MASS SPECTROMETRY OF PRENYLATED FLAVONOIDS

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Abstract-The fragmentation patterns originating from the degradation of prenyl group(s) in positive ion electron ionization (EI), fast-atom bombardment (FAB) and chemical ionization (CI) mass spectrometry (MS) of prenylated flavonoids were reviewed. The EI spectra showed the characteristic fragmentation patterns reflecting the location of prenyl group in the flavonoid compounds, whereas the FAB and CI spectra showed relatively monotonous patterns. It was described how the EI and FAB fragmentation patterns are useful for the identification of prenylated flavonoids.

CONTENTS

1. INTRODUCTION

Mass spectrometry (MS) is a very useful technique for the determination of the structure of organic compounds, as well as of the molecular weight, since the spectrum for a given compound shows a characteristic fragmentation pattern reflecting the structure. In particular, the electron ionization (EI) method is very excellent in reproducibility of the spectral pattern as well as the measurement requires only a small amount (a few micrograms) of sample, so that it is of significance for the structural determination of organic compound to study the EI fragmentation.

Electron impact fragmentation of flavonoids has already been reviewed by some workers.[1-3] They mainly have treated on the flavonoid-skeletal

destruction which results in the fragments originated from A- and B-rings, and a *retro*-Diels-Alder (RDA) cleavage. On the other hand, a number of flavonoids having one or more isoprenoid groups have been isolated so far.[4] As summarized by Venkataraman *et al.*,[5] the EI spectra of isopentenylated flavonoids give characteristic fragmentation patterns reflecting the location of prenyl (3,3-dimethylallyl) group(s) in the higher mass region. The pioneering works on the EI fragmentation of prenyl group(s) were done by Reed *et al.*,[6] Ritchie *et al.*[7] and Stout *et al.*[8] They indicated that in EI-MS of prenylated compounds the prenyl group adjacent to a hydroxy or a methyl group results in the fragment ion with the loss of C_4H_8 (56 mass units),[7] whereas the prenyl group adjacent to a methoxyl group results in the fragment ion with the loss of C_3H_7 (43 mass units).[8] Although the latter indication was utilized to elucidate the structure of geranylated compounds,[9] it is doubtful since the proposed structure was subsequently revised.[10]

We have recently reported the feature of fragmentation in the EI, fast-atom bombardment (FAB) and chemical ionization (CI) mass spectra of prenylated flavonoids[11-13] and other isoprenoid substituted phenolic compounds.[14] The EI spectra give a great variety of fragmentation patterns originating from the degradation of prenyl group(s), while the FAB and CI spectra give relatively monotonous patterns. The fragmentation patterns in EI-MS of the prenylated flavonoids generally consist of the fragment peaks corresponding to (M - 15), (M - 43), (M - 55), (M - 56) and (M - 68) ions originating from the degradation of the prenyl group, and also the EI spectra rarely show the peaks of (M - 57), (M - 69) and (M - 71) ions. The fragmentation patterns of prenylated flavonoids are exactly dependent on the adjacent functional group(s) and the location of prenyl group. The diversity of the fragmentation patterns suggests that the structure of prenylated flavonoids can be partially determined by the EI fragmentation pattern. In fact, so-called 6-prenylated and 8-prenylated flavones (and isoflavones) can be distinguished from each other by means of their EI spectral patterns.[13,15] In this review, we describe how the EI fragmentation pattern is useful for the determination of the location of prenyl group attached to flavonoid. Furthermore, it is described that the FAB spectral patterns of prenylated flavonoids are useful for the structural determination.

2. ELECTRON IONIZATION MASS SPECTRA

2.1 Characteristic Fragmentation Patterns

In this section, typical fragmentation patterns originating from the degradation of the prenyl group attached to 3-, 6- or 8-position of the flavonoids are described.

2.1.1 3-Prenylated Flavones[11]

The EI spectrum of morusin (1), which was isolated from the root bark of Japanese mulberry tree,[16] shows a typical fragmentation pattern of 3-prenylated flavones (Figure 1 and Scheme 1). The characteristic fragments

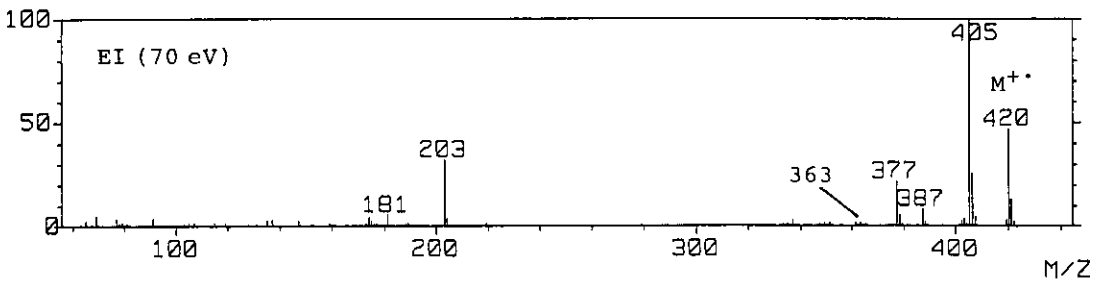
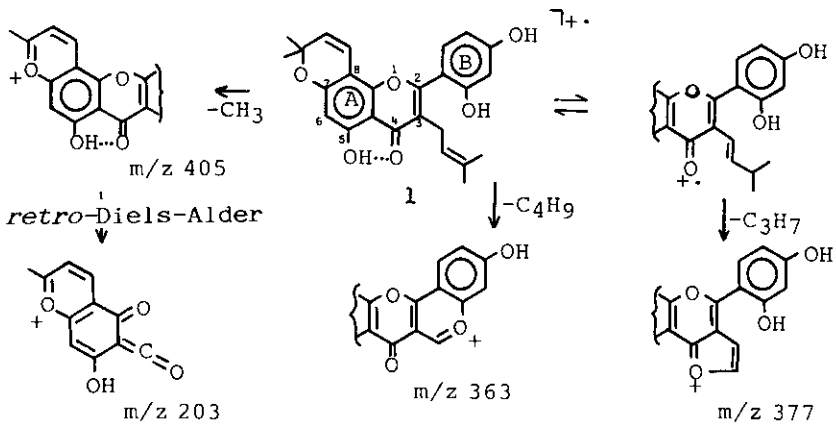


Figure 1 EI mass spectrum of morusin (1).



Scheme 1

originated from the degradation of the prenyl group occur at m/z 377 and 363. The fragment at m/z 363 can be obviously observed in the B/E-constant

linked scan EI (B/E-EI) mass spectrum of the molecular ion $M^{+\cdot}$ of (1).[17] The fragmentation pattern originating from the degradation of the 3-prenyl group can be characterized by the fragment (M - 43) and (M - 57) ions which are formed by the loss of neutral fragments C_3H_7 and C_4H_9 , respectively, from the $M^{+\cdot}$ ion. In fact, the pattern can be observed also in the EI spectra of other 3-prenylated flavones.[11,12]

2.1.2 6-Prenylated Flavones and Isoflavones[13]

The EI spectrum of a synthesized 6-prenylated flavone (2) gives the intense fragments at m/z 279 and 267 by the loss of neutral fragments C_3H_7 and C_4H_7 , respectively, from the $M^{+\cdot}$ at m/z 322 (Figure 2 and Scheme 2).[13] The fragmentation pattern can be characterized by the fragments (M - 43) and (M - 55) ions. The pattern can be observed also in the EI spectra of other 6-prenylated flavones[6] and 6-prenylated isoflavones.[13,15,18-26]

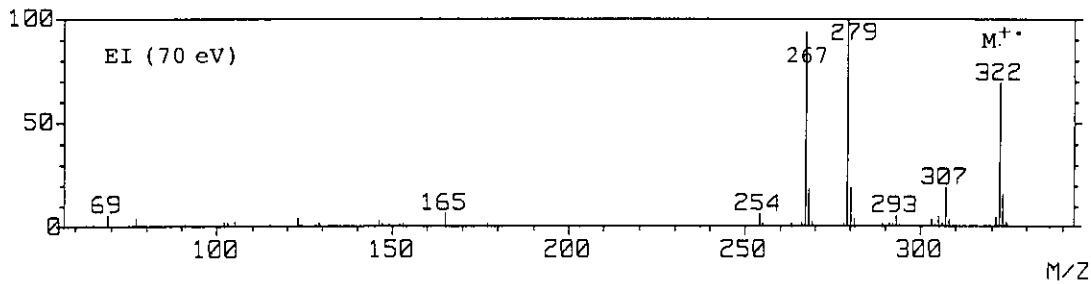
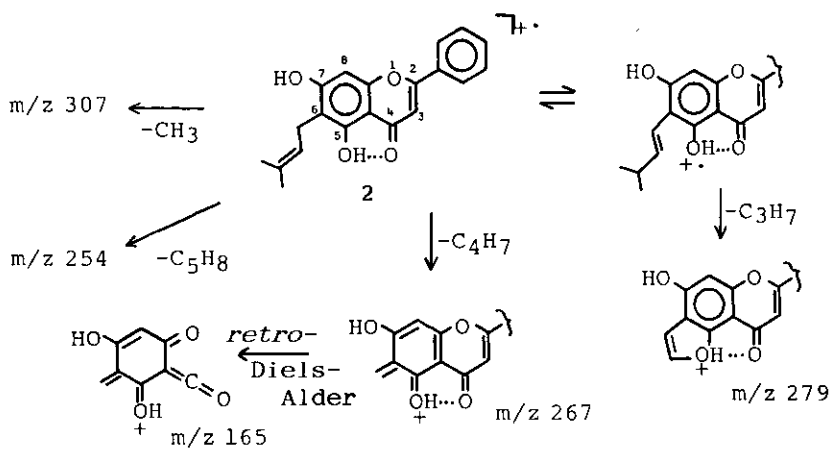


Figure 2 EI mass spectrum of the 6-prenylated flavone (2).



