The Electron Spin Resonance Spectra of Alkyl Aryl Ether Radical Cations

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Radical cations of alkyl aryl ethers may be generated in a flow system by means of oxidation of the ethers by cerium(IV) in concentrated sulphuric acid solution. The spin distributions and *g* values are similar to those in corresponding phenol radical cations. The 1,3-benzodioxoles give rise to particularly intense spectra which characteristically have triplet splittings close to 2.0 mT, which can be explained in terms of the molecular orbital theory of hyperconjugation. The relatively marked stability of the cations from the 1,3-benzodioxoles made it possible to obtain intelligible data from some complex natural products containing this group. Evidence from the spectra for various types of conformational isomerism is discussed.

RADICAL CATIONS of *p*-dialkoxybenzenes have been studied extensively by e.s.r. spectroscopy in non-aqueous solvents.[1,2] They may be prepared in the same way as the corresponding cations of *p*-hydroquinone [3-6] derivatives, by mild oxidation of the parent molecules in a static system.

By analogy with the relationship between phenoxyl and the *p*-benzosemiquinone anion radical [7,8] it is to be expected that most aromatic ether radical cations would be short-lived and this would explain the comparative rarity of e.s.r. data of this class of compounds in the literature.

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[1] W. F. Forbes, P. D. Sullivan, and H. M. Wang, *Canad. J. Chem.*, 1966, **44**, 1501.
[2] P. D. Sullivan, *J. Phys. Chem.*, 1970, **74**, 2563.
[3] I. C. P. Smith and A. Carrington, *Mol. Phys.*, 1967, **12**, 439.
[4] W. F. Forbes, P. D. Sullivan, and H. M. Wang, *Canad. J. Chem.*, 1967, **45**, 267.
[5] P. D. Sullivan and J. R. Bolton, *J. Amer. Chem. Soc.*, 1968, **90**, 5366.
[6] P. D. Sullivan, *J. Phys. Chem.*, 1971, **75**, 2195.
[7] T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 1964, 213.
[8] W. T. Dixon, M. Moghimi, and D. Murphy, *J.C.S. Faraday II*, 1974, **70**, 1713.

However, we have been able, in certain cases, to observe fully protonated phenoxyl radicals [9,10] (phenol radical cations) in strong sulphuric acid solution by means of cerium(IV) oxidation in a flow system. It was, therefore, not too surprising when the same technique was found to be adequate for generating aromatic ether radical cations in sufficient concentrations for the observation of their e.s.r. spectra.

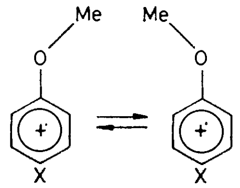
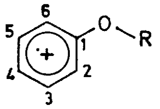


TABLE 1
E.s.r. parameters for benzene radical cation derivatives
(signs of spin densities in brackets)



	Coupling constants (mT = ±0.005 mT)						g Values
Substituents	a_1	a_2	a_3	a_4	a_5	a_6	±0.000 05
1-OMe *	a_{OMe} = 0.50	0.44	0.02	1.06	(−) 0.11	0.55	2.003 2
1-OCH_2Me *	a_{OCH_2} = 0.50	0.43	0.03	1.05	(−) 0.10	0.54	2.003 3
1-OMe,4-Me *	a_{OMe} = 0.43	0.35	0.02	a_{Me} = 1.525	(−) 0.08	0.43	2.003 2
1-OMe,4-F †	a_{OMe} = 0.45	0.45	0.0	a_F = 3.175	0.0	0.45	2.003 85
1-OMe,4-OH *	a_{OMe} = 0.32	0.22	0.19		0.19	0.30	2.003 6
1,4-$(OMe_3)_2$ * (*cis*)	a_{OMe} = 0.33	0.27	0.27	a_{OMe} = 0.33	0.18	0.18	2.003 7
(*trans*)	a_{OMe} = 0.35	0.15	0.30	a_{OMe} = 0.35	0.15	0.30	2.003 7
1,3-$(OMe)_2$	a_{OMe} = 0.30	0.0	a_{OMe} = 0.30	1.075	(−) 0.21	1.075	2.003 3
(A) 1,2-$(OMe)_2$	a_{OMe} = 0.325	a_{OMe} ± 0.325	0.0	0.49	0.49	0.0	2.003 4
1,2,3-$(OMe)_3$	a_{OMe} = 0.205	a_{OMe} = 0.525	a_{OMe} = 0.205	(−) 0.045	0.625	(−) 0.045	2.003 8
(B) 1,2(OCH_3CH_2O)	a_{OCH_2} = 0.25	a_{OCH_2} = 0.25	(−) 0.04	0.465	0.465	(−) 0.04	2.003 4

* Assignments according to the system used in ref. 2. † Very poor spectrum, but large doublet splitting and g value clearly seen.

