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Characterisation of electron beam generated transformation products of Irganox 1010 by particle beam liquid chromatography–mass spectrometry with on-line diode array detection

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Abstract

Transformation products of Irganox 1010 [pentaerythritol tetrakis-3-(3,5-di-*tert.*-butyl-4-hydroxyphenyl) propionate], in food contact polymers subjected to electron beam irradiation have been analysed by particle beam LC–MS with on-line UV diode array detection. It has been shown that the principal transformation products arise via loss of sub-units of the parent molecule, and the subsequent transformation of these sub-units. A total of 56 transformation products has been detected, for some of which structures are proposed. These results are compared to previous work on Irganox 1330 [1,3,5-trimethyl-2,4,6-tris(3′,5′-di-*tert.*-butyl-4-hydroxybenzyl)benzene], where transformations to yield *p*-quinone methide type structures were shown to occur.

1. Introduction

In previous papers we have reported on the effects of both gamma and electron beam irradiation in air on various hindered phenol and related arylphosphite antioxidants present in food contact polyolefins [1–4]. The overall trend observed has been that as the exposure to radiation increases, so the amount of antioxidant remaining decreases. This decrease in available antioxidant has been attributed to its transformation to other products via reactions with peroxo and other radicals present in the oxidising polymer.

Our recent work has concentrated on the characterisation of solvent extractable transformation products from hindered phenol and related antioxidants in polypropylene subjected to ionising radiation [5,6]. Initial studies on Irganox 1076 [octadecyl-3(3,5-di-*tert.*-butyl-4-hydroxyphenyl) propionate], Irganox 1010 [pentaerythritol tetrakis-3-(3,5-di-*tert.*-butyl-4-hydroxyphenyl) propionate] and Irganox 1330 [1,3,5-trimethyl-2,4,6-tris-(3,5-di-*tert.*-butyl-4-hydroxybenzyl)benzene] were reported [5]. We employed particle beam liquid chromatography–mass spectrometry (PB-LC–MS) [7] in conjunction with data obtained using high-performance liquid chromatography (HPLC) with diode array detection (DAD) in an off-line mode to characterise the transformation products. We noted that the data obtained in our early experiments with PB-

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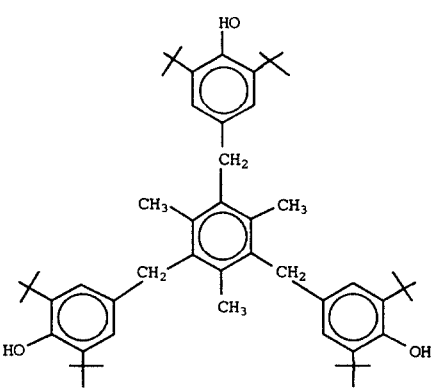
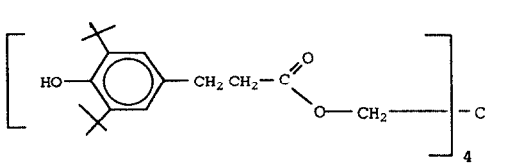
LC–MS in an isocratic mode were not adequate to enable characterisation of all transformation products observed [5].

A second paper reporting more detailed work on the transformation products of Irganox 1330 has been published [6]. We showed that the principal transformation products of Irganox 1330 (structure **1**) under irradiation conditions arise via oxidation processes to yield quinone methide type structures and also via side chain losses arising from cleavage of *tert.*-butyl groups. Irganox 1010 (structure **2**) has the potential to undergo similar transformation processes under irradiation conditions to yield one or more sub-units of structure **2** transformed into a quinone methide structure i.e., structure **3**. However Irganox 1010 might also be expected to yield transformation products containing a cinnamate type sub-unit (structure **4**). Transformation products containing the same number of quinone methide or cinnamate sub-units will show the same relative molecular mass (M_r). Of these isomeric structures, the cinnamate form is likely to be preferred on the grounds of aromaticity and extended conjugation.



(1)



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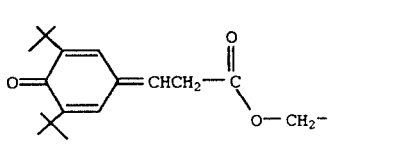

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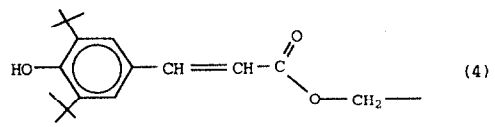


(4)

Since these sub-units may be present in any combination the following possibilities exist where in these structures (**2s**) refers to one sub-unit of structure **2**: $(\mathbf{2s})_3$–C–(**3**), $(\mathbf{2s})_3$–C–(**4**), $(\mathbf{2s})_2$–C–$(\mathbf{3})_2$, $(\mathbf{2s})_2$–C–$(\mathbf{4})_2$ etc.

We have also observed that in our previous work losses of the above sub-units from the parent antioxidant occur to yield transformation products with a variety of new substituents. In particular, cleavage of one or more of the above sub-units with the formation of alcohol or aldehyde functional group residues on what remains of the parent molecule is possible, as well as reductive cleavage to leave methyl groups [5,6].

A further class of transformation products expected would be related to the above compounds but exhibit losses of *tert.*-butyl groups.

In anticipation of such a complex mixture of transformation products it was decided to use gradient elution PB-LC–MS with the UV-DAD detector connected on line, and in this paper we report evidence for the structures of the major solvent extractable transformation products of Irganox 1010 obtained using this approach.