Scheme 2

2.1.3 8-Prenylated Flavones and Isoflavones[13]

The EI spectrum of a synthesized 8-prenylated flavone (3)[13] gives a characteristic pattern containing the intense fragments at m/z 307, 267 and 254 by the loss of neutral fragments CH_3 , C_4H_7 and C_5H_8 , respectively, from the $M^{+\cdot}$ at m/z 322 (Figure 3 and Scheme 3). The fragmentation pattern originating from the degradation of 8-prenyl group can be characterized by the fragment (M - 15), (M - 55) and (M - 68) ions. The pattern can be also observed in the EI spectra of 8-prenylated isoflavones[13,15] and flavonols.[11]

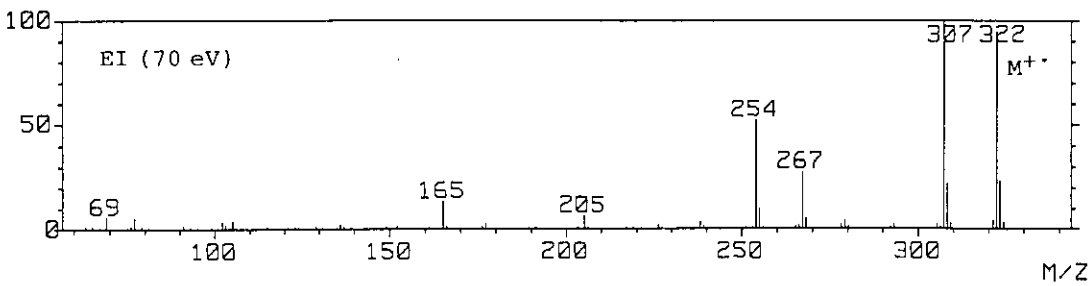
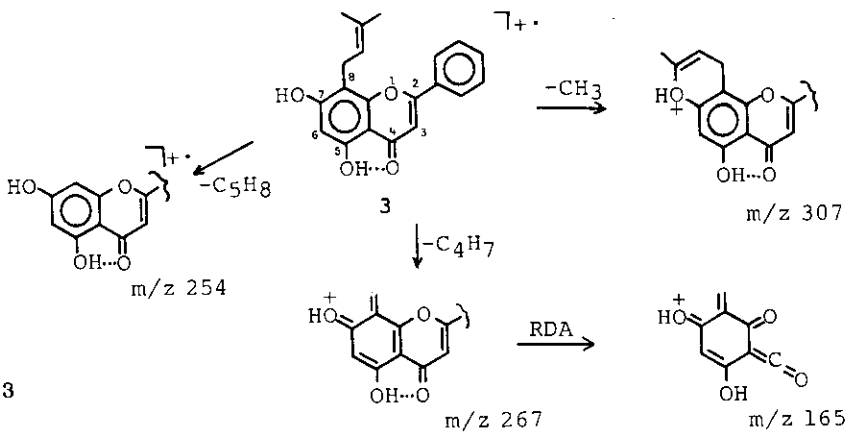


Figure 3 EI mass spectrum of 8-prenylated flavone (3).

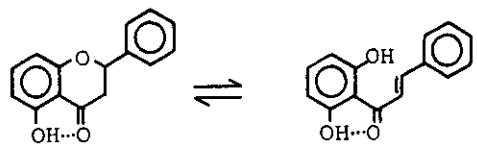


Scheme 3

2.1.4 6- and 8-Prenylated Flavanones and Chalcones

The EI-MS study of prenylated flavanones has been treated by some workers so far.[27-30] In general, the EI spectra of flavanones show more extensive

fragments than those of flavones and isoflavones. This is due to a thermal isomerization between flavanone and the corresponding chalcone in the ion source of the mass spectrometer prior to ionization [31-33] (Scheme 4).



Scheme 4

Both 6- and 8-prenylated flavanones,[13,34-36] and a prenylated chalcone[37] give the fragment (M - 15), (M - 43) and (M - 55) ions originating from the degradation of the prenyl group in their EI spectra. Furthermore, the EI spectral patterns of 6- and 8-prenylated flavanones[13,35] and of 8-prenylated flavanone and the corresponding chalcone[38] are good similar each other. Figures 4(a) and (b) are the EI spectra of synthesized 6- and 8-prenylated flavanones (**4** and 5), respectively.[13] These spectral patterns are very similar so that it is difficult to distinguish between these compounds by EI-MS. Both EI patterns for (**4**) and (**5**) may arise from the

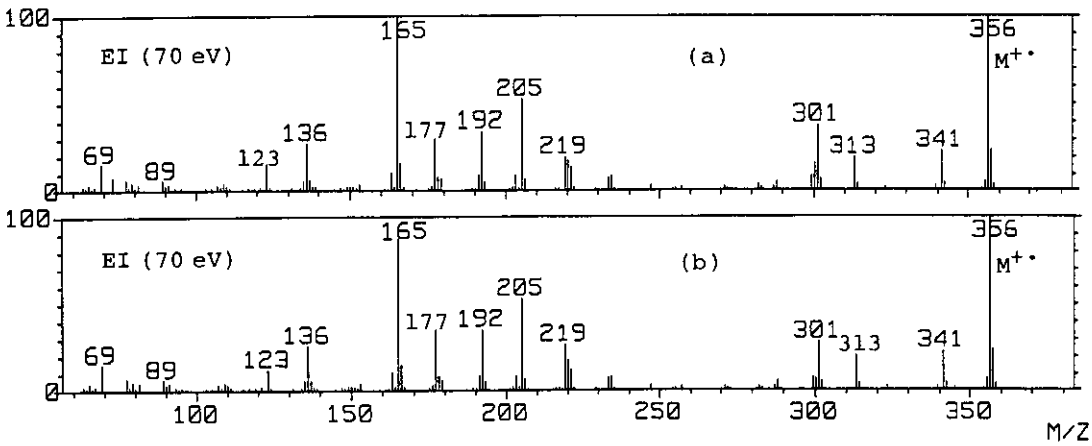
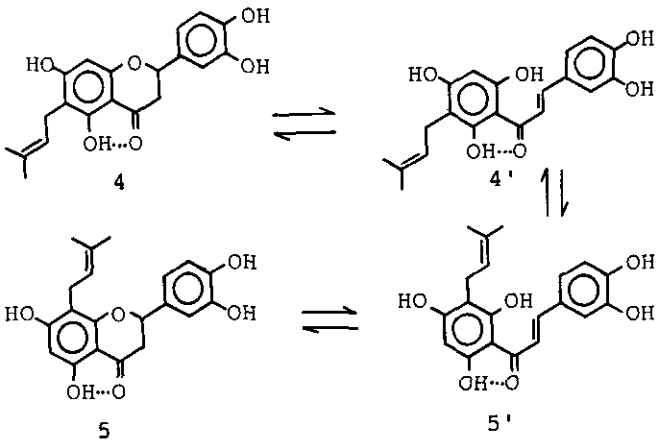


Figure 4 EI mass spectra of (a) 6- and (b) 8-prenylated flavanones (**4** and 5).

thermal isomerization of the molecular ions $M^{+\cdot}$ (m/z 356) giving the four isomers (**4**), (**4'**), (**5**) and (**5'**) (Scheme 5). As is described in the subsequent chapter 3.2.1, however, (**4**) and (**5**) are distinguishable from each

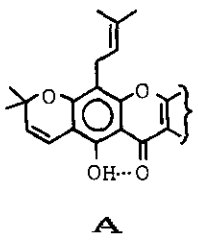
other by means of their FAB spectral patterns.



