1884 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(6), 1884—1888 (1975) [Vol. 48, No. 6

The High Resolution Mass Spectra of Shionane and Friedelane Derivatives

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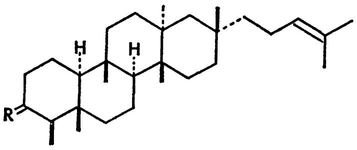
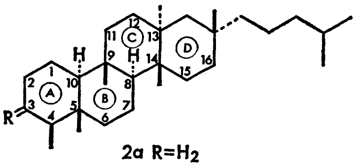
(Received November 8, 1974)

High resolution mass spectra of shionane and friedelane derivatives were measured and characteristic fragmentation patterns were described.

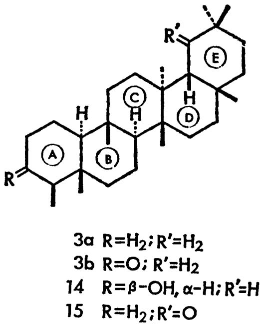
In the course of structure study of shionone (**1**),[1] a triterpene ketone, $C_{30}H_{50}O$, isolated from roots of *Aster tataricus* L., low resolution mass spectra of shionone (**1**) and several derivatives were measured.[2] We now wish to describe studies on the characteristic fragmentation patterns of a shionane-type skeleton (**2a**) as well as those of a friedelane-type skeleton (**3a**) by high resolution mass spectrometry. These two frameworks bear a common partial structure in respect to A/B/C/D rings.



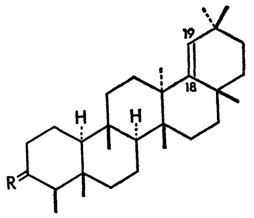
1 R=O
9 R=β-OH,α-H



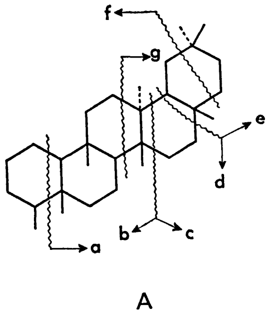
2a R=H2
2b R=O



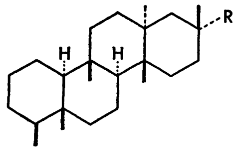
3a R=H2; R'=H2
3b R=O; R'=H2
14 R=β-OH, α-H; R'=H2
15 R=H2; R'=O



4a R=H2
4b R=O



A



5 R=-CH2CH2CO2Me
6 R=-CH2CO2Me
7 R=-CO2Me
8 R=-CH2CH2CH=C(Me)Me
11 R=-CH2CH2CH2C(Me)=CH2
12 R=-CH2CH2CH2COMe

Courtney *et al.* examined the mass spectra of several friedelin derivatives and described fission patterns as shown in **A**. The cleavages **c**, **e**, and **f** were described to be characteristic for friedelin derivatives with a hydroxyl, an acetoxyl or a carbonyl group in ring E, **a** and **d** for compounds with a carbonyl group at C_3, and **b** and **g** for a friedelane skeleton.[3]

Later, Budzikiewicz *et al.* reported cleavages **b** and **g** as well as the subsequent fragmentations for friedel-18-ene (**4a**) and friedel-18-en-3-one (**4b**)[4].

In the high resolution mass spectra of methyl tri-, tetra-, and pentanorshionanoates (**5**, **6**, and **7**), obtained by degradation reactions of the side chain of shion-24-ene (**8**), prominent peaks are classified into two groups: one group consists of peaks which vary with the side chain length, and the other is composed of peaks which are independent of the side chain (Table 1).

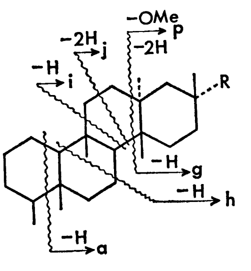
The peaks due to $(M-15)^+$, $(M-31)^+$, $(M-71)^+$, $(M-139)^+$, $(M-179)^+$, $(M-194)^+$, $(M-207)^+$, and $(M-239)^+$ showed characteristic shifts by 14 mass units for **5** and **6**, and for **6** and **7**. It is obvious that these peaks are due to the species including the side chain. These compounds exhibit the molecular ions and the $(M-15)^+$ ions with high intensities, as well as the $(M-31)^+$ ions due to a fission between the acyl group and the oxygen atom with weak intensities.