2. Experimental

2.1. Irradiation

Samples of polypropylene homopolymer stabilised with Irganox 1010 (0.25%, w/w) were prepared by sintering to produce small pellets which were then subjected to irradiation from a 4.5-MeV Dynamitron Continuous Electron Beam facility (50 kGy).

2.2. Extraction

The irradiated stabilised polypropylene (0.5 g) was heated under reflux in chloroform (10 ml) for 4.5 h to extract the transformation products. The extract was then microfiltered using a 0.45 mm pore size nylon 66 membrane filter and

1.0-cm Whatman GF/D pre-filter. The resulting extract was evaporated almost to dryness under oxygen-free nitrogen in a screw cap vial. Ethyl acetate (3 ml) was then added to the extract to precipitate oligomers. After re-microfiltration the extract was evaporated down to 0.5 ml prior to HPLC analysis.

2.3. High-performance liquid chromatography

The HPLC instrumentation comprised a Gilson binary gradient system for solvent programming and a Philips PU4021 multichannel UV–vis detector. The resulting data were processed using a Dell 210 microcomputer equipped with the Philips analytical PU 6003 Diode Array Detector system (3.0). The column employed was a 10 cm × 4.6 mm Spherisorb ODS2 analytical column fitted with a 5 cm × 4.6 mm Spherisorb ODS2 guard column.

Gradient elution was employed using the following mobile phases: (A) methanol–water (10:90, v/v); (B) ethyl acetate–methanol (57:43, v/v). Flow-rate: 0.7 ml/min. Solvent programme comprised initial 65% B for 15 min, linear gradient 65–90% B in 30 min, 90% B for 15 min and a step to 100% B which was held for 15 min. The diode array detector was set to acquire 1 spectrum/s over the range 250–390 nm.

2.4. Particle beam liquid chromatography–mass spectrometry

The HPLC system described above was connected in series with a VG Masslab (Manchester, UK) Trio 1 quadrupole mass spectrometer equipped with a VG LINC–particle beam LC–MS interface. Data were acquired in the full scan mode at 3 s/scan over the mass range 50–950 daltons under electron impact (70 eV) ionisation. All data were processed using a VG Lab Base data system.

3. Results and discussion

Our simultaneous UV–MS experiment provided three pieces of evidence for each peak: (i) the relative retention behaviour in the reversed-phase separation, (ii) the nature of the UV spectrum, and (iii) the mass spectrum. In total we were able to detect 56 different components, on the basis of UV and/or mass spectral information (complete spectra or extracted ion chromatograms). Most of these components were present at such low concentrations, however, that it was not possible to obtain satisfactory spectra using our on-line technique. In order to identify such peaks it would be necessary to undertake significant preconcentration or to use preparative chromatography. On the basis of spectral and chromatographic information we are able to propose identities for 9 of the 56 transformation products. We have synthesised three of our proposed compounds, and obtained an authentic sample of a fourth, and shown that in each case the mass spectra are very similar to those of the transformation products.

Inspection of the complete diode array data set showed that all the major peaks absorb significantly at 275 nm. The 275 nm chromatogram Fig. 1 shows twelve peaks I to XII with absorbances above 0.05 eluting before Irganox 1010 (peak XIII). On the basis of their retention behaviour the twelve transformation products giving rise to these peaks fall into three groups: (a) peaks I to III, (b) peaks IV to VIII, and (c) peaks IX to XII.

Group (a), peaks I, II and III, elute in the initial 15-min isocratic region [65% B, i.e. methanol–ethyl acetate–water (31:37:32)]. Given the reversed-phase nature of the separation these three transformation products are therefore expected to have much the most polar structures and/or lowest relative molecular masses (M_r).

Group (b), peaks IV to VIII, elute during the gradient portion of the chromatogram with retention times between 15 and 45 min, and are expected to be of steadily decreasing polarity and/or increasing M_r.

Group (c), peaks IX to XII, with retention times between 45 and 60 min, are expected to be of significantly lower polarity and/or higher M_r, since they elute during the second isocratic portion of the run [90% B, i.e. methanol–ethyl acetate–water (40:51:9)] as does Irganox 1010 itself (peak XIII).

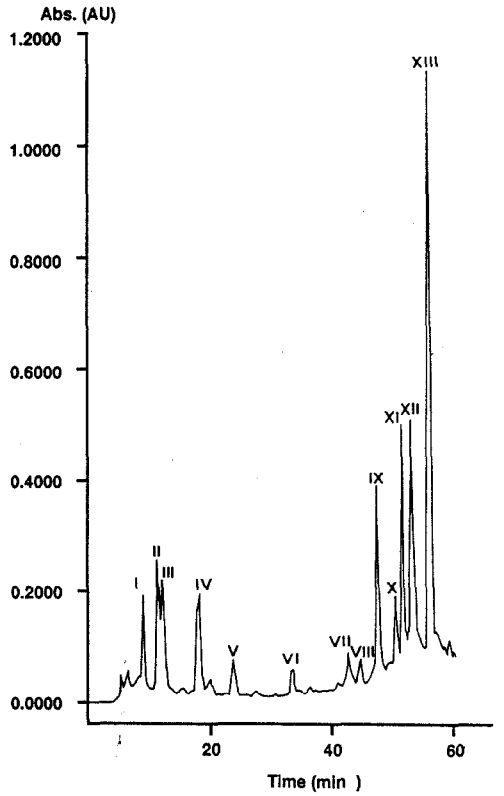


Fig. 1. UV absorption chromatogram (275 nm) of extract of irradiated polypropylene homopolymer originally stabilised with Irganox 1010.

