MASS SPECTROMETRIC STUDIES

ON ORGANIC COMPOUNDS.

A thesis presented for the degree of

DOCTOR OF PHILOSOPHY

to

The University of Glasgow

by

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C O N T E N T S.

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CHAPTER I.

INTRODUCTION.

Goldstein, in 1886, was the first to observe positively charged electrical entities[1] and Wien later showed that these rays were deflected by a magnetic field.[2] The first mass spectrograph was developed by Thomson who, in 1910,[3] passed a collimated beam of ions through a combined electrostatic and magnetic field. The ions emerging from this field were detected on a photographic plate in a series of parabolic curves according to their mass to charge ratio. In this way he demonstrated the existence of stable isotopes.

The work of Thomson on isotopes was extended by Aston[4] who, in 1919, introduced an instrument with consecutive electrostatic and magnetic fields. The lines of focus of ions of different mass to charge ratio fell on a plane, so that a photographic plate could be used for detection of the mass spectrum. Mass spectrographs, as such instruments were known, were best suited to the accurate measurement of mass, a disadvantage being the lack of accuracy of relative ion abundance measurements.

The first mass spectrometer, constructed by Dempster, appeared about the same time.[5] The mass dispersion was achieved by deflection through 180° in a homogeneous magnetic field. In this case it was important to use an ion source which provided an essentially monoenergetic ion beam. Mass spectrographs and mass spectrometers are differentiated according to the method of detection of the ion beam. Thus Dempster's mass spectrometer used electrical detection, making the instrument capable of accurate ion abundance measurements.

Both Aston's mass spectrograph and Dempster's mass spectrometer had only single-focusing properties. The former had velocity focusing and the latter direction focusing. Velocity focusing is the focusing of a beam of ions, homogeneous in mass, moving in the same initial direction, but at different speeds, and direction focusing is the focusing of a beam of ions, homogeneous in mass, moving at the same speed, but in different initial directions. Instruments which incorporate both of these properties are known as double-focusing instruments.

Herzog[6] developed the theory of double-focusing instruments and the Mattauch-Herzog design[7] is widely used today. It uses consecutive electrostatic and magnetic fields which deflect the ion beam in opposite directions, detection usually being by a

photographic plate. Electrical detection can also be employed. The other commonly used double-focusing instrument follows the design of Johnson and Nier,[8] the electrostatic and magnetic fields deflecting the ion beam in the same direction and using electrical detection. At the expense of sensitivity, these instruments can give very high mass resolution by the use of narrow slits.

The most common ion source used today for organic compound analysis is the Nier electron bombardment source.[9] This gives a degree of velocity focusing within the ion gun and is therefore suitable for use with instruments which have only direction focusing properties. Other methods of ion production which are finding increasing application are photon impact,[10] field ionization,[11] high voltage spark[12] and chemical ionization.[13]

Similarly, other instruments have been developed which use different principles of mass analysis. One of the most common is the time-of-flight mass spectrometer[14] which dispenses with the need for a bulky and expensive magnet. Pulses of ions are accelerated down a field-free tube, mass separation being due to differences in flight time of ions of different mass. Radio-frequency techniques have been

used to achieve mass separation in instruments of the Bennett[15] and Redhead[16] type. The quadrupole[17] mass spectrometer is of different design, but still employs radio-frequency fields. The omegatron[18] and the mass synchrometer[19] use radio-frequency techniques in conjunction with magnetic fields.

Although their potential usefulness in chemical analysis was recognised by Thomson, mass spectrometers were so unreliable that they were not much used until the electronic advances which accompanied World War II were incorporated. The first industry to make use of them was the petroleum industry, where the need for analysis of hydrocarbon mixtures was great. The method of analysis developed[20,21] depended on

(i) the reproducibility of the mass spectrum of a given compound under fixed operating conditions;

(ii) the mass spectrum of a mixture being a linear superposition of the mass spectra of the components of the mixture; and

(iii) the direct proportionality of the sensitivity for the reference peak of a component to the partial pressure of that component in the mixture.

Initially, since the sample had to be examined in gaseous form, only gases were studied. The introduction of heated inlet systems[22,23] allowed the sample to be heated before passing through a leak to the ionization chamber and thus extended the range of compounds which could be examined.

However, many compounds were too involatile or thermally unstable to obtain meaningful spectra in this way. This was overcome to a large extent by the development of methods[24] for the direct introduction of samples into the ionization chamber. Vacuum lock techniques are now used to allow samples to be changed without breaking the vacuum in the mass spectrometer. A further advantage of this method is the very small amount of sample ($\sim 10^{-9}$ g.) which is required for a mass spectrum.

More sophisticated methods of mixture analysis have now been developed[25] and the combination of gas-liquid chromatography-mass spectrometry[26] has had great success in the analysis of small samples of multi-component mixtures. This latter method has been made possible by the introduction of fast-scanning mass spectrometers. Also, the concentration of sample reaching the source of the mass spectrometer has

been improved by the use of the molecular separators of Ryhage[27] and Biemann[28] for the removal of carrier gas.

A vast number of compounds have now been examined by mass spectrometry and there have been two main approaches towards a theory which will encompass all of this data. The first is the quasi-equilibrium theory initially developed by Rosenstock, Wallenstein, Wahrhaftig and Eyring in 1952.[29] It assumes that ionization has taken place by a Franck-Condon transition and that the time of residence of the ion in the source is sufficient to permit any excess electronic energy to be randomly distributed over the molecular ions. The energies normally employed in an electron bombardment source are such that the ions formed are distributed over a very large number of electronically excited states. The mass spectrum is assumed to result from a series of competing unimolecular dissociations for which the reaction rates can be calculated from a suitable form of the absolute rate theory. Good agreement has been found between the calculated and observed mass spectra of some small molecules, but although the theory has been steadily tested and improved,[30] it has not yet advanced to the state where it can be used for complex organic molecules.

A more empirical and easily applied approach has been the one that uses the same basic principles as organic solution chemistry, i.e., resonance; inductive and steric effects; stabilities of carbonium ions, etc. The formation of abundant ions in the mass spectrum was suggested by McLafferty[31] to depend on the relative stabilities of

(a) the ion and the neutral fragment;

(b) the bonds of the decomposing ion; and

(c) the possibility of fragmentation through a transition state.

One of the assumptions of this approach was that of charge localization at favoured positions in the molecule. Djerassi[32] and his school used the charge localization concept to rationalize many mass spectral fragmentations and a recent paper considers the compatibility of this concept with the quasi-equilibrium theory.[34] In contrast, Biemann[35] proposed a set of empirical rules summarising known fragmentation, but without the inclusion of the charge localization principle. With Mandelbaum[36] he has shown that charge is not irreversibly localized at any particular site in the molecule.

The effectiveness of this type of approach was greatly enhanced when it was demonstrated by Beynon[37] that differences in

the nuclear packing fraction[38] of the elements make it possible to determine the elemental constitution of an ion. The only requirement is the high resolving power produced by the double-focusing instruments mentioned above.

Precise mass determination, using a mass spectrograph, can be accomplished by recording the high resolution spectrum of the sample and a calibration compound on a photographic plate. The distance on the plate between ions of the sample and ions of the calibration compound is related to the mass difference. Biemann[39] introduced a system whereby a computer was used for the calculation of the masses of all the ions in the spectrum. The data presentation was in the form of an "element map" - separate columns being used for different heteroatom content. Two other variations on the form of the mass spectral presentation are due to Burlingame[40] and McLafferty[41]. The processing of the data has been speeded up in systems which have become fully automated.[42,43].

Instruments using Nier-Johnson geometry were severely handicapped when performing mass measurements by the peak-matching technique.[44] This method was time consuming and only a few of the most important ions could be measured in this way. However, methods have now been devised[45,46] for element map

production from such instruments, even at the high scan speeds required when coupled to a gas liquid chromatograph. This can involve recording of the spectrum of the sample and reference compound on magnetic tape and subsequent computer analysis[45] or a more direct coupling between mass spectrometer and computer.[46] The time interval between the ions is related to their mass difference.

The flood of mass spectral data, partly brought about by these techniques, which has appeared in the last few years, has resulted in the formation of two international journals.[47] It has also been accompanied by a more critical approach to the subject, with greater efforts being made to establish ion structures and reaction mechanisms. A review[48] of the methods employed has recently appeared and some are mentioned below.

One of the longest established methods for the study of mass spectrometric reactions has been the use of isotopic labelling. Normally, hydrogen atoms have been replaced by deuterium atoms, but ^{13}C, ^{15}N and ^{18}O are among other labels used. The value of deuterium labelling experiments have been amply demonstrated by the work of Djerassi and his school.[49] Results must be interpreted with care, however, since scrambling of hydrogen atoms has been observed in both alkyl[50] and aryl[51] compounds

on electron impact.

A much used kinetic approach has been that of substituent effects.[52] McLafferty and Bursey[53] found that such effects in the mass spectra of benzoyl compounds could be related to the Hammett σ constants for the substituents. It has been demonstrated that this technique can be applied to many mass spectral problems, including the elucidation of the principal paths leading to the formation of a particular ion[54] and the identity or otherwise of ion structures.[55] However, some authors have questioned the validity of this approach as applied to mass spectrometry.[56,57]

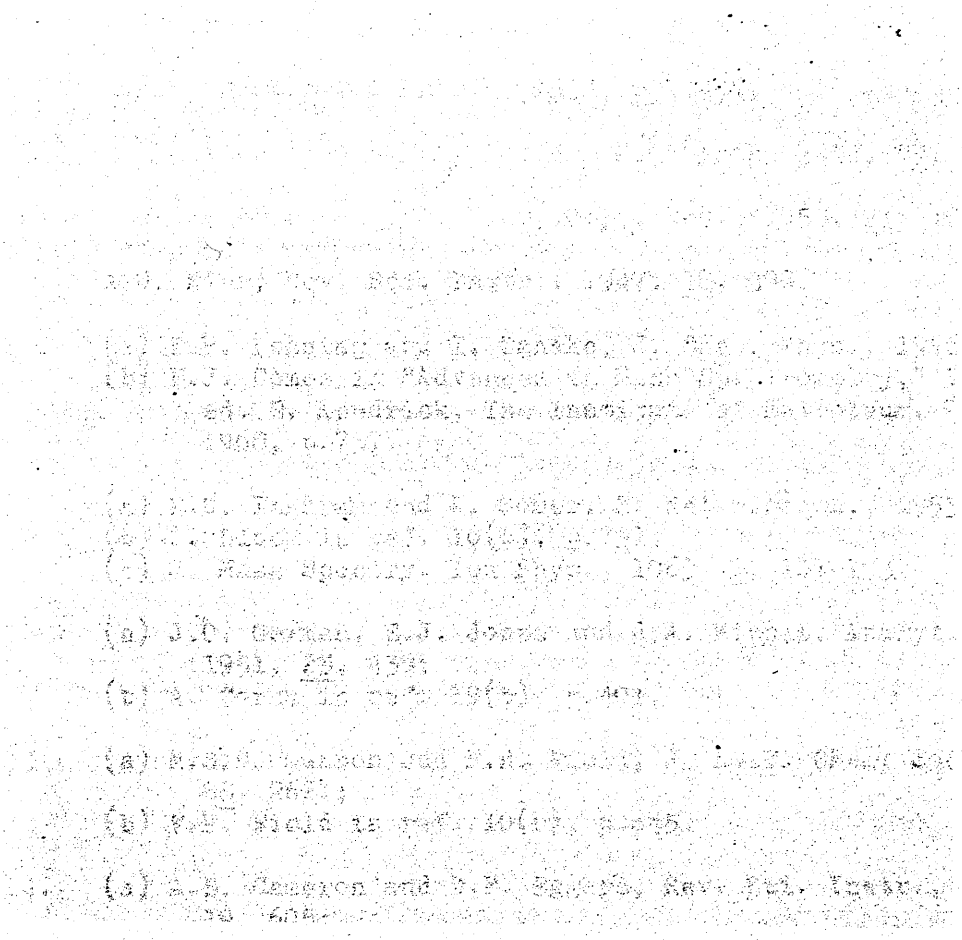
Metastable ions have always been a great source of information to the organic mass spectroscopist[58] and systems have now been devised[59,60] which allow the detection of pure metastable spectra without interference from normal ions. In double-focusing instruments only metastable ions decomposing after the electrostatic analyser could be observed, but ions decomposing in the field free region between the source and the electrostatic analyser can now be observed.[59] In this way many more metastable decompositions have been studied and McLafferty[61] has used "metastable ion characteristics" for the deduction of ionic structures.

The ultimate aim of mass spectroscopists must be the analysis of structure by computational methods. Low resolution spectra can be used for this by comparison of the spectrum of an unknown compound with the spectra in a data bank.[62] Much of the difficulty with this system is that best results are obtained only if compounds have been run on the same instrument under the same conditions.

Interpretation of high resolution data by computer is hampered by the great number of skeletal rearrangement reactions which occur in the mass spectrometer.[63] To this end it is still valuable to study organic fragmentation patterns and to correlate structure with particular rearrangements. The major success in computer-aided interpretation of spectra has been in the field of peptides.[64] This has been facilitated by the well defined nature of their breakdown on electron impact.

Approaches have been made towards the interpretation of the spectra of unknown compounds by computer.[65] Also, the vast amount of data obtained when the mass spectrometer is operated in the "metastable mode"[59] has led Barber *et al.*[66] to devise a semi-automatic system for recording this data. Subsequent computer processing can lead to the production of "fragmentation maps"[66] The incorporation of the analysis of fragmentation

pathways into computer programmes for interpretation of spectra seems likely to bring about progress in this relatively new and developing field.



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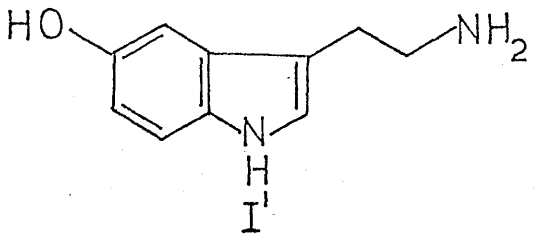
CHAPTER 2.

INDOLOSTEROIDS.

Introduction.

5-hydroxytryptamine, I', is a biologically active drug[1] with a particularly important effect on the central nervous system.

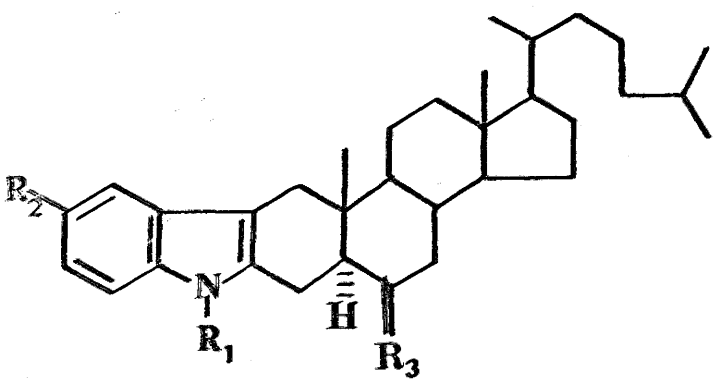


I'

However, its action differs and its mode of action is not understood. In order to study this, a series of indolosteroids were prepared[1] to simulate the 5-hydroxytryptamine. As the active groups would appear to be the hydroxyl and amino groups, attempts were made to synthesise compounds with the hydroxyl and amino groups in corresponding positions (carbon 5' on the indole ring and carbon 6 in the steroid nucleus). Steroids themselves are biologically very active, so many of the derivatives were from 5α-cholestane which has only small activity.

The general method of preparation of the compounds shown on the pages overleaf was by using variations of the Fischer indole synthesis.[2] The first indolosteroid prepared in this way was in 1908,[3] although the product was not realised to be an indole until the following year.[4] The structure of this compound, formed by refluxing 5β-cholestan-3-one and phenyl hydrazine in glacial acetic acid, was finally proved to be XX in 1965.[5]

FIGURE 1



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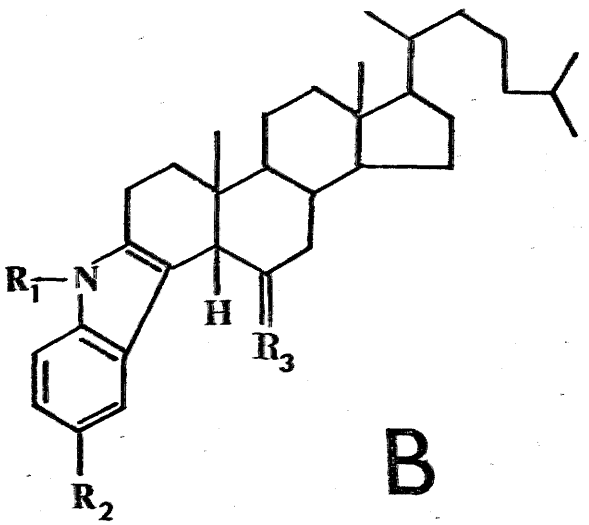

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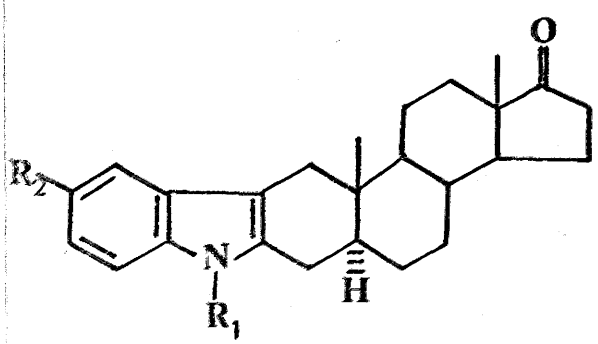
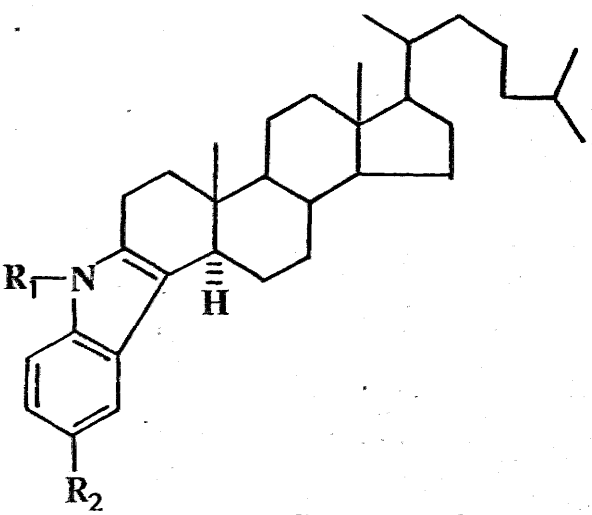




	R_1	R_2
XXVI	CH_3	H
XXVII	$PhCH_2$	H
XXVIII	H	$PhCH_2O$

	R_1	R_2
XXIX	H	H
XXX	CH_3	H
XXXI	$PhCH_2$	H

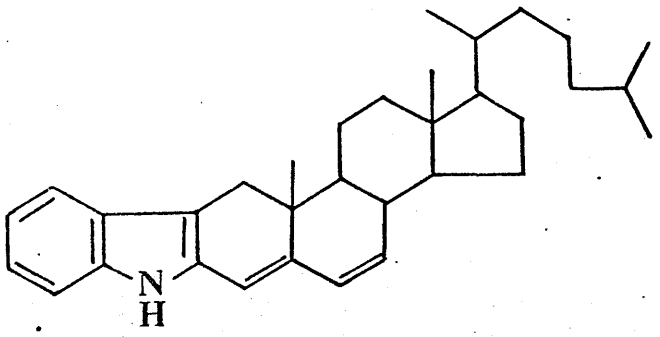
TABLE I (COMPOUNDS A).

Compound.	R_1	R_2	R_3
I.	H	H	H_2
II.	CH_3	H	H_2
III.	$PhCH_2$	H	H_2
IV.	H	CH_3	H_2
V.	H	CH_3O	H_2
VI.	H	$PhCH_2O$	H_2
VII.	H	C_1	H_2
VIII.	H	H	O
IX.	CH_3	H	O
X.	$PhCH_2$	H	O
XI.	H	CH_3	O
XII.	H	C_1	O
XIII.	H	Br	O
XIV.	H	H	NOH
XV.	$PhCH_2$	H	NOH
XVI.	$PhCH_2$	H	$\beta H, \alpha NO_2$
XVII.	H	CH_3O	$\beta H, \alpha NO_2$
XVIII.	H	$PhCH_2O$	$\beta H, \alpha NO_2$
XIX.	H	C_1	$\beta H, \alpha NO_2$

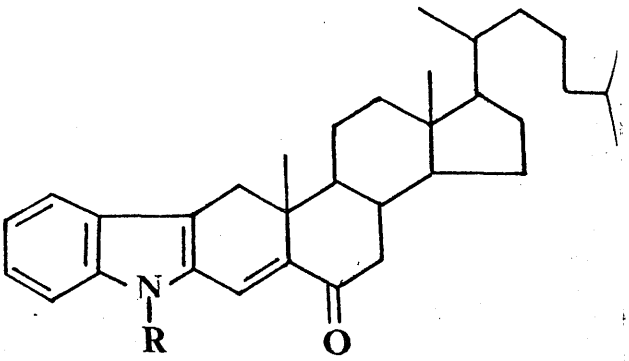
TABLE II (COMPOUNDS B).

Compound.	R_1	R_2	R_3
XX.	H	H	H_2
XXI.	$PhCH_2$	H	H_2
XXII.	H	CH_3	H_2
XXIII.	$PhCH_2O$	H	H_2
XXIV.	CH_3	H	O

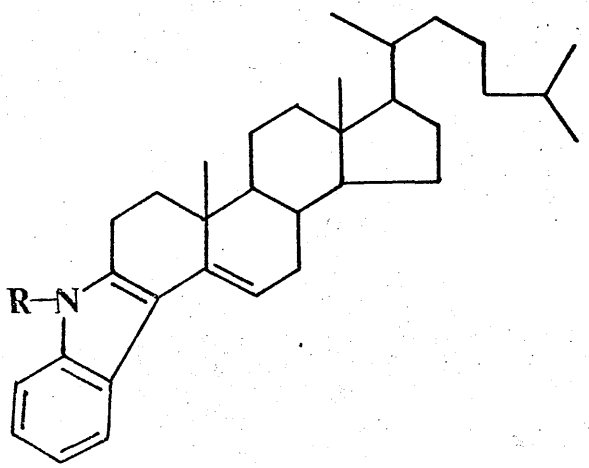
FIGURE 2



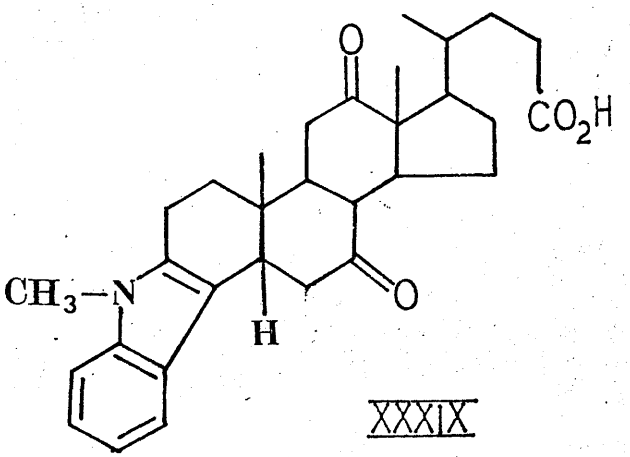
XXXII



	R
XXXIII	H
XXXIV	CH_3
XXXV	$PhCH_2$



	R
XXXVI	H
XXXVII	CH_3
XXXVIII	$PhCH_2$



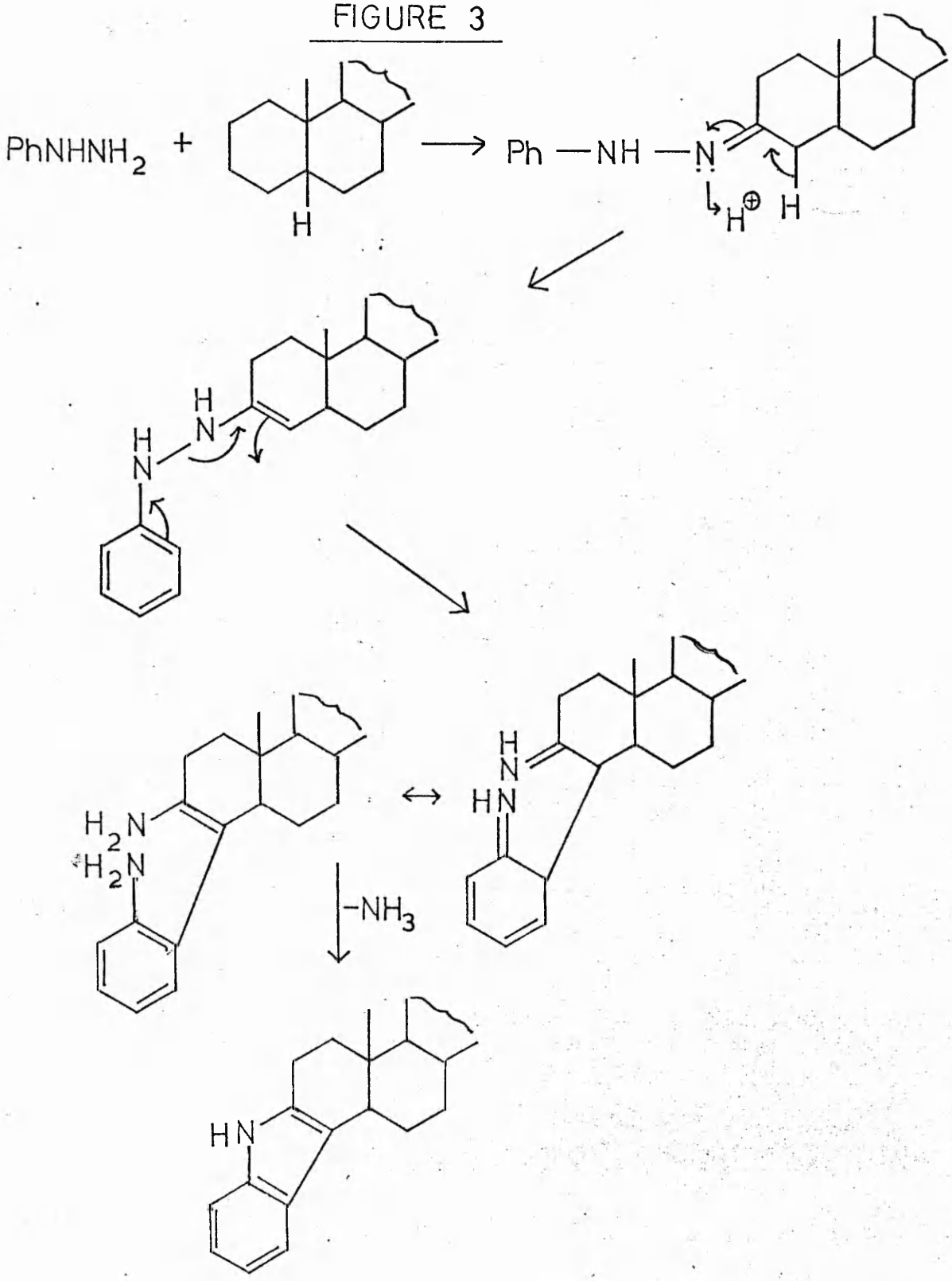
XXXIX

The mechanism for formation of indoles by this method is thought[3] to involve formation of an ene-hydrazine intermediate after initial hydrazone production, as shown in Figure 3. Many intermediates have been isolated for the remaining stages in other systems and two possibilities are shown. It is clear that the direction of indolization, to give compounds of types A (linear) or B (angular), is governed by the direction of ene-hydrazine formation, which is equivalent to the direction of enolization of the ketone. Hence 5α-cholestan-3-one, which preferentially enolizes towards C-2[6], gives mainly the linear indolosteroid, I, and 5β-cholestan-3-one yields mainly the angular compound.XX.[5]

The preparation of such a large number of compounds involved various starting compounds and the most favourable enolization is often difficult to predict, since changes that may seem insignificant often alter the pattern completely. For example, 5α-cholestan-3-one will exchange all four α-hydrogen atoms (although C_2 is favoured), whereas introduction of substituents on ring B make only hydrogen atoms on carbon atom 2 exchangeable.[7] It was thus decided to start a mass spectrometric study of these compounds in an attempt to find an easy method of differentiating between the angular and linear indolosteroids, as no simple method of doing this was known.

Perhaps one of the greatest triumphs of organic mass spectrometry

FIGURE 3



to date has been in the field of alkaloid chemistry - particularly indole alkaloids. The structure of these biologically important molecules has long been of interest and in 1960 the first structural elucidation of an alkaloid by mass spectrometry was reported by Biemann.[8] Such compounds are ideally suited for mass spectrometry, having an aromatic part to the molecule which generally stays intact and an alicyclic part in which most fragmentation occurs. Intense ions are normally formed, due to stabilisation by the aromatic system, or by heteroatoms or unsaturation in the alicyclic part of the molecule. As in many cases whole families of these alkaloids exist, differing only in small substituents, the mass spectrometric shift technique can be of use in identifying them. This has been demonstrated, for example, for a group of Iboga alkaloids.[9] There has since been such a flood of papers on the mass spectrometry of alkaloids that at least one book has been published on the subject.[10]

Since the first publication of the mass spectrum of 5α-cholestane by Reed,[11] there has been an almost equal amount of interest generated in the steroid field in spite of the fact that the functional groups which are found in these compounds (commonly carbonyl or hydroxyl) do not have a strong directing influence on the fragmentation.[12] In many cases the positions of the functional group are not made clear by the mass spectrum. This can be overcome by the use of

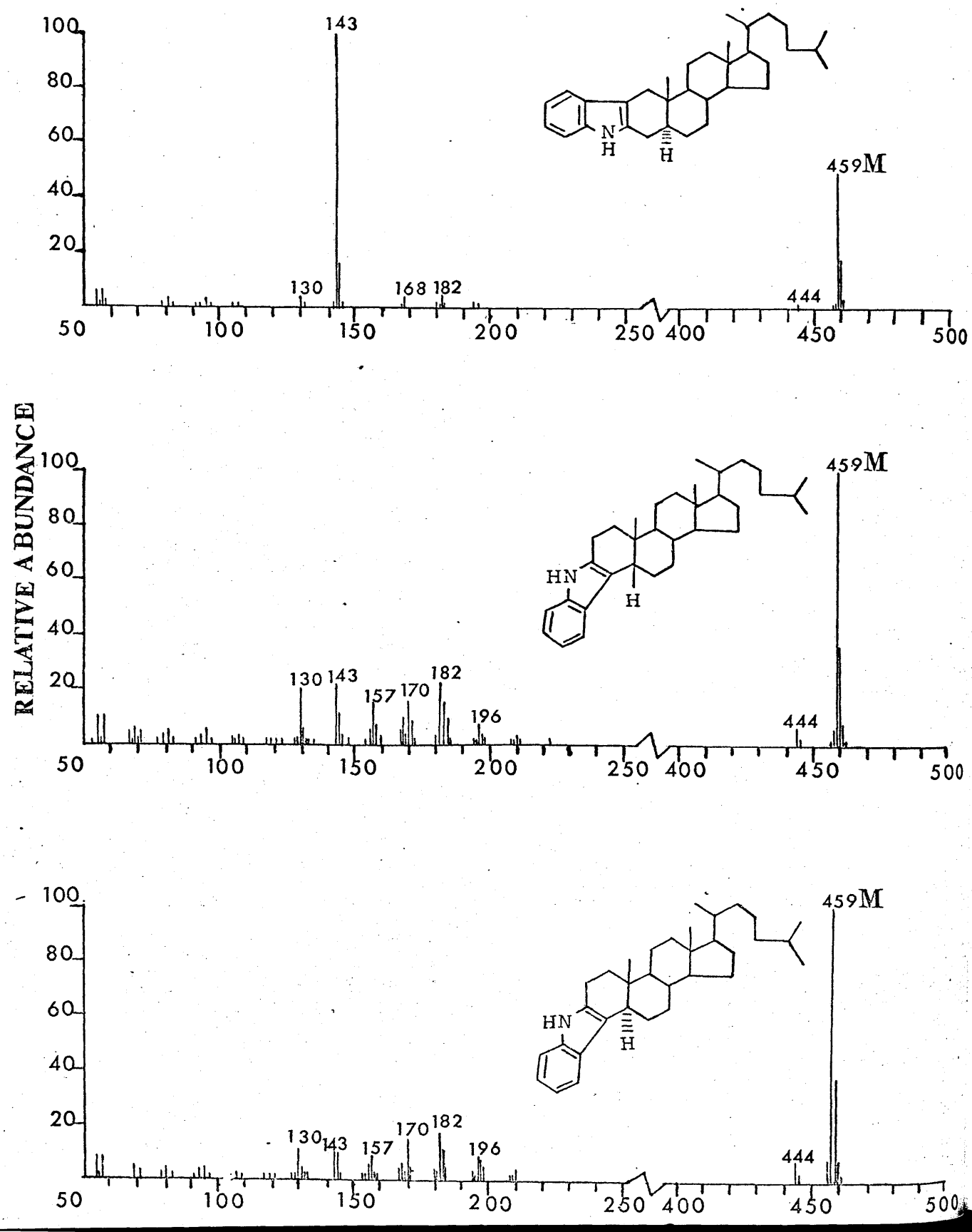
derivatives such as ketals[13] or dimethylamines.[14] These, however, have the disadvantage that subtle differences can be overlooked, e.g., although there are intensity differences in the mass spectra of cholestan-3-one and coprostan-3-one, the spectra of the corresponding ketals are virtually identical.[15]

Djerassi and co-workers have done much work on the steroidal ketones,[16] emphasis being placed on deuterium labelling for elucidation of the many complex hydrogen rearrangements accompanying fragmentation.

This group has worked on oestrogens[17] and α,β unsaturated ketones[18] and, in contrast to the results with ketones, it is found that in many of these cases the fragmentation is directed by charge localization on the π electron system, giving good correlation with structure. These cases and also the indole alkaloids mentioned above, gave reason to believe that the mass spectra of the angular and linear indolosteroids could be sufficiently different for unambiguous structure determination.

The structure of the compounds discussed below have been determined by degradation, gas-liquid chromatography, or by the use of chemical analogies.[1,19]

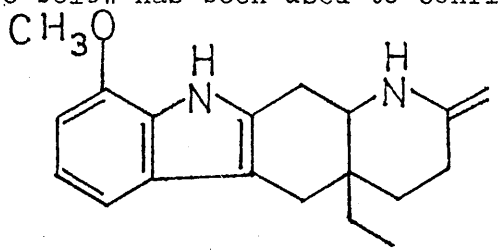
FIGURE 4


RELATIVE ABUNDANCE
100
80
60
40
20
143
130
168
182
444
459M
N
H
H
50
100
150
200
250
400
450
500
HN
H
130
143
157
170
182
196
HN
H

Discussion.

5α-cholestano (3,2-b) indole and simple related compounds.

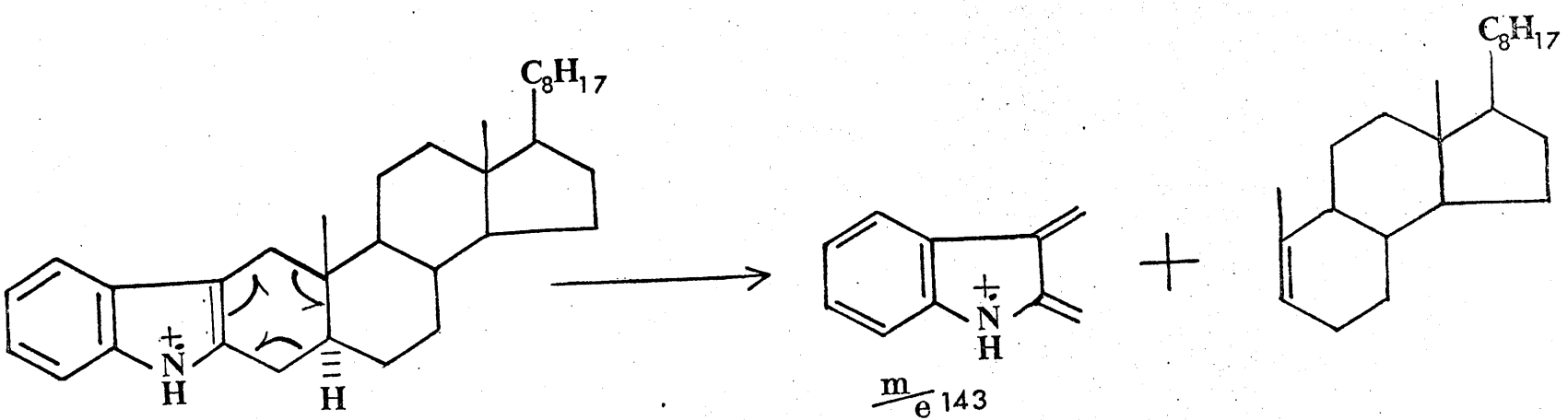
The mass spectrum of this compound is shown in Figure 4 with the corresponding 5α-and 5β-angular compounds. The base peak in the spectrum occurs at m/e 143 corresponding to a retro-Diels-Alder[20] fragmentation (Figure 5). This peak is by far the most important in the spectrum, being 36.1%Σ_{50}. The occurrence of a peak corresponding to the retro-Diels-Alder reaction in the mass spectrum of the indole below has been used to confirm[21] the linear structure



of this compound. However, as can be seen in Figure 4, the angular compounds also exhibit the m/e 143 peak, although the intensity is much reduced. In the linear case the high abundance is due to the stability of the ion formed, the tricyclic olefin eliminated and the facile six-membered rearrangement required for its formation.

The m/e 143 peak is accompanied by an ion at m/e 144 which is too intense to be solely the isotope peak (6%Σ_{50}). This ion at m/e 144 is said to be ubiquitous in the spectra of indole alkaloids.[22]

FIGURE 5



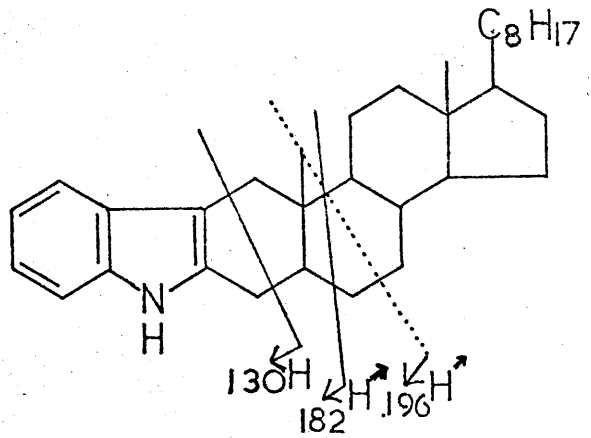
Also ions formed by retro-Diels-Alder reactions are often accompanied by ions one mass unit higher.