TABLE 2
g Values of radicals $(C_6H_{6-n}X_n)^+$

	1-X	1,2-X_2	1,3-X_2	1,4-X_2	1,2,3-X_3
X = O^-	2.004 6	2.004 45	2.003 9	2.004 55	2.004 4
X = OH	2.002 9	2.003 55	2.003 1	2.003 5	2.003 9
X = OMe	2.003 2	2.003 4	2.003 3	2.003 7	2.003 8

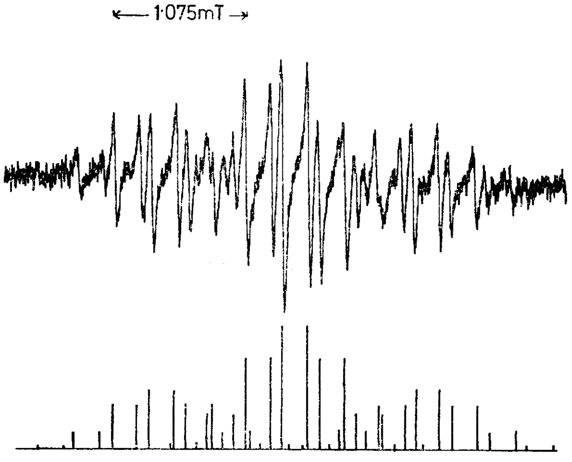


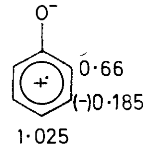
FIGURE 1 Spectrum from 1,3-dimethoxybenzene

Radical Cations of Derivatives of Methoxybenzene.— Many of the spectra we obtained from anisole derivatives were badly resolved due to a poor signal : noise ratio. Further difficulties in analysis arose from complications arising from the type of isomerism investigated by Sullivan *et al.*[2,6]

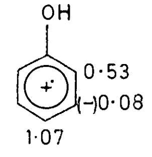
Nevertheless in some cases clear spectra were obtained (see Figure 1) and the results are given in Table 1.

Two major points arise from this set of e.s.r. parameters.

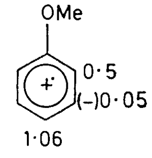
First, the spin distributions (averaged over the conformations of the OMe groups) are similar to those in radicals in which the OMe groups are replaced by OH and also to those in the corresponding radicals where OMe is replaced by Ō. The odd electron density on the ring is usually a little smaller than in the latter case.



phenyoxyl [8]



phenol cation [10]



anisole cation
(averaged)

Secondly, the g values of these radicals are similar to those of corresponding phenol cations and much nearer to the free-spin value (see Table 2) than is the case with corresponding phenoxyl radicals.

The radical cation (B) from 1,4-benzodioxan gave a particularly interesting e.s.r. spectrum (see Figure 2)

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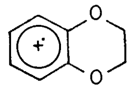
[9] W. T. Dixon and D. Murphy, *J.C.S. Faraday II*, 1976, 135.
[10] W. T. Dixon and D. Murphy, *J.C.S. Faraday II*, 1976, 1221.

which showed the alternating line widths often observed in the e.s.r. spectra of radicals containing aliphatic six-membered rings,[11,12] arising from intermediate rates of exchange between equivalent conformations.


(B)

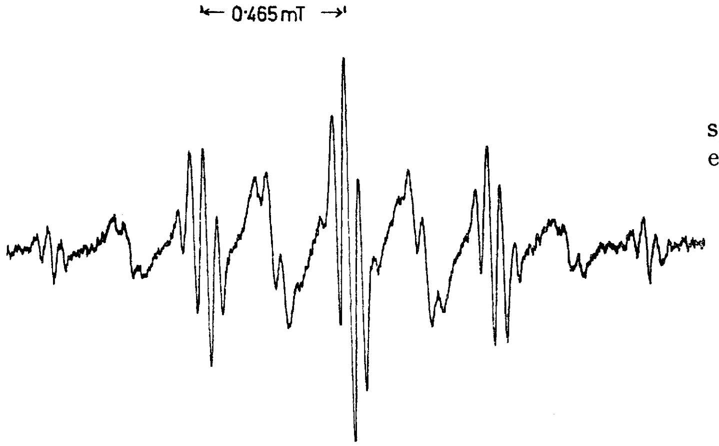
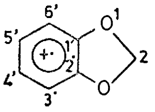


