Tetrahedron Vol. 27, pp 2691 to 2700 Pergamon Press 1971. Printed in Great Britain

# MASS SPECTROMETRY OF ORGANIC COMPOUNDS—VI*

## ELECTRON-IMPACT SPECTRA OF FLAVONOID COMPOUNDS

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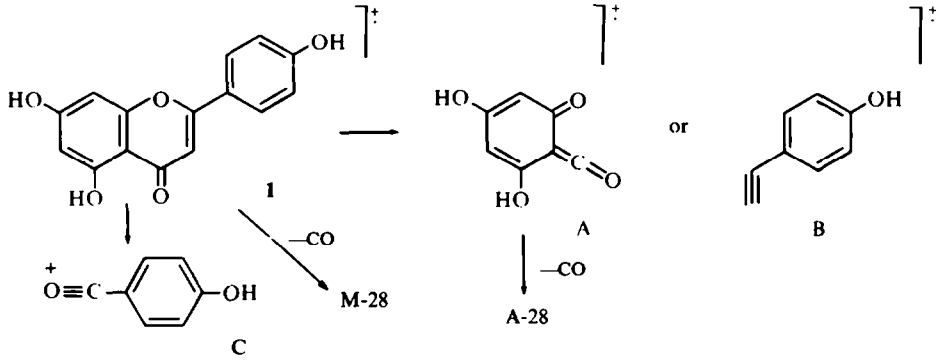
(*Received in USA* 18 *March* 1971; *Received in the UK for publication* 30 *March* 1971)

**Abstract**—The mass spectra of some simple flavones, flavonols, and their permethyl ethers have been examined. A new fragmentation pathway of 6-methoxyflavones is discussed, and the formation of $(M—H)^+$ and $(M—H_3O)^+$ ions is discussed. It is shown that significant structural information can be obtained from the mass spectra of polyhydroxyflavones and their ethers.

### INTRODUCTION

THE mass spectra of flavonoid compounds have been discussed in a number of recent papers.[2–9] and in this paper I wish to summarize these earlier results and to extend them to include some recent results from this laboratory which indicate that mass spectrometry is a suitable tool for partial structure identification of flavones and their methyl ethers. The discussion which follows has been restricted to the spectra of the flavones, the flavonols (3-hydroxyflavones), and their ether derivatives.

Flavones do not possess a site of facile bond rupture, and hence the molecular ion is always an intense ion in the mass spectrum of these compounds. Flavones with fewer than four OH groups show ions of moderate intensity due to the retro-Diels-Alder (RDA) reaction.[2–6] as illustrated below for the case of apigenin (1).[2] I have adopted Audier's convention[5] of referring to the RDA fragments containing ring A




SCHEME 1

* For Part V, see Ref. 1.

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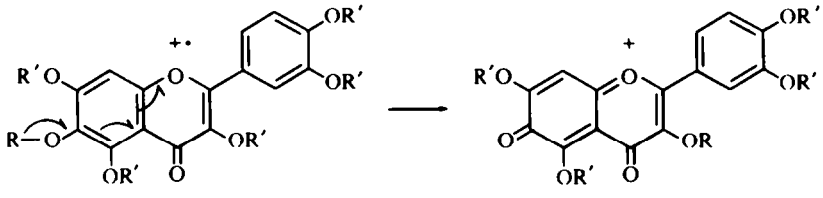
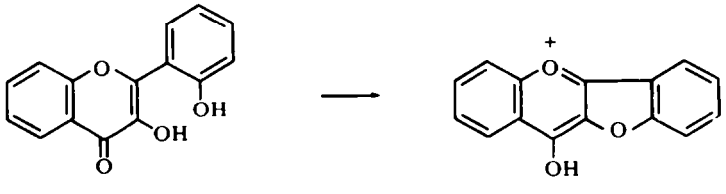
and ring C as A and B respectively. Other significant fragmentation modes of simple flavones include the formation of an (M-1) ion "of uncertain origin," an (M-CO) ion, an (A-CO) ion, and an aroyl cation C composed of ring C and a carbonyl group from ring B. This ion is especially significant in the spectra of the 3-hydroxyflavones. Flavones containing an OH group in ring C also show an ion D with mass A + 1. Finally, as would be expected for such highly aromatic compounds, substantial peaks due to doubly charged ions are frequently observed.