The rest of the spectrum is weak and normal common steroid cleavages, such as the loss of the sidechain + 42 mass units[23] have been almost completely suppressed. However, most of the other significant ions in the spectrum would appear to be formed by cleavage across rings A and B of the steroid nucleus with hydrogen transfer to give m/e 130, m/e 182 and m/e 196 as shown in Figure 6. Ions also appear at m/e 180 and m/e 194 with formulae as shown in Table 3, which suggest they have been formed from m/e 182 and m/e 196 respectively by H_2 loss. It can be seen that the driving force for these ions would be the stability of the even electron ions formed. The only significant odd electron ions in this part of the spectrum are at m/e 181 and m/e 167 with metastable ions at m/e 167.1 (calculated 167.1) and m/e 153.1 (calculated 153.2) for their formation from m/e 196 and m/e 182 respectively.

TABLE 3.

Nominal Mass	Mass Observed	Mass Calculated	Formula Assigned.
130	130.0656	130.0657	C_9H_8N
143	143.0734	143.0735	$C_{10}H_9N$
167	167.0719	167.0735	$C_{12}H_9N$
180	180.0814	180.0813	$C_{13}H_{10}N$
182	182.0965	182.0930	$C_{13}H_{12}N$
194	194.0964	194.0970	$C_{14}H_{12}N$
196	196.1113	196.1127	$C_{14}H_{14}N$

FIGURE 6



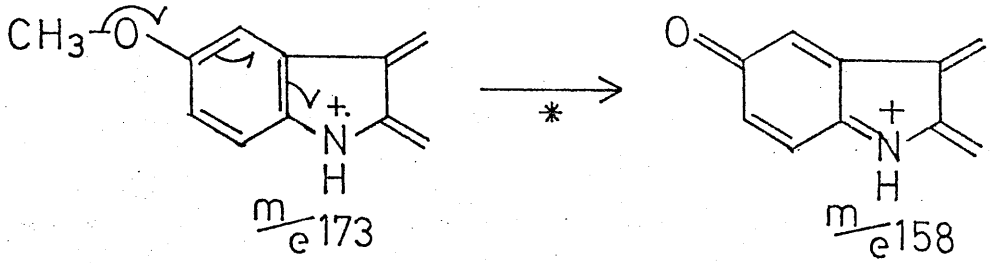
As can be seen from Figure 4, the ions below m/e 130 occur at masses consistent with their being hydrocarbon in nature (m/e 55, 57, etc.) and it is difficult to attach any structural significance to them.

It is known that the shape of a metastable peak[24] is a function of the structure of the parent and daughter ions. Similarly, the abundance of a metastable peak is related to the rate constant of the reaction and thus to the structure of the products. The shapes and abundances of metastable ions[25] have therefore been used to correlate ion structures. If the ratio of the metastable ion to the precursor or daughter ion is identical for different compounds, then it is concluded that the precursor ions are identical.

The metastable peak for the retro-Diels-Alder decomposition of the molecular ions of 5α-cholestano (3,2-b) indole is very broad and intense and is centred at m/e 44.6 (calculated 44.6). It is roughly Gaussian in shape and the ratio $[\text{m/e } 44.6]^+/[M]^+$ is 2×10^{-3}.

As discussed below, this metastable ion is absent from the spectra of 5β-and 5α-cholestano (3,4-b) indole. Although the detection of metastable peaks depends on the intensity of the spectrum obtained, in all the spectra below it was possible to observe metastable peaks which gave a ratio $[m^*]/[\text{base peak}] \approx 10^{-4}$ and in many cases the detection limit was lower than this.

FIGURE 7



The features of the spectra of the linear indolosteroids (II, IV, V and VII in Table I and Figure I) are virtually identical to those of the spectrum of 5α-cholestano (3,2-b) indole. In all cases the base peak is that formed by retro-Diels-Alder transition and they have associated strong metastable peaks shown in Table 4. In the chloro-compound (VII) the data is for chlorine 35.

TABLE 4.

Compound	RDA ion m/e	Intensity % Σ 50	m^* obs. m/e	m^* calc. m/e	Process.
II	157	26.7	52.1	52.1	$473^+ \longrightarrow 157^+$
IV	157	23.2	52.1	52.1	$473^+ \longrightarrow 157^+$
V	173	30.6	61.2	61.2	$489^+ \longrightarrow 173^+$
VII	177	24.1	63.6	63.6	$493^+ \longrightarrow 177^+$

This suggests that the presence of the intense retro-Diels-Alder ion and associated metastable are characteristic of the linear indolosteroids.

5α-cholestano (3,2-b) N-methylindole (II) has a metastable peak at m/e 128.4 (calculated 128.4) for the loss of the methyl radical from the m/e 157 ion, but this loss is not observed from 5α-cholestano (3,2-b) 5'-methylindole (IV). This is similar to results on simple indole systems[26]. The ion at m/e 173 in Figure 7 also loses a methyl radical to give the highly conjugated m/e 158, with a metastable peak at m/e 144.3 (calculated 144.3) for the process.

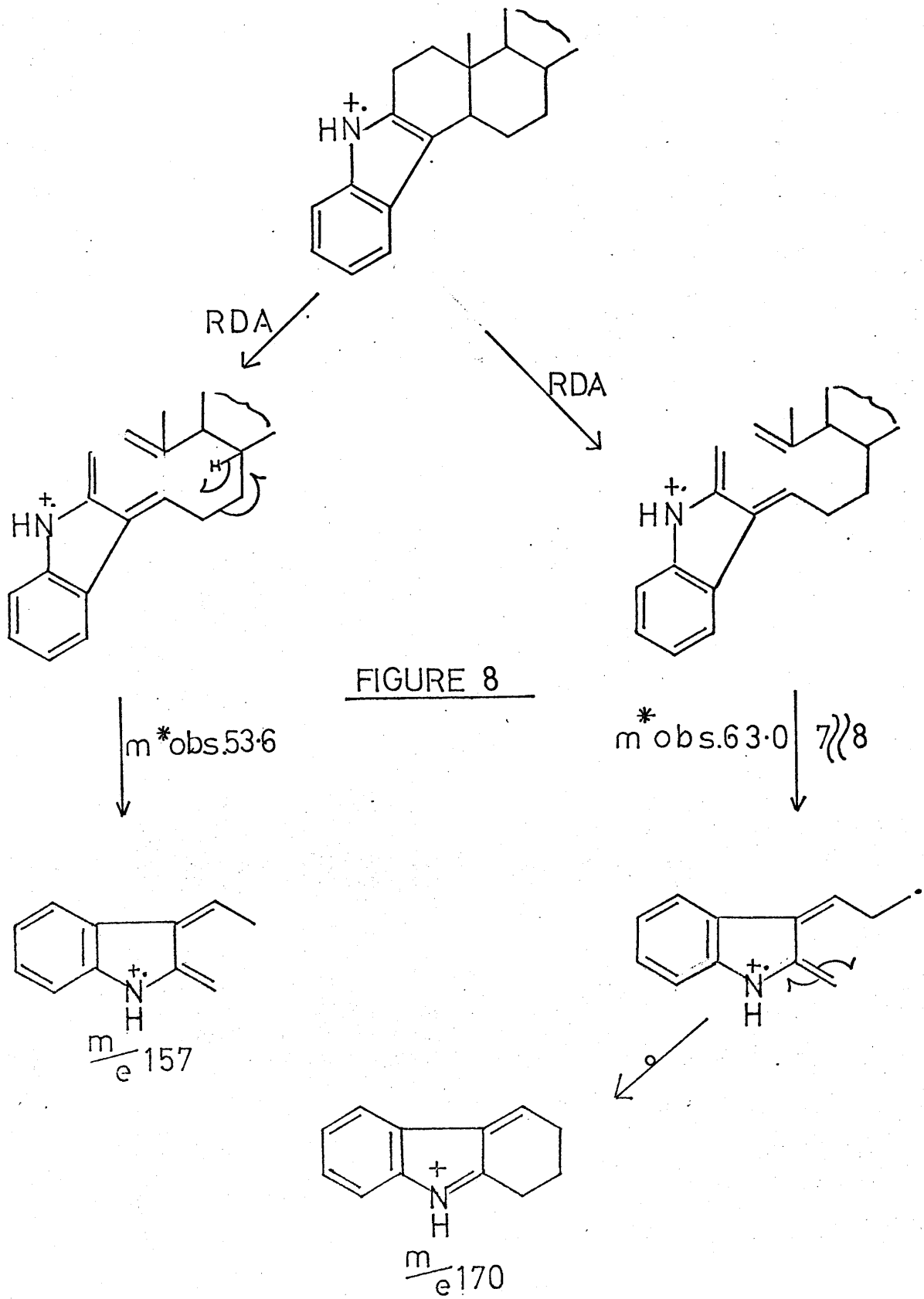


FIGURE 8

Simple angular indolosteroids.

The spectra of 5α- (XXIX) and 5β-cholestano (3,4-b) indole (XX) will be considered together since they are very similar (Figure 4) with only small intensity differences. In many cis-trans isomeric steroids there is a good correlation between the thermodynamic stability of the compounds and the relative intensities of the parent ions.[27] In accord with this it is usually found that trans fused rings A and B have a higher parent ion intensity than the cis isomer, due to the release of strain on fragmentation of the latter. Similar results are obtained in this case, with a parent intensity for the 5α isomer of 23% Σ_{50} and 20% Σ_{50} for the 5β compound.

Although most of the ions in these spectra are observed to a much smaller extent in the spectrum of the linear compound, the ions at m/e 157 and m/e 170 are virtually absent from its spectrum (< 1% relative intensity). Likely routes for the formation of these ions are shown in Figure 8. Once again the initial step is the favoured retro-Diels-Alder reaction. The ion at m/e 170 is then formed by

simple cleavage of the C7 - C8 bond and may cyclise to give the structure shown. Cleavage of the C6 - C7 bond with accompanying hydrogen transfer (not necessarily from the site shown) yields the m/e 157 ion.

The major fragment ion in both these spectra occurs at m/e 182 being 4.5% Σ_{50} in the 5β compound and 3.9% Σ_{50} in the 5α compound. Figure 9 shows a possible mode of formation by cleavage of the C9 - C10 bond and hydrogen transfer to C9. The breaking of the C5 - C6 bond as shown is now particularly favoured, as it is both allylic and benzylic. However, there are obviously many other possible mechanisms for the formation of this ion. For example, initial benzylic cleavage could be followed by rotation about the C9 - C10 bond to give hydrogen transfer to C6, before the final bond breaking.

The other ions may be formed by similar cleavages with hydrogen transfer both to and from the charged fragment. In contrast to the linear indolosteroids, many more metastable peaks are observed for the molecular ion decomposition and these are in Table 5.

TABLE 5.

m^* observed	m^* calculated	Transition	Intensity
430.0	429.5	$459^+ \rightarrow 444^+$	S
404.7	404.7	$459^+ \rightarrow 431^+$	W
308.0	308.0	$459^+ \rightarrow 376^+$	W
305.0	304.7	$459^+ \rightarrow 374^+$	W
261.0	260.8	$459^+ \rightarrow 346^+$	W
73.8	73.8	$459^+ \rightarrow 184^+$	W
72.1	72.2	$459^+ \rightarrow 182^+$	M
63.0	63.0	$459^+ \rightarrow 170^+$	M
53.7	53.7	$459^+ \rightarrow 157^+$	M

S = strong W = weak M = medium.

The increased abundance of methyl radical loss from the two angular compounds as compared to the above linear compounds is accompanied by an intense metastable peak at m/e 430 which is absent in the linear case. The $[m/e\ 430.0]/[M]^+$ ratio is 2.2×10^{-3} for the 5β-and 2.7×10^{-3} for the 5α-compound. It is noted that a fairly large error is associated with the assignment of mass to this metastable peak (see Table 5 above).

This may be due to confusion caused by normal ions of similar intensity which occur around this mass and to the close spacing

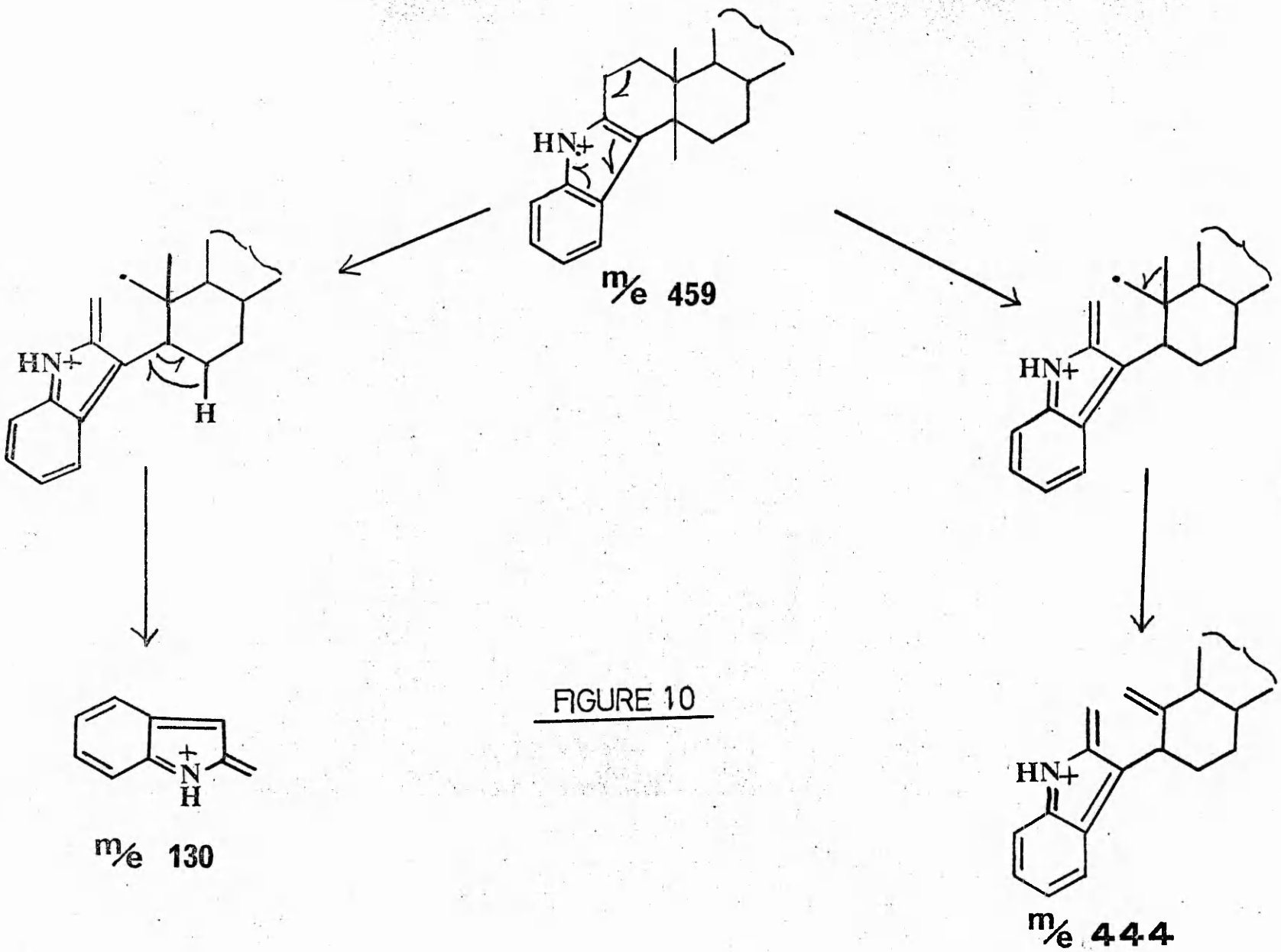


FIGURE 10

between peaks at such high mass. Alternatively, a metastable peak may also be present for the transition $(M + 1)^+ \rightarrow (M - 14)^+$ (calculated 430.5). Overlapping of these two peaks could lead to what is apparently a single peak, with a maximum higher than the expected mass.

A possible mode of formation of this ion is shown in Figure 10. Initial benzylic cleavage is followed by loss of the C-19 methyl group to give the ion at m/e 444. This benzylic cleavage would also give rise to the ion at m/e 130 as shown. However, in the linear compounds, this cleavage would lead to the breakdown of the molecular ion, by the retro-Diels-Alder decomposition, to m/e 143, as this facile cyclic rearrangement is irreversible in these compounds.

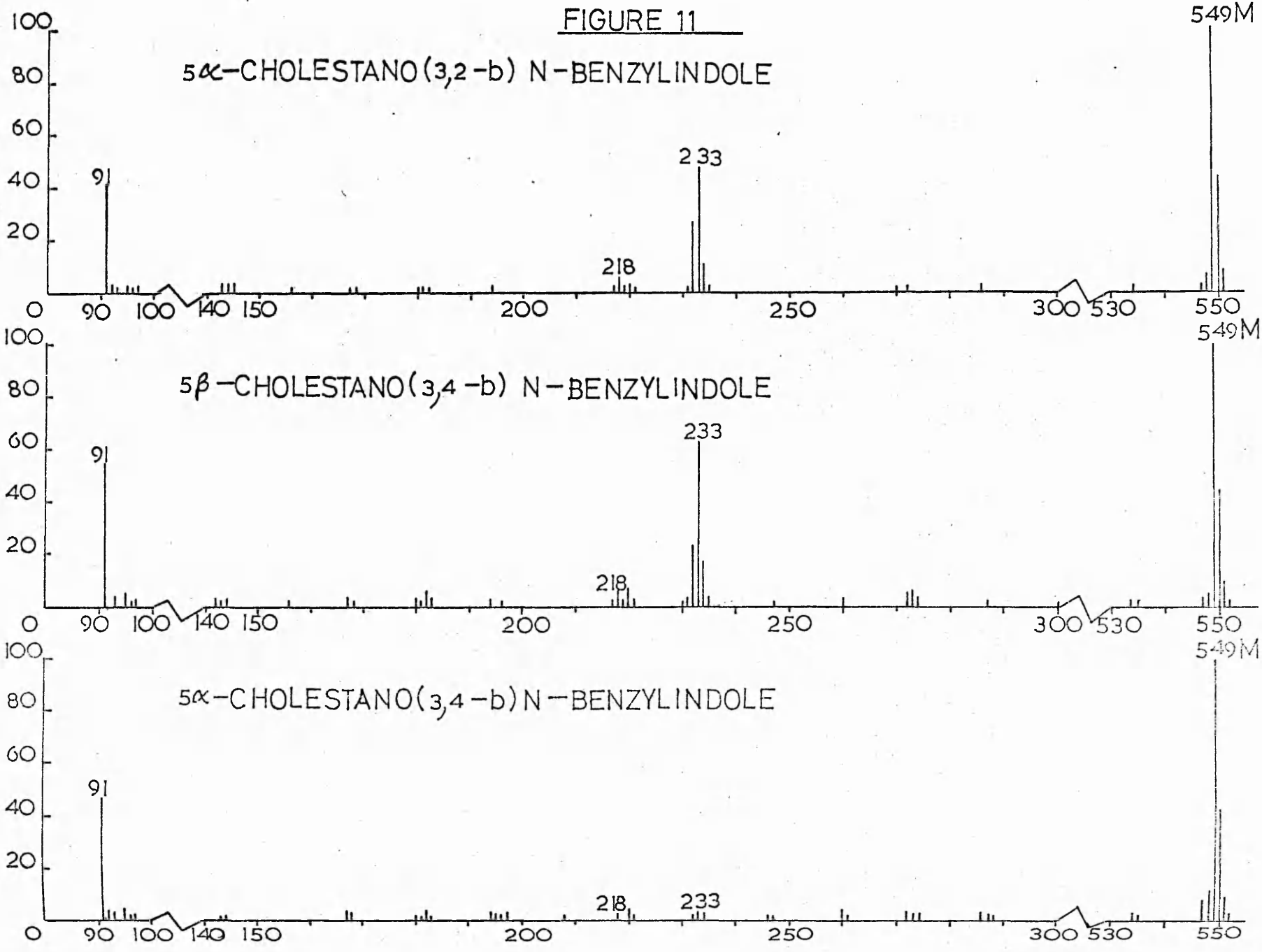
Although the formation of the ion at m/e 444 is shown as a two-step process, it could equally well be considered as a concerted mechanism. The intensity of the m/e 444 ions is still not high and, since they are accompanied by abundant metastable ions, the conclusion is drawn that the process for the formation is one with a low energy of activation and a low frequency factor.[27a] This is often the case, for example,

when a reaction involves skeletal rearrangement. Also, since no metastable ion is observed for the formation of the m/e 444 ion in the linear compounds, it would appear that this is a simple cleavage reaction. Further evidence to support this postulate is given in the section on compounds with unsaturation in the steroid nucleus.

5β-cholestano (3,4-b) 5'-methylindole (XXII) and 5α-cholestano (3,4-b) N-methylindole (XXX) have spectra which show the same breakdown pattern as the other angular compounds, after allowance has been made for the mass shift caused by the methyl groups. The metastable peaks for the loss of a methyl group from the parent are once again intense and occur at m/e 444.0 (calculated 443.5).

The examination of these simple linear and angular indolosteroids has thus shown that mass spectral interpretations can be used to differentiate between the two structural types. It has also shown that the presence or absence of particular metastable ions can be correlated with structure and that simple substitutions

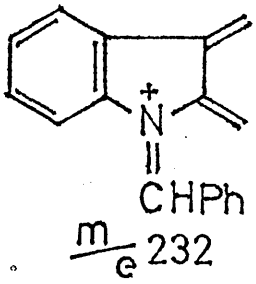
FIGURE 11


5α-CHOLESTANO(3,2-b) N-BENZYLINDOLE
549M
233
91
218
100
80
60
40
20
0
90
100
140
150
200
250
300
530
550
5β-CHOLESTANO(3,4-b) N-BENZYLINDOLE
549M
233
91
218
5α-CHOLESTANO(3,4-b)N-BENZYLINDOLE
549M
91
218
233

do not affect this. The effect of different substituents on the mass spectra of these compounds is discussed below.

Simple N-benzyl substituted indolosteroids.

The spectrum of 5α-cholestano (3,2-b) N-benzylindole (III) is shown in Figure 11 with the 5α- and 5β-angular compounds. The introduction of the benzyl group has led to a stabilization of the molecular ion with respect to the ion formed by the retro-Diels-Alder reaction (m/e 233). The only other major ions in the spectrum are the tropyllium ion at m/e 91 and the ion at m/e 232 which is formed by the loss of a hydrogen atom from m/e 233 (m^* observed 231.0, m^* calculated 231.0). The driving force for the loss of the hydrogen atom is the fully conjugated ion formed which is shown below.



m/e 232

A metastable peak at m/e 204.0 (calculated 204.0) shows that m/e 233 breaks down by loss of a methyl radical. Mass measurement has confirmed the formulae of the ions at m/e 233 (mass observed

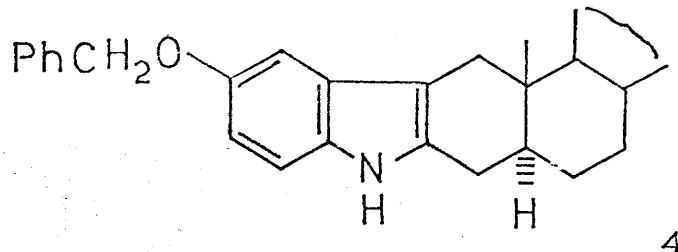
233.1185, mass calculated 233.1204) and m/e 218 (mass observed 218.0969, mass calculated 218.0970) as $C_{17}H_{15}N$ and $C_{16}H_{12}N$ respectively.

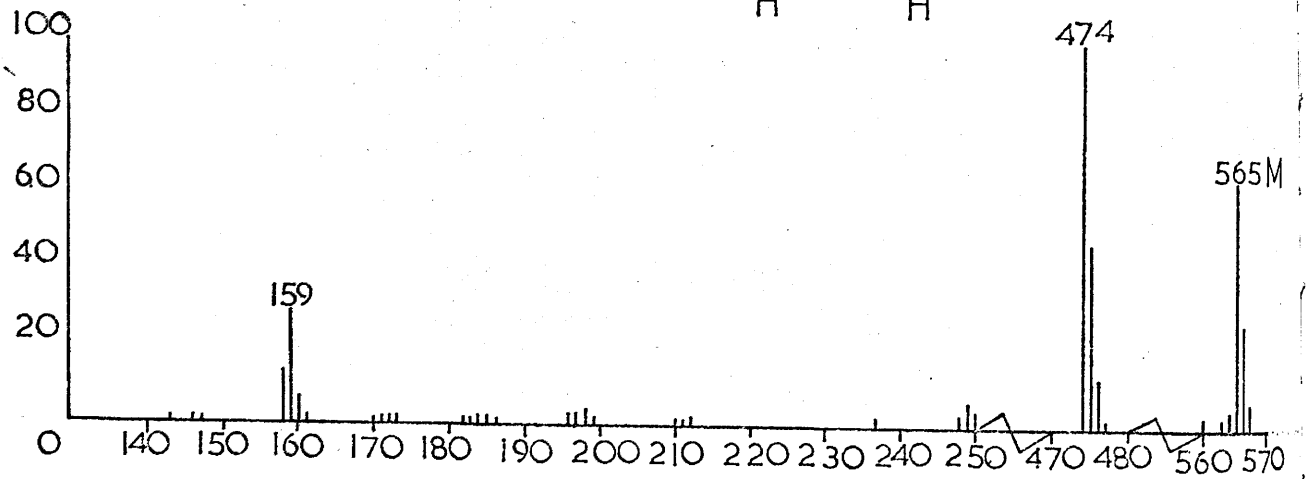
A review of bis-aryl compounds[28] has shown that many eliminate one or more of the bridging atoms, often with accompanying hydrogen loss. An example of this is methyl radical loss from stilbene and in a series of papers[29] on this compound and some of its analogues, evidence has been given for cyclisation, rather than phenyl migration, for the formation of this ion. Evidence is also provided for the reaction occurring from the first electronically excited state. Labelling results have shown that the atoms eliminated are a central carbon and hydrogen, plus ortho-hydrogens from the rings. The loss of methyl from m/e 233 would therefore appear to be due to the loss of the methylene group attached to the nitrogen with an aromatic hydrogen atom. To determine the origin of this hydrogen atom, labelling studies would be required.

5β-cholestano (3,4-b) N-benzylindole (XXI) has a mass spectrum (Figure 11) which is very similar to the linear compound. The ion at m/e 233 is probably formed by cleavage 11110 and 4115 and its high abundance is probably accounted for by the steric interaction of the bulky benzyl group with the already strained "boat" form of the steroidal ring A in this compound. The metastable ion for the

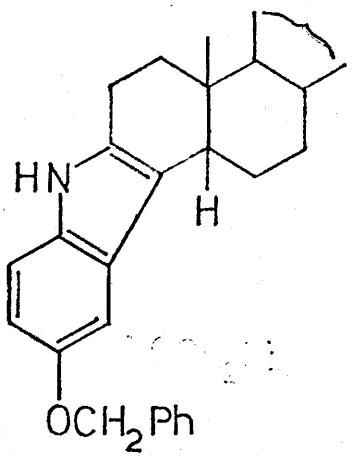
FIGURE 12

VI





XXIII



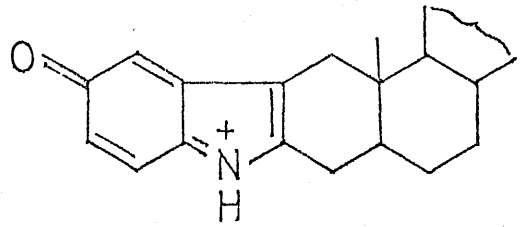
formation of m/e 233 from the molecular ion is at m/e 98.9 (calculated 98.9) and is also observed for the linear compound. The only real difference between compounds XXI and III is the metastable ion at m/e 519.5 (calculated 519.4) in the spectrum of XXI for the loss of the methyl group from the parent ion.

In contrast, the spectrum of 5α-cholestano (3,4-b) N-benzylindole, XXXI, has only two intense ions, the molecular ion and the tropyllium ion at m/e 91. All other fragmentations are weak, but the diagnostic metastable peak for the loss of methyl from the parent ion is still intense, with the ratio [m/e 519.5]/[m/e 549] being 1.9×10^{-3}.

The other N-benzyl compounds are discussed in the appropriate sections below.

Simple benzyloxyindolosteroids.

The effect of the introduction of the benzyloxy substituent on to the indole ring can be seen in Figure 12. Although most indole alkaloids[10] and the indolosteroids above show fragmentation of the steroid part of the molecule, the base peak in the spectrum occurs at m/e 474. This is formed by benzylic cleavage of the indole substituent to give the ion below (illustrated for compound VI).



m/e 474

The driving force for this reaction must be the stability of the ion formed by the favourable benzylic cleavage and also the stable radical of mass 91 which is eliminated.

In both cases the m/e 474 peak is accompanied by a peak one mass unit higher which is too intense to be simply the isotope peak, and is probably formed by loss of the benzyl substituent with transfer of the hydrogen to oxygen.

There is a metastable peak at 53.2 in the spectrum of 5α-cholestano (3,2-b) N-benzyloxyindole for the breakdown of the m/e 475 ion to m/e 159 by the retro-Diels-Alder decomposition. This indicates the extra stability of the even electron ion at m/e 474 to the odd electron species m/e 475. It is possible that the metastable ion at m/e 53.2 is for the process m/e 474 → m/e 159 as the calculated value for this process is 53.3. The retro-Diels-Alder decomposition of the molecular ion common to most linear indolosteroids has been suppressed to give only a small peak at

FIGURE 13a

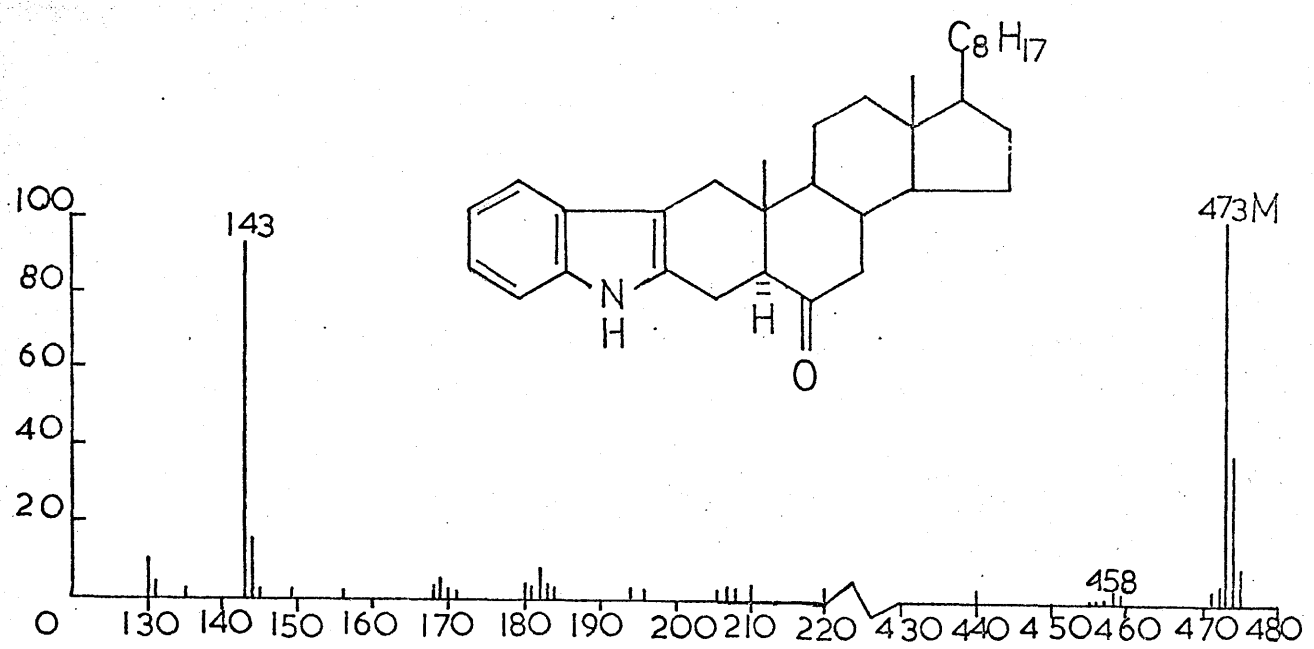
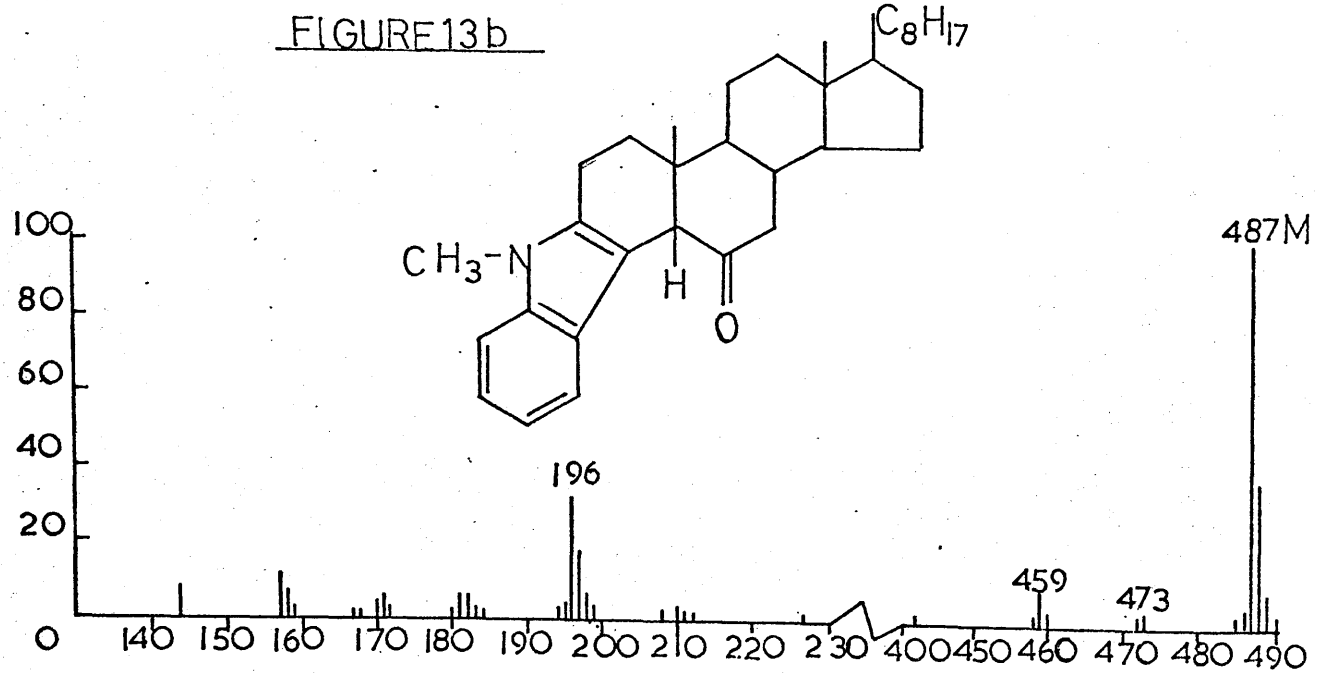


FIGURE 13b



m/e 249 (m^* observed 109.7, calculated 109.7 for $565^+ \rightarrow 249^+$).

5β-cholestano (3,4-b) N-benzyloxyindole does not have an important ion at m/e 159. A metastable peak at m/e 44.9 (calculated 44.9) shows the fragmentation at m/e 475 to form m/e 146 which is analogous to the ion at m/e 130 in the angular compounds, without indole substituents (see Figure 10). In this case the metastable peak for the loss of methyl from the molecular ion is absent.

Although the benzyloxy group gives rise to ions which dominate the spectrum in these two compounds, the ions at m/e 159 and 146 are indicative of the position of indole fusion to the steroid nucleus.

6-oxo- and 17-oxo- Indolosteroids.

It has been stated that the introduction of a keto group into a steroidal nucleus does not strongly direct the fragmentation. A study of 6-keto steroids[7] has shown that only three peaks can be attributed directly to the ketone substituent. It is thus not surprising that 6-oxo-5α-cholestano (3,2-b) indole (VIII) should have a mass spectrum (Figure 13a) which shows little difference to other simple linear indolosteroids.

Although the molecular ion has become the base peak of the spectrum, the m/e 143 ion formed by retro-Diels-Alder decomposition

(m^* observed 43.2, calculated 43.2 for $473^+ \longrightarrow 143^+$) still carries a large fraction of the ion current. (24.1% Σ_{50}). Many steroidal ketones show the loss of H_2O, CH_3 and $(CH_3 + H_2O)$ from their molecular ions.[7] 6-oxo-5α-cholestano (3,2-b) indole shows these losses to a small extent and the metastable peaks below are observed in this spectrum.

m^* observed.	m^* calculated.	Process.
443.6	443.5	$473^+ \longrightarrow 458^+ + 15$
437.9	437.7	$473^+ \longrightarrow 455^+ + 18$
409.5	409.3	$473^+ \longrightarrow 440^+ + 33$

Although there is a metastable peak for the process involving loss of $(H_2O + CH_3)$ from the parent ion, it is certain that this is not a one step loss, although it may be a concerted process. Metastable peaks have been observed for two step fragmentations,[30] and Seibl[31] has noted such a peak for the $[M-(H_2O + CH_3)]$ ion in ergosterol.

