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THE MASS SPECTRA OF QUINONOID PIGMENTS: CHARACTERISTIC CLEAVAGE PROCESSES OF γγ-DIMETHYLALLYL AND OTHER SIDE-CHAINS

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This paper firstly demonstrates the application of mass spectrometry in the structure determination of γγ-dimethylallyl and other side-chains attached to various anthraquinonoid pigments and secondly it provides mass spectral confirmation of the structures proposed in the immediately preceeding paper of this issue for harunganin, and related pigments. In the following discussion the Roman numerals refer to the structures given in the preceeding paper.

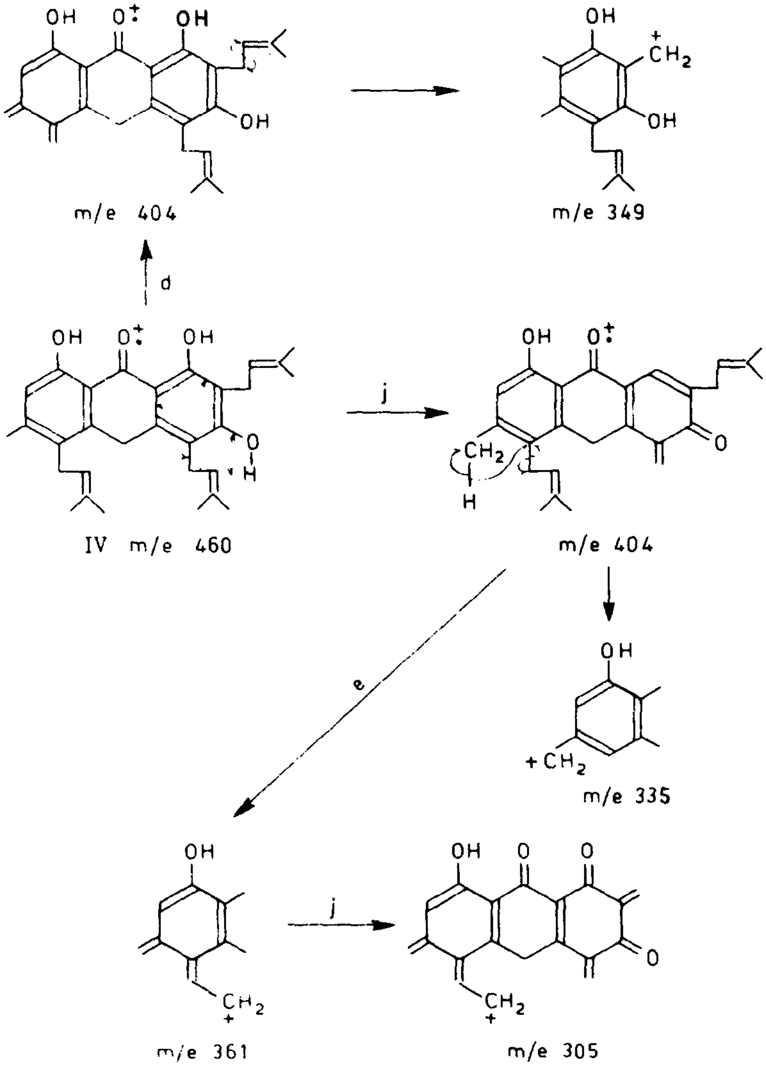
The mass spectra of harunganin (VI) and its ethers (VII) and (VIII) are similar except for the expected shifts of 14 and 28 mass units due to the extra methyl group in (VII) and the two extra methyl groups in (VIII). The principal peaks in the spectra which are listed in Table I, are due to ions whose formation can be interpreted in terms of the successive cleavage of three γγ-dimethylallyl side chains; five different mechanisms, (a)-(e), which are involved may be formulated as illustrated.