The situation with the simple flavones is thus that fragmentation proceeds by well-defined pathways to yield relatively simple spectra which may be interpreted to indicate the number of substituents on rings A, B and C. Unfortunately the position with more highly substituted flavones is more complex, a situation which has led some authors to comment that "little structural information may be culled from mass spectra in this [highly oxygenated] series."[4] The useful diagnostic RDA fragmentation is almost entirely absent in the spectra of flavones with four or more oxygen substituents[7] (OH or OMe groups), and the spectra are dominated by such ions as the molecular ion, the (M-15) ion, the (M-28) ion, and the (M-43) ion. However, two useful correlations have been developed for special cases. The mass spectra of derivatives of quercetagetin **2** have been shown to yield an intense ion corresponding to loss of the substituent R from the O atom at C-6, presumably because the



**2**: R, R′ = H or $CH_3$ **3**

product ion **3** is well-stabilised.[7] Such stabilisation could in principle also apply to flavones substituted at C-8 and C-3, but Bowie and Cameron show that OMe substituents at C-3 are eliminated preferentially as an acetyl radical (either in a concerted or stepwise fashion), and they suggest that this elimination is diagnostic for an OMe group at C-3 in O-alkylquercetagetin derivatives. Secondly, 2′,3-dihydroxyflavone **4** was shown to lose 17 mass units to give as its base peak an ion of postulated structure **5**.[8] suggesting that this fragmentation might be diagnostic for 2′,3-dihydroxyflavones.



**4** **5**

Finally, the question of water loss from flavones bearing OMe groups in the 5-position has been studied.[9] It was shown that while all flavones with a 5-OMe group exhibited

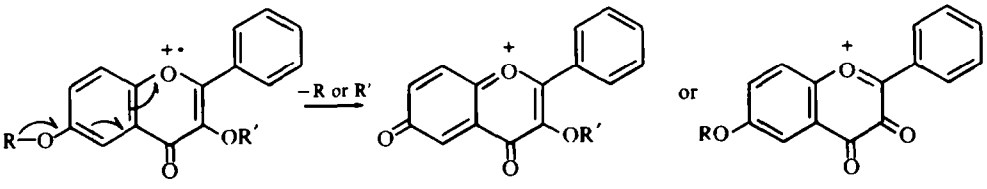
(M-17) and (M-18) peaks. a sufficient number of flavones *without* this group also showed significant loss of 17 and 18 mass units to vitiate a simple "*ortho*-effect" explanation of the phenomenon in these complex situations.

In summary. while much is known about the fragmentation pathways of the simpler flavones. the complex flavones lack clearly identifiable fragmentation pathways.

## DISCUSSION

The principal peaks in the mass spectra of the flavones **6–24** are given in Table 1. The major conclusions deduced from analysis of these spectra and other spectra in the literature are discussed below.

**(M-H)$^+$**. Loss of hydrogen from the molecular ion is a significant process in two distinct situations. In the first case. loss of hydrogen is observed from all the samples examined which contain a free 3-OH group (e.g. **16**. **18**. **20**). with the sole exception of the 2′.3-dihydroxyflavone **22** where fragmentation is dominated by the intense (M-OH)$^+$ ion. Similar intense (M-H)$^+$ ions have been observed in the spectra of 6-hydroxyquercetagetin derivatives.[7] and both observations may be rationalized by the assumption that loss of hydrogen occurs from the 3- or the 6-OH group to give the stable quinonoid ions **26** or **27** (scheme 2. R = R′ = H).

