

Figure 1. E.s.r. spectrum of pentadienyl radical (2a) at ambient temperature.

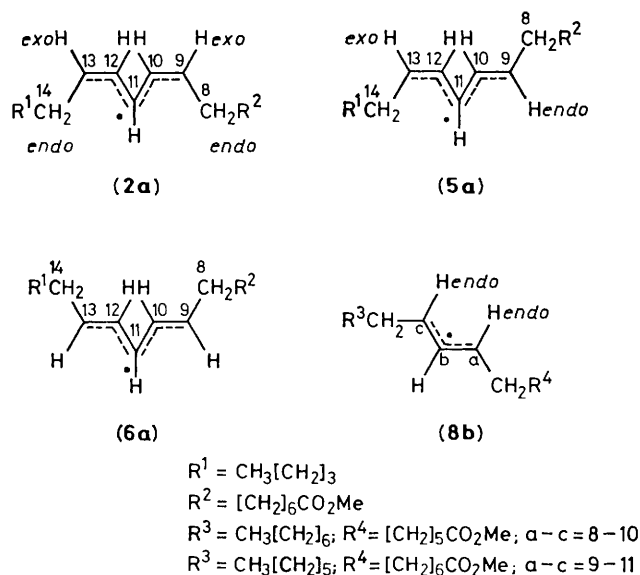


Table 1. E.s.r. parameters for pentadienyl and allyl radicals from olefinic lipids.

Radical	T/K	hfs ^a /mT
(2a)	290	H (10,12) 0.315
		CH ₂ (8,14 <i>endo</i>) 0.780
		H (9,13 <i>exo</i>) 0.980
(5a)	315	H (11) 1.110
		H (10,12) 0.315
		CH ₂ (<i>endo</i>) 0.780
		CH ₂ (<i>exo</i>) 0.900
		H (9 <i>endo</i>) 0.900
(6a)	310	H (13 <i>exo</i>) 0.980
		H (11) 1.110
		H (10,12) 0.315
		2CH ₂ (<i>exo</i>) 0.900
		H (9,13 <i>endo</i>) 0.900
(8b)	270	H(11) 1.110
		H (b) 0.37
		H (a,c <i>endo</i>) 1.29
		2CH ₂ (<i>exo</i>) 1.29

^a All hfs were checked by computer simulation of the spectra.

radicals which can be observed by e.s.r. spectroscopy.^{6,7} Attempts to observe the e.s.r. spectra of the radicals (2a) in a similar fashion were unsuccessful until material freshly purified from hydroperoxides and other trace impurities was used. The e.s.r. spectrum shown in Figure 1 was obtained by photolysis of a deoxygenated mixture of methyl linoleate and di-*t*-butyl peroxide at ambient temperature. The spectra could be obtained in hydrocarbon solutions, but were most intense in neat di-*t*-butyl peroxide. The spectrum was analysed (see Table 1) and the hyperfine splittings (hfs) were checked

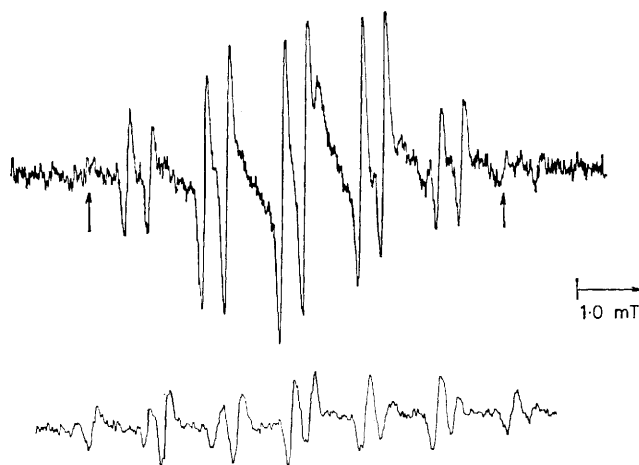
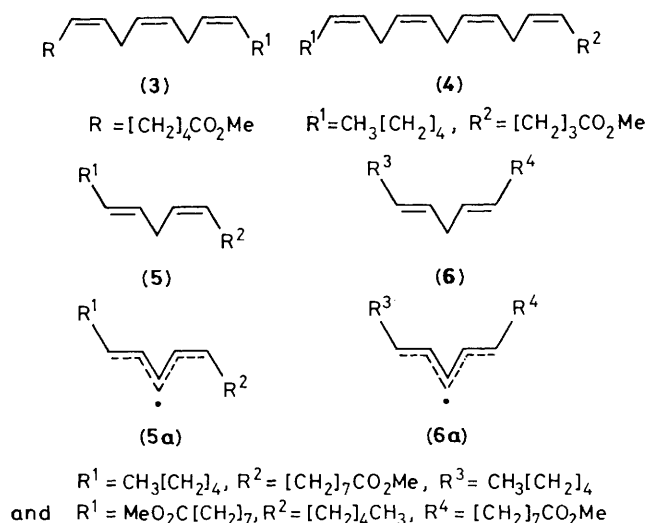
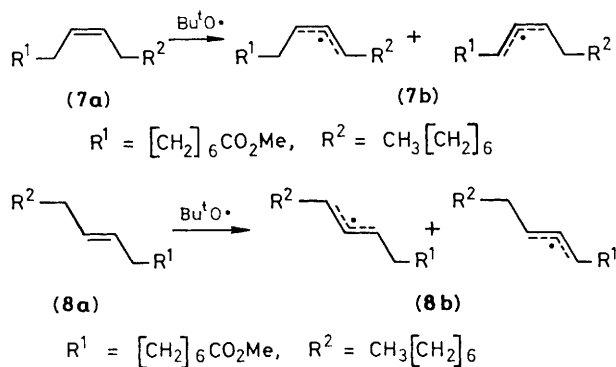