TABLE 1

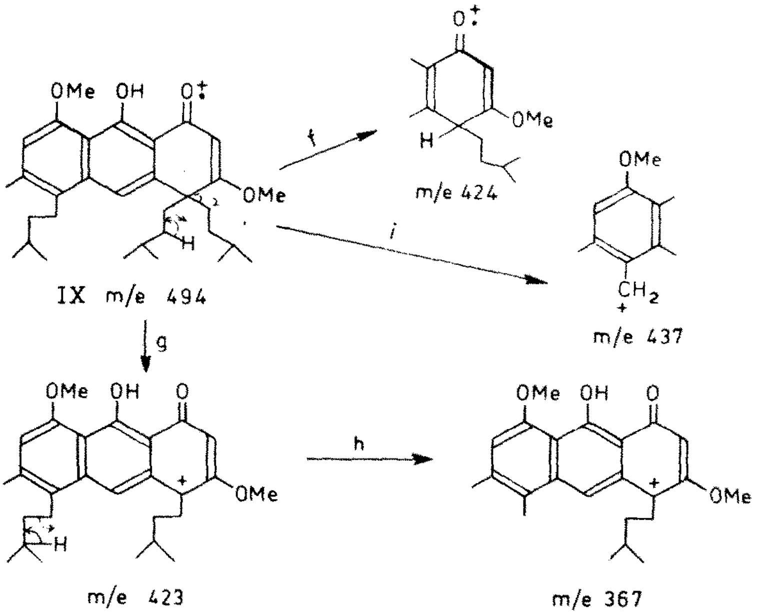
Principal Peaks in Mass Spectra of (VI), (VII) and (VIII)

VI			VII		VIII		Corresponding ion reactions
m/e	460	(59)*	474	(40)*	488	(36)*	
m/e	417	(2)	431	(1)	455	(2)	(e)
m/e	404	(25)	418	(19)	432	(1)	(d)
	392	(100)	406	(64)	420	(91)	(a)
	391	(89)	405	(100)	419	(79)	(b)
	361	(14)	375	(15)	389	(4)	
	349	(44)	363	(34)	377	(13)	(e) + (a)
	336	(70)	350	(48)	364	(15)	(d) + (a)
	335	(61)	349	(60)	363	(31)	(d) + (b)
	323	(73)	337	(71)	351	(100)	(b) + (a)
	305	(26)	319	(24)	333	(16)	
	293	(43)	307	(27)	321	(18)	(e) + (a) + (c)
	281	(70)	295	(26)	309	(17)	
	280	(77)	294	(41)	308	(5)	(d) + (a) + (c)

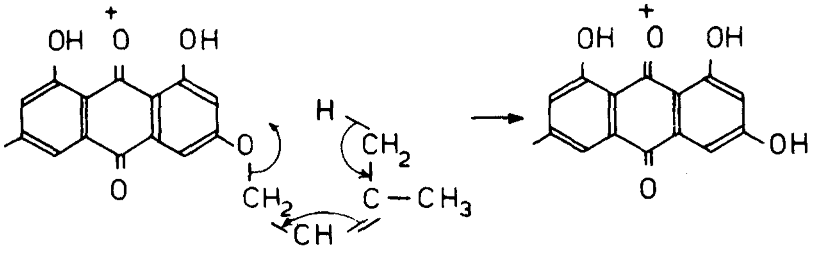
* Relative intensity of base peak (100%)


m/e 404
m/e 349
d
j
IV m/e 460
m/e 404
e
m/e 335
j
m/e 361
m/e 305

Consistent with the presence of saturated side chains in dimethylhexahydroharunganin (IX), its spectrum shows peaks at M-70 and M-71 rather than at M-68 and M-69 which characteristically occur in the spectra of (VI), (VII), and (VIII). The principal peaks are at m/e 494 (parent), 424, 423, 367 and 297; there is a meta-stable transition $423^{+} \rightarrow 367^{+}$ +56. The successive cleavage of three isoamyl side chains can be described by the mechanisms (f)-(i).



The mass spectrum of (II) which had its parent peak at m/e 338 and base peak at m/e 270 was identical with the mass spectrum of emodin from the peak at m/e 270 to the low mass end of the spectrum. Thus the molecular ion of emodin was presumably formed from (II) by the side-chain cleavage as depicted.



II m/e 338 m/e 270

Other peaks in the spectrum of both (II) and emodin at m/e 242, 241, 213, 185 and 157, were due to the successive loss of CHO and/or CO, which reactions have been found by Beynon (1) to be characteristic of hydroxy-anthraquinone as is also the peak at m/e 139 due to a stabilized tricyclic hydrocarbon ion.