FIGURE 2 Spectrum from 1,4-benzodioxan

TABLE 3

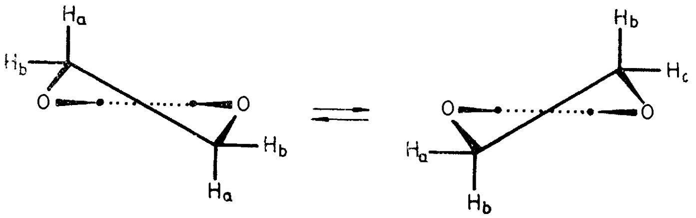
E.s.r parameters (a/mT) for radicals obtained from the oxidation of substituted 1,3-benzodioxoles by Ce^{IV} in $H_2SO_4,4H_2O$



	Substituents	a_2	a_3'	a_4'	a_5'	a_6'	g Value
(C)		2.19 (2)	(−) 0.04	0.49	0.49	(−) 0.04	2.0039
	4'-CHO	2.28 (2)	0.025		0.405	0.0	2.004 35
	4'-CO_2H	2.325 (2)	0.04		0.425	0.0	2.004 15
	4'-CN	2.42 (2)	0.0	a_N = 0.0	0.40	0.0	2.004 05
(F)	4'-Me	1.94 (2)	(−) 0.075	a_{Me} = 0.795	0.515	(−) 0.025	2.0038
(G)	4'-CH_2CO_2H	2.04 (2)	(−) 0.06	a_{CH_2} = 0.465	0.49	(−) 0.025	2.0039
	4'-OMe	1.445 (2)	(−) 0.045	a_{OMe} = 0.265	0.625	(−) 0.045	2.0040
	4'-OH	1.35	0.0		0.625	(−) 0.04	2.003 95
(D)	4'-O^- *	0.65 (2)	0.195		0.795	(−) 0.11	2.0043
	4'-CH=$CHCO_2H$	1.85 (2)	(−) 0.11	$a_{\beta CH}$ = 0.40	0.40	(−) 0.04	2.0038
				$a_{\beta CH}$ = 0.19			
	4'-$(CH_2)_2CO_2H$	2.025 (2)	(−) 0.07	a_{CH_2} = 0.675	0.51	(−) 0.025	2.0038
	4'-CH_2CH=CH_2	1.99 (2)	(−) 0.075	a_{CH_2} = 0.725	0.525	(−) 0.025	2.0038
(E)	4'-CH_2OH *	2.00	(−) 0.075	a_{CH_2} = 1.05	0.50	(−) 0.025	2.0038
	4'-CH_2Cl,5'-Cl	1.95 (2)	(−) 0.075	a_{CH_2} = 0.89	a_{Cl} = 0.125	(−) 0.025	2.004 95
	3'-Me	2.14 (2)	a_{Me} = 0.04	0.42	0.53	(−) 0.06	2.0039
	3'-$CH(Me_2)_2$	2.145 (2)	a_{CH} = 0.0	0.415	0.52	(−) 0.06	2.0039
	3'-OMe	1.925 (2)	a_{OMe} = 0.15	0.085	0.605	(−) 0.085	2.0040
(H)	3'-OMe,5-$CH_2CH(Me)\overset{+}{N}H_3$	1.85 (2)	a_{OMe} = 0.15	0.08	a_{CH} = 0.56, 0.49	(−) 0.03	2.0040

* Oxidation by Ce^{IV} in 0.5 mol dm^{-3} H_2SO_4.

Radical Cations from 1,3-*Benzodioxoles*.—The radical cations of 1,3-benzodioxoles form a class which is distinct from those of the other aromatic ethers investigated. The e.s.r. spectra are naturally very much simplified by the small number of aliphatic protons interacting with the odd electron. However, even allowing for this, the spectra are remarkably intense (see Figure 3) indicating either high stability or greater ease of formation of the radical cations, or both. A remarkable feature of the e.s.r. spectra of these radical cations was the large splitting arising from the methylene protons (see Table 3).