Species $(M-71)^+$, $(M-139)^+$, $(M-179)^+$, and $(M-207)^+$ due to fissions **a**, **h**, **i**, and **g**, respectively, are derived from the two-bond fission between a quarternary and a tertiary carbon atoms and between a tertiary or a quarternary and a secondary carbon atoms, followed by loss of an additional hydrogen from the charged species.

The species due to $(M-194)^+$ is originated by rupture of bonds C_8–C_{14} and C_{11}–C_{12}. Although the latter is a bond between two secondary carbon atoms, the fission **j** occurred with relative ease (relative intensities: 20, 10, and 36% for **5**, **6**, and **7**, respectively).

The (M-239) peaks, observed in the spectra of **5** and

6, are considered to be due to species **p** which could be derived by the fission **g** followed by loss of a methoxyl group and two hydrogen atoms. These fissions are shown as in **B**.



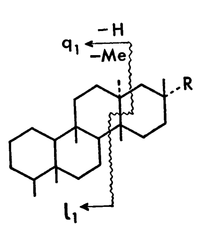
B

On the other hand, the peaks at *m/e* 329, *m/e* 259, *m/e* 233, *m/e* 217, *m/e* 205, *m/e* 193, *m/e* 191, *m/e* 179, *m/e* 177, *m/e* 149, *m/e* 137, *m/e* 135, *m/e* 123, *m/e* 109, *m/e* 95, *m/e* 81, *m/e* 69, and *m/e* 55 are independent of the side chain length.

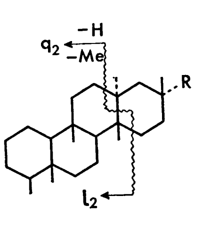
The fragment **k** at *m/e* 329 ($C_{24}H_{41}$) is derived from the scission of the side chain of **5**, **6**, and **7**.

It has been reported that fission **b** due to two-bond fission between C_{13} and C_{18} and between C_{14} and C_{15} in friedelin (**3b**)[3,4] and friedel-18-ene (**4a**)[4] followed by loss of one hydrogen atom gives species at *m/e* 273 and 259, respectively. Although intense peaks due to fission **b** were observed in the spectra of friedelane derivatives (**3a**, **14**, and **15**), these peaks due to fission **b** in the spectra of **6** and **7** were rather weak. Friedelane derivatives and a few shionane derivatives were accompanied by species **b**′, derived from the two-bond fission **b** without loss of one hydrogen atom.

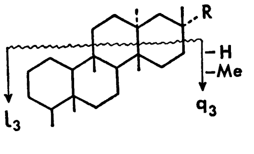
Peaks at *m/e* 233 ($C_{17}H_{29}$) were observed in the spectra of **5**, **6**, and **7**. The fragmentation process has remained obscure, because four alternative scissions such $\mathbf{l}_1$, $\mathbf{l}_2$, $\mathbf{l}_3$, or $\mathbf{l}_4$ including three-bond fission in ring C and D could be considered (**C**$_1$—**C**$_4$). The fragment **q** at *m/e* 217 ($C_{16}H_{25}$) observed for **2a**, **5**, **6**, and **8** is seemed to be due to scission **l** accompanied by loss of one hydrogen atom and a methyl group (**C**$_1$—**C**$_4$).



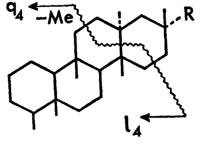
C1



C2



C3



C4

In a friedelane series, the corresponding scission **q** gives the peak at *m/e* 217 for **3a**, **4a**, and **15**, and a peak at *m/e* 233 for **14**.

By the two-bond fission of C_{12}—C_{13} and C_8—C_{14}, a charged species **m** (*m/e* 206) containing rings A and B was formed, which was followed by loss of a hydrogen atom to give species **m**′ (*m/e* 205) for **5** and **6**. The counterpart to give a species **g** was discussed above.

