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A STUDY OF SANTONINS AND THEIR DERIVATIVES BY MASS SPECTROMETRY

N. WASADA, T. TSUCHIYA[a], E. YOSHII[b] and E. WATANABE[c]

Joint Contribution from [a]Government Chemical Industrial Research Institute, Tokyo, 1, Honmachi, Shibuyaku, [b]Faculty of Pharmaceutical Science, Toyama University, Toyama, and [c]Japan Electron Optics Laboratory, Akishimashi, Tokyo

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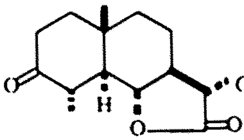
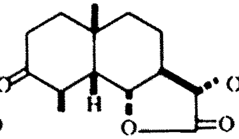
Abstract—Fragmentation patterns of santonins and their derivatives under electron impact have been investigated by the use of high resolution mass spectra and a deuterium labelling technique. The relationship between conformation of santonins and their spectra is discussed.

THE mass spectra of santonins and their derivatives have been investigated in order to obtain information on the fragmentation of fused ring lactones. The mass spectra



α-Tetrahydro-santonin



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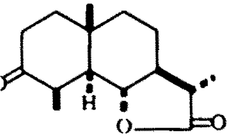

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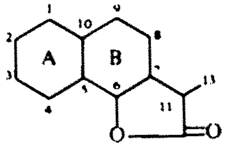
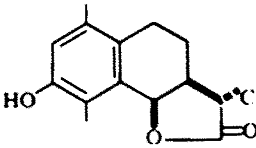
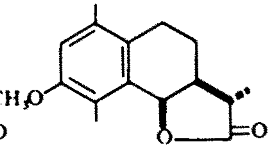
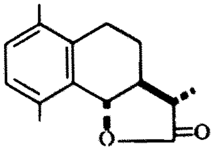




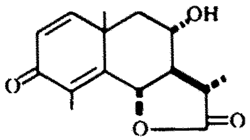
α-Desmotropo-santonin



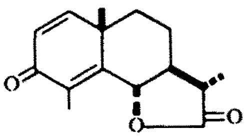
α-Desmotropo-santonin methyl ether



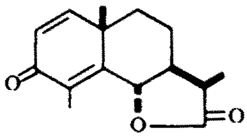
Hyposantonin



Artemisin



α-Santonin



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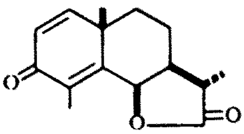
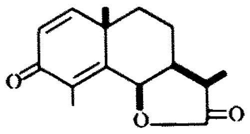
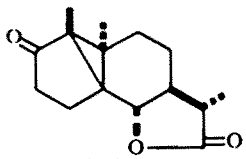


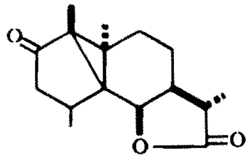
C-Santonin



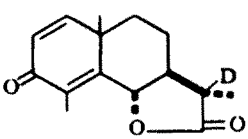
D-Santonin



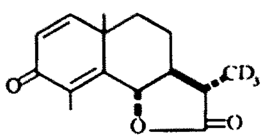
Dihydrolumi-santonin



Dihydrolumi-6-epi-santonin



11d$_1$-α-Santonin



13d$_3$-α-Santonin

of aliphatic lactones have been investigated[1, 2] and recently, a few peaks of the mass spectrum of α-santonin and a proposed fragmentation mechanism of one of the main peaks have been reported.[3]

Thirteen santonins, including isomers, derivatives of santonin, and two deuterated santonins have now been investigated.

Table 1 shows the pattern coefficient of santonins based on Σ_{90}. Table 2 shows the atomic composition of main peaks of α-santonin determined by high resolution spectrum. The last column of Table 2 shows the atoms expelled. Main peaks of mass spectra of compounds investigated are reproduced in Figs. 1–10.

