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Mass Spectra of Pentacyclic Triterpenoids

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Mass spectra of more than one hundred saturated and unsaturated pentacyclic triterpenoids were examined. In general, the presence of nuclear double bond(s), vicinal methyl groups and functional group(s) controls the fragmentation behavior, and therefore the basic carbon skeleton with double bond(s) and functional group(s) of unknown compounds can be identified by consideration of the fragmentation pattern.

Keywords mass spectra; fragment ion; triterpenoid; migrated triterpenoid; hopane; fernane; gammacerane; lupane; oleanane; ursane

Mass spectrometry has been used as an important tool for structure elucidation of triterpenoids for three decades. Mass spectra (MS) of pentacyclic triterpenoids belonging to the oleanane, ursane and some migrated oleanane and ursane groups were first reported by Djerassi *et al.*1) However, systematic reports for many other types of compounds have not been published yet. This paper deals with MS of pentacyclic triterpenoid hydrocarbons and their derivatives belonging to hopane and its migrates (neohopane, pteronane, fernane, adianane and filicane), gammacerane and its migrates (neogammacerane and swertane), lupane and its migrates (neolupane and lactucane), oleanane and its migrates (taraxerane, multiflorane, glutinane and friedelane), and taraxastane and its migrates (ursane and bauerane). Compounds having a different carbon skeleton with the same double bond location show very similar fragment patterns in the MS.

Results and Discussion

Hopane, Adiantane, Trisnorhopane, Hakonane, Gammacerane, Lupane and Taraxastane Groups The most characteristic fragmentation of all the compounds of these groups in the MS is initiated by cleavage of the C(8)–C(14) bond. For example, hopane (**1**) gave the most important fragment ion at *m*/*z* 191 (**a**), formation of which can be explained as follows. That is, the C(8)–C(14) bond of ring C cleaves first, and then C(8) or C(14) becomes positively charged to give fragment ion **a** or **b** (Chart 2). Hop-22(29)-ene (**2**, carries a double bond on the right-hand part of the molecule) and 21α*H*-adiantane [**3**, lacks the C(30) methyl group] gave the fragment ions at *m*/*z* 189 (**b**) and *m*/*z* 177 (**b**), respectively, as an abundant or a base peak (Table I). The fragment ions, *m*/*z* 191 (**a**) or equivalents were also strong in the MS of the compounds belonging to the adiantane, trisnorhopane, hakonane, gammacerane, lupane and taraxastane groups. Some compounds that have similar structure to **1** at rings A, B and C gave the characteristic fragment ion **a** due to cleavage of the C(8)–C(14) bond in the molecule. Also a fragment ion **b** was observed at similar intensity to the fragment ion **a**. Compounds belonging to the hopane and lupane groups afforded a fragment ion at *m*/*z* 367 due to loss of the side chain from the molecule as a less intense peak. However, hop-21-ene (**4**) and hop-17(21)-ene (**5**) gave the fragment ion at *m*/*z* 367 as a much more abundant peak. This can be explained by assuming the stability of the ions from the latter two compounds differs from that of the former compounds. Also fragment ions at *m*/*z* 341 (**c**) and *m*/*z* 231 (**d**) were observed abundantly in **4** and a fragment ion **d** in **5**. The fragment ion **d** is considered to arise by cleavage of the C(13)–C(18) bond, causing rearrangement of the

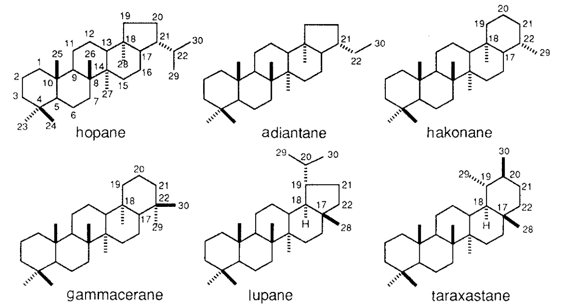

Chart 1

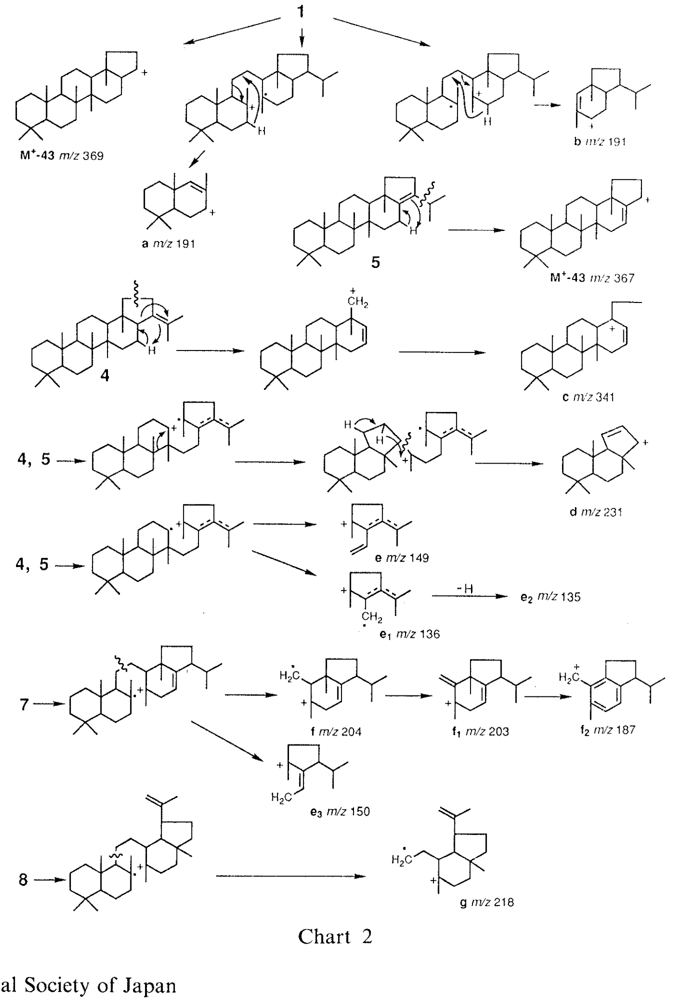

Chart 2

TABLE I. MS of Compounds Belonging to the Hopane, Adiantane, Hakonane, Gammacerane, Lupane and Taraxastane Groups