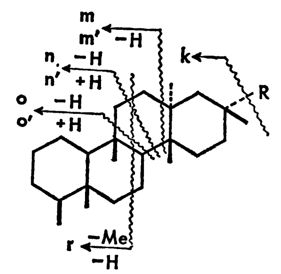
The two-bond fission of C_{11}—C_{12} and C_8—C_{14} could produce either a charged species containing rings A and B or ring D. The latter charged species gives a species **j**, mentioned above. The former charged species, on removal of a hydrogen atom, affords a species **n** (*m/e* 191) for **5**, **6**, and **7**, whereas by abstraction of an additional hydrogen atom from the leaving moiety gives species **n**′ (*m/e* 193).

The species at *m/e* 177 due to fragmentation **o** is formed by cleavage of two bonds (C_8–C_{14} and C_9–C_{11}) followed by loss of an additional hydrogen atom from the charged species. This fission is visualized by the rupture involving the quarternary C_9 and C_{14} centers. In the case of **5**, the species **o** ($C_{13}H_{21}$, *m/e* 177.1642, obs. 177.1637) was accompanied by $C_{12}H_{17}O$ (*m/e* 177.1279, obs. 177.1280) with weak intensity, which was likely due to a species **p** derived from the two-bond fission of C_{12}–C_{13} and C_8–C_{14} accompanied by loss of two hydrogen atoms and a methoxyl group (*cf.* **B**). This was supported by the appearance of the corresponding peak at *m/e* 163.1106 ($C_{11}H_{15}O$) in the mass spectrum of **6**. The fragment ion **o** constitutes the counterpart of ion **i**.

The above mentioned fission of the two bonds (C_8–C_{14} and C_9–C_{11}) and a subsequent hydrogen abstraction gave species **o**′, which were observed with nearly the same intensities as those due to the species **o**.

Peaks **r** were observed at *m/e* 149 for **2a**, **5**, **6**, **7**, and **8** with considerably high intensities. It is considered that this peak is produced from the three-bond fission of C_6–C_7, C_8–C_9, and C_{11}–C_{12} followed by loss of one methyl group and one hydrogen atom. In friedelane derivatives, the corresponding rupture **r** gives peaks at *m/e* 149 for **15**, at *m/e* 163 for **3b**, and at *m/e* 165 for **9** and **14**.

Fragmentation patterns independent of the side chain length can be depicted as in **D**.



D

Although we can find other common peaks at *m/e* 263 ($C_{17}H_{27}O_2$ for **5** and **6**) and *m/e* 249 ($C_{16}H_{25}O_2$ for **5**, **6**, and **7**) for these compounds, it is likely that each fragment may be produced by a different mode of scission in each compound. These fragmentation patterns are therefore left undetermined.

Compositions of the species in low mass range less

TABLE 1. HIGH RESOLUTION MASS SPECTRAL DATA

	M^+	$(M-15)^+$	**a**	**h**	**i**	**i′**	**j**
Shionone (**1**)	426.3836 (92)	411.3604 (16)	341.3170 (100)	273.2546 (21)			218.2022 (27)
Shonane (**2a**)	414.4246 (48)	399.3971 (57)	343[b]	275.2746 (71)			220.2151 (36)
Shionanone (**2b**)	428.4019 (15)	413.3756 (6)	343.3353 (32)	275.2739 (16)			220.2181 (29)
Methyl trinor-shionanoate (**5**)	416.3679 (93)	401.3437 (28)	345.2762 (18)	277.2154 (56)	237.1842 (10)		222.1620 (30)
Methyl tetranor-shionanoate (**6**)	402.3483 (66)	387.3266 (33)	331.2643 (9)	263.2011 (47)	223.1682 (5)		208.1437 (19)
Methyl pentanor-shionanoate (**7**)	388.3331 (100)	373.3082 (100)	317.2494 (67)	249.1828 (80)			194.1292 (27)
Shion-24-ene (**8**)	412.4065 (63)	397.3861 (22)	341.3197 (6)	273.2578 (24)			218.2035 (15)
Shion-24-en-3β-ol (**9**)	428.4027 (54)	413.3794 (14)	341[b]	273.2589 (19)			218.2038 (14)
Friedelane (**3a**)	412.4065 (33)	397.3813 (16)	341[b]	273.2564 (4)	233.2266[d] (49)		218.2014 (42)
Friedelin (**3b**)	426.3870 (90)	411.3638 (63)	341.3209 (26)	273[b]			218.2022 (26)
Friedel-18-ene (**4a**)	410.3919 (53)	395.3692 (100)		271.2389 (16)			[g]
Friedelan-3β-ol (**14**)	428.4014 (84)	413.3758 (44)		273.2585 (7)			218.2003 (9)
Friedelan-19-one (**15**)	426.3822 (41)		[c]	287.2353 (2)		248.2145 (8)	233.1903 (5)

