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Further Mass Spectral Studies of Flavones

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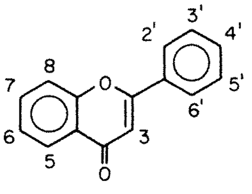
Further evidence supporting the structure of the $[M-1]^+$ ion found in the mass spectrum of flavone as being the [dibenzo-β-tropolone $-$ H]$^+$ species was obtained by comparison of linked scan measurements performed in flavone, 3-deuteroflavone, 5,6,7,8-tetradeuteroflavone, 2′,3′,4′,5′,6′-pentadeuteroflavone and dibenzo-β-tropolone. This fragmentation process has also been demonstrated in the case of 3-methoxyflavone by high-resolution measurements, deuterium labelling, metastable decompositions and evaluation of the subspectra of 9-methoxyfluorenol, fluorenone and biphenylene. The structure of the ion at *m/z* 181 in the spectrum of flavone was found to be the [2-phenylbenzoxetane $-$ 1]$^+$ species.

INTRODUCTION

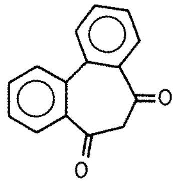
In a previous work[1] we proposed a [dibenzo-β-tropolone $-$ H]$^+$ structure for the intense (~30%) ion radical generated after electron impact induced fragmentation of flavone (**1**). The loss of the hydrogen atom occurs from the *B*-ring of flavones since 5,6,7,8-tetradeuteroflavone (**3**) provides a $[M-H]^+$ ion, while 2′,3′,4′,5′,6′-pentadeuteroflavone (**4**) gives a $[M-D]^+$ ion. The [dibenzo-β-tropolone $-$ H]$^+$ ion further decomposes by the successive expulsion of two carbon monoxide residues to provide, after ring contraction, a fragment at *m/z* 165. The latter subsequently behaves as the $[M-H]^+$ ion derived from fluorene (**16**) as substantiated by the similarity of the appropriate subspectra.

In this report we provide further evidence of this fragmentation mechanism by studying in detail the mass spectral behaviour of dibenzo-β-tropolone (**13**). Furthermore, the extension of this fragmentation process to the case of 3-methoxyflavone (**7**) is demonstrated by the evaluation of deuterated analogues, linked scan studies of metastable decompositions and comparison of subspectra with those of molecules that generate the appropriate comparison ions.



1

2: 3-*d*-**1**
3: 5,6,7,8-d_4-**1**
4: 2′,3′,4′,5′,6′-d_5-**1**
5: 3-OH-**1**
6: 3-OH-2′,3′,4′,5′,6′-d_5-**1**
7: 3-OCH_3-**1**
8: 3-OCD_3-**1**
9: 3-OCH_3-2′,3′,4′,5′,6′-d_5-**1**
10: 3-OCD_3-2′,3′,4′,5′,6′-d_5-**1**
11: 7-Br-**1**
12: 4′-Br-**1**



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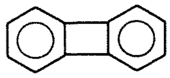

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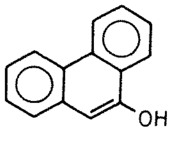

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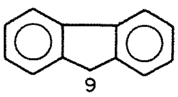

16

17: 9-OH-**16**
18: 9-OCH_3-**16**
19: 9-OCD_3-**16**
20: 9-O-**16**

RESULTS AND DISCUSSION

In order to obtain further evidence supporting the structure of the [dibenzo-β-tropolone $-$ H]$^+$ ion originating after electron impact induced loss of an hydrogen atom from the *B*-ring of flavone (**1**), followed by cleavage of the central ring (Scheme 1) and subsequent recyclization to the tricyclic species, a detailed mass spectral study of dibenzo-β-tropolone[2] (5,7-dioxo-6,7-dihydro-5*H*-dibenzo[*a*,*c*]cycloheptane-(**13**)) was performed. The spectra depicted in Fig. 1 clearly show that both flavone (**1**) and dibenzo-β-tropolone (**13**) give rise to $[M-1]^+$ ions at *m/z* 221, although with different intensities. This is due to the fact that in **13** the major fragmentation process is the

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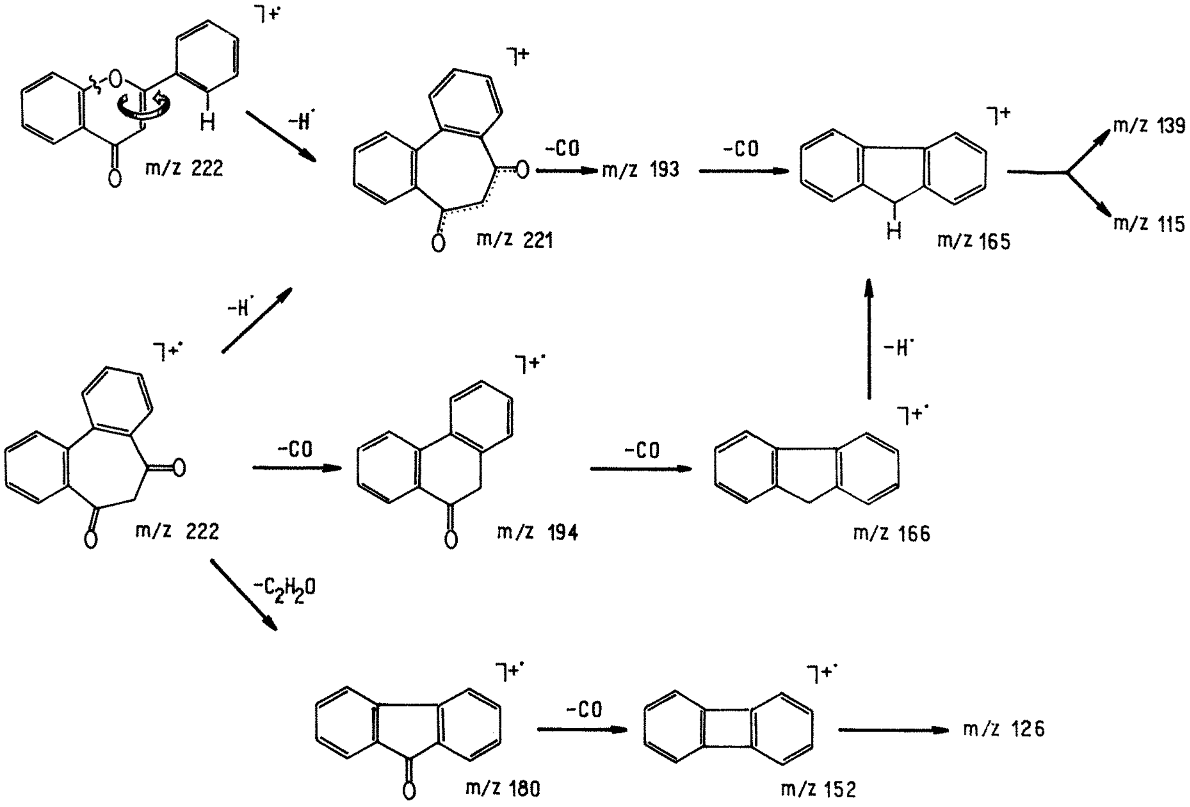


