

# Mass Spectrometric Studies of Dehydro- $\alpha$ -lapachone and Dehydro-*iso*- $\alpha$ -lapachone

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Mass spectra, dehydro- $\alpha$ -lapachone, dehydro-*iso*- $\alpha$ -lapachone

Mass spectral fragmentation studies of dehydro- $\alpha$ -lapachone and dehydro-*iso*- $\alpha$ -lapachone, isolated from the heartwood of *Tabebuia rosea*, have been made. The fragmentation patterns in the case of two compounds are essentially similar and have been discussed.

We have recently isolated dehydro- $\alpha$ -lapachone and dehydro-*iso*- $\alpha$ -lapachone from the petroleum ether extract of the heartwood of *Tabebuia rosea*<sup>1</sup>. The two compounds are isomeric substituted 1,4-naphthoquinones having one ethereal oxygen atom in the cyclic form. The mass spectrometric fragmentation of 1,4-naphthoquinones has been studied by a number of workers<sup>2–6</sup>. The fragmentation behaviour of 1,4-naphthoquinones and their derivatives is essentially similar to that of other quinones; the preliminary cleavage taking place about the ketonic oxygen atoms by elimination of CO molecules. In the present case, however, a second possibility also arises, *i.e.* the initial fragmentation may also occur about the cyclic ethereal oxygen atom<sup>7</sup>. The peaks found in the mass spectra of these two compounds support the latter speculation. The mass spectral data of compounds I and II are given in Table I. The intensity of molecular ion

peak, which is also the base peak, has been arbitrarily taken as 100%. Both compounds give distinct molecular ions at mass 240, which forms the base peak as can be predicted from the structures of such compounds. The absence of an associated  $M+2^+$  ion peak of comparable intensity further supports the paranaphthoquinonoid nature of the compound<sup>8</sup>.

The molecular ion may be formed by the removal of one electron either from the ketonic oxygen or from the ethereal oxygen, thus giving two types of possibilities of fragmentation.

In case of dehydro- $\alpha$ -lapachone, (Fig. 1) the peak observed at mass 225, is formed by elimination of one methyl radical from the side chain giving ion **a**. The latter may lose one molecule of ketene leading to the formation of an ion **b** of mass 183 or it may eliminate one molecule of CO thereby forming ion **c** of mass 197. The formation of ion **b** involves the rearrangement of one hydrogen atom. The high intensity of ion **b** can be explained by the rearrangement of the initially formed ion into the more stable tertiary carbonium ion. The ion **d** of mass 155 is formed from ion **b** after the elimination of one molecule of CO. The ion **d** involves the ring cleavage thereby forming ion **e**, which loses the side chain  $C_4H_3$  and thus changing into ion **f** having mass 104. This ion is highly characteristic for naphthoquinones having no substituents in benzenoid ring<sup>2</sup>. This ion decomposes in usual manner involving the successive elimination of CO and  $C_2H_2$  molecules giving rise to other characteristic peaks of naphthoquinones at masses 76 and 50 respectively<sup>2</sup>. On the other hand, the appearance of an abundant ion of mass 169 shows that ion **c** further loses one more molecule of CO forming ion **g**. The latter undergoes elimination of one molecule of ketene forming ion of mass 127, which further decomposes into ions of masses 76 and 50 successively. As already mentioned, in case of such compounds, the initial

Table I. Mass spectral data of compounds I and II <sup>a</sup>.

S.No.	<i>m/e</i>	Ion composition	Relative intensities	
			I	II
1.	240 ( $M^+$ )	$C_{15}H_{12}O_3^+$	100	100
2.	225	$C_{13}H_9O_3^+$	99.2	96.6
3.	212	$C_{14}H_{12}O_2^+$	98.8	98.8
4.	197	$C_{13}H_9O_2^+$	98.4	98.2
5.	184	$C_{13}H_{12}O^+$	25.6	27.2
6.	183	$C_{12}H_7O_2^+$	57.6	66.4
7.	169	$C_{12}H_9O^+$	62.6	60.0
8.	155	$C_{11}H_7O^+$	39.0	33.1
9.	127	$C_{10}H_7^+$	30.0	15.7
10.	104	$C_7H_4O^+$	71.4	71.0
11.	101	$C_8H_5^+$	34.6	30.2
12.	76	$C_6H_4^+$	62.6	57.8
13.	50	$C_4H_2^+$	40.0	28.9

a. The NMR and IR spectra of these compounds are consistent with the assigned structures.