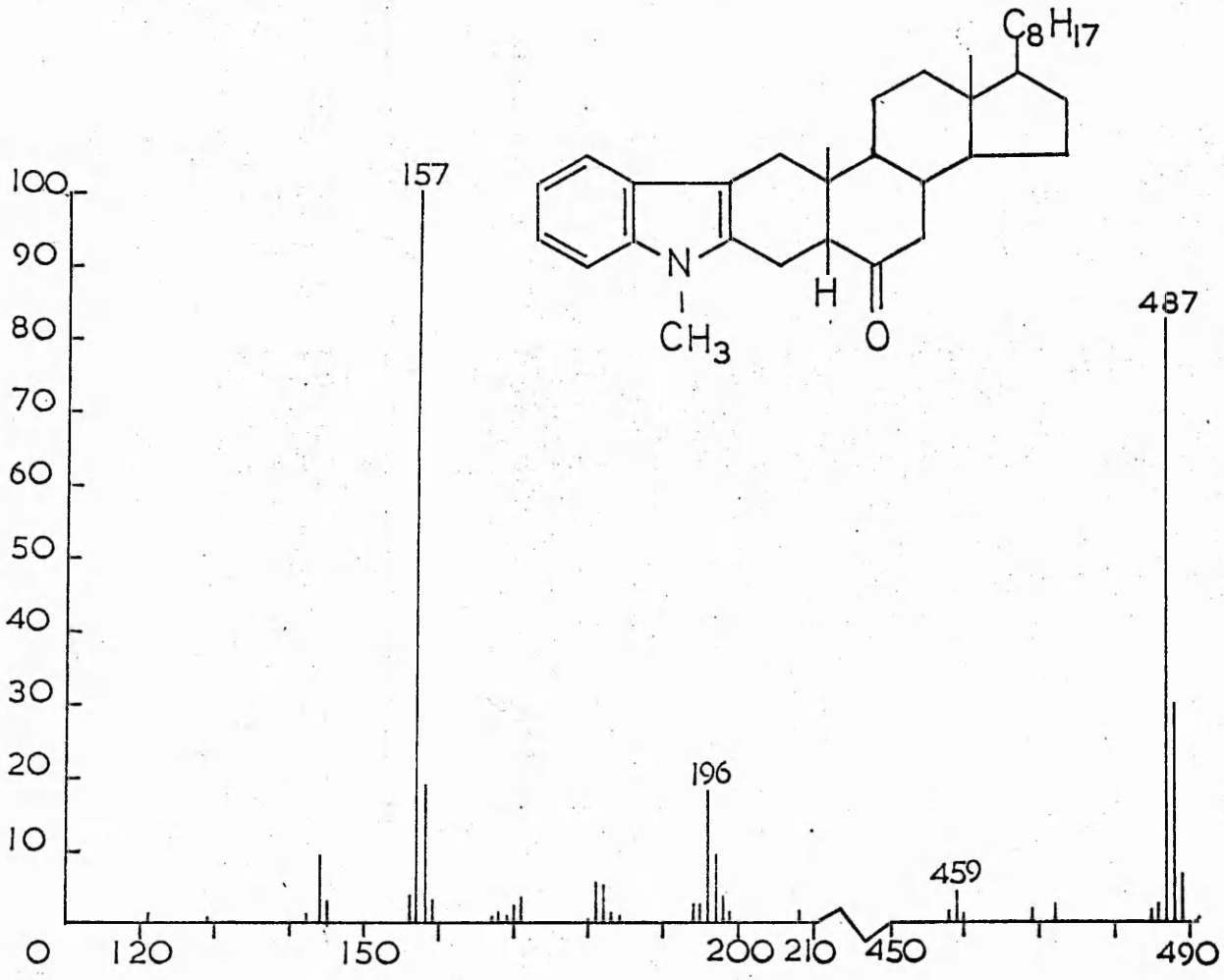
The other compounds in Table I, with the ketone group at C - 6 (IX - XIII) all behave in an analogous manner on electron impact.

Only one angular indolosteroid (XXIV) was available with the ketone substituent. It was noted that an impurity peak was present at m/e 501 (5% relative intensity) in this compound, but enough was not available for purification. However, the main interpretation was substantiated by the presence of the appropriate metastable peaks.

Figure 13(b) shows that the keto group has not substantially changed the general fragmentation pattern which is characteristic of the angular indolosteroids. The most intense fragment ion is at m/e 196 which is indicative of fragmentation across ring B (as for m/e 182 in figure 9). m/e 196 was mass measured to confirm that none of the ions has an oxygen contribution. The result was a singlet of formula $C_{14}H_{14}N$ (mass observed 196.1120, calculated 196.1126). However, this ion is formed both from m/e 487 (m^* observed 79.0, calculated 78.9) and m/e 459 (m^* observed 83.8, calculated 83.7).

The ion at m/e 459 (M - 28) has been shown by high resolution measurements (mass observed 459.3890, calculated 459.3865 formula assigned $C_{33}H_{49}N$) to be solely due to the loss of carbon monoxide from the molecular ion. This has been observed in steroidal ketones.[16] An intense metastable ion is present at m/e 432.6

FIGURE 14


C8H17
N
CH3
H
O
100
90
80
70
60
50
40
30
20
10
0
120
150
157
196
200
210
450
459
487
490

(calculated 432.9). The steric compression in the angular compound must be high enough to produce the carbon monoxide expulsion in preference to the $\left[M-(CH_3 + H_2O)\right]$ ion.

The observation of the differences between the linear and angular indolosteroids with a ketone group was of use in the examination of a compound which was believed to be 6-oxo-5β-cholestano (3,2-b) N-methylindole. The spectrum is shown in Figure 14 with the proposed structure of the compound.

The base peak in the spectrum corresponds to the retro-Diels-Alder fragmentation and there is a weak metastable at m/e 50.6 (calculated 50.6) for this degradation. In contrast to 6-oxo-5α-cholestano (3,2-b) N-methylindole (IX), the compound had an intense m/e 196 ion and also a metastable peak for the loss of carbon monoxide to m/e 459 (m^* observed 432.9, m^* calculated 432.6). Although there is an (M - 18) ion, there is no $\left[M-(CH_3 + H_2O)\right]$, so the spectrum would seem to have features of both the linear (IX) and angular (XXIV) compounds. It was concluded that this compound may in fact be a mixture of these two. Gas-liquid chromatography was used[19] to confirm this, by comparison with the authentic samples.

Similar results were obtained for the compound XXXIX shown in

FIGURE 15

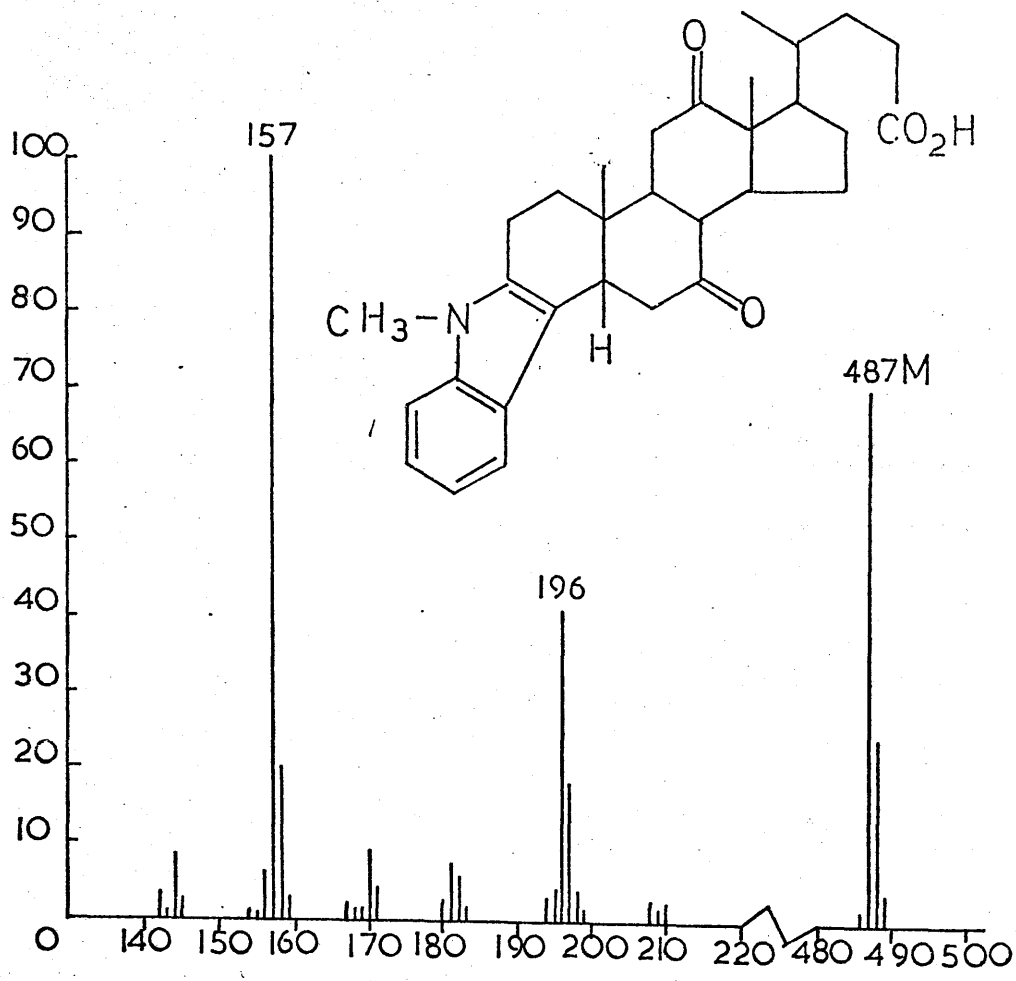

100
90
80
70
60
50
40
30
20
10
0
140
150
160
170
180
190
200
210
220
480
490
500
157
196
487M
O
CO_2H
CH_3-N
H
O

Figure 15. Although no other similar compounds had been run, the high intensity of both m/e 157 and m/e 196 suggested that a mixture of the linear and angular compounds were present. Once again gas-liquid chromatography[19] has shown that there are two compounds present, although their identification has not been confirmed.

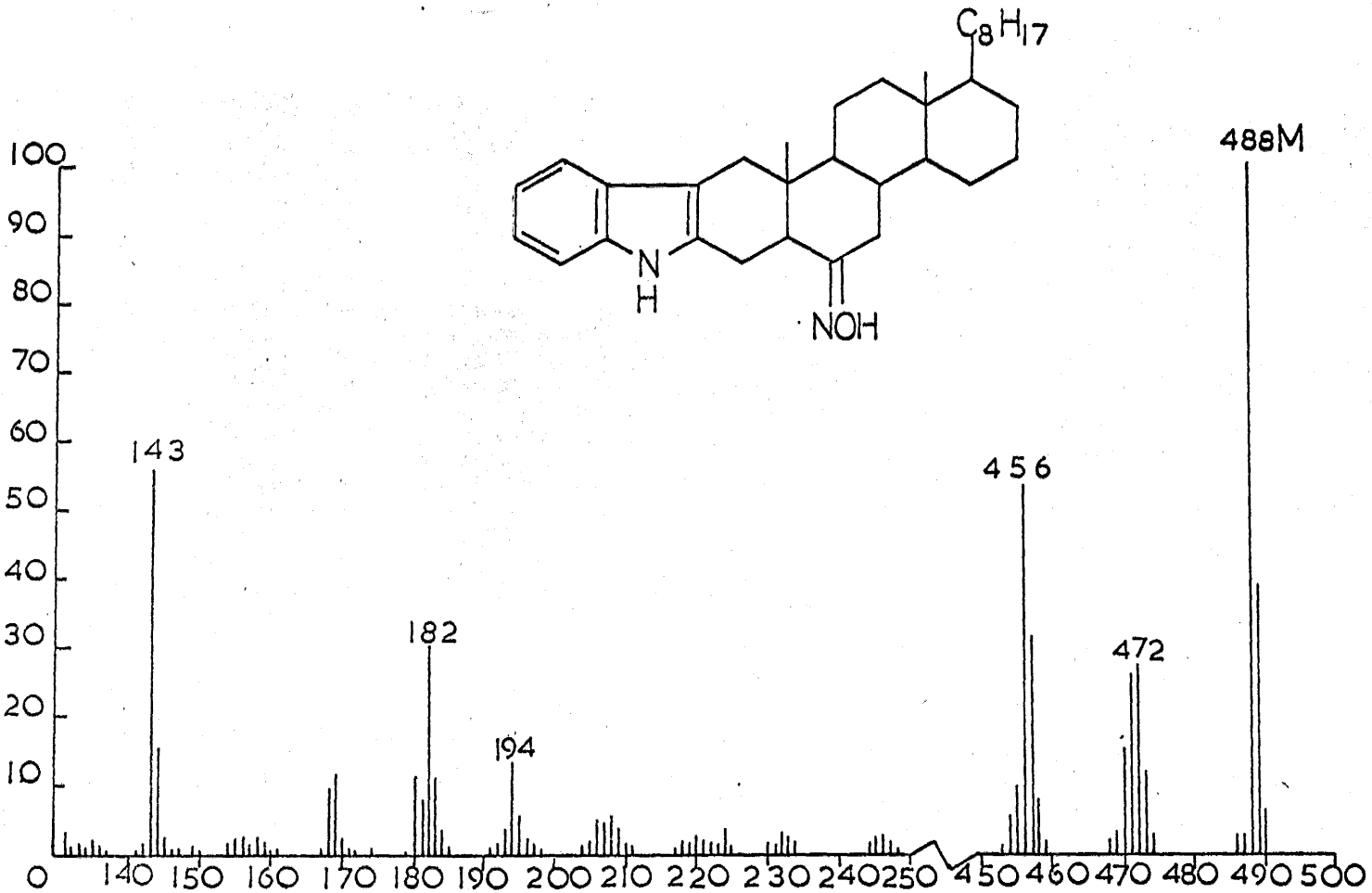
The introduction of the carbonyl group at C-17 has no effect on the general fragmentation of the indolosteroids. Even the loss of water or carbon monoxide from the molecular ion has been suppressed. The N-benzyl (XXVII) and 5'-benzyloxy compounds (XXVIII) behave as described previously for the linear compounds, whilst the base peak in the spectrum of the N-methyl compound (XXVI) is at m/e 157 ($34.8\% \Sigma_{50}$) for the retro-Diels-Alder decomposition of the parent ion. The intensity of the peaks at the low mass end of the spectra have dropped considerably, due to the absence of the sidechain at C-17.

6-oximino and 6α-nitro indolosteroids.

The effect of these substituents will be discussed briefly as only linear compounds where available in each case.

It has been previously shown[32] that oxime groups do not exert a strong directing influence on the fragmentation of steroids. This

FIGURE 16


C8H17
N
H
NOH
488M
456
143
182
194
472
100
90
80
70
60
50
40
30
20
10
0
140 150 160 170 180 190 200 210 220 230 240 250 450 460 470 480 490 500

can be seen in Figure 16. The spectrum of the oxime (XIV) shows losses typical of this group, such as oxygen atom, hydroxyl and water losses. This is accompanied by the normal loss of the steroidal methyl group. The series of peaks from m/e 456 upwards is formed by combinations of these losses. A metastable peak is observed at m/e 426.0 (calculated 426.0) for the transition m/e $488^{+} \longrightarrow 456^{+}$. This may be explained as being due to consecutive losses of hydroxyl and methyl groups, analogous to the $[M-(CH_3 + H_2O)]$ ion in the ketone spectra.

The ion at m/e 456 decomposes to m/e 194 as shown by the metastable at m/e 82.5 (calculated 82.5). This corresponds to ring B cleavage, although a mass measurement would be required to determine the composition of this ion. The m/e 182 ion is probably formed from the molecular ion by ring B cleavage, initiated by the oxime group. It can be seen that the retro-Diels-Alder peak at m/e 143 is of much less importance, its intensity being only 6.8% Σ_{50}. The N-benzyl compound (XV) behaves in a similar manner although, as before, this substituent leads to a stabilization of the molecular ion with respect to fragment ions.

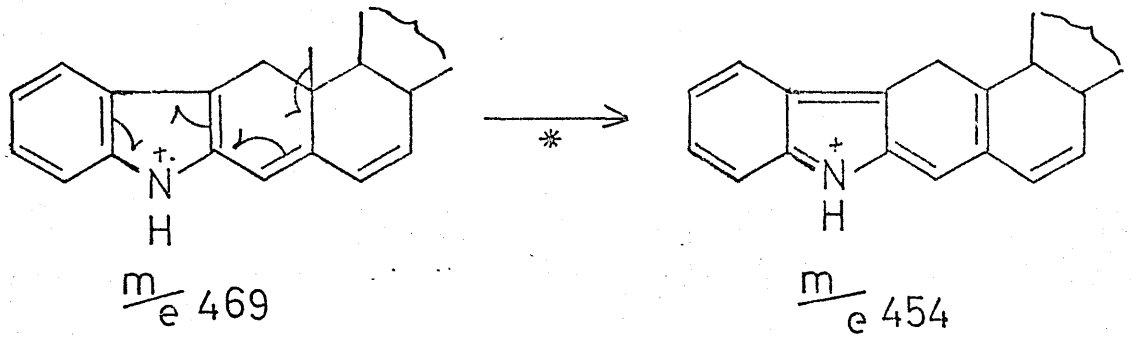
The spectrum of 6α-nitro-5α-cholestano (3,2-b) 5'-methoxyindole is shown in Figure 17. Although there has been a marked reduction

in the intensity of the retro-Diels-Alder ion at m/e 173 (m^* observed 56.0, m^* calculated 56.0, for the process $534^+ \rightarrow 173^+$), the nitro group obviously does not exert as strong an influence on the fragmentation pattern as does the oximino group. A metastable peak at m/e 440.0 (calculated 440.1) indicates that the parent ion decomposes by loss of HNO_2 to m/e 487. This loss is also observed in the other nitro compounds examined (XVI, XVIII and XIX), but in all cases they behaved, in general, like the correspondingly substituted linear indolosteroids.

Indolosteroids with unsaturation on steroidal nucleus.

The spectrum of cholest-4,6-dieno (3,2-b) N-methylindole (XXXII) is relatively simple. The parent ion is the base peak ($27.1\% \Sigma_{50}$) and the only important fragment ion is at m/e 222 ($4.1\% \Sigma_{50}$). This is probably formed by cleavage of the C9 - C10 and C7 - C8 bonds of ring B with a hydrogen transfer to the charged fragment.

It was observed that although this is a linear indolosteroid, the (M - 15) fragment ion (2.9% relative intensity) had a strong metastable peak associated with its formation (m^* observed 439.8, m^* calculated 439.5 for the decomposition $469^+ \rightarrow 454^+$). This would indicate the formation of this ion by the process shown



m/e 469

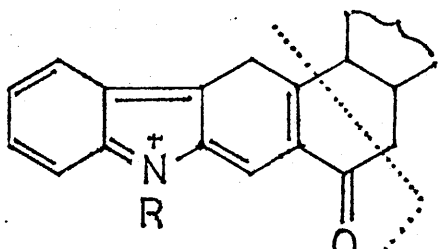
m/e 454

FIGURE 18

opposite in Figure 18 as in the case of the angular compounds.

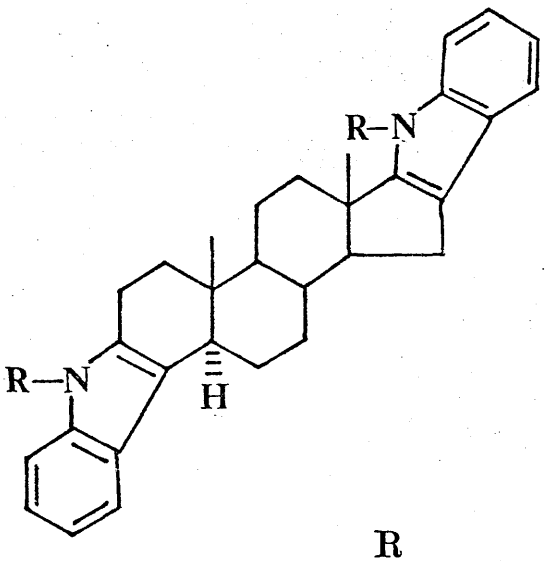
The spectrum of cholest-5-eno (3,4-b) indole (XXXVI) shows an even more dramatic simplification of the spectrum with a parent ion intensity of 35% Σ_{50}. The most important fragment ion is at m/e 209 formed by retro-Diels-Alder decomposition of ring B. (1.3%) This may have been expected to have been a more abundant ion, but this is not the case, probably due to delocalisation of the π electrons over the indole ring system. Similar results were obtained for compounds XXXVII and XXXVIII with parent ion intensities of 41.3% Σ_{50}. and 42.7% Σ_{50} respectively. However, the latter compound had 8.5% Σ_{50} intensity for the tropyllium ion at m/e 91.

The spectra of the α,β unsaturated ketones XXXIII - XXXV follow the same general fragmentation pattern. In contrast to the ketones mentioned previously, they exhibit neither loss of water nor carbon monoxide from the molecular ions. The major breakdown is the loss of a methyl radical, presumably the C19 radical, to give the highly conjugated ion shown below.

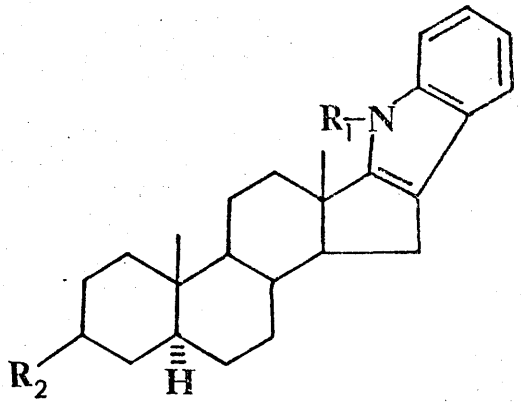


(M−15) (I)

FIGURE 19

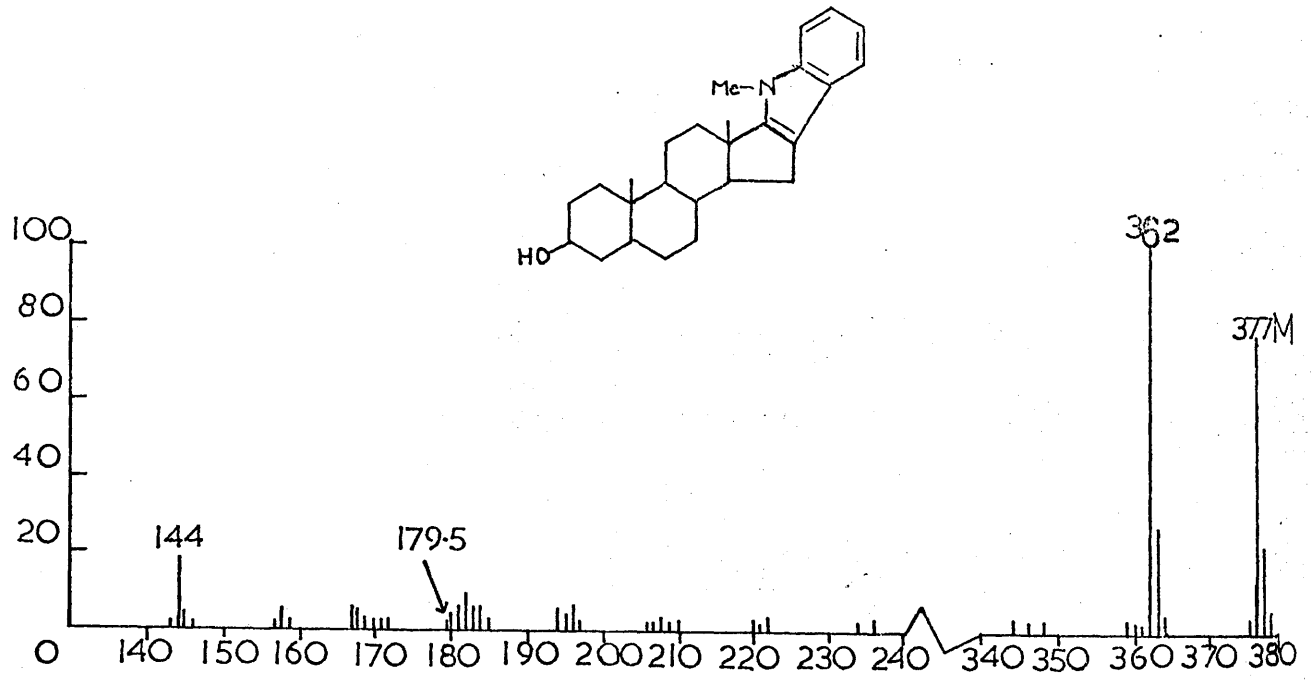


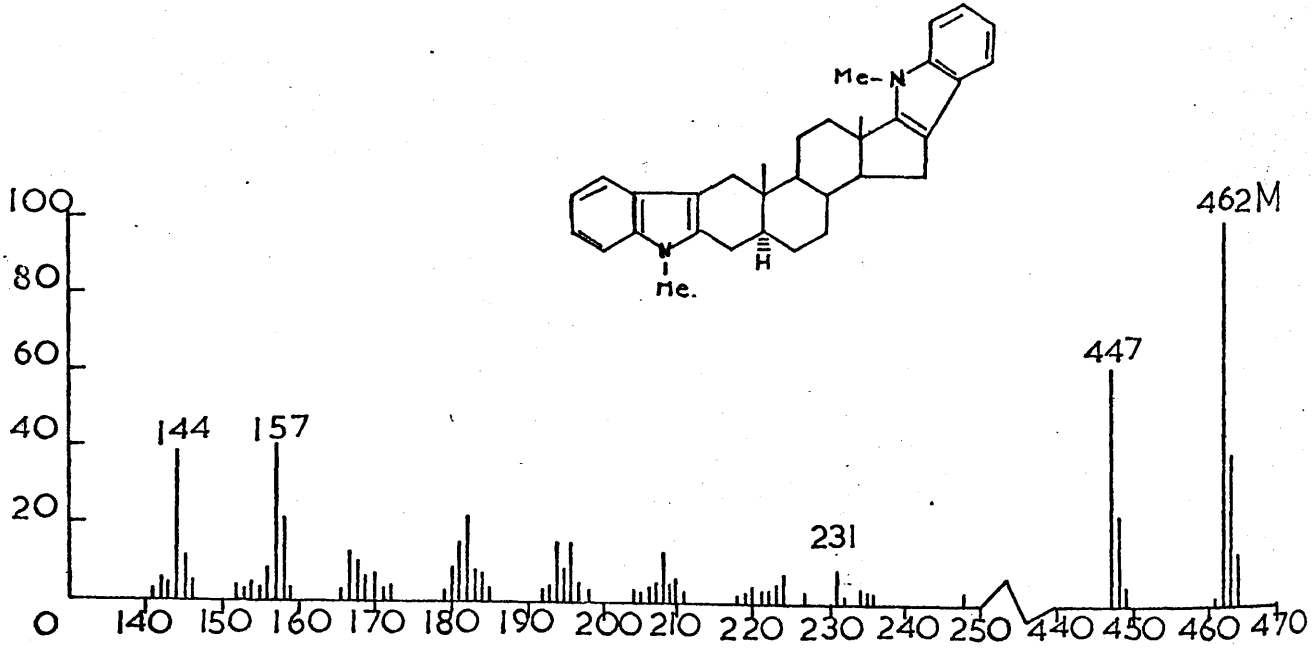
	R
XXXX	CH_3
XXXXI	$PhCH_2$



	R_1	R_2
XXXXII	CH_3	OH
XXXXIII	CH_3	CH_3COO
XXXXIV	$PhCH_2$	CH_3COO

FIGURE 20


Me-N
HO
100
80
60
40
20
0
144
179·5
362
377M
140 150 160 170 180 190 200 210 220 230 240 340 350 360 370 380


Me-N
N
Me.
H
100
80
60
40
20
0
144
157
231
447
462M
140 150 160 170 180 190 200 210 220 230 240 250 440 450 460 470

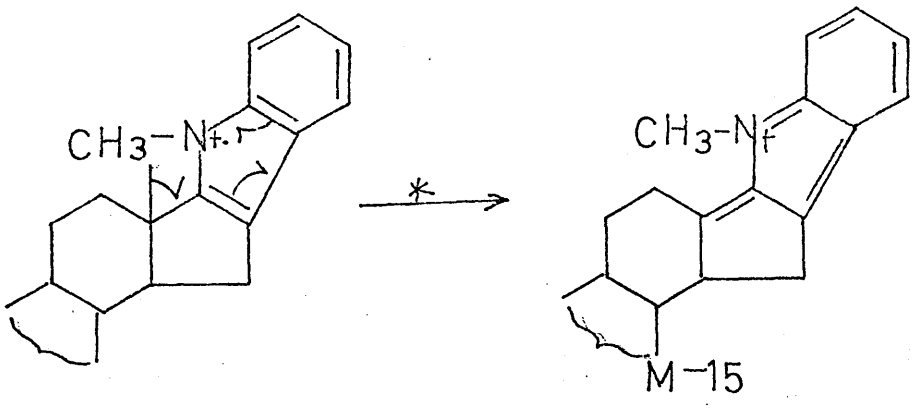


FIGURE 21a

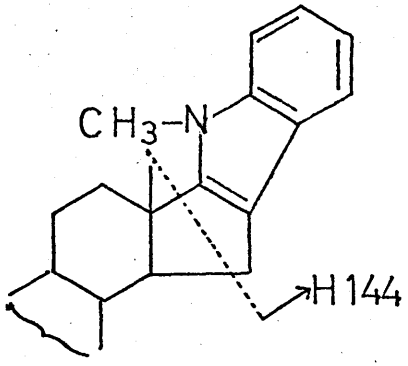


FIGURE 21b

This then decomposes by fragmentation (1) e.g., for XXXIII there is a metastable at m/e 82.5 (calculated 82.5) for $456^+ \rightarrow 194^+$. This ion further breaks down by loss of carbon monoxide to m/e 166 (m^* observed 142.1, calculated 142.0). The formation of the other important fragment ion (m/e 180 in XXXIII) is probably by cleavage of C5 - C6 and C9 - C10 bonds with hydrogen transfer to the neutral fragment.

Compounds with an indole ring fused on steroidal ring D.

The compounds investigated are shown in Figure 19 and the spectrum of 3β-hydroxy-5α-androstano (17,16-b) N-methylindole (XXXXII) is in Figure 20. The base peak observed in the spectrum is the (M - 15) ion. The steric crowding between the N-methyl group and the C - 18 angular methyl gives rise to the formation of m/e 362 as shown in Figure 21a. A metastable peak is found at m/e 349.5 (calculated 349.5) for this decomposition.

The metastable peak analysis below shows that m/e 362 decomposes to m/e 344 and m/e 144.

m^* observed.	m^* calculated.	Process.
327.0	327.0	$362^+ \rightarrow 344^+ + 18$
57.2	57.1	$362^+ \rightarrow 144^+ + 218$

Figure 21b shows the expected decomposition to give m/e 144. However, the only metastable observed for its formation is from the (M - 15)ion. Analogous metastable ions are found in the spectra of compounds XXXXIII and XXXXIV and it was noted that the metastable for the formation of m/e 144 from the parent was not present.for any of these compounds. The acetoxy compounds mentioned show a similar fragmentation pattern with the elimination of acetic acid in place of water.

An interesting peak in the spectrum of XXXXII is that at m/e 179.5. This doubly charged ion represents the loss of water from the parent, the ion formed at m/e 359 being stable though not intense.

The spectrum of the di-indole (XXXX) compound is shown in Figure 20 and we see that the most important fragment ion is the loss of methyl, presumably from the C - 18 methyl group. It can be seen that the formation of m/e 144 as above (m^* observed, 46.4 m^* calculated 46.4 for $447^+ \longrightarrow 144^+$) is as important as the retro-Diels-Alder fragmentation to give m/e 157. There is no metastable peak for this last process from either the molecular or the (M - 15) ion.

The overall fragmentation of the benzyl substituted di-indole (XXXXI) is similar to compounds XXXX, though as with other benzyl substituted compounds the fragment ions are less intense.

Conclusion.

The mass spectral investigation of the indolosteroids has shown it to be possible to differentiate between the linear and angular structures, although introduction of a benzyl substituent on the indole nitrogen atom, or of a benzyloxy group on the indole ring (C5) makes the spectra obtained very similar. The fragmentation of these compounds can be explained in many cases by postulating charge localization on the nitrogen atom. The linear compounds suffered decomposition mainly by the retro-Diels-Alder reaction, whereas the angular compounds show various ions formed by cleavage of rings A and B of the steroid nucleus. A metastable peak associated with the loss of methyl from the molecular ions has been shown to be characteristic of simple angular compounds, as well as unsaturated linear and angular indolosteroids.

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EXPERIMENTAL.

The mass spectra were determined on an A.E.I. M.S.9 mass spectrometer using the direct insertion lock. The ionizing voltage was 70eV and the trap current 100μA. The source temperature was maintained at 240° - 260°C unless otherwise stated.

Mass measurements were carried out at a resolution of 10,000 on a 10% valley definition.

The mass spectra are tabulated overleaf.

5α-CHOLESTANO(3,2-b)INDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
53	0.7	123	0.6	180	2.5
55	6.5	128	0.5	181	1.6
56	1.5	129	0.5	182	4.3
57	6.0	130	4.2	183	0.9
58	2.6	131	1.3	184	0.6
77	0.7	133	0.5	193	0.5
79	1.7	142	1.0	194	1.6
81	3.8	143	100.0	195	0.6
82	0.5	144	16.5	196	1.9
83	1.8	145	2.3	197	0.5
91	1.5	155	0.5	305	0.6
93	1.8	156	0.8	331	0.5
95	3.2	157	0.7	444	0.9
97	0.9	158	0.6	457	0.5
105	1.5	159	0.5	458	1.7
107	1.8	160	0.5	459	50.5M
115	0.6	167	1.9	460	18.5
117	0.6	168	3.1	461	3.6
119	0.7	169	0.6		
121	0.7	170	0.9		

5α-CHOLESTANO(3,2-b)N-METHYLINDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
51	0.5	90	3.2	143	0.9	194	2.3
52	1.1	91	0.6	144	4.6	195	1.6
53	0.5	93	2.3	145	1.9	196	4.1
55	6.2	95	3.2	147	0.5	197	1.2
56	2.2	96	0.6	149	0.5	198	0.6
57	6.9	97	1.5	155	0.6	207	0.7
66	2.0	105	1.2	156	4.2	208	1.4
67	0.6	107	1.5	157	100.0	209	0.6
68	4.4	109	1.3	158	16.8	210	1.9
69	1.3	111	0.7	159	1.7	211	0.5
70	3.2	115	0.6	167	0.8	319	1.2
77	0.6	117	0.5	168	0.6	320	0.5
79	1.3	119	0.7	169	0.6	333	0.5
81	3.3	121	0.7	170	0.7	345	0.9
82	0.7	123	0.6	172	0.5	347	0.5
83	2.2	128	0.5	180	0.6	360	0.8
84	0.5	129	1.0	181	2.0	447	0.5
85	0.9	130	0.7	182	2.6	448	1.4
86	1.6	131	0.7	183	0.7	449	0.7
88	2.3	142	1.8	184	0.9	471	2.2

5α-CHOLESTANO(3,2-b)N-METHYLINDOLE (Contd.)

m/e	%Abund.
472	3.0
473	79.8M
474	29.8
475	5.2
476	0.6

5α-CHOLESTANO(3,2-b)N-BENZYLINDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
50	0.7	73	2.1	98	0.9	128	0.5
51	0.8	74	0.5	99	0.6	129	1.2
52	0.5	77	1.4	101	0.5	130	1.6
53	1.4	78	0.6	104	0.5	131	1.1
54	1.2	79	2.7	105	2.4	133	1.0
55	12.4	80	0.7	106	0.7	135	0.9
56	3.9	81	6.2	107	2.5	137	0.7
57	12.2	82	1.5	108	0.7	142	3.0
58	0.7	83	3.8	109	2.5	143	3.0
60	2.1	84	1.1	110	0.7	144	3.0
61	0.5	85	2.0	111	1.3	145	0.9
63	0.5	87	0.7	115	1.3	147	0.8
64	0.6	89	0.8	116	0.5	149	0.8
65	1.2	91	42.5	117	1.0	156	1.1
66	0.5	92	3.8	119	1.3	157	0.7
67	4.0	93	2.8	120	0.5	159	0.6
68	1.4	94	0.8	121	1.7	161	0.7
69	7.9	95	2.4	122	0.5	167	1.3
70	2.3	96	1.0	123	1.4	168	1.2
71	4.9	97	2.6	125	0.7	180	2.4

5α-CHOLESTANO(3,2-b)N-BENZYLINDOLE (Contd.)

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
181	1.3	234	10.3	547	1.7
182	1.5	235	1.3	548	3.3
183	0.7	259	0.5	549	100.0M
190	0.5	260	0.7	550	44.0
193	0.5	270	1.0	551	9.4
194	2.3	271	0.5	552	0.9
195	0.7	272	1.4		
196	0.7	273	0.7		
197	0.7	274	0.5		
204	0.6	284	0.7		
206	0.6	286	1.4		
208	0.5	287	0.5		
217	1.7	395	0.8		
218	5.8	409	0.5		
219	1.3	421	0.6		
220	2.3	436	0.6		
221	1.0	459	0.6		
231	1.0	464	0.5		
232	27.7	534	1.8		
233	48.7	535	0.8		

5α-CHOLESTANO(3,2-b)5'-METHYLINDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
50	0.7	77	1.8	101	0.8	130	0.5
51	0.8	78	0.8	105	2.5	131	1.0
52	0.6	79	2.9	106	0.6	133	1.1
53	1.9	80	1.0	107	2.6	135	1.1
54	1.5	81	7.3	108	0.8	137	0.9
55	15.5	82	2.3	109	3.0	142	0.6
56	4.2	83	4.8	110	0.9	143	1.1
57	13.9	84	1.7	111	1.9	144	4.1
58	0.9	85	2.9	112	0.7	145	2.2
60	3.4	87	1.3	113	0.5	146	0.6
61	0.8	89	0.9	115	1.1	147	0.9
64	0.7	91	2.9	117	0.8	149	1.2
65	0.8	92	0.8	119	1.4	151	0.6
67	3.9	93	2.9	120	0.6	152	0.7
68	1.9	94	0.8	121	2.2	154	0.5
69	11.2	95	5.4	122	0.6	155	0.7
70	2.8	96	1.4	123	1.6	156	4.2
71	7.1	97	3.6	124	0.5	157	100.0
73	3.5	98	1.5	125	0.9	158	20.5
74	0.7	99	0.9	129	1.5	159	2.8

5α-CHOLESTANO(3,2-b)5'-METHYLINDOLE (Contd.)

m/e	%Abund.	m/e	%Abund.
160	0.5	208	1.6
161	0.8	209	0.7
163	0.5	210	1.7
166	0.5	241	0.5
167	1.0	259	0.6
168	0.6	319	0.8
169	0.6	458	1.3
170	0.9	459	0.7
171	0.7	471	0.9
180	1.0	472	2.6
181	1.8	473	64.0M
182	2.5	474	25.9
183	0.8	475	4.4
184	0.9	476	0.6
185	0.6		
194	2.4		
195	1.5		
196	3.7		
197	1.1		
198	0.5		

5α-CHOLESTANO(3,2-b)5'-METHOXYINDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
53	0.5	121	0.6	175	1.8	489	81.0
55	4.5	123	0.5	181	0.5	490	30.5M
56	1.2	130	0.5	182	0.5	491	5.2
57	4.6	132	0.5	186	0.6	492	0.6
67	1.8	133	0.6	188	0.6		
69	3.2	142	1.0	196	0.5		
70	0.6	143	0.6	197	0.9		
71	1.9	147	0.6	198	1.5		
77	0.5	153	0.7	200	0.7		
79	1.2	153.5	0.5	210	1.3		
81	2.9	158	10.6	211	0.7		
83	1.4	159	1.7	212	2.3		
91	1.1	160	4.3	213	0.6		
93	1.6	162	1.1	214	0.5		
95	2.6	168	1.3	224	1.0		
97	0.8	169	0.9	226	1.3		
105	1.3	170	0.6	474	1.5		
107	1.6	172	0.5	475	0.7		
109	1.0	173	100.0	487	1.0		
119	0.8	174	18.8	488	3.2		

5α-CHOLESTANO(3,2-b)5'-BENZYLOXYINDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
50	0.7	80	0.5	117	0.7	155	0.6
51	0.6	81	6.2	118	0.7	156	0.7
53	0.8	82	0.8	119	1.4	157	0.7
54	0.5	83	3.0	120	0.5	158	14.0
55	9.1	84	0.5	121	1.4	159	30.7
56	2.2	85	0.8	123	0.9	160	6.2
57	11.1	91	24.2	129	0.6	161	1.3
58	0.5	92	2.9	130	2.7	167	0.6
60	0.5	93	3.3	131	1.4	168	0.9
63	0.6	94	0.7	132	2.8	169	0.9
65	2.5	95	5.2	133	1.3	170	1.1
67	3.1	96	0.7	134	0.6	171	1.0
68	0.8	97	1.6	135	0.8	172	1.1
69	8.8	105	2.4	142	0.7	173	1.4
70	1.2	106	0.5	143	1.0	174	0.6
71	4.1	107	3.1	144	0.7	175	0.5
73	0.5	108	0.5	145	0.9	182	1.1
77	0.9	109	2.2	146	2.8	183	1.6
78	0.5	111	0.7	147	1.4	184	2.1
79	2.1	115	0.5	149	0.5	185	1.2

5α-CHOLESTANO(3,2-b)5'-BENZYLOXYINDOLE (Contd.)