Figure 2. Top. E.s.r. spectrum of allyl radicals (8b) obtained on hydrogen abstraction from methyl elaidate, by $\text{Bu}^t\text{O}\cdot$ radicals. The arrows indicate signals arising from secondary alkyl radicals (see the text). Bottom. E.s.r. spectrum of allyl radicals obtained on hydrogen abstraction from 1-palmitoyl-2,3-dielaidoyl *rac*-glycerol, by $\text{Bu}^t\text{O}\cdot$ radicals.

by computer simulation of the spectrum. Comparison of the e.s.r. parameters with those of pentadienyl-^{6,7} and of alkyl-substituted pentadienyl radicals⁸ indicates that the spectrum is due to pentadienyl radicals (2a) and the hfs were unambiguously assigned to specific hydrogens (see Table 1). The observation of radical (2a) and the absence of any other radicals in the spectrum indicates that *t*-butoxyl radicals generated in the initial photolytic step mainly abstract hydrogen from the bisallylic position (C-11); abstraction from other sites must be 2–3 times slower. Pentadienyl radicals with the same e.s.r. parameters were observed on hydrogen abstraction from the hydrocarbon (1b). Hydrogen abstraction from the two bisallylic positions in methyl γ -linolenate (3) and the three bisallylic positions in methyl arachidonate (4) also gave rise to pentadienyl radicals which, as would be expected, were spectroscopically indistinguishable from each other and from (2a). *t*-Butoxyl radicals abstracted hydrogen from the *cis*, *trans*-mixture (5) and the *trans*, *trans*-ester (6) (stereoisomers of methyl linoleate) to give pentadienyl radicals which were distinct from each other and from (2a). The e.s.r. parameters and the assignments of the hfs to specific hydrogens, made by comparison with alkyl-substituted pentadienyls,⁸ are in Table 1. The internal consistency of the hfs between the three isomeric radicals provides confirmation of the assignments.



Photolysis of di-*t*-butyl peroxide solutions of methyl oleate (7a) and its *trans* isomer methyl elaidate (8a) gave rise to e.s.r. spectra which can be attributed to the allyl-type radicals (7b) and (8b) (Figure 2, upper spectrum), respectively. The hfs of the radical from (8a) are similar to those of allyl-^{9,10} and alkyl-substituted allyl radicals¹⁰⁻¹³ and the assignments of the hfs to specific hydrogens shown in the table were made by comparison with those model radicals. As would be expected the two radicals (8b) are spectroscopically indistinguishable. The spectra of (8b) were unchanged with time and temperature, but the spectrum from (7b) showed two overlapping sets of signals and changed during photolysis until it became identical with that from (8b). This prevented unambiguous assignment of the hfs for radical (7b). If the radicals are formed in the thermodynamically most stable conformations shown in (7b) and (8b), these results may imply that there is some interconversion of (7b) to (8b) at 330 K occurring directly or, possibly, *via* reversible addition of *t*-butoxy radicals to the double bond in (7a). Alternatively, radical (7b) preferentially abstracts hydrogen so as to give *trans*-olefins. This latter possibility seems unlikely.

In the spectra obtained with methyl oleate and elaidate weak signals can also be observed for some of the outer lines of the

secondary alkyl radicals obtained on hydrogen abstraction from the non-allylic methylene groups (see Figure 2); the inner lines are obscured by overlap with the main allyl radical.

E.s.r. spectra of allyl radicals derived from triacylglycerols can also be observed on photolysis of solutions containing di-*t*-butyl peroxide and a triacylglycerol with one or more oleate or elaidate units. For example the e.s.r. spectrum from 1-palmitoyl-2,3-dielaidoyl *rac*-glycerol is similar to that from methyl elaidate (Figure 2, bottom): the main radical is derived by hydrogen abstraction from one of the four allylic sites. The much larger triacylglycerol radicals tumble less efficiently and the line broadening evident in Figure 2 (lower spectrum) is probably due to incomplete averaging of the anisotropic dipolar coupling.

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