

On the Mass Spectra of Several Furanocoumarins having Various Isoprenoidal Residues

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Mass spectra of several disubstituted furanocoumarins, namely phellopterin, byakangelicol, byakangelicin, anhydrobyakangelicin, neobyakangelicol and alloisoimperatorin were elucidated. The mass spectra of these compounds are characteristic respectively, especially on cleavages of their side chains.

The results are shown in Fig. 1—6 and Chart 1—6.

Recently we obtained several furanocoumarins from the root of *Angelica dahurica* BENTH. et HOOK.²⁾ Then, we studied the mass spectra of the 5,8-disubstituted psoralen-type furanocoumarins, namely phellopterin, byakangelicol, byakangelicin, anhydrobyakangelicin, neobyakangelicol and alloisoimperatorin. The mass spectra of furanocoumarins were reported in several papers, for instance N.S. Vul'fson,³⁾ C.S. Barnes,⁴⁾ T. Furuya,⁵⁾ M. Nakayama,⁶⁾ J.P. Kutney⁷⁾ and their co-workers interpreted the fragmentations of the compounds. However, most of these papers explained the cleavages of furanocoumarin skeletons with methoxyl or hydroxyl groups. And N.S. Vul'fson, *et al.*³⁾ accounted for the mass spectra of furanocoumarins with isoprenoidal residues, but none of 5,8-disubstituted compounds. Furthermore, many flavones, chromones, xanthenes and quinones with isoprenoidal side chains are known, and a few reports⁸⁻¹¹⁾ have been described on the mass spectra of these compounds.

Phellopterin

The mass spectrum of phellopterin did not afford its molecular ion (m/e 300), and the absence of the ion is found in this compound only among its analogues. Compared with the mass spectra³⁾ of imperatorin and isoimperatorin having the same side chain, its fragmentation is similar to both. Its molecule generated a major ion (m/e 232) and a significant ion (m/e 69) by β -cleavage in its long side chain accompanied with hydrogen transfer by the first electron attack, then the ion (m/e 232) produced three ions of m/e 217, 189 and 161 as the result of the losses of a methyl group and two molecules of CO. Production of its base peak (m/e 202) is probably due to direct decomposition from the molecular ion by contemporaneous losses in two side chains, and this suggestion is supported by the following fact. This base peak is considered to be same with the molecular ion of xanthotoxol,⁴⁾ because the mass spec-

- 1) Location: 2-2-1 Oshika, Shizuoka-shi, 420, Japan.
- 2) Y. Saiki, K. Morinaga, O. Okegawa, S. Sakai, Y. Amaya, A. Ueno, and S. Fukushima, *Yakugaku Zasshi*, **91**, 1313 (1971).
- 3) N.S. Vul'fson, V.I. Zaretskii, and V.G. Zaikin, *Dokl. Akad. Nauk S.S.S.R.*, **155**, 1104 (1964) [*Chem. Abst.*, **61**, 1737 (1964)].
- 4) C.S. Barnes and J.L. Occolowitz, *Austral. J. Chem.*, **17**, 975 (1964).
- 5) T. Furuya, H. Kojima, and H. Sato, *Chem. Pharm. Bull.* (Tokyo), **15**, 1362 (1967).
- 6) M. Nakayama, S. Eguchi, A. Matsuo, S. Hayashi, S. Hishida, and Y. Kato, *Shitsuryo Bunseki*, **20**, 89 (1972).
- 7) J.P. Kutney, G. Eigendorf, and T. Inaba, *Org. Mass Spectr.*, **5**, 249 (1971).
- 8) A. Peter, P. Stainton, and M. Barber, *J. Heterocycl. Chem.*, **2**, 262 (1965).
- 9) P.H. McCabe, R. McCrindle, and R.D.H. Murray, *J. Chem. Soc. (C)*, **1967**, 145.
- 10) E. Ritchie, W.C. Taylor, and J.S. Shannon, *Tetrahedron Letters*, **1964**, 1437.
- 11) F. Bohmann and K.-M. Kleine, *Chem. Ber.*, **99**, 885 (1966).

