by the alkaline degradation reaction, which invariably involves opening of the pyrone ring. In the course of our work on oxidation processes of some groups of natural products, we have studied the autoxidation, in alkaline solution, of coumarins containing hydroxyl groups in the aromatic ring. Under our conditions oxidation accompanies the alkaline degradation, and the intermediate semiquinone anion radicals involved in the combined process are conveniently studied by ESR spectroscopy.[2] We report here the useful relationships between the structures of the initial coumarins and the information gained from an ESR study of the radicals formed during these autoxidation reactions.

Experimental Section

Materials. Caffeic acid (3,4-dihydroxycinnamic acid), chlorogenic acid [3-(3,4-dihydroxycinnamoyl)quinic acid], 7-hydroxycoumarin, 7-hydroxy-4-methylcoumarin, esculetin (6,7-dihydroxycoumarin),

4-methylesculetin, and 4-methyldaphnetin (7,8-dihydroxy-4-methylcoumarin) were purchased from Ralph N. Emanuel Ltd., Wembley, England.

6-Hydroxycoumarin-3-carboxylic acid was prepared from 2,5-dihydroxybenzaldehyde and malonic ester by means of the Knoevenagel reaction.[3] Decarboxylation of this compound yielded 6-hydroxycoumarin.

6-Hydroxy-3-methylcoumarin and 7-hydroxy-3-methylcoumarin were prepared by means of the Perkin reaction, condensing the appropriate dihydroxybenzaldehyde with a mixture of propionic anhydride and sodium propionate.[4] 6-Hydroxy-3-phenylcoumarin was prepared in a similar manner employing acetic anhydride and sodium phenylacetate.[5]

6-Hydroxy-4-methylcoumarin and 6-hydroxy-3,4-dimethylcoumarin were synthesized by means of the Kostanecki–Robinson reaction, condensing 2,5-dihydroxyacetophenone with acetic anhydride–sodium acetate and propionic anhydride–sodium propionate, respectively.[6]

6-Hydroxy-4-phenylcoumarin was prepared in a similar manner from 2,5-dihydroxybenzophenone. The latter was prepared from hydroquinone dimethyl ether according to the method of Bogert and Howells,[7] but with some modification during the last stage of the synthesis. The demethylation of 2-hydroxy-5-methoxybenzophenone, carried out strictly according to the procedure of these workers, proved unsuccessful. However, the demethylation process could be carried out by the following method.

The monomethyl ether (10 g) was refluxed for 3 h with 50 ml of hydriodic acid (sp gr 1.70) and 20 ml of acetic anhydride, the mixture poured into cold water, and the yellow product crystallized from benzene (yield 81%, mp 124–125°C).

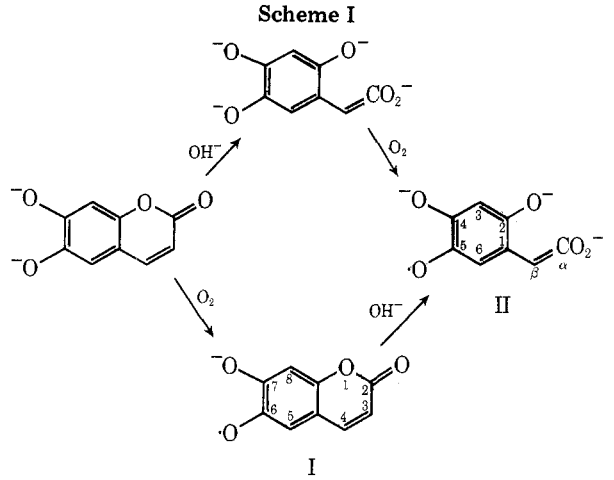
Autoxidations and ESR Spectra. Autoxidation of the coumarins was carried out by addition of sodium hydroxide solution to a solution of the coumarin (0.02 M in 50% aqueous ethanol), and shaking the mixture in air. This was then transferred to an aqueous cell in the cavity of a Varian E-3 instrument and the spectrum recorded. In general the observation of secondary radicals was favored by high pH and longer exposure to the air.

The 7-hydroxycoumarins were autoxidized under the same conditions, but with the additional presence of 0.5 M hydrogen peroxide.