Scheme 5

2.1.5 Other Fragmentation Patterns

8-Prenylated flavonoids characterized by a common partial structure with the linear alignment of 2,2-dimethylpyran ring (**A**), show a characteristic fragmentation pattern in EI-MS. Figure 5 is the EI mass spectrum of broussoflavonol A (6).[39] The characteristic fragments at m/z 407 and 395



A

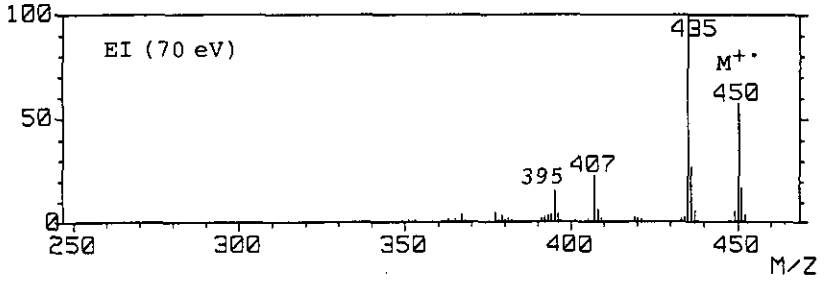
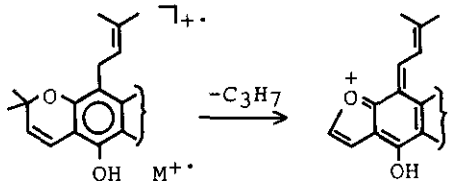


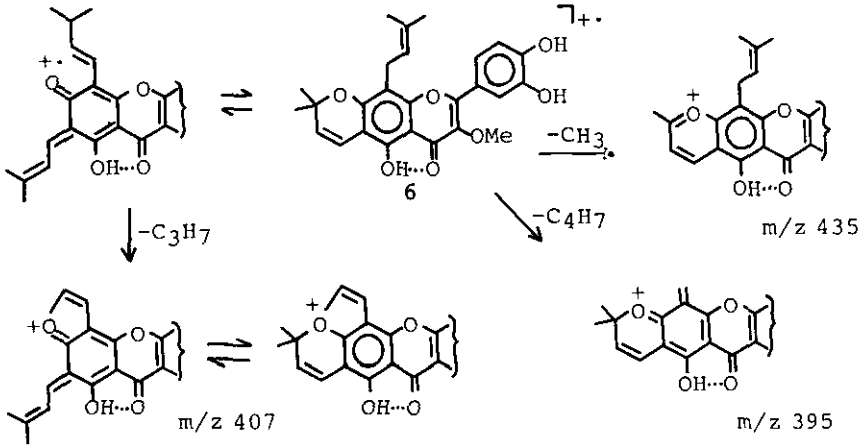
Figure 5 EI mass spectrum of broussoflavonol A (6).

are originated from the loss of neutral fragments C_3H_7 and C_4H_7, respectively, from the $M^{+\cdot}$ at m/z 450. This fragmentation pattern can be observed in the EI spectra of other flavonoids containing the common partial structure **A**.[40-43] Although it has been believed so far that the fragment

(M - 43) ion is formed by the degradation of a 2,2-dimethylpyran ring as shown in Scheme 6,[40,41] we proposed another mechanism as shown in Scheme 7 since the pyran ring gives a characteristic degradation pattern in FAB-MS rather than EI-MS.[11]

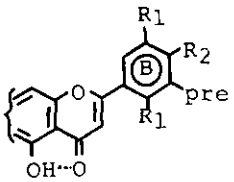


Scheme 6

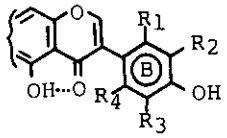


Scheme 7

The EI fragmentation pattern originating from the degradation of the prenyl group attached to B-ring varies according to the position and/or adjacent functional group(s). Some EI spectral data are shown in Figure 6 with the fragments and the relative intensity (%). Although the EI fragmentation of the prenyl group in the B-ring has not yet been studied, the diversity of the EI-MS data suggests that the EI fragmentation patterns are useful for the location of prenyl group in the B-ring.



7 and 8



9 - 14

	R_1	R_2
7	OH	OH
8	H	OMe

pre: prenyl

	R_1	R_2	R_3	R_4
9	OH	pre	H	OMe
10	OH	pre	H	H
11	OH	pre	OMe	H
12	pre	OH	H	OMe
13	H	pre	OMe	H
14	OH	pre	H	H

EI-MS data

	$M^{+\cdot}$	M-15	M-43	M-55	M-56	M-57	M-68	M-69	M-71	ref
7	33	100	30			5				44
8	100	38	16					10		45
9	48	23	4							46
10	100	10	70	100	44					47
11	93	6	13	50	100				20	48
12	95	10	12	17	20		23	9		48
13	100	19		91	57			12		48
14	73		49	100		29				49

Figure 6 Some flavonoids having a prenyl group attached to B-ring and the EI spectral data with the relative intensity (%).

2.2. Characteristic Fragment Ions

2.2.1 (M - 15) Ion

As shown in Figures 1 and 5, in the EI spectra of prenylated flavonoids the fragment (M - 15) ion by the loss of a methyl radical CH_3 from a 2,2-dimethylpyran ring can often be observed. In the absence of the pyran ring, on the other hand, an intense (M - 15) ion peak can be observed in the EI spectra of 8-prenylated flavones and isoflavones (see Figure 3). In general, the EI fragmentation of the prenyl group adjacent to hydroxyl group(s) seems to result in the (M - 15) ion.[5,10,13,19-21,25,47,50] This can be supported by the EI spectrum of a model compound I (15)[10] (Figure 7 and Scheme 8).

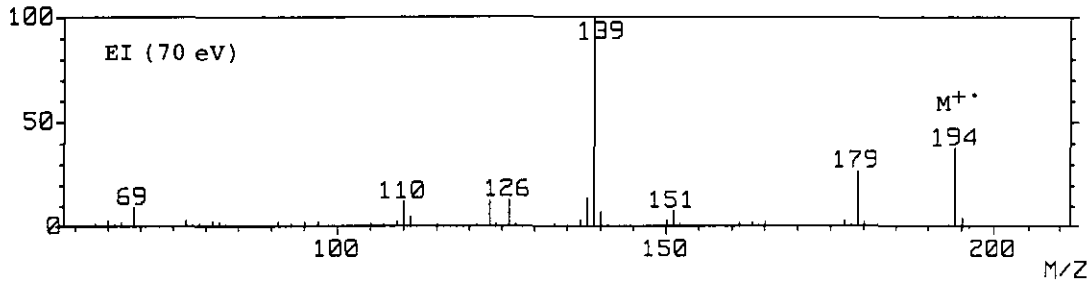
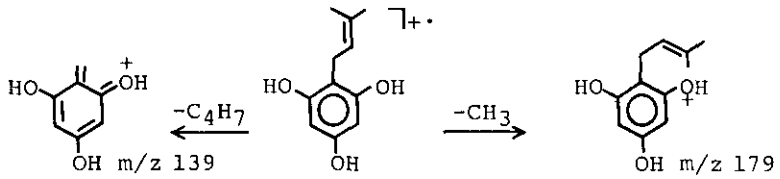


Figure 7 EI mass spectrum of the model compound I (15).



Scheme 8 15

2.2.2 (M - 43) Ion

The fragment (M - 43) ion is formed by the loss of neutral fragment C_3H_7 from the prenyl group attached to 3-, 6-, 8-positions and B-ring as shown in Figures 1, 2, 5 and 6, respectively. A typical fragmentation for the (M - 43) ion can be observed in the EI spectrum of albanin A (16)[51] (Figure 8 and Scheme 9). The (M - 43) ion formation may be explained as an influence of the adjacent carbonyl group, except for the case of the prenyl group attached to B-ring, as shown in Schemes 1, 6 and 9.
On the other hand, Matsuura *et al.*[52] have proposed that in the photo-

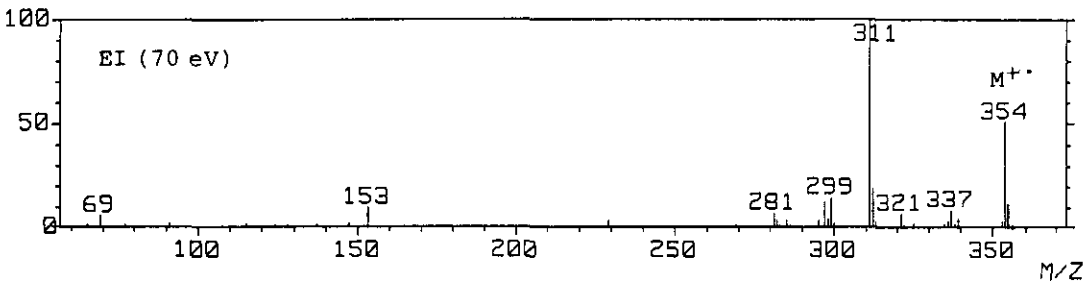
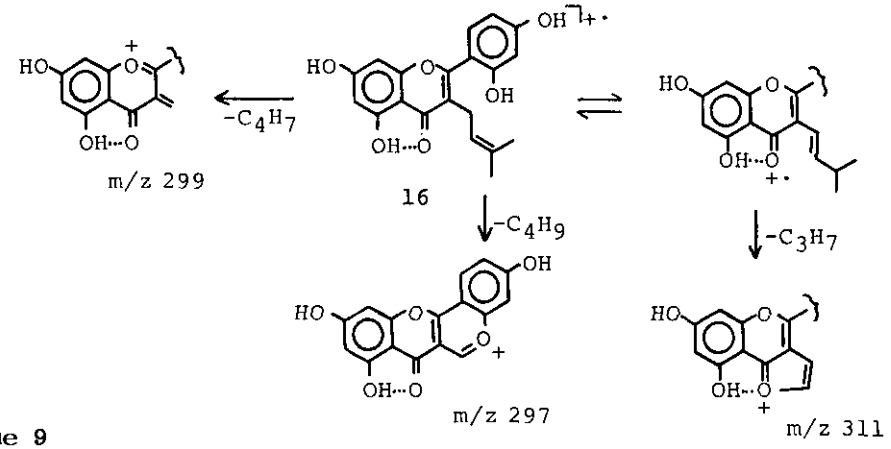
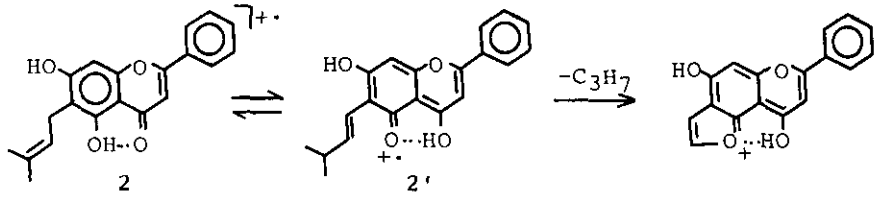


Figure 8 EI mass spectrum of albanin A (16).