Scheme 1

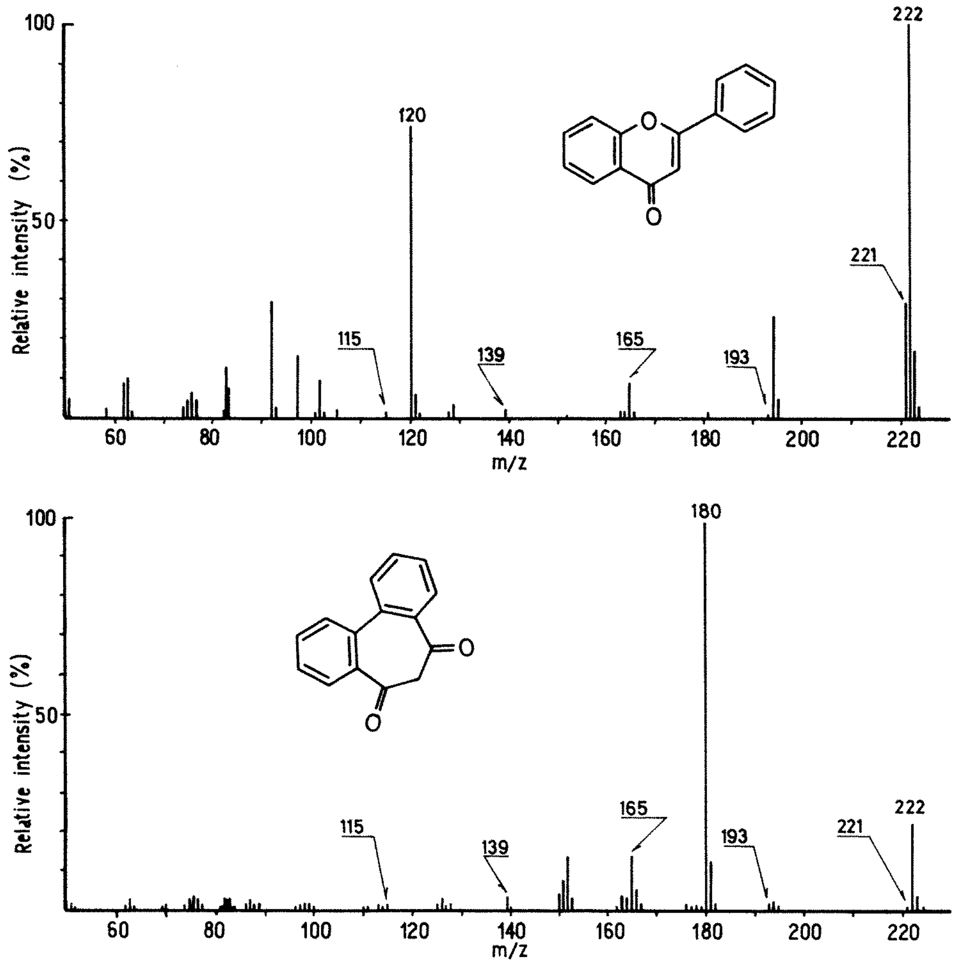


Figure 1. Mass spectra of flavone (**1**) and dibenzo-β-tropolone (**13**).

expulsion of kethene, thus providing the very stable (100%) ion at *m/z* 180.

Furthermore, the use of a linked scan of the deflection voltage and of the magnetic field, either in the search for daughter ions or for parent ions, shows that for dibenzo-β-tropolone (**13**) the sequence $[M-H]^+ \rightarrow [M-H-CO]^+ \rightarrow [M-H-CO-CO]^+ \rightarrow [M-H-CO-CO-C_2H_2]^+$, which corresponds to the peaks at *m/z* 221 → 193 → 165 → 139, is present, as well as the fragmentation *m/z* 165 → 115. These data are in excellent agreement with those corresponding to the same transitions in the mass spectrum of flavone (**1**) as can be seen in Fig. 2. Therefore the fragmentation subspectrum corresponding to this sequence in dibenzo-β-tropolone (**13**) has been located in that of flavone (**1**).

At this point it seems necessary to define the concept 'mass subspectrum'. This indicates cases where the peaks due to a fragmentation route in a given compound are found in the spectrum of another molecule.

In addition, the first elimination of a CO residue in dibenzo-β-tropolone (**13**) produces the ion at *m/z* 194, which is the keto form of 9-phenanthrol (**15**). This is further substantiated by the study of **15**, in which the sequences $[M]^{+\cdot} \rightarrow [M-CO]^+$ and $[M-H]^+ \rightarrow [M-H-CO]^+ \rightarrow [M-H-CO-C_2H_2]^+$ corresponding to peaks at *m/z* 194 → 166 and 193 → 165 → 139 are present, as is also the fragmentation *m/z* 165 → 115. Also, the $[\text{fluorene}-H]^+$ subspectrum, responsible for the fragmentations *m/z* 165 → 139 and *m/z* 165 → 115 in fluorene (**16**), is placed in those of flavone (**1**) and of dibenzo-β-tropolone (**13**).