	g	**k**	**d**	**b**	**b′**	**l**	**m**
Shionone (**1**)	205.1958 (43)	343.3022 (42)			274.2296 (19)	247.2039 (30)	220.1807 (28)
Shionane (**2a**)	207.2105 (19)	329.3213 (36)		259[b]	260[b]	233.2278 (79)	
Shionanone (**2b**)	207.2109 (16)	343.3010 (22)				247.2058 (16)	220.1820 (21)
Methyl trinor-shionanoate (**5**)	209.1555 (24)	329.3194 (13)				233.2264 (73)	206.2045 (11)
Methyl tetranor-shionanoate (**6**)	195.1366 (26)	329.3192 (26)		259.2449 (5)	260.2504 (22)	233.2257 (78)	
Methyl pentanor-shionanoate (**7**)	181[b]	329.3188 (40)		259.2409 (20)		233.2262 (47)	
Shion-24-ene (**8**)	205.1944 (23)	329.3220 (31)		259.2427 (16)		233.2267 (58)	206.2016 (13)
Shion-24-en-3β-ol (**9**)	205.1954 (19)	345[b]			276.2439 (9)	249.2214 (9)	
Friedelane (**3a**)	205.1947[e] (45)		288.2817 (5)	259.2404 (70)	260.2489 (26)	233.2266[d] (49)	206.2012 (27)
Friedelin (**3b**)	205.1965 (42)		302[b]	273[b]	274.2344 (68)	247.2048 (32)	220.1846 (16)
Friedel-18-ene (**4a**)	203.1789 (47)		288.2804 (11)		260.2480 (16)	233.2267 (21)	206.2027 (11)
Friedelan-3β-ol (**14**)	205.1955 (19)		304[b]	275.2374 (41)	276.2438 (25)	249.2224 (20)	
Friedelan-19-one (**15**)	[f]		288.2847 (8)	259.2417 (69)	260.2467 (19)		

than *m*/*e* 137 were examined by high resolution mass spectrometry. Since these species would be formed through multi-step fissions, their fragmentation patterns are not discussed here.

The high resolution mass spectra of shionone (**1**), shionane (**2a**), shionanone (**2b**), shion-24-ene (**8**), and shion-24-en-3β-ol (**9**) and the low resolution mass spectra of shion-3-ene (**10**), shion-25-ene (**11**), norshionan-25-one (**12**), and shionan-3β,29-olide (**13**) are well interpreted by the fragmentation patterns above mentioned (Tables 1 and 2).

The $C_{14}H_{23}^+$ (*m*/*e* 191) peaks in the mass spectra of shionone (**1**), shionanone (**2b**), and friedelin (**3b**) are considered to be derived from the fragment **m′** and subsequent loss of a carbon monoxide molecule.

Introduction of a carbonyl group at C_{19} causes con-

OF SHIONANE AND FRIEDELANE DERIVATIVES[a]