TABLE 1. PATTERN COEFFICIENT OF α-, β-, C-, AND D-SANTONIN

m/e	α	β	C	D	m/e	α	β	C	D
247	0·9	0·9	1·3	1·0	146	1·8	1·2	1·1	1·1
246	5·3	5·1	7·9	6·1	145	2·0	1·9	3·8	3·6
231	2·7	2·4	1·8	1·0	144	0·6	0·4	1·2	1·2
218	0·7	0·6	2·0	1·6	135	4·3	5·5	3·5	3·5
203	1·8	1·5	2·1	1·3	134	2·1	2·3	3·3	3·0
191	1·5	1·9	0·2	0·1	133	1·2	1·2	1·2	1·0
190	1·9	1·9	0·7	0·6	131	1·0	0·9	1·2	1·5
187	0·9	1·1	1·9	2·7	129	1·4	1·2	2·3	2·3
175	2·7	2·3	1·6	1·2	128	1·2	0·8	1·7	1·9
174	1·4	1·1	1·9	2·1	122	2·3	2·5	0·8	0·7
173	6·8	5·7	6·5	5·4	121	2·6	2·3	1·2	1·0
172	2·4	2·2	1·8	1·8	120	1·1	0·9	1·5	1·1
163	1·6	1·9	0·3	0·4	119	1·8	1·7	1·5	1·4
162	1·3	1·1	0·7	0·6	117	1·1	0·9	1·3	1·3
161	1·8	1·9	1·3	1·2	115	1·7	2·0	2·0	2·1
159	1·2	0·9	2·8	3·1	108	1·0	1·1	3·6	3·2
158	0·8	0·5	1·1	1·2	107	2·4	2·2	2·6	2·4
157	1·2	1·0	1·8	1·3	106	0·8	0·6	1·4	1·3
149	1·5	2·5	0·8	1·8	105	2·2	1·9	2·6	2·4
148	1·1	1·1	1·2	1·2	93	1·2	1·0	0·7	0·7
147	2·2	1·8	1·4	1·2	92	1·2	1·0	0·7	0·7
					91	7·5	6·2	5·6	5·2

CEC 21-103C, ionizing voltage, 70 eV

Fragmentation of α-santonin

m/e 231, (M-15). The expelled group is CH_3. From the spectra of deuterated compounds, the Me group on the lactone ring was found intact. Although this result does not indicate the contribution of the Me groups at C-4 and at C-10, usually, the contribution from the angular Me group to the peak is considerable.

m/e 228, (M-18). The (M-18) peaks of the measured compounds except artemisin were small. McFadden *et al.*[1] reported that aliphatic lactones give a significant (M-18) peak as the chain length increases to three or more carbons and suggested that this length permits a steric configuration that is favourable to the transfer of a

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[1] W. H. McFadden, E. A. Day and M. J. Diamond, *Analyt. Chem.* 37, 89 (1965).

[2] L. Friedman and F. A. Long, *J. Am. Chem. Soc.* 75, 2832 (1953).

[3] D. G. Boocock and E. S. Waight, *Chem. Comm.* 90 (1966)

TABLE 2. MASS AND ATOMIC COMPOSITION OF FRAGMENT IONS OF α-SANTONIN

m/e	Experimentally determined mass	Composition of fragment					Composition of expelled fragment		
		^{13}C	C	H	O		C	H	O
231	231·1035		14	15	3	−2	1	3	
228	228·1156		15	16	2	+2		2	1
218	218·1300		14	18	2	1	1		1
	218·0919		13	14	3	2	2	4	
203	203·1055		13	15	2	−1	2	3	1
	203·0680		12	11	3	−3	3	7	
191	191·1357	1	12	18	1	0	2		2
	191·1065		12	15	2	0	3	3	1
190	190·1335		13	18	1	+2	2		2
	190·1001		12	14	2	+1	3	4	1
175	175·1131		12	15	1	+1	3	3	2
	175·0730		11	11	2	−3	4	7	1
174	174·1029	1	11	13	1	3	3	5	2
			12	14	1	−1	3	4	2
	174·0656		11	10	2	−2	4	8	
173	173·0971		12	13	1	0	3	5	2
	173·0595		11	9	2	0	4	9	1
172	172·0873		12	12		2	3	6	2
161	161·0964		11	13	1	−2	4	5	2
	161·0621		10	9	2	+2	5	9	
147	147·1170		11	15		0	4	3	2
	147·0799		10	11	1	1	5	7	2
146	146·1085		11	14	0	−1	4	4	3
	146·0736		10	10	1	0	5	8	2
135	135·1174		10	15		0	5	3	3
	135·0810		9	11	1	0	6	7	2

JMS-01S. ionizing voltage. 30 eV

hydrogen. Santonins have an insignificant (M-18) peak though they have steric configuration that is favourable to the reaction suggested by McFadden *et al.*[1] This result may be due to the santonin molecule being less flexible than the chain of aliphatic lactones, and the shortening of the C-4-CH_3 bond resulting from hyperconjugation may decrease the chance of hydrogen transfer to the ethereal oxygen atom.