Although the original work reported the metastable decompositions of flavone (**1**) and their tetradeutero (**3**) and pentadeutero (**4**) analogues, the study of 3-deuteroflavone (**2**) was still missing. Thus, linked scan measurements of the latter also showed the presence of the fragmentation route $[M]^{+\cdot} \rightarrow [M-H]^+ \rightarrow [M-H-CO]^+ \rightarrow [M-H-CO-CO]^+$, corresponding to *m/z* 223 → 222 → 194 → 166.

The combined evidence herein presented further confirms the structure of the $[M-H]^+$ ion derived from flavone (**1**), as shown in Scheme 1. The extension of this mechanism to other flavones has already been suggested by us. It is now further substantiated for the most significant case, that of 3-methoxyflavone (**7**).

The fragments corresponding to 3-methoxyflavone (**7**) and to its 3-trideuteromethoxy analogue (**8**) have already been reported.[1] In addition, we now prepared 3 methoxy 2′,3′,4′,5′,6′ pentadeuteroflavone (**9**) and 3 trideuteromethoxy-2′,3′,4′,5′,6′-pentadeuteroflavone (**10**) and performed mass spectral studies on the four molecules.

Linked scan measurements of the metastable transitions of 3-methoxyflavone (**7**) provided evidence for the existence of the sequence $[M]^{+\cdot} \rightarrow [M-H]^+ \rightarrow [M-H-CO]^+ \rightarrow [M-H-CO-CO]^+$, corresponding to ions at *m/z* 252 → 251 → 223 → 195, the composition of the ions being verified by high-resolution measurements. In other words, after initial expulsion of an H, there are two successive eliminations of CO to provide fragment *a* in Scheme 2. This postulation is further consistent with the metastable transitions of the three deuteriated analogues (**8–10**) of 3-methoxyflavone (**7**). Thus, for 3-trideuteromethoxyflavone (**8**) the sequence *m/z* 255 → 254 → 225 → 198 → 180 → 152 → 126 is evident,

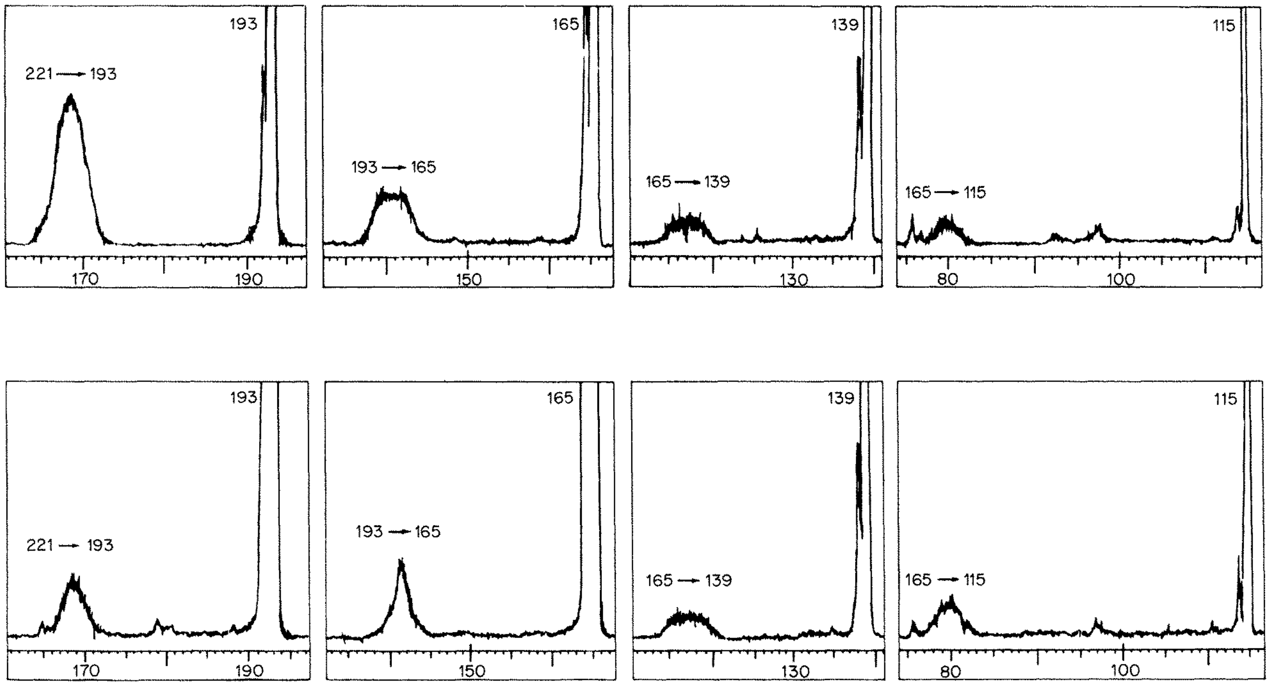
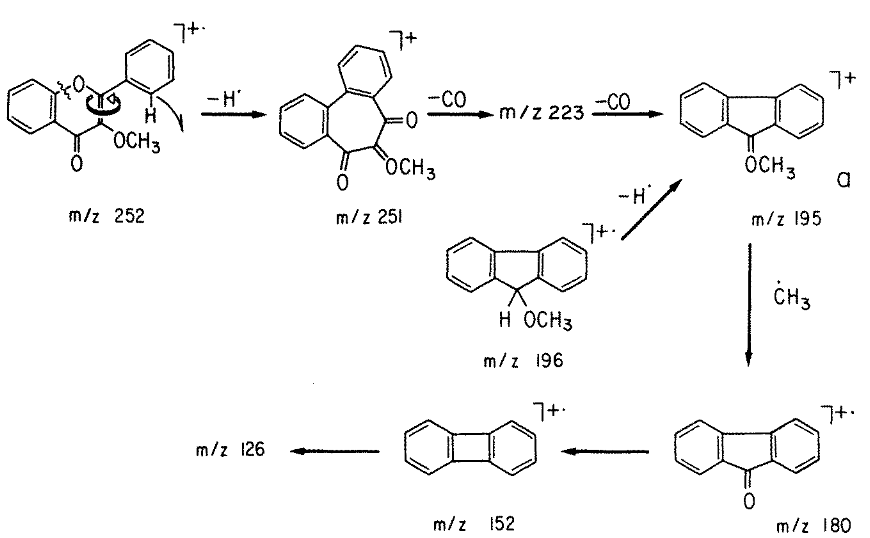


