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MASS SPECTRAL FRAGMENTATION STUDIES OF TRITERPENES RELATED TO SERRATENEDIOL[1,2]

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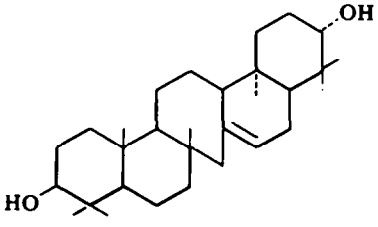
Abstract—A detailed investigation of the mass spectral fragmentation patterns of triterpenes of the serratenediol family has been carried out. This study reveals that the application of mass spectrometry to the structural elucidation of these compounds can be invaluable. Characteristic fragmentations, particularly in the 7-membered C ring, allow definite allocations to structure and functionality in this series.



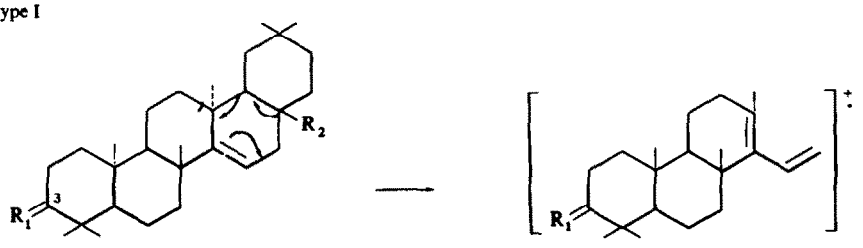
I

RECENT structural studies on the neutral triterpenes of the bark of Sitka spruce[4,5] [*Picea sitchensis* (Bong.) Carr] have led to the accumulation of a considerable volume of data concerning their modes of cleavage in the mass spectrometer. These compounds are derivatives of the pentacyclic triterpene, serratenediol (I), in which ring C is 7-membered and the double bond is in the Δ^{14} position. Recent investigations have indicated that these compounds are of rather widespread occurrence in nature and, in addition to Sitka spruce, derivatives of serratenediol have now been isolated from club mosses,[6,7] ferns,[8] and the bark of pine[9] species. Often these compounds are present in complex mixtures which are difficult to separate. Their subsequent isolation in minute quantities necessitated the application of physical methods to aid in structure elucidation. The purpose of the present paper is to indicate how mass spectrometry can assist structural determinations in this series and also to show how the presence of the 7-membered carbocyclic ring C affects the fragmentation process in this system.

The application of mass spectrometric methods to the study of pentacyclic triterpenes of various structural types was discussed in an important and fundamental paper by Djerassi *et al.*[10] The mode of cleavage of the Δ^{14}-taraxerenes is relevant to our discussion and it is briefly mentioned using as examples the compounds taraxerone (II), taraxerol (III) and myricadiol diacetate (IV).

An important cleavage process (Type I) in this series is the retro Diels–Alder collapse of ring D as shown below yielding the diene fragment, A. Subsequent elimination of the C-3 substituent gives rise to the ion B (*m/e* 284) and further loss of a Me group yields ion C (*m/e* 269). The location of ion A at *m/e* 300 for taraxerone, *m/e* 302 for taraxerol and *m/e* 344 for myricadiol diacetate illustrates the expected dependency on functionality at C-3 in providing the appropriate *m/e* value.