Compound	M$^+$	M$^+-15$	M$^+-43$	**a**	**b**	Other fragments	Ref.
Hopane (**1**)	412 (8)	397 (8)	369 (11)	191 (100)[h]	191 (—)[h]		2
22-Hydroxyhopane	428 (4)	413 (3)	369 (4)	191 (100)	207 (30)	410 (5) (M$^+-18$), 189 (81) (*b*-18)	3
29-Hydroxyhopane	428 (6)	413 (6)	369 (8)	191 (64)	207 (100)	189 (10) (**b**-18)	4
30-Hydroxyhopane	428 (5)	413 (2)	369 (7)	191 (64)	207 (100)	189 (10) (**b**-18)	4
30-Oxohopane	426 (17)	411 (7)	369 (8)	191 (98)	205 (100)		4
Hop-22(29)-ene (**2**)	410 (30)	395 (9)	—	191 (100)	189 (94)		5
Hop-21-ene (**4**)	410 (50)	395 (13)	367 (34)	191 (100)	189 (100)	341 (52) (**c**), 231 (28) (**d**), 149 (57) (**e**), 135 (94) (**e**$_2$)	5
Hop-21-en-3-one	424 (60)	409 (21)	381 (100)	205 (74)	189 (91)	355 (100) (**c**′), 245 (33) (**d**′), 149 (86) (**e**), 135 (118) (**e**$_2$)	6
Hop-17(21)-ene (**5**)	410 (59)	395 (17)	367 (100)	191 (71)	189 (46)	231 (81) (**d**), 149 (24) (**e**), 136 (100) (**e**$_1$), 135 (112) (**e**$_2$)	5
Hop-17(21)-ene-23, 23-d_2 (**6**)	412 (60)	397 (19)	369 (100)	193 (74)	189 (42)	233 (84) (**d**), 149 (20) (**e**), 136 (104) (**e**$_1$), 135 (107) (**e**$_2$)	7
Hop-17(21)-en-3-one	424 (25)	409 (17)	381 (100)	205 (8)	189 (20)	245 (27) (**d**), 149 (15) (**e**), 136 (58) (**e**$_1$), 135 (57) (**e**$_2$)	6
Hop-16-ene (**7**)	410 (29)	395 (53)	367 (21)	191 (100)	189 (47)	204 (16) (**f**), 203 (9) (f_1), 187 (15) (**f**$_2$), 150 (22) (**e**$_3$), 107 (50) (**e**$_3$-43)	8
21αH-Hopane[a]	412 (20)	397 (17)	369 (10)	191 (100)[i]	191 (—)[i]		9
22-Hydroxy-21αH-hopane	428 (10)	413 (4)	369 (3)	191 (100)	207 (19)	410 (16) (M$^+-18$), 189 (87) (**b**-18)	8
21αH-Hop-22(29)-ene	410 (39)	395 (15)	—	191 (100)	189 (82)		8
Adiantan-22-one[b]	412 (24)	397 (10)	369 (8)	191 (100)[j]	191 (—)[j]		9
21αH-adiantane (**3**)[c]	398 (14)	383 (13)	369 (2)	191 (100)	177 (100)		7
21αH-adiantan-22-one[d]	412 (27)	397 (7)	369 (4)	191 (100)[k]	191 (—)[k]		9
Trisnorhopan-21α-ol	386 (14)	371 (10)	—	191 (100)	165 (99)	353 (4) (M$^+-15-18$), 147 (46) (**b**-18)	7
Trisnorhopan-21β-ol	386 (13)	371 (9)	—	191 (100)	165 (55)	353 (4) (M$^+-15-18$), 147 (22) (**b**-18)	7
Trisnorhopan-21-one	384 (13)	369 (9)	—	191 (100)	163 (19)		10
17αH-Trisnorhopane	370 (21)	355 (11)	—	191 (100)	149 (33)		7
17αH-Trisnorhopan-21-ol A	386 (10)	371 (2)	—	191 (100)	165 (10)	368 (5) (M$^+-18$), 147 (44) (**b**-18)	7
17αH-Trisnorhopan-21-ol B	386 (13)	371 (6)	—	191 (100)	165 (16)	368 (6) (M$^+-18$), 147 (11) (**b**-18)	7
17αH-Trisnorhopan-21-one	384 (14)	369 (9)	—	191 (100)	163 (9)		10
Hakonanol	414 (8)	—	—	191 (100)	193 (26)	396 (4) (M$^+-18$), 175 (24) (**b**-18)	9
Ketohakonanol	428 (8)	—	—	191 (100)	—	410 (4) (M$^+-18$), 395 (3) (M$^+-15-18$)	9
Hakon-17(22)-ene	396 (8)	381 (5)	—	191 (100)	175 (21)	231 (88) (**d**)	9
Hakon-21-ene	396 (38)	381 (13)	—	191 (100)	175 (96)		9
Hakon-22(29)-ene	396 (21)	—	—	191 (100)	175 (37)		9
Gammacerane	412 (8)	397 (5)	—	191 (100)[l]	191 (—)[l]		7
Gammaceran-21-yl acetate[e]	470 (12)	455 (3)	—	191 (100)	249 (13)	410 (7) (M$^+-60$), 189 (53) (**b**-60)	11
Gammacer-16-en-3β-ol	426 (38)	411 (12)	—	207 (38)	189 (100)[m]	393 (21) (M$^+-15-18$), 204 (31) (**f**), 203 (23) (**f**$_1$), 189 (—) (**a**-18)[m], 187 (88) (**f**$_2$), 150 (30) (**e**$_3$), 135 (31) (**e**$_3-15$)	12
Gammacer-16-en-3β-yl acetate	468 (10)	453 (2)	—	249 (2)	189 (100)[n]	408 (20) (M$^+-60$), 393 (18) (M$^+-15-60$), 204 (24) (**f**), 203 (34) (**f**$_1$), 189 (—) (**a**-60)[n], 187 (79) (**f**$_2$), 150 (21) (**e**$_3$), 135 (47) (**e**$_3-15$)	12
Lup-20(29)-ene(**8**)	410 (40)	395 (14)	367 (5)	191 (100)	189 (60)	218 (60) (**g**), 204 (39) (**f**), 203 (41) (**f**$_1$)	11
Lup-20(29)-en-3β-yl acetate[f]	468 (16)	453 (4)	—	249 (10)	189 (100)[o]	408 (23) (M$^+-60$), 218 (28) (**g**), 204 (38) (**f**), 203 (46) (**f**$_1$), 189 (—) (**a**-60)[o]	13
Lup-20(29)-en-3-one	424 (37)	409 (12)	381 (4)	205 (100)	189 (39)	218 (31) (**g**), 204 (31) (**f**), 203 (29) (**f**$_1$)	13
Taraxast-20-ene	410 (22)	395 (9)	—	191 (100)	189 (26)	204 (9) (**f**)	14
Taraxast-20-en-3β-yl acetate	468 (23)	453 (10)	—	249 (19)	189 (100)[p]	408 (21) (M$^+-60$), 393 (19) (M$^+-15-60$), 218 (11) (**g**), 204 (24) (**f**), 203 (23) (**f**$_1$), 189 (—) (**a**-60)[p]	12
Taraxast-20(30)-ene	410 (42)	395 (10)	—	191 (100)	189 (25)	204 (23) (**f**)	7
Taraxast-20(30)-en-3β-yl acetate[g]	468 (11)	453 (1)	—	249 (14)	189 (100)[q]	408 (12) (M$^+-60$), 393 (8) (M$^+-15-60$), 218 (10) (**g**), 204 (21) (**f**), 203 (20) (**f**$_1$), 189 (–) (**a**-60)[q]	12

a) Isohopane. *b*) Adiantone. *c*) Isoadiantane. *d*) Isoadiantone. *e*) Tetrahymanyl acetate. *f*) Lupenyl acetate. *g*) Taraxasteryl acetate. Relative intensities are shown in parentheses. *h*—*q*) Total intensities of two peaks.

C(8)–C(14) bond to C(8)–C(13) (Chart 2). The fragment ion **d** originated in the left-hand part of the molecule, because hop-17(21)-ene-23,23-d_2 (**6**) gave the ion at *m*/*z* 233 (Table I). On the other hand, the fragment ions at *m*/*z* 149 (**e**), *m*/*z* 136 (**e**$_1$) and *m*/*z* 135 (**e**$_2$) originated in the right-hand part of **4** and **5**. The fragment ion **c** seems to be due to the cleavage of ring E of **4** (Chart 2). Hop-16-ene (**7**) gave the fragment ions at *m*/*z* 187 (**f**$_2$) and *m*/*z* 150 (**e**$_3$), which showed the presence of the Δ^{16} double bond in the molecule (Chart 2). The compounds of the lupane, gammacerane and hakonane groups gave similar fragment patterns to the corresponding compounds of the hopane group (Table I). However, lup-20(29)-ene (**8**) gave the fragment ion at *m*/*z* 218 (**g**) as a much more abundant peak (Chart 2).

Neohopane, Neolupane, Oleanane, Ursane and Neogammacerane Groups In the MS of triterpenoid hydrocarbons with a C(12)–C(13) double bond belonging to these groups the fragment ion at *m*/*z* 218 (**g**′) was the most

Table II. MS of Compounds Belonging to the Neohopane, Neolupane, Oleanane and Ursane Groups