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
186	1.2	247	0.6	447	1.0
187	0.5	248	1.7	458	0.6
195	0.7	249	6.8	460	0.5
196	2.2	250	4.0	474	100.0
197	1.7	251	0.8	475	49.8
198	3.3	252	0.5	476	11.5
199	1.6	264	0.5	477	1.6
200	0.6	276	0.7	559	0.7
206	0.6	286	0.6	560	1.5
209	0.6	288	0.7	561	0.6
210	1.7	302	0.8	562	0.5
211	1.2	306	0.5	563	2.7
212	1.8	320	1.6	564	4.7
213	0.8	321	0.5	565	65.8M
224	0.6	334	1.1	566	27.5
234	0.5	346	0.8	567	5.8
235	0.7	360	0.7	568	0.8
237	1.5	388	0.5		
238	0.5	398	0.8m*		
239	0.5	446	2.6		

5α-CHOLESTANO(3,2-b)5'-CHLOROINDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
50	0.5	81	6.3	111	1.4	155	0.7
51	0.5	82	1.4	115	1.0	161	0.9
53	1.3	83	4.0	117	0.5	162	0.5
54	0.9	84	1.0	119	1.3	163	0.5
55	11.8	85	2.0	120	0,5	164	2.5
56	2.9	91	2.2	121	1.3	165	0.8
57	12.9	92	0.5	123	1.2	166	1.0
58	0.7	93	2.9	125	0.7	167	1.3
60	1.1	94	0.7	129	0.6	168	0.6
64	1.2	95	5.2	131	0.6	169	0.7
65	0.5	96	1.1	133	0.9	169.5	0.5
67	4.1	97	2.8	135	0.9	176	0.6
68	1.3	98	0.8	137	0.6	177	100.0
69	9.1	99	0.5	141	0.5	178	16.6
70	1.8	105	2.4	142	2.7	179	33.0
71	4.9	106	0.5	143	2.0	180	5.8
73	1.1	107	2.6	144	0.5	181	1.9
77	1.1	108	0.5	145	0.5	182	0.6
79	2.6	109	2.3	147	0.7	190	0.5
80	0.6	110	0.5	149	0.6	191	0.5

5α-CHOLESTANO(3,2-b)5'-CHLOROINDOLE (Contd.)

m/e	%Abund.	m/e	%Abund.
192	0.7	493	53.0M
193	0.5	494	19.9
194	0.7	495	20.5
195	0.6	496	6.5
201	0.5	497	2.0
202	1.1		
203	0.5		
204	0.9		
214	1.6		
215	0.9		
216	2.4		
217	0.9		
218	1.0		
228	1.1		
229	0.5		
230	1.5		
231	0.6		
232	0.6		
459	0.6		
488	0.7		

6-OXO-5α-CHOLESTANO(3,2-b)INDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
53	0.5	107	1.7	156	1.0	206	1.0
55	5.7	109	1.7	157	0.5	207	1.4
56	1.3	115	0.5	158	0.5	208	1.1
57	7.2	117	0.7	159	0.5	209	0.6
58	0.6	119	0.6	161	0.5	210	1.5
67	2.1	121	1.7	167	0.5	211	0.5
68	0.5	123	0.6	168	2.6	212	0.7
69	4.2	129	0.5	169	5.4	220	1.1
70	0.7	130	10.3	170	1.0	232	0.6
71	3.2	131	4.4	171	1.2	247	0.5
77	0.6	132	0.5	175	0.6	319	0.6
79	1.5	133	0.7	180	3.7	345	0.5
81	3.1	135	1.4	181	2.8	360	0.6
82	0.5	142	0.8	182	7.5	440	0.7
83	2.1	143	93.5	183	2.4	455	0.5
91	1.0	144	15.5	184	1.7	456	0.6
93	2.2	145	1.7	193	0.5	457	0.6
95	3.2	147	0.7	194	2.3	458	2.2
97	1.0	149	1.0	195	0.7	459	1.2
105	1.0	155	0.7	196	2.0	471	1.5

6-OXO-5α-CHOLESTANO(3,2-b)INDOLE (Contd.)

m/e	%Abund.
472	3.1
473	100.0M
474	37.0
475	7.8
476	0.9

6-OXO-5α-CHOLESTANO(3,2-b)N-METHYLINDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
53	0.8	108	1.0	159	1.6	221	0.6
55	6.6	115	1.0	167	1.7	222	0.7
56	2.0	116	0.5	168	1.0	224	0.8
57	7.1	117	0.7	169	0.9	234	0.7
58	2.1	119	0.5	170	0.9	333	0.8
67	2.1	121	1.0	171	0.6	359	0.7
68	0.5	128	0.6	180	1.4	374	0.7
69	3.6	129	1.0	181	4.0	469	0.5
70	0.8	130	0.8	182	5.1	470	0.5
71	2.8	131	0.7	183	1.0	471	0.5
77	0.9	135	0.8	184	0.8	472	2.1
79	1.6	142	1.9	194	3.7	473	1.0
81	2.5	143	0.9	195	2.5	485	1.7
83	1.3	144	10.2	196	6.8	486	2.6
91	1.5	145	2.6	197	2.3	487	95.0 M
93	2.0	149	0.6	198	1.7	488	35.5
95	2.1	155	0.6	208	1.9	489	7.0
97	0.6	156	4.9	209	0.5	490	0.9
105	1.0	157	100.0	210	1.3		
107	1.3	158	15.0	220	0.6		

6-OXO-5α-CHOLESTANO(3,2-b)N-BENZYLINDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
50	1.0	72	0.5	97	4.3	120	0.7
51	1.1	73	4.3	98	1.5	121	3.3
52	0.7	74	0.9	99	0.8	122	0.8
53	2.2	77	2.1	101	0.9	123	2.1
54	1.6	78	1.1	103	0.5	124	0.6
55	19.2	79	3.9	104	0.6	125	1.1
56	5.5	80	1.2	105	2.9	128	0.8
57	20.5	81	8.0	106	0.7	129	2.0
58	1.3	82	2.3	107	3.1	130	1.9
59	0.5	83	6.2	108	0.9	131	1.3
60	4.1	84	1.9	109	4.1	133	1.6
61	0.9	85	3.2	110	1.1	134	0.5
63	0.5	87	1.4	111	2.2	135	2.1
65	1.9	89	1.1	112	0.6	136	0.6
66	0.6	91	63.0	113	0.6	137	1.2
67	6.3	92	5.6	115	1.4	139	0.5
68	2.4	93	4.0	116	0.8	140	0.5
69	13.0	94	1.0	117	1.1	141	0.5
70	3.3	95	7.0	118	0.4	142	3.4
71	10.1	96	1.9	119	1.8	143	3.1

6-OXO-5α-CHOLESTANO(3,2-b)N-BENZYLINDOLE (Contd.)

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
144	2.3	182	3.4	231	3.1	286	0.9
145	1.0	183	0.9	232	33.0	300	0.6
147	1.0	184	0.5	233	63.9	409	0.9
149	1.5	185	0.6	234	14.6	435	0.8
151	0.6	193	0.7	235	1.7	450	0.7
154	0.6	194	4.3	241	0.7	459	0.6
155	0.6	195	1.0	245	0.6	472	1.0
156	1.4	196	0.6	246	0.7	473	0.6
157	1.1	204	0.8	247	0.5	545	1.2
159	0.7	205	0.6	257	0.6	546	0.9
161	0.8	206	1.1	258	1.4	547	1.0
163	0.6	208	0.8	259	0.9	548	2.0
167	2.7	210	0.6	260	0.7	549	1.1
168	1.8	217	1.5	270	1.8	561	1.8
169	0.6	218	6.3	271	1.3	562	2.7
175	0.6	219	1.5	272	2.7	563	100.0M
177	0.5	220	5.7	273	1.8	564	46.1
179	0.5	221	1.6	274	1.6	565	9.8
180	4.4	222	0.5	275	0.5	566	1.6
181	2.1	230	1.5	284	1.2		

6-OXO-5α-CHOLESTANO(3,2-b)5'-CHLORO-INDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
50	0.6	83	3.1	122	0.5	161	0.8
51	0.6	85	0.7	123	1.3	163	0.6
53	2.1	91	2.9	127	0.5	164	11.5
54	0.8	92	0.6	128	0.6	165	4.4
55	13.8	93	4.1	129	0.8	166	4.5
56	2.8	94	0.8	130	0.7	167	5.0
57	13.7	95	5.3	131	0.7	168	1.4
58	3.5	96	0.7	133	1.4	169	0.6
65	0.8	97	1.7	135	2.2	175	1.0
67	4.5	105	2.2	137	0.5	176	0.8
68	1.3	106	0.5	140	0.6	177	92.0
69	7.6	107	3.2	141	1.0	178	15.5
70	1.5	108	0.6	142	2.7	179	30.0
71	5.8	109	2.8	143	3.4	180	6.4
77	2.0	111	0.7	144	0.8	181	5.1
78	0.6	115	1.5	145	0.5	182	1.7
79	3.5	116	0.5	147	1.2	183	0.8
80	0.8	117	0.7	149	2.1	189	0.7
81	5.9	119	1.4	154	1.2	190	1.3
82	0.8	121	2.8	155	1.0	191	0.9

6-OXO-5α-CHOLESTANO(3,2-b)5'-CHLORO-INDOLE (Contd.)

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
192	1.0	230	3.0	474	1.2
193	0.8	231	0.9	489	0.8
194	0.8	232	1.1	490	0.8
201	1.8	240	0.8	491	0.9
202	3.3	241	1.7	492	2.3
203	1.4	242	1.5	493	1.1
204	2.5	243	1.2	494	0.9
205	1.0	244	2.1	505	2.4
206	0.9	245	0.8	506	3.3
207	0.6	246	1.4	507	100.0M
214	4.0	247	1.0	508	28.0
215	2.7	254	1.0	509	28.0
216	6.5	255	0.5	510	12.9
217	3.0	256	0.7	511	2.4
218	3.1	266	0.7		
219	1.2	268	0.6		
220	0.7	353	0.6		
227	0.5	394	0.7		
228	2.4	472	1.1		
229	0.9	473	2.0		

6-OXO-5α-CHOLESTANO(3,2-b)5'-METHYLINDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
50	0.7	83	2.2	133	0.9	171	0.7
51	0.6	85	0.6	135	1.3	172	0.6
53	1.4	91	2.3	142	0.5	173	0.5
54	0.7	93	2.7	143	1.0	175	0.5
55	8.6	94	0.5	144	10.5	180	2.1
56	3.1	95	3.4	145	3.6	181	3.5
57	8.5	96	0.5	146	0.8	182	6.0
58	7.5	97	1.0	147	0.7	183	1.3
65	0.6	105	1.4	149	1.1	184	1.1
67	3.3	107	1.9	154	0.6	193	0.6
68	1.0	109	1.8	155	0.8	194	4.2
69	4.8	115	0.7	156	4.4	195	3.3
70	1.2	117	0.7	157	90.0	196	7.6
71	3.9	119	0.8	158	16.5	197	2.5
77	1.3	121	1.6	159	2.1	198	2.2
78	0.5	123	0.7	166	0.5	207	0.7
79	2.4	128	0.6	167	1.6	208	2.5
80	0.5	129	0.6	168	0.9	209	0.9
81	3.6	130	0.5	169	0.9	210	1.8
82	0.6	131	0.8	170	1.2	220	1.0

6-OXO-5α-CHOLESTANO(3,2-b)5'-METHYLINDOLE (Contd.)

m/e	%Abund.	m/e	%Abund.
221	1.4	486	4.5
222	1.3	487	100.0M
223	0.6	488	37.0
224	1.5	489	7.0
226	0.6	490	1.0
232	0.5		
234	1.2		
246	0.7		
247	0.6		
248	0.5		
333	0.7		
359	0.7		
374	0.7		
454	0.7		
469	1.1		
470	1.0		
471	1.0		
472	2.2		
473	1.1		
485	3.4		

6-OXO-5α-CHOLESTANO(3,2-b)5'-BROMO-INDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
53	1.8	91	3.3	128	0.5	163	0.6
54	0.6	92	0.6	129	1.6	166	0.8
55	17.8	93	6.7	130	1.5	167	10.6
56	2.9	94	0.8	131	1.0	168	3.0
57	16.0	95	8.6	133	1.6	169	0.6
58	0.7	96	1.0	135	2.9	175	0.7
65	0.6	97	2.5	137	0.6	177	0.6
67	5.8	105	2.6	141	1.4	179	1.1
68	1.3	107	4.8	142	7.6	180	4.8
69	10.5	108	0.7	143	8.2	181	13.1
70	1.4	109	4.7	144	1.8	182	3.7
71	8.1	110	0.5	145	0.7	183	1.2
77	1.8	111	1.0	147	1.2	192	0.7
79	4.7	115	2.1	149	3.3	193	0.9
80	0.8	116	0.7	154	1.5	194	1.6
81	9.0	117	0.6	155	1.2	195	1.1
82	1.0	119	1.5	156	0.5	196	0.5
83	5.3	121	4.0	157	0.7	204	0.6
84	0.5	122	0.6	159	0.6	205	1.2
85	1.1	123	1.6	161	0.8	206	1.1

6-OXO-5α-CHOLESTANO(3,2-b)5'-BROMO-INDOLE (Contd.)

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
207	1.3	246	0.9	289	0.6	549	1.0
208	9.2	247	1.2	290	1.6	550	2.2
209	3.5	248	2.0	292	0.6	551	93.6M
210	9.6	250	1.1	298	0.5	552	36.8
211	3.4	258	2.8	300	0.6	553	100.0
217	0.7	259	1.8	310	0.5	554	35.9
218	0.8	260	3.4	312	0.5	555	5.9
219	0.9	261	2.5	326	0.7	556	0.9
220	0.5	262	2.4	438	0.5		
221	69.5	263	0.9	440	0.5		
222	11.9	264	0.7	472	3.4		
223	68.6	272	1.5	473	5.9		
224	10.9	273	0.5	474	2.1		
225	0.9	274	3.1	518	0.5		
231	0.5	275	0.7	520	0.5		
233	0.5	276	1.7	535	0.6		
234	1.0	285	1.0	536	2.0		
235	0.8	286	0.8	537	0.9		
236	1.0	287	1.4	538	1.7		
245	0.6	288	1.7	539	0.6		

6-OXIMINO-5α-CHOLESTANO(3,2-b)INDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
50	0.6	83	5.1	117	1.5	144	15.5
51	0.6	84	0.8	118	1.1	145	2.3
53	2.1	85	1.3	119	1.8	146	0.8
54	1.0	91	3.7	120	2.5	147	0.8
55	16.9	92	0.8	121	2.0	149	0.9
56	4.5	93	5.5	122	0.7	150	0.5
57	20.5	94	1.5	123	1.2	154	1.4
58	1.2	95	8.5	128	1.0	155	1.7
65	0.7	96	1.2	129	1.1	156	2.5
67	4.4	97	2.5	130	8.9	157	1.4
68	1.4	103	0.6	131	3.1	158	2.4
69	11.9	105	3.0	132	1.1	159	1.9
70	2.4	106	1.4	133	1.3	160	0.7
71	8.0	107	3.4	134	1.0	161	0.7
77	2.0	108	1.0	135	2.0	167	0.7
78	0.7	109	3.7	136	1.2	168	9.5
79	4.4	110	0.5	137	0.5	169	11.3
80	1.3	111	0.8	141	0.5	170	2.3
81	8.0	115	1.3	142	1.4	171	0.6
82	1.4	116	0.9	143	56.1	172	0.5

6-OXIMINO-5α-CHOLESTANO(3,2-b)INDOLE (Contd.)

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
174	0.6	208	5.6	245	2.0	346	1.1
179	0.6	209	3.8	246	2.4	357	0.6
180	11.7	210	1.3	247	1.8	360	0.5
181	7.8	211	0.7	248	0.6	375	0.6
182	30.5	217	0.8	258	0.6	385	0.5
183	11.0	218	1.8	259	0.7	426	1.0m*
184	3.5	219	1.5	260	0.7	427	1.2
185	0.9	220	2.7	261	1.0	428	0.5
191	0.5	221	1.8	263	0.5	429	0.5
192	1.5	222	1.5	301	0.5	439	0.7
193	3.4	223	1.1	302	1.1	440	1.9
194	13.1	224	3.6	303	0.5	441	0.8
195	5.5	225	0.9	316	0.7	442	0.5
196	2.0	230	1.7	317	0.7	453	0.9
197	1.1	231	1.2	327	1.2	454	5.2
198	0.7	232	3.0	328	1.0	455	9.5
204	1.0	233	2.2	329	1.0	456	53.5
205	1.5	234	1.4	333	0.5	457	31.0
206	4.8	235	0.9	342	0.8	458	7.9
207	4.4	244	1.3	343	0.8	459	1.3

6-OXIMINO-5α-CHOLESTANO(3,2-b)INDOLE (Contd.)

m/e	%Abund.
468	2.0
469	3.0
470	15.0
471	25.7
472	27.0
473	11.5
474	2.8
486	2.1
487	2.9
488	100.0M
489	38.9
490	6.1
491	1.0

6-OXIMINO-5α-CHOLESTANO(3,2-b)N-BENZYLINDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
50	2.5	76	0.9	102	0.6	128	1.3
51	2.5	77	3.2	103	0.9	129	1.5
52	1.4	78	2.4	104	0.8	130	2.7
53	3.4	79	5.9	105	3.8	131	1.9
54	1.8	80	1.9	106	1.9	132	1.5
55	20.5	81	8.3	107	4.3	133	2.2
56	8.9	82	2.2	108	1.9	134	1.7
57	24.0	83	5.3	109	4.1	135	2.8
58	1.0	84	1.2	110	0.7	136	0.9
59	0.8	85	1.2	111	0.9	137	0.6
63	1.6	89	1.0	115	1.9	139	0.5
64	0.9	90	1.0	116	1.0	140	0.5
65	4.1	91	100.0	117	1.8	141	0.6
66	1.0	92	9.8	118	1.2	142	2.3
67	7.4	93	6.4	119	2.3	143	3.9
68	2.4	94	2.3	120	3.8	144	4.5
69	12.9	95	9.4	121	2.7	145	1.4
70	4.6	96	1.6	122	1.0	146	1.3
71	9.5	97	2.6	123	1.6	147	1.3
72	0.5	98	0.5	127	0.7	148	0.6

6-OXIMINO-5α-CHOLESTANO(3,2-b)N-BENZYLINDOLE (Contd.)

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
149	1.1	174	0.9	205	2.2	234	7.2
152	0.9	175	0.7	206	3.1	235	1.9
153	0.5	176	0.6	207	2.8	236	0.6
154	1.0	178	0.7	208	3.8	241	0.5
155	1.1	179	1.2	209	2.0	242	0.6
156	1.3	180	7.9	210	1.0	243	0.8
157	1.6	181	5.3	216	0.7	244	2.9
158	1.2	182	6.4	217	2.7	245	6.2
159	1.1	183	2.3	218	5.1	246	3.7
160	0.6	184	0.9	219	3.3	247	2.1
161	0.6	191	0.9	220	8.6	248	1.4
165	0.6	192	1.6	221	4.1	249	0.9
166	0.9	193	2.3	222	1.5	254	0.8
167	4.2	194	9.8	223	0.9	255	0.6
168	2.7	195	3.2	224	0.6	256	1.2
169	1.0	196	1.5	229	0.7	257	1.5
170	0.8	197	0.6	230	3.0	258	2.5
171	0.6	202	0.6	231	3.5	259	1.7
172	0.7	203	0.5	232	12.0	260	1.5
173	0.5	204	2.1	233	19.5	261	1.3

6-OXIMINO-5α-CHOLESTANO(3,2-b)N-BENZYLINDOLE (Contd.)

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
262	0.5	297	4.3	326	0.7	393	0.6
268	1.0	298	4.5	327	0.6	394	0.6
269	1.1	299	3.8	328	1.5	406	0.6
270	7.5	300	1.7	329	1.9	407	0.5
271	6.2	301	1.2	330	1.1	408	0.7
272	13.9	302	0.5	334	0.9	409	0.5
273	7.9	308	1.2	335	2.5	417	0.7
274	2.3	309	1.5	336	2.1	418	1.0
275	0.6	310	2.6	337	1.7	419	0.7
281	1.1	311	2.2	338	1.0	424	0.6
282	1.1	312	1.7	339	0.6	425	0.5
283	1.5	313	1.0	340	0.5	431	0.7
284	7.9	314	1.0	349	0.5	432	1.0
285	6.1	315	0.6	351	1.0	433	0.9
286	2.3	320	1.5	352	0.5	434	0.5
287	1.1	321	1.2	353	0.5	435	0.6
288	0.7	322	3.0	354	5.5	438	0.5
294	0.7	323	2.4	355	1.6	446	0.5
295	1.0	324	1.6	391	0.5	447	1.1
296	4.3	325	1.1	392	0.7	448	0.6

6-OXIMINO-5α-CHOLESTANO(3,2-b)N-BENZYLINDOLE (Contd.)

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
449	0.5	475	0.8	531	2.7	563	23.5
450	0.7	476	0.6	532	1.6	564	6.7
451	0.5	477	0.6	533	0.9	565	1.0
452	0.6	485	0.5	534	0.5	576	5.2
453	0.5	487	0.7	541	0.7	577	4.6
454	3.0	488	0.7	542	0.7	578	89.0M
455	2.3	489	0.7	543	5.1	579	39.5
456	1.1	491	0.6	544	8.5	580	8.5
457	0.9	492	0.7	545	30.5	581	1.2
460	0.5	493	0.5	546	23.9		
461	0.6	503	0.7	547	16.9		
465	0.6	515	0.6	548	6.2		
466	0.5	516	0.8	549	1.7		
468	1.3	517	0.9	556	0.6		
469	1.5	518	0.7	557	0.6		
470	1.4	519	0.5	558	3.6		
471	5.1	527	0.6	559	3.7		
472	2.4	528	1.9	560	35.5		
473	0.9	529	3.5	561	26.5		
474	0.7	530	4.8	562	53.0		

6α-NITRO-5α-CHOLESTANO(3,2-b)N-BENZYLINDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
90	0.7	110	2.2	130	3.4	150	0.6
91	85.0	111	5.0	131	2.9	151	1.2
92	8.3	112	1.8	132	0.9	152	0.7
93	7.9	113	1.4	133	2.9	153	0.7
94	2.7	114	0.5	134	1.1	154	1.0
95	14.8	115	3.3	135	2.9	155	1.3
96	4.2	116	1.5	136	0.9	156	1.7
97	9.8	117	2.7	137	2.0	157	2.7
98	4.6	118	1.3	138	1.1	158	1.0
99	1.8	119	4.0	139	0.9	159	2.0
100	0.8	120	1.7	140	0.6	160	0.5
101	2.1	121	5.5	141	1.1	161	1.5
102	0.8	122	1.5	142	3.1	162	0.5
103	1.1	123	3.9	143	5.6	163	1.1
104	1.4	124	1.3	144	3.8	165	1.1
105	8.4	125	2.6	145	2.6	166	0.8
106	2.1	126	0.8	146	0.6	167	2.8
107	7.0	127	0.7	147	2.0	168	2.4
108	2.0	128	1.6	148	0.6	169	1.2
109	7.4	129	4.3	149	2.8	170	1.1

6α-NITRO-5α-CHOLESTANO(3,2-b)N-BENZYLINDOLE (Contd.)

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
171	1.5	196	1.4	222	0.8	257	1.1
172	0.5	197	0.6	227	0.5	258	1.6
173	1.3	199	0.7	228	0.7	259	2.0
175	0.7	200	0.6	229	0.6	260	1.8
177	0.7	201	0.7	230	1.8	261	0.5
178	0.7	202	0.5	231	2.8	270	5.6
179	1.1	203	0.7	232	22.3	271	2.5
180	4.9	204	1.0	233	42.5	272	4.7
181	2.7	205	1.0	234	16.0	273	2.2
182	2.7	206	2.1	235	2.6	274	1.2
183	1.3	207	1.2	236	0.5	275	0.6
184	0.6	208	1.8	241	1.1	284	4.2
185	1.4	209	0.8	242	0.6	285	2.4
187	0.7	210	0.5	243	0.5	286	1.9
189	0.8	213	1.0	244	0.9	287	0.9
191	0.7	217	1.8	245	1.3	288	0.5
192	1.0	218	5.3	246	1.8	296	0.7
193	1.8	219	2.0	247	0.9	297	0.7
194	5.8	220	6.7	248	0.9	298	1.1
195	1.8	221	2.1	256	0.8	299	0.9

6α-NITRO-5α-CHOLESTANO(3,2-b)N-BENZYLINDOLE (Contd.)

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
300	0.9	532	0.8	592	0.8
301	0.7	538	0.8	593	1.7
310	0.5	543	0.7	594	100.0M
312	0.5	544	1.0	595	45.4
324	0.5	545	3.7	596	10.0
434	0.6	546	2.4	597	1.6
440	1.2	547	5.2		
441	0.7	548	5.4		
451	0.8	549	5.2		
454	0.6	550	2.0		
455	0.6	551	0.5		
459	1.4	560	2.3		
460	0.5	561	1.4		
466	1.3	562	2.0		
467	0.6	563	1.0		
468	0.5	564	3.4		
481	0.9	565	1.7		
504	0.5	578	0.6		
505	0.5	579	1.2		
524	0.5	580	0.5		

6α-NITRO-5α-CHOLESTANO(3,2-b)5'-METHOXYINDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
53	0.5	106	0.5	157	0.5	185	0.7
55	6.9	107	2.6	158	7.1	186	2.1
56	1.6	109	1.5	159	2.5	187	1.3
57	8.3	111	0.5	160	6.4	188	0.9
58	0.5	117	0.6	161	1.6	196	1.0
67	1.9	119	1.2	162	0.5	197	1.3
69	4.8	121	1.0	166	0.7	198	2.8
70	0.7	123	0.6	166.5	0.5	199	1.0
71	3.8	130	0.6	167	0.8	200	1.7
77	0.6	131	1.0	168	0.6	201	0.5
79	1.7	132	0.5	171	0.5	210	4.6
81	4.1	133	0.8	172	0.9	211	1.9
82	0.5	135	0.5	173	53.5	212	4.9
83	2.4	142	0.8	174	16.5	213	1.4
84	0.5	143	0.9	175	2.1	214	0.5
91	1.5	144	0.5	180	0.6	224	3.7
93	2.2	145	0.8	181	0.7	225	1.4
95	3.7	146	0.5	182	0.8	226	1.9
97	1.2	154	0.5	183	0.5	227	0.5
105	2.9	155	0.5	184	0.5	238	1.1

6α-NITRO-5α-CHOLESTANO(3,2-b)5'-METHOXYINDOLE (Contd.)

m/e	%Abund.	m/e	%Abund.
239	0.5	536	7.5
240	0.7	537	1.1
250	0.5		
380	0.7		
421	0.6		
472	0.7		
485	0.8		
486	1.5		
487	3.6		
488	3.2		
489	2.9		
490	1.0		
502	0.5		
503	0.5		
504	0.9		
505	0.5		
519	1.3		
520	0.6		
534	100.0M		
535	38.5		

6α-NITRO-5α-CHOLESTANO(3,2-b)5'-BENZYLOXYINDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
50	0.6	83	3.8	118	0.5	156	1.0
51	0.6	84	0.5	119	1.6	157	0.9
53	0.6	85	0.7	120	0.5	158	11.5
55	11.0	89	0.5	121	1.3	159	19.9
56	2.6	90	0.5	123	0.8	160	5.7
57	13.8	91	41.4	129	0.5	161	1.2
58	0.7	92	4.1	130	1.6	167	0.7
63	0.6	93	3.4	131	1.8	168	1.3
65	2.7	94	0.5	132	0.9	169	1.2
67	3.0	95	5.9	133	1.1	170	1.0
68	0.5	96	0.5	135	0.7	171	1.6
69	8.1	97	1.8	142	0.7	172	1.6
70	1.4	105	3.8	143	1.2	173	1.5
71	6.2	106	0.7	144	0.8	174	0.6
77	1.0	107	3.2	145	1.6	180	0.5
78	0.5	108	0.5	146	3.2	181	0.7
79	2.2	109	1.9	147	1.2	182	1.8
80	0.5	110	0.5	149	0.5	183	2.1
81	5.9	111	0.7	154	0.5	184	2.1
82	0.7	117	1.0	155	0.9	185	1.5

6α-NITRO-5α-CHOLESTANO(3,2-b)5'-BENZYLOXYINDOLE (Contd.)

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
186	0.9	226	0.5	365	2.0	488	0.5
187	0.5	234	0.8	366	0.6	489	1.1
194	0.6	235	0.5	379	1.0	490	0.7
195	1.1	236	1.5	391	1.1	491	0.5
196	3.5	237	0.5	406	1.1	497	0.5
197	3.1	238	0.5	407	1.5	503	0.8
198	3.5	246	0.5	430	0.6	504	0.5
199	1.1	247	0.5	433	0.6	519	100.0
200	0.5	248	0.8	442	1.1m*	520	42.5
201	0.5	249	2.5	444	0.5	521	9.7
208	0.8	250	3.9	449	0.5	522	1.5
209	1.7	251	0.7	450	0.5	548	0.5
210	2.7	252	0.5	470	0.5	561	1.2
211	1.4	260	0.5	471	0.7	562	1.1
212	1.2	262	0.5	472	2.5	563	2.1
220	0.5	264	0.6	473	1.7	564	2.9
222	0.7	276	0.7	474	2.9	565	1.3
223	0.7	286	0.5	475	1.9	576	0.5
224	1.0	288	0.5	476	0.5	577	0.5
225	0.8	300	0.5	487	0.6	578	0.7

6α-NITRO-5α-CHOLESTANO(3,2-b)5'-BENZYLOXYINDOLE (Contd.)

m/e	%Abund.
579	0.5
580	1.1
581	0.7
595	1.3
596	0.6
608	0.8
609	3.2
610	82.0M
611	36.4
612	8.8
613	1.5

6α-NITRO-5α-CHOLESTANO(3,2-b)5'-CHLORO-INDOLE.

Source temperature 190°C.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
91	6.1	118	0.7	143	3.9	168	2.4
92	1.0	119	4.0	144	1.4	169	1.4
93	8.4	120	1.0	145	2.4	170	0.5
94	1.4	121	3.9	146	0.6	171	0.8
95	16.0	122	0.6	147	2.1	173	1.3
96	1.9	123	2.6	149	1.6	175	1.0
97	5.2	124	0.5	151	0.7	176	0.7
98	0.7	125	0.9	154	2.0	177	92.0
99	0.5	128	0.8	155	1.8	178	25.5
105	10.3	129	1.5	156	0.6	179	32.0
106	1.8	130	1.2	157	2.0	180	9.5
107	8.7	131	2.7	158	0.7	181	5.9
108	1.2	132	0.6	159	2.2	182	1.8
109	5.9	133	2.7	160	0.6	183	0.6
110	0.7	134	0.7	161	2.1	185	0.7
111	2.4	135	2.3	163	1.0	187	0.8
113	0.6	137	1.0	164	8.6	189	0.7
115	2.0	140	0.7	165	1.5	190	2.4
116	0.7	141	1.1	166	3.1	191	1.6
117	1.8	142	3.8	167	4.1	192	2.5

6α-NITRO-5α-CHOLESTANO(3,2-b)5'-CHLORO-INDOLE (Contd.)

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
193	2.1	220	0.6	266	0.7	494	2.3
194	2.6	227	0.8	267	0.5	495	0.8
195	1.4	228	9.0	268	1.0	503	1.2
196	0.8	229	4.4	270	0.7	504	2.2
199	0.5	230	6.4	280	0.5	505	1.1
201	1.7	231	2.6	282	0.8	506	3.9
202	4.0	232	1.9	283	0.5	507	1.7
203	1.9	233	0.6	284	0.7	508	2.8
204	3.7	240	1.1	315	1.6	509	1.0
205	1.3	241	1.1	378	0.7	510	0.6
206	1.4	242	2.3	380	0.6	523	0.6
207	1.1	243	1.4	384	0.6	536	0.8
208	0.7	244	2.0	476	1.2	537	1.3
213	0.5	245	0.7	477	0.5	538	100.0M
214	9.5	246	0.7	478	0.5	539	37.5
215	4.1	254	1.1	489	1.8	540	39.5
216	10.8	255	0.6	490	2.0	541	13.0
217	3.4	256	1.2	491	9.3	542	2.4
218	3.7	257	0.5	492	5.6		
219	1.3	258	1.2	493	5.2		

5β-CHOLESTANO(3,4-b)INDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
50	0.5	85	0.5	128	1.1	158	7.8
53	1.2	91	2.4	129	2.1	159	1.7
54	0.5	93	3.6	130	20.5	159.5	0.5
55	10.5	94	0.6	131	5.4	161	0.6
56	2.3	95	5.3	132	1.1	163	0.5
57	10.0	96	0.6	133	1.1	167	5.0
58	0.5	97	1.4	135	1.0	168	9.0
65	0.5	105	2.3	142	0.5	169	3.4
67	4.2	106	1.0	143	22.2	170	15.5
68	0.8	107	3.0	144	11.5	171	7.3
69	6.6	108	0.6	145	3.5	172	1.1
70	1.1	109	2.0	146	0.5	173	0.5
71	4.2	111	0.5	147	0.9	180	3.4
77	1.5	115	0.6	149	0.6	181	3.1
78	0.5	117	1.2	152	0.7	182	22.2
79	3.4	118	0.6	152.5	0.5	183	15.5
80	0.5	119	1.4	154	1.4	184	9.2
81	5.8	121	1.5	155	1.8	185	2.0
82	0.7	123	1.0	156	5.0	194	2.2
83	2.7	127	0.5	157	15.8	195	1.2

5β-CHOLESTANO(3,4-b)INDOLE (Contd.)

m/e	%Abund.	m/e	%Abund.
196	7.4	346	1.5
197	4.2	347	0.5
198	2.8	374	0.9
206	0.5	376	3.0
208	1.4	390	0.5
209	1.0	402	0.5
210	3.2	403	0.5
211	0.9	416	0.5
220	0.5	430	0.5
222	1.1	444	6.0
224	0.6	445	1.9
234	0.5	457	1.4
236	0.7	458	5.5
250	0.6	459	100.0M
264	0.5	460	36.5
278	0.5	461	7.5
304	0.5	462	0.9
305	1.0		
306	0.5		
319	0.5		

5β-CHOLESTANO(3,4-b)N-BENZYLINDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
50	0.7	79	3.0	105	2.5	133	1.0
51	0.7	80	0.8	106	0.6	135	0.9
53	1.6	81	6.1	107	2.9	137	0.6
54	1.1	82	1.4	108	0.6	142	2.9
55	15.0	83	3.9	109	2.3	143	2.6
56	4.7	84	1.1	110	0.6	144	1.8
57	14.5	85	2.0	111	1.3	145	0.8
58	0.8	87	0.7	115	1.4	147	0.8
60	2.2	89	0.7	116	0.7	149	0.9
61	0.6	91	55.7	117	1.0	154	0.6
65	1.4	92	4.7	119	1.4	155	0.5
67	4.2	93	3.1	120	0.5	156	1.5
68	1.4	94	0.7	121	1.9	157	0.8
69	9.4	95	4.6	122	0.5	159	0.6
70	2.5	96	1.0	123	1.2	161	0.8
71	6.1	97	2.8	125	0.7	163	0.5
73	2.2	98	0.9	128	0.6	167	2.8
74	0.6	99	0.6	129	1.2	168	1.4
77	1.5	101	0.5	130	2.0	169	0.5
78	0.7	104	0.5	131	1.1	170	0.6

5β-CHOLESTANO(3,4-b)N-BENZYLINDOLE (Contd.)

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
180	2.5	233	63.8	300	1.0
181	1.6	234	17.9	395	0.8
182	5.4	235	2.6	421	0.7
183	1.4	246	0.9	436	0.9
193	0.6	247	1.4	459	0.5
194	2.1	248	0.8	464	0.6
195	0.9	258	0.5	466	0.5
196	1.0	259	0.7	534	2.3
197	0.7	260	2.7	535	1.0
205	0.6	261	0.9	547	2.1
207	0.7	270	0.6	548	4.6
217	1.2	271	0.8	549	100.0M
218	5.5	272	5.4	550	44.1
219	1.1	273	5.6	551	9.0
220	6.5	274	2.5	552	1.3
221	2.4	275	0.6		
222	0.5	284	0.7		
230	1.1	286	1.6		
231	2.0	287	1.3		
232	23.2	288	0.6		

5β-CHOLESTANO(3,4-b)5'-METHYLINDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
50	0.7	78	0.6	109	2.3	142	0.5
51	0.8	79	4.6	110	0.5	143	1.7
52	0.5	80	1.0	111	1.1	144	21.5
53	2.2	81	7.5	115	0.9	145	5.2
54	1.0	82	1.2	116	0.5	146	1.0
55	16.5	83	3.9	117	1.0	147	0.9
56	5.2	84	0.6	118	0.5	149	0.7
57	15.0	85	1.3	119	1.6	152	0.5
58	1.5	91	3.7	120	1.2	154	1.9
60	0.7	92	0.7	121	1.6	155	1.5
63	0.5	93	4.3	123	1.0	156	2.1
65	0.9	94	1.0	125	0.5	157	20.5
66	0.5	95	5.2	128	1.2	158	13.5
67	5.5	96	0.9	129	0.9	159	2.8
68	1.7	97	2.2	130	0.9	160	0.5
69	10.5	98	0.5	131	0.5	161	0.5
70	2.4	105	2.5	132	0.9	167	2.8
71	7.4	106	0.6	133	1.1	168	2.8
73	0.5	107	2.9	135	1.0	169	2.3
77	2.0	108	0.7	137	0.5	170	6.7

5β-CHOLESTANO(3,4-b)5'-METHYLINDOLE (Contd.)