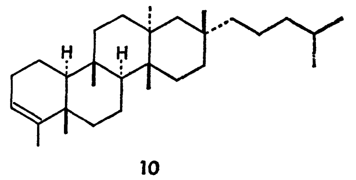
	m′	**n**	**n′**	**o**	**o′**	**p**	**q**
Shionone (**1**)	219.1739 (10)	205.1596 (27)	207.1753 (30)	191.1441 (13)	193.1578 (12)		231.1738 (12)
Shionane (**2a**)	205.1961 (17)	191.1764 (17)	193[b]	177.1663 (28)	179.1792 (29)		217.1931 (19)
Shionanone (**2b**)	219.1733 (6)	205.1602 (11)	207.1746 (11)	191.1429 (6)	193.1599 (8)		
Methyl trinorshionanoate (**5**)	205.1944 (13)	191.1803 (8)	193.1952 (11)	177.1637 (29)	179.1796 (13)	177.1280 (5)	217.1954 (19)
Methyl tetranorshionanoate (**6**)	205.1928 (9)	191.1785 (19)	193.1930 (10)	177.1619 (43)	179.1776 (28)	163.1106 (5)	217.1947 (9)
Methyl pentanorshionanoate (**7**)		191.1779 (27)	193[b]	177.1631 (33)	179[b]		
Shion-24-ene (**8**)	205.1944 (23)	191.1801 (32)	193.1957 (14)	177.1634 (32)	179.1796 (32)		217.1960 (14)
Shion-24-en-3β-ol (**9**)				193.1577 (9)			
Friedelane (**3a**)	205.1947[e] (45)	191.1754 (33)	193.1906 (3)	177.1630 (41)	179.1784 (50)		217.1951 (51)
Friedelin (**3b**)		205.1607 (42)	207.1738 (16)		193.1601 (32)		
Friedel-18-ene (**4a**)	205.1946 (16)	191.1794 (21)		177.1643[h] (68)	179.1770 (16)		217.1973 (47)
Friedelan-3β-ol (**14**)		207.1716 (7)		193.1586 (15)	195.1742 (10)		233.1902 (35)
Friedelan-19-one (**15**)	205.1970 (11)	191.1806 (22)		177.1637 (19)			217.1945 (55)

	r	**f**	**c**	**e**	**m′**−CO	**i**−CO	Base peak
Shionone (**1**)					191.1804 (21)		341.3170
Shionane (**2a**)	149.1310 (67)						123.1153
Shionanone (**2b**)					191.1787 (7)		109.1013
Methyl trinorshionanoate (**5**)	149.1326 (62)						109.1012
Methyl tetranorshionanoate (**6**)	149.1317 (71)						121.1020
Methyl pentanorshionanoate (**7**)	149.1301 (27)						373.3082 388.3331
Shion-24-ene (**8**)	149.1335 (56)						109.1017 123.1169
Shion-24-en-3β-ol (**9**)	165.1271 (19)						109.1014
Friedelane (**3a**)	149.1312 (100)						109.1013 149.1312
Friedelin (**3b**)	163.1111 (62)				191.1825 (42)		109.1011
Friedel-18-ene (**4a**)	149.1329 (26)						111.1170 395.3692
Friedelan-3β-ol (**14**)	165.1273 (100)						165.1273
Friedelan-19-one (**15**)	149.1318 (27)	357.3148 (8)	165.1289 (5)	139.1119 (100)		219.2092 (16)	139.1119

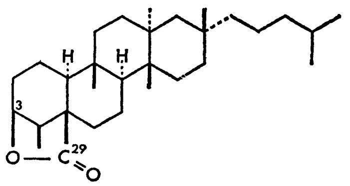
a) Peaks higher than *m/e* 100 are registered. Numbers in parentheses refer to relative intensities. b) *m/e* Value, observed in a low resolution mass spectrum, but not detected in a high resolution mass spectrum, because error of the *m/e* value exceeded ±5 milli mass units. c) A peak at *m/e* 355 was not observed, but *m/e* 357.3148 ($C_{25}H_{41}O$), due to fission **a** followed by addition of H, was observed. d) Maybe due to fissions **i** and **l**. e) Maybe due to fissions **g** and **m′**. f) A peak at *m/e* 219 was not observed, but *m/e* 221.1900 ($C_{15}H_{25}O$), due to fission **g** followed by addition of H, was observed. g) A peak at *m/e* 216 was not observed, but *m/e* 217.1973 ($C_{16}H_{25}$), due to fission **j** followed by loss of H (not 2H), was observed. h) Or due to a species "**jj**", described in the reference 4.