Compound	M^+	M^+-15	M^+-43	**a**	$\mathbf{g}'$	$\mathbf{g}'-15$	$\mathbf{g}'-43$	Other fragments	Ref.
Neohop-12-ene (**9**)	410 (7)	395 (2)	367 (1)	191 (28)	218 (100)	203 (33)	175 (48)	189 (22) ($\mathbf{g}'-29$)	15
Neohop-12-en-3β-ol[a]	426 (4)	411 (1)	—	207 (6)	218 (100)	203 (56)	175 (78)	408 (32) (M^+-18), 393 (20) ($\mathrm{M}^+-15-18$), 365 (18) ($\mathrm{M}^+-18-43$), 189 (62) ($\mathbf{g}'-29$)	16
Neohop-12-en-3β-yl acetate	468 (9)	453 (3)	—	249 (2)	218 (100)	203 (32)	175 (42)	408 (21) (M^+-60), 393 (10) ($\mathrm{M}^+-15-60$), 365 (9) ($\mathrm{M}^+-15-43$), 189 (34) ($\mathbf{g}'-29$)	16
18αH-Neohop-12-ene	410 (8)	395 (5)	367 (1)	191 (20)	218 (57)	203 (15)	175 (100)	189 (7) ($\mathbf{g}'-29$)	15
Neohop-18-ene	410 (33)	395 (11)	367 (8)	191 (78)	218 (78)	203 (30)	175 (22)	205 (42) ($\mathbf{f}_3$), 204 (100) (f'), 189 (48) ($\mathbf{b}'$), 161 (78) ($\mathbf{f}'-43$)	17
Neohop-13(18)-ene (**10**)	410 (31)	395 (4)	367 (3)	191 (100)	218 (60)	203 (25)	175 (26)	205 (63) ($\mathbf{f}_3$), 204 (37) ($\mathbf{f}'$)	5
Neohop-13(18)-ene-23, 23-d_2	412 (51)	397 (5)	369 (3)	193 (100)	218 (79)	203 (26)	175 (28)	205 (67) ($\mathbf{f}_3$), 204 (43) ($\mathbf{f}'$)	7
Neohop-13(18)-en-3-one	424 (32)	409 (3)	381 (3)	205 (100)[g]	218 (6)	203 (9)	175 (7)	205 (—) ($\mathbf{f}_3$),[g] 204 (14) ($\mathbf{f}'$)	6
Neolup-12-ene	410 (19)	395 (6)	—	191 (66)	218 (100)	203 (83)	175 (20)	135 (84) (**h**)	18
Neolup-12-en-3β-ol	426 (12)	411 (2)	—	207 (24)	218 (100)	203 (73)	175 (25)	408 (11) (M^+-18), 393 (4) ($\mathrm{M}^+-15-18$), 365 (5) ($\mathrm{M}^+-18-43$), 189 (100) ($\mathbf{g}'-29$), 135 (68) (**h**)	18
Neolup-12-en-3β-yl acetate	468 (11)	453 (2)	—	249 (6)	218 (100)	203 (88)	175 (32)	408 (12) (M^+-60), 393 (5) ($\mathrm{M}^+-15-60$), 365 (8) ($\mathrm{M}^+-43-60$), 189 (100) ($\mathbf{g}'-29$), 135 (89) (**h**)	18
Neolup-12-en-3-one (**11**)	424 (26)	409 (7)	—	205 (95)[h]	218 (84)	203 (100)	175 (33)	205 (—) ($\mathbf{f}_3$),[h] 189 (85) ($\mathbf{g}'-29$), 135 (181) (**h**)	18
Neolup-13(18)-en-3β-yl acetate	468 (57)	453 (2)	425 (2)	249 (9)	218 (42)	203 (30)	175 (23)	205 (100) ($\mathbf{f}_3$), 204 (83) (**f**)	18
Olean-12-ene	410 (6)	395 (2)	—	191 (16)	218 (100)	203 (46)	—		5
Olean-12-en-3β-ol[b]	426 (5)	411 (4)	—	207 (9)	218 (100)	203 (48)	—	408 (3) (M^+-18), 189 (18) ($\mathbf{g}'-29$, $\mathbf{a}-18$)	13
Olean-12-en-3β-yl acetate	468 (2)	453 (1)	—	249 (1)	218 (100)	203 (43)	—	408 (3) (M^+-60), 189 (19) ($\mathbf{g}'-29$, $\mathbf{a}-60$)	12
Methyl 3β-acetoxyl-olean-12-en-28-oate[c]	512 (3)	497 (1)	—	249 (10)	262 (62)	—	—	452 (6) (M^+-60), 437 (2) ($\mathrm{M}^+-15-60$), 203 (100) ($\mathbf{g}'-59$), 189 (24) ($\mathbf{a}-60$)	13
18αH-Olean-12-ene	410 (12)	395 (18)	—	191 (30)	218 (100)	203 (40)	—		5
Olean-13(18)-ene	410 (28)	395 (22)	—	191 (76)	218 (86)	203 (44)	—	205 (100) ($\mathbf{f}_3$), 204 (46) (**f**), 189 (46) ($\mathbf{g}'-29$)	5
Olean-13(18)-en-3β-yl acetate	468 (58)	453 (30)	—	249 (7)	218 (99)	203 (54)	—	408 (13) (M^+-60), 393 (18) ($\mathrm{M}^+-15-60$), 205 (100) ($\mathbf{f}_3$), 204 (73) (**f**), 189 (69) ($\mathbf{a}-60$, $\mathbf{g}'-29$)	7
Olean-18-ene[d]	410 (24)	395 (30)	—	191 (56)	218 (32)	203 (22)	—	205 (38) ($\mathbf{f}_3$), 204 (100) ($\mathbf{f}''$), 189 (90) ($\mathbf{b}''$)	5
Olean-18-en-3β-yl acetate	468 (14)	453 (14)	—	249 (4)	218 (16)	203 (24)	—	205 (46) ($\mathbf{f}_3$), 204 (100) ($\mathbf{f}''$), 189 (100) ($\mathbf{a}-60$, $\mathbf{b}''$)	12
Olean-18-en-3-one	424 (42)	409 (35)	—	205 (67)[i]	218 (24)	203 (16)	—	205 (—) ($\mathbf{f}_3$),[i] 204 (64) ($\mathbf{f}''$), 189 (70) (**b**), 177 (100) ($\mathbf{f}_3-28$)	13
Urs-12-en-3β-ol[e]	426 (7)	411 (1)	—	207 (11)	218 (100)	203 (15)	—	408 (2) (M^+-18), 393 (1) ($\mathrm{M}^+-15-18$), 189 (12) ($\mathbf{a}-18$, $\mathbf{g}'-29$)	13
Urs-12-en-3β-yl acetate	468 (5)	453 (3)	—	249 (2)	218 (100)	203 (26)	—	408 (5) (M^+-60), 393 (4) ($\mathrm{M}^+-15-60$), 189 (28) ($\mathbf{g}'-29$, $\mathbf{a}-60$)	12
Methyl 3β-acetoxyl-urs-12-en-28-oate[f]	512 (3)	497 (2)	—	249 (20)	262 (100)	—	—	452 (5) (M^+-60), 437 (3) ($\mathrm{M}^+-15-60$), 203 (91) ($\mathbf{g}'-59$), 189 (28) ($\mathbf{a}-60$)	13
Urs-13(18)-en-3β-yl acetate	468 (16)	453 (7)	—	249 (16)	218 (96)	203 (58)	—	408 (12) (M^+-60), 393 (18) ($\mathrm{M}^+-15-60$), 205 (100) ($\mathbf{f}_3$), 204 (50) ($\mathbf{f}'''$)	7

a) Neomotiol. *b*) β-Amyrin. *c*) Acetate of methyl oleanolate. *d*) Germanicol. *e*) α-Amyrin. *f*) Acetate of methyl ursolate. Relative intensities are shown in parentheses. *g*—*i*) Total intensities of two peaks.