trum of an analogous compound, imperatorin³⁾ exhibits occurrence of the same ion (m/e 202) and is quite similar to that of phellopterin especially on several fragment ions of m/e 174, 161 and 145 and their intensities. An alternative interpretation that the base peak (m/e 202) can be derived from another major ion (m/e 232) by elimination of formaldehyde is excluded, because of absence of the peak (m/e 202) in the mass spectra of byakangelicol and byakangelicin in spite of production of the ion (m/e 232) as shown on Fig. 2 and 3. Therefore, the occurrence of the base peak (m/e 202) comes from the molecular ion by α - and β -cleavages in both side chains, and this phenomenon is quite unique. The fragmentation of phellopterin is proposed as shown on Chart 1.

Byakangelicol

The mass spectrum of byakangelicol is characterized by the presence of a considerably intense molecular ion (m/e 316, 18%), by the β -cleavage in its long side chain and by an intense

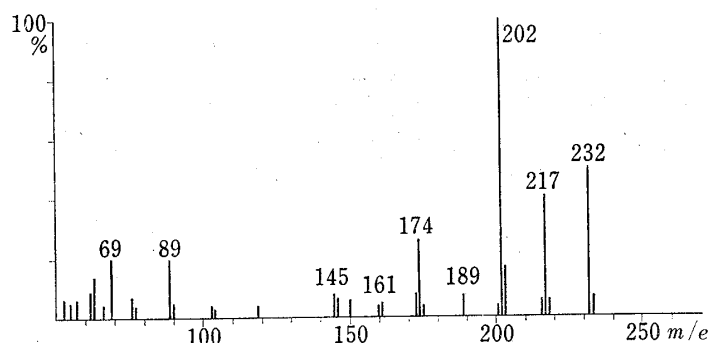
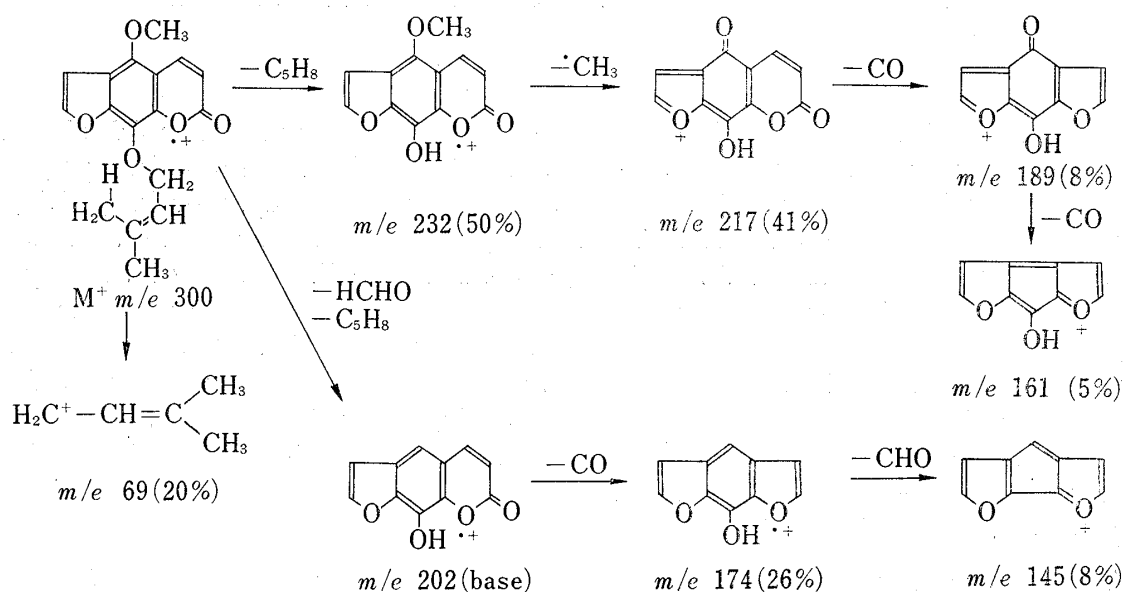