Type I



II; $R_1 = O$; $R_2 = Me$

III: $R_1 = \alpha$-OH, β-H; $R_2 = Me$

IV: $R_1 = \alpha$-OAc, β-H; $R_2 = CH_2OAc$

V: $R_1 = H_2$; $R_2 = Me$

VI: $R_1 = \alpha$-OMe, β-H; $R_2 = Me$

A

$-R_1H$

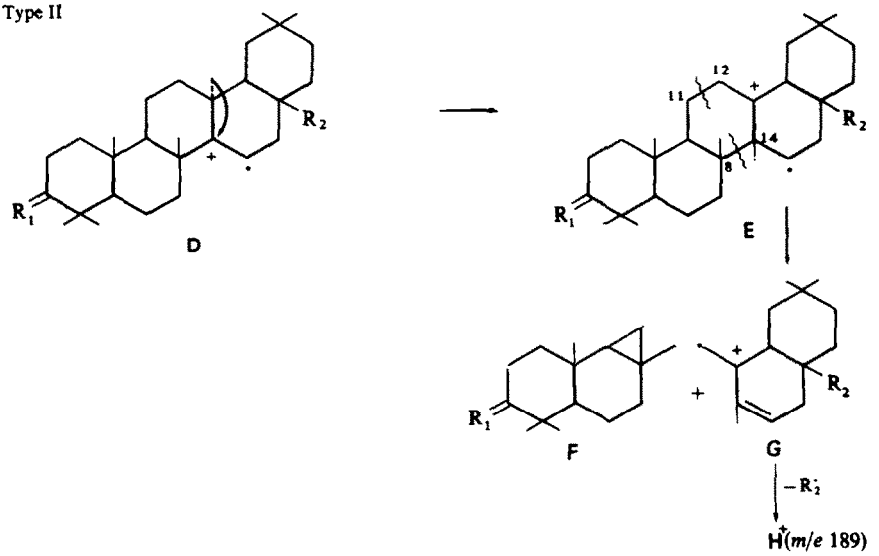
$B^{+\cdot}$ *m/e* 284

$-CH_3\cdot$

C^+ *m/e* 269

A second important cleavage in this family occurs in ring C involving rupture of the 8,14 and 11,12 bonds. Although these authors found it more difficult to explain this process, they postulated a mechanism (Type II) for this fragmentation in which the molecular ion, D, generates a new carbonium ion species, E, which in turn leads to

Type II



D

E

F

G

$-R_2\cdot$

H^+ (*m/e* 189)

the ions G and H by appropriate cleavages as shown. Species G (*m/e* 204) is the most abundant in the spectra of taraxerol and taraxerone and gives rise to an abundant satellite ion, H (*m/e* 189), by elimination of the substituent, R_2, at the C-17 position.

It is now appropriate to compare the similarities and/or differences which prevail in the taraxerene and serratene series in order to illustrate the features which characterize the latter compounds. For this purpose, the mass spectra of both families were determined under as similar conditions as possible, since it was felt that only under these circumstances could reasonably accurate comparisons be made.

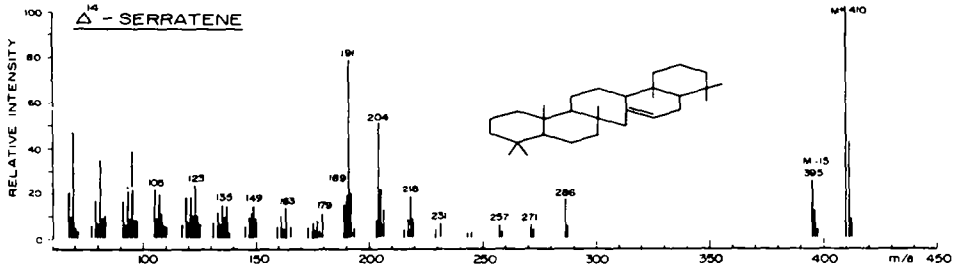


FIG. 1. Mass Spectrum of Δ^{14}-Serratene

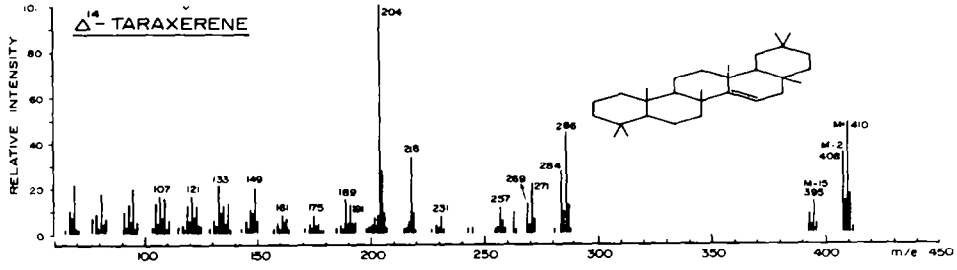
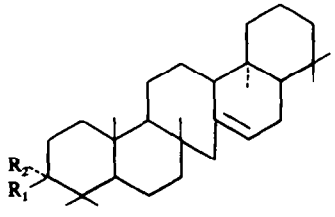


FIG. 2. Mass Spectrum of Δ^{14}-Taraxerene

We turn initially to the mass spectra of Δ^{14}-taraxerene (V) and Δ^{14}-serratene (VII) as illustrated in Figs. 1 and 2.

