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The Mass Spectra of Chalcones, Flavones and Isoflavones*

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The fragmentation of flavonoid compounds by electron impact has been studied and the following results described: 1) Chalcones gave the usual fragmentation pattern; however, 2′-hydroxy chalcones showed complex spectra according to the isomerization of chalcone to flavanone. 2) The fragmentation pathways of flavones were decided by comparison with many kinds of halogen-substituted flavones. 3) Isoflavone gave the M-1 ion as the base peak, and no loss of CO was observed.

A few reports on the mass spectral investigation of flavonoids have been published.[1] However, the fragmentation pathways of these compounds on electron impact have not always been established. The mass spectra of flavone and halogen-substituted flavones have been recorded; the natural isotopic abundance of halogen made the structures of most fragment ions clear. 2′-Hydroxychalcone and 2′-hydroxyhalochalcones give complex spectra because of the isomerization of chalcone to flavanone in the spectrometer. Furthermore, the mass spectra of isoflavones have been determined; in them M-1 ions are always characteristic base peaks and no loss of CO is observed, unlike as in flavones.

Experimental

All the mass spectra were obtained with an Hitachi RMU-6D Mass Spectrometer. Mass spectra were recorded with 70 V. electron energy and an 80 μamp. ionizing current. The temperature of the ion source was 250°C. All the samples were synthesized according to the known procedure.[2]

Results and Discussion

Chalcones.—The mass spectra of 4′-methoxychalcone (I) and 4-methoxychalcone (II) have been determined (Fig. 1). Both I and II give the molecular ion (a, a′) (m/e 238), the M-1 ion (b, b′) (m/e 237) and the M-CH_3 ion (c, c′) (m/e 223) as common fragments. The peaks at m/e 103 (e) and m/e 131 (f) in I are shifted to m/e 133 (e′) and m/e 161 (f′) in II respectively; moreover, the peaks at m/e 105 (d′) and m/e 77 (g′) in II are shifted to m/e 135 (d) and m/e 107 (g) in I respectively. The difference between the two compounds is the location of the methoxyl group, that is, 30 mass units.

The spectra of the two compounds are very similar, but the process of cleavage is not fully identical; for instance, the phenyl cation (g′) (m/e 77) in II is due to the loss of CO from the benzoyl cation (d′) which was formed by the fragmentation of the methyl radical from the molecular ion (a′) followed by the cleavage of the c′ cation. However, an abnormally abundant phenyl cation (h) in I arises from the methoxyphenyl cation (g) and the styryl cation (e). All these pathways are ascertained by means of the presence of metastable ions (Table I). Furthermore, the supposition that the (h) ion deos not arise by the simple

TABLE I. METASTABLE IONS OF METHOXYCHALCONES

Reaction	Metastable
4′-Methoxychalcone	
$238^+ \rightarrow 223^+ + 15$	209
$238^+ \rightarrow 135^+ + 103$	76.5
$238^+ \rightarrow 103^+ + 135$	46.2
$223^+ \rightarrow 131^+ + 92$	77
$135^+ \rightarrow 28^+ + 107$	58
$103^+ \rightarrow 77^+ + 26$	56.5
4-Methoxychalcone	
$238^+ \rightarrow 223^+ + 15$	209
$238^+ \rightarrow 161^+ + 77$	109
$223^+ \rightarrow 105^+ + 118$	49.5
$161^+ \rightarrow 133^+ + 28$	109.5
$105^+ \rightarrow 77^+ + 28$	56.5

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[1] a) J. H. Beynon, "Mass Spectrometry and its Application to Organic Chemistry," Elsevier Publishing Company, Amsterdam (1960), p. 270.
b) R. I. Reed and J. M. Wilson, *J. Chem. Soc.*, **1963**, 5949.
c) C. S. Barnes and J. L. Occolowitz, *Austral. J. Chem.*, **17**, 975 (1964).
d) H. Budzikiewicz, C. Djerassi and D. H. Williams, "Structure Elucidation of Natural Products by Mass Spectrometry," Vol. II Holden Day, Inc., Sanfrancisco (1964), p. 262.