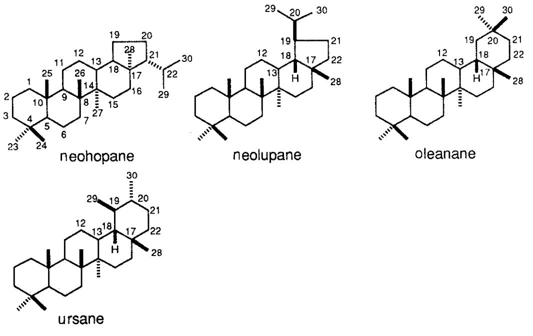

Chart 3

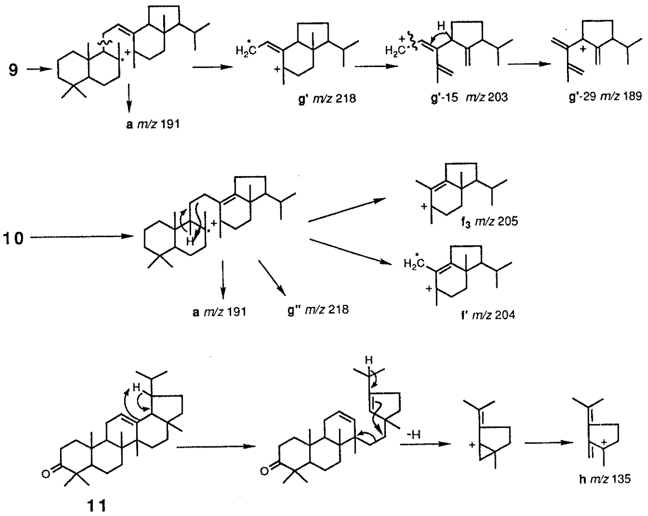

Chart 4

important one. For example, in the case of neohop-12-ene (**9**), the C(8)–C(14) bond cleaves first in the same way as in hopane (**1**), the neighboring carbon [C(14)] of double bond becomes positively charged, and then the allylic bond [C(9)–C(11)] cleaves to give the fragment ion $\mathbf{g}'$ (Chart 4). The fragment ion at *m*/*z* 203 and *m*/*z* 175, which were formed by loss of methyl or isopropyl group from $\mathbf{g}'$, were also observed. Neohop-13(18)-ene (**10**) afforded the same base peak **a** as the hopane group compounds. Furthermore, the fragment ion $\mathbf{g}''$ is observed abundantly in the MS of **10**. Also the fragment ions at *m*/*z* 205 ($\mathbf{f}_3$) and *m*/*z* 204 ($\mathbf{f}'$) were derived by cleavage of the C(8)–C(14) and C(11)–C(12) bonds (Chart 4). The compounds of the neolupane group, for example, neolup-12-en-3-one (**11**), gave abundantly the fragment ion at *m*/*z* 135 (**h**) due to cleavage of the C(13)–C(18) and C(15)–C(16) bonds in the molecule, as well

TABLE III. MS of Compounds Belonging to the Pteronane, Lactucane and Taraxaerane Groups

Compound	M^+	M^+-15	M^+-43	**i**	**i**-15	**a**	**j**	**k**	**k**-15	**k**-43	**l**, $\mathbf{l}_1$, $\mathbf{l}_2$	Other fragments	Ref.
Pteron-14-ene (**12**)	410 (50)	395 (64)	367 (8)	286 (4)	271 (21)	191 (72)	257 (60)	204 (100)	189 (40)	161 (48)	121 (56)		17
Pteron-14-en-7-one	424 (33)	409 (100)	381 (10)	300 (7)	285 (6)	205 (17)	257 (6)	204 (16)	189 (15)	161 (2)	123 (49)		17
Pteron-14-en-7α-ol	426 (64)	411 (30)	383 (6)	302 (2)	287 (4)	207 (10)	257 (14)	204 (62)	189 (27)	161 (22)	123 (40)	408 (70) (M^+-18), 393 (67) ($M^+-15-18$), 271 (100) (**m**)	17
Lactuc-14-en-3β-yl acetate	468 (9)	453 (7)	—	344 (74)	329 (36)	249 (2)	257 (10)	204 (100)	189 (26)[b]	161 (26)	122 (123)	408 (3) (M^+-60), 393 (7) ($M^+-15-60$), 365 (3) ($M^+-15-60$), 284 (19) (**i**-60), 269 (31) (**i**$-15-60$), 189 (—) (**k**-15)[b]	7
Lactuc-14-en-3β-ol	426 (8)	411 (8)	—	302 (65)	287 (46)	207 (10)	257 (13)	204 (100)	189 (32)	161 (30)	122 (151)	408 (8) (M^+-18), 393 (21) ($M^+-15-18$), 365 (8) ($M^+-15-18$)	7
Taraxer-14-ene	410 (12)	395 (14)	—	286 (56)	271 (60)	191 (18)	257 (24)	204 (100)	189 (28)	—	121 (28)		14
Taraxer-14-en-3β-yl acetate[a]	468 (10)	453 (8)	—	344 (40)	329 (20)	—	257 (12)	204 (100)	189 (30)	—	121 (32)	284 (14) (**i**-60), 269 (28) (**i**$-15-60$)	12
Taraxer-14-en-7α-ol (**13**)	426 (32)	411 (13)	—	302 (100)	287 (25)	207 (10)	257 (25)	204 (44)	189 (19)	—	123 (30)	271 (11) (**m**), 269 (31) (**i**$-15-18$), 256 (68) (**m**-15)	14
Taraxer-14-en-7-one (**14**)	424 (34)	409 (48)	—	300 (14)	285 (9)	205 (52)	257 (17)	204 (40)	189 (43)	—	123 (100)	406 (100) (M^+-18)	14

a) Taraxeryl acetate. Relative intensities are shown in parentheses. *b*) Total intensities of two peaks.

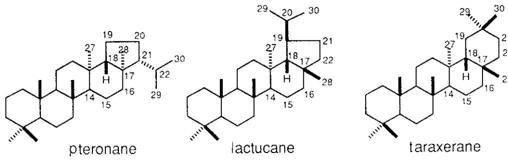

Chart 5

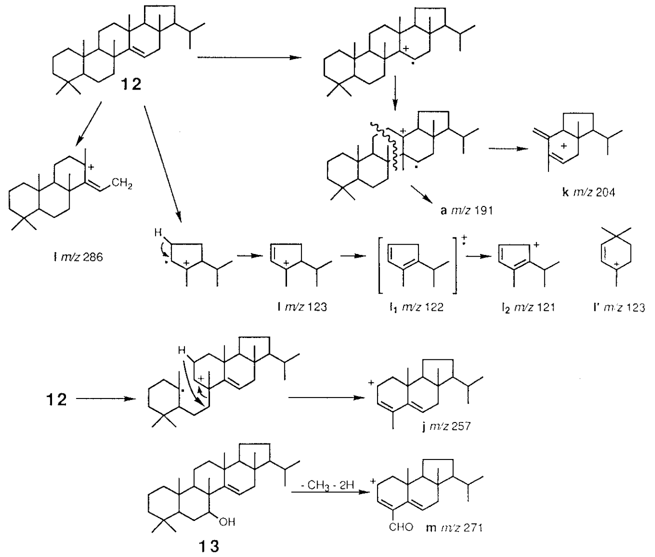

Chart 6

as the ion $\mathbf{e}_2$ (Chart 4).

Compounds belonging to the neolupane, oleanane, ursane and neogammacerane groups with a C(12)–C(13) double bond also show similar fragment patterns to the compounds of the neohopane group (Table II).

Pteronane, Lactucane and Taraxerane Groups In the MS of pteron-14-ene (**12**), the fragment ion at *m*/*z* 204 (**k**) was the most important. It is proposed that the fragment ion **k** is formed by the following steps. In the molecular ion of **12** the missing electron is preferentially lost from the double bond, and the C(13) methyl group migrates to give the radical ion. Then fission of the C(11)–C(12) and C(8)–C(14) bonds affords the stable diene **k**.[1] The fragment ion at *m*/*z* 257 (**j**) appears comparatively abundant, and this ion is formed by fission of the C(7)–C(8) and C(9)–C(10) bonds. On the other hand, the fragment ion at *m*/*z* 286 (**i**) was observed only at weak intensity (Chart 6).

In the compounds of the taraxerane and lactucane groups the fragment ion **i** was as strong as the ion **k**, while pteron-14-en-7α-ol (**13**) shows the fragmention at *m*/*z* 271 (**m**) as a base peak. Taraxer-14-en-7-ene (**14**) also gave the fragment ions at *m*/*z* 406 (M^+-18) and *m*/*z* 123 (**l'**, base peak) (Chart 6).

Fernane, Swertane, Multiflorane, Bauerane and Serratane Groups The MS of three compounds having the double bond at the 7, 8 and 9(11) positions of the fernane group showed rather similar fragment patterns. That means the position of the double bond can not be distinguished from the fragment patterns (Fig. 1). A probable mechanism involves formation of each fragment through the same intermediate. In the MS of fern-7-ene (**15**), fern-8-ene (**16**) and fern-9(11)-ene (**17**), the fragment ion at *m*/*z* 243 (**o**) is the most important one, consisting of the left-hand part of the molecule. The C(13)–C(14) bond between ring C and D cleaves first, C(14) becomes positively charged, and then each compound produces the same intermediate, followed by fission of the C(12)–C(13) and C(15)–C(16) bonds to give the fragment ion **o**. Furthermore, the fragment ion at *m*/*z* 231 (**p**) was formed in a similar way to the ion **o**. That is, the C(13)–C(14) bond of each compound cleaves first to give the same intermediate, and then the fragment **p** is formed by rupture of the C(15)–C(16) bond. The fragment ions at *m*/*z* 217 ($\mathbf{q}_1$) and *m*/*z* 191 (**s**) originate from the right-hand part of the molecule through the same C(13) ion intermediate formed by cleavage of the C(13)–C(14) bond. The MS of the compounds of the fernane group exhibits an additional fragment ion at *m*/*z* 257 (**n**) derived from the left-hand part of the molecule. Also the fragment ion at *m*/*z* 205 (**r**) is produced from the right-hand part of the molecule by cleavage in ring C (Chart 8). In sum, the most