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
171	12.0	209	1.5	278	0.5	417	0.6
172	6.2	210	7.2	292	0.7	430	0.5
173	1.0	211	4.1	319	0.6	458	4.6
180	2.2	212	2.3	320	1.5	459	1.6
181	5.2	213	0.5	321	0.7	471	3.3
182	7.9	220	0.6	333	0.7	472	7.9
183	3.1	221	0.5	334	0.5	473	100.0M
184	13.5	222	1.6	345	1.6	474	40.0
185	7.0	223	1.1	346	0.8	475	8.3
186	1.1	224	2.4	347	0.5	476	1.0
193	0.5	225	0.8	359	0.6		
194	4.2	234	0.6	360	1.9		
195	3.7	235	0.5	361	0.7		
196	21.0	236	1.1	388	1.0		
197	17.0	237	0.5	389	0.5		
198	8.3	238	0.5	390	2.6		
199	1.4	248	0.6	391	0.8		
206	0.5	250	0.7	403	0.6		
207	0.5	252	0.5	404	0.5		
208	2.7	264	0.8	416	0.5		

5β-CHOLESTANO(3,4-b)5'-BENZYLOXYINDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
51	0.5	83	3.7	122	0.6	157	0.6
53	0.6	84	1.4	123	1.1	158	1.3
54	0.5	85	3.9	129	0.6	159	3.1
55	7.2	89	0.5	130	0.6	160	5.8
56	1.6	91	17.2	131	0.9	161	1.1
57	8.6	92	2.1	132	0.5	167	0.5
58	0.5	93	2.9	133	1.0	168	0.7
60	0.5	94	0.6	134	0.5	169	0.8
65	1.8	95	6.3	135	1.0	170	2.1
67	2.8	96	0.8	137	0.5	171	1.4
68	0.8	97	1.7	143	1.0	172	2.1
69	7.9	105	1.8	144	0.7	173	2.1
70	1.3	107	2.7	145	1.7	174	1.5
71	3.2	108	0.5	146	17.8	175	0.5
73	0.6	109	2.4	147	2.5	182	0.8
77	0.9	111	0.7	148	0.6	183	1.1
78	0.5	117	0.9	149	0.7	184	2.3
79	2.1	118	0.7	154	0.5	185	1.6
81	5.3	119	1.2	155	0.5	186	3.1
82	1.1	121	1.9	156	0.7	187	1.0

5β-CHOLESTANO(3,4-b)5'-BENZYLOXYINDOLE (Contd.)

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
196	1.7	238	0.7	334	0.8	566	36.2
197	2.1	248	0.5	346	0.6	567	7.5
198	6.4	249	1.1	360	0.5	568	1.1
199	5.6	250	1.5	398	0.8m*		
200	4.1	251	0.5	446	0.8		
201	0.7	252	0.7	452	0.5		
207	0.6	262	0.5	458	0.6		
210	1.8	263	0.9	460	0.7		
211	1.1	264	0.9	472	1.8		
212	4.1	266	0.6	473	2.6		
213	2.1	268	1.1	474	100.0		
214	1.5	276	1.3	475	47.0		
222	0.5	277	0.5	476	10.3		
224	0.7	288	1.5	477	1.3		
225	0.5	289	1.2	480	0.5		
226	1.0	290	0.9	550	2.2		
234	0.7	312	0.8	551	1.0		
235	0.5	313	0.5	563	3.1		
236	4.9	314	0.5	564	6.3		
237	1.1	320	1.1	565	80.9M		

6-OXO-5β-CHOLESTANO(3,4-b)N-METHYLINDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
53	0.7	119	0.5	181	5.9	227	1.3
55	5.1	121	0.6	182	5.4	236	0.5
56	1.2	131	0.8	183	1.6	263	0.5
57	4.8	133	0.6	184	1.8	374	0.6
67	1.7	135	0.5	185	0.5	402	0.5
68	0.5	143	0.5	194	2.2	431	0.5
69	2.8	144	8.5	195	3.0	432	0.6
70	0.5	145	0.5	196	31.0	433	0.7m
71	1.7	156	0.7	197	17.0	442	1.2
77	0.6	157	11.0	198	6.8	443	0.5
79	1.5	158	6.1	199	2.7	458	1.8
81	2.4	159	1.1	200	0.5	459	8.2
83	1.1	167	1.8	208	1.4	460	2.9
91	1.2	168	1.1	209	0.8	461	0.5
93	1.8	169	0.6	210	2.5	469	0.9
95	2.0	170	4.4	211	1.7	472	2.4
97	0.5	171	5.8	212	1.0	473	1.1
105	0.9	172	1.2	222	0.7	485	1.2
107	1.2	173	0.5	223	0.5	486	3.2
109	0.8	180	1.4	224	0.9	487	100.0M

6-OXO-5β-CHOLESTANO(3,4-b)N-METHYLINDOLE (Contd.)

m/e	%Abund.
488	37.0
489	7.0
490	1.1
501	4.8i
502	1.7

17-OXO-5α-ANDROSTANO(3,2-b)N-METHYLINDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
50	0.5	82	0.6	118	0.5	152	1.1
51	0.6	83	1.3	119	0.7	154	0.6
53	1.2	85	0.5	121	0.7	155	0.8
54	0.5	91	2.3	123	1.0	156	5.6
55	4.0	92	0.6	124	0.5	157	100.0
56	1.1	93	1.6	125	0.5	158	15.2
57	1.7	94	0.5	127	0.5	159	1.5
64	0.5	95	2.2	128	1.1	159.5	0.8
65	0.7	96	0.6	129	1.5	160	0.5
66	0.5	97	1.6	130	1.0	163	0.5
67	2.4	105	1.6	131	0.8	165	0.5
68	0.6	106	0.5	133	0.5	165.5	1.5
69	2.2	107	1.1	135	0.5	166	0.7
70	0.5	108	0.5	137	0.5	167	1.5
71	0.7	109	1.5	142	2.3	168	1.0
77	2.0	110	0.5	143	1.0	169	0.6
78	0.5	111	0.8	144	3.5	170	0.6
79	1.9	115	1.8	145	1.4	171	0.5
80	0.5	116	0.9	149	0.5	178.5	1.0
81	2.8	117	0.9	151	0.5	179	0.7

17-OXO-5α-ANDROSTANO(3,2-b)N-METHYLINDOLE (Contd.)

m/e	%Abund.
180	1.5
181	2.2
182	1.9
183	0.5
184	0.5
194	2.3
195	1.5
196	2.1
197	0.8
208	1.0
210	0.8
374	1.5
375	49.5M
376	14.5
377	2.1

17-OXO-5α-ANDROSTANO(3,2-b)N-BENZYLINDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
50	0.6	80	0.7	109	1.4	142	4.3
51	0.9	81	3.9	111	0.7	143	3.6
53	1.7	82	0.9	115	2.6	144	5.2
54	0.6	83	1.3	116	1.3	145	1.3
55	5.9	85	0.6	117	1.1	147	0.6
56	1.0	89	0.5	118	0.5	149	0.5
57	2.0	90	0.5	119	1.5	152	0.5
58	0.6	91	73.0	120	0.7	154	0.9
63	0.5	92	5.7	121	1.3	155	0.6
64	0.9	93	2.8	122	0.5	156	1.5
65	2.2	94	0.6	123	0.9	157	0.8
66	0.6	95	2.5	127	0.6	158	0.5
67	3.5	96	0.6	128	1.1	159	0.7
68	0.9	97	1.5	129	1.1	161	0.7
69	2.5	103	0.6	130	2.3	163	0.5
70	0.6	104	0.6	131	1.3	165	0.5
71	0.9	105	3.3	133	0.8	166	0.6
77	2.9	106	0.7	135	0.5	167	2.9
78	0.8	107	1.8	140	0.6	168	1.8
79	3.3	108	0.5	141	0.6	169	0.5

17-OXO-5α-ANDROSTANO(3,2-b)N-BENZYLINDOLE (Contd.)

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
179	0.7	217	2.2	449	0.5
180	4.4	218	7.2	450	2.7
181	2.0	219	1.5	451	100.0M
182	1.9	220	2.2	452	36.3
183	0.6	230	1.8	453	6.0
190	0.7	231	4.1	454	0.8
191	0.5	232	36.2		
192	0.8	233	56.4		
193	0.9	234	11.0		
194	3.7	235	1.2		
195	1.4	258	0.5		
196	1.1	259	0.4		
197	0.6	260	0.5		
199	0.5	270	0.8		
203.5	1.3	271	0.5		
204	1.3	272	0.9		
205	0.6	273	0.7		
206	0.9	284	0.5		
207	0.4	286	0.8		
208	0.6	436	0.6		

17-OXO-5α-ANDROSTANO(3,2-b)5'-BENZYLOXYINDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
53	0.6	118	0.7	157	0.8	197	0.8
55	2.2	119	1.2	158	15.5	198	1.2
57	0.5	120	0.5	159	13.2	199	0.5
61	0.5	121	0.6	160	2.5	219	0.5
65	1.8	128	0.5	161	0.5	220	0.7
67	1.5	129	0.7	167	0.7	221	0.5
69	0.9	130	4.3	168	1.1	222	0.6
77	1.1	131	1.9	169	0.9	235	0.5
79	1.5	132	2.8	170	0.8	237	0.5
81	2.1	133	0.9	171	0.7	248	0.6
91	24.0	134	0.5	172	0.7	249	2.6
92	2.1	142	0.8	173	0.7	250	1.5
93	1.6	143	1.0	180	0.5	320	1.1
95	1.0	144	0.6	181	0.5	322.5	0.5
97	1.0	145	0.7	182	0.9	374	0.6
103	0.6	146	1.1	183	0.9	375	0.5
105	1.8	147	0.5	184	1.1	376	100.0
107	1.2	154	0.8	185	0.6	377	28.5
115	0.6	155	0.7	195	0.5	378	4.1
117	0.9	156	0.8	196	1.2	379	0.5

17-OXO-5α-ANDROSTANO(3,2-b)5'-BENZYLOXYINDOLE (Contd.)

m/e	%Abund.
465	0.6
466	2.0
467	37.5M
468	12.8
469	2.1

5α-CHOLESTANO(3,4-b)INDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
53	0.7	107	2.6	147	0.6	185	0.8
55	8.7	109	1.7	149	0.6	193	0.5
56	1.7	115	0.5	152	0.6	194	2.4
57	8.7	117	1.0	154	1.6	195	1.4
58	0.5	118	0.5	155	1.9	196	8.4
67	3.0	119	1.0	156	5.8	197	7.4
68	0.5	121	1.4	157	8.8	198	4.5
69	5.4	123	0.8	158	2.6	199	0.7
70	0.8	128	1.0	159	1.4	206	0.6
71	3.4	129	1.8	167	3.3	207	0.5
77	0.9	130	10.7	168	5.8	208	1.5
79	2.5	131	4.7	169	2.9	209	1.6
81	4.4	132	0.9	170	14.1	210	3.3
83	2.2	133	0.9	171	4.6	211	0.8
91	1.8	135	0.9	172	0.6	220	0.7
93	3.1	138	0.7	180	3.2	221	0.5
95	4.4	143	9.7	181	2.5	222	1.1
97	1.0	144	9.9	182	16.7	224	0.6
105	1.5	145	2.4	183	10.0	234	0.7
106	0.9	146	0.5	184	5.7	236	0.8

5α-CHOLESTANO(3,4-b)INDOLE (Contd.)

m/e	%Abund.	m/e	%Abund.
250	0.6	460	37.8
304	0.6	461	7.7
305	1.1	462	0.9
306	0.5		
319	0.6		
330	0.9		
331	0.5		
346	1.3		
347	0.5		
374	0.7		
376	1.2		
378	0.5		
402	0.6		
403	0.5		
430	0.5		
444	7.1		
445	2.5		
457	7.8		
458	8.2		
459	100.0M		

5α-CHOLESTANO(3,4-b)N-METHYLINDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
50	0.5	97	0.7	149	0.5	185	1.4
51	0.6	105	0.9	152	0.5	194	2.4
53	0.7	107	1.2	154	0.5	195	1.6
55	5.6	109	0.9	155	0.5	196	8.0
56	2.6	115	0.6	156	0.6	197	4.9
57	5.9	117	0.5	157	5.2	198	2.8
67	2.0	119	0.5	158	5.8	208	1.5
68	0.6	121	0.6	159	1.4	209	1.2
69	3.1	128	0.6	159.5	0.5	210	3.6
70	1.1	129	0.6	167	1.2	211	3.7
71	2.3	130	0.5	168	1.2	212	1.7
77	0.7	131	0.7	169	1.1	220	0.5
78	0.5	132	0.5	170	3.1	222	0.8
79	1.5	133	0.5	171	2.3	223	0.7
81	1.9	135	0.5	172	0.9	224	1.6
82	0.5	143	0.5	180	0.9	234	0.6
83	1.3	144	6.2	181	1.7	236	0.6
91	1.7	145	2.9	182	2.5	317	0.5
93	1.6	146	0.7	183	1.4	318	0.9
95	1.9	147	0.5	184	5.8	319	0.5

5α-CHOLESTANO(3,4-b)N-METHYLINDOLE (Contd.)

m/e	%Abund.
344	0.7
358	0.5
359	0.7
387	0.5
456	0.5
457	0.6
458	3.7
459	1.7
471	8.7
472	10.9
473	100.0M
474	37.2
475	6.7
476	0.8

5α-CHOLESTANO(3,4-b)N-BENZYLINDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
51	0.8	77	1.5	105	2.6	135	1.0
52	1.0	78	0.8	106	1.3	137	0.7
53	1.8	79	2.8	107	2.6	142	0.7
54	1.4	80	0.8	108	0.7	143	1.0
55	14.3	81	4.8	109	2.5	144	1.0
56	4.5	82	1.3	110	1.6	145	0.8
57	13.5	83	3.7	115	1.0	147	0.7
58	0.7	84	1.1	117	1.0	149	0.7
60	1.5	85	1.6	118	0.5	154	0.8
63	0.5	87	0.5	119	1.3	155	0.6
64	0.7	89	0.9	120	0.5	156	0.9
65	1.6	91	47.2	121	1.9	157	0.8
66	0.8	92	4.6	122	0.6	159	0.6
67	13.4	93	2.8	123	1.3	161	0.5
68	1.5	94	0.9	125	0.5	163	0.5
69	8.2	95	4.5	128	0.7	167	2.1
70	2.5	96	1.5	129	1.0	168	1.8
71	5.4	97	1.8	130	2.2	169	0.6
73	1.5	98	1.1	131	1.0	170	0.8
74	0.6	99	0.5	133	1.0	171	0.4

5α-CHOLESTANO(3,4-b)N-BENZYLINDOLE (Contd.)

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
180	2.2	222	0.6	285	0.5	548	12.5
181	1.4	232	2.0	286	2.4	549	100.0M
182	3.9	233	2.4	287	3.3	550	43.7
183	1.5	234	3.3	288	1.5	551	9.8
184	0.5	235	0.8	298	0.5	552	1.3
193	0.7	244	0.6	299	0.7		
194	2.2	246	1.4	300	1.4		
195	1.0	247	1.0	301	0.5		
196	1.7	248	0.7	395	1.1		
197	1.1	258	0.6	396	0.6		
204	0.5	259	0.9	409	0.6		
206	0.8	260	4.2	421	1.1		
207	0.5	261	1.2	422	0.5		
208	1.0	270	0.9	436	0.9		
210	0.6	271	0.5	459	0.5		
217	0.7	272	4.5	464	0.6		
218	1.6	273	3.6	534	3.4		
219	0.6	274	3.2	535	1.5		
220	4.2	275	0.5	546	0.5		
221	1.9	284	0.6	547	8.0		

CHOLEST-4,6-DIENO(3,2-b)N-METHYLINDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
53	0.6	107	0.9	182	0.7	230	1.2
55	5.8	109	1.3	193	0.6	231	3.7
56	1.2	111	0.6	194	7.2	232	4.3
57	6.2	119	0.7	195	5.1	233	1.5
67	2.0	121	0.5	196	1.2	234	1.8
69	3.8	122	0.7	204	0.7	235	0.5
70	0.7	123	0.7	205	1.2	243	0.5
71	2.6	129	0.6	206	0.8	244	5.1
77	0.6	130	0.5	207	3.5	245	3.4
79	1.3	131	0.6	208	6.7	246	5.3
81	3.0	133	0.5	209	1.6	247	1.5
82	0.5	135	0.5	216	0.6	248	1.4
83	1.7	143	0.8	217	1.4	257	0.6
85	0.6	144	1.3	218	1.9	258	1.4
91	1.2	145	0.5	219	1.7	259	0.7
93	1.9	150	0.6	220	4.8	260	2.2
95	3.6	157	2.1	221	3.3	261	0.9
96	0.5	158	1.0	222	15.0	262	0.8
97	1.1	180	0.6	223	2.9	270	0.5
105	1.1	181	1.5	229	0.5	272	0.6

CHOLEST-4,6-DIENO(3,2-b)N-METHYLINDOLE (Contd.)

m/e	%Abund.
274	0.5
286	0.5
300	0.5
315	0.5
341	0.6
356	0.5
453	1.4
454	2.9
455	1.3
467	1.2
468	2.5
469	100.0M
470	39.8
471	10.5
472	0.8

6-OXO-CHOLEST-4-ENO(3,2-b)INDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
50	0.5	81	8.9	113	0.5	151	0.6
53	1.7	82	1.9	117	0.5	152	0.7
54	0.9	83	6.8	119	1.1	153	0.7
55	16.1	84	1.2	121	2.4	155	0.6
56	3.4	85	3.0	123	2.0	163	0.8
57	18.1	91	2.5	125	1.0	165	0.7
58	1.5	92	0.6	128	0.5	166	3.9
60	0.5	93	6.1	129	0.5	167	3.7
65	0.6	94	1.0	130	1.6	168	2.5
67	5.7	95	9.2	131	0.6	177	0.6
68	2.7	96	1.6	133	1.5	178	0.6
69	11.5	97	4.4	135	3.9	179	1.5
70	2.1	98	0.7	136	0.6	180	28.2
71	9.1	99	0.6	137	1.0	181	11.6
72	0.5	105	2.0	139	0.5	182	6.5
73	0.6	107	4.1	142	0.7	183	1.1
77	1.7	108	0.6	143	1.7	191	0.8
78	0.5	109	5.5	144	1.5	192	1.1
79	4.3	110	1.0	147	0.6	193	2.4
80	1.0	111	2.4	149	3.0	194	26.0

6-OXO-CHOLEST-4-ENO(3,2-b)INDOLE (Contd.)

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
195	5.4	232	1.2	457	15.7
196	1.1	233	0.9	458	3.0
204	1.5	234	1.4	469	2.5
205	1.3	236	0.5	470	4.4
206	4.7	244	0.6	471	100.0M
207	3.2	245	0.5	472	38.2
208	9.9	246	1.5	473	6.8
209	2.6	247	1.5	474	0.9
210	3.1	248	0.9		
211	0.6	257	1.3		
217	1.2	258	0.5		
218	1.7	260	1.1		
219	0.7	300	0.5		
220	5.6	358	0.6		
221	1.9	441	1.4		
222	1.7	442	1.6m*		
223	2.6	443	0.9		
224	0.8	454	2.0		
230	1.6	455	5.6		
231	0.7	456	43.5		

6-OXO-CHOLEST-4-ENO(3, 2-b)N-METHYLINDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
53	1.1	97	1.3	163	0.5	209	4.6
55	9.7	105	1.2	165	0.5	210	0.8
56	1.5	107	3.0	167	0.7	217	0.6
57	10.7	109	3.1	168	0.7	218	1.3
67	3.5	111	0.5	169	0.5	219	1.2
68	0.6	111.5	0.5	179	1.4	220	3.6
69	6.0	119	0.9	180	4.9	221	2.2
70	0.6	121	1.5	181	2.7	222	8.3
71	4.7	123	0.9	182	1.6	223	1.9
77	1.1	131	0.6	192	0.6	224	1.5
79	2.8	133	1.1	193	1.4	231	0.6
80	0.5	135	2.6	194	23.8	232	1.1
81	5.5	143	0.5	195	11.4	233	0.6
82	0.5	144	1.0	196	5.2	234	3.7
83	2.6	145	0.5	197	0.9	235	1.2
91	1.6	147	0.5	204	0.7	236	1.3
93	4.3	149	1.8	205	1.1	237	1.4
94	0.5	152	0.7	206	1.2	238	0.6
95	5.6	157	0.9	207	1.8	244	1.2
96	0.5	158	0.6	208	21.8	245	0.6

6-OXO-CHOLEST-4-ENO(3,2-b)N-METHYLINDOLE (Contd.)

m/e	%Abund.	m/e	%Abund.
246	1.0	485	100.0M
247	0.9	486	37.4
248	0.9	487	7.1
258	0.5	488	1.1
260	1.2		
261	0.6		
262	0.6		
274	0.8		
331	0.5		
342	0.5		
372	0.5		
456	1.6m*		
457	0.7		
468	1.4		
469	5.4		
470	38.0		
471	13.8		
472	2.5		
483	0.9		
484	1.7		

6-OXO-CHOLEST-4-ENO(3,2-b)N-BENZYLINDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
50	0.5	97	1.5	193	1.7	255	0.6
53	0.8	105	1.1	194	3.0	256	1.6
55	8.5	107	3.0	195	0.5	257	0.5
56	1.6	108	0.5	204	1.2	268	0.7
57	10.3	109	2.9	205	0.9	269	0.5
65	1.0	111	0.5	206	1.0	270	9.6
67	3.4	121	1.3	207	1.0	271	5.5
69	6.5	123	0.8	208	1.2	272	2.6
70	0.9	132	1.3	217	0.8	273	0.5
71	4.7	134	2.8	218	1.1	282	0.5
77	0.8	149	2.0	219	0.6	283	0.6
79	2.8	152	0.5	220	0.6	284	16.1
81	5.4	163	0.5	222	0.5	285	4.4
83	2.7	165	0.7	230	0.9	286	0.9
85	0.7	169	1.5	233	7.0	296	1.3
91	51.2	170	6.7	234	1.5	297	1.1
92	4.2	171	1.7	244	0.7	298	6.5
93	4.8	172	0.9	246	0.6	299	1.5
95	5.9	191	0.5	247	0.6	300	0.9
96	0.6	192	0.6	254	1.0	310	1.7

6-OXO-CHOLEST-4-ENO(3,2-b)N-BENZYLINDOLE (Contd.)

m/e	%Abund.	m/e	%Abund.
311	0.6	561	100.0M
312	0.8	562	48.5
313	1.1	563	9.9
314	0.5	564	1.3
320	0.6		
322	0.5		
324	0.5		
336	0.9		
337	0.5		
338	0.5		
350	0.5		
532	1.8m*		
533	1.0		
534	0.5		
545	9.8		
546	35.7		
547	14.3		
548	2.9		
559	1.3		
560	1.9		

CHOLEST-5-ENO(3,4-b)INDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
53	0.5	117	0.6	182	2.0	219	0.8
55	4.5	119	0.8	183	1.0	220	1.6
56	0.9	121	0.5	184	0.8	221	0.8
57	4.6	123	0.6	192	0.6	222	1.0
67	1.7	130	2.8	193	1.0	230	0.5
69	2.8	131	0.6	194	3.0	231	0.5
70	0.6	133	0.6	195	1.4	232	1.0
71	2.0	135	0.7	196	1.9	233	0.7
77	0.6	143	0.8	197	2.1	234	1.9
79	1.2	144	2.1	198	0.6	235	0.9
81	2.2	145	0.6	204	0.6	236	0.7
83	1.5	154	0.5	205	0.6	246	0.5
85	0.5	156	0.8	206	1.2	248	1.0
91	1.0	157	0.6	207	0.9	344	0.5
93	1.4	167	1.3	208	2.8	372	0.5
95	2.3	168	1.7	209	3.7	441	0.5
97	0.8	169	0.6	210	1.9	442	3.5
105	0.9	170	1.0	211	0.5	443	1.4
107	1.3	180	1.9	217	0.7	455	1.9
109	0.9	181	1.4	218	1.0	456	4.7

CHOLEST-5-ENO(3,4-b)INDOLE (Contd.)

m/e	%Abund.
457	100.0M
458	37.5
459	6.9
460	1.0

CHOLEST-5-ENO(3,4-b)N-METHYLINDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
55	2.9	158	1.9	223	3.8	474	1.4
56	0.8	167	0.5	224	1.4		
57	3.5	168	0.5	231	0.5		
67	1.2	170	0.6	232	0.6		
69	1.9	180	0.8	233	1.1		
71	1.3	181	1.2	234	0.6		
79	0.8	183	0.6	235	0.5		
81	1.5	194	1.3	246	0.6		
83	1.1	195	1.0	247	0.5		
91	0.7	196	1.3	248	1.1		
93	0.8	197	0.8	249	0.6		
95	1.4	206	0.5	262	0.7		
97	0.6	207	0.7	455	0.5		
105	0.6	208	2.2	456	3.5		
107	0.7	209	0.9	457	1.6		
109	0.6	210	1.2	469	1.9		
130	0.5	211	1.0	470	5.6		
144	2.6	220	0.8	471	100.0M		
145	0.6	221	0.6	472	38.5		
157	0.7	222	2.7	473	8.5		

CHOLEST-5-ENO(3,4-b)N-BENZYLINDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
55	3.3	180	0.9	286	0.6
56	0.7	182	0.5	287	0.6
57	3.6	192	0.5	298	0.9
67	1.0	193	0.9	299	2.3
69	2.1	194	0.9	300	1.1
71	1.4	196	0.6	322	0.6
79	0.7	204	0.5	457	0.5
81	1.6	206	0.8	462	0.5
83	0.9	207	0.5	531	0.5
91	20.5	208	2.0	532	2.4
92	1.8	217	0.5	533	1.1
93	1.1	218	0.7	545	1.9
95	1.7	220	1.5	546	4.9
105	0.5	232	0.7	547	100.0M
107	0.9	233	0.5	548	44.5
109	0.6	234	1.1	549	10.5
119	0.6	260	0.6	550	2.1
130	0.6	270	0.5		
167	0.6	272	0.6		
168	0.5	284	0.5		

5α-ANDROSTANO(3,2-b:17,16-b)N,N'-DIMETHYL-DI-INDOLE

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
50	1.3	73	0.9	96	0.6	128	2.6
51	1.5	74	0.5	97	1.5	129	3.5
52	0.7	76	0.5	98	0.5	130	3.2
53	1.5	77	2.9	101	0.5	131	4.0
54	1.0	78	1.0	102	1.3	132	1.6
55	6.0	79	3.5	103	1.3	133	1.5
56	2.1	80	0.6	104	0.7	140	0.6
57	3.8	81	3.0	105	3.3	141	1.3
58	0.5	82	0.7	106	0.6	142	4.4
59	0.8	83	1.3	107	2.5	143	3.0
60	2.0	84	0.5	108	0.5	144	38.9
61	0.6	85	1.4	115	4.2	145	10.0
63	0.8	86	1.1	116	1.7	146	3.2
64	0.5	87	0.6	117	2.3	147	0.6
65	0.8	89	0.5	118	0.8	151	0.6
67	2.5	91	4.3	119	1.1	152	3.4
68	0.7	92	0.7	120	0.5	153	1.4
69	1.3	93	3.4	121	2.0	154	2.5
70	0.8	94	0.5	125	6.4	155	1.7
71	1.3	95	2.1	127	1.2	156	7.8

5α-ANDROSTANO(3,2-b:17,16-b)N,N'-DIMETHYL-DI-INDOLE (Contd.)

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
157	40.8	191	0.6	219	1.4	248	1.3
158	20.0	192	1.2	220	3.0	249	0.7
159	2.8	193	2.0	221	1.6	250	0.9
160	0.5	194	15.0	222	1.7	258	0.5
165	0.8	195	7.4	223	2.9	260	0.8
166	1.5	196	14.0	224	6.8	261	0.5
167	11.5	197	2.8	227	1.4	262	0.8
168	8.2	198	1.5	228	0.6	264	0.6
169	4.2	203	0.6	230	0.6	274	0.6
170	6.1	204	1.1	231	7.1	276	0.5
171	1.8	205	1.1	232	1.5	288	0.7
172	2.1	206	1.9	233	0.9	290	10.0
178	0.7	207	2.0	234	2.1	291	2.3
179	1.3	208	11.0	235	1.4	302	0.6
180	6.3	209	3.4	236	1.3	305	2.0
181	14.0	210	4.2	237	0.5	306	1.1
182	21.0	211	1.1	244	0.6	317	1.1
183	6.4	216	0.6	245	0.5	319	0.8
184	5.8	217	0.8	246	0.9	445	0.6
185	1.4	218	1.6	247	0.6	446	0.9

5α-ANDROSTANO(3,2-b:17,16-b)N,N'-DIMETHYL-DI-INDOLE (Contd.)

m/e	%Abund.
447	62.0
448	22.0
449	3.6
450	0.5
461	1.1
462	100.0 M
463	39.8
464	7.0
465	0.9

5α-ANDROSTANO(3,2-b:17,16-b)N,N'-DIBENZYL-DI-INDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
50	0.8	79	1.5	111	0.8	154	0.8
51	0.6	81	2.2	115	1.4	155	0.8
53	0.8	82	0.8	116	0.7	156	1.6
54	0.7	83	1.9	117	0.9	157	0.9
55	4.5	84	0.7	119	0.7	158	1.4
56	1.4	85	1.2	121	0.9	159	0.6
57	3.7	89	0.5	123	0.5	165	0.5
60	1.5	90	0.5	125	0.5	166	0.7
61	0.9	91	100.0	128	0.8	167	3.9
63	0.5	92	8.9	129	1.3	168	3.8
65	2.3	93	1.7	130	4.6	169	1.1
67	1.9	95	1.5	131	1.6	170	1.1
68	0.8	96	0.7	132	0.6	179	0.6
69	3.3	97	1.4	133	1.4	180	5.1
70	0.9	98	0.6	137	0.5	181	2.7
71	1.9	103	0.5	141	0.5	182	3.3
73	1.5	105	1.6	142	2.0	183	0.8
74	0.5	106	0.5	143	2.8	184	0.7
77	1.0	107	1.0	144	5.9	192	0.7
78	0.5	109	0.8	145	2.1	193	1.2

5α-ANDROSTANO(3,2-b:17,16-b)N,N'-DIBENZYL-DI-INDOLE (Contd.)

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
194	5.7	234	6.1	274	1.1	395	0.8
195	1.5	235	1.3	275	0.6	508	0.6
196	1.3	236	0.6	284	3.2	509	2.0
204	0.9	243	0.5	285	1.4	510	1.2
205	0.7	244	0.8	286	2.1	523	0.6
206	1.5	245	0.7	287	0.6	524	1.1
207	0.8	246	1.5	298	0.8	584.5	1.9m*
208	1.2	247	0.6	299	0.6	597	0.5
209	0.5	248	0.8	299.5	4.6	598	0.8
210	0.5	254	0.5	300	2.5	599	43.5
217	1.4	256	0.8	300.5	0.5	600	21.5
218	4.7	257	0.7	307	5.7	601	4.8
219	1.4	258	4.1	307.5	2.8	602	0.7
220	11.0	259	1.8	308	0.8	612	2.9
221	3.1	260	2.0	310	0.5	613	3.5
222	1.3	261	0.6	312	0.5	614	99.0M
230	1.1	270	3.5	324	0.5	615	48.0
231	1.2	271	1.5	366	3.1	616	12.0
232	9.5	272	2.6	367	0.9	617	1.9
233	10.2	273	1.0	381	0.8		

3β-HYDROXY-5α-ANDROSTANO(17,16-b)N-METHYLINDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
53	1.4	106	0.5	145	4.3	179	0.5
55	4.4	107	2.5	146	1.7	179.5	2.2
56	0.6	109	0.5	147	0.5	180	3.7
57	1.7	115	1.3	152	0.8	181	5.3
58	0.5	116	0.6	153	0.5	182	9.6
65	0.6	117	1.3	154	0.8	183	5.5
67	3.1	118	0.5	155	0.5	184	4.8
68	0.5	119	1.4	156	0.7	185	1.0
69	1.4	121	0.6	157	1.4	192	0.5
77	1.8	127	0.5	158	5.4	193	0.8
79	3.0	128	1.1	159	1.1	194	4.9
81	3.2	129	0.8	164.5	0.5	195	3.3
83	0.6	130	1.0	165	0.6	196	5.8
91	3.8	131	2.1	166	0.9	197	1.6
92	0.5	132	0.9	167	5.2	198	0.9
93	2.9	133	0.7	168	4.7	204	0.6
95	1.9	141	0.7	169	2.1	205	0.5
103	0.6	142	0.5	170	2.6	206	1.0
104	0.5	143	1.4	171	1.2	207	1.0
105	2.9	144	22.0	172	1.3	208	2.4

3β-HYDROXY-5α-ANDROSTANO(17,16-b)N-METHYLINDOLE (contd.)

m/e	%Abund.	m/e	%Abund.
209	1.3	345	0.8
210	1.1	346	1.0
218	0.8	348	1.3m*
219	0.7	359	2.0
220	2.0	360	1.8
221	1.2	361	1.5
222	2.8	362	100.0
223	0.8	363	27.3
224	0.5	364	4.0
232	0.5	375	0.6
234	1.1	376	3.1
235	0.8	377	76.0M
236	2.0	378	22.0
237	0.6	379	3.3
248	0.6		
250	0.8		
262	0.5		
290	1.0		
320	0.6		
344	2.9		

3β-ACETOXY-5α-ANDROSTANO(17,16-b)N-METHYLINDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
50	1.0	73	5.8	98	1.6	120	6.7
51	0.9	74	1.0	99	0.7	121	1.6
52	0.5	75	0.5	101	0.9	122	0.5
53	2.5	77	3.0	102	0.6	123	1.5
54	2.3	78	0.8	103	0.8	124	0.7
55	18.0	79	5.5	104	0.6	125	1.2
56	4.9	80	1.1	105	4.9	126	0.6
57	14.5	81	7.0	106	1.1	127	0.9
58	1.4	82	2.7	107	4.2	128	1.6
59	0.6	83	5.8	108	1.1	129	2.8
60	7.0	84	1.9	109	2.5	130	1.6
61	2.5	85	4.1	110	1.1	131	3.1
65	1.2	87	1.2	111	2.5	132	1.3
66	0.7	91	6.8	112	0.8	133	1.5
67	7.9	92	1.1	113	0.8	134	0.5
68	2.5	93	5.3	115	2.2	135	0.9
69	6.2	94	1.2	116	0.9	137	1.0
70	3.3	95	5.7	117	2.0	138	0.9
71	6.7	96	1.9	118	0.7	139	0.9
72	0.5	97	4.7	119	2.4	140	0.6

3β-ACETOXY-5α-ANDROSTANO(17,16-b)N-METHYLINDOLE (Contd.)

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
141	1.1	167	7.8	195	4.6	223	1.0
142	0.9	168	6.1	196	7.5	224	1.0
143	2.5	169	2.5	197	2.1	228	0.5
144	34.5	170	3.7	198	1.3	232	0.7
145	6.5	171	2.1	199	1.4	233	0.6
146	2.6	172	2.5	204	0.9	234	1.9
147	1.1	173	0.7	205	0.8	235	1.3
149	1.3	178	0.6	206	1.3	236	2.6
151	0.7	179	0.9	207	1.5	237	1.0
152	1.3	180	4.1	208	3.4	238	0.6
153	0.9	181	7.0	209	1.9	246	0.5
154	1.1	182	14.5	210	1.7	248	1.1
155	0.9	183	7.6	211	0.5	249	0.6
156	1.3	184	6.3	213	0.6	250	1.3
157	2.6	185	1.8	217	0.5	251	0.5
158	8.2	187	0.8	218	1.0	256	0.6
159	2.1	191	0.5	219	1.0	258	0.8
161	0.6	192	0.8	220	2.5	260	0.5
165	1.8	193	1.3	221	1.8	262	0.7
166	1.3	194	6.5	222	3.4	276	0.5

3β-ACETOXY-5α-ANDROSTANO(17,16-b)N-METHYLINDOLE (Contd.)