Scheme 9

chemical study of flavonoids the irradiation of ultraviolet (uv) light to the flavonoid results in an intramolecular hydrogen abstraction between the 5-hydroxy and the 4-carbonyl groups, e.g., the compound (2) may yields a tautomer (2') by the uv irradiation (Scheme 10). Such an isomerization may occurs by an electron impact excitation. From analogy with 3-prenylated flavonoids (Scheme 9), therefore, the fragment (M - 43) ion formation in the EI spectra of 6-prenylated flavones and isoflavones can be explained as the influence of the adjacent carbonyl group.



Scheme 10

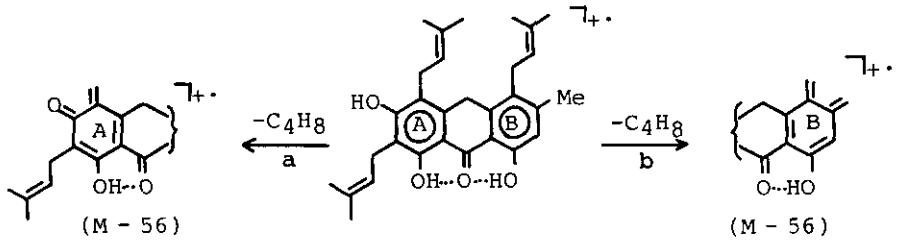
2.2.3 (M - 55) Ion

The peak of (M - 55) ion can be observed in the EI spectra of prenylated flavonoids as a most familiar fragment. As shown in Schemes 2, 3, 7 and 8, the fragment (M - 55) ion is formed through a simple cleavage with the loss

of a neutral fragment C_4H_7 from the prenyl group. In particular, the simple cleavage fragmentation seems to frequently occur when the prenyl group adjoins hydroxyl group(s), whereas the (M - 55) peak in the EI spectra of the compounds having a prenyl group adjacent to methoxyl group(s) is weak in the relative intensity.[10,45,53]

2.2.4 (M - 56) Ion

The fragment (M - 56) ion can often be observed in the EI spectra of certain flavonoids having prenyl group(s) attached to B-ring.[47,48] The fragment can be formed by a hydrogen rearrangement. This fragmentation was at first reported by Ritchie *et al.*[7] in the EI spectrum of prenylated quinoids, e.g., compound (17). They suggested two mechanisms for the (M - 56) ion formation (processes a and b in Scheme 11). The (M - 56) ion formation in the EI-MS



Scheme 11

of flavonoids having prenyl group(s) attached to B-ring may be explained by the process a in Scheme 11, i.e., the process occurring by the six-membered cyclic transition state between prenyl and the adjacent hydroxyl group.[7] In the EI spectra of other prenylated flavonoids,[11,13] however, such a fragment is only a few percents in the relative intensity. In general, therefore, the process a can not be accepted for the (M - 56) ion formation.

On the other hand, the fragment (M - 56) ion can be characteristically observed in the EI spectra of isoprenylated flavans.[14,55,56] For instance, Figure 9 is the EI spectrum of kazinol B (18)[14] and the fragmentations are shown in Scheme 12. For their flavans, we can find a common partial structure **B**. The partial structure **B** can be found also in the

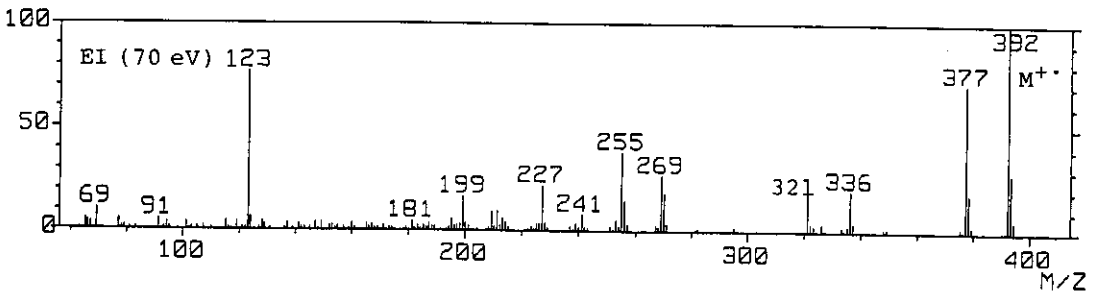
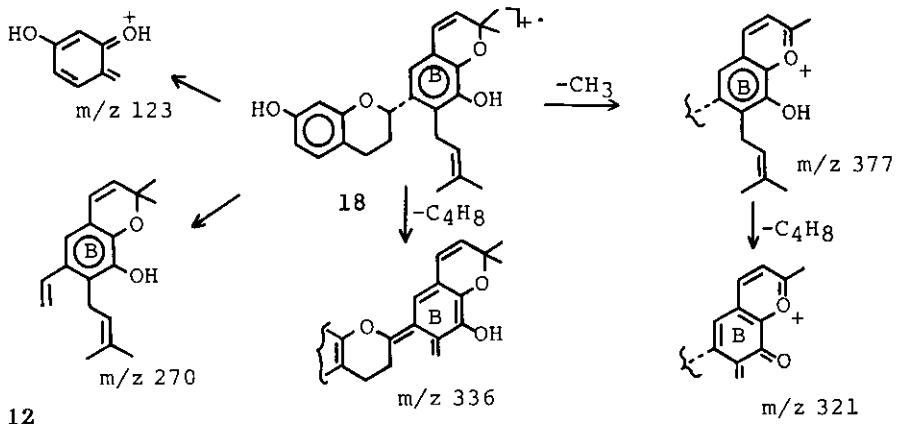
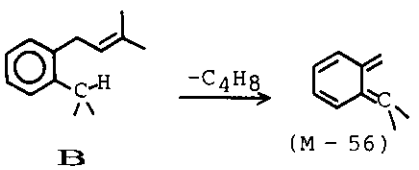


Figure 9 EI mass spectrum of kazinol B (18).



Scheme 12

compound (17). For the (M - 56) ion formation, therefore, the process b in Scheme 11 seems most likely process. The process can be generally explained as shown in Scheme 13.



Scheme 13

2.2.5 (M - 68) Ion

The fragment (M - 68) ion originating from the loss of a prenyl group C_5H_8 with a hydrogen rearrangement can be observed in the EI spectra of 8-prenylated flavones and isoflavones (see 2.1.3).[11,13,15,53] This fragment peak can be observed also in the EI spectra of other prenylated flavonoids, sanggenon A (19)[57] and sanggenon L (20).[58] The EI spectrum of (19) and the fragmentations are shown in Figure 10 and Scheme 14, respectively.

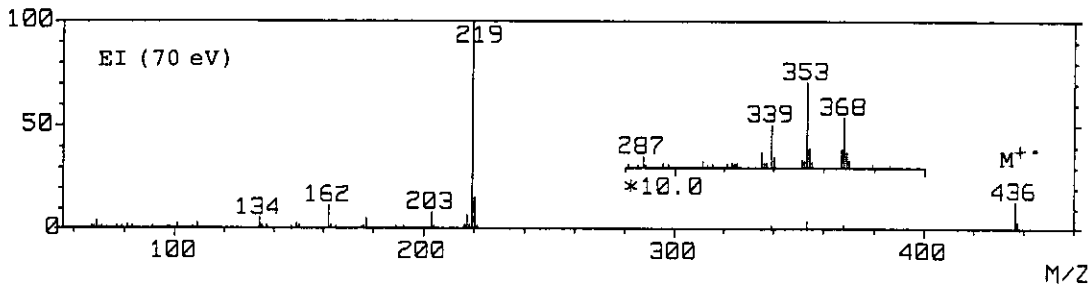
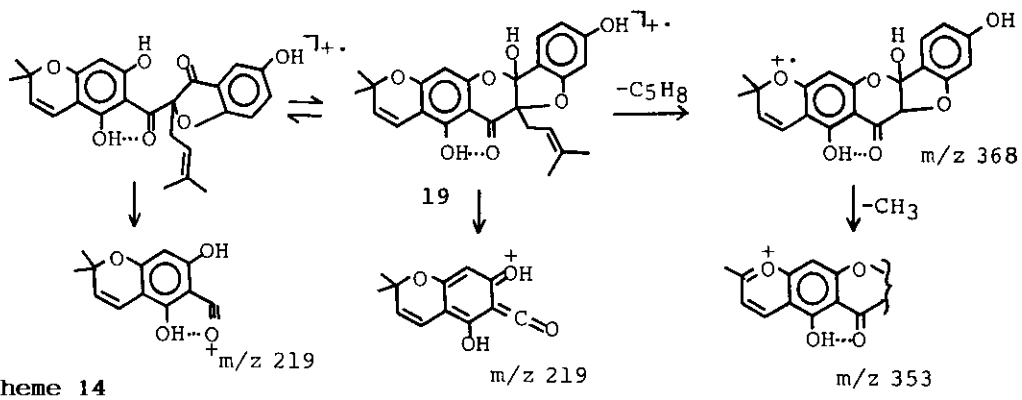


Figure 10 EI mass spectrum of sanggenon A (19).