TABLE IV. MS of Compounds Belonging to the Fernane, Swertane, Serratane, Multiflorane and Bauerane Groups

Compound	M$^+$	M$^+$−15	M$^+$−43	**n**	**o**	**p**	**q**, **q**$_1$	**r**	**s**	Other fragments	Ref.
Fern-7-ene (**15**)	410 (23)	395 (90)	367 (1)	257 (25)	243 (100)	231 (19)	217 (8)	205 (9)	191 (8)		5
Fern-7-en-3β-yl acetate[a]	468 (13)	453 (30)	—	255 (29)[k]	241 (51)[l]	229 (16)[m]	217 (4)	205 (11)	191 (2)	408 (55) (M$^+$−60), 393 (100) (M$^+$−15−60), 365 (39) (M$^+$−43−60), 301 (27) (**n**)	16
Fern-7-en-3-one	424 (32)	409 (86)	—	271 (22)	257 (100)	245 (16)	217 (2)	205 (2)	191 (2)		16
Methyl fern-7-en-28-oate	454 (31)	439 (100)	—	257 (7)	243 (66)	231 (26)	—	—	—	395 (4) (M$^+$−59), 379 (57) (M$^+$−15−60)	19
9βH-Fern-7-ene	410 (69)	395 (87)	367 (13)	257 (34)	243 (100)	231 (39)	217 (25)	205 (48)	191 (25)		5
Fern-8-ene (**16**)	410 (19)	395 (69)	367 (1)	257 (21)	243 (100)	231 (18)	217 (6)	205 (6)	191 (6)		5
Fern-8-ene-23, 23-d_2	412 (26)	397 (66)	369 (1)	259 (16)	245 (100)	233 (15)	217 (3)	205 (9)	191 (8)		7
Methyl fern-8-en-28-oate	454 (22)	439 (88)	—	257 (6)	243 (100)	231 (26)	—	—	—	395 (3) (M$^+$−60), 379 (62) (M$^+$−15−60)	19
Fern-9(11)-ene (**17**)	410 (24)	395 (89)	367 (1)	257 (24)	243 (100)	231 (19)	217 (7)	205 (8)	191 (9)		5
Fern-9(11)-ene-23, 23-d_2	412 (22)	397 (75)	369 (1)	259 (18)	245 (100)	233 (16)	217 (5)	205 (12)	191 (11)		7
Fern-9(11)-en-3β-yl acetate[b]	468 (21)	453 (43)	—	255 (22)[k]	241 (49)[l]	229 (14)[m]	217 (5)	205 (10)	191 (11)	408 (47) (M$^+$−60), 393 (100) (M$^+$−15−60), 365 (18) (M$^+$−43−60), 301 (46) (**n**)	19
Fern-9(11)-en-3-one	424 (32)	409 (71)	381 (1)	271 (19)	257 (100)	245 (20)	218 (12)	205 (12)	191 (9)		16
Fern-9(11)-en-23-ol	426 (26)	411 (90)	383 (1)	273 (14)	259 (100)	247 (13)	217 (6)	205 (14)	191 (13)		7
Fern-9(11)-en-24-ol	426 (22)	411 (75)	383 (2)	273 (17)	259 (100)	247 (15)	217 (9)	205 (17)	191 (13)		20
Fern-9(11)-en-23-al	424 (21)	409 (63)	381 (2)	271 (15)	257 (100)	245 (14)	217 (7)	205 (10)	191 (9)		7
Fern-9(11)-en-24-al	424 (16)	409 (54)	381 (4)	271 (16)	257 (100)	245 (16)	217 (8)	205 (10)	191 (8)		20
Fern-9(11)-en-24-oic acid[c]	440 (21)	425 (61)	397 (2)	287 (18)	273 (100)	261 (15)	217 (4)	205 (14)	191 (11)		20
Methyl fern-9(11)-en-28-oate	454 (32)	439 (100)	—	257 (5)	243 (60)	231 (18)	—	—	—	395 (1) (M$^+$−60), 379 (53) (M$^+$−15−60)	19
8βH-Fern-9(11)-ene	410 (20)	395 (84)	—	257 (29)	243 (100)	231 (28)	217 (9)	205 (9)	191 (9)		5
Ferna-7,9(11)-diene	408 (100)	393 (28)	365 (5)	255 (86)	—	—	—	—	—		5
Ferna-7,9(11)-diene-23, 23-d_2	410 (100)	395 (28)	367 (2)	257 (47)	—	—	—	—	—		7
24-Norferna-4(23),9(11)-diene	394 (26)	379 (87)	351 (1)	241 (21)	227 (100)	215 (20)	217 (8)	205 (8)	191 (10)		21
Swert-7-en-3β-yl acetate	468 (19)	453 (58)	—	315 (10)	301 (91)	289 (100)	217 (7)	205 (15)	191 (8)	408 (8) (M$^+$−60), 393 (54) (M$^+$−15−60), 255 (31) (**n**−60), 241 (81) (**o**−60), 229 (93) (**p**−60)	22
Swert-8-en-3β-yl acetate[d]	468 (40)	453 (57)	—	315 (8)	301 (100)	289 (93)	217 (8)	205 (22)	191 (13)	408 (4) (M$^+$−60), 393 (45) (M$^+$−15−60), 255 (15) (**n**−60), 241 (45) (**o**−60), 229 (48) (**p**−60)	23
Swert-8-en-3β-ol[e]	426 (29)	411 (60)	—	273 (13)	259 (100)	247 (83)	217 (5)	205 (12)	191 (8)	408 (9) (M$^+$−18), 393 (38) (M$^+$−15−18), 255 (15) (**n**−18), 241 (71) (**o**−18), 229 (63) (**p**−18)	23
Swert-9(11)-en-3β-yl acetate[f]	468 (59)	453 (91)	—	315 (9)	301 (100)	289 (99)	218 (6)	205 (18)	191 (11)	408 (6) (M$^+$−60), 393 (52) (M$^+$−15−60), 255 (15) (**n**−60), 241 (45) (**o**−60), 229 (48) (**p**−60)	23
Swert-9(11)-en-3β-ol[g]	426 (55)	411 (100)	—	273 (15)	259 (99)	247 (8)	217 (8)	205 (14)	191 (15)	408 (20) (M$^+$−18), 393 (52) (M$^+$−15−18), 255 (16) (**n**−18), 241 (43) (**o**−18), 229 (42) (**p**−18)	23
Multiflor-7-ene (**18**)	410 (8)	395 (20)	—	257 (13)	243 (68)	231 (63)	218 (27)	205 (39)	191 (31)	204 (100) (**t**)	5
Multiflor-7-en-3β-yl acetate[h]	468 (12)	453 (11)	—	315 (3)	301 (25)	289 (23)	218 (22)	205 (64)	191 (18)	408 (2) (M$^+$−60), 393 (8) (M$^+$−15−60), 262 (100) (**t**), 202 (46) (**t**−60)	14
Multiflor-8-ene (**19**)	410 (16)	395 (23)	—	257 (10)	243 (100)	231 (74)	218 (27)	205 (44)	191 (43)		5
Multiflor-9(11)-ene (**20**)[i]	410 (16)	395 (19)	—	257 (12)	243 (70)	231 (56)	218 (100)	205 (41)	191 (90)		5
Bauer-7-en-3β-yl acetate	468 (14)	453 (15)	—	315 (4)	301 (16)	289 (92)	218 (3)	205 (24)	191 (6)	408 (10) (M$^+$−60), 393 (27) (M$^+$−15−60), 255 (15) (**n**−60), 241 (21) (**o**−60), 229 (100) (**p**−60)	12
Bauer-8-en-3β-yl acetate[j]	468 (17)	453 (13)	—	315 (3)	301 (15)	289 (86)	218 (5)	205 (21)	191 (4)	408 (9) (M$^+$−60), 393 (32) (M$^+$−15−60)	12
Serrat-7-ene (**21**)	410 (48)	395 (100)	—	257 (28)	243 (96)	231 (23)	218 (15)	—	—	204 (45) (**f**″), 191 (77) (**b**‴)	24
Serrat-7-ene-3,21-dione	433 (100)	423 (32)	—	271 (7)	257 (3)	245 (9)	232 (27)	—	—	219 (64) (**f**$'_3$), 218 (81) (**f**⁗), 205 (90) (**b**‴)	25

a) Motiyl acetate. *b*) Fernenyl acetate. *c*) Davallic acid. *d*) Isopichierenyl acetate. *e*) Isopichierenol. *f*) Pichierenyl acetate. *g*) Pichierenol. *h*) Multiflorenyl acetate. *i*) Walsurene. *j*) Isobauerenyl acetate. Relative intensities are shown in parentheses. *k*) **n**−60. *l*) **o**−60. *m*) **p**−60.