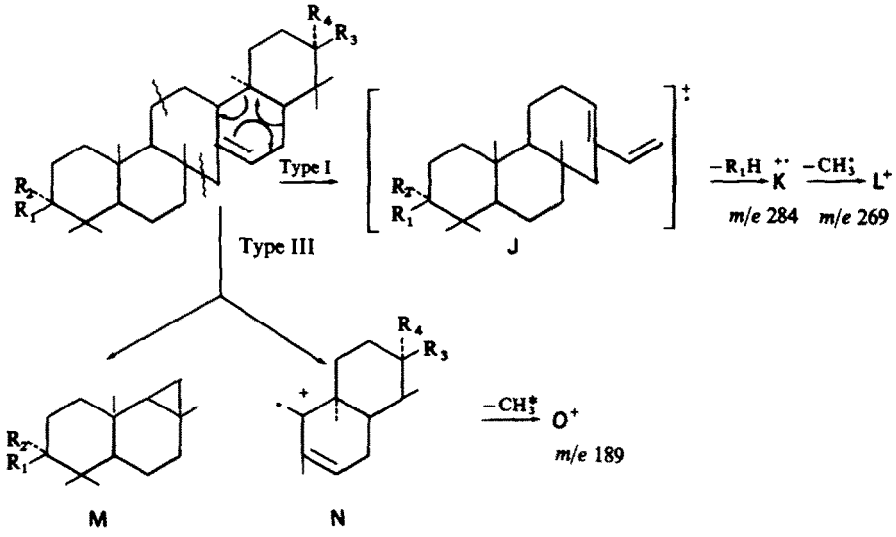


VII: $R_1 = R_2 = H$
VIII: $R_1 = OMe$; $R_2 = H$

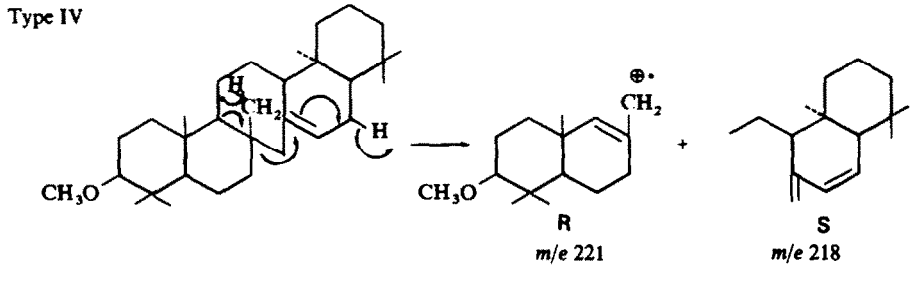
It is clear that, in the Δ^{14}-taraxerene system, the retro Diels–Alder fragmentation (Type I) is an important cleavage process (ion A, *m/e* 286, 44·5%; A-Me, *m/e* 271,

21·6%). In Δ14-serratene, however, this pathway appears very much less dominant (ion J, *m/e* 286, 16·9%; J-Me, *m/e* 271, 5·7%), probably because the 7-membered ring C is a weak point in the molecule and undergoes preferential fragmentation.

The base peak in the spectrum of Δ^{14}-taraxerene occurs at *m/e* 204 (ion G) and establishes that type II fragmentation is highly significant. The satellite ion H (*m/e* 189) arising from ion G by the loss of a Me group is much less abundant (14·8%). This type of fragmentation (Type III) is also important in the Δ^{14}-serratene system (ion N, *m/e* 204, 49·8%; ion O, *m/e* 189, 14·7%).



The two ring systems are clearly distinguishable by the abundance of another ion, R (*m/e* 191, 76·8%), in the serratene case, which is obviously arising from another fragmentation pathway of importance in this series (Type IV). The corresponding ion in the taraxerene analogue is much less abundant (*m/e* 191, 12·1%) and possible reasons for this difference are presented later.



The contrast in emphasis on these three cleavage pathways is further illustrated by comparison of the spectra of 3β-methoxy-Δ^{14}-taraxerene (VI, sawamilletin), and 3β-methoxy-Δ^{14}-serratene (VIII), which are shown in Figs. 3 and 4. The low resolution mass spectrum of sawamilletin has recently been published[11] as part of a

study on the triterpene methyl ethers occurring in Gramineae plants. Here once again, we note the importance of the retro Diels–Alder cleavage (Type I) mode in the Δ^{14}-taraxerene system (ion A, *m/e* 316, 50·6%) versus its low utilization in the case of the Δ^{14}-serratene compound (ion J, *m/e* 316, 5·5%).

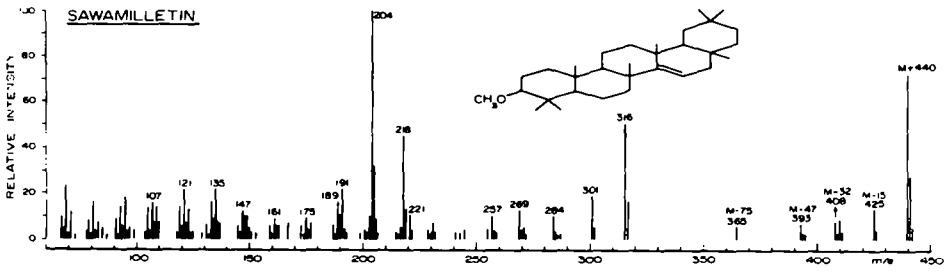


FIG. 3. Mass Spectrum of Sawamilletin 3 (β-Methoxy-Δ^{14}-Taraxerene)