Figure 2. B^2/E scans for the ions at *m/z* 193, 165, 139 and 115 of (a) flavone (**1**) and (b) dibenzo-β-tropolone (**13**). On the MAT-112 these transitions are calculated for the reaction $m_1 \rightarrow m_2$ as $m_1 = m_2(M_2/M_1)$, where m = nominal value of focused ion and M_1 = value read on the spectrum.



Scheme 2

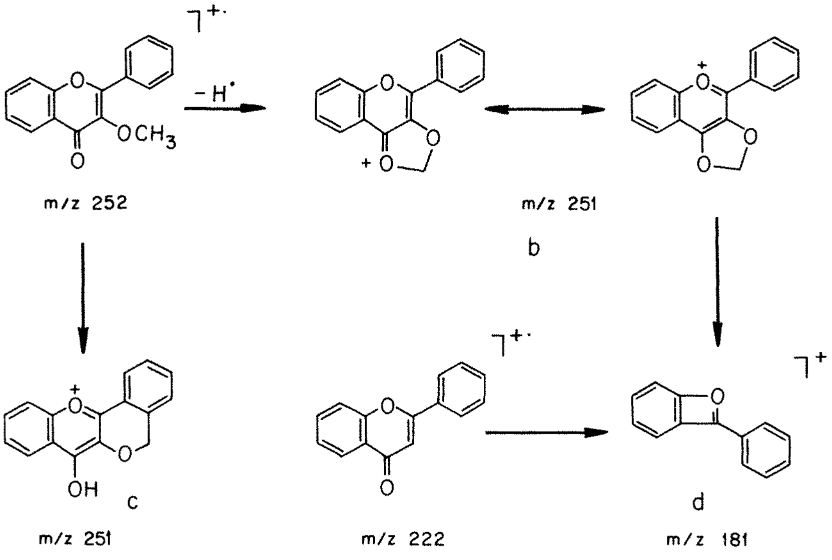
for 3-methoxy-2′,3′,4′,5′,6′-pentadeuteroflavone (**9**) the sequence *m/z* 257→255→227→199→184 and for 3 trideuteromethoxy 2′,3′,4′,5′,6′-pentadeuteroflavone (**10**) the sequence *m/z* 260→258→230→202→184. These data indicate that a more complete representation of the fragmentation route involving the $[M-H]^{+\cdot}$ in 3-methoxyflavone (**7**) can be summarized as the sequence $[M]^{+\cdot}\rightarrow[M-H]^{+}\rightarrow[M-H-CO]^{+}\rightarrow[M-H-CO-CO]^{+}\rightarrow[M-H-CO-CO-CH_3]^{+}\rightarrow[M-H-CO-CO-CH_3-CO]^{+}\rightarrow[M-H-CO-CO-CH_3-CO-C_2H_2]^{+}$, indicated in Scheme 2. The elemental composition of the ions is given in the Experimental section.

In order to further substantiate the decomposition of the fragment labelled as *a* in Scheme 2, which appears at *m/z* 195 in the spectrum of 3-methoxyflavone (**7**) and at *m/z* 198 from 3-trideuteromethoxyflavone (**8**), samples of 9-methoxyfluorene (**18**) and 9-trideuteromethoxyfluorene (**19**) were prepared. Linked scan measurements of these two molecules gave the sequence *m/z* 195→180→152 for **18** and 198→180→152 for **19**, corresponding to $[M-H]^{+}\rightarrow[M-H-CH_3]^{+}\rightarrow[M-H-CH_3-CO]^{+}$ and $[M-H]^{+}\rightarrow[M-H-CD_3]^{+}\rightarrow[M-H-CD_3-CO]^{+}$, respectively.

Since the peak at *m/z* 180 corresponds to the molecular ion of fluorenone (**20**), the metastable decompositions of this tricyclic ketone were also recorded, showing the existence of the sequence $[M]^{+\cdot}\rightarrow[M-CO]^{+}\rightarrow[M-CO-C_2H_2]^{+}$ at *m/z* 180→152→126. Finally, for the evaluation of the peak at *m/z* 152, the data of biphenylene (**14**)[3] were also measured, thus showing the transition $[M]^{+\cdot}\rightarrow[M-C_2H_2]^{+}$ at *m/z* 152→126.

The combined evidence herein presented demonstrates that Scheme 2 corresponds to the mass spectral fragmentation route of 3-methoxyflavone (**7**) involving the [dibenzo-β-tropolone − H]$^{+}$ intermediate.

It was proposed sometime ago[4] that for 3-methoxyflavones the H atom is lost from the methoxyl group. Thus, it was formulated that the ionized CO group displaces an H atom with the formation of the stabilized intermediate *b*, as shown in Scheme 3. This assumption was later rejected[5], based on the fact that



Scheme 3

Table 1. Low-resolution ion intensities in the vicinity of the molecular ion of 3-methoxyflavones at 70 eV

Compound	$[M]^{+\cdot}$	$[M-1]^+$	$[M-2]^+$
7	69.4	100	—
8	63.0	100	5.5
9	53.6	26.4	100
10	52.9	24.0	100

perdeuteromethylated flavanols do not provide a comparable $[M-D]^+$ and that a $[M-H]^+$ was still present. However, no detailed intensity data for the corresponding $[M-H]^+$ and $[M-D]^+$ ions were provided. The formation of the $[M-H]^+$ ions in these molecules was then attributed to the probable loss of an aromatic proton and its structure was therefore formulated as the tetracyclic species *c*.