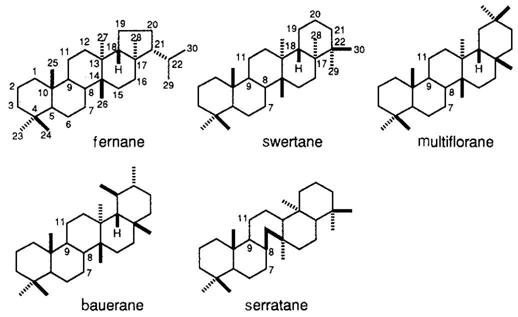

Chart 7

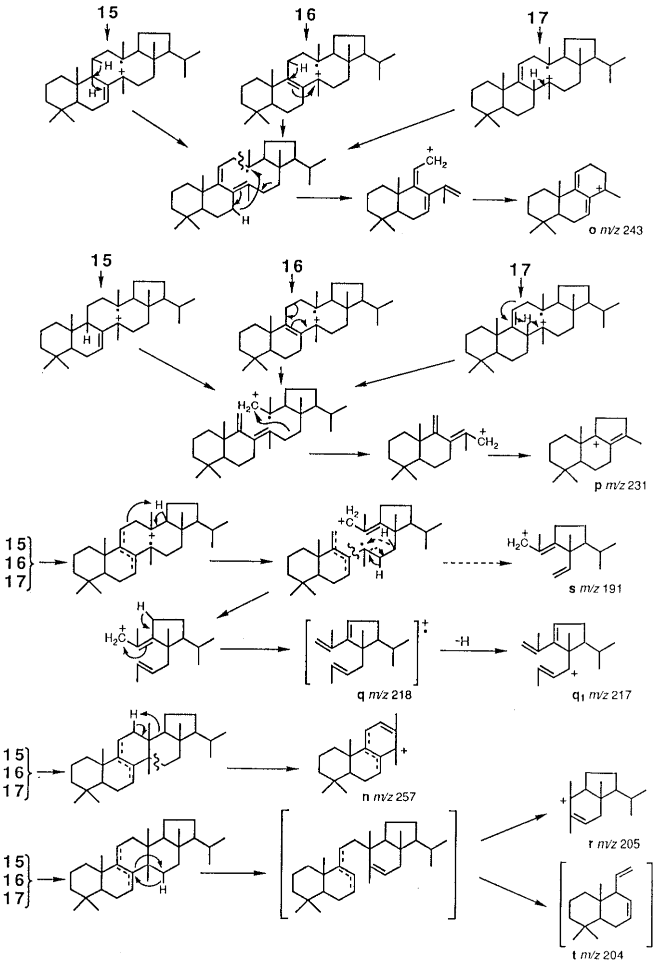

Chart 8

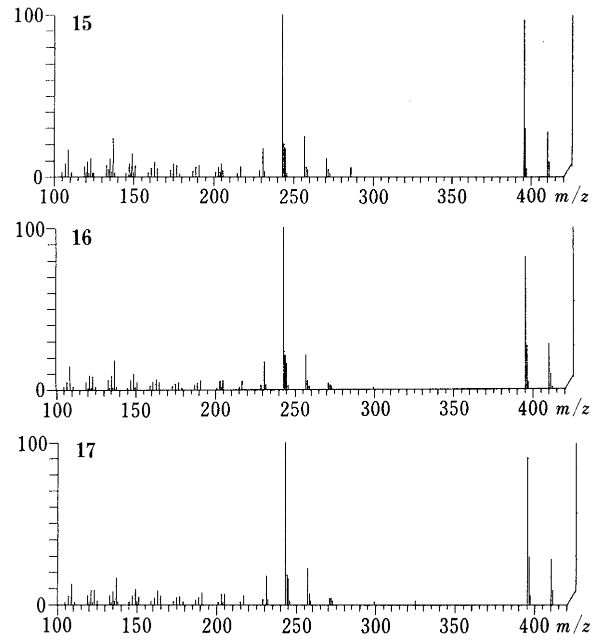

Fig. 1. MS of Fern-7-ene (**15**), Fern-8-ene (**16**) and Fern-9(11)-ene (**17**)

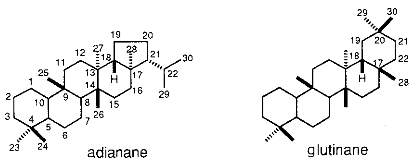

Chart 9

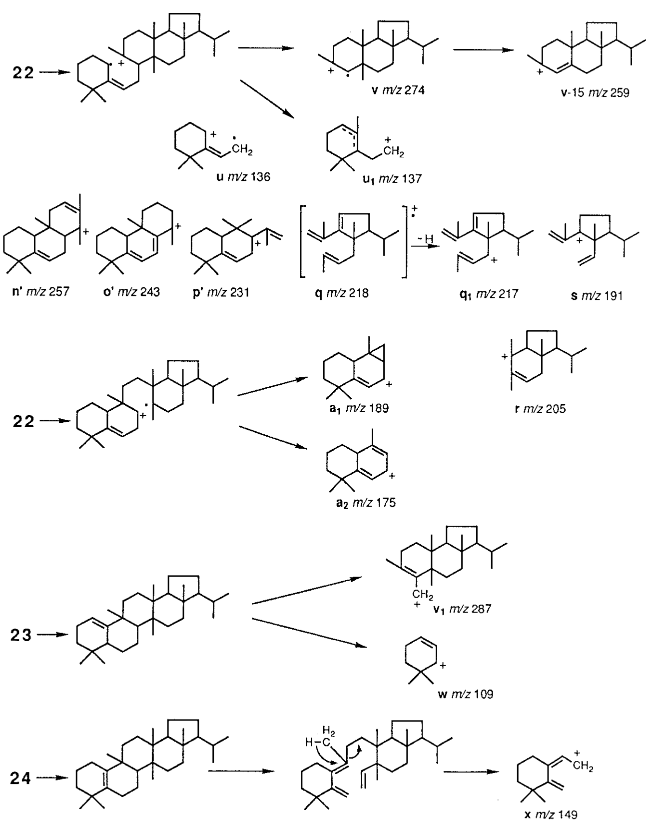

Chart 10

characteristics fragment ions of the fernane group hydrocarbons are *m*/*z* 257 (**n**), *m*/*z* 243 (**o**) and *m*/*z* 231 (**p**), and the other fragment ions are not abundant.

In the MS of multiflor-7-ene (**18**), multiflor-8-ene (**19**) and multiflor-9(11)-ene (**20**), the most characteristic fragment ions were **n**, **o** and **p**, such as the fragment ions from **15**, **16**, **17** of the fernane group. In addition, the fragment ions at *m*/*z* 218 (**q**), *m*/*z* 205 (**r**), *m*/*z* 204 (**t**) and *m*/*z* 191 (**s**) were stronger than those of fernenes (Table IV). In particular, **18** gave the fragment ion at *m*/*z* 204 (**t**) as the base peak, comprising the left-hand part of the molecule (Chart 8). The formation of ion **t** is considered to be formally initiated by cleavage of the C(8)–C(14) and C(12)–C(13) bonds, but it seems more reasonable to assume double hydrogen transfer [as indicated for the formation of ion **r** coupled with back transfer of one of the C(11) hydrogens] to avoid the unfavorable cleavage of the bond next to a double bond.[1] The MS of serrat-7-ene (**21**) gave the same fragment ions at *m*/*z* 257 (**n**), *m*/*z* 243 (**o**) and *m*/*z* 231 (**p**)