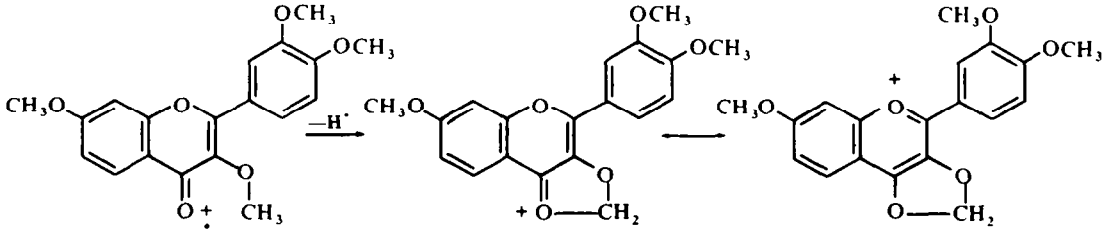



**25** **26** **27**

R. R′ = H or $CH_3$

SCHEME 2

Secondly. an H atom is lost from all the flavone methyl ethers examined which have an OMe group at either the 3-position (**17**. **19**. **21**. **23**. **24**) or the 5-position (**7**. **10**. **17**. **21**. **23**. **24**). with the exception of compound **15** where another more facile fragmentation takes place. The H atom is probably lost from the 3- or the 5-OMe group. and it is proposed that the ionized CO group displaces an H atom from one of these groups with the formation of the stabilized intermediate **28** (scheme 3). An analogous




**19** **28**

SCHEME 3

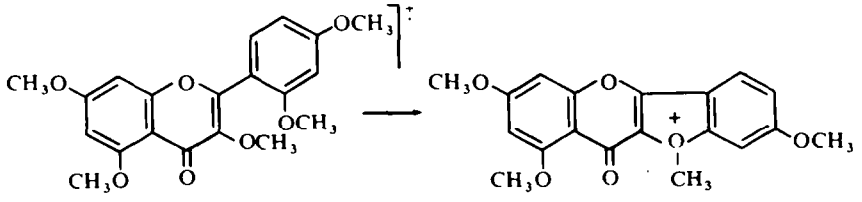
mechanism has been proposed to account for the loss of the C-6 Me group from 2-hexanone observed in the first field-free region of a double focusing mass spectrometer,[10] and the loss of an Me group from 1-ethoxy anthraquinones.[11] In support of this mechanism, the intensity of the $(M-H)^+$ ion relative to other fragment ions increases significantly at low ionizing voltage: thus for compound **17** the intensity of $(M-H)^+$ expressed as $\Sigma_{50}$ is 8% at 70 eV and 40% at 14 eV. An increase in relative intensity of this order of magnitude is characteristic of fragmentations with low energies of activation,[12] such as that proposed here.

**$(M-CH_3)^+$.** This ion is abundant in the mass spectra of all the 6- and 8-methoxyflavones examined (**13–15** and references 7, 9, 13–16). It is almost certain that formation of the stable quinonoid cation **26** (or the isomeric cation derived from an 8-methoxyflavone) from the precursor **25** (Scheme 2, R = $CH_3$) provides the driving force for this fragmentation, which is so facile that competing fragmentations such as the formation of the $(M-H)^+$ ion are greatly reduced in importance in, for example, compound **15**. The 3-methoxyflavones examined (**17**, **19**, **21**, **23**, **24**) also display a moderately intense or intense peak at $(M-CH_3)$, presumably due to formation of the stabilized cation corresponding to **27** from **25** (R′ = $CH_3$). In this case, however, loss of an Me radical appears not to compete so effectively with other processes such as loss of an H atom (compounds **17**, **21** and **23**), and the intensity of the $(M-CH_3)^+$ ion is correspondingly reduced. The observation of an intense $(M-CH_3)$ peak is thus diagnostic for a 3-, 6- or 8-methoxyflavone, but failure to observe this peak does not necessarily exclude the presence of a 3-OMe group.

**$(M-OH)^+$ and $(M-OH_2)^{+\cdot}$.** The origin of these ions in compounds analogous to **22**[8] and to the 3- and 5-methoxyflavones examined[7,9] has been previously discussed.

**$(M-OH_3)^{+\cdot}$.** A number of the flavone methyl ethers examined yielded intense or moderately intense ions corresponding to the loss of 19 mass units, or $H_3O$, from the molecular ion. It was noted that only those compounds (**17**, **19**, **21**, **23**, **24**) which had OMe groups in *both* the 3- and the 5-positions gave this ion, and although its origin is obscure it could thus be of diagnostic importance in the structural analysis of flavonoid methyl ethers.