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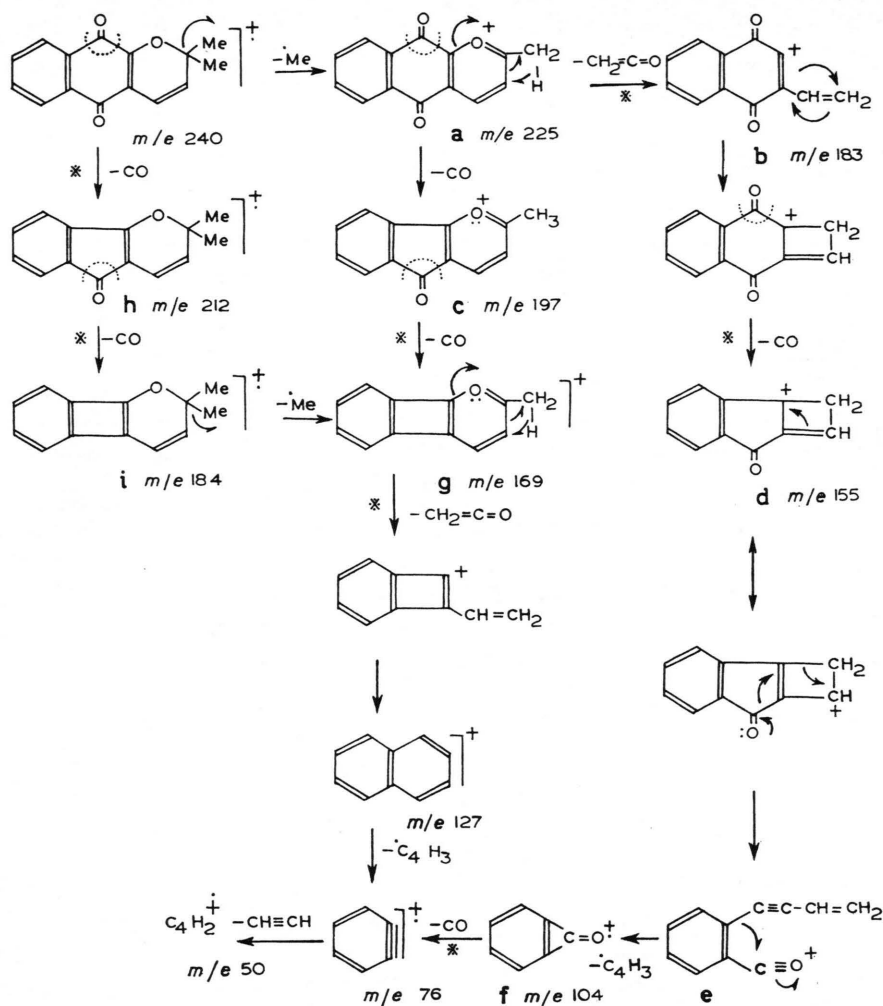


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cleavage may occur in quinonoid ring also. In conformity to this pattern of cleavage, peaks are observed at masses 212 and 184, which are formed by successive elimination of two molecules of CO from the molecular ion. The ion **e** of mass 184 may lose  $\text{CH}_3$  radical leading to the formation of ion **g**.

The various fragmentation processes discussed above are further substantiated by the appearance of appropriate metastable peaks except that an expected metastable peak at  $m/e$  172.5 for the fragmentation of ion **a**  $m/e$  225  $\rightarrow$  ion **c**  $m/e$  197 involving the elimination of CO molecule does not appear. However, such limited exceptions do not altogether exclude the possibility of this type of

fragmentation<sup>9</sup>. These metastable transitions have been indicated by an asterisk in Fig. 1.