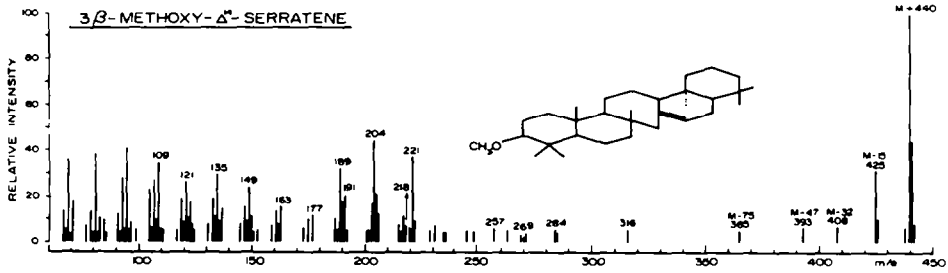


FIG. 4. Mass Spectrum of 3β-Methoxy-Δ^{14}-Serratene

In contrast, the second fragmentation mechanism (Type II) again leads to the formation of the most abundant fragment in the spectrum of sawamilletin (ion G, *m/e* 204), and this then gives rise to ion H (*m/e* 189, 16·6%) as confirmed by the presence of a metastable ion at *m/e* 175·5. In the case of the Δ^{14}-serratene analogue, rupture of ring C via a similar pathway (Type III) gives the fragment ion, N (*m/e* 204, 44·0%), and its satellite ion, O (*m/e* 189, 32·5%). This type of process is, therefore, an important one in *both* ring systems.

Further, the type IV cleavage process is once again emphasized in the fragmentation of 3β-methoxy-Δ^{14}-serratene (ion R, *m/e* 221, 37·5%) versus its abundance in the spectrum of sawamilletin (*m/e* 221, 10·4%).

The elemental compositions of the more important ions in the mass spectra of these two C-3 methyl ether derivatives have been determined by high resolution mass spectrometry and the results are given in Table 1. The compositions of these ions are in agreement with the fragmentation processes so far discussed.

It is now opportune to discuss the origin of the third fragmentation mode (Type IV) in the spectra of the Δ^{14}-serratenes which is also an important one in the saturated

TABLE 1. COMPOSITION AND ABUNDANCE OF MAJOR FRAGMENTS IN THE SPECTRA OF SAWAMILLETIN AND 3β-METHOXY-Δ^{14}-SERRATENE

Sawamilletin				3β-Methoxy-Δ^{14}-serratene			
Ion	*m/e*	Elemental composition	Relative intensity	Ion	*m/e*	Elemental composition	Relative intensity
M^+	440	$C_{31}H_{52}O$	72·4	M^+	440	$C_{31}H_{52}O$	100
M-15	425		13·5	M-15	425	$C_{30}H_{49}O$	32·0
M-32	408		7·7	M-32	408		6·5
M-47	393		6·8	M-47	393		6·5
A	316	$C_{22}H_{36}O$	50·6	J	316	$C_{22}H_{36}O$	5·5
A-15	301	$C_{21}H_{33}O$	19·5	K	284	$C_{21}H_{32}$	5·5
B	284	$C_{21}H_{32}$	9·9	L	269	$C_{20}H_{29}$	3·0
C	269	$C_{20}H_{29}$	12·8	R	221	$C_{15}H_{25}O$	37·5
	221	$C_{15}H_{25}O$	10·4	N	204	$C_{15}H_{24}$	44·0
G	204	$C_{15}H_{24}$	100	O	189	$C_{14}H_{21}$	32·5
H	189	$C_{14}H_{21}$	16·6		191		20·5
	191		21·6		149		24·0
	147		11·9		135		30·0
	135		21·6				

and the Δ^{13} series. One possible explanation is that the fragment, M, comprising rings A and B and arising from Type III cleavage, is too unstable to exist, but rapidly loses a methyl group to yield the important fragments of type R. This explanation does not appear to be acceptable because in the Δ^{13} series, ion N, which would arise as a companion fragment in Type III cleavage and which in fact is a major ion in the Δ^{14} series, is non-existent. Moreover, as we shall presently see, ions of this type arise even in the saturated serratane system where there is no possibility of allylic activation. We, therefore, postulate a rearrangement process (Type IV) in ring C giving rise to ions R and S as shown. A similar proposal has been advanced by Djerassi[10] to explain some of the fragments in his study on pentacyclic triterpenes.

The variation of the masses of ions R and S with changes in functionality at positions C-3 and C-21 is indicated in Table 2. In all cases, fragment R is abundant and one of

TABLE 2. FRAGMENTS ARISING FROM TYPE IV REARRANGEMENT IN RING C

Ion R			Ion S		
C-3 Function	*m/e*	Abundance	C-21 Function	*m/e*	Abundance
H	191	high	H	218	low
OCH_3	221	high	OCH_3	248	low
OH	207	high	OH	234	low
=O	205	high	=O	232	low
OAc	249	low	OAc	276	absent

the major species in the spectrum. The other fragment, S, is less plentiful, but has always been found to be present except when the C-21 functional group is acetate. In the case of Δ^{14}-serratene itself, species S is a fairly abundant fragment (*m/e* 218, 18%).