[2] F. C. Chen and T. H. Tsai, *J. Taiwan Pharm. Association*, **4**, 42 (1952) [*Chem. Abstr.*, **49**, 5374 (1955)]; F. C. Chen, C. T. Chang, T. T. Shi and T. Lin, *J. Chinese Chem. Soc.*, Ser. II, **1**, 159 (1954) [*Chem. Abstr.*, **50**, 2476 (1956)].

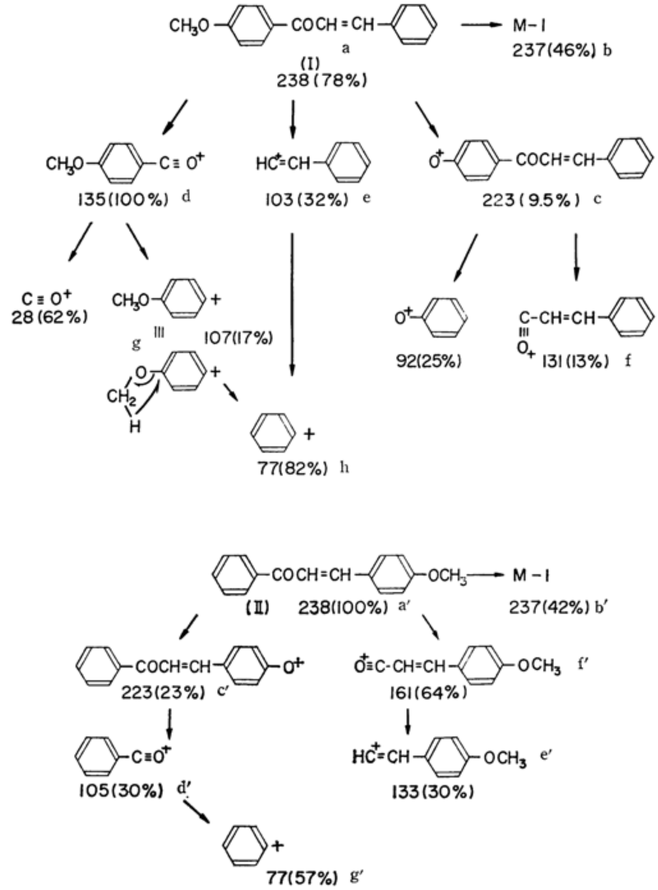


Fig. 1. Fragmentation of 4′-methoxy-(I) and 4-methoxychalcone (II).

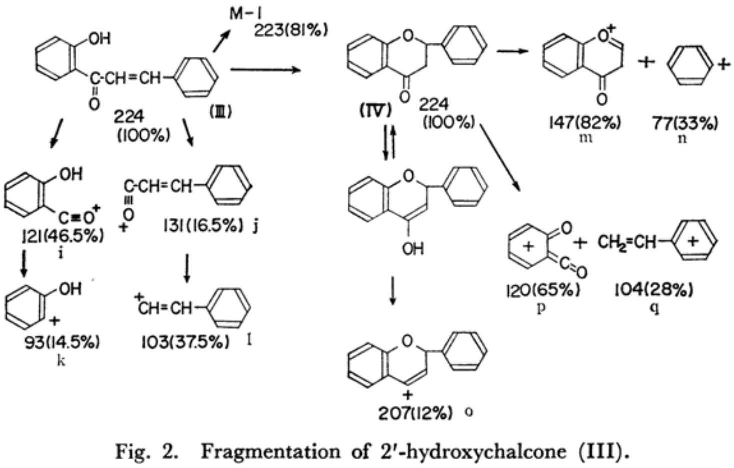
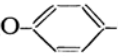


Fig. 2. Fragmentation of 2′-hydroxychalcone (III).

cleavage of the molecular ion (a) is supported by the fact that no CH_3O--$COCH{=}CH^+$ ion appears in the spectrum of I.