**$(M-CH_3O)^+$.** This ion forms the base peak in the spectrum of compound **23**, indicating that the characteristic fragmentation of 2′,3-dihydroxyflavones is retained in their methyl ethers (scheme 4). A number of other methylated flavones also yield




**23**

SCHEME 4

$(M-CH_3O)$ peaks of moderate intensity, but the intensity of this peak in the spectrum of **23** suggests that it can be used as a diagnostic tool for 2′,3-dimethoxyflavones.

**$(M-CH_3CO)^+$.** These ions are significant in the spectra of the 6- and 8-methoxyflavones investigated (**13–15** and references 7, 13–16). Metastable and high resolution

TABLE 1. RELATIVE INTENSITIES OF THE PRINCIPAL IONS IN THE MASS SPECTRA OF FLAVONES 6–24[a]

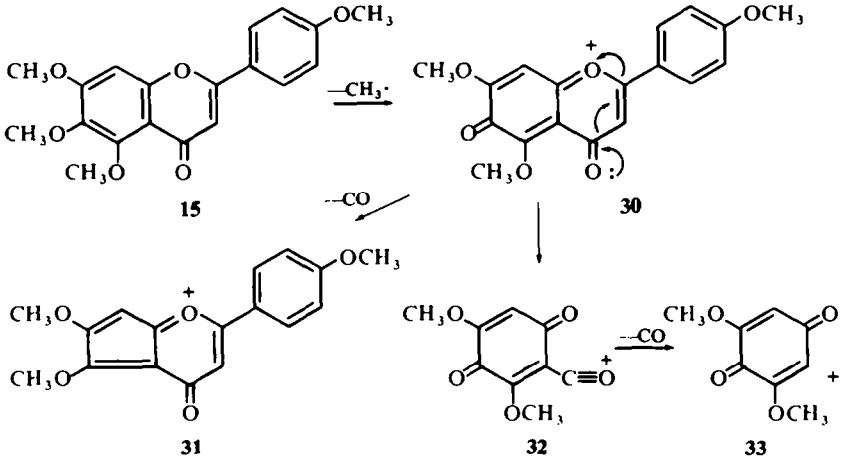
| | | $M^+$ | $(M-1)^+$ | $(M-CH_3)^+$ | $(M-OH)^+$ | $(M-OH_2)^{+\cdot}$ | $(M-OH_3)^+$ | $(M-CO)^+$ | $(M-CHO)^+$ | $(M-CH_3O)^+$ | $(M-CH_3CO)^+$ | $(M-CH_2O_2)^{+\cdot}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **6** | 5,7-OH | 100 | | | | | | 12 | | | | |
| **7** | 5,7-OMe | 100 | 60 | | 22 | | | 8 | 42 | 22 | 8 | 45 |
| **8** | 5-OH-4'-OMe-7-Me | 100 | 5 | | | | | | | | 6 | |
| **9** | 5-OH-4',7-OMe | 100 | 8 | | | | | | 8 | | 8 | |
| **10** | 4',5,7-OMe | 100 | 62 | | 8 | | | 7 | 32 | 21 | 6 | 40 |
| **11** | 7-OH-3',4'-OMe | 68 | | 6 | | | | 6 | 11 | | 10 | 17 |
| **12** | 3',4',7-OMe | 100 | | 11 | | | | 6 | | | 20 | |
| **13** | 4',5,7-OH-6-OMe | 96 | | 63 | | | | | | | 100 | 24 |
| **14** | 4',5-OH-6,7-OMe | 100 | | 100 | | | | | 43 | 15 | 55 | 30 |
| **15** | 4',5,6,7-OMe | 25 | | 100 | | | | | | 5 | 8 | 6 |
| **16** | 3,5,7-OH | 100 | 45 | | | | | 34 | 20 | | | |
| **17** | 3,5,7-OMe | 47 | 100 | 10 | 7 | 7 | 39 | | 11 | 21 | 5 | 8 |
| **18** | 3,3',4',7-OH | 100 | 38 | | 32 | | | 14 | 10 | | | |
| **19** | 3,3',4',7-OMe | 100 | 85 | 70 | 6 | 6 | 9 | | 8 | 28 | 45 | 7 |
| **20** | 3,4',5,7-OH | 100 | 24 | | | | | 28 | 18 | | | |
| **21** | 3,4',5,7-OMe | 78 | 100 | 12 | | 5 | 25 | | 7 | 9 | 5 | |
| **22** | 2',3,4',5,7-OH | 67 | | | 100 | | | 5 | 13 | | | |
| **23** | 2',3,4',5,7-OMe | 74 | 50 | 19 | | | 12 | | 10 | 100 | | 6 |
| **24** | 3,3',4',5,5',7-OMe | 100 | 39 | 98 | | | 7 | | 7 | 28 | 9 | 8 |