Scheme 14

Furthermore, the fragment (M - 68) ion can be observed in the EI spectrum of a model compound II (21)[10] (Figure 11). The fragmentation pattern of (21), which contains the intense fragment (M - 15), (M - 55) and (M - 68) ions, is similar to of the EI spectrum of 8-prenylated flavone (3) (see Figure 3). However, it is unusual that in EI-MS of prenylated flavonoids the fragment (M - 68) ion can be observed as an intense peak, so that the appearance of intense (M - 68) ion peak in the EI spectra seems to be useful for the

determination of the location of prenyl group.

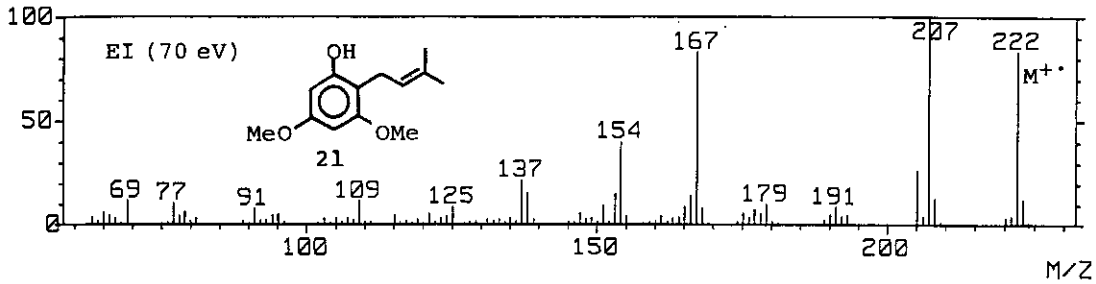
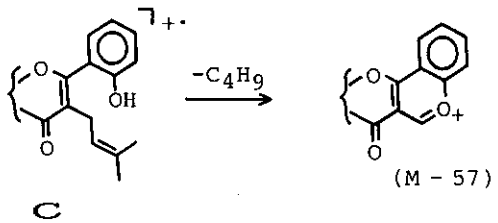


Figure 11 EI mass spectrum of the model compound II (21).

2.2.6 Other Fragment (M - 57), (M - 69) and (M - 71) Ions

Further fragment (M - 57), (M - 69) and (M - 71) ions originating from the degradation of the prenyl group can be often observed in the EI spectra of prenylated flavonoids. As described in the section 2.1.1, the fragment (M - 57) ion can be observed in the EI spectra of 3-prenylated flavones having a common partial structure C. The fragmentation occurs as shown in Scheme 15. This mechanism has been already reported by Deshpande *et al.*[59]



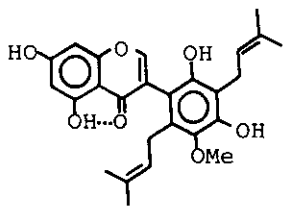
C

Scheme 15

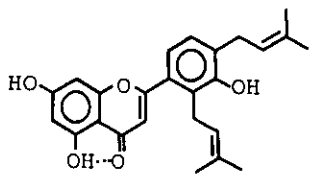
That is, in EI-MS of 3-geranylated flavones,[59,60] the corresponding fragment (M - 125) ion can be observed in their EI spectra. Furthermore, the fragment (M - 57) ion can be observed also in the EI spectra of the flavonoids having a prenyl group attached to B-ring, although the fragmentation mechanism is not clear.

The fragment (M - 69) ion has been reported in the EI-MS data of the

flavonoids having two prenyl groups attached to B-ring,[47,61] e.g., the compounds (22)[47] and (23)[61].

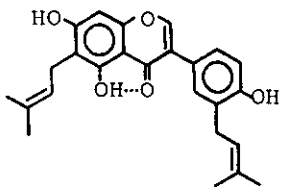


22

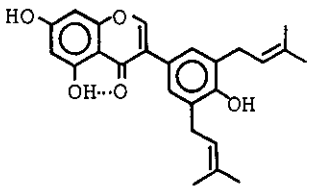


23

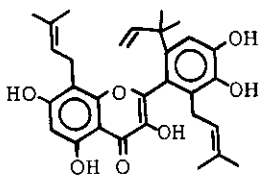
The fragment (M - 71) ion can be observed in the EI spectra of various prenylated flavonoids.[22,36,42,43,47,61] In particular, the EI spectra of the compounds (24)[22] and (25)[36] give the intense (M - 71) ion peaks.



24

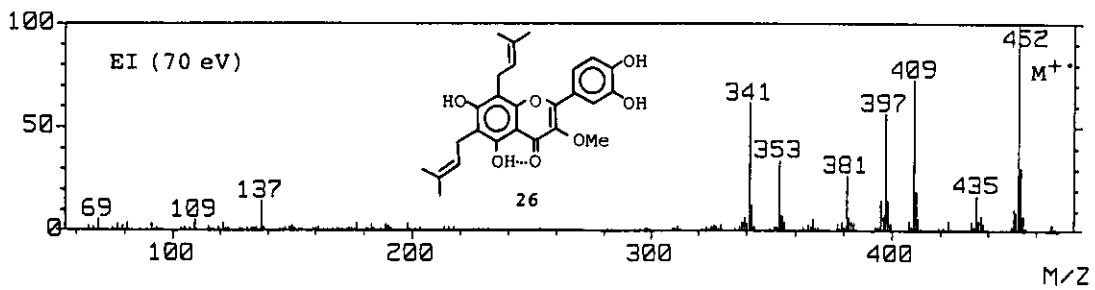


25



27

Broussoflavonols B (26)[39] and C (27)[62] also show the fragment (M - 71) ion peak in their EI spectra (Figure 12). It can be proved by the high



26

Figure 12 EI mass spectrum of broussoflavonol B (26).

resolution data that in Figure 12 a fragment at m/z 381 has an elemental composition $C_{21}H_{17}O_7$ by the loss of neutral fragment C_5H_{11} from the

$M^{+\cdot}$ at m/z 452, but the mechanism for the (M - 71) ion formation is not yet clear.

2.3 Successive Fragmentations

In the case of the flavonoids having two prenyl groups, e.g., **(26)**, further fragmentations originating from the degradation of prenyl group occur from the characteristic fragment (M - 43) and (M - 55) ions. In this section, typical fragment (M - CH_3 - 56), (M - C_3H_7 - 56) and (M - C_4H_7 - 56) ions, of which we called as successive fragments, originated from the further fragmentation will be described.

2.3.1 (M - CH_3 - 56) Ion

A successive fragment (M - CH_3 - 56) ion can be often observed in the EI spectra of the prenylated flavonoids containing 2,2-dimethylpyran ring, e.g., see Figure 9 and Scheme 12. The EI spectrum of kuwanon B **(28)**[11,63] shows such a fragment ion at m/z 349 (Figure 13 and Scheme 16). Furthermore, the successive fragment (M - CH_3 - 56) ions have been reported in the EI-MS data of 6,8-diprenylated flavones.[64,65]

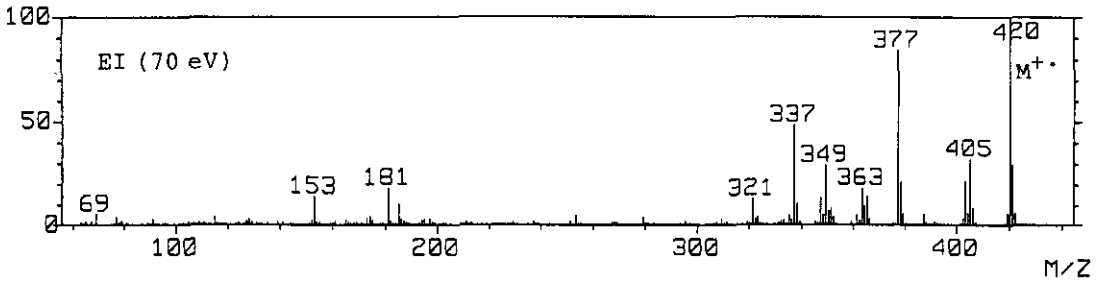
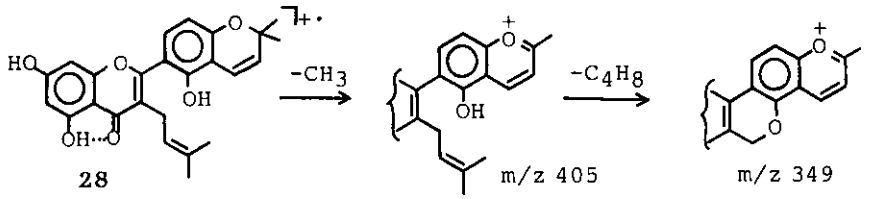


Figure 13 EI mass spectrum of kuwanon B **(28)**.