The spectrum of 2′-hydroxychalcone (III) is interpreted in the same way as in the case of either I or II (Fig 2. Table II). The peaks at *m/e* 121 (i), *m/e* 131 (j), *m/e* 93 (k) and *m/e* 103 (l) must arise from 2′-hydroxychalcone itself. However, that the chalcone gives rise to the M–C_6H_5 ion (m) and the M–OH ion (o) is not conceivable; these cations, m and o, most probably arise from the loss of the phenyl radical and the hydroxyl radical respectively from the heat-isomerization product of the chalcone,

Table II. Mass spectra of 2'-hydroxychalcone and 2'-hydroxyhalochalcones

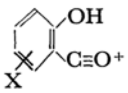
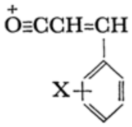
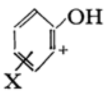
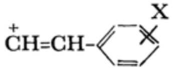
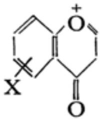
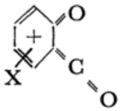
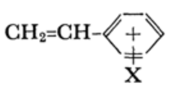
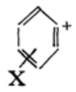
				Fragments from chalcone				Fragments from flavanone				
	M	M-1	M-X					M-OH				
2'-Hydroxychalcone (III)	224 (100)	223 (81)		X=H 121 (47)	X=H 131 (16)	X=H 93 (14)	X=H 103 (37)	207 (12)	X=H 147 (82)	X=H 120 (65)	X=H 104 (28)	X=H 77 (33)
2'-Hydroxy-3-chlorochalcone (V)	258 (100) 260 (41)	257 (74) 259 (42)	223 (12.5)	X=H 121 (60)	X=Cl 165 (56) 167 (5)	X=H 93 (16)	X=Cl 137 (11) 139 (5)	241 (12) 243 (4)	X=H 147 (95)	X=H 120 (69)	X=Cl 138 (7) 140 (5)	X=Cl 111 (7) 113 (3)
2'-Hydroxy-4-chlorochalcone (VI)	258 (100) 260 (34)	257 (72) 259 (36)	223 (12.5)	X=H 121 (33)	X=Cl 165 (18) 167 (6)	X=H 93 (16)	X=Cl 137 (16) 139 (9)	241 (15) 243 (5)	X=H 147 (40)	X=H 120 (38)	X=Cl 138 (29) 140 (12)	X=Cl 111 (8) 113 (3)
2'-Hydroxy-3-bromochalcone (VII)	302 (100) 304 (78)	301 (56) 303 (67)	223 (15)	X=H 121 (52)	X=Br 209 (6) 211 (5.5)	X=H 93 (18)	X=Br 181 (5) 183 (5)	285 (9.5) 287 (9)	X=H 147 (52)	X=H 120 (62)	X=Br 182 (8) 184 (7.5)	X=Br 155 (1) 157 (1)
2'-Hydroxy-4'-bromochalcone (VIII)	302 (100) 304 (97)	301 (78) 303 (91)	223 (23)	X=Br 199 (31) 201 (32)	X=H 131 (26)	X=Br 171 (6) 173 (6)	X=H 103 (50)	285 (13) 287 (12)	X=Br 225 (75) 227 (72)	X=Br 198 (24) 200 (24)	X=H 104 (87)	X=H 77 (46.5)
2'-Hydroxy-5'-bromochalcone (IX)	302 (100) 304 (97)	301 (78) 303 (91)	223 (12.5)	X=Br 199 (20) 201 (19)	X=H 131 (21)	X=Br 171 (5) 173 (4.5)	X=H 103 (56)	285 (7.5) 287 (6.5)	X=Br 225 (48) 227 (47)	X=Br 198 (96) 200 (95)	X=H 104 (83)	X=H 77 (42.5)
2'-Hydroxy-5'-chlorochalcone (X)	258 (100) 260 (44)	257 (67) 259 (42)	223 (9)	X=Cl 155 (31) 157 (9)	X=H 131 (16)	X=Cl 127 (9) 129 (7)	X=H 103 (45)	241 (9.5) 243 (3)	X=Cl 181 (63) 183 (22)	X=Cl 154 (76) 156 (50)	X=H 104 (58)	X=H 77 (58)