Results and Discussion

Structure and Formation of Anion Radicals. Coumarins containing two ortho hydroxyl groups in the aromatic ring appear to behave like substituted catechols,[8] and are autoxidized in mildly alkaline solution to give well-resolved ESR spectra corresponding to the *o*-semiquinone anions. Esculetin, for example, in dilute alkaline solution, gives rise initially to an ESR spectrum ascribed to radical I (Scheme I and Figure 1). This spectrum, however, slowly decays and is replaced by that due to radical II, formed by opening of the pyrone ring under the alkaline conditions employed. This latter spectrum is observed immediately if strong alkali (5% NaOH) is employed in the autoxidation mixture. An identical spectrum with that of radical II is observed on autoxidation of caffeic acid (3,4-dihydroxycinnamic acid) under the same strongly alkaline conditions, a secondary radical of the type observed by Stone and Waters[8] in their study of substituted catechol semiquinones. A primary oxidation product of caffeic acid can be observed on autoxidation in mildly alkaline solution (see Table I).

Scheme I



I II

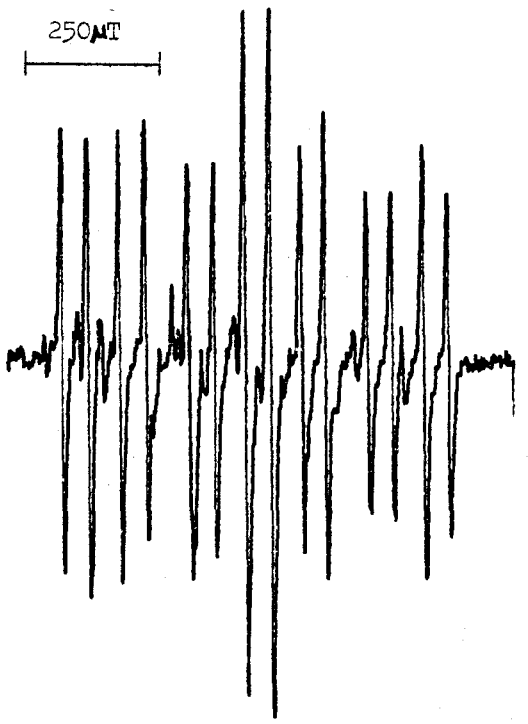
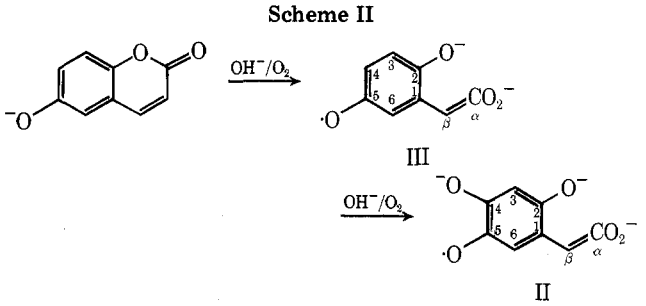


Figure 1. ESR spectrum of the primary radical (I) from esculetin (6,7-dihydroxycoumarin).

In the case of 6-hydroxycoumarins, semiquinone radical formation occurs only as a result of pyrone ring opening (Scheme II), giving spectra with hyperfine splittings highly characteristic of para semiquinones (see Table I).[9] On more prolonged autoxidation in strongly alkaline solution, hydroxylation leads to the observation of secondary species,[9] the semiquinones of trihydroxycinnamic acids, and identical with the species formed by ring opening of the esculetins.

Scheme II



The 7-hydroxycoumarins form resorcinol derivatives in alkaline media,[1b] leading to no stable radical anions. However, in the presence of hydrogen peroxide, hydroxylation of the resorcinol can occur,[10] to again give the trihydroxycinnamic acid semiquinones (Scheme III). The latter are thus definitely

Scheme III

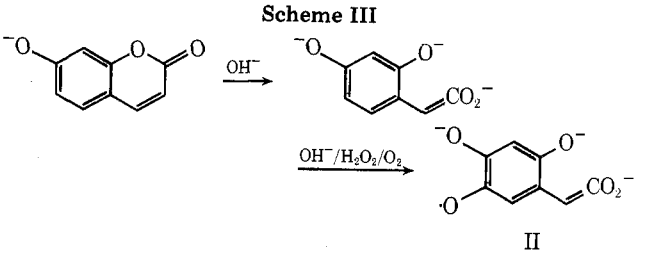


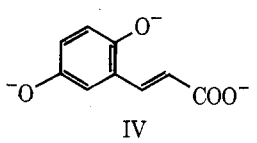
Table I. Radicals Observed during the Autoxidation of Hydroxycoumarins, with Their Hyperfine Splitting Constants