[a] Only peaks of intensity greater than 5% of base peak were recorded

TABLE 1—*continued*

| | | $(A+H)^+$ | $A^{+\cdot}$ | $(A-H)^{+\cdot}$ | $(A-CH_3)^+$ | $(A-CO)^+$ | $(A-CH_3CO)^+$ | $B^{+\cdot}$ | $(B-CH_3)^+$ | $C^+$ | $(C-CO)^+$ | $(M-CO)^{+\cdot}/2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **6** | 5,7-OH | | 20 | | | 14 | | 6 | | 12 | 14 | 12 |
| **7** | 5,7-OMe | | | | 6 | 11 | 10 | 15 | | 22 | 30 | 20 |
| **8** | 5-OH-4′-OMe-7-Me | | 19 | | | 11 | | 18 | 5 | 6 | | 7 |
| **9** | 5-OH-4′,7-OMe | 9 | 11 | 5 | | | | 15 | 5 | | | |
| **10** | 4′,5,7-OMe | | | | | | 7 | 35 | 11 | 7 | 5 | 18 |
| **11** | 7-OH-3′,4′-OMe | 100 | 9 | | | 9 | | 27 | 11 | | | 42 |
| **12** | 3′,4′,7-OMe | 15 | | 5 | | | 5 | 23 | 12 | | | 9 |
| **13** | 4′,5,7-OH-6-OMe | | | | 15 | | 31 | 13 | | 13 | 19 | |
| **14** | 4′,5-OH-6,7-OMe | | | | 18 | | 45 | | | 10 | 12 | |
| **15** | 4′,5,6,7-OMe | | | | 5 | | 12 | 5 | | | | |
| **16** | 3,5,7-OH | 8 | | | | 12 | | | | 50 | 85 | 8 |
| **17** | 3,5,7-OMe | 13 | 5 | | | 10 | | | | 40 | 45 | 20 |
| **18** | 3,3′,4′,7-OH | 62 | | | | 12 | | 8 | 11 | 62 | 20 | 6 |
| **19** | 3,3′,4′,7-OMe | 19 | 5 | | 6 | 6 | 9 | | | 12 | | 9 |
| **20** | 3,4′,5,7-OH | 13 | | | | 8 | | 8 | | 47 | 22 | 8 |
| **21** | 3,4′,5,7-OMe | 6 | | | | | | | | 17 | | 14 |
| **22** | 2′,3,4′,5,7-OH | 55 | | 7 | | 9 | | 13 | 5 | 25 | 7 | 25 |
| **23** | 2′,3,4′,5,7-OMe | 26 | | | 9 | | | | | 9 | | 26 |
| **24** | 3,3′,4′,5,5′,7-OMe | 10 | | | | | | | | 6 | 14 | 13 |

evidence (Tables 2 and 3 and reference 7) indicate that the ions are formed by loss of CO from the ($M-CH_3$) ion. Since compounds **13–15** do not contain a 3-methoxyl group, loss of CO must occur from the quinonoid ion **30** (Scheme 5) to give an ion of




SCHEME 5

possible structure **31** (or an open-chain isomer). Loss of CO from **30** would be expected to occur readily by analogy with the facile loss of CO from benzoquinones and naphthoquinones.[17] Similar intense or moderately intense ($M-CH_3CO$) peaks are also observed in the spectra of the 3-methoxyflavones investigated (**17**, **19**, **21**, **24**), where loss of Me followed by CO presumably occurs from the 3-position, while a few compounds with no OMe groups in the 3-, 6- or 8-positions (**7–12**) also gave moderate or weak peaks at (M-43). It may thus be concluded that the observation of an *intense* peak at (M-43) is diagnostic for a 3-, 6-, or 8-substituted methoxyflavone, but the observation of a weak peak at this mass is inconclusive.