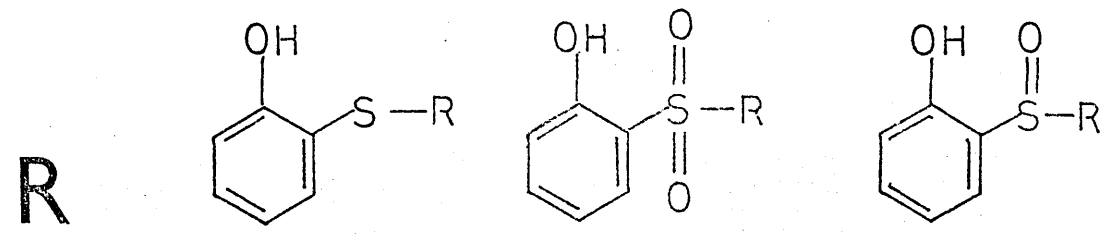
m/e	%Abund.
290	2.0
291	0.6
304	0.5
305	0.6
344	3.8
345	1.1
346	0.7
358	1.4
359	1.3
360	1.8
361	0.8
376	1.1
404	100.0
405	31.0
406	4.6
407	0.5
418	1.8
419	73.9 M
420	24.6
421	3.6

3β-ACETOXY-5α-ANDROSTANO(17,16-b)N-BENZYLINDOLE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
53	0.6	119	1.2	181	2.0	217.5	1.9
55	2.3	121	0.7	182	2.1	218	2.3
57	0.6	128	0.6	183	0.7	219	0.7
60	0.8	129	0.8	187	0.6	220	12.2
65	1.6	130	2.3	189.5	0.5	221	2.8
67	2.4	131	1.4	192	0.5	222	1.3
69	1.0	133	0.7	193	0.7	232	0.7
77	1.1	143	1.1	194	2.4	234	2.7
79	2.4	144	1.8	195	0.7	235	0.7
81	3.1	145	0.9	196	0.5	244	0.6
91	100.0	154	0.7	197	0.5	246	1.0
92	7.0	155	0.6	199	0.6	256	0.5
93	2.9	156	0.7	203	0.6	258	2.5
95	1.9	157	0.7	204	0.8	259	2.0
105	3.0	166	0.5	205	0.6	260	1.8
106	0.5	167	2.8	206	1.4	270	0.7
107	2.8	168	3.6	207	0.7	271	0.5
109	0.5	169	1.2	208	0.9	272	1.6
115	0.6	170	0.9	210	1.5	273	0.6
117	1.1	180	3.1	217	0.7	298	0.7

3β-ACETOXY-5α-ANDROSTANO(17,16-b)N-BENZYLINDOLE (Contd.)

m/e	%Abund.
312	0.7
366	0.8
420	9.2
421	2.8
422	0.7
434	0.8
435	7.5
436	3.2
437	0.9
452	0.7
466	1.2m*
480	69.2
481	25.0
482	4.0
483	0.6
494	1.3
495	69.5M
496	25.4
497	4.2
498	0.6



R			
CH_3	I	XIII	XXV
CH_3CH_2	II	XIV	XXVI
$CH_3(CH_2)_2$	III	XV	XXVII
$(CH_3)_2CH$	IV	XVI	XXVIII
$CH_3(CH_2)_3$	V	XVII	XXIX
$CH_3CH_2CH(CH_3)$	VI	XVIII	XXX
$(CH_3)_2CHCH_2$	VII	XIX	XXXI
$(CH_3)_3C$	VIII	XX	XXXII
$(CH_3)_2CH(CH_2)_2$	IX	XXI	XXXIII
$CH_3CH=CHCH_2$	X	XXII	XXXIV
$PhCH_2$	XI	XXIII	XXXV
$PhCH(CH_3)$	XII	XXIV	XXXVI

FIGURE 1.

CHAPTER 3.

MASS SPECTRA OF SOME ORGANO-SULPHUR COMPOUNDS.

Introduction.

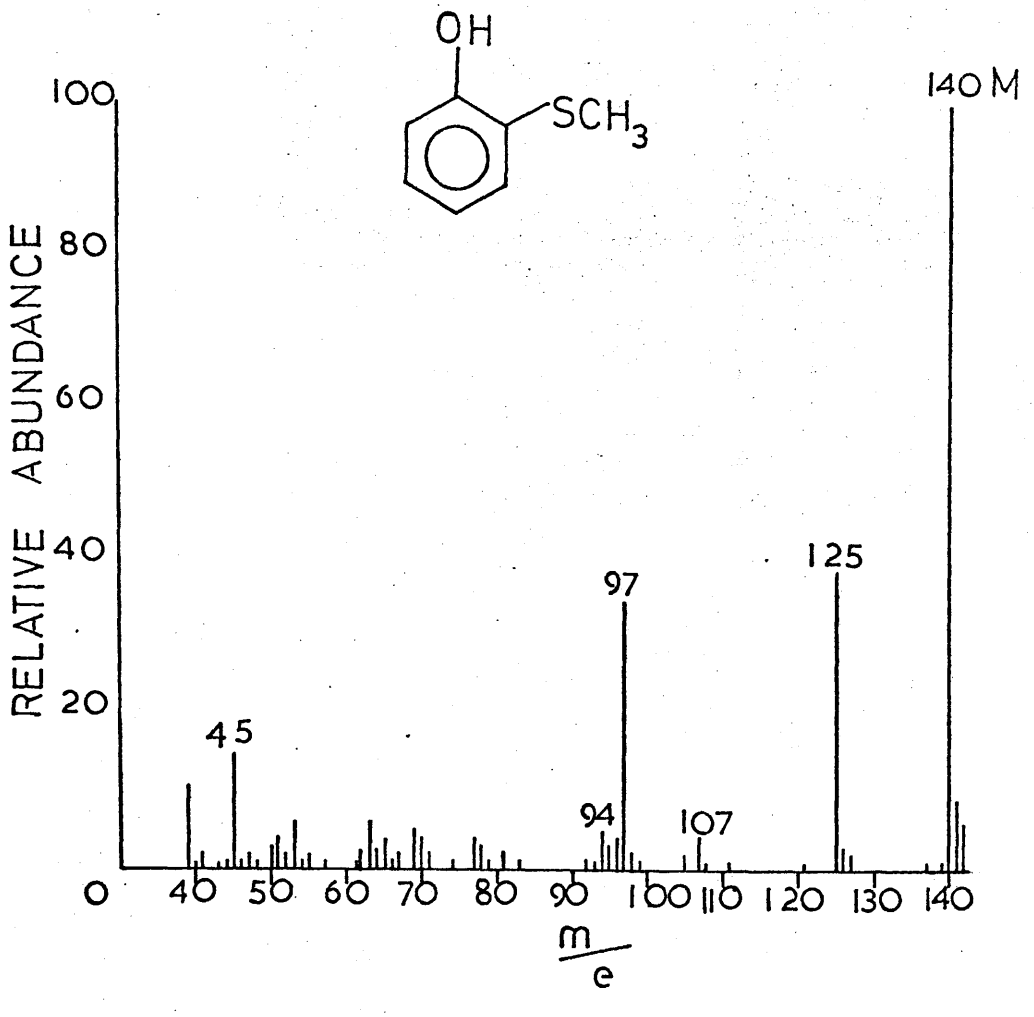
A vast number of skeletal rearrangement ions have been observed[1,2,3] in the mass spectra of organo-sulphur compounds. These are often accompanied by the loss of neutral fragments like sulphur, sulphur monoxide and sulphur dioxide. The importance of a clear understanding of skeletal rearrangement reactions in mass spectrometry made it of interest to study the sulphides, sulphones and sulphoxides shown in Figure I.

Discussion.

A. Sulphides.

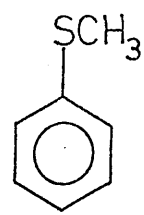
In a review article,[1] Brown and Djerassi refer to systematic studies on sulphides[4,5,6] and disulphides[4,7,8] which clearly show that many skeletal rearrangements with attendant sulphur loss are possible. However, it has been proposed[6,7] that an unsaturated site on the molecule is a necessary prerequisite for significant rearrangement. This is supported by the fact that higher dialkyl sulphides[9] fragment by simple cleavage reactions, sometimes accompanied by hydrogen rearrangements. Also, the fact that

FIGURE 2


OH
SCH3
140 M
125
97
45
94
107
100
80
60
40
20
0
RELATIVE ABUNDANCE
40 50 60 70 80 90 100 110 120 130 140
m/e

methyl compounds (e.g. Me_2S[4], Me_2S_2[7] and PhSMe[5,6]) show a greater propensity to undergo skeletal rearrangements as compared with other alkyl substituted analogues, has been attributed[6,7] to the lack of competing reactions possible with a methyl group. This latter statement is substantiated by the spectrum of 2-hydroxyphenyl methyl sulphide (I) which is shown in Figure 2.

Although thioanisole (a)[5,6] has an ion at m/e 91 (25% relative



(a)

abundance) due to the loss of a sulfhydryl radical, substitution of an ortho-hydroxyl group has reduced this ion to 3.6% of the base peak. Similarly, the important peak due to the loss of CH_2S from the molecular ion in the thioanisole spectrum, has fallen to only 5.3% in this case. A metastable peak was only observed for the transition involving sulfhydryl loss (m^* observed 81.8; calculated 81.8 for the transition $140^+ \longrightarrow 107^+$).

As can be seen from Figure 3, the dominant process, in the mass spectrum of 2-hydroxyphenyl methyl sulphide, is the formation of the ion at m/e 97. Initial loss of the methyl radical is

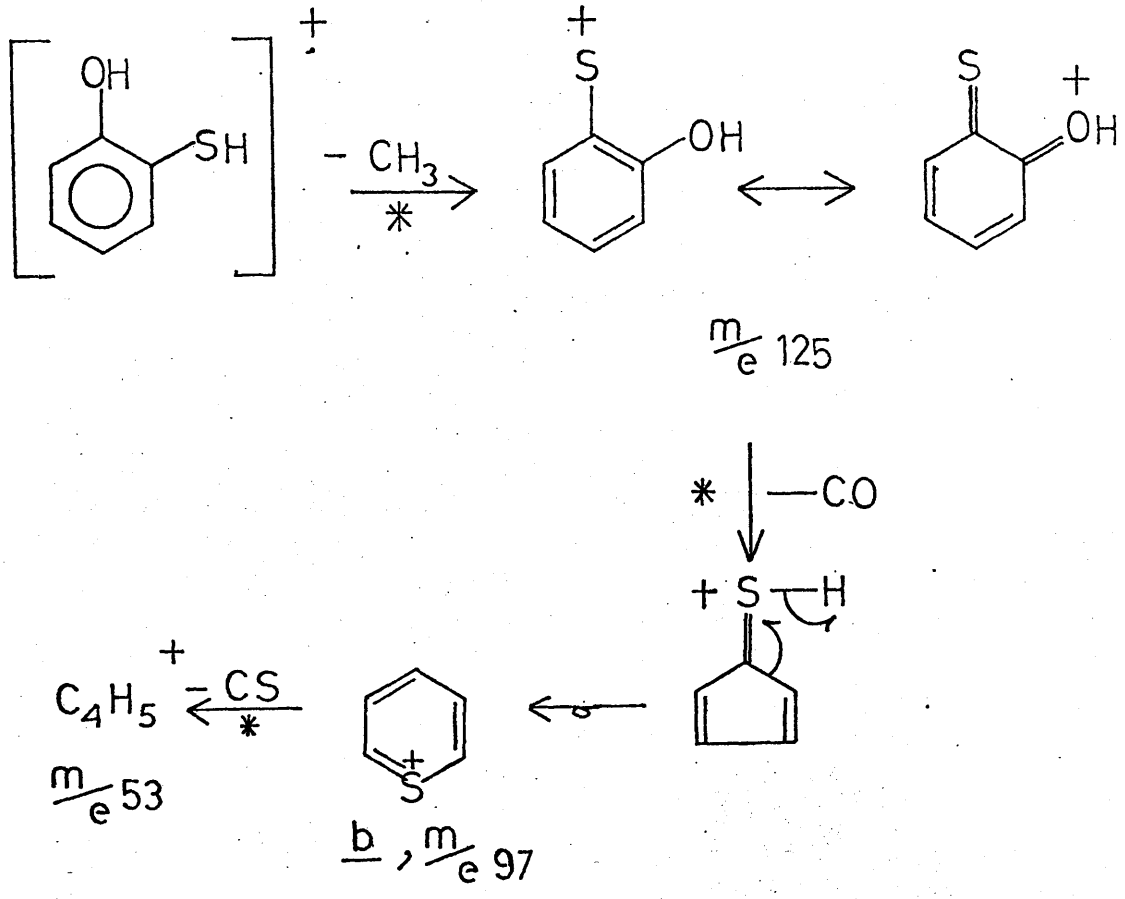


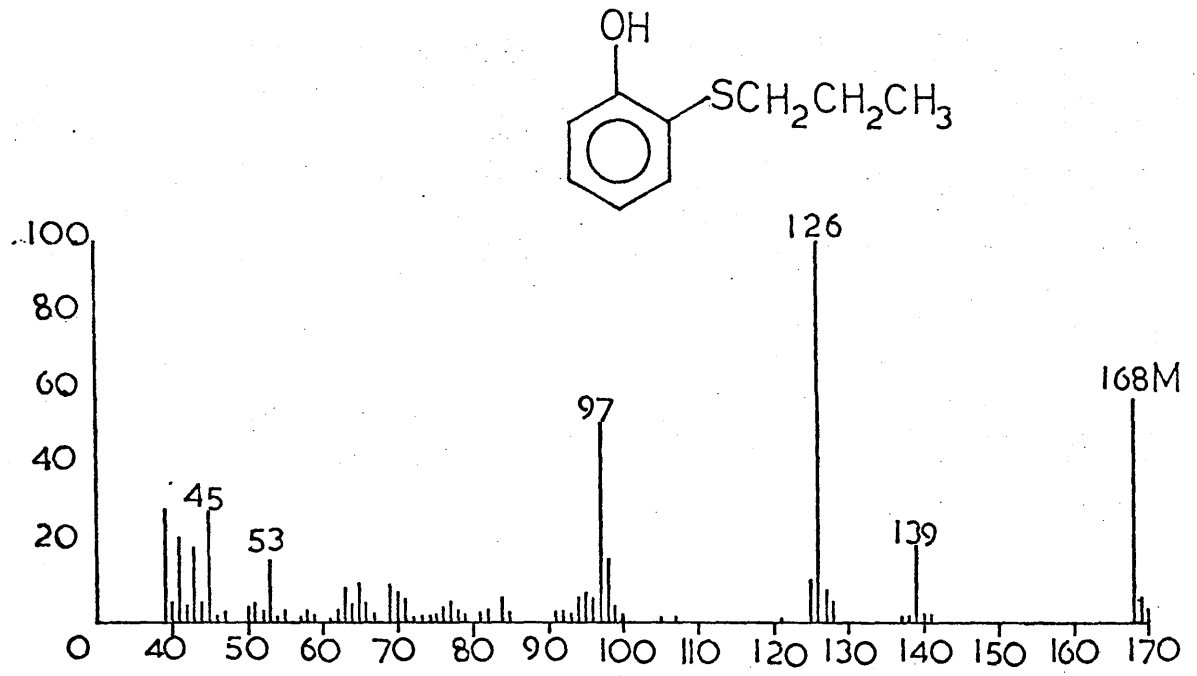
FIGURE 3

followed by carbon monoxide elimination. The ion at m/e 97 may isomerise to give the stable thiopyrilium ion, b which has been postulated for the ion at m/e 97 in the spectra of isomeric alkyl thiophenes.[10] Further breakdown, by elimination of carbon monosulphide, is supported by the presence of a metastable ion at m/e 29.0 (calculated 29.0).

Ions common to the spectra of many of these compounds are the thioformyl ion at m/e 45 and the cyclopropenyl ion at m/e 39. The ion at m/e 121 can only have the formula $C_7H_5S^+$ arising by loss of H_3O from the parent ion. This cation must have enhanced stability, as it has been observed in the spectra of many aromatic sulphur compounds.[6] The origin of the ions at m/e 69, 70 and 71 are mentioned below.

The spectra of the n-propyl (III) and the isopropyl (IV) substituted sulphides are shown in Figure 4 and are typical of the other compounds with alkyl substituents (II - IX). The base peak occurs at m/e 126 in all the spectra except that of the ethyl sulphide (II), in which the molecular ion is the most intense peak. Figure 5 shows the major breakdown pathways, asterisks indicating transitions which are supported by metastable peaks in most of the spectra. Mass measurements on the ethyl sulphide (II) were used to confirm the formulae of some of the ions and are shown below in Table I.

FIGURE 4


OH
SCH2CH2CH3
100
80
60
40
20
0
126
168M
97
45
53
139
40 50 60 70 80 90 100 110 120 130 140 150 160 170

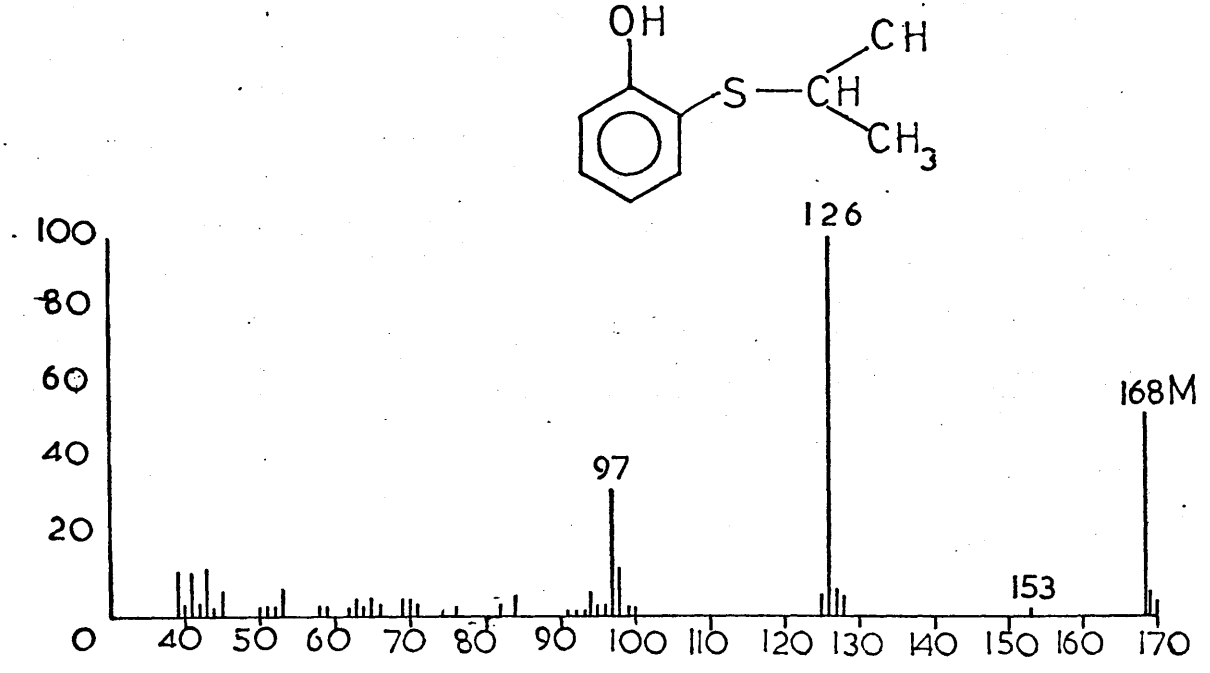
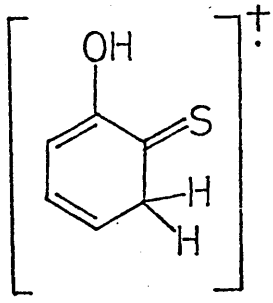

OH
S
CH
CH
CH3
100
80
60
40
20
0
126
168M
97
153
40 50 60 70 80 90 100 110 120 130 140 150 160 170

TABLE I.

Nominal Mass	Mass Observed	Mass Calculated	Formula Assigned.
137	137.0051	137.0061	C_7H_5OS
126	126.0148	126.0139	C_6H_6OS
125	125.0068	125.0061	C_6H_5OS
98	98.01881	98.01902	C_5H_6S
97	97.01111	97.01120	C_5H_5S
96	96.00332	96.00337	C_5H_4S
84	84.00194	84.00337	C_4H_4S
71	70.99462	70.99555	C_3H_3S
70	69.98790	69.98772	C_3H_2S

The most important ion (m/e 126) in the spectra of the sulphides III-IX is formed by olefin elimination from the parent ion. This is represented as having occurred by hydrogen transfer to sulphur and is supported by the work of MacLeod and Djerassi,[11] who studied labelled n-butoxybenzene and n-butylthiobenzene. In this way they have shown that only a maximum of 19% of the olefin elimination ions can have been formed by McLafferty rearrangement of the n-butylthiobenzene molecular ion. This would result in the alternative type of structure c for these ions. However, a recent paper[12] has used



c

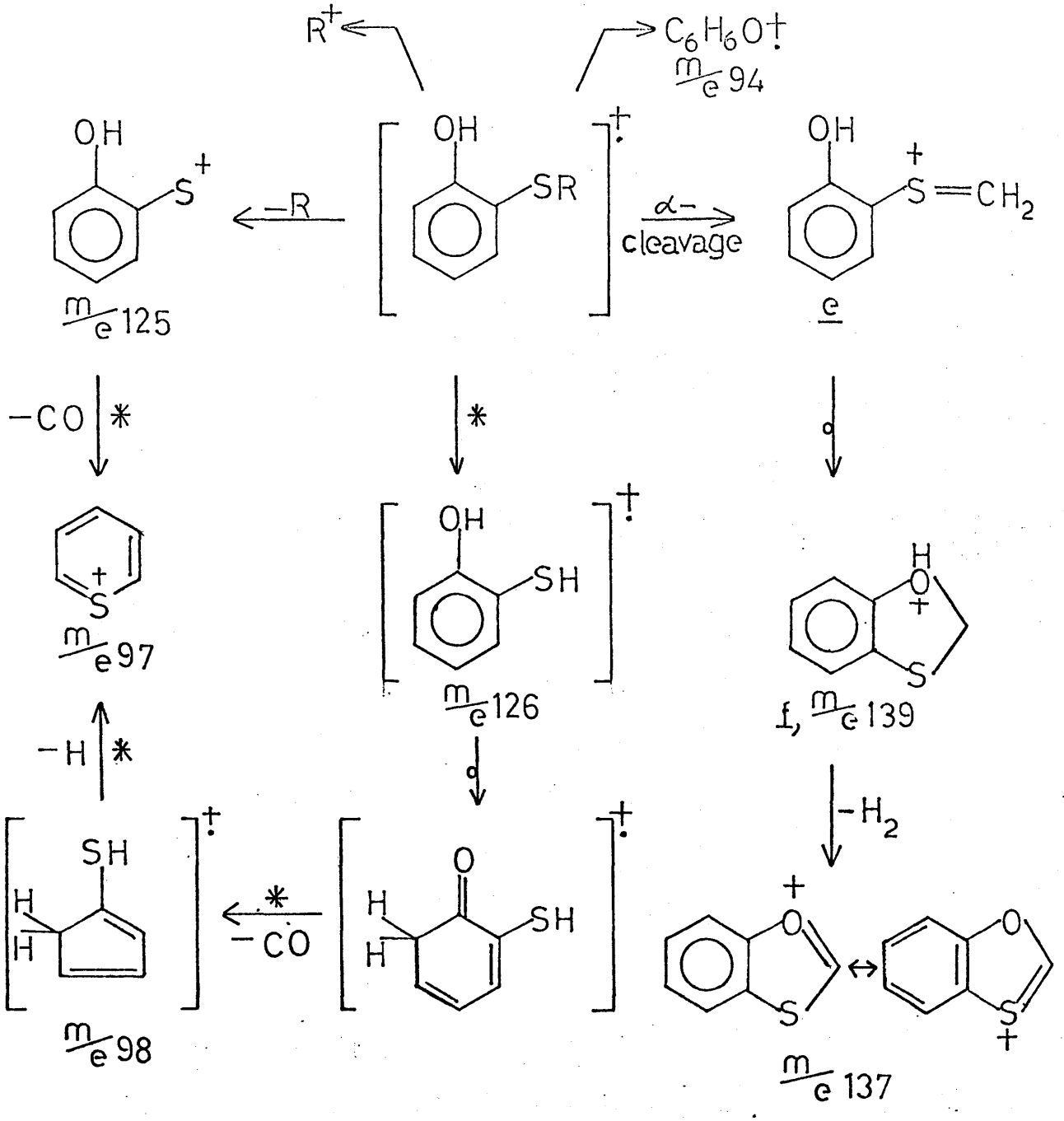
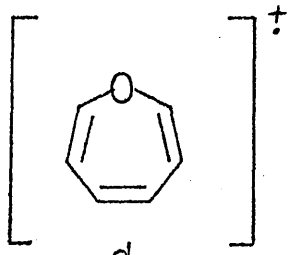

R+
C6H6O+·
m/e 94
OH
SR
+·
−R
α-cleavage
S+
m/e 125
S+=CH2
e
−CO
*
SH
m/e 97
m/e 126
H
O+
S
f, m/e 139
−H
−H2
m/e 98
−CO
O
m/e 137

FIGURE 5

energetic considerations to arrive at the conclusion that this ion in alkoxybenzenes and alkylthiobenzenes is most likely to have structure c. A study of substituted ethoxybenzenes[13] has led to the conclusion that the corresponding ions in these compounds may have oxepin structure, d. The structure of these ions would

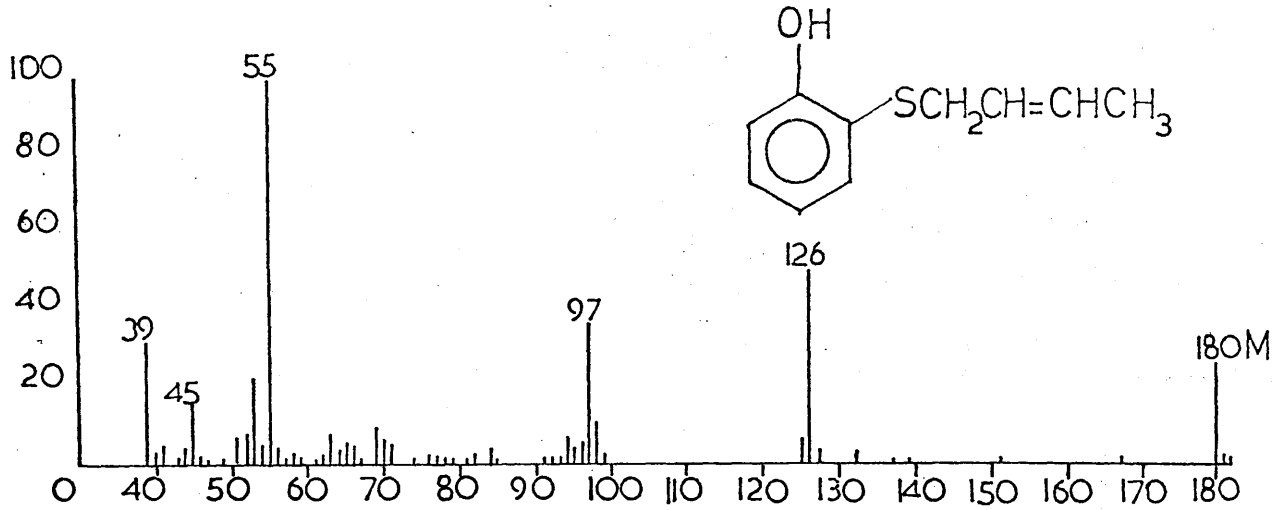


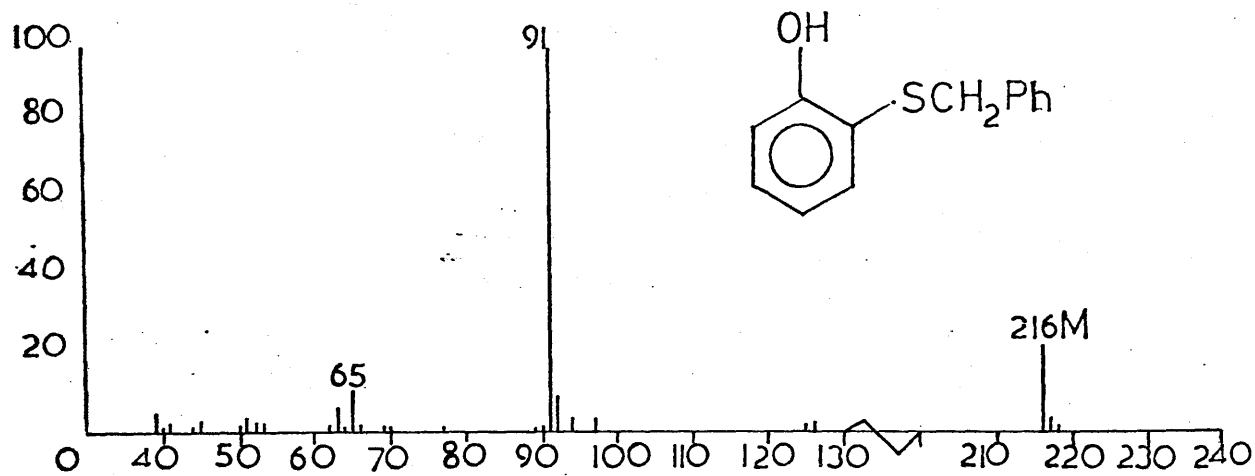
d

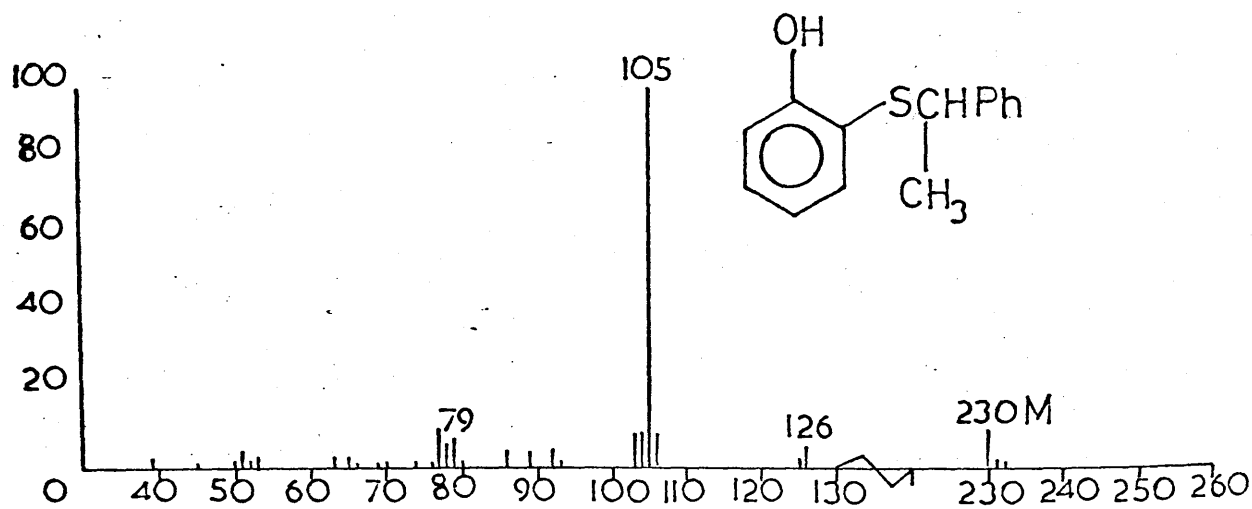
thus still seem to be in doubt and it seems probable that they have no simple unique structure.

A further variant of the structure of m/e 126 has to be postulated for the degradation by loss of carbon monoxide and a hydrogen atom, the driving force probably being the formation of the thiopyrilium cation at m/e 97. Another probable route for the formation of this ion is by initial alkyl loss from the molecular ion and subsequent carbon monoxide elimination, although the metastable peak for the former process is absent. The ions at m/e 69, 70, 71 and 84 have all been observed in the spectra of thiophenols[14] and they seem likely to have been formed from m/e 126. The formulae of m/e 70, 71 and 89 have been confirmed by the mass measurements above and m/e 69 is therefore most likely to be C_3HS^+.

FIGURE 6


OH
SCH2CH=CHCH3
100
80
60
40
20
0
55
39
45
97
126
180M
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180


OH
SCH2Ph
100
80
60
40
20
0
91
65
216M
40 50 60 70 80 90 100 110 120 130 210 220 230 240


OH
SCHPh
CH3
100
80
60
40
20
0
105
79
126
230M
40 50 60 70 80 90 100 110 120 130 230 240 250 260

Many dialkyl sulphides[9] and aryl alkyl sulphides[6,15] exhibit α-cleavage ions in their mass spectrum. In the compounds II - IX, however, α-cleavage ions are only important when the alkyl substituent is not branched at the carbon attached to sulphur. Although the lower intensity of α-cleavage ions in thioethers as compared to their oxygen analogues has been attributed to increased carbon-sulphur cleavage,[16] Keyes and Harrison[17] have used appearance potential data to suggest that this decrease is due to the inability of sulphur to stabilise the α-cleavage ions. In a series of 2-alkylthio-5-aminothiazolo (5,4-d) pyrimidines, Tatematsu[18] et al. have found the α-cleavage ions to be of negligible importance.

The extra stability required for the formation of the m/e 139 ions in the compounds II, III, V, VII and IX may be derived from the formation of the cyclic structure f. Five-membered ring formation in mass spectrometry has been shown to occur in many arylureas and related compounds.[19] It is supported in this case by the ion at m/e 137 which has the formula C_7H_5OS. This ion would seem much more likely to be formed from an ion of structure f rather than e. The reason that the corresponding α-cleavage ion in compounds IV, VI and VIII are not important may be steric effects in the cyclisation step, or simply that more δ-hydrogen atoms favour the formation of the (M-olefin) fragment.

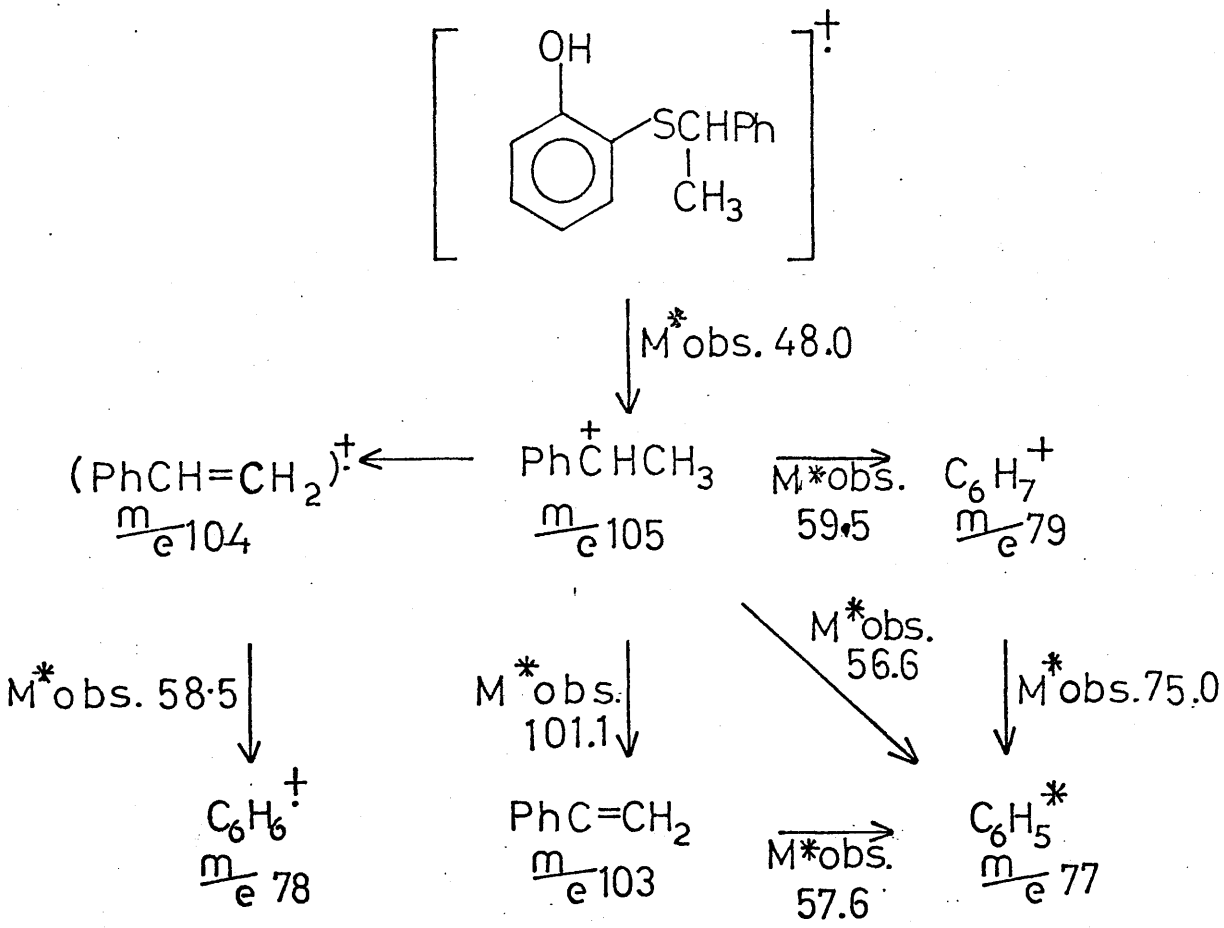

OH
SCHPh
CH3
M* obs. 48.0
(PhCH=CH2)+·
m/e 104
PhCHCH3+
m/e 105
M* obs. 59.5
C6H7+
m/e 79
M* obs. 58.5
C6H6+·
m/e 78
M* obs. 101.1
PhC=CH2
m/e 103
M* obs. 56.6
M* obs. 57.6
M* obs. 75.0
C6H5*
m/e 77

FIGURE 7

Substitution of the alkyl group by the unsaturated groups in the sulphides X, XI and XII would be expected[6,7] to give rise to an increase in skeletal rearrangement ions of the type $(ABC)^+ \rightarrow (AC)^+ + B$. However, this is not observed. The spectra of these compounds are shown in Figure 6.

But-2-enyl 2-hydroxyphenyl sulphide (X) forms the base peak in the spectrum by simple carbon-sulphur bond cleavage. The α-cleavage ion is of low intensity, as its formation would involve unfavourable vinylic cleavage. A recent study[20] on phenyl vinyl sulphides has shown many rearrangement ions and the conclusion is reached that $(M - SH)$, $(M - SH_2)$ and $(M - SH_3)$ ions are characteristic of alkenyl sulphides. It would appear that this only applies to compounds which have vinyl substituents.

The spectra of sulphides XI and XII are dominated by hydrocarbon fragments, as has been observed for benzyl phenyl sulphide,[6] the lack of rearrangement ions being attributed to the very ready formation of the tropyllium ion at m/e 91. Similarly, the spectrum of compound XII has m/e 105 as the base peak, the subsequent fragmentation, shown by metastable peak analysis, being in Figure 7.

The assignments are not all unambiguous but appear the most probable (e.g., m^* observed 101.1 could also be for the process $103^+ \rightarrow 102^+ + 1$).

B. Sulphones.

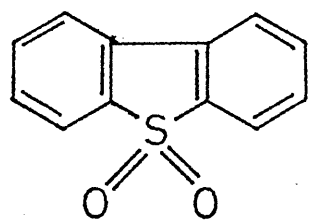
The mass spectra of dialkyl sulphones[20,21] display charge localization at oxygen rather than sulphur. There are three major fragmentation pathways:

(a) cleavage of the carbon-sulphur bond;

(b) β-bond cleavage; and

(c) olefin elimination accompanied by single or double hydrogen rearrangement to the charged fragment.