The mass spectrum of (III) was quite similar to that of (II) except for the displacement of the peaks to a lower mass range by 14 units. Also consistent with the anthrone-quinone relationship of (III) with (II) was the fact that whereas (II) exchanged the two hydrogen atoms of the two hydroxyl groups for deuterium with deuterium oxide in the mass spectrometer, (III) exchanged four, the additional two being presumably due to the anthrone-anthrol equilibrium.

The mass spectrum of (IV) had strong peaks at m/e 460, 404, 361, 349, 335, 305 and 293 and meta-stable peaks which suggested the occurrence of the following transitions:

$$\begin{tikzcd}
 & 460^+ \arrow[r] & 404^+ \arrow[dll] \arrow[dd] \arrow[drr] & + \; {}^+56 & \\
361^+ \; +43 & & & & 335^+ \; +69 \\
 & & 349^+ \; +55 & &
\end{tikzcd}$$

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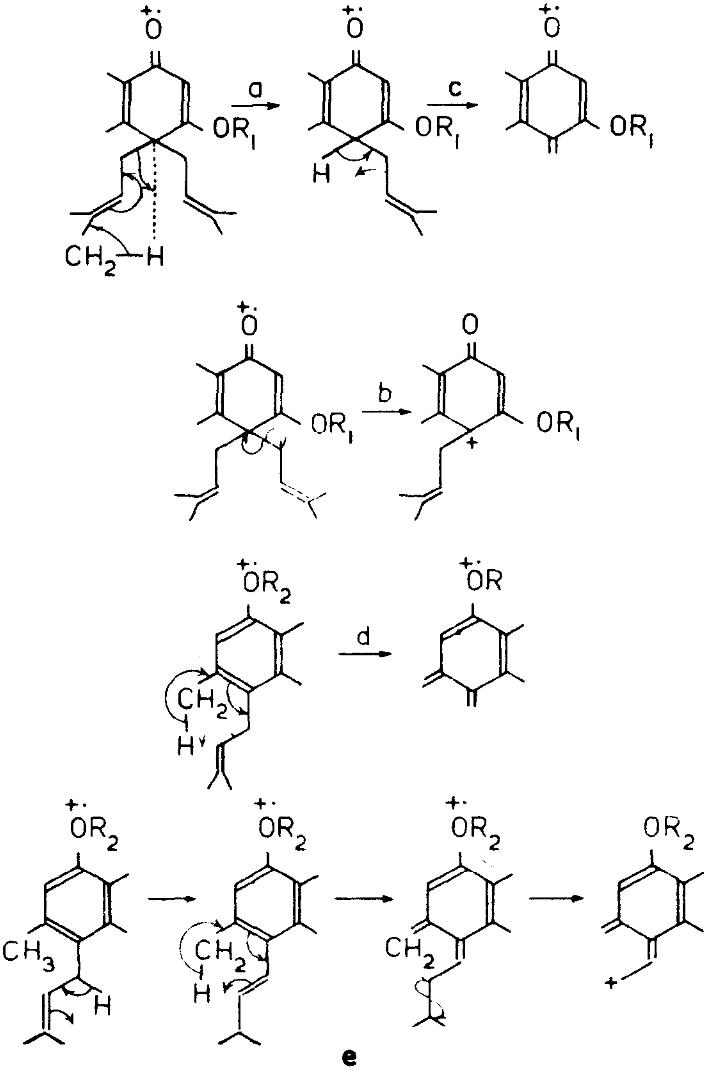
(1) J.H. Beynon, <u>Mass Spectrometry and Its Applications to Organic Chemistry</u>, p.360. Elsevier, Amsterdam (1960).

The spectrum of (IV-O-d_5), formed by exchange of (IV) with deuterium oxide within the ion source of the mass spectrometer, not only contained an M-56 peak at m/e 409 but also an M-57 peak at m/e 408. This suggested that besides reaction (d) there occurs a corresponding reaction (j) in which a hydroxyl group replaces the methyl group in the six-membered cyclic transition state. The dissociation of (IV) may be formulated as below.



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