TABLE 2. EXACT MASS MEASUREMENTS OF REPRESENTATIVE IONS*

| Compound | Measured mass | Composition | Calculated mass | Assignment |
|---|---|---|---|---|
| 7 | 236·0851 | $C_{16}H_{12}O_2$ | 236·0837 | $[M-H_2O-CO]^+$ |
| 11 | 162·0679 | $C_{10}H_{10}O_2$ | 162·0680 | $B^+$ |
| | 147·0465 | $C_9H_7O_2$ | 147·0446 | $[B-CH_3]^+$ |
| | 137·0258 | $C_7H_5O_3$ | 137·0238 | $[A+H]^+$ |
| 13 | 257·0448 | $C_{14}H_9O_5$ | 257·0450 | $[M-CH_3CO]^+$ |
| | 166·9976 | $C_7H_3O_5$ | 166·9981 | $[A-CH_3]^+$ |
| 14 | 271·0606 | $C_{15}H_{11}O_5$ | 271·0604 | $[M-CH_3CO]^+$ |
| | 181·0165 | $C_8H_5O_5$ | 181·0137 | $[A-CH_3]^+$ |
| 18 | 137·0212 | $C_7H_5O_3$ | 137·0238 | $C^+$ |
| 19 | 165·0530 | $C_9H_9O_3$ | 165·0551 | $C^+$ |

* Made at a resolving power of one in 12.000.

**RDA fragments** $(A + H)^+$, $A^{+\cdot}$, $(A\text{-}H)^+$. As has been pointed out previously, these ions are in general significant only for flavones bearing fewer than four oxygen substituents, although the (A + H) peak can be intense in the spectra of 3-hydroxyflavones with as many as five oxygen substituents (compound **22**). On the other hand, apigenin trimethyl ether (**10**) shows only weak peaks due to this fragmentation, so it is a somewhat unreliable indicator of molecular structure and substitution pattern.

TABLE 3. METASTABLE TRANSITIONS OF SELECTED IONS*

| Compound | Transition | $m_1/m_2$ or m* observed | m* Calculated |
|---|---|---|---|
| **13** | 285(M-$CH_3$) → 257(M-$CH_3CO$) | 1·108 | 1·108 |
| **14** | 299(M-$CH_3$) → 271(M-$CH_3CO$) | 1·103 | 1·102 |
| | 299(M-$CH_3$) → 181(A-$CH_3$) | 1·652 | 1·651 |
| **15** | 342(M) → 195(A-$CH_3$) | 1·750 | 1·752 |
| | 327(M-$CH_3$) → 195(A-$CH_3$) | 1·678 | 1·677 |
| **23** | 371(M-H) → 353(M-$H_3O$) | 1·055 | 1·051 |
| **19** | 342(M) → 341(M-H) | 340·0 | 340·0 |
| **21** | 342(M) → 341(M-H) | 340·0 | 340·0 |
| | 341(M-H) → 323(M-$H_3O$) | 306·0 | 305·8 |
| | 342(M) → 327(M-$CH_3$) | 312·0 | 312·6 |
| | 135(C) → 107(C-28) | 84·9 | 84·9 |

* Transitions for compounds **13–23** obtained by the defocussing technique; transitions for compounds **19–21** measured in the normal manner.

**$(A\text{-}CH_3)^+$**. The spectra of compounds **13–16** and also of some other 6- or 8-methoxyflavones[14–16] show intense to moderate peaks corresponding to the RDA fragment A less one Me group; exact mass measurement confirmed this assignment (Table 2). This peak has not been noted in the spectra of previously examined flavones.[2–9] and it is proposed that it arises by fragmentation of the $(M\text{-}CH_3)^+$ ion, as indicated in Scheme 5, **30** (arrows) → **32**. Metastable measurements (Table 3, compounds **14** and **15**) confirm that the $(A\text{-}CH_3)^+$ ion does indeed arise from $(M\text{-}CH_3)^+$ in one step, adding support to the mechanism proposed. The $(A\text{-}CH_3)^+$ ions should thus be useful diagnostic ions for the structural elucidation of 6- and 8-methoxyflavones, with the proviso that they may be of low intensity in the spectra of 3,6-dimethoxyflavones.[9]