28 m/z 405 (M - CH_3) m/z 349 (M - CH_3 - 56)

Scheme 16

2.3.2 (M - C_3H_7 - 56) Ion

The successive fragment (M - C_3H_7 - 56) ions can be observed in the EI spectra of 3-,[5,11] and 6-prenylated flavonoids having another prenyl group in the molecules,[11,22,50,60,66,67] and in the EI-MS data of flavanone and isoflavones having two prenyl groups.[68-70] A typical example can be shown in the EI spectrum of kuwanon C (29)[11,63] (Figure 14 and Scheme 17).

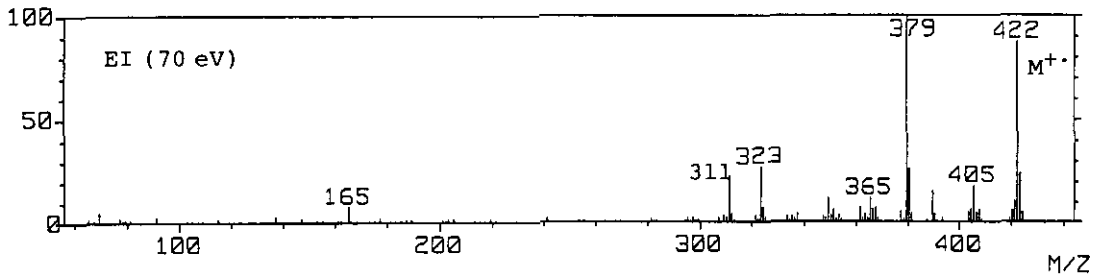
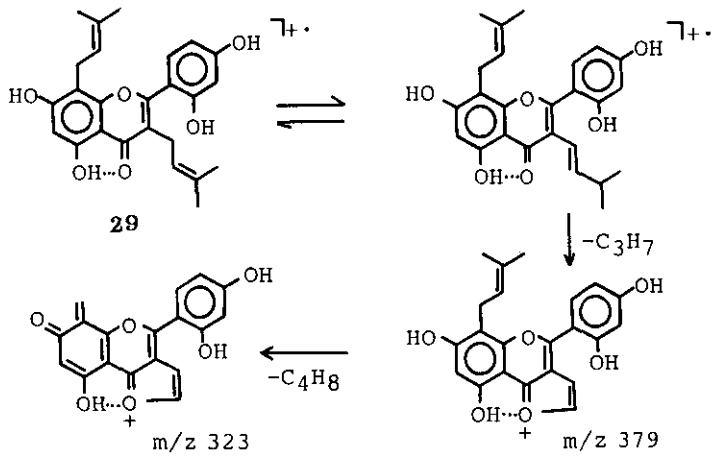


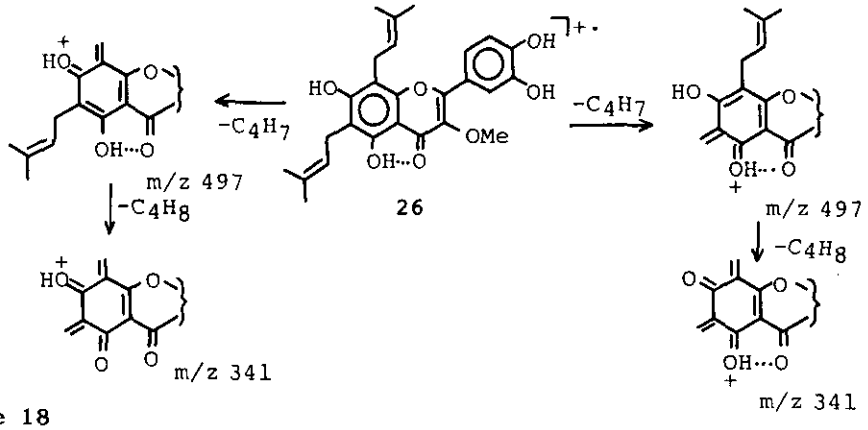
Figure 14 EI mass spectrum of kuwanon C (29).



Scheme 17

2.3.3 (M - C_4H_7 - 56) Ion

The successive fragment (M - C_4H_7 - 56) ions can be often observed in the EI spectra of the flavonoids having two prenyl groups.[11,22,48,61,64-67,70] A typical example can be seen in the EI spectrum of broussoflavonol B (26), as shown in Figure 12. The fragmentation is shown in Scheme 18.



Scheme 18

3. FAST-ATOM BOMBARDMENT MASS SPECTRA

The technique of fast-atom bombardment (FAB) ionization, pioneered by Barber and his colleagues,[71-73] is very useful for the determination of the molecular weight and structure of complex compounds such as polar antibiotics, polypeptides, glycosides, organic salts and other large molecules. Although the prenylated flavonoids, except for glycosides, can be successfully measured by EI-MS, we studied the FAB spectra of the flavonoids by comparing with those of the EI and CI spectra in order to learn the features of fragmentation in FAB-MS.[11,12,14,74] In this section, we describe the characteristic fragmentation in the FAB spectra and the identification of the prenylated flavonoids using FAB fragmentation patterns.

3.1 Characteristic Fragmentation Patterns

3.1.1 Monoprenylated Flavonoids

The FAB spectra of monoprenylated flavonoids generally show a characteristic fragment (MH - 56) ion peak by the loss of a neutral fragment C_4H_8 from the protonated molecules MH^+,[11,13] regardless of its location of prenyl group. Figures 15(a) and (b) are the FAB spectra of morusin (1) and

anhydroicaritin (**30**),[75] respectively. The fragmentations for these compounds can be illustrated as shown in Scheme 19.

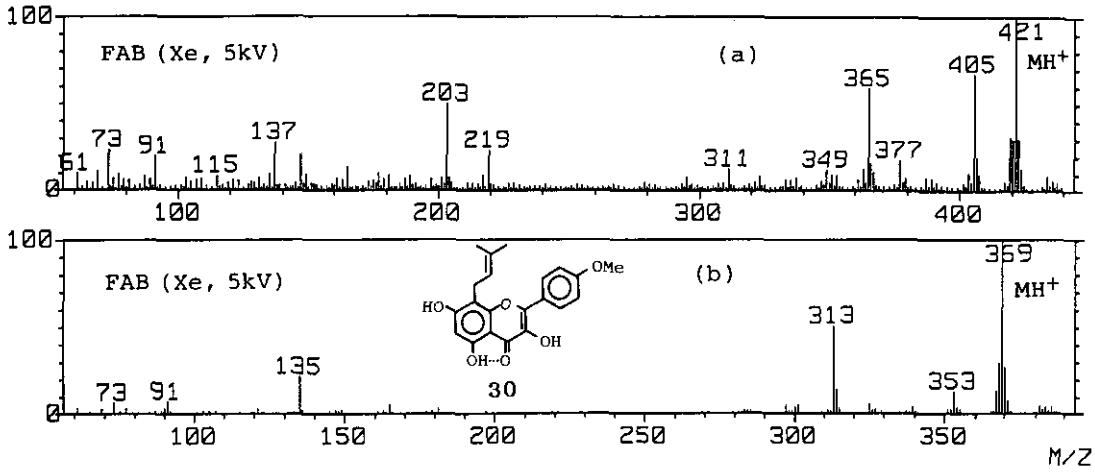
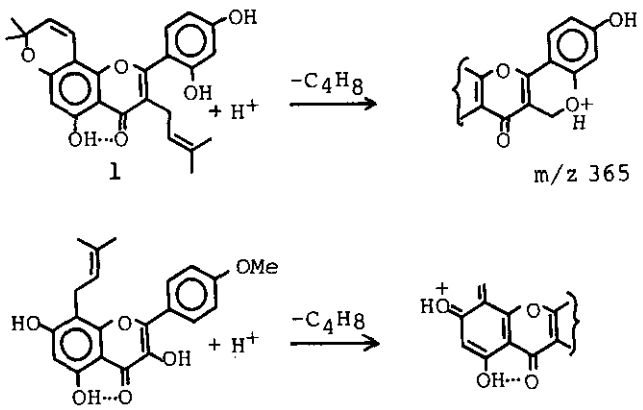


Figure 15 FAB mass spectra of (a) morusin (1) and (b) anhydroicaritin (**30**).