It will be recalled that an ion was detected at *m/e* 218 (33·7%) in the fragmentation of taraxerene (Fig. 1). This type of cleavage probably also arises by a Type IV rearrangement in the six-membered ring C in this system. The fragments corresponding to ions of type R and S (designated R′ and S′) which are present in the spectra of the five taraxerene derivatives studied by us are summarised in Table 3. Unfortunately, none of these compounds contains a substituent in ring E. It is seen that the situation in the taraxerene case (except in taraxerone) is the reverse of that in the serratene series. Thus, the relative abundance of fragments bearing rings D and E is high in the former, whereas in the latter, the predominant species contains rings A and B.

TABLE 3. POSSIBLE TYPE IV REARRANGEMENT FRAGMENTS IN THE SPECTRA OF TARAXERENES

	R′		S′	
Compound	*m/e*	Relative intensity	*m/e*	Relative intensity
Taraxerene	191	12·1	218	33·7
Taraxerol	207	5·3	218	20·3
Taraxerone	205	43·5*	218	13·8
Taraxeryl acetate	249	1·3	218	20·4
Sawamilletin	221	10·4	218	45·2

* Adjacent to major fragment at *m/e* 204 (84%).

It is now clear that the assignment of an unknown pentacyclic triterpene to the Δ^{14}-serratene or Δ^{14}-taraxerene series is greatly assisted by a consideration of the mass spectral fragmentation patterns. As the discussion has indicated, the controlling influence in the fragmentation is the Δ^{14} double bond in the taraxerene system; in the serratene case, it is the fission of the 7-membered ring.

It is now of interest to direct attention to the use of mass spectrometry in the location of functional groups on the Δ^{14}-serratene skeleton. A summary is given in Tables 4 and 5 of the important fragments in the mass spectra of 17 compounds which we have studied in this series. The fragments marked with an asterisk have been measured under high resolution and their elemental compositions determined. In all cases, these were in agreement with the retro Diels–Alder (Type I) and Types III and IV fragmentation mechanisms as presented in this publication. The results for the compounds bearing ketone functions, however, require further comment and will be discussed separately. The value of Table 4 in determining whether a substituent is present in ring A or ring E is readily apparent, and so far, all the naturally occurring Δ^{14}-serratenes identified have possessed functional groups attached only to these two rings.* Thus, for example, in the case of an unknown alcohol, one might prepare the acetate derivative. A shift of 42 units to higher mass in ion J would indicate the presence of the grouping in rings A or B. Conversely, if ion N was shifted by a corresponding amount, then the functional group would, of course, be present in rings D or E. Consultation of Table 4 also underlines the fact that ion R must comprise rings A and B. Thus, the mass of this fragment changes from *m/e* 191 in the unsaturated

* The compound, tohogenol, isolated by Inubushi[12] from the club moss, *Lycopodium serratum* has an OH substituent at C-14, but does not contain a Δ^{14} double bond.

hydrocarbon to *m/e* 221 in the C-3 OMe derivatives, to *m/e* 207 where there are C-3 OH functions, and to *m/e* 205 and 249 in the corresponding ketones and acetates.

In the case of the compounds with ketonic functions, the retro Diels–Alder cleavage process was observed to be absent or very insignificant. Moreover, when the weak fragment ions attributed to type L (*m/e* 269) were examined under high resolution, doublets were observed corresponding to the elemental compositions, $C_{19}H_{25}O$ and $C_{20}H_{29}$. In the spectrum of 3β-methoxy-21-keto-Δ^{14}-serratene, the ratio was

TABLE 4. RELATIVE ABUNDANCE OF MAJOR FRAGMENTS IN THE SPECTRA OF Δ^{14}-SERRATENES

Functionality	J		N		R	
	m/e	%†	*m/e*	%	*m/e*	%
3-H_2; 21-H_2	286	16·9	204	49·8	191	76·8
3β-OMe; 21-H_2	316*	5·5	204*	44·0	221*	37·5
3α-OMe; 21-H_2	316*	7·6	204*	48·2	221*	75·0
3β-OH; 21β-OH	302	16·2	220	30·2	207	53·3
3β-OH; 21α-OH	302	6·6	220	54·2	207	100
3α-OH; 21β-OH	302	7·3	220	25·4	207	38·4
3-keto; 21-keto	300	3·6	218	45·0	205	42·5
3β-OMe; 21β-OH	316*	5·8	220*	31·5	221*	52·4
3α-OMe; 21β-OH	316*	13·0	220*	31·5	221*	63·5
3α-OMe; 21α-OH	316	3·8	220	50·4	221	100
3β-OMe; 21:keto			218*	51·5	221*	66·0
3α-OMe; 21-keto			218*	43·5	221*	100
3β-OMe; 21β-OAc	316	4·8	262	12·0	221	44·2
3α-OMe; 21β-OAc	316	6·1	262	11·0	221	39·6
3β-OMe; 21β-OMe	316	7·7	234	10·2	221	20·9
3α-OMe; 21β-OMe	316	16·0	234	17·8	221	43·9
3β-OAc; 21β-OAc	344	9·4	262	14·2	249	10·6

* Elemental composition determined by high resolution measurements.