Fig. 1. phellopterin

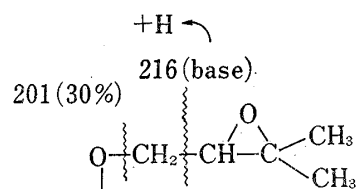
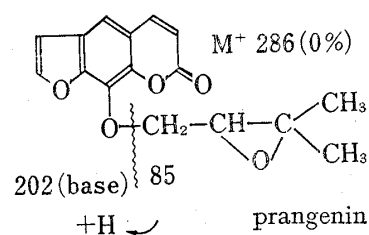
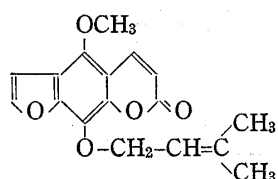


Chart 2. Mass Spectral Patterns³⁾ of Prangenin and Oxypeucedanin

ion (m/e 59). Mono-substituted linear furanocoumarins connected with C-O juncture did not afford their molecular ions except oxypeucedanin hydrate, while di-substituted analogues generated considerably predominant molecular ions except phellopterin. The base peak (m/e 232) and another major ion (m/e 85) of byakangelicol are produced by β -cleavage on the long chain, and this feature is same with the case of phellopterin. The second intense ion (m/e 217) is derived from the base peak as the case of phellopterin. Compared with another compound prangenin³⁾ that includes the same long chain in its molecule at the same position, their mass spectral patterns are quite similar to each other on their cleavages. However, oxypeucedanin and byakangelicol, which have the same chain on opposite sides of their benzene nuclei, differ distinctly each other in their mass spectral patterns. Namely, γ -cleavage is predominant in oxypeucedanin, while β -cleavage is so in byakangelicol. This spectral distinction is remarkable and significant, and is due to their positional correlations among their side chains and two oxygen atoms of furan and coumarin rings.

The ion (m/e 59) is usually found in the spectra of many compounds possessing tertiary hydroxy-isopropyl group such as α -terpineol¹²⁾ and myrcenol,¹³⁾ therefore oxypeucedanin hydrate and byakangelicin containing such group exhibit this ion naturally. However, byakangelicol lacking of such group produced this ion in considerable intensity that is more than in the case of byakangelicin. This feature is notable in comparison with the mass spectra³⁾ of oxypeucedanin and prangenin in which the ion (m/e 59) did not appear in spite of possession of same side chain in their molecules.

Another ion (m/e 203) is weak and minor, however it is presumably derived from the fragment ion (m/e 232) by the losses of one molecule of CO and a hydrogen atom, therefore its structure is thought to be quite different from the base peak (m/e 202) of phellopterin in spite of difference of m/e 1. Moreover, this ion (m/e 203) is also found in the mass spectra of phellopterin, byakangelicin, anhydrobyakangelicin and neobyakangelicol. The fragmentation of byakangelicol is proposed as shown on Chart 3.

Byakangelicin

The mass spectrum of byakangelicin is similar to that of byakangelicol except a few differences. The long side chain of byakangelicin is splitted into several portions, and then