The raw total ion chromatogram is shown in Fig. 2 scaled to 100% for the Irganox 1010 peak XIII. Peaks appear with retention times approximately 0.5 min longer than in the UV chromatogram, reflecting the fact that the diode array detector and mass spectrometer were connected in series. Although there is some deterioration in peak shape, the loss of chromatographic resolution compared with the UV trace is not too severe.

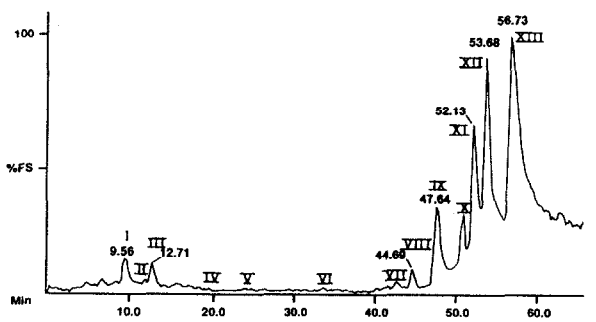
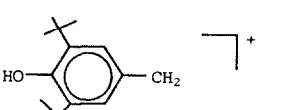


Fig. 2. Total ion chromatogram of same polypropylene extract as in Fig. 1. FS = full scale.

Peaks I and III in group (a) are clearly visible in the total ion chromatogram, but in group (b), for the gradient elution part of the run, the only obvious peak is peak VIII. All five of the peaks IX to XIII show clearly in group (c). The fact that only eight of the thirteen peaks seen in the UV chromatogram appear clearly in the total ion chromatogram is not unexpected, since without calibration neither UV absorbance nor LC–MS ion intensity give a good indication of the amount of material present. It was possible to locate peaks II, V, VI and VII using the mass spectrometer data system, but no mass spectral peak could be found for peak IV. Although peak X shows up reasonably strongly on the raw total ion chromatogram, it was not possible to obtain an interpretable mass spectrum for this component.

Fig. 3 shows the UV and mass spectra for the Irganox 1010 peak (peak XIII). The major UV absorption band in the range 260–300 nm (λ_{max} 285 nm) is characteristic of phenolic compounds, and similar bands are found in most of the transformation products. The upper mass range of the spectrometer precludes detection of a molecular ion for Irganox 1010 (M_r 1178). The base peak at m/z 219 is attributed to the fragment ion with structure **5** formed by cleavage of the carbon–carbon bond β to the aromatic ring. Significantly this m/z 219 peak is found in many of the transformation products. Similarly, the ion at m/z 259 (tentative structure 6) which gives the second most abundant peak in the mass spectrum of Irganox 1010, is also found in the high M_r transformation products giving rise to peaks IX and XI.



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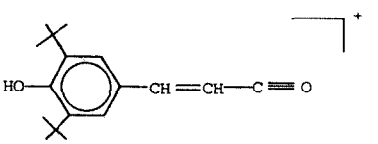

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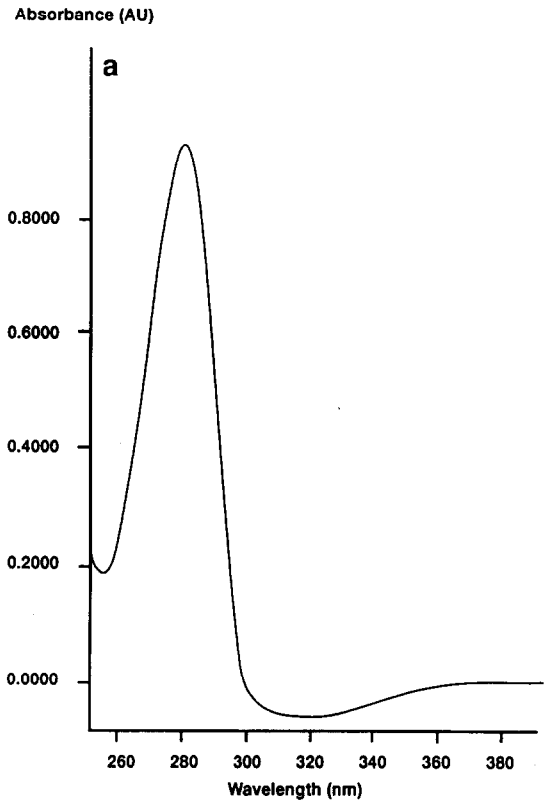