† Relative intensity of the fragments with base peak arbitrarily taken as 100.

found to be 3:1 in favour of the oxygen-bearing ion, and with the 3α-analogue, the ratio was 2:1. Clearly, the oxygenated fragments were due to another type of cleavage which was only observed in the case of the ketones. This raises the possibility that the fragments observed at *m/e* 284 in these compounds may also arise by a different mechanism, although the elemental compositions agreed with the expected values for ions of type K.

The acid-catalysed isomerization of the double bond from the Δ^{14} into the Δ^{13} position of the serratene system has been discussed by Inubushi,[6] and recently, we have isolated the first naturally occurring example of a Δ^{13}-serratene from the bark of Sitka spruce[5] [*Picea sitchensis* (Bong.) Carr]. It is, therefore, of interest to describe the characteristic fragmentations occurring in this system, and these are illustrated by the fragmentation patterns of the 3α-methoxy-21β-hydroxy (IX) and 3α-methoxy-21-keto (X) derivatives as presented in Figs. 5 and 6.

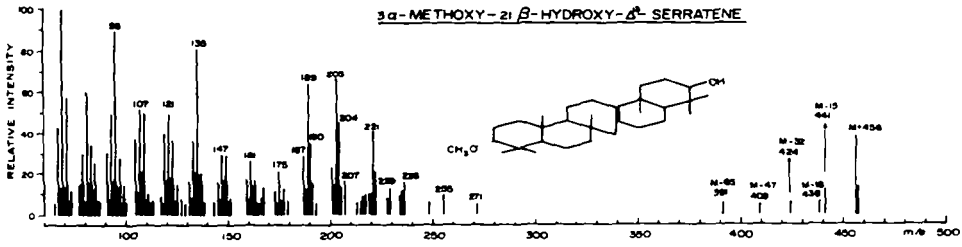


FIG. 5. Mass Spectrum of 3α-Methoxy-21β-Hydroxy-Δ^{13}-Serratene

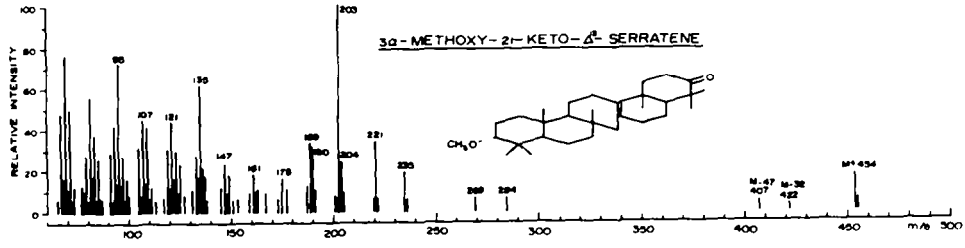
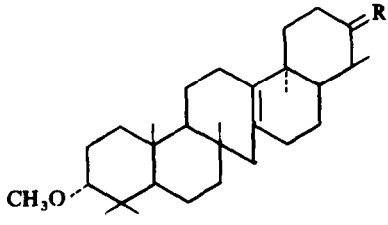


FIG. 6. Mass Spectrum of 3α-Methoxy-21-Keto-Δ^{13}-Serratene

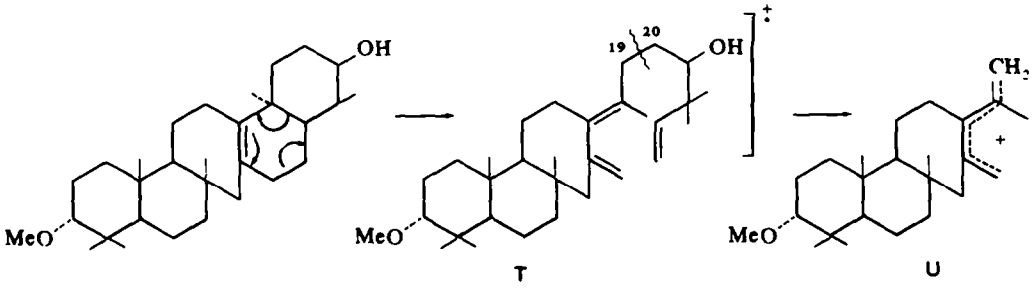


IX: R = 

X: R = O

The first point of interest concerns the complete disappearance of the retro Diels–Alder cleavage mode in this system. One notes the presence of low abundance fragments at *m/e* 284 and *m/e* 269 in the ketone where one should observe the satellite ions of type K and L. Once more, however, high resolution mass spectrometry has indicated that these cannot be retro Diels–Alder fragments as the elemental composition of the *m/e* 284 ion is $C_{20}H_{28}O$ (not $C_{21}H_{32}$) and that of the *m/e* 269 fragment is $C_{19}H_{25}O$ (not $C_{20}H_{29}$). This result is not surprising, since the location of the double bond at the Δ^{13} position eliminates retro Diels–Alder fragmentation of the type discussed in the Δ^{14} series. Thus, attempts to formulate the process in ring D would now give rise to species T which would have to undergo further cleavage before fragments of lower mass than the parent ion could arise. Although such a cleavage might reasonably be expected to occur at the C_{19}—C_{20} bond to generate a species,

U, there is, however, no evidence for this process in the spectrum of either compound IX or X.