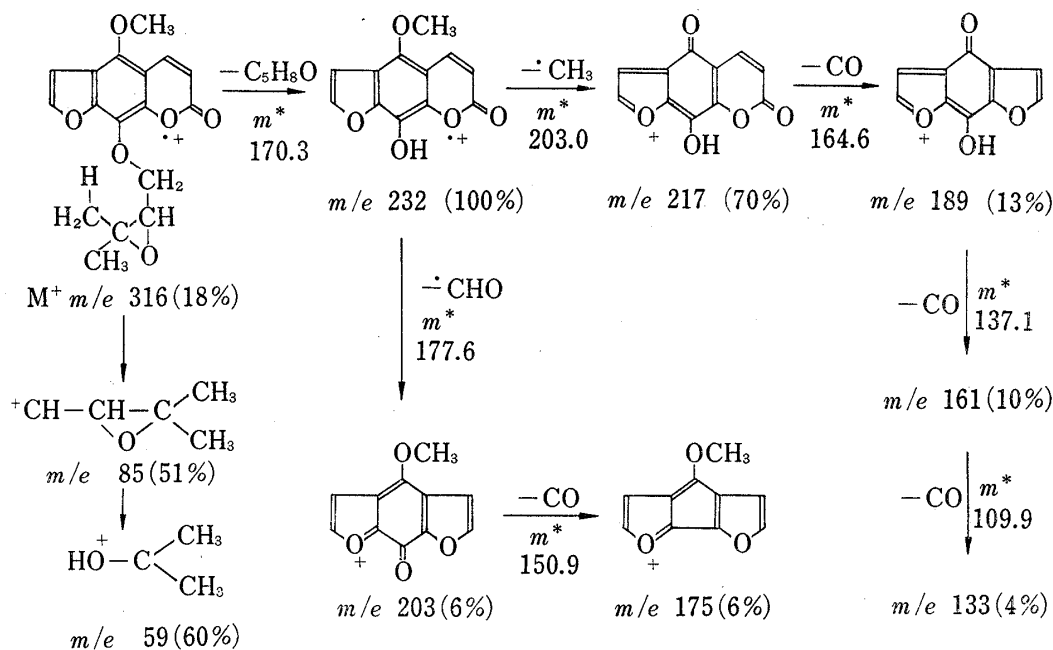


Chart 3. Proposed Fragmentation of Byakangelicol

12) E. von Sydow, *Acta Chem. Scand.*, **17**, 2504 (1963).

13) K.L. Stevens, L. Jurd, and G. Manners, *Tetrahedron*, **28**, 1939 (1972).

several minor ions are observed at m/e 319, 316, 245, 59 and 43. Compared with oxypeucedanin hydrate possessing the same side chain, the mass spectrum of byakangelicin is also similar to each other in produced process of their base peaks by β -cleavage of their long side chains, however the intensity of another ion (m/e 59) is remarkably less than that of oxypeucedanin hydrate, and than even that of byakangelicol having no hydroxy-isopropyl group mentioned above.

As a matter of fact, it seems strange that the mass spectra of byakangelicin and oxypeucedanin hydrate resemble each other on cleavages of their long side chains while those of byakangelicol and oxypeucedanin differ apparently as mentioned above in spite of their same structural correlation.

Anhydrobyakangelicin

The mass spectrum of anhydrobyakangelicin is characterized by the presence of an intense molecular ion (m/e 316), by a peculiar ion (m/e 245) caused by the loss of C_4H_6O by γ -fission,

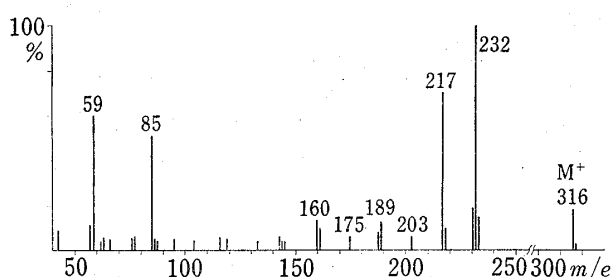


Fig. 2. Byakangelicol

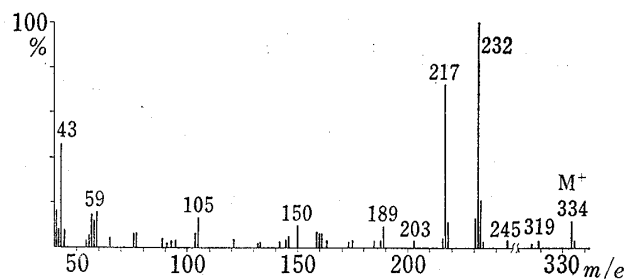
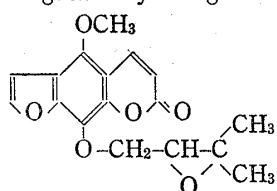
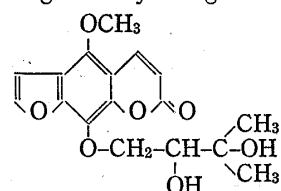