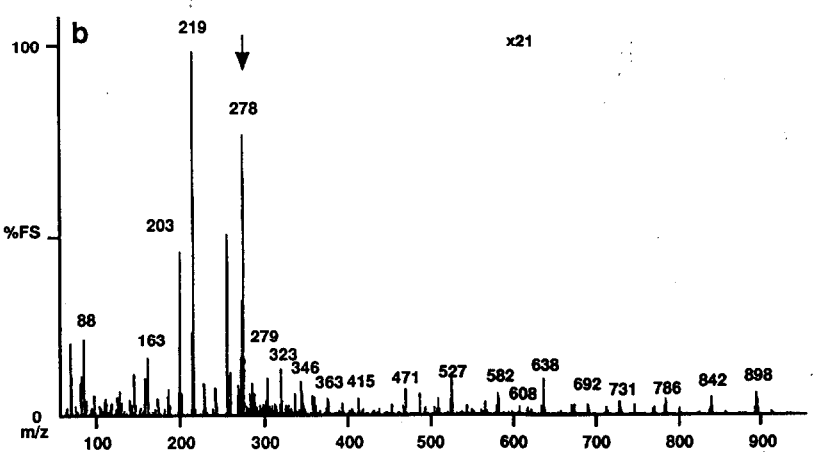
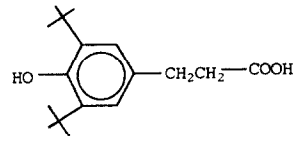
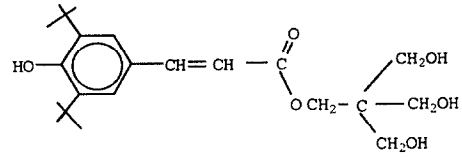
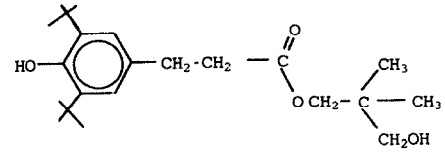
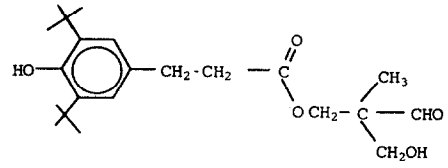
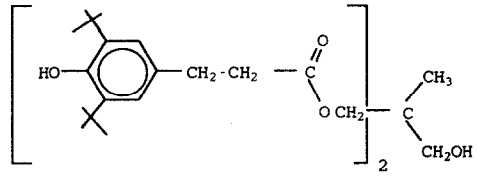
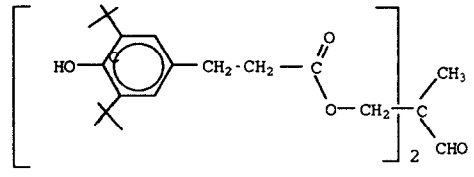
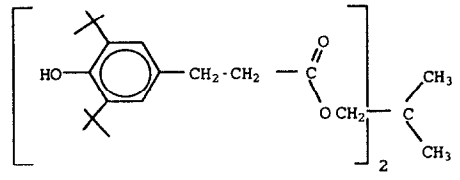
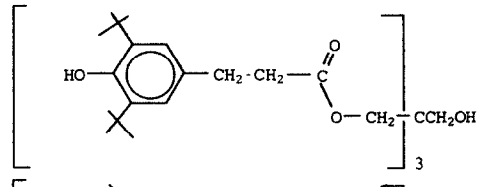
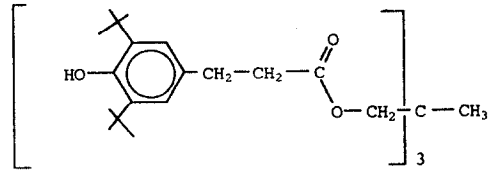


Fig. 3. (a) Diode array UV spectrum of peak XIII (Irganox 1010) for chromatogram of Fig. 1. (b) Mass spectrum of peak XIII (Irganox 1010) for chromatogram of Fig. 2.

Table 1
Proposed structures for major transformation products of Irganox 1010 after 50 kGy electron beam irradiation

Chromatographic peak number	M_r (u)	Proposed structure
I[a]	278	
II	394	
III[a]	364	
V	378	
		tentative structure (see text)
VI	640	
VII	638	
VIII[a]	624	
IX	916	
XI[a]	900	
XII	> 1000	Simple cleavage of *tert.*-butyl groups

[a] Identity confirmed by synthesis or comparison with authentic standards.

Table 1 shows our proposed structures for transformation products corresponding to nine of the peaks, together with a much more tentative possible structure for peak V. All these peaks except peak II show UV spectra similar to Irganox 1010, with the main absorption band extending from 260 to 300 nm with λ_{max} in the range 280–285 nm characteristic of phenolic compounds. Fig. 4 shows examples for peaks I and IX. We conclude that the only major chromophore in such compounds is the Irganox 1010 subgroup.

None of the UV spectra provide evidence of quinone methide structure **3** similar to those found in our work with Irganox 1330 [6]. Such structures would show a characteristic intense absorption at significantly longer wavelengths, extending to 380 nm with λ_{max} at about 345 nm.

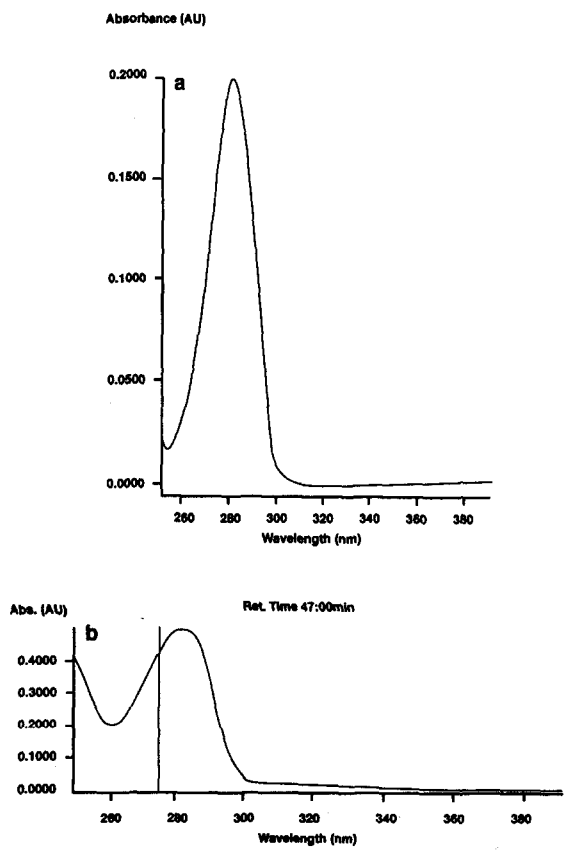


Fig. 4. (a) Diode array UV spectrum of peak I. (b) Diode array UV spectrum of peak IX.