**$(A\text{-}CH_3CO)^+$**. This ion, like the $(A\text{-}CH_3)^+$ ion, is most intense in the spectra of 6-methoxyflavones. It is presumably arises by simple loss of CO from the $(A\text{-}CH_3)^+$ ion **32** to give the ion **33** (Scheme 5). A few compounds which do not yield intense $(A\text{-}CH_3)^+$ peaks do show peaks corresponding to $(A\text{-}CH_3CO)^+$ (**10**, **12**), but these ions are of low intensity and would not be confused with the $(A\text{-}CH_3CO)^+$ ion from a 6-methoxyflavone.

**RDA fragments $B^{+\cdot}$** and **$(B\text{-}15)^{+\cdot}$**. These ions are most abundant in the spectra of flavones with up to three oxygen substituents, and provide useful diagnostic peaks. The more fully oxygenated flavones do not give abundant ions of this composition.

**$C^+$ and $(C\text{-}CO)^+$.** These ions are moderately abundant in the spectra of nearly all the flavones examined, and their abundance is roughly inversely proportional to the abundance of the RDA fragments $A^{+\cdot}$, $(A\text{-}15)^+$, and $B^{+\cdot}$. They are thus important diagnostic ions, inasmuch as they yield information on the composition of ring C and hence, by difference, on the composition of ring A also. In particular, if a fully methylated flavone which does not show intense RDA fragments is examined, the possible mass numbers at which fragments C can occur are restricted to a small number of possibilities, namely the ions at *m/e* 105, 135, 165, and 195 for flavones unsubstituted and mono, di, and trisubstituted, respectively, in ring C. In such a case, if attention is limited to ions with these *m/e* values, *the most intense ion will be the one corresponding to ion C*, even when all the fragments examined are of relatively low intensity. This "rule" has been tested on a number of flavones whose spectra are reported in the literature,[2-9] and has been found to hold in most of the cases examined. Partially methylated flavones can be dealt with by a simple extension of the *m/e* values considered. The observation of a second ion with *m/e* (C-28) is confirmatory evidence for the fragmentation proposed.

*Doubly charged ions.* Peaks due to doubly charged ions are moderately intense in the spectra of all the flavones examined, as would be expected from such highly unsaturated molecules. Although these peaks frequently fall in the same part of the spectrum as the significant structural peaks due to fragments A, B, and C, they can be distinguished from the latter by the presence of isotope peaks at non-integral masses, and hence they need not cause any confusion in interpretation. Interestingly enough, the doubly charged ion at *m/e* (M-28)/2 is usually the most intense such ion in the spectrum, although the reason for this is not clear.

## CONCLUSION

This work demonstrates that considerable structural information about an unknown flavone sample can be obtained from a study of its mass spectrum. In particular, the presence of OMe groups in the 3, 5, 6 and 8 positions and the substitution on ring C may be readily deduced from mass spectral data.

## EXPERIMENTAL

Samples were all commercially available (A. G. Fluka, Switzerland, and Aldrich Chemical Co.), with the exception of **13–15** which were available from earlier work in this laboratory.[18] Mass spectra were obtained on an AEI MS-902 mass spectrometer (at low resolving power unless otherwise stated) with a source temp of 200°.

*Methylation of flavones.* The flavone (10–50 mg) was dissolved in anhyd acetone (5 ml) and treated with an excess $K_2CO_3$ and $Me_2SO_4$. The mixture was heated under reflux for 6 hr, cooled, and treated with excess conc ammonia soln, followed by a few drops of 10% NaOH aq. Water was then added to the soln until the product just began to separate, and separation was allowed to proceed overnight. The product was then filtered off, washed, and recrystallized from aqueous acetone or acetone/petrol. All samples prepared in this way had m.pts in agreement with literature values.[19]

*Acknowledgments*—Financial support from the Research Foundation of the State University of New York is gratefully acknowledged.

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