Table V. MS of Compound Belonging to the Adianane and Glutinane Groups

Compound	M^+	M^+-15	M^+-43	$\mathbf{n}'$	$\mathbf{o}'$	$\mathbf{p}'$	$\mathbf{a}_1$	$\mathbf{a}_2$	$\mathbf{u}, \mathbf{u}_1$	$\mathbf{v}$	$\mathbf{v}-15$	$\mathbf{r}$	$\mathbf{s}$	Other fragments	Ref.
Adian-5-ene (**22**)	410 (10)	395 (12)	367 (1)	257 (2)	243 (8)	231 (32)	189 (22)	175 (25)	136 (79)	274 (100)	259 (98)	205 (19)	191 (16)		5
Adian-5-en-3β-ol[a]	426 (2)	408 (26)	—	273 (14)	259 (—)[c]	—	205 (—)[d]	191 (—)[e]	152 (38)	274 (100)	259 (93)[c]	205 (19)[d]	191 (11)[e]		26
Adian-5-en-3β-yl acetate	468 (1)	453 (2)	—	255 (2)[f]	241 (2)[g]	229 (2)[h]	187 (9)[i]	173 (16)[j]	134 (52)[k]	274 (100)	259 (99)	205 (17)	191 (14)	408 (7) (M^+-60), 393 (6) ($M^+-15-60$)	26
Adian-5-en-3-one	424 (6)	409 (6)	381 (4)	271 (3)	257 (1)	245 (10)	203 (5)	189 (18)	150 (20)	274 (100)	259 (70)	205 (17)	191 (16)		26
Methyl adian-5-en-28-oate	454 (13)	439 (9)	—	257 (8)	243 (32)	231 (2)	189 (19)	175 (6)	136 (89)	318 (55)	303 (20)	249 (10)	189 (19)[l]	258 (100) ($\mathbf{v}-60$)	19
Adian-1(10)-ene (**23**)	410 (100)	395 (85)	367 (15)	257 (25)	243 (74)	231 (40)	189 (57)	175 (47)	137 (139)	274 (42)	259 (26)	205 (77)	191 (85)	287 (42) ($\mathbf{v}_1$), 273 (59) ($\mathbf{v}_1-14$) 218 (30) (**q**), 217 (26) ($\mathbf{q}_1$), 109 (370) (**w**)	17
Adian-5(10)-ene (**24**)	410 (100)	395 (69)	367 (1)	257 (9)	243 (11)	231 (16)	189 (5)	175 (34)	137 (76)	274 (8)	259 (4)	205 (77)	191 (49)	218 (10) (**q**), 217 (8) ($\mathbf{q}_1$), 149 (41) (**x**)	5
Adiana-1(10), 5-diene	408 (100)	393 (22)	365 (9)	255 (12)	241 (6)	229 (14)	187 (26)	173 (27)	135 (13)	—	—	205 (15)	190 (76)[m]	203 (68) ($\mathbf{r}-2$H)	5
Glutin-5-ene	410 (16)	395 (9)	—	257 (3)	243 (3)	231 (8)	189 (17)	175 (23)	136 (67)	274 (100)	259 (82)	205 (42)	191 (12)		17
Glutin-5-en-3β-yl acetate[b]	468 (5)	—	—	255 (2)[f]	241 (2)[j]	229 (3)[h]	187 (9)[i]	173 (23)[j]	134 (38)[k]	274 (100)	259 (73)	205 (28)	191 (9)		17
Glutin-5-en-3-one	424 (10)	409 (8)	—	271 (2)	257 (2)	245 (15)	203 (9)	189 (16)	150 (25)	274 (100)	259 (78)	205 (41)	191 (13)		17

a) Simiarenol. *b*) Glutinyl acetate. Relative intensities are shown in parentheses. *c*—*e*) Total intensities of two peaks. *f*) $\mathbf{n}'-60$. *g*) $\mathbf{o}'-60$. *h*) $\mathbf{p}'-60$. *i*) $\mathbf{a}_1-60$. *j*) $\mathbf{a}-60$. *k*) $\mathbf{t}-60$. *l*) $\mathbf{s}-60$. *m*) $\mathbf{s}-$H.

Table VI. MS of Compounds Belonging to the Filicane and Friedelane Groups

Compound	M^+	M^+-15	M^+-43	$\mathbf{y}$	$\mathbf{z}$	$\mathbf{n}''$	$\mathbf{o}''$	$\mathbf{p}''$	$\mathbf{t}_1$	$\mathbf{a}_1'$, $\mathbf{a}_3$	$\mathbf{a}_2'$	$\mathbf{v}$	$\mathbf{v}-15$	$\mathbf{r}$	$\mathbf{q}, \mathbf{q}_1$	$\mathbf{s}$	Ref.
Filicane	412 (27)	397 (26)	369 (4)	342 (9)	327 (42)	259 (16)[b]	245 (8)	233 (14)	205 (—)[c]	191 (—)[d]	177 (43)	274 (3)	259 (—)[b]	205 (44)[c]	218 (10)	191 (100)[d]	27
Filican-3α-ol	428 (36)	413 (38)	385 (3)	358 (12)	343 (48)	275 (11)	261 (5)	249 (3)	221 (17)	207 (12)	193 (14)	274 (7)	259 (27)	205 (23)	—	191 (100)	28
Filican-3-one	426 (25)	411 (25)	383 (3)	356 (6)	341 (40)	273 (16)	259 (16)[e]	247 (8)	219 (20)	205 (—)[f]	191 (—)[g]	274 (10)	259 (—)[e]	205 (26)[f]	217 (8)	191 (100)[g]	28
Filic-3-ene (**25**)	410 (88)	395 (54)	367 (14)	340 (4)	325 (38)	257 (18)	243 (29)	231 (29)	203 (41)	189 (36)	175 (43)	274 (29)	259 (19)	205 (32)	218 (21)	191 (100)	5
Filic-3-en-6β-ol	426 (11)	411 (15)	383 (2)	356 (3)	341 (21)	273 (26)	259 (9)	247 (5)	219 (13)	205 (—)[h]	191 (—)[i]	274 (11)	259 (9)	205 (—)[h]	217 (8)	191 (100)[i]	7
Filic-3-en-6-one	424 (7)	409 (30)	381 (3)	354 (8)	339 (5)	271 (12)	257 (4)[j]	245 (7)	217 (10)	203 (12)	189 (19)	274 (3)	257 (—)[j]	205 (9)	217 (10)	191 (100)	7
Filic-3-en-25-ol	426 (21)	411 (10)	383 (4)	—	—	273 (10)	259 (8)	247 (7)	219 (10)	177 (100)	191 (—)[k]	—	—	205 (54)	217 (13)	191 (35)[k]	7
Filic-3-en-23-al	424 (14)	409 (14)	381 (2)	354 (5)	339 (26)	271 (11)	—	245 (6)	217 (23)	203 (14)	189 (16)	274 (8)	—	205 (10)	217 (23)	191 (100)	27
Filic-3-en-23-oic acid	440 (27)	425 (23)	397 (3)	370 (9)	355 (41)	287 (15)	273 (15)	261 (5)	233 (30)	219 (13)	205 (–)[l]	274 (2)	259 (4)	205 (22)[l]	218 (5)	191 (100)	7
Filic-4(23)-ene	410 (51)	395 (46)	367 (6)	340 (7)	325 (46)	257 (19)	243 (26)	231 (23)	203 (39)	189 (37)	175 (43)	274 (11)	259 (23)	205 (26)	218 (9)	191 (100)	27
Friedelan-3-one[a]	426 (91)	411 (29)	—	—	341 (18)	273 (100)	259 (15)	247 (33)	219 (26)	205 (—)[m]	191 (—)[n]	274 (57)	259 (15)	205 (90)[m]	218 (75)	191 (55)[n]	29
Friedel-3-ene (**26**)	410 (35)	395 (37)	—	—	—	257 (30)	243 (9)	231 (30)	203 (12)	189 (39)	175 (52)	274 (22)	259 (17)	205 (74)	218 (100)	191 (52)	5
Friedel-4(23)-ene	410 (66)	395 (100)	—	—	325 (2)	257 (93)	243 (16)	231 (71)	203 (57)	189 (52)	175 (71)	274 (21)	259 (34)	205 (67)	218 (34)	191 (41)	7

a) Friedelin. Relative intensities are shown in parentheses. *b*—*n*) Total intensities of two peaks.