From the mass spectrum of dehydro-*iso-a*-laphone, it appears that this compound also follows the same fragmentation pattern (Fig. 2) as its isomer discussed above. In this case also, the molecular ion may fragment in two ways. The highly abundant ion of mass 225 formed by elimination of CH<sub>3</sub> radical from the molecular ion is stabilized by resonance. The ion **j** can lose one CO molecule or ketene molecule forming ions of masses 197 **k** and 183 **l** respectively. The high intensity of these ions can be attributed to their stabilization by resonance. The ion **k** can eliminate one molecule of CO followed by loss of ketene molecule. On the other hand,

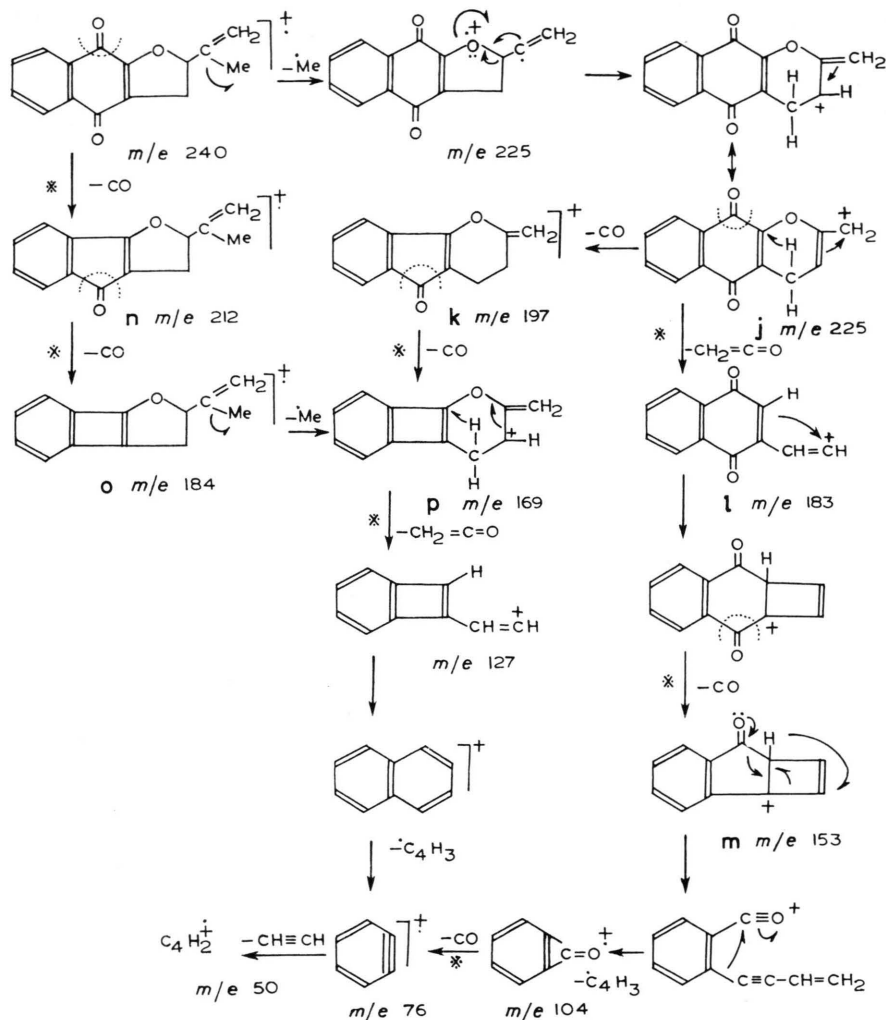


Fig. 2. Mass spectral fragmentation pattern of dehydro-*iso*- $\alpha$ -lapachone.

ion **l** loses one molecule of CO forming an ion of mass 155 **m**, which changes into the characteristic ion of mass 104 as in the case of dehydro- $\alpha$ -lapachone. Elimination of CO molecule from the quinonoid ring of molecular ion leads to the formation of ion **n** of mass 212, which further loses one more molecule of CO forming ion **o** of mass 184. The ion **o** eliminates one methyl radical forming resonance stabilized ion of mass 169 **p** which breaks down in the usual way.

In this case also metastable peaks are observed at appropriate places thereby supporting the proposed fragmentation process.

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