Scheme 19

A few exceptions for the fragmentation MH^+ - 56 can be found in the FAB spectra of sanggenons A (**19**)[57] and L (**20**).[58] These compounds give the fragment (MH - 68) ion by the loss of a neutral fragment C_5H_8 from the MH^+ ions in their FAB spectra, e.g., see Figure 16 and Scheme 20 for the compound (**19**).[12]

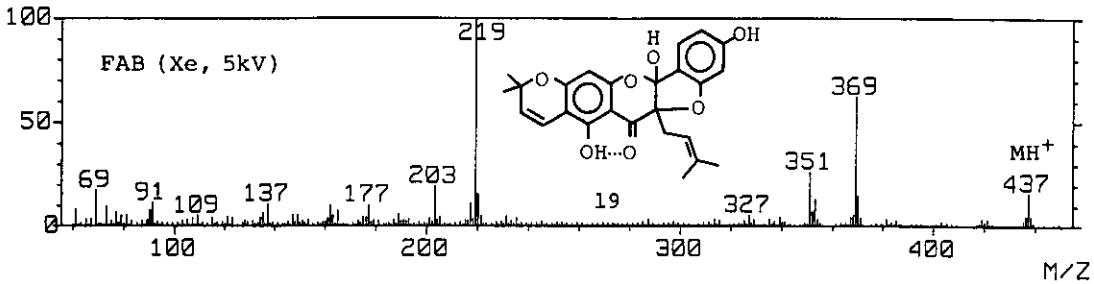
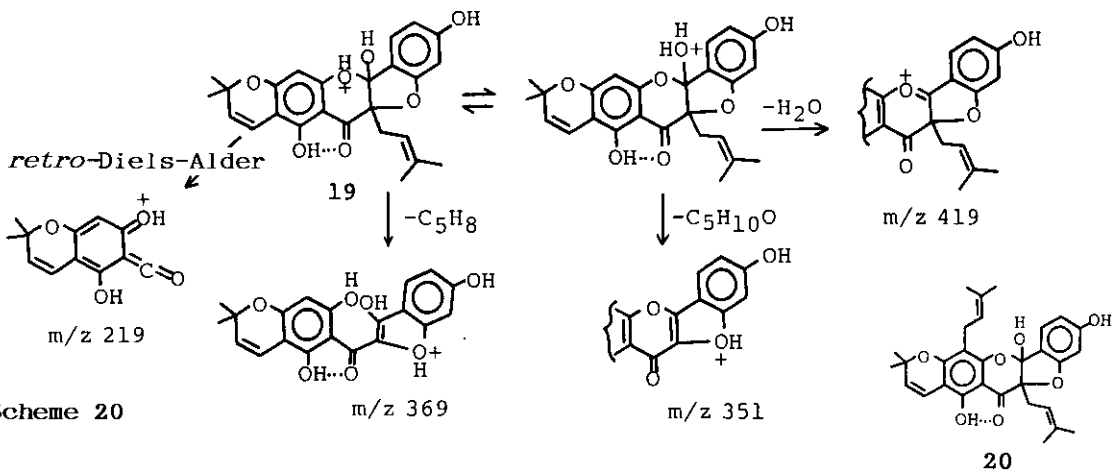


Figure 16 FAB mass spectrum of sanggenon A (19).



Scheme 20

3.1.2 Diprenylated Flavonoids

Broussoflavonol B (26) and kuwanon C (29), having two prenyl groups, give the characteristic two fragment (MH - 56) and (MH - 56 - 56) ions originating from the degradation of the prenyl group(s) in their FAB spectra[11] as shown in Figures 17(a) and (b), respectively. These patterns seem to be monotonous compared with the corresponding EI spectral patterns (see Figures 12 and 14). The fragmentation pattern in FAB-MS seems to be useful for characterization of the presence of two prenyl groups in the molecule. However, the FAB spectrum of sanggenon L (20) gives the fragment peaks corresponding to (MH - 68) and (MH - 68 - 56) ions,[14] as partially described in the section 3.1.1.

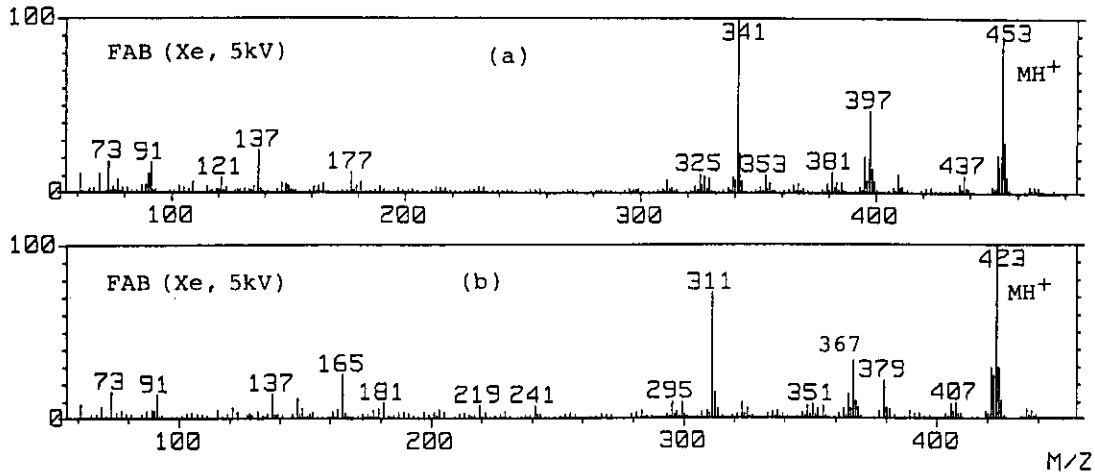


Figure 17 FAB mass spectra of (a) broussoflavonol B (**26**) and (b) kuwanon C (**29**).

3.2 Identification of Prenylated Flavonoids

3.2.1 6- and 8-Prenylated Flavonoids

As described in the section 2.1, 6- and 8-prenylated flavanones can not be distinguished from each other by means of their EI spectral patterns, whereas 6- and 8-prenylated flavones and isoflavones are distinguishable. The difficulty for the flavanones is due to a thermal isomerization as shown in the Scheme 5. We now employed the FAB technique in order to avoid the effects of thermal isomerization. The FAB spectra of 6-prenylated and 8-prenylated flavanones (**4** and **5**) are shown in Figures 18(a) and (b), respectively. The characteristic fragments at m/z 301 and 165 are formed by the loss of the neutral fragment C_4H_8 from the MH^+ ions at m/z 357 and by the *retro*-Diels-Alder cleavage from the fragment at m/z 301, respectively. The fragmentation patterns in Figure 18 indicate that the loss of C_4H_8 from MH^+ ion of 8-prenylated flavavone (**5**) is less likely to occur than that from the corresponding ion of 6-prenylated flavanone (**4**). The tendency can be observed also in the FAB spectra of 6- and 8-prenylated flavones and isoflavones,[13] though the reason is not clear. This suggests the possibility that 6- and 8-prenylated flavonoids are distinguishable by means of their FAB spectra.

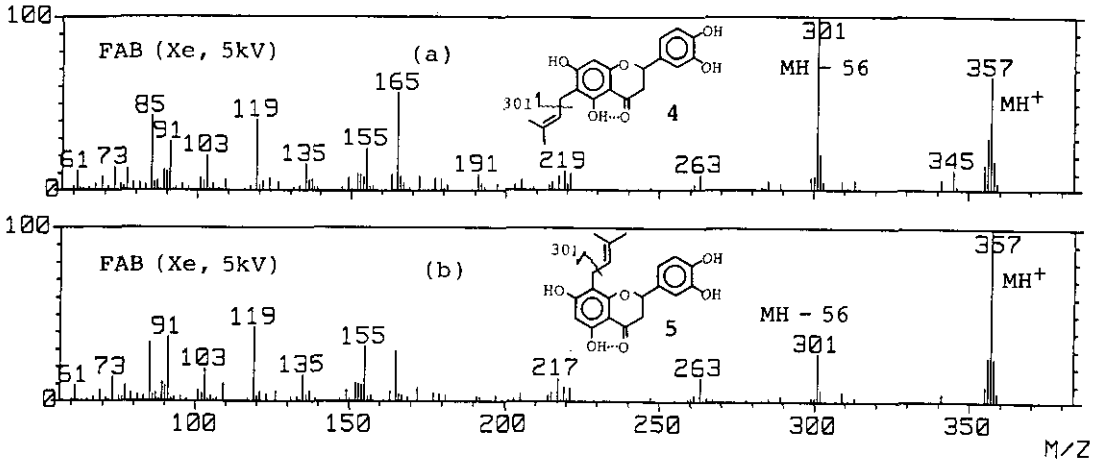


Figure 18 FAB mass spectra of (a) 6-prenylated and (b) 8-prenylated flavanons (**4** and **5**).