According to the spectra of deuterated santonins, though the hydrogen atoms bonded with the C-13 atom do not contribute to the loss of a water molecule, part of the C-11 hydrogen is lost as HDO. These results are in keeping with the hydrogen atoms in the water molecule lost from decalone.[4] It was shown by deuteration that the hydrogen atoms of the lost water molecule are randomly picked from every position in the decalone molecule. A metastable peak appears at *m/e* 212 which can be assigned to the transition,

$$246^{+} \rightarrow 228^{+} + 18$$

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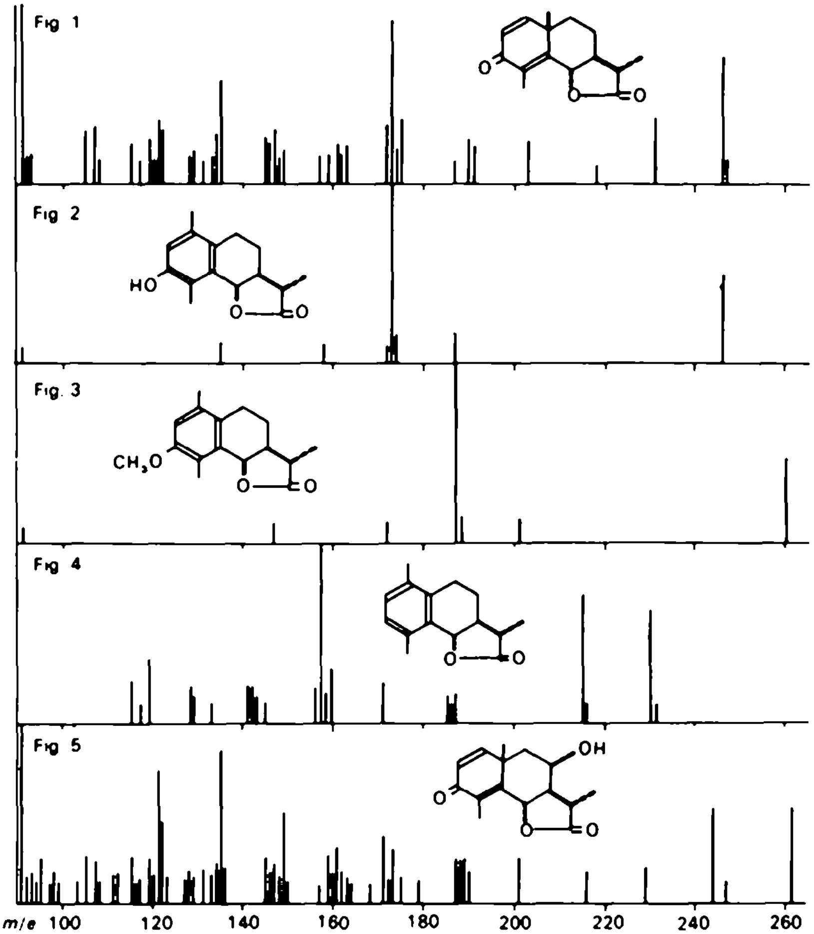
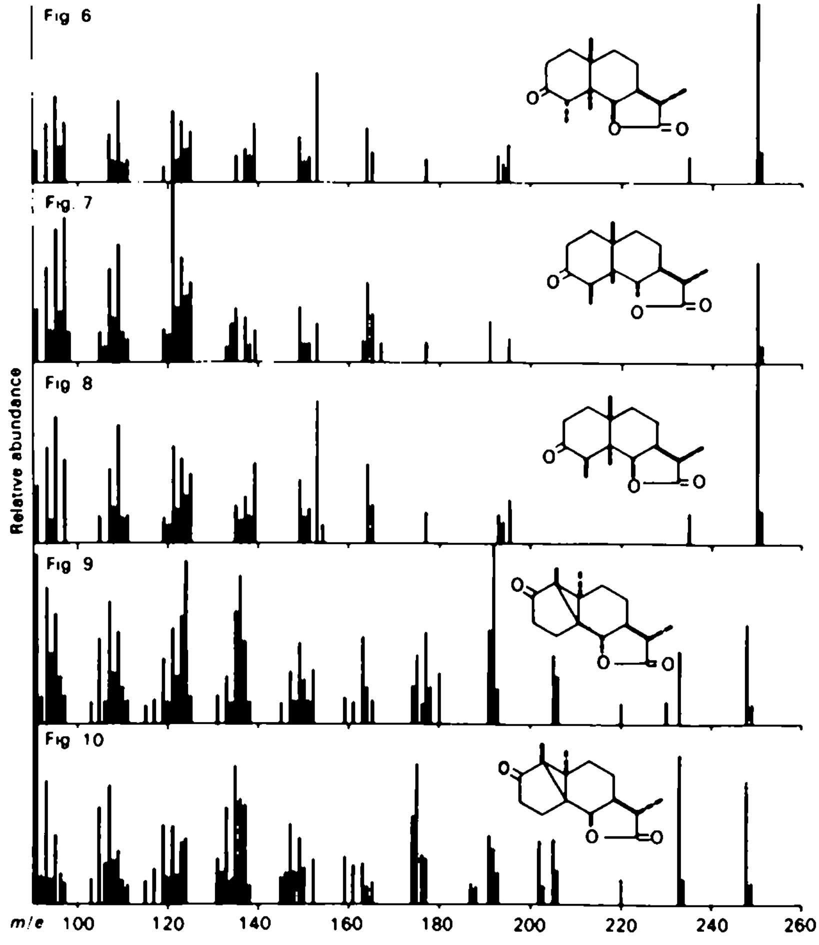
[4] E. Lund, H. Budzikiewicz, J. M. Wilson and C. Djerassi, *J. Am. Chem. Soc.* 85, 941 (1963)