Table III. Mass spectra of flavone and haloflavones

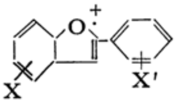
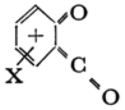
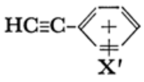
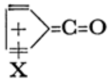
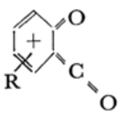
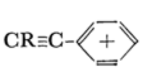
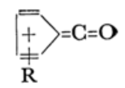
	M	M-1	M-CO 			
			X=X′=H	X=H	X′=H	X=H
Flavone (I)	222	221	194	120	102	92
	(100)	(33)	(52)	(80)	(12)	(43)
			X=Cl, X′=H	X=Cl	X′=H	X=Cl
6-Chloroflavone (II)	256	255	288	154	102	126
	(100)	(16)	(14)	(95)	(19)	(27)
	258	257	230	156		128
	(36)	(22)	(4)	(31)		(10)
			X=Cl, X′=H	X=Cl	X′=H	X=Cl
7-Chloroflavone (III)	256	255	228	154	102	126
	(100)	(23)	(48)	(50)	(37)	(35)
	258	257	230	156		128
	(31)	(21)	(14)	(15)		(11)
			X=Cl, X′=H	X=Cl	X′=H	X=Cl
8-Chloroflavone (IV)	256	255	228	154	102	126
	(90)	(12)	(15)	(100)	(15)	(20)
	258	257	230	156		128
	(25)	(15)	(7)	(44)		(7)
			X=H, X′=Cl	X=H	X′=Cl	X=H
4′-Chloroflavone (V)	256	255	228	120	136	92
	(92)	(13)	(32)	(100)	(12)	(70)
	258	257	230		138	
	(31)	(20)	(9)		(4)	
			X=Br, X′=H	X=Br	X′=H	X=Br
6-Bromoflavone (VI)	300	299	272	198	102	170
	(100)	(12)	(13)	(89)	(36)	(29)
	302	301	274	200		172
	(96)	(29)	(12.5)	(83)		(28.5)
			X=Br, X′=H	X=Br	X′=H	X=Br
7-Bromoflavone (VII)	300	299	272	198	102	170
	(100)	(20)	(45)	(50)	(60)	(30)
	302	301	274	200		172
	(98)	(37)	(44)	(49)		(29)
			X=Br, X′=H	X=Br	X′=H	X=Br
8-Bromoflavone (VIII)	300	299	272	198	102	170
	(100)	(13)	(15)	(87)	(22)	(13)
	302	301	274	200		172
	(96)	(28)	(15)	(84)		(12.5)
			X=I, X′=H	X=I	X′=H	X=I
6-Iodoflavone (IX)	348	347	320	246	102	218
	(100)	(7)	(8)	(52)	(14)	(20)
			X=I, X′=H	X=I	X′=H	X=I
7-Iodoflavone (X)	348	347	320	246	102	218
	(100)	(13)	(27)	(30)	(20)	(15)
			X=H, X′=I	X=H	X′=I	X=H
4′-Iodoflavone (XI)	348	347	320	120	228	92
	(100)	(5)	(14)	(75)	(9)	(41)

TABLE IV. MASS SPECTRA OF ISOFLAVONES

	M	M-1			
Isoflavone (II)	222 (91.5)	221 (100)	R=H 120 (40)	R=H 102 (11)	R=H 92 (34)
7-Methoxy-isoflavone (III)	252 (95)	251 (100)	R=OCH$_3$ 150 (50)	R=H 102 (10)	R=OCH$_3$ 122 (30)
2-Methyl-7-acetoxy-isoflavone (IV)	M 294 (13)	M-42 252 (81)	M-42-1 251 (100)	R=OH 136 (2)	R=CH$_3$ 116 (8)

that is, flavanone (IV). Other peaks at *m/e* 120 (p) and *m/e* 104 (q) which are never observed in the spectrum of chalcone without a hydroxyl group at C-2′, are also well-explained through the isomerization of III to IV.