Such quinone methide structures would have the same M_r as the corresponding cinnamate, being two mass units less than that of compound containing the fully saturated Irganox 1010 subunit.

3.1. Peak I

This peak shows a UV spectrum (Fig. 4a) which is very similar to that of Irganox 1010, indicating an intact phenolic group, without further conjugation. The mass spectrum (Fig. 5a) with a relatively intense molecular ion at m/z 278, base peak at m/z 263 due to the expected loss of CH_3 from the *tert.*-butyl groups, and significant fragment ion at m/z 219 as found in Irganox 1010 itself, is very similar to that of an authentic sample of 3-(3,5-di-*tert.*-butyl-4-hydroxyphenyl)propanoic acid (Fig. 5b). A B/E linked scan mass spectrum of the authentic sample confirmed that both m/z 263 and m/z 219 arise directly from fragmentation of the molecular ion. The low mass and relatively high polarity of this carboxylic acid are consistent with the fact that this compound has the shortest retention time of all the identified transformation products.

3.2. Peak II

The mass spectrum (Fig. 6a) shows a weak molecular ion at m/z 394. This is the only peak with a significantly different UV spectrum (Fig. 6b) to that of Irganox 1010: the absorption band is much broader, extending to beyond 320 nm, with λ_{max} at 290 nm. This is characteristic of cinnamate type compounds (structure **4**), with extended conjugation.

3.3. Peak III

The single sub-unit structure assigned to this peak (M_r at m/z 364) is shown in Table 1.

This substance was synthesised, and comparison between the mass spectrum of the authentic sample and the transformation product was used to confirm assignments.

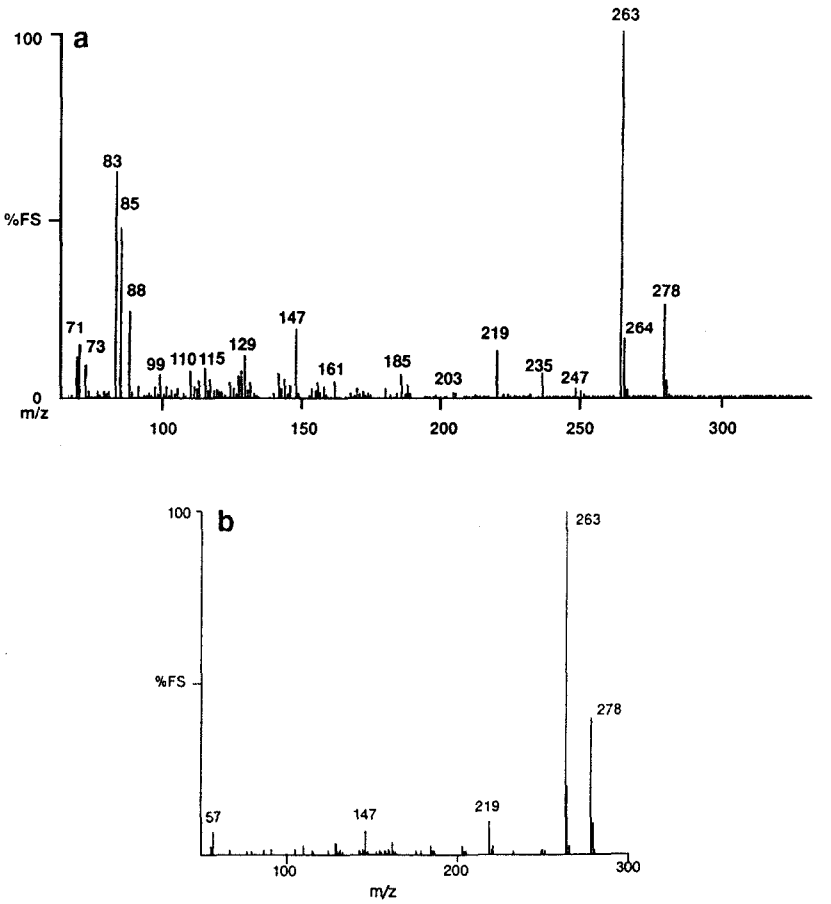


Fig. 5. (a) Mass spectrum of peak I. (b) Mass spectrum of an authentic sample of 3-(3,5-di-*tert.*-butyl-4-hydroxyphenyl) propanoic acid.

3.4. Peak V

On the basis of its UV spectrum (phenolic) and mass spectrum (apparent molecular ion at 378) peak V would be consistent with the single sub-unit structure shown in Table 1. However, such a structure is more polar than the proposed structure for peak III, and would therefore be expected to elute significantly earlier in the chromatogram. The actual identity of peak V is therefore uncertain.

3.5. Peaks VI, VII, and VIII

Peaks VI to VIII have been assigned to the structures containing two 1010 type sub-units. The mass spectra of these three compounds show characteristic ions corresponding to structure **6** as well as the other principal fragmentation routes discussed. Confirmation of these assignments was achieved by synthesis of the compound with the structure proposed for peak VIII. The mass spectra of peak VIII and the synthetic sample are shown in Fig. 7a and b, respectively.