Registry no.	Radical anion	Hyperfine splittings, μT[a]					
		Pyrone ring		Aromatic ring			
		a_3	a_4	a_5	a_6	a_7	a_8
305-01-1	6,7-Di-OH-coumarin	338	106	234			47
529-84-0	6,7-Di-OH-4-Me-coumarin	278	58 (Me)	220			45
2107-77-9	7,8-Di-OH-4-Me-coumarin	152	33 (Me)	308	51		
		Side chain		Aromatic ring			
		a_α	a_β	a_2	a_3	a_4	a_5	a_6
636-01-1	2,5-Di-OH-cinnamic acid	85	170		240	213		213
59433-76-0	α-Me-2,5-di-OH-cinnamic acid	100 (Me)	153		236	230		180
57707-19-4	β-Me-2,5-di-OH-cinnamic acid	14	0 (Me)		254	222		184
59433-77-1	α-Ph-2,5-di-OH-cinnamic acid	70 (Ph)[b]	136		250	214		191
59433-78-2	β-Ph-2,5-di-OH-cinnamic acid	9	0 (Ph)		258	216		204
56437-15-1	2,4,5-Tri-OH-cinnamic acid	175	283		44			132
59433-79-3	α-Me-2,4,5-tri-OH-cinnamic acid	259 (Me)	320		47			69
59433-80-6	β-Me-2,4,5-tri-OH-cinnamic acid	24	0 (Me)		47			96
59433-81-7	α,β-DiMe-2,4,5-tri-OH-cinnamic acid	58 (Me)	0 (Me)		50			96
59433-82-8	α-Ph-2,4,5-tri-OH-cinnamic acid	177 (Ph)[b]	294		44			95
59433-83-9	β-Ph-2,4,5-tri-OH-cinnamic acid	19	0 (Ph)		45			113
59433-84-0	α-CO_2H-2,4,5-tri-OH-cinnamic acid		250		40			125
59433-85-1	α-CO_2H-2,3,5-tri-OH-cinnamic acid		67			67		501
59433-86-2	α,β-Di-Me-2,3,5-tri-OH-cinnamic acid	10 (Me)	0 (Me)			62		422
57707-18-3	β-Me-2,3,4-tri-OH-cinnamic acid	6	0 (Me)				83	540
331-39-5	3,4-Di-OH-cinnamic acid	130	236	23			119	282
59434-09-2	3,4-Di-OH-cinnamoylquinic acid	120	240	63			120	260

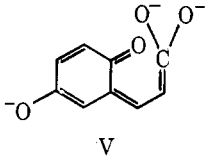
[a] Numbering systems for radicals as given in the text. [b] Total splitting from phenyl group.

characterized by their formation from a variety of different starting materials.

In view of obtaining identical ESR spectra from autoxidation of the *trans*-cinnamic acid derivative, caffeic acid, and from ring opening of coumarins, it appears that the radicals we observe in both cases have adopted the more stable trans configuration with respect to the side chain double bond. In fact, there is good evidence for suggesting that during the oxidative degradation of coumarins, semiquinones with the cis configuration are either not formed at all to any appreciable extent, or are not sufficiently long lived for observation. For example, while the trans forms of *o*-hydroxycinnamic acid anions appear to contain a truly aromatic ring (IV), the corresponding cis forms are best represented by *o*-quinonoid structures such as V.[1b]



IV

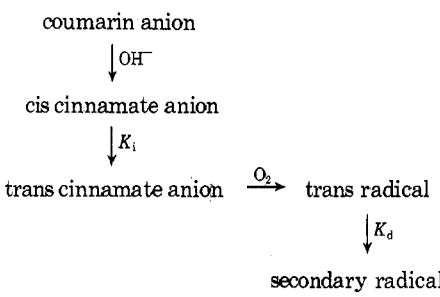


V

In this case, while the trans forms are readily autoxidized in the ring to give long-lived semiquinone radical anions, the cis forms are expected to be more resistant to the oxidation process, which may not occur to any appreciable extent under such relatively mild oxidizing conditions. A number of such cases of resistance to autoxidation have been found where the aromaticity of the quinol anion is disturbed by substituents.[11] In any event, the shorter lifetimes of radical anions from cis forms such as V, if produced at all, would probably preclude their observation in the presence of more stable semiquinones.