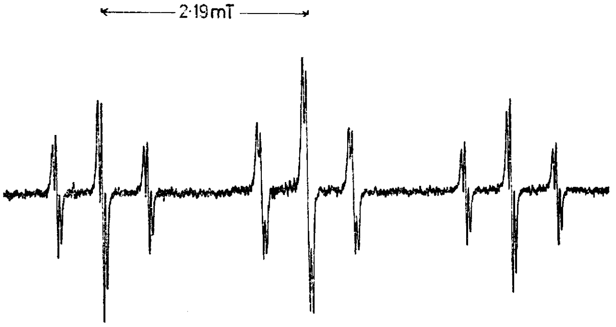


FIGURE 3 Spectrum from 1,3-benzodioxole

A less spectactular property of these radicals is that their g values are somewhat higher than those of corresponding dimethoxybenzene radical cations (compare Tables 1 and 3).

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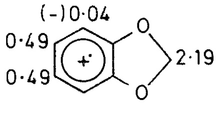
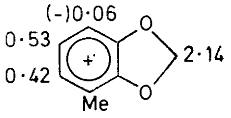
[11] W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 1964, 4850.

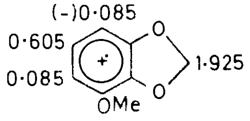
[12] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147.

Assignments of Coupling Constants.—The assignments of the larger ring-proton splittings could be made by comparison with those in corresponding phenoxyl or semiquinone anion radicals. The small splittings were assigned by means of graphical techniques[8] assuming that the splitting pattern varies smoothly with substitution. A good example is that of the 3′-substituted 1,3-benzodioxole radical cations where the trends of the coupling constants are particularly clear-cut.

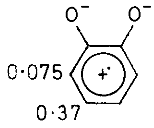
In the case of cinnamic acid derivatives, the coupling constants in the side-chain were assigned on the basis of previous work on radicals from hydroxycinnamic acids.[13]

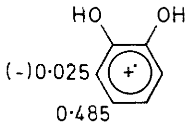


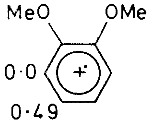




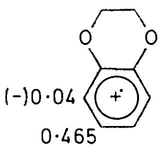
Hyperfine Splittings in Benzodioxole Radical Cations.—The large splittings of the protons of the methylene-dioxy-group in these radicals contrasts with the fact that the ring-proton coupling constants are similar to those in closely related radicals.







(A)



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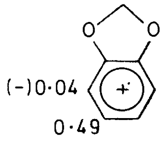
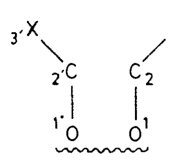


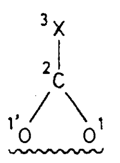
(C)

It therefore appears that the spin distributions in these radicals are all closely similar, implying that the spin density on the oxygen atoms is approximately the same along the series. This possibility can be used in the explanation of the large hyperfine splittings in radical (C).

MO Hyperconjugation Model.—The aliphatic proton splittings in radicals (A) and (C) both arise from hyperconjugation[2,14] and should be proportional to the spin densities on the adjacent oxygen atoms. However, it is necessary to consider the alkoxy fragments in more detail to see why the splittings in these two cases differ so much.



(A)



(C)

The odd electron goes into an orbital, in each case, which is not very different from a non-bonding orbital and which is symmetrical with respect to reflection through the symmetry plane mid-way between the two oxygen atoms. The relevant secular equations for calculating spin delocalisation due to hyperconjugation are, for (A) as follows:

$$\begin{cases}(2\alpha_c - 2E_0)C_2 + 2\beta_{12}C_1 + 2\beta_{23}C_3 = 0\\ 2\beta_{23}C_2 + (2\alpha_x - 2E_0)C_3 \qquad\qquad = 0\end{cases}$$

and for (C)

$$\begin{cases}(\alpha_c - E'_0)C_2 + 2\dot{\beta}_{12}C_1 + \beta_{23}C_3 = 0\\ \beta_{23}C_2 + (\alpha_x - E'_0)C_3 \qquad\qquad = 0\end{cases}$$

where α_c and α_x are the coulomb integrals of the carbon π-orbital and the hydrogen group orbital of π-symmetry, respectively; β_{12} and β_{23} are resonance integrals, and C the coefficients of the atomic orbitals. E_0 and E'_0 are the energies of the odd $\bar{e}$ orbitals in the two cases and we expect that $(E_0 - E'_0)$ is small. The spin density (ρ_x) in the hydrogen group orbital 'x' is then calculated to be

for (A) $\rho_x = C_3{}^2 =$

$$\beta_{12}{}^2\left[\beta_{23} - \frac{(\alpha_x - E_0)(\alpha_c - E_0)}{\beta_{23}}\right]^{-2} C_1{}^2 \approx \frac{\beta_{12}{}^2}{\beta_{23}{}^2}\rho_0$$