Table 1 summarizes the data corresponding to the loss of an hydrogen or a deuterium atom in 3-methoxyflavone (**7**) and its deuterated analogues (**8**–**10**). It can be seen that deuteration of the methoxyl group (**7** to **8**) produces an approximate ratio of 24:1 of $[M-H]^+$ to $[M-D]^+$ ions, suggesting that the methylenedioxy-containing ions (*b* in Scheme 3) contribute moderately to the overall picture. In contrast, deuteration at the *B*-ring of 3-methoxyflavone (**7** to **9**) gives rise to an 1:4 ratio of $[M-1]^+$ to $[M-2]^+$ ions, indicating that the loss of an aromatic hydrogen is indeed a major fragmentation route. However, this aromatic hydrogen loss is mainly responsible for the [dibenzo-β-tropolone $-$ H]$^+$ species (Scheme 2) since the change of a OCH_3 for a OCD_3 (**9** to **10**) is accompanied by a very small modification of the $[M-1]^+$ to $[M-2]^+$ ion ratio. Thus, it seems clear that the contribution of the tetracyclic species *c* to the overall peak at $[M-1]^+$ is limited, that of the methylenedioxy-containing ions (*b* in Scheme 3) is moderate and the one corresponding to the [dibenzo-β-tropolone-H]$^+$ ion appears to be the major one.

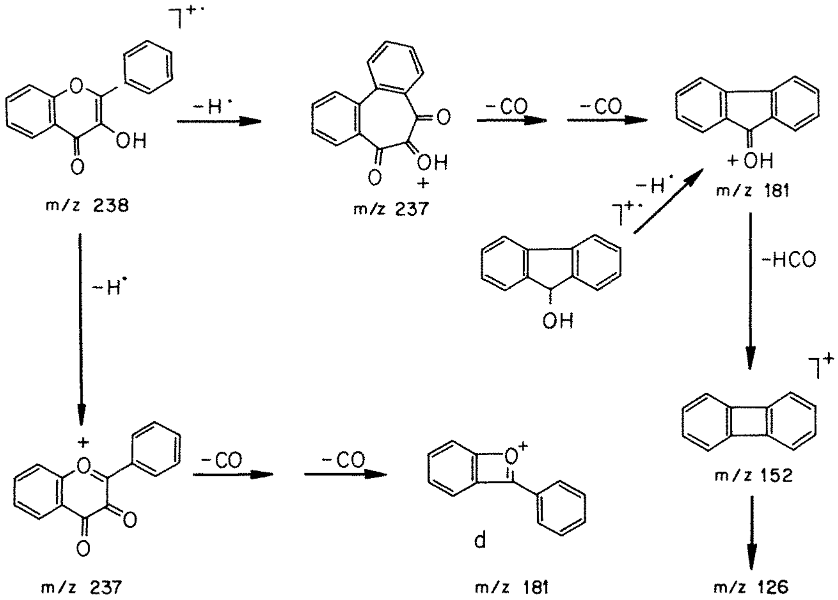
As a consequence of the above results, it was decided to look for additional evidence supporting the moderately important route, that is responsible for the ion labelled as *b* in Scheme 3. A low-intensity (3.2%) fragment at *m/z* 181 in the mass spectrum of 3-methoxyflavone (**7**) turned out to be informative in this respect. Linked scan measurements provided evidence that the ion at *m/z* 181 originates from the $[M-1]^+$ ion at *m/z* 251 and from the $[M-43]^+$ at *m/z* 209, the latter fragment already being reported[4] as $[M-(CH_3+CO)]^+$ or as $[M-CH_3CO]^+$.

An exhaustive analysis of linked scans and high-resolution measurements on several compounds provided the transition $[M-H]^+ \rightarrow [M-H-C_3H_2O_2]^+$ for 3-methoxyflavone (**7**) corresponding to *m/z* 251→181, the transition $[M-D]^+ \rightarrow [M-D-C_3D_2O_2]^+$ corresponding to *m/z* 253→181 in the case of 3-trideuteromethoxyflavone (**8**), the transition $[M-H]^+ \rightarrow [M-H-C_3H_2O_2]^+$ with values 256→186 for 3-methoxy-2′,3′,4′,5′,6′-pentadeuteroflavone (**9**) and $[M-D]^+ \rightarrow [M-D-C_3D_2O_2]^+$ at *m/z* 258→186 in 3-trideutero-2′,3′,4′,5′,6′-pentadeuteroflavone (**10**). In the case of **10** this was also verified by Accelerating Voltage Scan (AVS) in the first field-free sector of the spectrometer, between the accelerating potential and the magnetic field, and in the second field-free sector, between the magnetic field, and the electrostatic sector, by use of the direct analysis of daughter ions (DADI) technique. The loss of 70 atomic mass units ($C_3H_2O_2$) or 72u ($C_3D_2O_2$) from fragments $[M-H]^+$ or $[M-D]^+$ in compounds **7**–**10** points toward the postulation of a [2-phenylbenzoxetane $-$ 1]$^+$ fragment as represented by *d* in Scheme 3.

Further evidence in support of ion *d* became evident from the mass spectral studies of other flavones. Thus, in the case of the parent molecule (**1**) there is also a low-intensity (1.2%) ion at *m/z* 181, which after high-resolution measurements was shown to have the composition $C_{13}H_9O$. Linked scan measurements to find the origin of this ion indicated that it arises directly from the molecular ion at *m/z* 222 by the uncommon loss of 41u. Similarly, measurements in 3-deuteroflavone (**2**) showed the transition 223 ($[M]^{+\cdot}$) → 181 ($[M-42]^+$), 5,6,7,8-tetradeuteroflavone (**3**) gave 226 ($[M]^{+\cdot}$) → 185 ($[M-41]^+$), 2′,3′,4′,5′,6′-pentadeuteroflavone (**4**) gave 227 ($[M]^{+\cdot}$) → 186 ($[M-41]^+$), 7-bromoflavone (**11**) gave 300 ($[M]^{+\cdot}$) → 259 × ($[M-41)$ and 4′-bromoflavone (**12**) also gave 300 ($[M])^{+\cdot}$ → 259 × ($[M-41]^+$). In the case of the bromoflavones (**11** and **12**) these transitions were also verified by AVS and DADI measurements.