In support of these ideas is the difficulty we have experienced in obtaining spectra of primary radicals (Scheme II) from 6-hydroxycoumarins containing substituents in the 3 position, where cis to trans isomerizations are known to be relatively slow under our conditions.[1b] No sign of primary radicals was observed in two of these cases, from the 3-carboxyl and 3,4-dimethyl derivatives. If our premise that we observe only trans forms is correct, then the chances of observing the primary species will decrease with the decreasing rate of cis to trans isomerization of the anion precursor. When

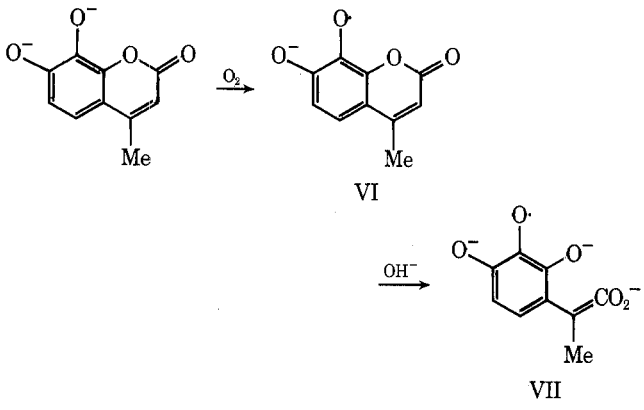
Scheme IV



the isomerization rate is very slow relative to the rate at which primary radicals are destroyed, by further oxidation to secondary species via the quinone[9] (i.e., $k_i \ll k_d$), then the concentration of primary radicals may be sufficiently low to preclude observation. In such cases only secondary species will be observed, as we have found for the 3-carboxyl and 3,4-dimethyl derivatives. These observations could not be readily explained if we made the assumption that the radicals we observe during coumarin autoxidation were of the cis form.

In addition to not observing primary radicals from the 3-carboxyl- and 3,4-dimethyl-6-hydroxycoumarins, these are the only cases where a mixture of isomeric secondary species is obtained. These isomeric mixtures are a feature of the ESR spectra observed during autoxidation of alkyl-[9] and phenylquinols,[12] but the factors influencing the relative concentrations of each isomeric radical are not fully understood.

The autoxidation of 4-methyldaphnetin (7,8-dihydroxy-4-methylcoumarin) is readily understood in terms of formation of the primary catechol semiquinone (VI), and secondary formation of the ring-opened radical (VII), with hyperfine splittings highly characteristic of a pyrogallol semiquinone.[8]



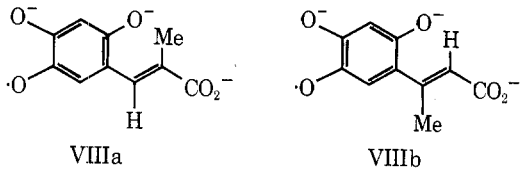
VI

VII

Hyperfine Splittings and Conformation. Little difficulty is encountered in identifying the radical intermediates from their ESR spectra and from a knowledge of the initial coumarin. The semiquinone ring splittings are unambiguously determined in the spectra of radicals containing a fully methylated extranuclear fragment (see Table I), and are found to be close to the corresponding splittings in unsubstituted semiquinones.[9] This relatively small effect of the side chain in the cinnamic acid semiquinones is comparable to that of a phenyl[12] or alkyl[9,13] group, as might be expected since the same types of mild interaction with the semiquinone nucleus will be involved. The aromatic ring proton splittings are also rather insensitive to the nature of substitution in the side chain (α or β substitution of protons by Me or Ph, see Table I), being chiefly dictated by the particular hydroxylation pattern of the ring.

For the semiquinones with an intact coumarin ring, the effect of the –OCO– grouping appears to be small with respect to the aromatic ring splittings. These radicals are all ortho semiquinones, the hyperfine splittings of which are in general fairly insensitive toward substitution in the nucleus.[8,14] As a result of these small substituent effects in both the open and closed ring radicals, the aromatic proton splittings are readily identified with particular hydroxylation patterns for the aromatic ring (see Table I). This information, together with the observed conditions of radical generation, could be of some value in the analysis of coumarins with indefinite structures.

The spin density distribution in the remaining extranuclear fragment of each radical is, on the other hand, highly dependent on whether or not the pyrone ring is open, and on any substitution of the proton at C_β or C_4 (see Table I). The effect of such substitution at C_β by a methyl group, for example, is very striking indeed, compared to the relatively small effect of a methyl group at the α position. This is illustrated in Figure 2, which shows the ESR spectra of the isomeric secondary radicals VIIIa and VIIIb. With β-methyl substitution (VIIIb),



VIIIa VIIIb

spin density is effectively cut off from the side chain protons, suggesting that conformational changes with respect to the bond joining this fragment and the aromatic ring are responsible for the widely different spectra.