m/e 218, (M-28). The peak is a doublet composed of $(M-C_2H_4)^+$ and $(M-CO)^+$ ions, and was revealed to contain C-11 and C-13 from the spectra of deuterated compounds. In all four santonins the $(M-CO)^+$ ion is more abundant than the $(M-C_2H_4)^+$ ion; in α-santonin, their intensity ratio is 4 to 1.



Mass spectra of: FIG. 1 α-santonin
FIG. 2 α-Desmotroposantonin
FIG. 3 α-Desmotroposantonin methyl ether
FIG. 4 Hyposantonin
FIG. 5 Artemisin

$(M-CO)^+$, $C_{14}H_{18}O_2^+$. The pattern coefficient of this ion of α- and β-santonins is appreciably smaller than that of C- and D-santonins. The expulsion of the CO group at C-3 and the carbonyl group in the lactone ring only were considered, as these processes involve the cleavage of just two bonds and the $(M-CO)^+$ ion is observed even at the lowest ionizing electron voltage applied. Therefore the expulsion of a CO group containing an ethereal oxygen atom in the lactone ring may be excluded as this process involves cleavage of three bonds instead of two. The contribution of either one of these two CO groups to the $(M-CO)^+$ peak cannot be estimated accurately from the present experimental results. But as desmotroposantonins and hyposantonin, which have no carbonyl group in the A ring, have only a minor $(M-28)^+$ peak (Figs 2, 3 and 4), and the CO group in benzoquinone and anthraquinone situated at a position in a ring similar to C-3 in santonin is expelled,[5-7] and as there is almost no peak in the spectra of aliphatic lactones,[1,2] it is inferred that an appreciable part of the peak is due to expulsion of a CO group in the A ring. Boocock *et al.* also postulated that the 3-oxo-group is almost certainly



Mass spectra of: Fig. 6. α-Tetrahydrosantonin
Fig. 7. β-Tetrahydrosantonin
Fig. 8. γ-Tetrahydrosantonin
Fig. 9. Dihydrolumisantonin
Fig. 10. Dihydrolumi-6-epi-santonin

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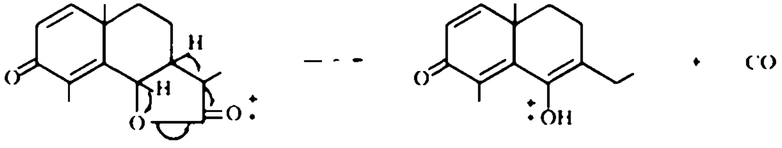
[5] J. H. Beynon, G. R. Lester and A. E. Williams, *J. Phys. Chem.* **63**, 1861 (1959)

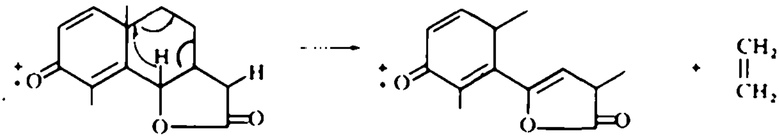
[6] J. H. Beynon, *Mass Spectrometry and its Applications to Organic Chemistry* p. 271 Elsevier (1960).

[7] J. H. Beynon and A. E. Williams, *Appl. Spectroscopy* **14**, 156 (1960).

the source of carbon monoxide lost, because the (M-CO) peak is considerably greater in the C-, D-santonins having the *cis*-fused lactone ring than in the α- and β-santonins in which the lactone is *trans*-fused and this fragmentation relieves steric strain which from models seems to be greater when the lactone ring has the *cis*-fusion.[3] However, other potential fragmentation pathways, e.g. the possibility of the following scheme, should not be excluded.