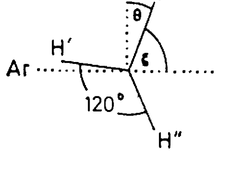
and for (C), $\rho_x = C_3{}^2 =$

$$4\beta_{12}{}^2\left[\beta_{23} - \frac{(\alpha_x - E_0')(\alpha_c - E_0)}{\beta_{23}}\right]^{-2} C_1{}^2 \approx \frac{4\beta_{12}{}^2}{\beta_{23}{}^2}\rho_0$$

where ρ_0 = spin density on the oxygen atom.

The splittings of the aliphatic protons will depend on the dihedral angles which in turn determine the nature of the hydrogen group orbitals ϕ_x; *i.e.* a combination of the hydrogen atomic orbitals, ϕ, ϕ' . . . , *etc.*

$$\begin{aligned}\sqrt{\tfrac{3}{2}}\,\phi_x &= \phi\sin\xi + \phi'\sin(120 + \xi) + \phi''\sin(240 + \xi)\\ &= \phi\cos\theta - \phi'\cos(60 + \theta) - \phi''\cos(60 - \theta)\end{aligned}$$



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[13] W. T. Dixon, M. Moghimi, and D. Murphy, *J.C.S. Perkin II*, 1975, 1189.

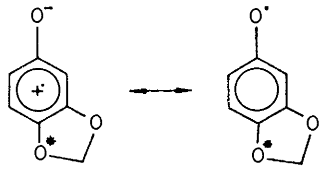
[14] A. Carrington and A. D. McLachlan, 'Introduction to Magnetic Resonance,' Harper and Row, London, 1967, p. 83; W. T. Dixon, 'Theory and Interpretation of Magnetic Resonance Spectra,' Plenum Press, London, 1972, ch. 6, p. 97.

The splittings in these two cases are

$a_A = \frac{1}{3}\rho_x \times 50.8$ mT (θ = 45°) *i.e.* rotational average
$a_O = \frac{1}{2}\rho_x \times 50.8$ mT (θ = 30°)

The expected ratio of the aliphatic coupling constants is therefore $\frac{a_A}{a_O} = \frac{\frac{1}{3}}{\frac{1}{2} \times 4} = \frac{1}{6}$. This agrees well with the observed ratio 3.25/21.9 = 1/6.7.

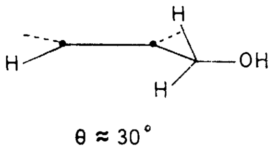
Another significant result is that for radical (D) from

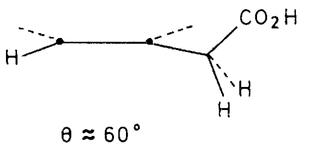


(D)

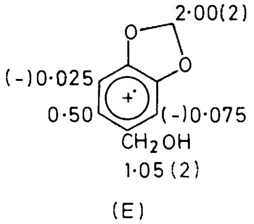
sesamol. In this case only the *para*-oxygen O* is expected to have a significant spin density. The methylene proton splitting is, therefore, correspondingly small (*i.e.* by a factor of *ca.* 4) compared with that in the parent 1,3-benzodioxole radical cation.

Steric Effects in the 1,3-*Benzodioxole Radical Cations*.—There are some rather clear-cut steric effects to be noted amongst these radicals. For example along the series (E)—(G) the aliphatic proton splittings indicate that in

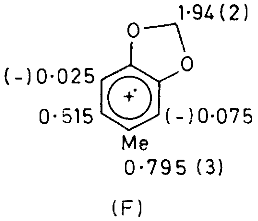




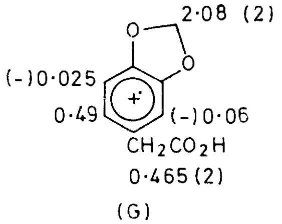
radical (G) the C–CO_2H bond is close to a plane perpendicular to the ring whereas in the radical (E) the CH_2–OH bond is near to the plane of the ring, on average.