Fig. 3. Byakangelicin



$m^* 203.0; 232 \rightarrow 217$

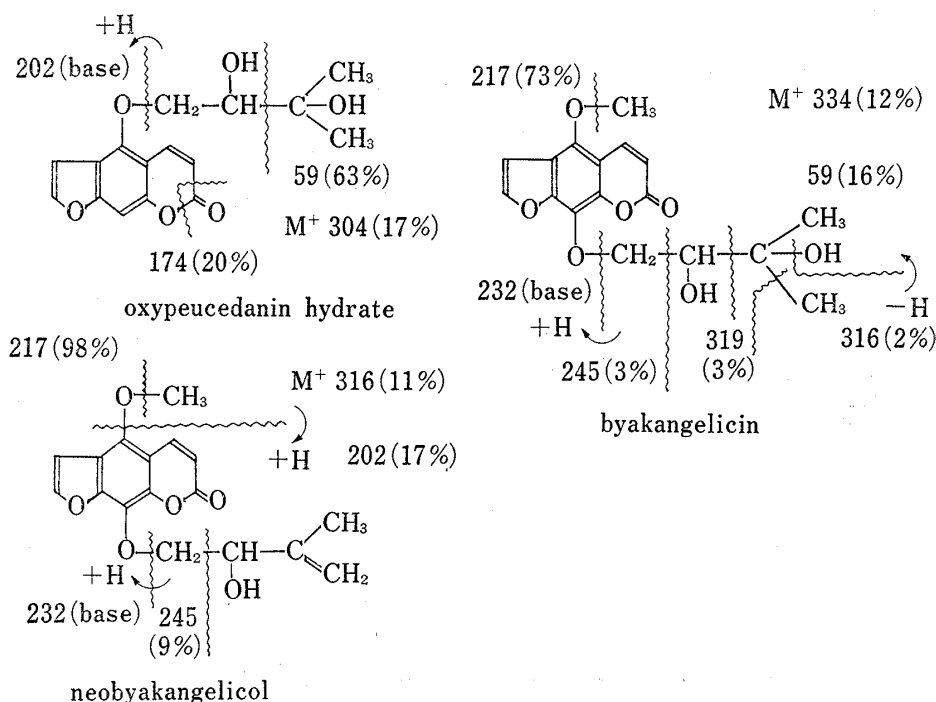


Chart 4. Mass Spectral Patterns of Oxypeucedanin Hydrate, Byakangelicin and Neobyakangelicol

and by a base peak (m/e 231) possessing a ketone-type structure. The base peak (m/e 231) is derived from β -cleavage on the side chain without hydrogen transfer, and it is unique in the mass spectrum of this compound and not found in those of the homologues with such long chains, but observed only in the case of the compounds having a small substituent such as methoxyl group.⁴⁾ The fragmentation of anhydrobyakangelicin is shown on Chart 5.

Neobyakangelicol

The mass spectrum of neobyakangelicol is also similar in most aspects to that of byakangelicol and byakangelicin, however it is also allied to that of anhydrobyakangelicin especially in a fragment ion (m/e 245), furthermore presence of a considerably intense peak (m/e 202) shows similarity to that of phellopterin. Therefore, the mass spectrum of this compound is characterized as an intermediate pattern possessing all spectral features of these homologues.