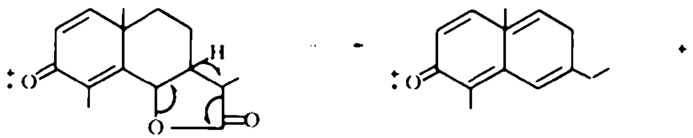


$(M\text{-}C_2H_4)^+$, $C_{13}H_{14}O_3^+$. Since this ion was found to contain both C-11 and C-13 from the spectra of deuterated compounds, the expelled C_2H_4 must come from C-8 and C-9. It is well established[8] that steroids lose C-6, 7 and C-8, 9 in a similar way. An analgous consideration leads to the following fragmentation scheme:



m/e 203, (M-43). The peak consists of a doublet composed of $C_{13}H_{15}O_2^+$ and $C_{12}H_{11}O_3^+$, the intensity ratio being 10 to 1. $C_{13}H_{15}O_2^+$, $(M\text{-}C_2H_3O)^+$. This more intense ion of the doublet contains C-11 and C-13. Since the ion is observed at ionizing electron voltage, V_E, down to about 9 eV, the ion is probably not produced by a rupture of many bonds, and based on the molecular structure of santonin, the lost C_2H_3O is not considered to be expelled as a fragment.

m/e 202, (M-44). C-11 and C-13 remain intact in the $(M\text{-}CO_2)^+$ ion. Since the ion is produced at low electron energies, a possible fragmentation pathway would be as follows:



a

The intensity of the $(M\text{-}CO_2)^+$ ions in santonins is in the following order

$$\alpha < \beta < C < D,$$

in accordance with the suggestion made by Boocock *et al.* for the $(M\text{-}CO)^+$ ion.

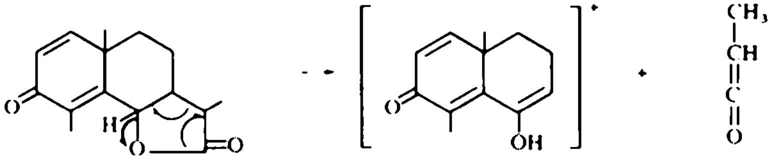
m/e 191, (M-55). The $C_{12}H_{15}O_2^+$ ion contains C-11 and C-13, and is observed at lower electron energies. There is no (M-55) peak in the spectrum of hyposantonin, which has an aromatic A ring and has no 3-oxo-group. Potentially the rupture of bonds 1–10 and 3–4 and an expulsion of a hydrogen atom would result in the ion. A similar rupture is known in the spectrum of p-benzoquinon,[5-7] though there is no hydrogen expulsion presumably because the molecule has no additional fused rings.

m/e 190, (M-56). A triplet consisting of $C_{13}H_{18}O^+$, $(M\text{-}C_2O_2)^+$; $C_{12}H_{14}O_2^+$,

[8] C. Djerassi, J. M. Wilson, H. Budzikiewicz and J. W. Chamberlin, *J. Am. Chem. Soc.* **84**, 4544 (1962)

$(M-C_3H_4O)^+$; and $C_{11}H_{10}O_3^{\cdot}$, $(M-C_4H_8)^+$ appears at m/e 190. The $C_{13}H_{18}O^+$ is the most intense and the $C_{12}H_{10}O_3^{\cdot}$ is the weakest. The spectra of deuterated compounds indicated that the intensity ratio $C_{13}H_{18}O^+ : C_{12}H_{14}O_2^{\cdot}$ is about 10:1.

The $C_{13}H_{18}O^+$ contains C-11 and C-13 and is observed at lower electron energies. The peaks in α- and β-santonins are about three times as intense as in C- and D-santonins. The $C_{12}H_{14}O_2^{\cdot}$ does not contain C-11 and C-13, and the fragmentation was assumed to be as follows:



A comparison of the intensities of m/e 190 and m/e 191 peaks reveals that the intensity ratio of these two peaks depends largely on the apparatus used for measurement, as is shown in Table 3, while intensity ratios of other peaks are about the same

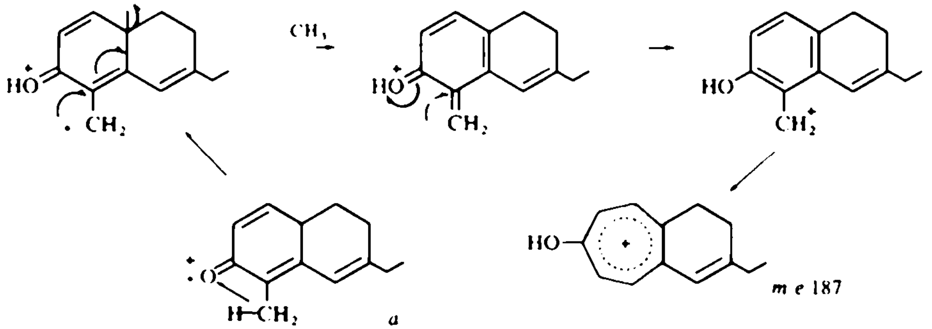
TABLE 3. THE DIFFERENCE OF ION INTENSITY

m/e		190	191
CEC 21-103C		35·8	28·6
Hitachi U6-B	Peak on the higher mass side	66·9	10·7
	Peak on the lower mass side	6·7	1·8

Arbitrary unit on each instrument. Only the ratios of peak heights should be compared.