3.2.2 Compounds Containing 2,2-Dimethylpyran Ring[11]

The FAB spectra of certain prenylated flavonoids containing a 2,2-dimethylpyran ring show the characteristic fragment (MH - C_4H_8 - 42) and (MH - C_4H_8 - 54) ions originating from the degradation of the pyran ring.[11] A typical example can be found in the FAB spectrum of morusin (**1**), as shown in Figure 19(a) and Scheme 21. The characteristic fragmentations

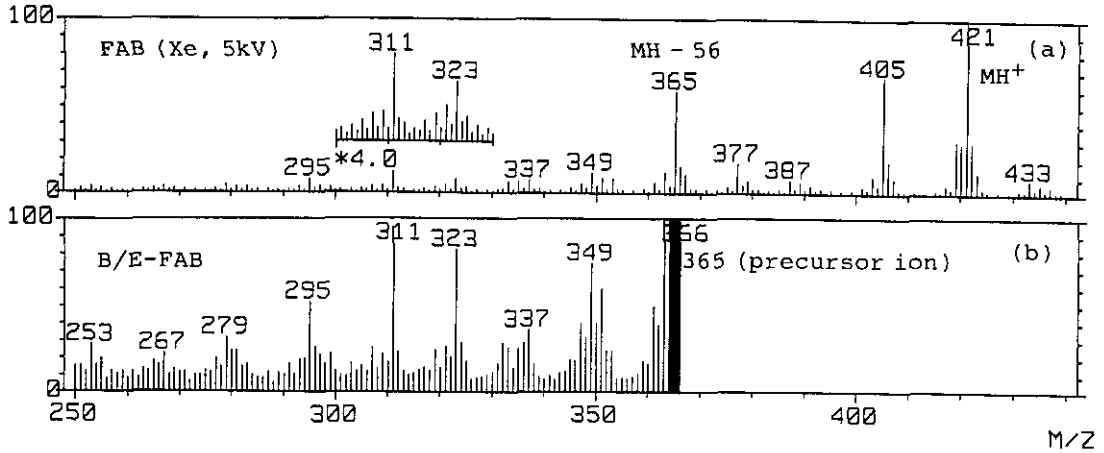
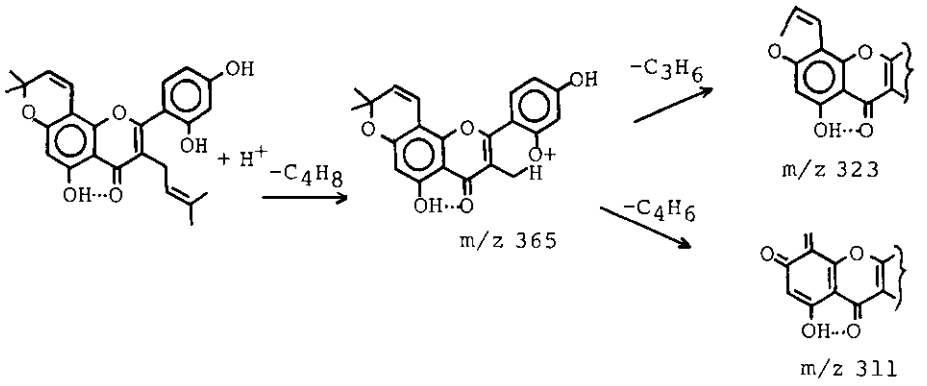


Figure 19 (a) FAB mass spectrum of (**1**) and (b) B/E linked scan FAB spectrum of the fragment ion at m/z 365.



Scheme 21

can be supported by the B/E-constant linked scan FAB spectrum of the fragment (MH - C_4H_8) ion at m/z 365, as shown in Figure 19(b).

Furthermore, the fragment (MH - C_4H_8 - 42) and (MH - C_4H_8 - 54) ions can be observed in the FAB spectrum of broussoflavonol A (6)[76] (Figure 20).

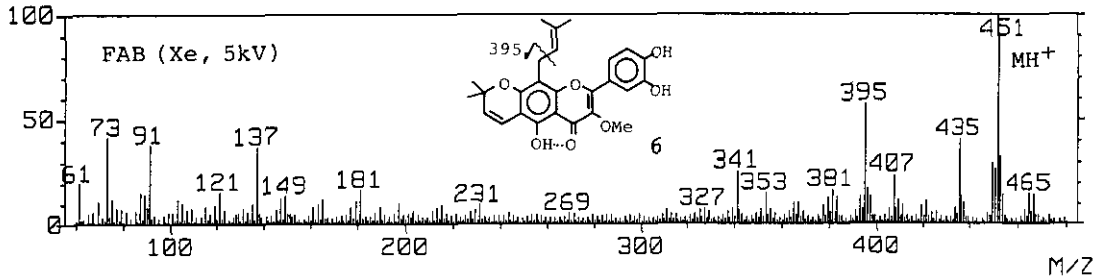


Figure 20 FAB mass spectrum of broussoflavonol A (6).

The characteristic fragment (MH - C_4H_8 - 42) and (MH - C_4H_8 - 54) ions can never be observed in the corresponding EI spectrum, so that the observation of their fragments in the FAB spectra of prenylated flavonoids seems to be useful for characterization of the presence of a 2,2-dimethylpyran ring.

4. CHEMICAL IONIZATION MASS SPECTRA

The chemical ionization (CI) method is not useful for the structural determination of prenylated flavonoids, since the CI spectra generally do not show the characteristic fragmentation pattern reflecting the chemical structure.[11,12,14] The CI spectra generally show the intense protonated molecule MH^+ ion peaks and only a few fragments which are weak in the relative intensity. The CI spectra of morusin (1),[11] broussoflavonol B (26),[11] sanggenon A (19)[12] and kazinol B (18)[14] are shown in Figures 21(a), (b), (c) and (d), respectively.

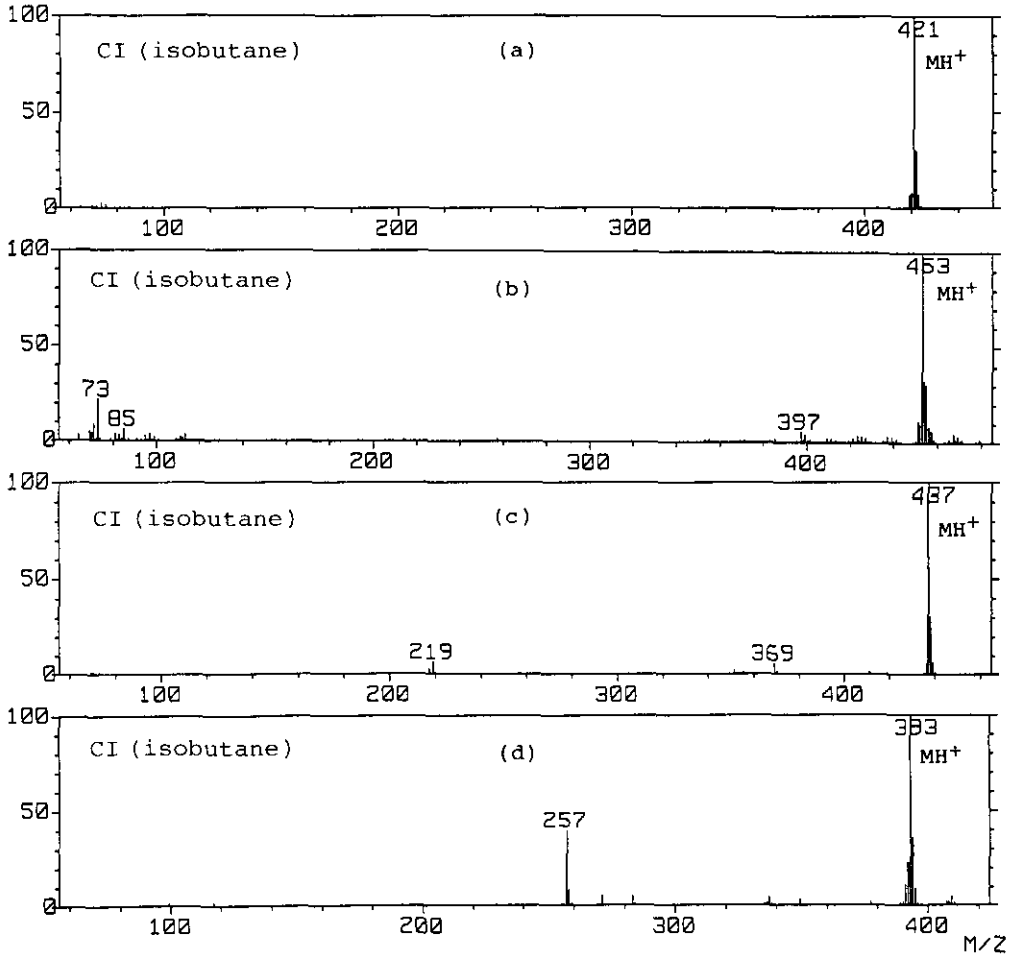


Figure 21 CI mass spectra of (a) morusin (1), (b) broussoflavonol B (26), (c) sanggenon A (19) and (d) kazinol B (18).

5. SUMMARY AND CONCLUSIONS

It is noteworthy that the EI spectra of prenylated flavonoids show a great variety of fragmentation patterns originating from the degradation of prenyl group(s). In this review, we described that the EI fragmentation patterns are very useful for the determination of the location of prenyl group. The fragmentation patterns are exactly dependent on the adjacent functional group(s) and the location of prenyl group. For more accurate determination of the location of prenyl group based on the EI fragmentation patterns, however, it is necessary to analyze the EI fragmentation of the simple prenylated compounds such as (15) and (21).

Furthermore, it was described that the FAB fragmentation patterns are useful for the identification of prenylated flavonoids.

In conclusion, we insist here that the EI and FAB spectra should be more positively used for the structural determination of organic compounds.

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