It may be noted in passing that the fragment occurring at *m/e* 269 in the case of compound X has the same elemental composition ($C_{19}H_{25}O$) as the fragments of similar mass found in the spectra of the two 21-keto-Δ^{14}-serratene derivatives to which reference has already been made. Moreover, in the case of the alcohol, IX, this fragment ion is also present, being removed now two units to higher mass (*m/e* 271). High resolution measurements on this latter fragment, on the other hand, reveal that the ion at *m/e* 271 is again a doublet composed of the species, $C_{19}H_{27}O$ and $C_{20}H_{31}$.

The second feature of the spectra of the Δ^{13} compounds is the absence of the Type III cleavage process which is so important in the Δ^{14}-serratene system. Thus, fragments of type N ought to be observed at *m/e* 220 in IX and at *m/e* 218 in X corresponding to cleavage of the two allylically activated 11, 12 and 8, 27 bonds in ring C. There is no fragment of this mass arising from the ketone, X, but a low abundance species (10·2%) is present at *m/e* 220 in the case of the alcohol, IX.

As may be seen from Figs. 5 and 6, the major fragment ions in the spectra of both Δ^{13} compounds are located at *m/e* 221, 203, 189 and 135. Quite clearly, the species at *m/e* 221 and 189 are synonymous with those arising from the Type IV fragmentation process which is so characteristic of the spectra of the Δ^{14}-serratenes. The very abundant fragments at *m/e* 203 are clearly typical of compounds in the Δ^{13} series. High resolution mass measurements of this fragment occurring in both spectra indicate the elemental composition, $C_{15}H_{23}$, which clearly reveals that this species has lost *both* of the oxygen functions. Ions of similar mass are prominent in the mass spectra of the Δ^{12}-oleanenes and Δ^{12}-ursenes. These have been studied by Djerassi and his group[13] who concluded, as a result of deuteration studies, that these fragments are formed from the retro Diels–Alder cleavage product by further loss of either of the Me groups attached to C-20 or that attached at C-17. All three Me groups were lost to about the same degree. Without having deuterium labelled derivatives of our compounds, we are unable to suggest how the prominent fragment ions at *m/e* 203 arise in the case of the Δ^{13}-serratenes.

The investigation of the relationships of the fragments at *m/e* 189, 203 and 221 is assisted by the presence of three metastable peaks measured at *m/e* 186·5, 175·4 and 161·6. The latter confirms that the fragment at *m/e* 221 loses methanol to yield the species at *m/e* 189, whereas that at 175·4 indicates that the species at *m/e* 203 can also give rise to an ion at *m/e* 189 via loss of 14 mass units. The metastable ion at

TABLE 5. RELATIVE ABUNDANCE OF MOLECULAR ION SATELLITES IN THE SPECTRA OF Δ^{14}-SERRATENE DERIVATIVES

Functionality	M		M-15		M-18		M-32		M-33		M-47		M-60		M-75	
	m/e	%†	*m/e*	%	*m/e*	%	*m/e*	%	*m/e*	%	*m/e*	%	*m/e*	%	*m/e*	%
3-H_2; 21-H_2	410	100	395	24·9												
3β-OMe; 21-H_2	440*	100	425*	32·0			408	6·5			395	6·5				
3α-OMe; 21-H_2	440*	100	425	8·0			408	1·7			395	5·0				
3β-OH; 21β-OH	442	100	427	19·1	424	20·0			409	16·2						
3β-OH; 21α-OH	442	9·5	427	4·1	424	1·8			409	2·5						
3α-OH; 21β-OH	442	19·3	427	4·7	424	25·4			409	9·1						
3-keto; 21-keto	438	100	423	20·1												
3β-OMe; 21β-OH	456*	11·4	441	5·1	438	13·6	424	4·3	423	10·7						
3α-OMe; 21β-OH	456*	24·9	441	1·5	438	31·9	424	7·8	423	5·0						
3α-OMe; 21α-OH	456	25·2	441	3·3	438	8·3	424	4·1			409	3·1				
3β-OMe; 21-keto	454*	60·5	439	2·5			422	5·1			407	4·0				
3α-OMe; 21-keto	454*	45·0	439	1·0			422	8·2			407	3·5				
3β-OMe; 21β-OAc	498	91·0	483	5·2									438	94·0	423	21·6
3α-OMe; 21β-OAc	498	100	483	3·3			466	4·8			451	2·3	438	19·0	423	4·6
3β-OMe; 21β-OMe	470	71·7	455	11·2			438	18·3			423	6·1				
3α-OMe; 21β-OMe	470	100	455	11·3			438	17·5			423	7·1				
3β-OAc; 21β-OAc	526	45·9	511	4·7									466	52·7	451	24·6

* Elemental composition determined by high resolution measurements.