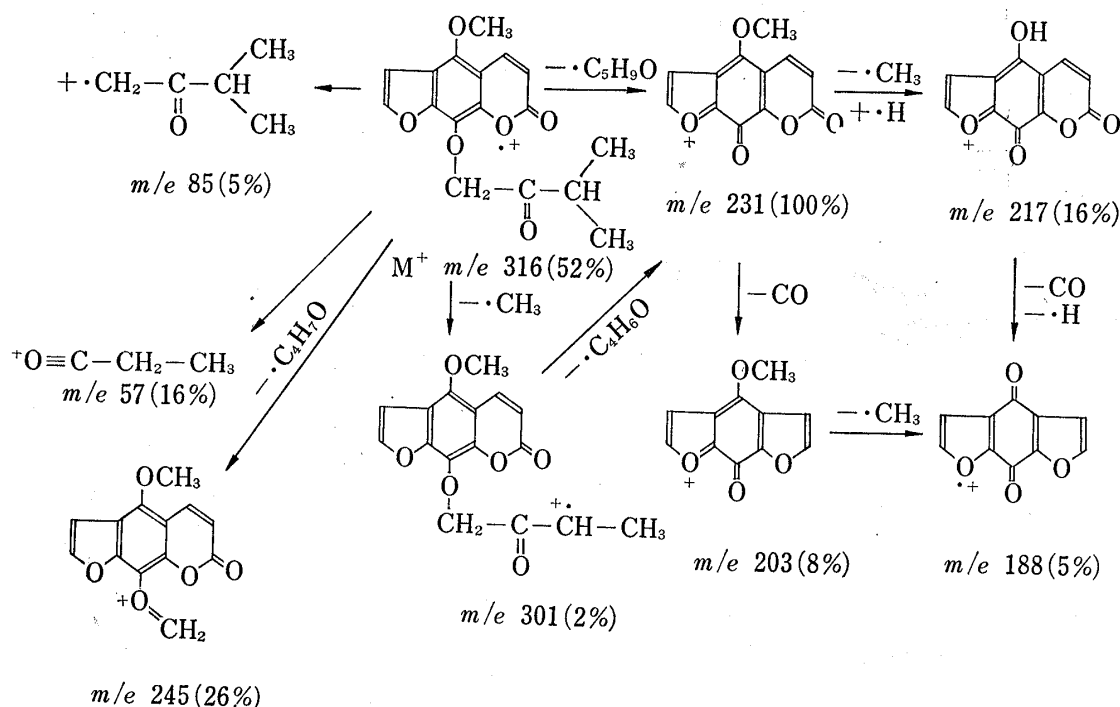


Chart 5. Proposed Fragmentation of Anhydrobyakangelicin

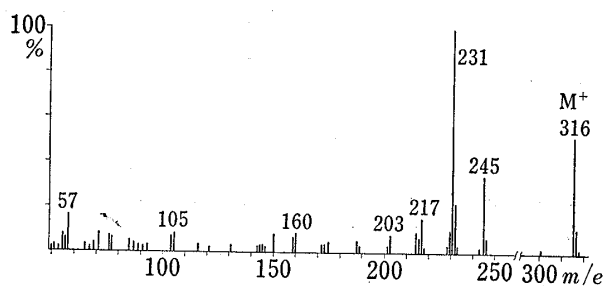


Fig. 4. Anhydrobyakangelicin

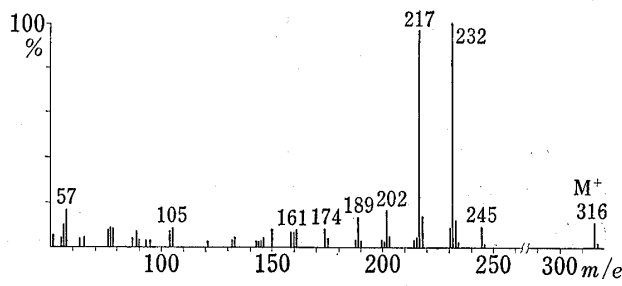
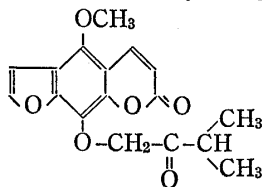
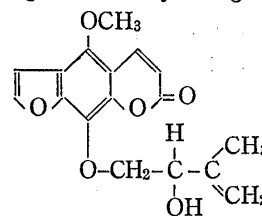