To examine the situation more closely, we can make use of a relatively simple qualitative model, to reflect the effects of such conformational changes on the delocalization of spin density from the semiquinone nucleus into the remaining fragment. Turning our attention first to the cinnamic acid semiquinones, since the side chain has little influence on spin

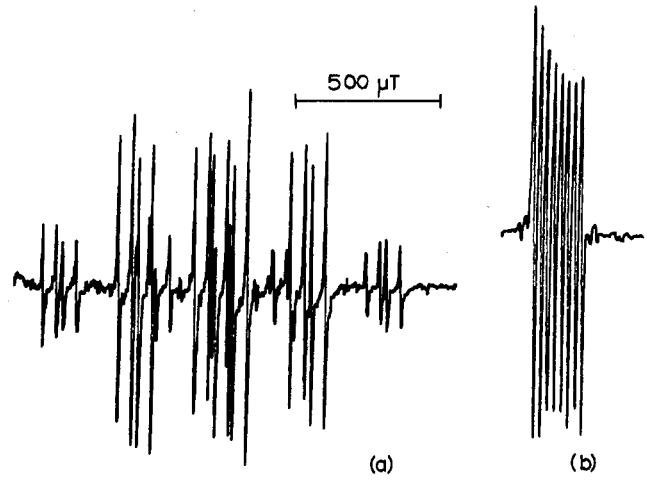


Figure 2. ESR spectra of the isomeric secondary radicals VIIIa and VIIIb from (a) 6-hydroxy-3-methylcoumarin and (b) 6-hydroxy-4-methylcoumarin.

densities in the aromatic ring, it may be treated, to a good approximation, simply as a substituent drawing spin density from the $p\pi$ orbital of the aromatic ring carbon to which it is attached. In this respect, the model is no different from that used to examine hyperconjugation in alkyl semiquinones,[15] or π–σ delocalization in aryl semiquinones.[16] In support of such a model is the observation that for a series of cinnamic acid semiquinones containing the same side chain but different aromatic ring hydroxylation patterns, the splittings from α and β protons are roughly proportional to the expected spin densities at the aromatic ring carbon, i.e., those found for corresponding ring positions in unsubstituted semiquinones.[9] Similar relationships have been found for alkyl[9] and aryl[16] splittings in a series of differently hydroxylated semiquinone anions.

For closed ring radicals, the model remains the same, since the –OCO– grouping should form an effective barrier to any spin transfer from its neighboring aromatic ring carbon. The problem is thus reduced to that of an "allylic fragment", made up of the nuclear ring carbon atom C_r, and the extranuclear carbons, C_α and C_β (Figure 3a). The extranuclear hyperfine splittings then arise by delocalization of spin density from the $p\pi$ orbital of C_r, and we can envisage two extreme mechanisms by which this delocalization can occur.

The mechanism of $p\pi$–$p\pi$ overlap (Figure 3b) will clearly lead to effective delocalization for a planar allylic system, but the resultant spin densities at C_α and C_β follow a $\cos^2\theta$ relation as the system leaves planarity (where θ is the dihedral angle between $p\pi$ orbitals on C_r and C_β). Near-planar allyl radicals[17] reflect the $p\pi$–$p\pi$ overlap mechanism, in agreement with MO theory, which predicts high positive spin density at C_α and a small negative value at C_β. Protons and alkyl groups at C_α and C_β, in this case, show splittings characteristic of π radicals (e.g., $a^H \sim a^{Me}$).[17]

The second mechanism is that of hyperconjugation or π–σ delocalization, whereby spin is transmitted by overlap of the $p\pi$ orbital of C_r with σ orbitals of the carbon framework.[16,18,19] The effectiveness of this spin transfer mechanism varies with $\sin^2\theta$, being most important in a perpendicular allylic system. The ESR spectrum of a near-perpendicular allyl radical has recently been observed,[20] confirming the view that hyperconjugation in these systems is very important for spin transfer to an atom directly bonded to C_β (Figure 3c), but falls off rapidly with distance from the radical center (C_r). With regard to the radicals under discussion in this paper, we can expect a strong hyperconjugative interaction, leading to positive spin density on a vinylic β proton, as the dihedral