The spectra of the following 2′-hydroxyhalochalcones have been determined (Table II): 2′-hydroxy-3-chloro-(V), 2′-hydroxy-4-chloro-(VI), 2′-hydroxy-3-bromo - (VII), 2′-hydroxy-4′-bromo-(VIII), 2′-hydroxy-5′-bromo-(IX) and 2′-hydroxy-5′-chlorochalcone (X). In all cases these hydroxyhalochalcones give molecular ions as the base peaks and M-X ions as the characteristic peaks. They also show both fragments from hydroxyhalochalcones (V-X) and the corresponding flavanones, as in the case of 2′-hydroxychalcone itself.

Flavones.—Barnes et al. reported that flavone (I) itself gives the molecular ion (*m/e* 222) as the base peak and shows the substantial loss of one hydrogen, thus giving an ion (*m/e* 221); one oxygen is readily eliminated as CO, but more readily by the retro-Diels-Alder fission of the heterocyclic ring, thus giving two ions, one with a quinonoid (*m/e* 120) (b), and the other a phenylacetylene (*m/e* 102) (c) structure. The d ion (*m/e* 92) arises from the loss of CO from the b ion (Fig. 3).

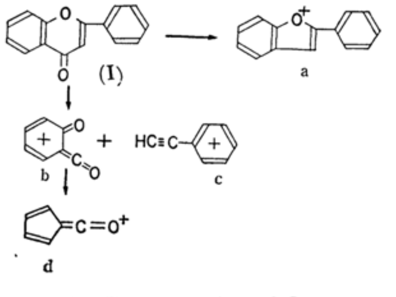


Fig. 3. Fragmentation of flavone.

The spectra of 6-chloro- (II), 7-chloro- (III), 8-chloro- (IV), 4′-chloro- (V), 6-bromo- (VI), 7-bromo- (VII), 8-bromo- (VIII), 6-iodo- (IX), 7-iodo- (X) and 4′-iodoflavone (XI) have also been determined. All the characteristic peaks arise from the haloflavones correspond to the peaks of the molecular ion, the M-1 ion, and to the a, b, c and d of flavone itself. Therefore, the breakdown process of flavone proposed by Barnes may be regarded as quite reasonable (Table III).

Isoflavones.—It has been reported[1a] that the spectrum of daidzein dimethyl ether (I) shows a peak at *m/e* 282 (molecular ion) as the base peak, other peaks at *m/e* 150 (a) and *m/e* 132 (b), and no M-CO ion (Fig. 4).

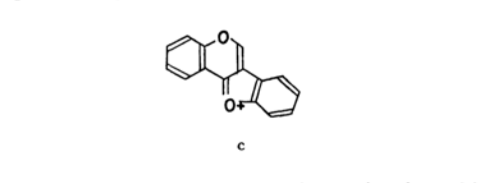
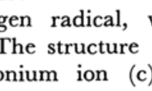


Fig. 4. Fragmentation of daidzein dimethyl ether.



c

However, according to our determination of isoflavone (II) and 7-methoxyisoflavone (III), M-1 ions appear as the base peaks. In the case of 2-methyl-7-acetoxyisoflavone (IV), the ion loses a ketene molecule from the molecular ion; then it loses one hydrogen radical, which appears as the base peak. The structure of the M-1 ion is probably an oxonium ion (c) results from the fragmentation of a hydrogen radical at C-2′ of the molecular ion. Because of the stability of the ion, no further fragmentation or loss of CO occurs, unlike as in flavones (Table IV).

Summary

The mass spectra of chalcones, flavones and isoflavones have been studied. From the metastable peaks or from a comparison with halogen-substituted compounds, the main fragmentation paths of chalcones and flavones on electron impact have been elucidated. The fragmentation of isoflavones, which give characteristic M-1 ions as base peaks has also been studied.

The authors wish to express their hearty thanks to Professor Koji Nakanishi for his encouragement throughout the course of this work.