Presumably, the material of the sample handling manifold, i.e. stainless steel in CEC 21-103C and glass in Htachi U6-B, could be the main cause of this phenomenon.

m/e 187, (M-59).$^+$ In the $C_{13}H_{15}O^+$, $(M-C_2H_3O_2)^+$ ion, C-11 and C-13 remain intact. From the molecular structure, the fragmentation pathway is inferred to be:



m/e 175, (M-71). α, β > C, D[*]. The peak is revealed to be a doublet consisting of $C_{12}H_{15}O^+$, $(M-C_3H_3O_2)^+$ and $C_{11}H_{11}O_2^{\cdot}$, $(M-C_4H_7O)^+$. The C-11 or C-13 content of the m/e 175 peak were calculated to be 5/8 from C-11-d_1-α-santonin and 5/9 from C-13-d_3-α-santonin, respectively. Since the intensity of the $C_{12}H_{15}O^+$ ion

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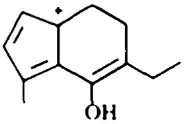
[*] This implies that the ion is more intense in α- and β-santonins than in C- and D-santonins according to the measurement with CEC 21-103C mass spectrometer.

is a little larger than that of the $C_{11}H_{11}O_2^+$ ion, it is inferred that the former ion contains C-11 and C-13 while the latter ion does not contain these atoms assuming each ion to consist of a single species. Appearance potential of m/e 175 ion is fairly large suggesting rupture of many bonds.

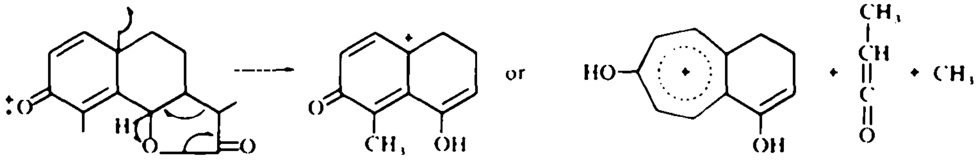
$C_{12}H_{15}O^+$. A metastable peak at m/e 140 indicates a reaction

$$218^{+\cdot} \rightarrow 175^{+} + 43$$

Presumably either one of carbonyls at C-3 or in the lactone ring is expelled first followed by another carbonyl and the C-10 methyl group. A potential structure of the ion may be as follows:



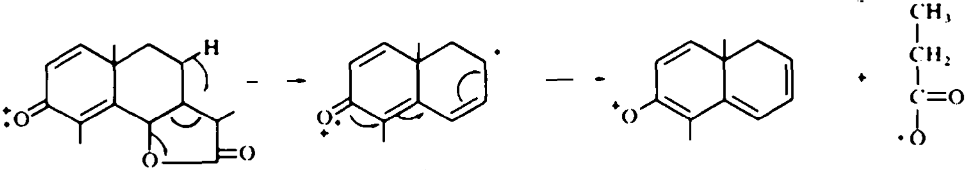
$C_{11}H_{11}O_2^+$. As C-11 and C-13 are inferred to be absent in the ion, the following reaction is probable:



m/e 173. (M-73). The peak was a triplet of $C_{12}H_{13}O^+$, $(M\text{-}C_3H_5O_2)^+$; $C_{13}H_{17}^+$, $(M\text{-}C_2HO_3)^+$; and $C_{11}H_9O_2^+$, $(M\text{-}C_4H_6O)^+$. The $C_{12}H_{13}O^+$ ion is by far the most intense and does not contain C-11 and C-13. A metastable peak at m/e 122 suggests the reaction:

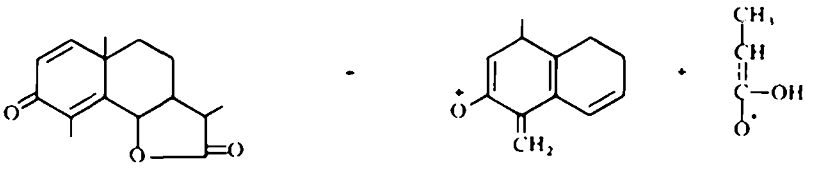
$$246^{+} \rightarrow 173^{+} + 73$$

The potential structure of the ion would be *b* or *c*.



b *c*

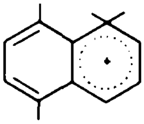
Boocock *et al.* showed that the hydrogen at C-2 remains intact in the formation of this ion and assumed a migration of the ring-junction methyl, postulating structure *d* for this ion.[3]