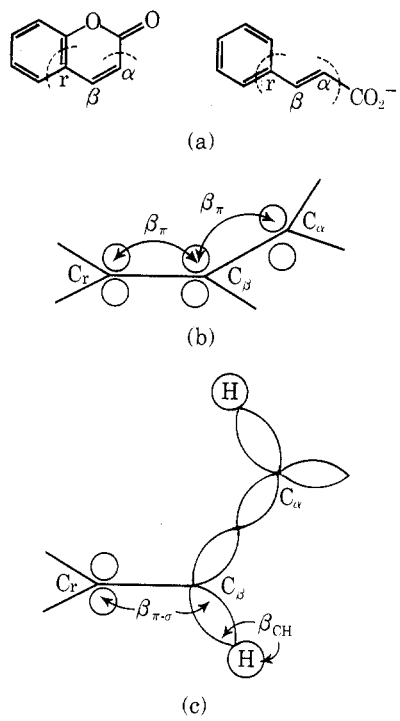


Figure 3. Mechanism of spin delocalization: (a) "allylic fragment" for closed ring and side chain; (b) π–π delocalization (θ = 0°); (c) σ orbitals of allylic fragment at θ = 90° showing effective π–σ overlap for a vinylic β proton.

angle approaches 90°, but much less significant interactions involving methyl and α protons.

In the model just described, we have rather artificially separated the total spin delocalization into that arising by two extremes of mechanism. However, the model is rather useful for gaining a qualitative picture of the dependence of extranuclear hyperfine splittings on the dihedral angle (i.e., conformational changes at the C_r–C_β bond).

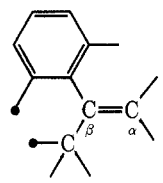
For any extranuclear hyperfine splitting, we can write

$$a^H = a^H{}_{\pi-\pi} + a^H{}_{\pi-\sigma} = a^H{}_{\pi-\pi(0°)} \cos^2\theta + a^H{}_{\pi-\sigma(90°)} \sin^2\theta$$

With this relationship in mind, it is instructive to examine certain trends in these hyperfine splittings with ring opening, and with substitution in the side chain or pyrone ring. For example, an examination of the extranuclear proton splittings in the closed ring radicals from 6,7-dihydroxycoumarins shows that the effect of introducing a 4-methyl group (β position) on the value of $a^H{}_3$ is small, and that $a^H{}_3(\alpha) > a^H{}_4(\beta)$. Clearly, in this case, the pyrone ring is held in a near-planar conformation wtth effective π–π delocalization, leading to large α splittings. However, when the constraints on planarity are removed by ring opening, we find $a^H{}_\beta > a^H{}_\alpha$, and the effect of a β-methyl group now is to reduce splittings drastically. We would expect some increase in the value of the dihedral angle θ on ring opening, and the observed splitting trends are consistent with a decrease in π–π overlap and an increase in the hyperconjugative interaction involving the β proton. The effect of a β-methyl group, as might be expected on steric grounds, is to further increase θ to a value approaching 90°.

The lack of splitting from the β-methyl protons is probably a fortuitous cancelling of small contributions from π–π spin (−Ve) and π–σ spin (+Ve), indicating that despite a favorable conformation for the latter mechanism, the separation of methyl protons from the radical center renders the contribution small compared to that for a vinylic β proton. Comparison of splittings from α protons and α-methyl protons, on the other hand, shows that they have comparable values in otherwise equivalent radicals. This is indicative of their major contribution coming from the π–π delocalization mechanism.

The presence of a methyl, phenyl, or carboxyl group at C_α has apparently little effect on the dihedral angle θ, suggesting that the only steric interactions responsible for the observed conformational effects are between the aromatic ring and the other group on C_β. The magnitude of the steric interactions



involved with the introduction of a β-methyl or β-phenyl group need not necessarily be very large to bring about a significant change in θ. A loss of stabilization by π–π delocalization of spin with increasing dihedral angle is expected to be somewhat compensated for by the increased hyperconjugation. The C_r–C_β bond will, of course, be subject to torsional vibrations, particularly in the open ring radicals, the average value of $\cos^2\theta$ determining the hyperfine splittings.

In conclusion, it may be stated that the ESR investigation of semiquinone intermediates formed during the alkaline autoxidation of hydroxylated coumarins can lead to structural, conformational, and mechanistic information. The cinnamic acid and coumarin semiquinones provide a particularly lucid example of how ESR hyperfine splitting data can be related, by simple qualitative theory, to conformational changes affecting the delocalization of spin.

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