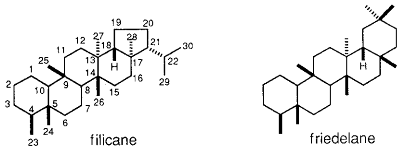

Chart 11

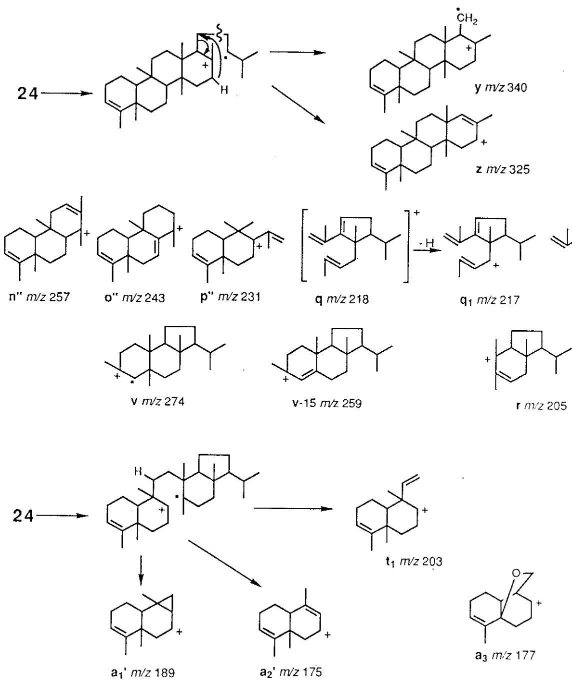

Chart 12

as those of the fernane group compounds and the fragment ions at *m/z* 204 (**f'''**) and *m/z* 191 (**b'''**) like those of the hopane group compounds (Table IV).

Adianane and Glutinane Groups The most important fragment ion of adian-5-ene (**22**) was *m/z* 274 (**v**), formed from the right-hand part of the molecule by cleavage of the allylic position of the double bond. In addition, the fragment ion at *m/z* 259 was formed by the loss of a methyl group from the ion **v**. On the other hand, the fragment ion of the left-hand part of the molecule was observed at *m/z* 136 (**u**). There were also fragment ions at *m/z* 257 (**n'**), *m/z* 243 (**o'**), *m/z* 231 (**p'**), *m/z* 218 (**q**), *m/z* 217 ($\mathbf{q_1}$) and *m/z* 191 (**s**), like those of the fernane group compounds. Among these fragment ions, the ion **p'** appears relatively abundant because *m/z* 231 is also formed by loss of the isopropyl group from the ion **v**. Furthermore, the fragment ions from the left-hand part of the molecule were observed at *m/z* 189 ($\mathbf{a_1}$) and *m/z* 175 ($\mathbf{a_2}$). Adian-1(10)-ene (**23**) gave the fragment ion at *m/z* 109 (**w**) as the strongest one, while adian-5(10)-ene (**24**) gave a relatively abundant peak at *m/z* 149 (**x**) (Chart 10).

Filicane and Friedelane Groups The MS of filic-3-ene (**25**) and friedel-3-ene (**26**) showed the fragment ions at *m/z* 191 (**s**) and *m/z* 218 (**q**) as a base peak, respectively. These ions originated from the right-hand part of the molecule, initiated by cleavage of the C(13)–C(14) bond. In addition, the fragment ions **n''**, **o''** and **p''**, which are equivalent to the characteristic ions, **n**, **o** and **p**, of the fernane group compounds, originated from the left-hand part of the molecules, were observed in the MS of these compounds too. The fragment ions at *m/z* 205 (**r**), *m/z* 203 ($\mathbf{t_1}$), *m/z* 189 ($\mathbf{a'_1}$) and *m/z* 175 ($\mathbf{a'_2}$) were observed in the MS of **25** and **26**, originated from cleavage of their C(8)–C(14) bond. There were also fragment ions at *m/z* 274 (**v**) and *m/z* 259 (**v** − 15) that are derived by cleavage of the C(9)–C(10) bond. The fragment ions at **v** and **v** − 15 are similar ions to those of **22**. Compound **25** gave the fragment ions at *m/z* 340 (**y**) and *m/z* 325 (**z**) due to cleavage of ring E, but these ions are not detected in the MS of **26** (Chart 12). In sum, compounds of the filicane and friedelane groups gave similar fragment patterns to each other, and many fragments in common with those of the fernane and multiflorane groups were observed (Table VI).

Experimental

The spectra were measured using a JEOL JMS-D 300 mass spectrometer. The ionization energy was 30 or 70 eV and the ionizing current was 300 μA. The samples were run using a direct inlet system heated at 250 °C. The relative intensities of the peaks were reported with reference to the most intense peak higher than *m/z* 100. The samples used were mainly isolated from Fern, Composite and Ericaceous plants (references are cited in the tables).

References and Notes

1) H. Budzikiewics, J. W. Wilson and C. Djerassi, *J. Am. Chem. Soc.*, **85**, 3688 (1963).
2) H. Ageta, K. Iwata and Y. Yonezawa, *Chem. Pharm. Bull.*, **11**, 408 (1963).
3) H. Ageta, K. Iwata and Y. Otake, *Chem. Pharm. Bull.*, **11**, 407 (1963).
4) H. Ageta, K. Shiojima, Y. Arai, T. Kasama and K. Kajii, *Tetrahedron Lett.*, **1975**, 3297.
5) H. Ageta, K. Shiojima and Y. Arai, *Chem. Pharm. Bull.*, **35**, 2705 (1987).
6) H. Fazakerley, T. G. Halsall and E. R. H. Jones, *J. Chem. Soc.*, **1959**, 1877.
7) Unpublished data from our laboratory.
8) K. Shiojima and H. Ageta, *Chem. Pharm. Bull.*, **38**, 347 (1990).
9) H. Ageta, K. Iwata, Y. Arai, Y. Tsuda, K. Isobe and S. Fukushima, *Tetrahedron Lett.*, **1966**, 5679.
10) K. Shiojima, Y. Arai and H. Ageta, *Phytochemistry*, **29**, 1079 (1990).
11) K. Masuda, K. Shiojima and H. Ageta, *Chem. Pharm. Bull.*, **31**, 2530 (1983).
12) K. Shiojima, K. Masuda, T. Lin, H. Suzuki and H. Ageta, *Tetrahedron Lett.*, **30**, 4977 (1989).
13) Y. Arai, Y. Kusumoto, M. Nagao, K. Shiojima and H. Ageta, *Yakugaku Zasshi*, **103**, 356 (1983).
14) H. Ageta and Y. Arai, *Phytochemistry*, **22**, 1801 (1983).
15) H. Ageta, K. Siojima and Y. Arai, *Chem. Commun.*, **1968**, 1105.
16) H. Ageta and T. Ageta, *Chem. Pharm. Bull.*, **32**, 369 (1984).
17) K. Shiojima, K. Masuda and H. Ageta, *Chem. Pharm. Bull.*, **38**, 79 (1990).
18) H. Ageta, K. Shiojima, K. Masuda and T. Lin, *Tetrahedron Lett.*, **22**, 2289 (1981).
19) K. Masuda, R. Kamaya, S. Ikegami, Y. Ikeshima and H. Ageta, *Chem. Pharm. Bull.*, **37**, 1673 (1989).
20) Y-Y. Lin, H. Kakizawa, Y. Shiobara and K. Nakanishi, *Chem. Pharm. Bull.*, **13**, 986 (1965).
21) Y. Tanaka, K. Tohara, K. Terasawa, M. Sawada and H. Ageta, *Shoyakugaku Zasshi*, **32**, 60 (1978).
22) A. K. Chakraraty, B. Das, S. C. Pakrashi, D. R. Mcphail and A. T. Mcphail, *J. Chem. Soc., Chem. Commun.*, **1989**, 438.
23) K. Shiojima, K. Masuda, Y. Ooishi, H. Suzuki and H. Ageta, *Tetrahedron Lett.*, **30**, 6873 (1989).
24) H. Ageta, K. Shiojima and K. Masuda, *Chem. Pharm. Bull.*, **30**, 2272 (1982).
25) Y. Inubushi, Y. Tsuda, T. Sano, T. Konita, S. Suzuki, H. Ageta and Y. Otake, *Chem. Pharm. Bull.*, **15**, 1153 (1967).
26) H. R. Arthur, W. H. Hui and R. T. Aplin, *Tetrahedron Lett.*, **1965**, 937.
27) H. Ageta and K. Iwata, *Tetrahedron Lett.*, **1966**, 6069.
28) H. Ageta, K. Iwata and S. Natori, *Tetrahedron Lett.*, **1964**, 3413.
29) G. Ourisson and T. Takahashi, *Chem. & Ind.*, **1955**, 1155.