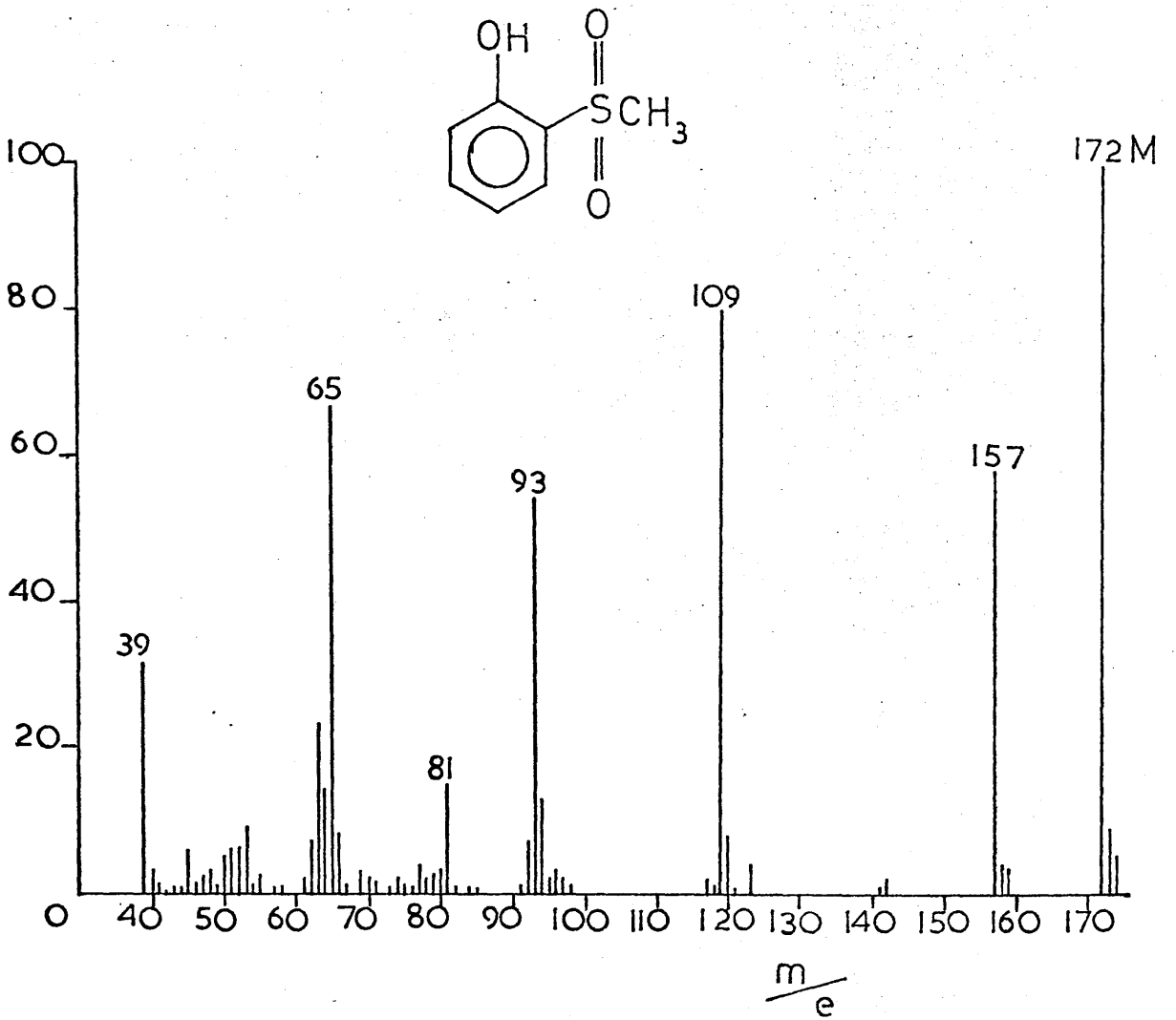
Diaryl sulphones[22-27] give a great number of rearrangement ions caused by aryl migration from sulphur to oxygen, again implying charge localization on the oxygen atom. This has resulted, for example, in the elimination of two molecules of carbon monoxide from the dibenzothiophene dioxide (A) parent ion.[24]



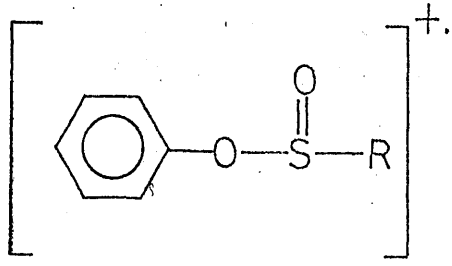
A

Studies have also been carried out on alkyl aryl sulphones.[20,21] The molecular ions of both methyl and ethyl phenyl sulphones[20]

FIGURE 8


OH
O
SCH3
O
100
80
60
40
20
0
39
65
81
93
109
157
172 M
40 50 60 70 80 90 100 110 120 130 140 150 160 170
m/e

rearrange to g. This is followed by elimination of CH_2SO and C_2H_4SO



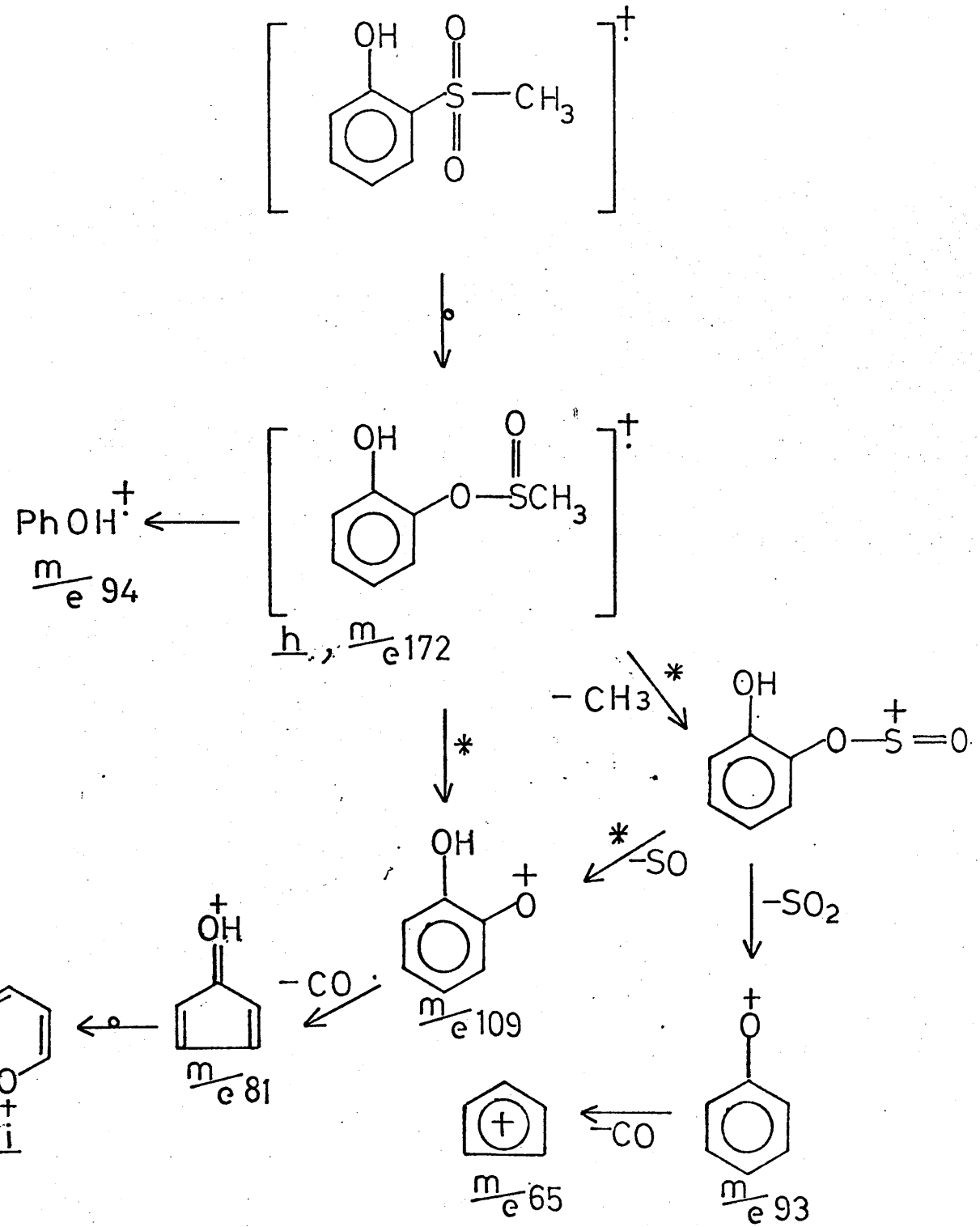
g

to give an ion at m/e 94 of 50% and 40% relative intensity respectively. They do not, however, show any carbon monoxide loss from the parent ion. In contrast, this rearrangement to the phenyl sulphinic ester was not observed in the spectra of n-butyl phenyl or n-hexyl phenyl sulphones.[21]

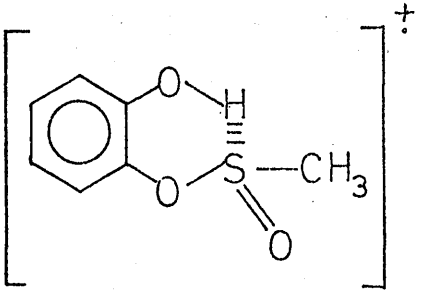
The mass spectrum of 2-hydroxyphenyl methyl sulphone (XIII) and the breakdown pathways are shown in Figures 8 and 9 respectively. As in the case of methyl phenyl sulphone,[20] fragmentation is preceded by aryl migration to give the ion h. However, this is followed by loss of CH_3SO without hydrogen transfer, as previously observed, a metastable ion for the process being observed at m/e 69.1 (calculated 69.1). The ion at m/e 109 can also be formed from the molecular ion by stepwise loss of a methyl radical and sulphur monoxide. This is supported by metastable ions at m/e 143.3 (calculated 143.3) and m/e 75.8 (calculated 75.7) respectively.

The virtual absence of hydrogen transfer can be attributed to

FIGURE 9


OH
O
S
CH3
O
PhOH+
m/e 94
h
m/e 172
- CH3
*
-SO
-SO2
-CO
m/e 109
m/e 81
m/e 93
m/e 65
-CO
i

chelation in the molecular ion, perhaps as shown below. The



use of models shows that the distance of closest approach of a methyl hydrogen atom to the aromatic ring is about 3Å, making hydrogen transfer unlikely.[28] However, the distance from the ethereal oxygen atom is unaffected and hence it would seem that the hydrogen transfer in the methyl phenyl sulphone occurred mainly by McLafferty rearrangement.

The peak at m/e 81 is probably formed from m/e 109 by loss of carbon monoxide and may have the fully aromatic pyrilium structure, i. The ion at m/e 93 has the formula $C_6H_5O^+$ as shown by the mass measurements in Table 2 below. By analogy with methyl phenyl sulphone, the origin of this ion was probably the (M - 15) ion with subsequent sulphur dioxide loss.

FIGURE 10a

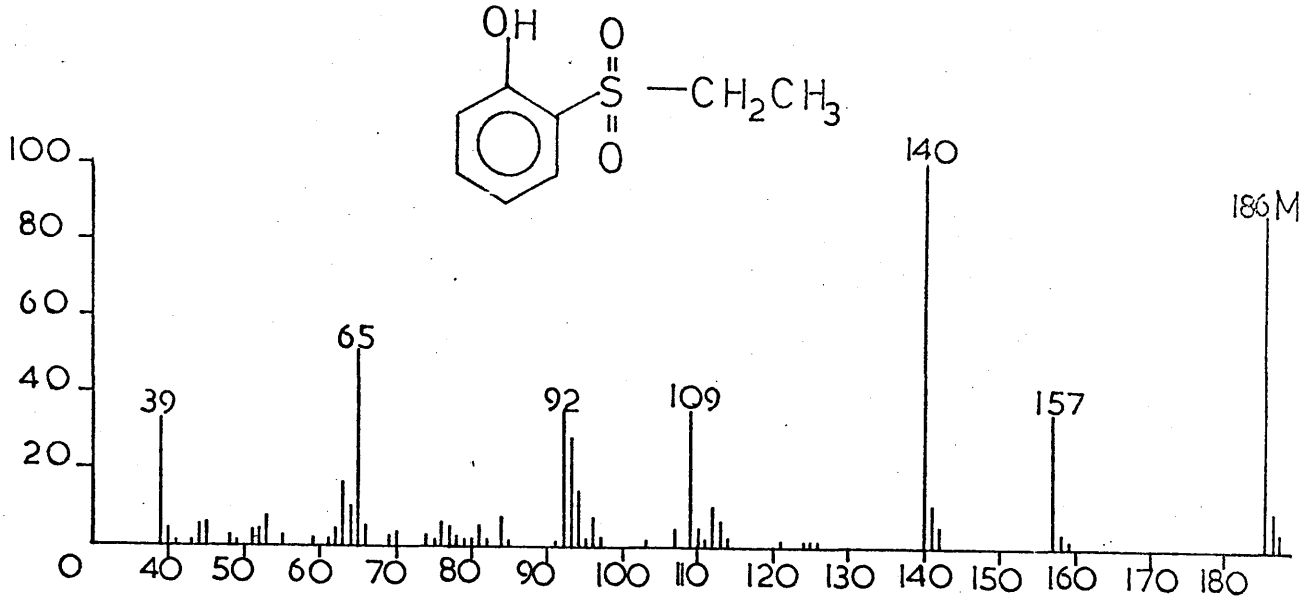


FIGURE 10b

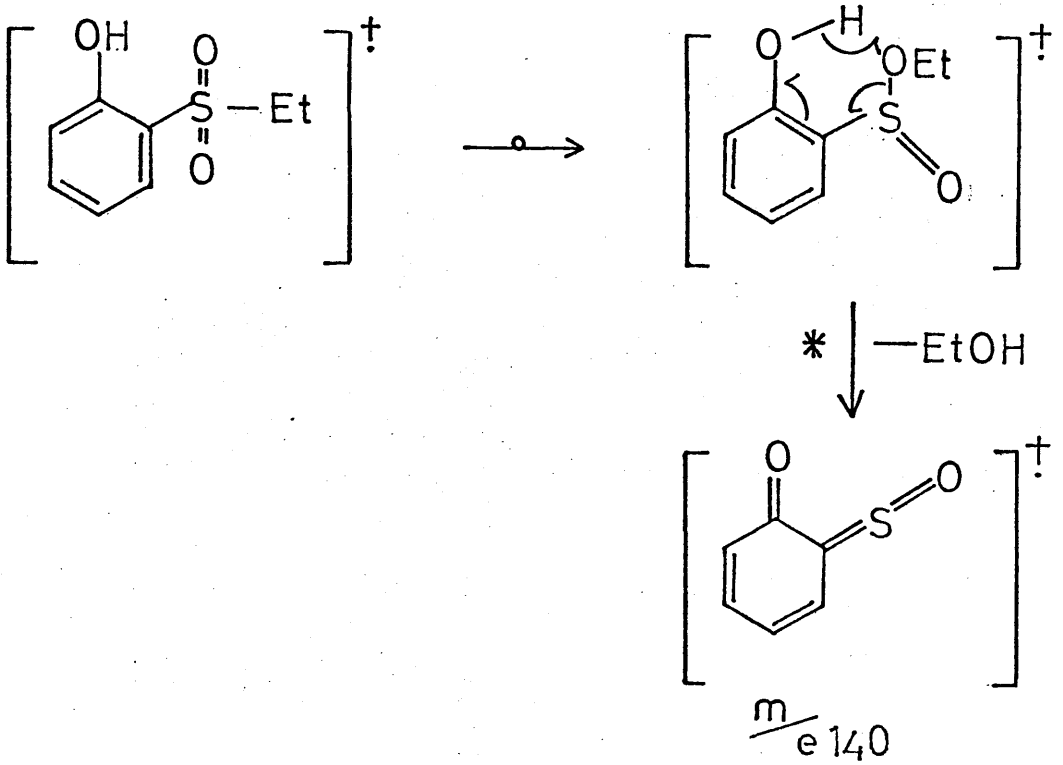


TABLE 2.

Nominal Mass	Mass Observed	Mass Calculated	Formula Assigned.
109	109.02893	109.02895	$C_6H_5O_2$
93	93.03399	93.03404	C_6H_5O
81	81.03400	81.03404	C_5H_5O

The mass spectrum of ethyl 2-hydroxyphenyl sulphone (XIV), (Figure 10a), differs from the methyl compound in that the base peak is at m/e 140. Once again, the ion at m/e 109 is intense and is indicative of rearrangement of the parent ion to the sulphinic ester. This is the only other of these compounds in which this rearrangement is of importance. The only metastable observed for its formation was at m/e 75.9 (calculated 75.7) for the loss of sulphur monoxide from m/e 157.

Although many of the other compounds have the base peak at m/e 140, only in the case of the ethyl compound is there a metastable ion for its formation from the molecular ion (m^* observed 105.3 (calculated 105.4) for the transition $186^+ \longrightarrow 140^+ + 46$).

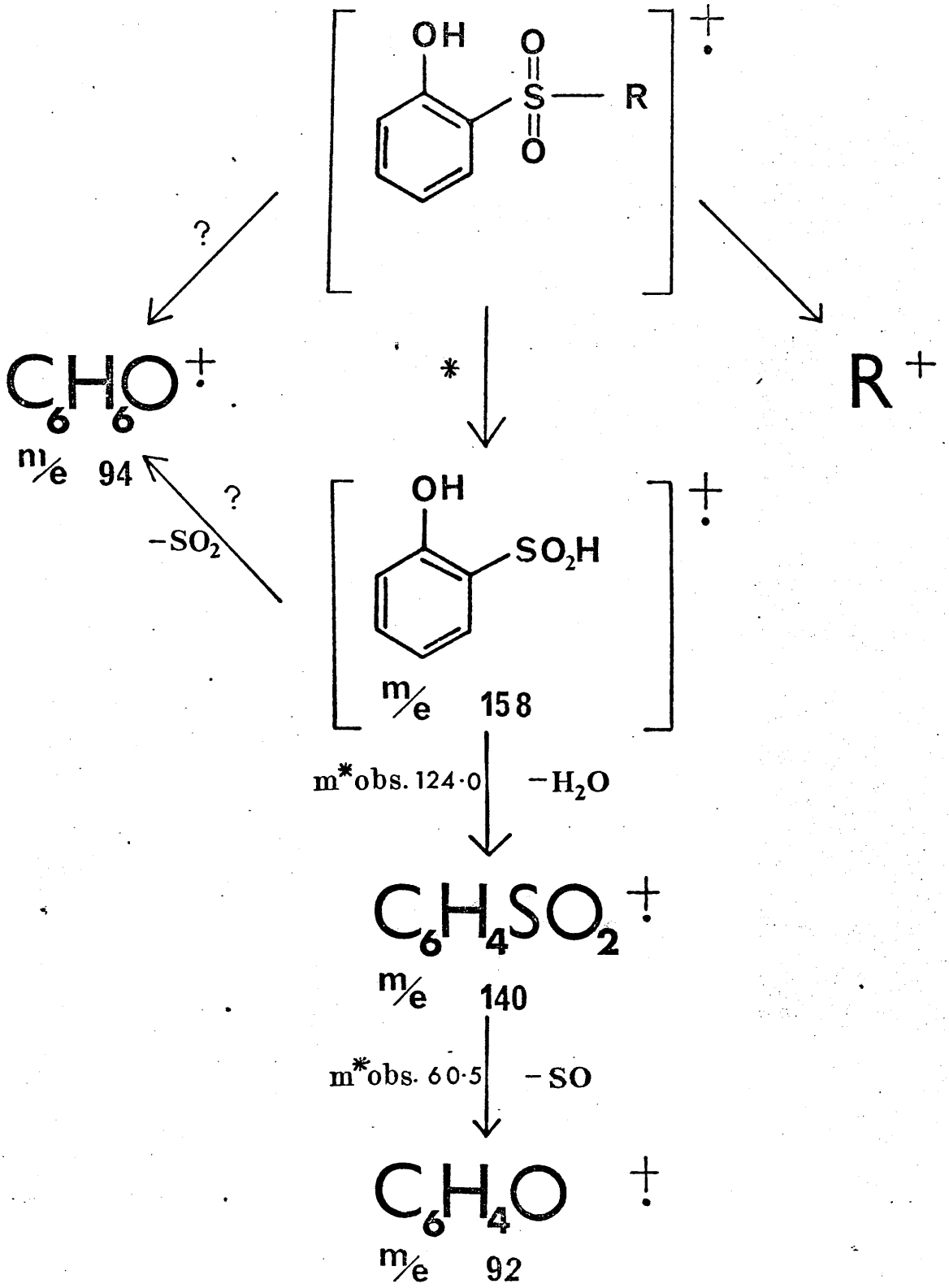
The only reasonable formula for m/e 140 involves loss of the elements of ethanol. Although, as mentioned above, the presence of a metastable peak does not prove that the loss occurs as a one-step process,[29] it very often is indicative of this.[30] The loss of ethanol in a single process would necessitate migration of the

ethyl group to oxygen, followed by the operation of an ortho-effect,[31] as shown in Figure 10b. Although alkyl migrations have been observed in many sulphur compounds,[2,3] skeletal rearrangement reactions tend to be more favoured when unsaturated substituents are present.[1] It is surprising, therefore, that the spectrum does not solely display aryl migration products. The driving force for the ethyl migration may be the stability of the ethanol eliminated and of the conjugated ion at m/e 140.

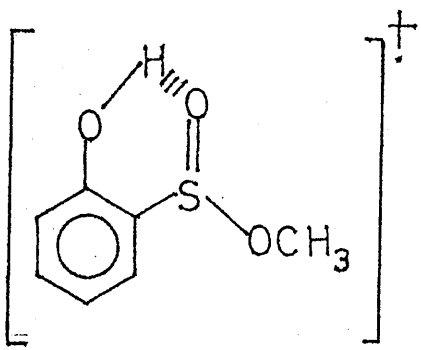
Formation of m/e 140 could also occur from m/e 158 and m/e 157, as shown by metastable ions in many of the other spectra. However, these metastable ions are absent in the spectrum of XIV and it thus seems likely that many of the m/e 140 ions are formed directly from the parent ion. This ion then undergoes decomposition by loss of carbon monoxide and sulphur monoxide to give m/e 112 and m/e 92 respectively, with a metastable ion at m/e 60.6 (calculated 60.5) for the latter process.

It is surprising that the mechanism involving the ethanol loss described above does not also operate for methyl 2-hydroxyphenyl sulphone. However, the m/e 140 ion ($M - CH_3OH$) has a relative intensity of only 1.5%, whilst m/e 141 ($M - CH_3O$) is 2.5% of the base peak. One possible explanation for this is that the ion

FIGURE 11


OH
O
S
O
R
+·
?
C6H6O+·
m/e 94
*
R+
OH
SO2H
+·
?
−SO2
m/e 158
m*obs. 124·0
−H2O
C6H4SO2+·
m/e 140
m*obs. 60·5
−SO
C6H4O+·
m/e 92

formed by methyl migration is still strongly chelated as shown below.



Rotation about the sulphur-carbon bond would be required for the methanol elimination reaction. Steric factors may have the effect of reducing the strength of the chelation in the case of the ethyl compound.

Figure 11 shows the general fragmentation of compounds XV-XXII. The constitution of the important ions has been confirmed by mass measurement on XVI, as shown below in Table 3.

TABLE 3.

Nominal Mass	Mass Observed	Mass Calculated	Formula Assigned.
158	158.003798	158.003763	$C_6H_6O_3S$
140	139.993388	139.993200	$C_6H_4O_2S$
96	96.003233	96.001372	C_5H_4S
94	94.041499	94.041862	C_6H_6O
92	92.026087	92.026213	C_6H_4O

The loss of water from m/e 158 implies that the hydrogen transferred

in the olefin elimination (M $\longrightarrow$ m/e 158) migrates to one of the sulphone oxygen atoms, as previously suggested for dialkyl sulphones.[21] In this paper, Aplin and Bailey also noted that double hydrogen rearrangement took place, similar to that occurring in esters greater than methyl.[32] They concluded that the double rearrangement ion increased with the length of the alkyl substituent and the hydrogen atoms transferred were mainly β-and γ-secondary hydrogen atoms. Similar results were obtained by Bowie et al.[20] Table 4 below shows the effect of changing the alkyl substituent on the simple cleavage ion (m/e 157), the single rearrangement ion (m/e 158) and the double rearrangement ion (m/e 159) in this series of compounds. The methyl and ethyl compounds discussed above showed only an ion at m/e 157, after corrections had been made for heavy isotopes.

TABLE 4.

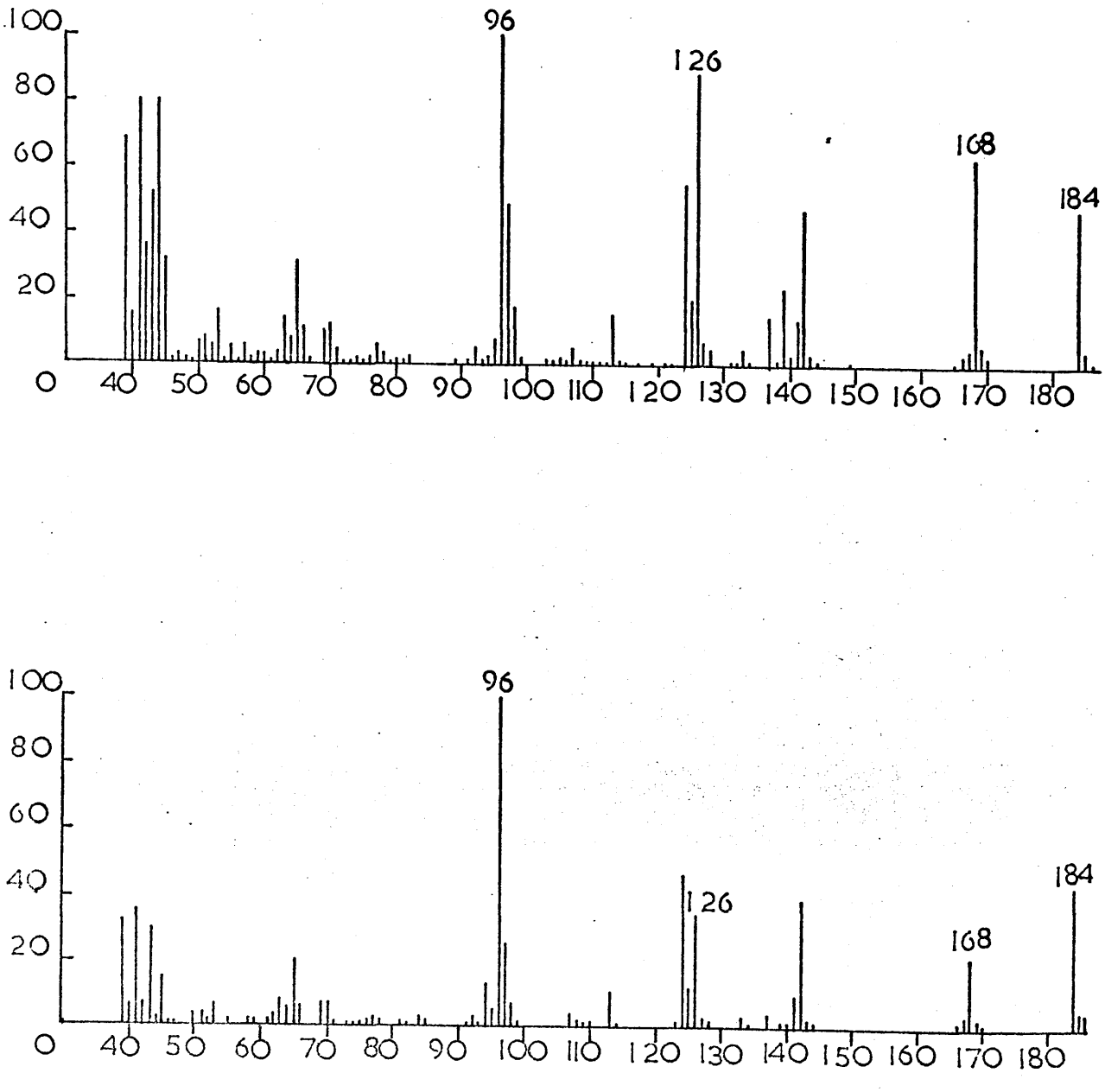
Compound.	Rel.Int.% m/e 157	Rel.Int.% m/e 158	Rel.Int.% m/e 159
XV.	3.7	2.6	-
XVI.	0.9	13.5	-
XVII.	4.0	6.1	0.9
XVIII.	1.0	17.0	3.4
XIX.	4.2	6.2	1.6
XX.	-	18.7	0.7
XXI.	4.6	12.0	15.8
XXII.	1.1	14.7	0.2

These results show that the single rearrangement ion is more important than the double rearrangement ion. However, this may be

due to the m/e 159 ion undergoing more rapid decomposition. The results also support the findings of Aplin and Bailey, and it is observed that the double rearrangement ion is most important for 2-hydroxyphenyl isopentyl sulphone (XXI). In this case the γ-hydrogen atom is tertiary and its migration is more favourable than for a secondary or a primary hydrogen atom. However, labelling experiments would be required to substantiate the origin of any of the transferred hydrogen atoms.

Although m/e 140 is the base peak in most of the sulphones XV - XXII, the compounds XX, XXI and XXII have base peaks corresponding to hydrocarbon fragments at m/e 57, m/e 43 and m/e 55 respectively. Similarly, the mass spectra of benzyl 2-hydroxyphenyl sulphone (XXIII) and 2-hydroxyphenyl 1-phenylethyl sulphone (XXIV) are dominated by hydrocarbon fragments. They have base peaks at m/e 91 and m/e 105 respectively and are very similar to the spectra of the corresponding sulphides. The loss of sulphur dioxide from the molecular ion, which is observed in many diaryl sulphones,[22-27] gives rise to small peaks in only two of the spectra. The ion occurs at m/e 184 (1.6%) in the spectrum of benzyl 2-hydroxyphenyl sulphone and at m/e 148 (3.6%) in the spectrum of but-2-enyl 2-hydroxyphenyl sulphone.

FIGURE 12



MIXTURE SPECTRA OF 2—HYDROXYPHENYL n—PROPYL SULPHOXIDE.

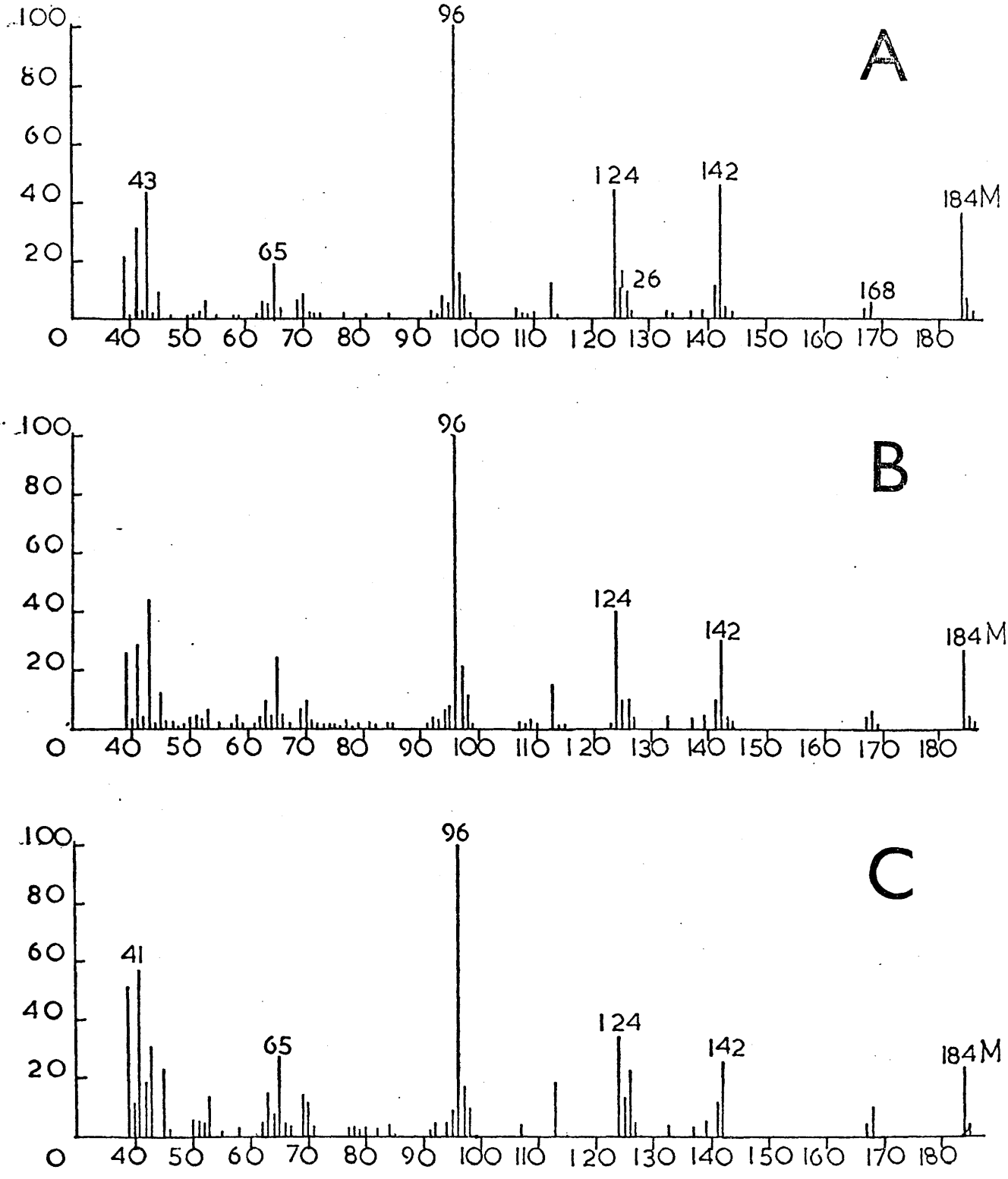
C. Sulphoxides.

Dialkyl sulphoxides[4,20] display few rearrangement ions in their mass spectra (with the exception of dimethyl sulphoxide). The most important ions are olefin elimination ions and hydrocarbon fragments. However, the introduction of unsaturation in methyl vinyl sulphoxide[4,33] gives rise to skeletal rearrangement ions. In common with sulphones, aromatic sulphoxides[20,26,27] show many abundant rearrangement ions and there is evidence of aryl migration from sulphur to oxygen.

The spectra of many sulphoxides show abundant peaks due to the loss of a single oxygen atom from the molecular ion.[20,26,27] The base peak in the spectrum of dibenzothiophene sulphoxide[26] is the $(M-O)^+$ ion. It was, therefore, no surprise when the sulphoxides in Figure 1 exhibited loss of 16 mass units from the molecular ion, although in common with other reported oxygen losses there were no metastable peaks to support the fact that this was electron impact induced. However, considerable variation was noticed in the ratio of the molecular ion to the $(M-16)^+$ ion on the examination of several spectra of the same compound.

Two of the spectra obtained of 2-hydroxyphenyl n-propyl sulphoxide (XXVII) are shown in Figure 12. The results implied that the sulphoxides were mixtures. This was reasonable, since they were obtained by oxidation of the corresponding sulphides.[34] Low electron voltage spectra substantiated this fact.

FIGURE 13



2-HYDROXYPHENYL n-PHENYL SULPHOXIDE.

The sulphoxide XXVII was selected for further investigation. Gas-liquid chromatography showed a small impurity peak which could correspond to the sulphide. Consequently, a mass spectrum was obtained by using combined gas-liquid chromatography-mass spectrometry (G.C.M.S.) and this is shown in Figure 13a. It can be seen that the $(M-16)^+$ ion is of much less importance than previously, in spite of the fact that the source temperature for this run was 290°C, some 130° higher than for the initial spectra. A sample of this compound was purified by recrystallising six times and its spectrum is shown in Figure 13b. The purity was checked by gas-liquid chromatography.

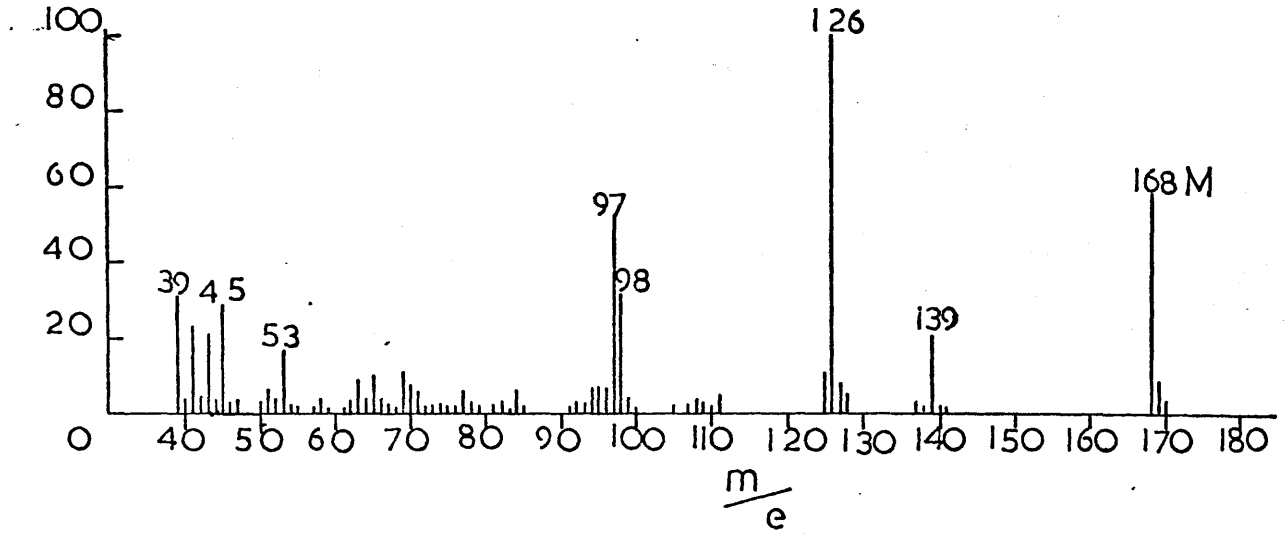
In view of the difficulties involved in multi-recrystallisation of many small samples and of obtaining G.C.M.S. results from many samples, it was considered to be worthwhile to attempt to obtain pure spectra by a method of mixture analysis first developed by Johnsen[35] and later by Meyerson.[36] This method is applicable to binary mixtures, although in favourable cases it can be extended to include more components. This investigation was further prompted by the fact that Dr. L. Monteiro had written a computer programme to carry out the tedious arithmetic associated with this method. This programme had not been properly tested and the data from this experiment seemed to offer this opportunity.

The method of analysis depends on there being two peaks in the spectrum, one of which can be uniquely attributed to one component and one to the other. If this condition does not hold, it may still be possible to carry out the analysis, using the peak from each component to which the other component contributes least. A further requirement is that two different mixture spectra (i) and (ii) must be available.