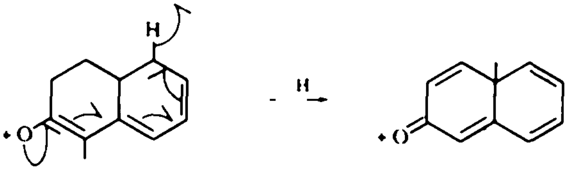
d

While the intensity of $(M\text{-}73)^+$ peaks in tetrahydrosantonins and lumi-santonins is about the same as that in four santonins, the intensity of the ions in hyposantonins and desmotroposantonin, which have an aromatic A ring, is very large (Figs 1–10). Instead of structure *b* or *c*, "naphtonium ion" structure *e* is proposed for these latter ions. The $(M\text{-}73)^+$ ion in artemisin is weak. A competent dehydration reaction due to the presence of hydroxyl group at C-8 would explain the phenomenon.

e

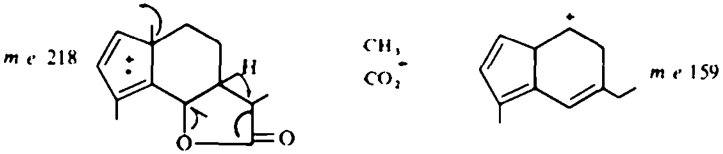


m/e 172, (M-74). A doublet consisting of $C_{13}H_{16}^{+}$, $(M\text{-}C_2H_2O_3)^+$ and $C_{12}H_{12}O^+$, $(M\text{-}C_3H_6O_2)^+$ appears. The $C_{12}H_{12}O^+$ is far more intense than the $C_{13}H_{16}^{+}$ and does not contain C-11 and C-13. An expulsion of a hydrogen atom from $C_{12}H_{13}O^+$ ion would result in the ion.

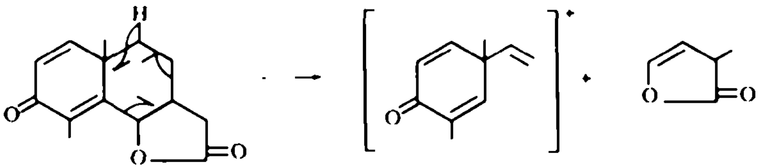


c

m/e 159, $C_{12}H_{15}$, $(M\text{-}C_3H_3O_3)^+$. A metastable peak at 116·5 suggests the following structure for this ion.



m/e 148, (M-98). The peak is a triplet consisting of $C_{10}H_{12}O^+$, $(M\text{-}C_5H_6O_2)^+$, $C_9H_8O_2^+$, $(M\text{-}C_6H_8O)^+$ and $C_{11}H_{16}^{+}$, $(M\text{-}C_4H_2O_3)^+$. The $C_{10}H_{12}O^+$ is by far the most intense and does not contain C-11.



m/e 91, C_7H_7, $(M\text{-}C_8H_{11}O_3)^+$. The ion does not contain C-11 and has the same atomic composition as the tropylium ion. The *m/e* 91 peak is very prominent in four santonins, artemisin and two dihydrolumisantonins and is of medium intensity in three tetrahydrosantonins, desmotroposantonin and its methyl ether and is weak in hyposantonin. Though we did not scrutinize the structure of the ion, it is interesting that the compounds which contain an aromatic A ring and which contain an A ring of a structure similar to santonin show an intense m/e 91 peak as is seen in Figs 1–10.

A comparison of the spectra of desmotroposantonin and its methyl ether (Figs. 2 and 3) reveals that almost all peaks in the higher mass region include the stable A ring. Similarly, important peaks in the higher mass region in the spectra of santonins contain an A ring which has a highly conjugated structure.

Intensity of parent ion and stability of molecule

Intensity of molecular ions in percentage of total ionization, I_p is known to be a measure of the stability of the ionized compounds.[9–11] In santonins, it is found that for B/C *cis* compounds C- and D-santonins, I_p values of 7·9% and 6·1%, respectively, are observed while the *trans* isomers give I_p values of 5·3% and 5·1%. These values are in agreement with the chemical experience that the *cis* compounds are more stable than the *trans* compounds, and among these *cis* compounds C-santonin is thermodynamically more stable than D-santonin.[12]

Stereochemical consideration

It has already been noted by many authors that certain stereochemical features can be related to characteristic mass spectrometric fragmentation process.[4, 8, 11–18]

While most of the peaks in the range of m/e > 150 are more intense in α- and β-santonins than those corresponding to each peak in C- and D-santonins, the intensity of a few peaks are in the reverse order. Table 4 shows the pattern coefficient of the more prominent peaks in the spectra of santonins in the range of m/e > 150, which are more intense in C- and D-santonins than in α- and β-santonins.