Fig. 5. Neobyakangelicol



Alloisimperatorin

Alloisimperatorin possesses an isoprenoidal chain by C-C juncture, therefore the nature differs from other furanocoumarins mentioned above. The mass spectrum of alloisimperatorin is very similar to that of alloimperatorin⁷⁾ except a few distinctions. Alloisimperatorin afforded a stable molecular ion (m/e 270) forming its base peak, then the ion was splitted into three ions of m/e 202, 255, and 215 which underwent respectively consecutive losses of CO.

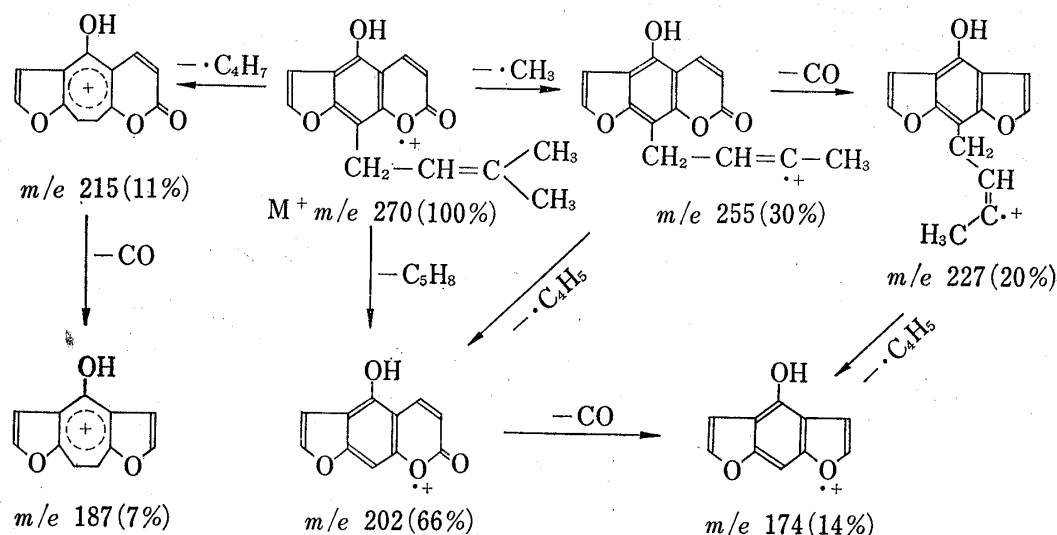


Chart 6. Proposed Fragmentation of Alloisimperatorin

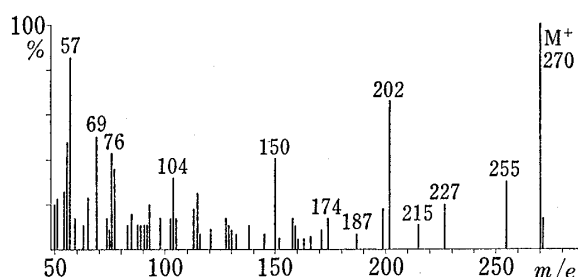
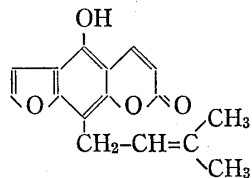


Fig. 6. Alloisimperatorin



The distinction between alloisimperatorin and alloimperatorin is observed on three ions at m/e 150, 69 and 57 which are major in the mass spectrum of the former. One of them (m/e 150) is too strange and puzzling to figure out.

Experimental

The mass spectra were determined on a Hitachi RMS-4 mass spectrometer using a direct inlet system. The source temperature was 200° to 250°. The applied energy of the electron beam was 80 eV.

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