Allylic Hydroperoxides from the Autoxidation of Methyl Oleate

By ROBERT F. GARWOOD, BHUPINDER P. S. KHAMBAY, and BASIL C. L. WEEDON*
(*Department of Chemistry, Queen Mary College, Mile End Road, London* E1 4NS)
and EDWIN N. FRANKEL
(*Northern Regional Research Centre, Agricultural Research Service, U.S. Department of Agriculture, Peoria, Illinois* 61604)

Summary Methods have been developed, using ^{13}C n.m.r. and mass spectrometry, for the analysis of all eight *cis* and *trans* allylic 8-, 9-, 10-, and 11-hydroperoxides formed on autoxidation of methyl oleate.

DESPITE many investigations on the autoxidation of methyl oleate (**1**) and related compounds, uncertainty remains concerning the quantitative composition of the mixtures of allylic hydroperoxides which are formed as the first isolable products.[1,2] Studies with authentic samples of methyl 8-, 9-, 10- and 11-hydroxyoctadecanoates, and with *cis* and *trans* methyl 12-hydroxyoctadec-10-enoate (**6**), reveal that the methods used by other workers to analyse mixtures of hydroperoxides from unsaturated fatty acids, and their derivatives, may give rise to significant errors. These can be avoided by the procedures outlined below which were checked with known mixtures of the authentic compounds listed above.

cis
$Me[CH_2]_7CH{=}CH[CH_2]_7CO_2Me$
(**1**)

$Me[CH_2]_yCH{=}CHCH(OH)[CH_2]_xCO_2Me$
(**2**) $x = 6, y = 7$
(**3**) $x = 7, y = 6$

$Me[CH_2]_yCH(OH)CH{=}CH[CH_2]_xCO_2Me$
(**4**) $x = 6, y = 7$
(**5**) $x = 7, y = 6$
(**6**) $x = 8, y = 5$

Methyl oleate (10—30 g) was stirred under O_2 and the reaction monitored by determination of the peroxide value. The resulting hydroperoxides were concentrated by liquid–liquid partition (80% EtOH and light petroleum, b.p. 40—60 °C), followed by t.l.c. (silica gel; 25% ether in light petroleum, b.p. 60—80 °C), and reduced to the corresponding allylic alcohols (**2**—**5**) with $NaBH_4$ in MeOH. The mixture of allylic alcohols was also concentrated by t.l.c., and the proportions of *cis* and *trans* isomers were then determined (±2%) by ^{13}C n.m.r. spectroscopy, using the peak heights of the resonances at δ 67·5 and 73·1 due to the hydroxylated allylic carbon atoms in the *cis* and *trans* isomers, respectively;† the corresponding resonances at δ 81·1 and 86·9 in both the crude and concentrated hydroperoxides indicated that the stereochemistry in the initial product had been retained. The *cis* allylic alcohols were separated from the *trans* by careful t.l.c. on silica gel (Merck, Kieselgel $HF_{254+366}$) impregnated with 5% $AgNO_3$, using C_6H_6–EtOAc–EtOH (80:18:2) as eluent. The two mixtures were hydrogenated [in EtOAc over 10% Pd/C; atmospheric pressure: no selective hydrogenolysis of *cis* and *trans* (**6**)] and the products were trimethylsilylated.[3] The four main constituents in the two mixtures were determined (±1%) by mass spectrometry (m.s.) (AEI MS902; direct insertion, 70 eV, 32 °C) using the relative abundancies of the intense lines due to both α-fissions of the trimethylsilyl ethers, and/or by g.l.c.–m.s. using the computer summation technique to avoid errors due to partial separation of the isomers.‡

† Although the percentage of *trans* isomers can be determined (±2%) by quantitative i.r. spectrometry, subtraction of this value from 100 does not afford a measure of the *cis* isomers since the allylic alcohols cannot be separated quantitatively by t.l.c. from other autoxidation products, and their derivatives, of similar polarity. Spectra were obtained at 22·63 MHz in $CDCl_3$. At 50·3 MHz both signals are resolved into three peaks, indicating that at higher fields isomers can be estimated directly.

‡ Neither m.s. nor g.l.c.–m.s. of the trimethylsilyl ethers from the allylic alcohols is suitable for quantitative purposes owing to allylic rearrangements under the conditions used.

TABLE

Allylic hydroperoxides from autoxidation of methyl oleate (as % of total hydroperoxides at peroxide values 300—1000; *cis* and *trans*, respectively, in parentheses).

Temp. /°C	8-OOH, Δ^9	9-OOH, Δ^{10}	10-OOH, Δ^8	11-OOH, Δ^9
25	26·4 (14·1, 12·3)	24·2 (1·1, 23·1)	22·8 (1·1, 21·7)	26·6 (13·7, 12·9)
40	26·6 (10·6, 16·0)	23·6 (1·6, 22·0)	23·4 (1·7, 21·7)	26·4 (10·1, 16·0)
75	25·1 (6·1, 19·0)	25·1 (2·7, 22·5)	24·9 (2·9, 22·0)	24·9 (5·4, 19·5)

Some typical results for the distribution of the allylic hydroperoxides from the autoxidation of methyl oleate are summarised in the Table. At 25 °C substitution without double bond migration gave comparable amounts of *cis* and *trans* isomers; that with double bond migration mainly, but not exclusively, gave the *trans* isomer. Though *cis* products were less evident at 75 °C, their relative importance with the 9- and 10-hydroperoxides increased. Except at higher temperatures, attack at C-8 and C-11 was slightly (but consistently) greater than that at C-9 and C-10. The significance of these findings for the mechanism of the autoxidation process will be discussed elsewhere.

We thank the United States Department of Agriculture for financial support, and the University of London for a Postgraduate Studentship (B.P.S.K.).

(*Received*, 1*st March* 1977; *Com.* 178.)

[1] E. N. Frankel in Symposium on Foods: 'Lipids and their Oxidation,' ed. W. H. Schutz, Avi, Westport, Connecticut, 1962; J. Mercier, *Compt. rend.*, 1969, **269**, 1002; M. V. Piretti, P. Capella, and G. Bonaga, *J. Chromatog.*, 1973, **92**, 196.

[2] E. N. Frankel, W. E. Neff, W. K. Rohwedder, B. P. S. Khambay, and B. C. L. Weedon, paper presented at the American Oil Chemists' Society Meeting, Chicago, Illinois, Sept. 1976. Abstract 182; *J. Amer. Oil Chem. Soc.*, 1976, **53**, 470A.

[3] C. C. Sweeley, R. Bentley, A. Makita, and W. Wells, *J. Amer. Chem. Soc.*, 1963, **85**, 2497.