(E)

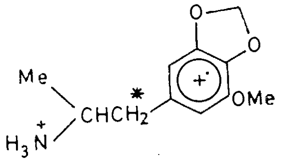


(F)



(G)

In the amphetamine derivative, radical (H), one would not expect a particularly large barrier to rotation about the $C{-}CH_2{}^*CH(CH_3)\overset{+}{N}H_3$ bond, so the non-equivalence of the two methylene protons H*, must be attributed to their being diastereotopic.[15]



(H)

Applications to Some Naturally Occurring Compounds.—The apparent stability of the cation radicals from benzodioxole derivatives enables us to observe radicals from naturally occurring compounds containing this grouping. With such materials as are relatively accessible (see below) we have found that oxidation under our conditions does lead to an e.s.r. spectrum dominated by the large triplet splitting of the methylene protons and centred, characteristically, at *g* = 2.004 0.

Although the spectra from these complex materials could not always be completely analysed because of several small splittings, the larger coupling constants could be measured and assigned consistently, according to the expected structure of the radicals and comparison with simple archetypes given in Table 3.

EXPERIMENTAL

E.s.r. spectra were obtained by flowing 10^{-2} mol dm^{-3} solutions or emulsions of the ethers in $H_2SO_4,4H_2O$ against 10^{-2} mol dm^{-3} cerium(IV) sulphate in $H_2SO_4,4H_2O$ in the flow systems described previously.[16] (Earlier work [10] had shown that when the solvent was $H_2SO_4,4H_2O$, resolution of the e.s.r spectra was optimum).

Most of the ethers were commercial materials; those which were not were prepared from the corresponding hydroxy-compounds by the methods given in references 17—19. All materials used were purified by the usual methods, and had physical constants which agreed well with those of the literature.

g Values were measured using Fremy's salt (*g* 2.005 5 [20]), itself standardised against the *p*-benzosemiquinone anion,[21] as an external standard. As the observed radical concentrations varied over a wide range (four orders of magnitude), an open-ended Pyrex ® capillary was placed through the cavity alongside the aqueous cell. By flowing Fremy's salt

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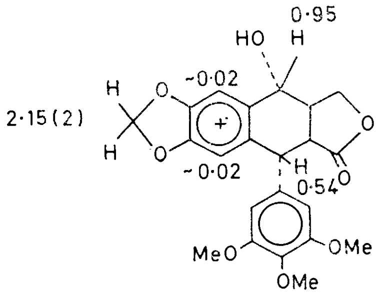
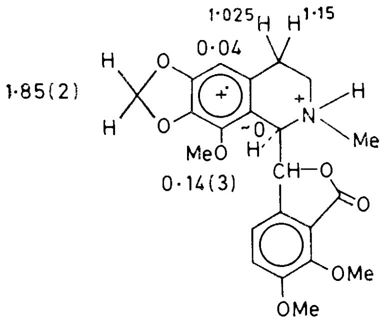
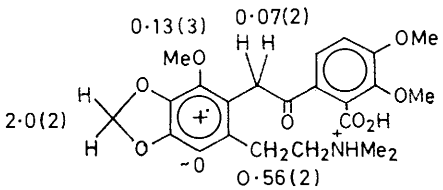


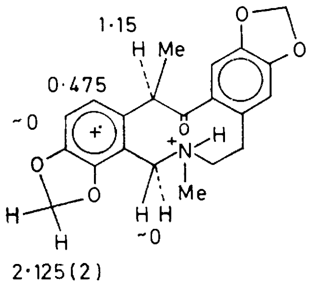
radical from podophyllotoxin



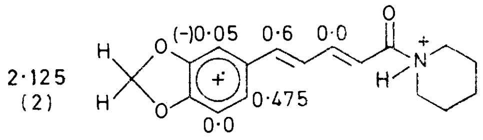
radical from narcotine



radical from narceine



radical from corycavine



radical from piperine

solutions of appropriate concentrations down through this capillary the standard signal could be adjusted to be commensurate with that from the radical being generated in the flow system.

Second-order effects were manifested in the broadening of the centre lines in the spectra of the 1,3-benzodioxole radical cations and in some cases the second-order splitting (*ca.* 0.01 mT) could just be resolved. Corresponding corrections to the *g*-values were not explicitly made since they were within the general experimental error.

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