TABLE 4. PATTERN COEFFICIENT OF PEAKS WHICH ARE MORE INTENSE IN C- AND D-SANTONINS THAN IN α- AND β-SANTONINS

m/e	α	β	C	D	Atomic composition
246	52·6	51·3	79·2	61·3	$C_{15}H_{18}O_3$
218	7·3	6·2	19·8	16·4	$C_{14}H_{18}O_2$
202	3·8	3·0	7·0	17·0	$C_{14}H_{18}O$
187	9·0	10·5	18·6	27·3	$C_{13}H_{15}O$
159	11·8	9·3	28·3	31·0	$C_{12}H_{15}$

CEC 21-103C, ionizing voltage, 70 eV
Ten times of values based on Σ_{90}

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Of the two components of the m/e 218 doublet, the $C_{14}H_{18}O_2^{+\cdot}$, $(M-CO)^+$ ion intensity varies with the molecular species. Provided that the structures inferred for the $(M-CO)^+$ ion and the m/e 159 ion are correct and that the influence of the difference in configuration in the C ring upon the fragmentation in the A ring is slight, the probability of a m/e 218 ion being produced is about the same in all four santonins. Consequently, the intensity difference of m/e 218 ion is considered to be due to a difference in stability of the ion, i.e. the extent of further breakdown of m/e 218 ions into secondary fragments depends on their stability. For instance, metastable peaks observed at m/e 115, 140·5, 122, 77·5, 75·3 and 67·5 suggest that the primary m/e 218 ion ruptures further into m/e 159, 175, 163, 130, 128 and 121 ions, respectively, the intensity of which is more abundant in α- and β-santonins than C- and D-santonins. These results suggest a lower stability of ions in the *trans* fused lactone systems than those of the *cis* structure. In any event, in the two pairs of stereoisomeric santonins (α, β and C, D) studied, the overall fragmentation patterns are sufficiently distinct so that their mass spectra can be used as secure criteria for purposes of differentiation.

EXPERIMENTAL

An analytical mass spectrometer, CEC 21 103C, and high resolution mass spectrograph of the type Mattauch-Herzog, JMS-01S and mass spectrometer, HITACHI U6-B were used. The former was used under a resolution of 1 part in 20,000. The U6-B, attached with an adapter for high resolution, which is essentially an electrostatic field, gives a resolution of 1 part in 12,000. Samples and the gas handling manifold, including reservoir, of mass spectrometers were heated to 120 130 C. The manifold was made of stainless steel in the case of CEC 21-103C, and was made of glass in the case of HITACHI U6-B. In the case of JMS-01, the samples were directly introduced into the ionization chamber with a glass capillary. The electron acceleration voltage was 70 eV in the case of the mass spectrometers and 30 eV in the case of the mass spectrograph. α-, β-, C-, and D-santonins were measured with low electron acceleration voltages down to about 9 eV, too. A Shimazu SR-2 comparator was used to measure the separation of mass spectral lines recorded with the JMS-01 mass spectrograph. The mass of ions was determined using PKF as an internal standard, and was calculated with a Nihondenki NEAC 2101 electronic computer.

Materials. Natural products were used for l-α-santonin, l-β-santonin, and artemisin. They were purified through recrystallization from EtOH. 6-epi-santonin (santonin C) and 6-epi-11α(H)-santonin (santonin D) were obtained by epimerization reaction of the corresponding natural santonins according to Ishikawa[19, 20]. Desmotroposantonin[21], hyposantonin[22], and tetrahydrosantonins[23] were prepared by well known methods. Photochemical preparation of lumisantonins from santonins was previously reported by one of the present authors (E.Y.)[20] and others[24].

rac-11d_1-*α-Santonin.* Deuterium exchange of *rac*-11-carboxy-santonin 11-epimers[25] was carried out by their repeated precipitation from a solution of 1:1 mixture of heavy water (99·75% d) and THF. The product was then decarboxylated at 190 200 C under 1 mm Hg. The yellow resinous distillate easily crystallized on trituration with ether and was recrystallized from benzene isopropyl ether to give colourless plates, m.p. 181 C, which by mass spectral analysis contained 49% d.

Dl-13d_3-*α-Santonin.* This compound was prepared according to a route reported[25] for the total synthesis of α-santonin. The yield of each step was comparable with that of the original report. The

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starting diethyl d$_3$-methyl malonate was obtained by deuteromethylation of diethyl malonate with d$_3$ methyl iodide[26] according to Fieser[27]

rac-13d$_3$-α-*Santonin* was recrystallized from MeOH isopropyl ether to give colourless plates, m.p 181·5°C Mass spectral analysis indicated the presence of 73% d$_3$, 2·9% d$_2$, and 1·8% d$_1$ species. The IR spectrum showed the bands at 2245 (C–D), 1775 (γ-lactone), 1650 (conjugated ketone), 1625 and 1610 cm^{-1} (conjugated double bonds)

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