Final evidence for the existence of a fragment of type *d* was obtained after careful study of 3-hydroxyflavone (flavanol (**5**)) and 3-hydroxy-2′,3′,4′,5′,6′-pentadueteroflavone (**6**). Comparison of the low-resolution data of **5** and **6** shows that for the initial loss of an hydrogen atom there are two competitive fragmentations. In these compounds the uncommon elimination[4] of the hydroxyl proton appears to occur to an extent of approximately 40%, and the loss of an aromatic proton from the *B*-ring of some 60%. These numbers are estimated taking into account the ion at *m/z* 241 (71%) in the mass spectrum of **6**, and making the pertinent isotope corrections. A more precise picture for the two competitive fragmentation processes involving the two structurally different $[M-H]^+$ ions was obtained from linked scan measurements.

In the case of 3-hydroxyflavone (**5**) the sequence $[M]^{+\cdot} \rightarrow [M-H]^+ \rightarrow [M-H-CO]^+ \rightarrow [M-H-CO-CO]^+ \rightarrow [M-H-CO-CO-HCO]^+ \rightarrow [M-H-CO-CO-HCO-C_2H_2]^+$ with values at *m/z* 238→237→209→181→152→126 became evident from the corresponding metastable transitions. This points to a route involving the corresponding [dibenzo-β-tropolone $-$ H]$^+$ ion, which was further tested from the data of 9-fluorenol (**17**). In the latter compound, on the one hand the hydroxyl group is lost to provide the [fluorene $-$ H]$^+$ ion (*m/z* 165) as evidenced by the metastable transition $[M]^{+\cdot} \rightarrow [M-OH]^+$ corresponding to *m/z* 182→165. The ion at *m/z* 165 further behaves as in the case represented in Scheme 1 since the transitions *m/z* 165→139 and



Scheme 4

165→115 are present. On the other hand, the benzylic hydrogen atom at C(9) in 9-fluorenol (**17**) is lost, since the sequence $[M]^{+\cdot} \rightarrow [M-H]^+ \rightarrow [M-H-HCO]^+ \rightarrow [M-H-HCO-C_2H_2]^+$ with values at *m/z* 182→181→152→126 was tested from the corresponding metastable transitions. The last transition is in agreement with that displayed in the mass spectrum of biphenylene (**14**).

The data of 3-hydroxy-2′,3′,4′,5′,6′-pentadeuteroflavone (**6**) were particularly informative for the [2-phenylbenzoxetane − 1]$^+$ ion. In compound **6** the transitions corresponding to the [dibenzo-*β*-tropolone − 1]$^+$ ion described for **5** are shifted by 4u after the initial formation of the corresponding [dibenzo-*β*-tropolone − 2]$^+$ ion. In addition, there is also an $[M-H]^+$ ion that decomposes by the successive expulsion of two CO residues. This $[M-1]^+$ is attributed to the already postulated[4] *α*-diketone species (Scheme 4) which finally leads to the ion *d*. An alternative structure for the ion at *m/z* 237, having an oxygen-protonated furan ring resulting from the loss of an hydrogen from C(2′) or C(6′), seems unlikely. This is due to the lack of further straightforward fragments in the mass spectra of flavonol (**5**) and of the deuterated moelcule **6**.

EXPERIMENTAL

Materials

Flavone (**1**), its deuterated analogues **3** and **4**, 7-bromo- (**11**) and 4′-bromo-flavone (**12**), 3-methoxy- (**7**) and 3-trideuteromethoxy-flavone (**8**) were available from previous NMR[6,7] and mass spectral[1] studies. 3-Deuteroflavone (**2**) was obtained by SeO_2 oxidation of 3,3′-dideuteroflavanone, which in turn was prepared by deuteration of commercially available flavanone with MeOD catalysed by TsOH. 3-Hydroxyflavone (**5**) was prepared by alkaline condensation of 2-hydroxyacetophenone with benzaldehyde, followed by hydrogen peroxide oxidation.[8] A similar reaction was performed for the preparation of 3-hydroxy-2′,3′,4′,5′,6′-pentadeuteroflavone (**6**) utilizing 2,3,4,5,6-pentadeuterobenzaldehyde, which in turn was obtained by Grignard reaction of pentadeuterobromobenzene with triethyl orthoformate.[9] Methylation of 3-hydroxy-2′,3′,4′,5′,6′-pentadeuteroflavone (**6**) with iodomethane or with trideuteroiodomethane in the presence of sodium gave 3-methoxy-2′,3′,4′,5′,6′-pentadeuteroflavone (**9**) and 3-trideuteromethoxy-2′,3′,4′,5′,6′-pentadeuteroflavone (**10**), respectively. Dibenzo-*β*-tropolone (**13**) was provided[12] by Prof. Ried (University of Frankfurt), while biphenylene (**14**), 9-phenanthrol (**15**), 9-fluorenol (**17**) and fluorenone (**20**) were commercially available. 9-Methoxyfluorene (**18**) and 9-trideuteromethoxyfluorene (**19**) were prepared by treatment of 9-fluorenol (**17**) with iodomethane and trideuteroiodomethane, respectively, in the presence of sodium. All new compounds (**2**, **5**, **6**, **10**, **18** and **19**) were characterized by ^1H NMR measurements at 90 MHz and their purities verified by thin-layer chromatography.