† Relative intensity of the fragments with base peak arbitrarily taken as 100.

186·5, which was found only in the spectrum of the alcohol, is puzzling as it would appear to suggest that the fragment at *m/e* 221 loses eighteen mass units to give the important species at *m/e* 203. As the fragment ion at *m/e* 221 is present in both the ketone and the alcohol, it is not thought to contain the OH function. Moreover, no corresponding metastable ion is observed in the spectrum of the ketone, although in this case, the *m/e* 203 fragment is the base peak.

In order to evaluate the importance of the Δ^{14} double bond in determining the fragmentation patterns in the serratene family, we turned finally to a study of the saturated serratane system. We illustrate this process with the spectra of β-serratan-3-one (XI) and β-serratan-3α-ol (XII) (Figs 7 and 8).

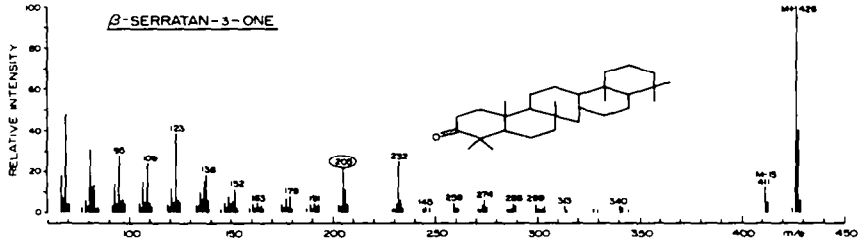


FIG. 7. Mass Spectrum of β-Serratan-3-one

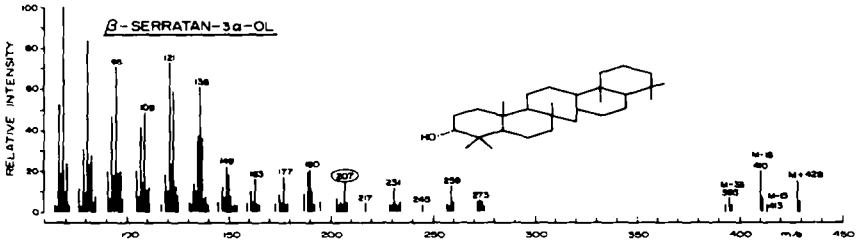
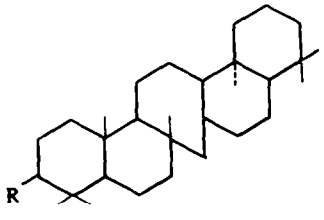
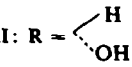


FIG. 8. Mass Spectrum of β-Serratan-3α-ol

The characteristic feature of the spectra in the saturated series is the low abundance of almost all fragments of mass greater than 150, with the exception of the molecular ion and its expected satellites. In Figs 7 and 8, one notes the expected absence of ions of types J, K and L associated with the retro Diels–Alder process and of type N



XI: R = O

XII: R = 

associated with the Type III fragmentation pathway. In Fig. 7, the only two major fragments of interest are those at *m/e* 205 (21·7%) and 232 (25%). The former could be plausibly derived from Type IV rearrangement, although there is no sign of the corresponding ion of type S arising from this process. The ion at *m/e* 232 is not explained by any process which we have discussed.

In the spectrum of β-serratan-3α-ol, we note the presence of fragments at *m/e* 207 (14%) and 189 (18·8%). Other fragments which are not explained are those at *m/e* 231 and *m/e* 259. In Table 6 is a summary of ions of type R arising from cleavage of serratane derivatives.

TABLE 6. TYPE IV REARRANGEMENT IONS FROM SERRATANE DERIVATIVES

Compound	Ion R	
	m/e	Relative intensity
α-Serratane	191	26·8
β-Serratane	191	42·0
β-Serratan-3-one	205	21·7
β-Serratan-3α-ol	207	14·0
3α-Methoxy-serratane*	221	17·1
3α-Methoxy-21-keto-serratane*	221	7·4
3α-Methoxy-21β-hydroxy-serratane*	221	12·0
3β-Methoxy-21β-hydroxy-serratane*	221	13·5

* Mixed α- and β-forms at C-14.

In summary, the presence of the 7-membered ring C in the serratene system exerts a predominating influence in the fragmentation processes of these molecules. The characteristic fragments which are observed in the mass spectra of this interesting family of pentacyclic triterpenes allow rapid assignment of structure and functionality. Thus, this technique is invaluable in the structure elucidation of these substances when only minute amounts are available.

EXPERIMENTAL

The mass spectra were measured on an Atlas CH4 or an AEI MS9 mass spectrometer. Samples were admitted into the ionization chamber using the direct insertion technique, the ionizing energy being maintained at 70 ev.

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