3.6. Peaks IX and XI

Peaks IX and XI are assigned to components containing three Irganox 1010 type sub-units. Peak IX has been assigned the structure shown in Table 1 on the basis of the mass spectral and

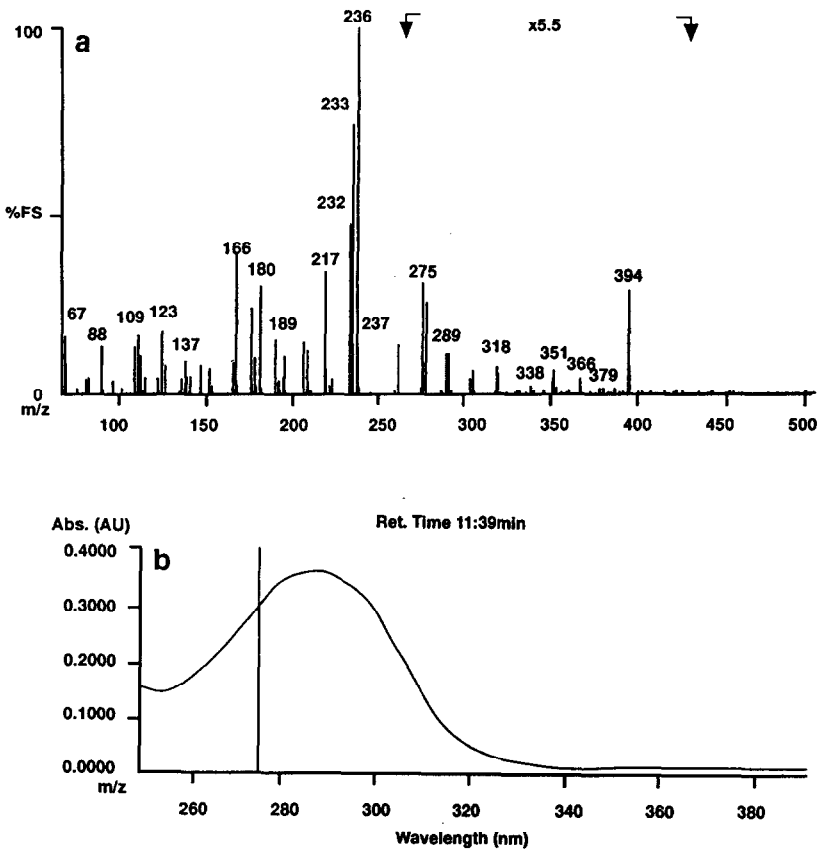


Fig. 6. (a) Mass spectrum of peak II. (b) Diode array UV spectrum of peak II.

UV evidence, Figs. 8 and 4b, respectively, and similarly for peak XI. In order to confirm these assignments an authentic sample of the compound with the structure proposed for peak XI was synthesised. A comparison between the mass spectrum obtained from peak XI and the synthetic sample is shown in Fig. 9a and b.

3.7. Peak XII

This peak elutes shortly before Irganox 1010 itself. On the basis of its high mass and the lack of any evidence of extended conjugation in the UV data we have tentatively explained it as arising via simple loss of a *tert.*-butyl group or groups from Irganox 1010, this type of transformation product having been previously identified in our work on Irganox 1330. [The relative molecular mass of this proposed substance, in common with that of Irganox 1010 (peak XIII) is above the mass range of the instrument used.]

It was not possible to assign structures for peaks IV and X.

In summary then we conclude that peaks I to III contain a single sub-unit, while peaks VI to VIII contain two sub-units, and peaks IX, XI and XII retain three of the four sub-units of Irganox 1010.

We have also identified one of the smaller peaks, with UV absorbance of much less than 0.05. This is the small peak seen in Fig. 1 between peaks V and VI. Its mass spectrum is shown in Fig. 10a, while Fig. 10b shows the mass spectrum of a synthesised sample of 2,2-dimethylpropyl-3-(3,5-di-*tert.*-butyl-4-hydroxyphenyl) propanoate (structure 7). The similarity