Table 2. Low resolution mass spectral data of shionane derivatives

	M$^+$	(M-15)$^+$	**a**	**h**	**j**	**g**	**k**	**b′**	**l**	**m**	**m′**	**n**	**n′**	**o**
Shion-3-ene (**10**)	412	397	343	275	220	207	327		231	204	203	189	191	175
Shion-25-ene (**11**)	412	397	341	273	218	205	329	260	233	206	205	191	193	177
Norshionan-25-one (**12**)	414	399	343	275	220	207	329	260	233	206	205	191	193	177
Shionan-3β,29-olide (**13**)	442	427	373	275	220	207	357		261	234	233	219	221	205

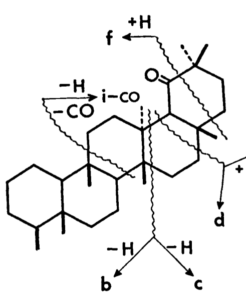


10



13

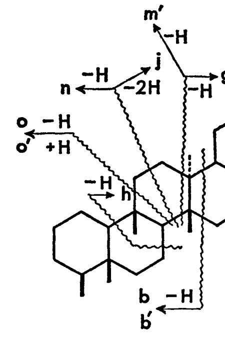
siderable changes in the fragmentation pattern of the friedelane skeleton. Among the fissions **b**, **c**, **d**, **e**, and **f** which are characteristic of a friedelane skeleton[3], two prominent peaks due to fissions **e** and **b** were observed in the mass spectrum of friedelan-19-one (**15**). The cleavage **f** seems to be not so important in the fragmentation of **15** (Figure **E**). A peak at *m/e* 219 was also observed. This ion could be explicable by the fragmentation (**i**—CO).



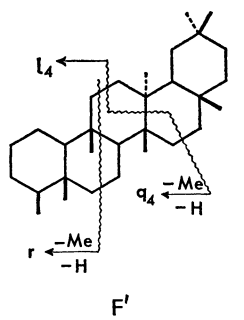
E

In conclusion, the cleavages **a**, **g**, **h**, **j**, **k**, **l**, **m** (**m′**), **n** (**n′**), **o** (**o′**), **q**, and **r** were shown to be characteristic of a shionane-type skeleton (**B**, **C**, and **D**).

The high resolution mass spectra of friedelin (**3b**), friedelane (**3a**), friedel-18-ene (**4a**), friedelan-3β-ol (**14**), and friedelan-19-one (**15**) confirmed the characteristic scissions **b′** (or **b**) and **g** described earlier.[3,4] The fissions **h**, **j**, **l**,† **m** (**m′**), **n**, **o** (**o′**), **q**,† and **r** were also considered to be characteristic of a friedelane-type skeleton (**F** and **F′**).



F



F′

Peaks due to the species **a** appeared for all shionane derivatives. The cleavages **b** and/or **b′** were observed constantly for friedelane derivatives, while peaks due to these scissions were absent in the spectra of some shionane derivatives (Tables 1 and 2). These observations are considered to be due to structure differences between the two skeletons of shionane and friedelane.

Experimental

The high and low resolution mass spectra were determined with a Hitachi RMU-7M double-focusing and a Hitachi RMU-6-Tokugata mass spectrometers, respectively, operating at 70 eV. The samples were introduced by direct inlet system at 100 to 180 °C. Shionane and friedelane derivatives were available from earlier studies.[1,2,5]

References

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4) H. Budzikiewicz, J. M. Wilson, and C. Djerassi, *J. Amer. Chem. Soc.*, **85**, 3688 (1963); They also described a formation of ion "q" and its related ions (analogues of species "g" in their text) from friedelin, friedelane, friedel-18-en-3-one and friedel-18-ene. However, the mass numbers of these ions are not compatible with their formulae.

5) T. Fukuda, T. Tsuyuki, Y. Tanahashi, and T. Takahashi, This Bulletin, **40**, 370 (1967).

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† In Fig. **F′**, cleavages **l** and **q** are shown by **l**$_4$ and **q**$_4$, respectively. Other scissions **l**$_1$, **l**$_2$, and **l**$_3$, and **q**$_1$, **q**$_2$, and **q**$_3$ analogous to those shown in **C**$_1$, **C**$_2$, and **C**$_3$, are also applicable for these cleavages **l** and **q**, respectively.