Methods

All mass spectra were determined using a Varian MAT 112S spectrometer operated at 70 eV and 0.7 mA. For the search for daughter ions during metastable decompositions, the scan of the magnetic field strength (*B*) and the voltage of the electrostatic analyzer (*E*) were linked to maintain constant the ratio *B*/*E*. Alternatively, the daughter ion search was also performed in the second field-free region of the spectrometer, that is, after the magnetic field and previous to the electrostatic sector, by use of the DADI technique. For the search for parent ions, the relation B^2/E was maintained constant, or alternatively, Accelerating Voltage Scan (AVS) in the first field-free sector, between the accelerating potential and the magnetic field, was employed. The high-resolution measurements were performed with peak matching at a resolution better than 6000 in the 10% valley definition and with an error smaller than 20 ppm. The ion source was carefully equilibrated with deuterium oxide immediately prior to the introduction of deuterated molecules. The ion source was always kept at 200 °C and the absolute pressure was lower than 2×10^{-6} Torr. Direct sample inlet between 40 and 150 °C was used.

Mass spectral data

Those data corresponding to compounds **1**, **3**, **4**, **7**, **8**, **11**, **12** and **16** were reported previously,[1] except the high-resolution data of **7** and **8**. Ions of intensity less than 2% are not tabulated except in those cases in which they are of specific interest.

3-Deuteroflavone (2). *m/z* (% relative abundance): 225(2.6), 224(17.0), $[M]^{+\cdot}$ 223(100.0), 222(26.9), 221(2.0), 196(4.0), 195(26.3), 194(2.0), 181(1.2), 166(7.9), 165(3.2), 152(1.2), 140(2.6), 139(1.2), 129(2.6), 122(2.0), 121(6.9), 120(90.9), 105(2.0), 104(2.0), 103(11.9), 102(2.0), 98(4.6), 97.5(19.0), 93(3.0), 92(32.8), 91(2.0), 90(2.6), 88(2.0), 83.5(2.0), 83(8.5), 82.5(9.9), 82(4.0), 78(2.0), 77(8.9), 76(5.9), 75(4.6), 74(2.0), 71(2.0), 70.5(2.0), 70(3.0), 69.5(2.0), 65(3.0), 64(16.4), 63(10.5), 62(2.6), 53(2.6), 52(3.0), 51(4.9).

3-Hydroxyflavone (5). *m/z* (% relative abundance): 240(2.1), 239(17.2), $[M]^{+\cdot}$ 238(100), 237(86.2), 210(4.9), 209(3.2), 182(2.8), 181(12.4), 165(1.9), 153(3.9), 152(5.8), 121(3.9), 120(1.6), 119(7.3), 105(12.5), 104(3.2), 93(2.8), 92(4.4), 90(3.2), 89(5.4), 77(16.3), 76(7.0), 75(2.1), 65(3.6), 64(4.1), 63(4.7), 51(7.5).

3-Hydroxy-2′,3′,4′,5′,6′-pentadeuteroflavone (6). *m/z* (% relative abundance): 245(3.5), 244(18.2), $[M]^{+\cdot}$ 243(100), 242(41.2), 241(71.1), 240(5.8), 215(8.0), 214(3.5), 187(2.3), 186(10.6), 185(14.2), 170(2.3), 169(2.3), 158(3.4), 157(6.0), 156(5.3), 155(2.6), 123(3.5), 122(4.8), 121.5(8.8), 121(4.4), 120(2.8), 110(5.3), 109(3.5), 108(2.3), 107.5(7.6), 107(2.3), 106(2.6), 105(2.3), 104(4.1), 95(3.5), 94(6.4), 93(6.4), 92(6.0), 83(2.3), 82(15.4), 81(4.4), 78(5.3), 77(4.1), 76(7.1), 66(5.8), 65(4.4), 64(4.1), 63(3.5), 62(2.3), 54(6.4), 51(3.5).

3-Methoxyflavone (7). *m/z* (composition): 223.0741 ($[C_{15}H_{11}O_2]^+$), 209.0595 ($[C_{14}H_9O_2]^+$), 195.0788 ($[C_{14}H_{11}O]^+$), 181.0631 ($[C_{13}H_9O]^+$), 180.0542 ($[C_{13}H_8O]^+$), 152.0620 ($[C_{12}H_8]^+$).

3-Trideuteromethoxyflavone (8). *m/z* (composition): 181.0652 ($[C_{13}H_9O]^+$).

3-Methoxy-2′,3′,4′,5′,6′-pentadeuteroflavone (9). *m/z* (% relative abundance): 259(2.2), 258(9.3), $[M]^{+\cdot}$ 257(53.6), 256(26.4), 255(100), 254(5.9), 242(2.0), 241(3.0), 240(4.4), 239(9.3), 238(6.8), 237(9.0), 236(2.7), 228(6.8), 227(7.6), 226(3.9), 225(15.8), 224(2.2), 214(7.3), 213(2.2), 211(2.7), 210(3.9), 209(3.4), 200(2.2), 199(11.0), 187(2.2), 186(10.2), 185(2.2), 183(2.9), 182(2.5), 181(2.2), 171(3.9), 170(5.1), 169(3.9), 168(2.2), 158(2.5), 157(6.8), 156(7.1), 155(2.7), 154(2.2), 134(5.6), 129(2.2), 128.5(7.8), 127(4.4), 126.5(12.4), 126(5.1), 122(3.7), 121(14.4), 120(30.5), 114.5(2.2), 111(2.0), 110(13.6), 108(2.2), 107(3.9), 106(2.2), 105(2.5), 104(2.7), 94(12.2), 93(2.5), 92(13.6), 91(2.2), 85(2.2), 84(2.5), 83(2.7), 82(34.4), 81(2.5), 80(2.0), 78(3.9), 77(2.7), 76(6.4), 75(2.7), 74(2.0), 66(7.6), 64(5.4), 63(3.9), 54(8.3); *m/z* (composition: 186.0961 ($[C_{13}H_4D_5O]^+$).