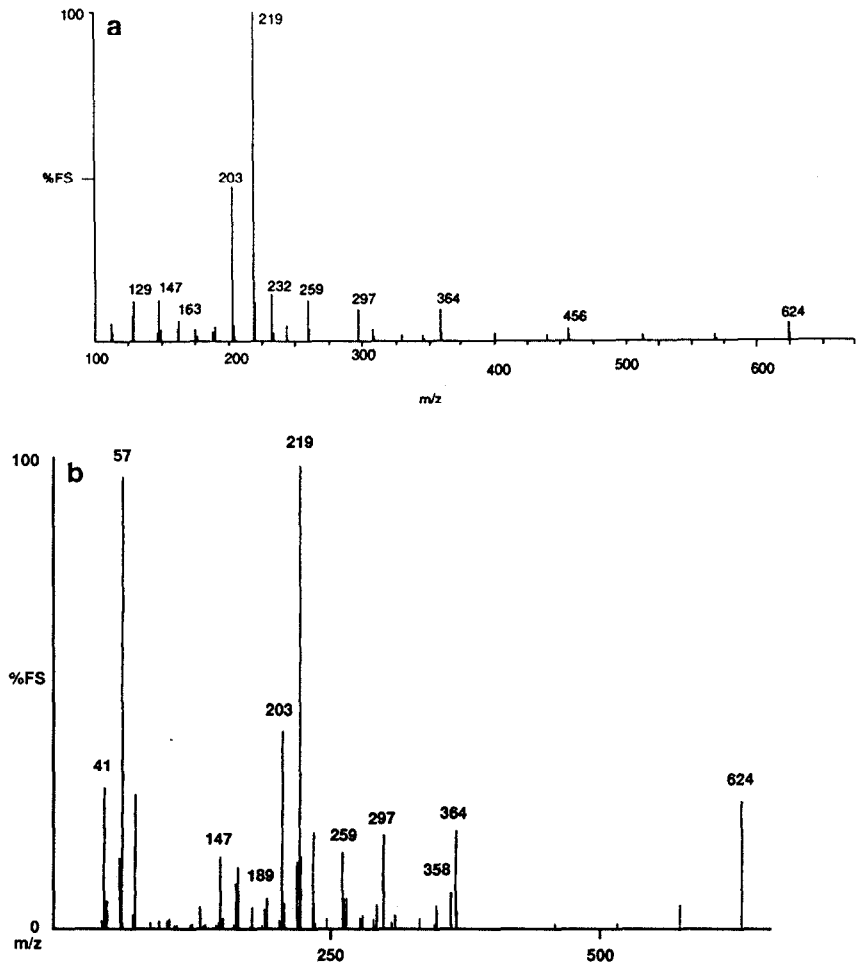


Fig. 7. (a) Mass spectrum of peak VIII. (b) Mass spectrum of a synthesised compound with the structure proposed for peak VIII.

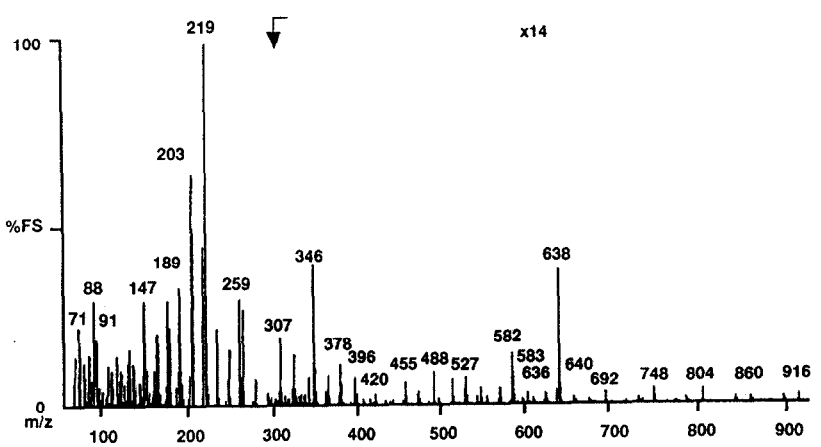


Fig. 8. Mass spectrum of peak IX.

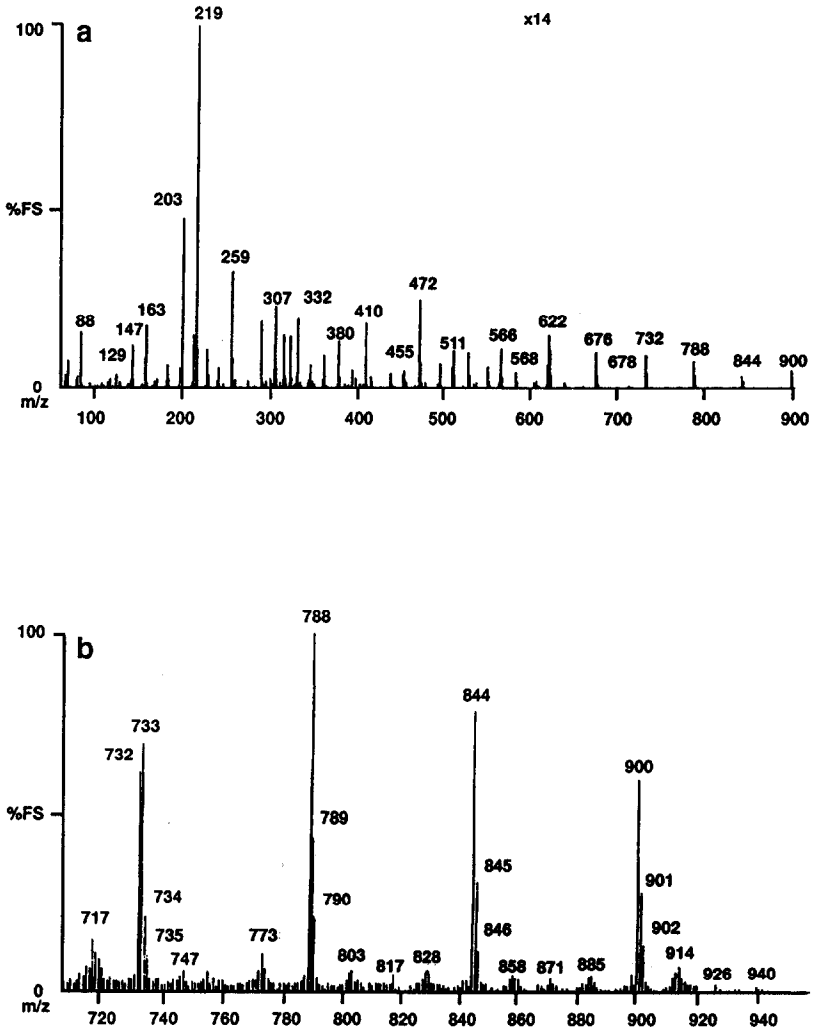
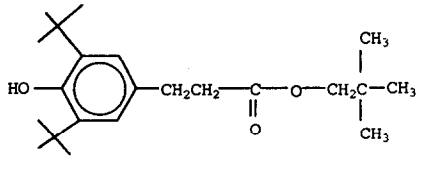


Fig. 9. (a) Mass spectrum of peak XI. (b) Mass spectrum of a synthesised compound with the structure proposed for peak XI.

between the two spectra is striking. This compound is the least polar of all the transformation products containing a single sub-unit, and is therefore the last of these to be eluted.



(7)

Overall the types of transformation products observed here appear to differ from those observed for Irganox 1330. In our work on Irganox 1330 we reported transformation to proceed via the formation of quinone methide type compounds. The difference in structure between the two antioxidants, principally the presence of the labile C–O bond in Irganox 1010 appears to lead to transformation proceeding via sub-unit losses. An overall scheme for this process is shown in Fig. 11.

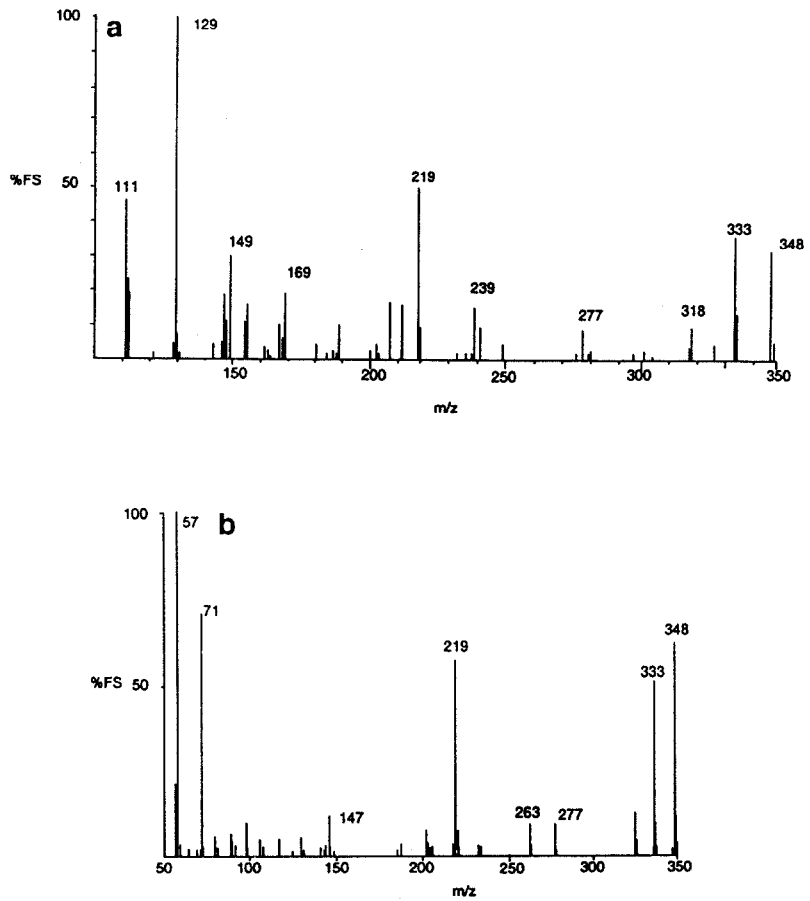


Fig. 10. (a) Mass spectrum of small peak eluting between peaks V and VI. (b) Mass spectrum of a synthesised compound with the structure proposed for the small peak eluting between Peaks V and VI.

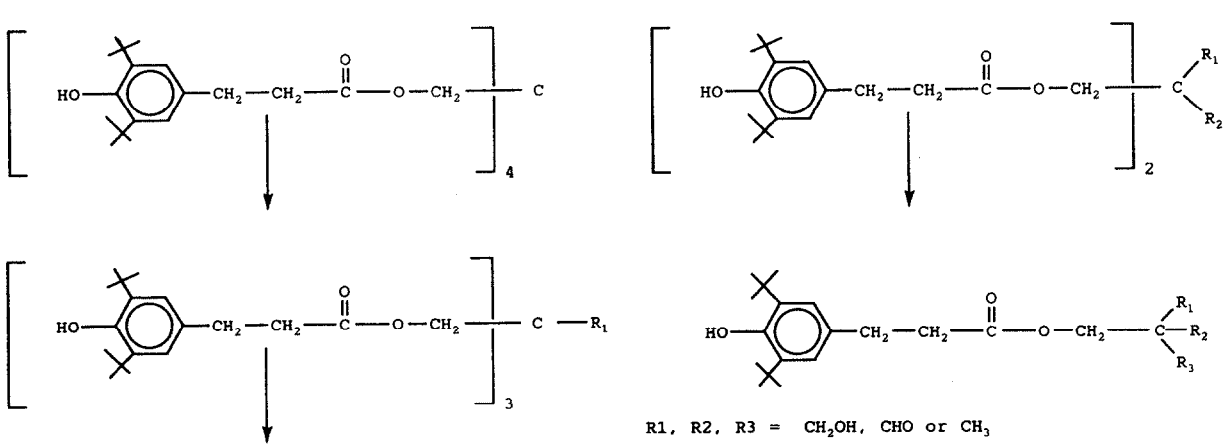


Fig. 11. Principal transformation processes for Irganox 1010 under electron beam irradiation.

4. Conclusions

Transformation of Irganox 1010 in food contact polymers subjected to electron beam irradiation gives rise to a complex mixture of products. The principal products arise via cleavage of C–O bonds leading to sub-unit losses. The formation of quinone methide species previously observed in our work on Irganox 1330 was not an important process in the transformation of Irganox 1010.

The combination of particle beam LC–MS with on-line UV diode array detection has proved a powerful analytical tool for this application.

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