3-Trideuteromethoxy-2′,3′,4′,5′,6′-pentadeuteroflavone (10). *m/z* (% relative abundance): 262(2.1), 261(10.4), $[M]^{+\cdot}$ 260(52.9), 259(24.0), 258(100), 257(5.8), 242(6.4), 241(3.3), 240(17.0), 239(2.1), 238(11.6), 231(2.1), 230(8.8), 229(2.1), 228(3.6), 227(3.3), 226(14.0), 215(2.1), 214(11.6), 213(1.8), 212(2.6), 211(3.3), 210(5.0), 202(5.0), 210(20.1), 200(9.9), 199(2.0), 187(2.0), 186(13.5), 185(2.6), 184(2.6), 183(2.6), 174(2.6), 172(2.0), 171(5.0), 170(6.6), 158(4.8), 157(12.1), 156(8.8), 155(4.1), 134(7.4), 131(2.6), 130(7.4), 128.5(2.1), 128(11.2), 123(2.1), 122(14.9), 121(4.1), 120(33.1), 110(25.1), 109(4.1), 106(3.6), 104(4.6), 95(2.5), 94(19.0), 93(3.3), 92(18.2), 84(2.5), 83(4.1), 82(41.3), 81(4.6), 78(5.0), 76(14.9), 75(4.3), 74(2.6), 66(11.9), 64(9.6), 63(5.9), 62(2.5), 54(17.5), 53(2.8), 52(2.8), 51(2.6); *m/z* (composition): 186.0982 ($[C_{13}H_4D_5O]^+$).

Dibenzo-β-tropolone (13). *M/z* (% relative abundance): 224(0.4), 223(3.4), $[M]^{+\cdot}$ 222(21.9), 221(0.4), 195(0.4), 194(1.7), 193(1.2), 181(10.6), 180(100.0), 166(4.8), 165(14.5), 164(2.8), 163(3.4), 152(13.1), 151(7.3), 150(3.7), 139(2.3), 126(2.8), 115(0.9), 83(2.1), 82(2.3), 76(2.8), 75(2.1), 63(2.5).

Biphenylene (14). *m/z* (% relative abundance): 154(1.2), 153(9.9), $[M]^{+\cdot}$ 152(100), 151(33.9), 150(15.3), 126(7.5), 76(10.6), 75(7.8), 74(3.7), 63(4.5).

9-Phenanthrol (15). *m/z* (% relative abundance): 196(1.8), 195(15.7), $[M]^{+\cdot}$ 194(100.0), 193(1.8), 180(1.4), 178(4.2), 167(4.6), 166(31.9), 165(63.3), 164(10.1), 163(10.4), 139(4.6), 115(3.5), 113(2.1), 97(7.4), 89(2.8), 88(2.2), 87(3.2), 86(2.2), 83.5(2.1), 83(11.5), 82.5(13.3), 82(16.0), 81.5(7.8), 81(3.6), 76(2.0), 75(2.2), 74(2.2), 70(2.1), 69.5(7.4), 69(2.2), 63(4.6), 62(2.2), 51(2.2).

9-Fluorenol (17). *m/z* (% relative abundance): 184(2.0), 183(13.1), $[M]^{+\cdot}$ 182(94.3), 181(100.0), 180(3.6), 166(3.5), 165(14.3), 164(3.0), 163(4.7), 154(3.8), 153(18.2), 152(30.8), 151(9.0), 150(3.5), 138(2.3), 126(3.3), 125(3.0), 114(2.0), 90(7.8), 89.5(9.0), 86(2.1), 81.5(3.2), 81(4.7), 80.5(3.2), 76(5.1), 75.5(5.0), 75(18.5), 74.5(3.3), 74(4.5), 73(3.5), 69(3.0), 63(2.1), 62(6.0), 61(2.3), 51(3.5).

9-Methoxyfluorene (18). *m/z* (% relative abundance): 198(1.9), 197(12.2), $[M]^{+\cdot}$ 196(64.7), 195(32.8), 182(8.4), 181(35.6), 180(16.0), 167(2.8), 166(16.9), 165(100.0), 164(12.9), 163(15.9), 162(3.2), 154(3.2), 153(18.8), 152(28.1), 151(8.4), 150(4.3), 139(7.5), 138(2.8), 137(2.8), 127(3.2), 126(5.1), 115(5.6), 113(3.2), 111(2.4), 110(2.8), 102(2.2), 101(2.2), 99(2.8), 98(4.1), 91(2.8), 90.5(2.8), 89(3.4), 88(2.8), 87(4.3), 86(3.2), 83(4.7), 82.5(19.3), 82(7.5), 81.5(8.8), 81(4.7), 77(3.2), 76.5(2.8), 76(8.4), 75.5(2.8), 75(4.3), 74(3.7), 70(2.8), 69.5(9.4), 69(2.4), 63(7.5), 57(2.4), 51(3.6).

9-Trideuteromethoxyfluorene (19). *m/z* (% relative abundance): 201(1.7), 200(16.1), $[M]^{+\cdot}$ 199(100.0), 198(44.9), 182(9.2), 181(30.3), 180(12.4), 166(13.2), 165(81.0), 164(7.8), 163(11.1), 162(2.0), 154(2.8), 153(13.2), 152(17.9), 151(6.5), 150(2.1), 139(4.0), 126(2.5), 99.5(5.0), 87(2.5), 83.5(3.0), 83(14.8), 82.5(4.7), 82(4.3), 76.5(3.0), 76(8.2), 75(2.4), 69.5(6.1), 63(3.4).

Fluorenone (20). *m/z* (% relative abundance): 182(2.0), 181(15.4), $[M]^{+\cdot}$ 180(100), 165(2.2), 153(7.0), 152(45.0), 151(23.1), 150(15.2), 149(2.2), 126(8.3), 125(3.3), 102(3.3), 101(2.2), 100(2.0), 99(4.2), 98(4.2), 90(4.2), 87(3.3), 86(2.9), 77(2.9), 76.5(3.3), 76(22.6), 75.5(4.0), 75(8.8), 74(5.5), 63(11.0), 62(3.7), 61(2.2), 51(4.0).

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