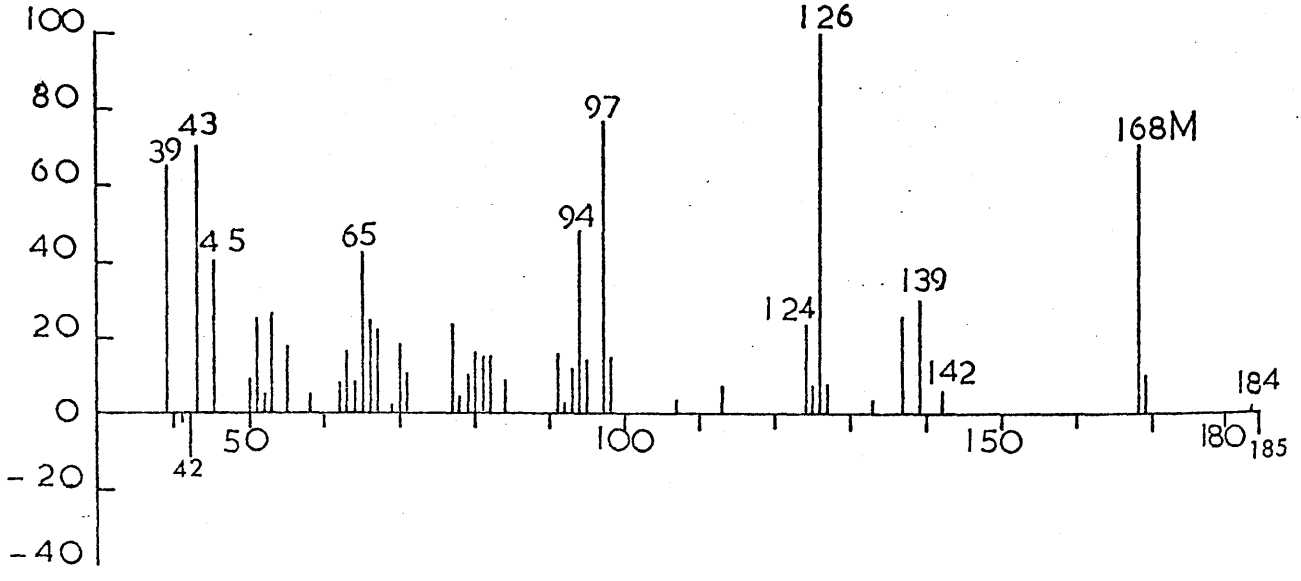
The first step in the analysis programme is to divide the intensities of ions in one of the spectra by those in the other. The unique peaks (or "best unique peaks") are located by finding the maximum and minimum ratios. One of the two mixture spectra (i) is multiplied by the minimum ratio and subtracted from the other (ii) to give the first pure component. The second mixture spectra (ii) is multiplied by the inverse of the maximum ratio and subtracted from the first (i) to give the second pure component.

If the analysis has not been successful, this is shown by negative peaks in the spectra. Therefore, at this stage, a test is made to find the number of negative peaks in the derived spectra. If this is greater than 25% of the total, the calculation should be repeated as follows. Mixture (i) is now multiplied by the inverse of the maximum ratio and subtracted from mixture (ii) to give the first pure component, etc. If this fails to yield reasonable

FIGURE 14



2-HYDROXYPHENYL n-PROPYL SULPHIDE.



DERIVED SPECTRUM OF 2-HYDROXYPHENYL n-PROPYL SULPHIDE.

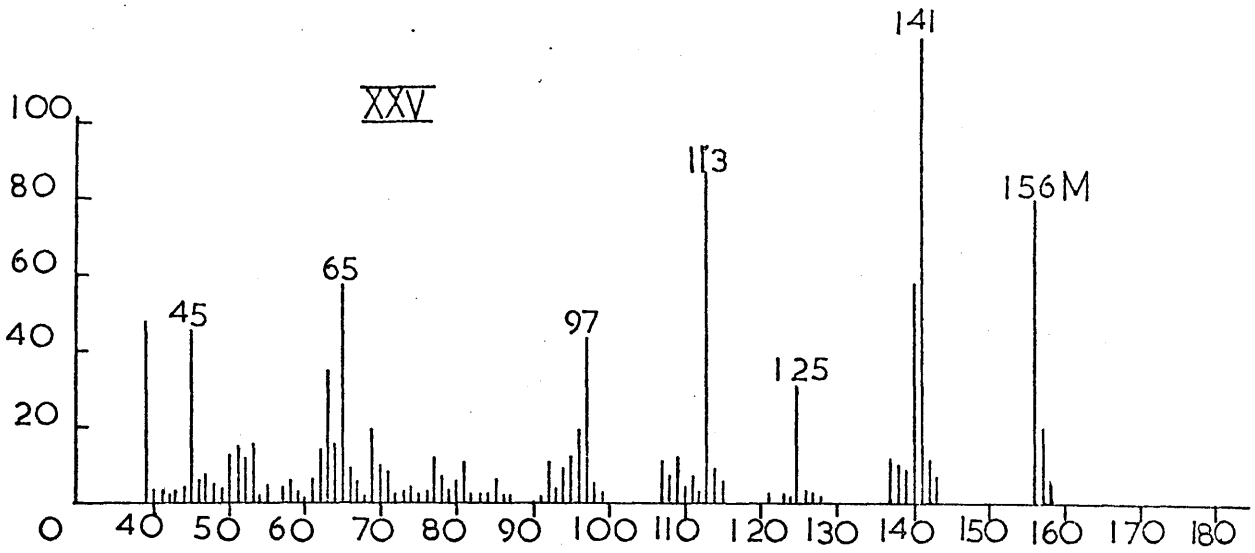
results, the reason may be that there are no unique peaks, or perhaps a third component is present.

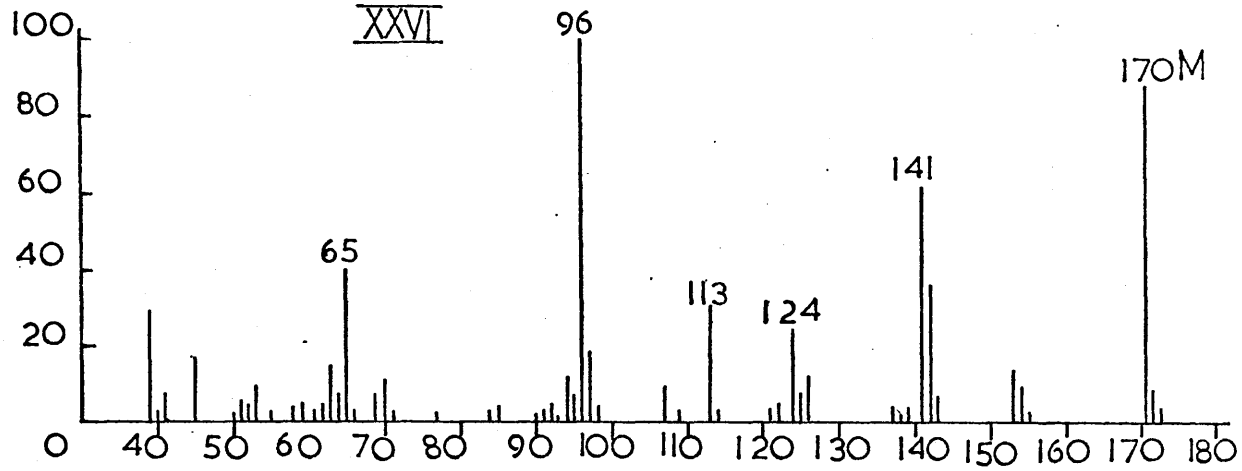
This approach was used on the two runs of 2-hydroxyphenyl n-propyl sulphoxide shown in Figure 12. The two spectra were obtained as in the experimental section. The best results from the analysis were obtained by omitting peaks of intensity below 2.5% of the base peak, since the uncertainty of the measurement is greater for these peaks. The resultant spectrum is shown in Figure 13c, several negative peaks of intensity $\leqslant 1\%$ having been omitted. It can be seen that, despite some minor differences, the agreement is good between the derived spectrum and the "pure spectra" obtained by the other methods.

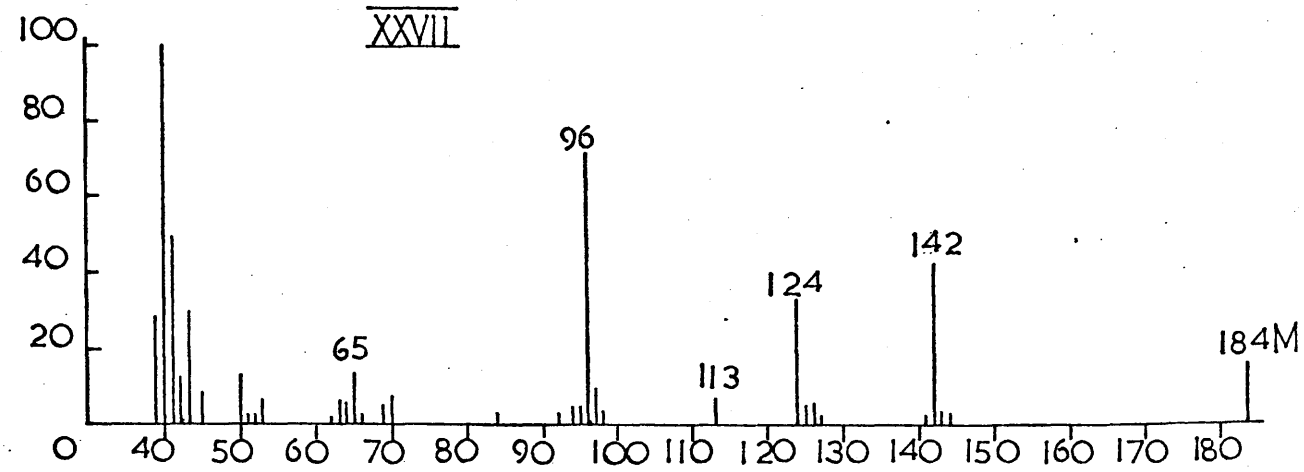
Figure 14 gives a comparison of the spectrum of 2-hydroxyphenyl n-propyl sulphide (III) as obtained previously and the derived spectrum obtained by the mixture analysis. It can be seen that the agreement is not as good as for the corresponding sulphoxides, although it is obviously much closer than either of the two mixture spectra in Figure 12. The negative peaks at m/e 41, 42 and 185 are indicative of the poorer result.

However, these results made this approach seem worth continuing and the compounds XXVI and XXVIII - XXXIV were subjected to this analysis, using two mixture spectra obtained as before in each case.

FIGURE 15







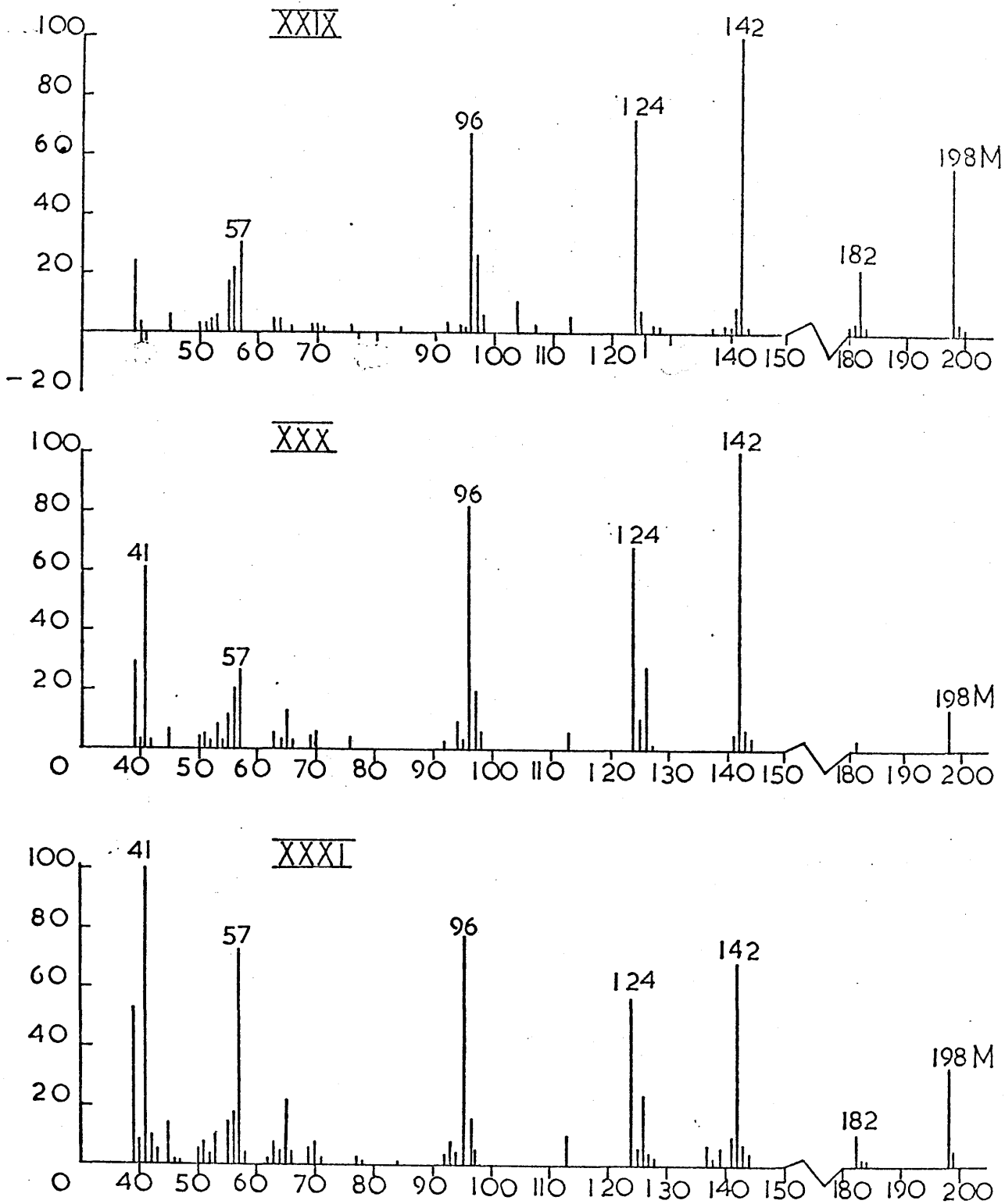
SULPHOXIDES.

Ions below 2.5% relative intensity were omitted from the data, as was m/e 44 which often had a background contribution. Little variation was found in the mass spectrum of 2-hydroxyphenyl methyl sulphoxide (XXV) and no analysis was carried out on this compound.

Initial results were poor in that the computer gave failures on many of the mixtures. It was found on consultation with the computing department that the programme was not carrying out the alternative procedure mentioned above, i.e., when the first set of derived spectra showed large numbers of negative peaks, the alternative calculation was not performed. The programme was corrected and the derived spectra obtained for the sulphoxides are shown in Figures 15 - 17. The corrected programme, which is in KDF9 Algol, is in the appendix.

The results show that the unique peak condition for the analysis has essentially been fulfilled. Only one of the sulphoxide (XXIX) spectra (Figure 16) has negative peaks. The major contribution to the spectra by the peaks caused by the $(M-16)^+$ ions and their breakdown products (e.g., m/e 126) has been greatly reduced. Their intensities are now of the same order as those in the pure 2-hydroxyphenyl n-propyl sulphoxide spectrum. Similarly, the major ions are the same in all the spectra, but with the methyl (XXV) and ethyl (XXVI) compounds showing some difference. This is similar to the pattern

FIGURE 16



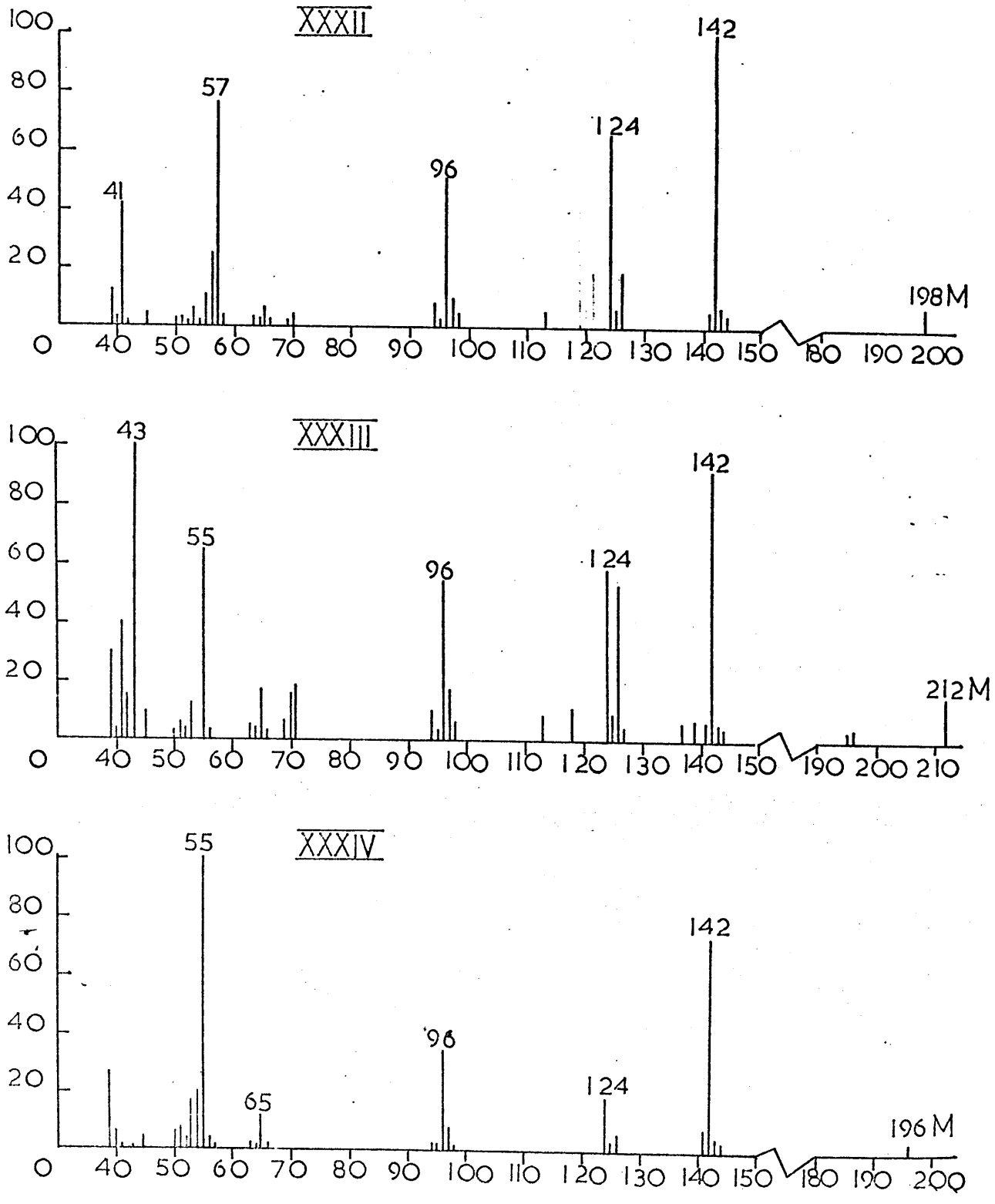
SULPHOXIDES.

followed by the sulphides and sulphones and further supports the validity of the results.

However, the derived spectrum of 2-hydroxyphenyl isopropyl sulphoxide (XXVIII), shown in Figure 15 shows that caution has to be used in considering the results obtained by this method. The base peak in the spectrum occurs at m/e 40 which is obviously in error. This may have arisen because the two mixture spectra were obtained on separate occasions, and on one of these there was a high background contribution to m/e 40. This can occur as the use of the direct insertion lock tends to give an increase in the air peaks, including argon. The other mixture spectra were obtained with the same sample, thus avoiding this problem. Alternatively, the error may have been due to the use of the direct insertion probe, causing sample pressure fluctuations which could upset the analysis. The other results do indicate the applicability of this method of analysis, even without using a leak between the sample and the source. The sulphide spectra obtained still showed some sulphoxide contribution, although they did approach the desired result.

The mass spectra of the sulphoxides were interpreted from the derived spectra and from the mass measurements made on the impure 2-hydroxyphenyl isobutyl sulphoxide (XXXI). This confirmed that the $(M-16)^+$ ion involved atomic oxygen loss and also confirmed the

FIGURE 17



SULPHOXIDES.

formulae of the ions m/e 139, 137 and 126 which are associated with the sulphide spectra. The measurements are in Table 4. Of necessity, metastable transitions were assigned using the mixture spectra, but omitting those associated with the sulphide spectra. Those observed in most of the spectra were also observed in the spectrum of the pure n-propyl substituted sulphoxide (XXVII).

TABLE 4.

Nominal Mass	Mass Observed	Mass Calculated	Formula Assigned.
182	182.0766	182.0765	$C_{10}H_{14}OS$
142	142.0091	142.0088	$C_6H_6O_2S$
141	141.0014	141.0010	$C_6H_5O_2S$
139	139.0217	139.0218	C_7H_7OS
137	137.0061	137.0061	C_7H_5OS
126	126.0142	126.0139	C_6H_6OS
124	123.9982	123.9983	C_6H_4OS
113	113.0053	113.0061	C_5H_5OS

The loss of an oxygen atom is only important for 2-hydroxyphenyl methyl sulphoxide (Figure 15) and this may be due in part to some sulphide present, although no variation in the spectrum was observed. The ion at m/e 140 then decomposes by methyl loss (m^* observed 111.6; calculated 111.5 for $140^+ \rightarrow 125^+$). to m/e 125. The other major

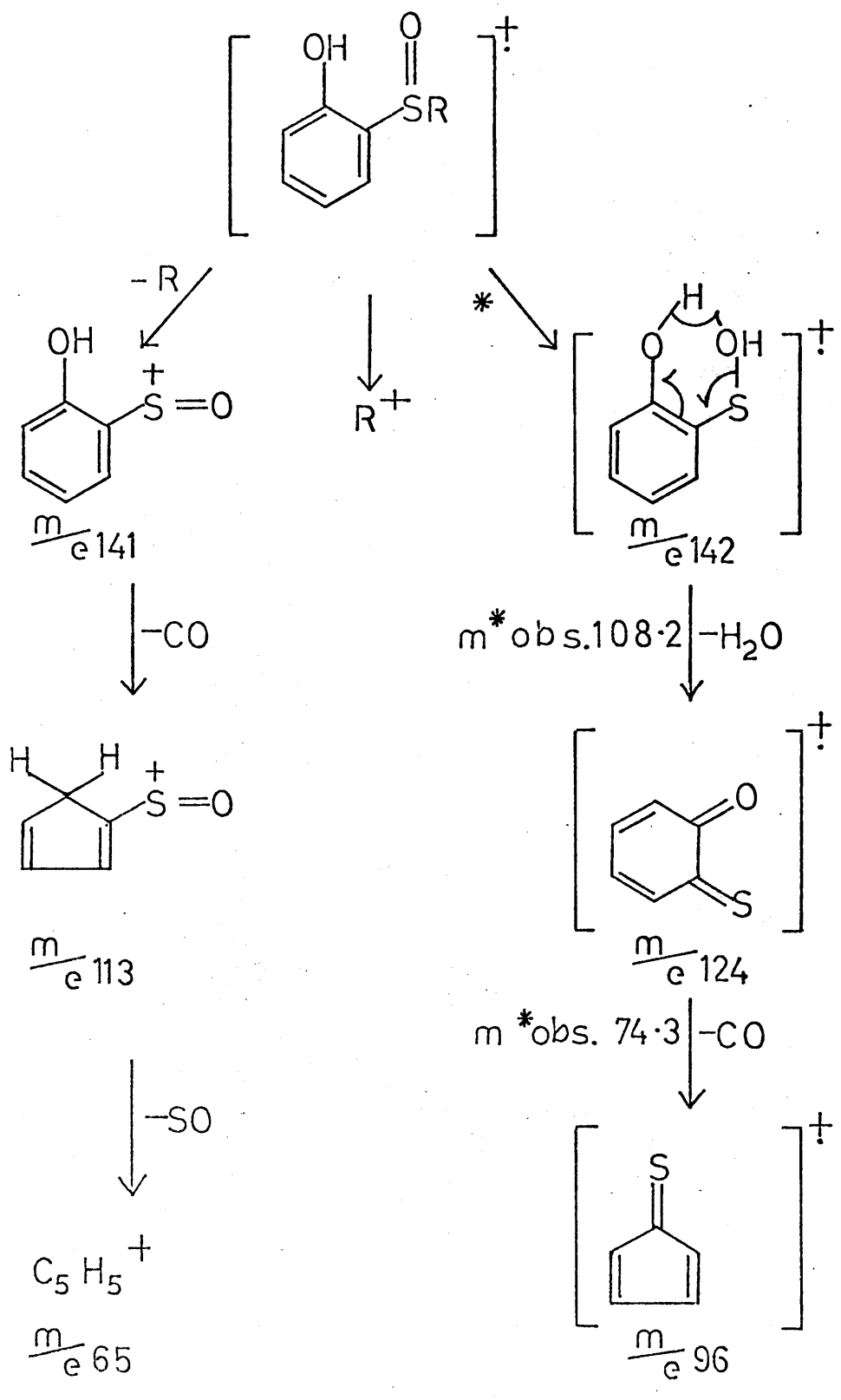

OH
O
SR
-R
R+
*
H
O
OH
S
m/e 141
m/e 142
-CO
m* obs. 108·2
-H2O
H
H
S=O
O
S
m/e 113
m/e 124
-SO
m* obs. 74·3
-CO
C5 H5+
m/e 65
m/e 96

FIGURE 18

process is loss of methyl from the molecular ion to m/e 141. This is followed by carbon monoxide elimination to give m/e 113, as shown by a metastable peak at m/e 90.7 (calculated 90.6). However, there is no evidence for important skeletal rearrangement ions, as is the case for the methyl sulphone (XIII).

Ethyl 2-hydroxyphenyl sulphoxide (Figure 15) shows the same general fragmentation as the other sulphoxides, although it is only in this compound that the loss of the alkyl substituent to give m/e 141 is important. Figure 18 shows the main breakdown pathways.

The most important and best substantiated fragmentation route is initiated by olefin elimination from the molecular ion as shown. With substituents greater than ethyl, metastable peaks were not observed for the alkyl loss and subsequent decomposition.

The spectra of the benzyl (XXXV) and 1-phenylethyl sulphoxides (XXXVI) were not further investigated because of their similarity to the corresponding sulphides and sulphones, and the consequent low intensity of all ions other than the hydrocarbon peaks.

Conclusion.

The mass spectra of the sulphides and sulphoxides do not show any abundant skeletal rearrangement ions. However, the 2-hydroxyphenyl methyl and ethyl sulphones show abundant rearrangement ions due to aryl migration to sulphur. The ethyl compound also shows an intense peak, probably originating from an alkyl migration.

It has also been shown that the sulphide impurity in the sulphoxides was amenable to removal by a known mixture analysis technique, even although the samples were run on a direct insertion probe.

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EXPERIMENTAL.

The mass spectra were determined on an A.E.I. M.S.12 mass spectrometer. The ionizing voltage was 70eV and the trap current 500μA. The temperature of the source was 150°C throughout and the compounds were introduced using the direct insertion lock. When running the sulphides care was taken to keep the source pressure below 5×10^{-7} torr to avoid dimerisation. The two mixture spectra, for each impure sulphoxide, were obtained by adjustment of the height of the probe shaft to give different spectra while keeping a constant monitor current reading.

Mass measurements were carried out on an A.E.I. M.S.9 instrument. The resolution was 20,000 on a 10% valley definition.

The mass spectrum of 2-hydroxyphenyl n-propyl sulphoxide, obtained by G.C.M.S., was run on the L.K.B. 9000 instrument in the Chemistry Department. A source temperature of 290°C was used.

The gas-liquid chromatographs were run on a Pye Argon chromatograph using a 1% SE 30 column. The runs were temperature programmed (70°C - 225°C) at 4° per minute.

The mixture analyses were carried out on the English Electric KDF9 computer. The data format was as below.

Number of mass numbers used; number of components in the mixture;

Mass number; intensity in mixture (i); intensity in mixture (ii); and so on for subsequent mass numbers.

The spectra of the sulphides and sulphones are tabulated overleaf.

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2-HYDROXYPHENYL METHYL SULPHIDE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
39	10.8	63	6.3	98	2.3
40	1.0	64	2.5	99	1.2
41	1.8	65	4.3	105	1.5
43	1.1	66	0.9	107	3.6
44	1.1	67	1.5	108	0.6
45	14.5	69	4.5	111	0.5
46	1.0	70	3.8	121	1.1
47	1.9	71	1.6	125	39.0
48	1.0	74	0.6	126	3.1
49	0.5	77	3.8	127	1.8
50	2.7	78	2.6	137	0.6
51	3.8	79	0.5	139	1.0
52	1.9	81	1.2	140	100.0M
53	6.6	83	0.5	141	9.2
54	0.5	92	0.8	142	5.2
55	1.6	93	1.2		
57	1.1	94	5.3		
58	0.7	95	2.4		
61	1.1	96	4.0		
62	2.2	97	34.6		

ETHYL 2-HYDROXYPHENYL SULPHIDE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
39	20.2	61	2.8	82	3.0	110	0.9
40	2.5	62	4.3	83	0.5	111	3.0
41	1.8	63	11.5	84	7.2	119	0.9
42	0.6	64	5.2	85	1.1	120	1.3
43	0.9	65	11.9	86	0.5	121	2.6
44	4.9	66	5.3	91	4.3	125	15.7
45	33.8	67	1.7	92	2.3	126	57.0
46	1.5	68	1.0	93	2.3	127	4.9
47	2.6	69	14.3	94	9.6	128	3.0
49	0.9	70	8.5	95	8.5	135	0.6
50	4.8	71	7.2	96	8.3	137	1.5
51	7.2	72	1.0	97	83.6	139	31.0
52	4.3	73	0.8	98	20.1	140	3.1
53	22.1	74	1.2	99	4.9	141	1.7
54	1.2	75	0.9	100	1.2	154	100.0M
55	2.2	76	0.5	103	0.9	155	8.7
57	1.4	77	5.1	105	0.5	156	4.8
58	3.6	78	1.9	107	1.0		
59	3.1	79	1.0	108	2.7		
60	1.1	81	1.7	109	1.4		

2-HYDROXYPHENYL n-PROPYL SULPHIDE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
39	31.3	60	0.5	81	1.4	111	2.3
40	4.1	61	1.2	82	2.5	121	0.5
41	22.7	62	2.5	83	0.5	125	11.6
42	4.3	63	9.0	84	5.9	126	100.0
43	21.3	64	4.5	85	0.8	127	7.7
44	4.8	65	10.0	91	1.4	128	4.9
45	29.3	66	4.7	92	1.9	137	2.7
46	1.7	67	1.7	93	1.7	139	20.0
47	3.0	68	0.7	94	6.5	140	2.2
48	0.5	69	10.7	95	6.7	141	1.4
49	0.7	70	7.3	96	6.5	153	0.5
50	3.3	71	5.9	97	52.0	168	58.7M
51	5.9	72	0.9	98	17.5	169	6.8
52	3.3	73	1.0	99	3.5	170	3.3
53	17.3	74	1.5	100	1.1		
54	1.2	75	0.9	105	0.5		
55	2.1	76	2.1	107	1.3		
57	1.0	77	5.5	108	2.1		
58	2.7	78	2.3	109	1.6		
59	1.1	79	1.1	110	0.7		

2-HYDROXYPHENYL ISOPROPYL SULPHIDE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
39	11.2	64	1.7	96	2.0	170	2.4
40	2.2	65	4.2	97	32.9		
41	10.8	66	2.4	98	12.1		
42	2.7	69	4.2	99	2.0		
43	12.5	70	2.4	100	0.8		
44	1.5	71	2.1	108	1.7		
45	6.2	73	0.6	109	0.7		
47	0.6	74	0.6	111	0.5		
50	1.6	76	1.2	119	0.5		
51	1.8	77	0.6	120	0.5		
52	1.3	81	0.6	125	5.4		
53	7.0	82	1.5	126	100.0		
54	0.5	83	0.5	127	7.0		
55	0.8	84	5.1	128	4.5		
57	0.5	85	0.5	137	0.6		
58	1.3	91	1.0	139	0.5		
59	1.5	92	0.8	151	0.6		
61	0.5	93	1.2	153	1.5		
62	1.1	94	6.3	168	54.4M		
63	3.4	95	1.8	169	5.1		

2-HYDROXYPHENYL n-BUTYL SULPHIDE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
39	20.5	60	0.8	85	0.8	126	100.0
40	5.4	61	1.0	90	0.8	127	7.9
41	32.6	62	1.2	91	1.5	128	5.1
42	3.3	63	4.6	92	1.0	137	2.7
43	7.5	64	2.5	93	1.2	138	0.5
44	9.8	65	7.5	94	12.3	139	11.9
45	16.7	66	5.9	95	5.6	140	1.7
46	1.0	67	1.5	96	2.7	141	0.6
47	1.2	68	0.8	97	25.1	182	41.2M
49	0.8	69	4.4	98	11.7	183	5.1
50	3.3	70	2.7	99	1.7	184	2.3
51	4.4	71	2.1	100	0.6		
52	2.1	74	0.8	107	1.2		
53	11.3	76	0.8	108	1.2		
54	2.1	77	3.6	109	1.0		
55	9.0	78	1.4	110	0.6		
56	8.2	79	1.0	111	1.0		
57	15.5	81	0.8	121	0.8		
58	1.5	82	1.4	122	1.0		
59	1.0	84	4.6	125	6.7		

2-HYDROXYPHENYL s-BUTYL SULPHIDE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
39	20.0	60	0.5	85	0.5	127	7.6
40	2.7	61	1.1	91	2.3	128	5.1
41	27.6	62	1.4	92	1.2	137	1.2
42	2.0	63	5.4	93	1.3	139	1.0
43	1.1	64	2.4	94	6.4	151	0.9
44	2.0	65	6.2	95	3.0	153	3.7
45	11.9	66	4.2	96	3.7	154	0.4
46	0.5	69	6.5	97	37.6	167	0.7
47	1.1	70	4.2	98	13.8	182	31.9M
49	0.6	71	4.0	99	2.4	183	4.0
50	2.6	72	0.6	100	0.9	184	1.7
51	4.2	73	0.5	107	0.5		
52	2.2	74	0.6	108	1.3		
53	14.3	76	0.6	109	1.1		
54	1.4	77	1.5	110	0.6		
55	5.9	78	0.5	111	0.5		
56	3.6	79	0.5	119	0.8		
57	17.1	81	1.0	120	0.7		
58	1.6	82	1.5	125	8.6		
59	2.5	84	4.6	126	100.0		

2-HYDROXYPHENYL ISOBUTYL SULPHIDE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
39	27.8	59	0.8	82	0.9	125	8.3
40	4.8	61	0.7	84	3.7	126	100.0
41	45.1	62	1.5	85	0.7	127	7.5
42	4.8	63	4.6	87	0.6	128	4.8
43	5.2	64	2.2	90	0.7	137	3.3
44	1.4	65	7.6	91	0.6	138	0.5
45	23.9	66	4.9	92	1.0	139	20.9
46	1.2	67	1.6	93	1.2	140	2.9
47	1.7	69	4.5	94	11.8	141	1.1
48	0.8	70	3.4	95	8.1	167	0.8
49	0.9	71	2.5	96	3.4	182	58.2M
50	3.3	72	0.5	97	26.0	183	6.7
51	4.0	73	0.7	98	9.0	184	3.1
52	2.1	74	0.9	99	1.7		
53	10.2	75	0.5	100	0.6		
54	1.2	76	1.2	107	1.3		
55	6.9	77	4.3	108	1.2		
56	8.7	78	2.0	109	1.1		
57	40.3	79	0.8	110	0.6		
58	2.1	81	0.7	111	1.6		

2-HYDROXYPHENYL t-BUTYL SULPHIDE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
39	44.9	59	1.5	82	1.1	128	5.9
40	9.4	61	1.5	84	4.5	129	0.8
41	67.9	62	3.0	91	1.9	135	0.9
42	3.8	63	7.9	92	1.1	167	1.9
43	1.9	64	3.0	93	1.9	182	14.9M
44	19.3	65	11.7	94	13.2	183	1.5
45	15.9	66	7.9	95	3.4	184	0.9
46	1.1	67	1.9	96	3.6		
47	1.3	68	0.9	97	37.7		
48	0.6	69	7.4	98	13.0		
49	1.5	70	4.9	99	2.3		
50	7.2	71	4.9	100	0.8		
51	8.1	73	1.1	105	0.8		
52	4.0	74	1.1	107	1.1		
53	19.4	75	0.8	108	1.7		
54	1.9	76	0.8	109	0.8		
55	9.4	77	2.3	110	1.7		
56	13.2	78	1.1	125	8.1		
57	67.9	79	1.5	126	100.0		
58	3.8	81	1.3	127	9.3		

2-HYDROXYPHENYL ISOPENTYL SULPHIDE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
39	12.1	61	0.6	91	1.0	141	0.5
40	3.0	62	0.7	92	0.6	153	1.0
41	16.5	63	2.5	93	0.7	168	0.5
42	7.5	64	1.4	94	6.6	196	35.8M
43	35.4	65	3.8	95	3.0	197	4.2
44	54.2	66	2.7	96	1.6	198	1.9
45	9.4	67	1.7	97	13.1		
46	0.7	68	0.5	98	4.9		
47	0.8	69	2.2	99	1.0		
49	0.5	70	5.4	107	0.9		
50	2.0	71	5.0	108	0.9		
51	2.3	72	0.5	109	0.6		
52	1.3	74	0.6	111	0.6		
53	6.5	76	1.0	125	6.3		
54	1.0	77	2.2	126	100.0		
55	15.6	78	1.0	127	7.3		
56	2.0	79	0.5	128	4.5		
57	1.7	81	0.5	137	2.5		
58	0.8	82	0.5	139	7.1		
59	0.8	84	2.2	140	1.4		

BUT-2-ENYL 2-HYDROXYPHENYL SULPHIDE.

m/e	%Abund.	m/e	%Abund.	m/e	%Aburd.	m/e	%Abund.
39	27.8	62	2.4	91	1.4	132	0.8
40	3.5	63	6.6	92	1.3	137	1.1
41	3.6	64	2.8	93	1.0	139	0.5
44	3.9	65	6.0	94	5.4	151	0.9
45	14.9	66	4.3	95	3.8	180	27.1M
46	1.0	67	0.8	96	5.4	181	3.2
47	1.3	69	9.4	97	34.9	182	1.5
49	1.2	70	5.7	98	9.8		
50	5.8	71	4.9	99	2.1		
51	7.7	72	0.6	100	0.7		
52	3.8	74	0.8	105	0.6		
53	22.3	75	0.5	107	0.6		
54	5.5	76	2.7	108	1.3		
55	100.0	77	1.7	109	0.7		
56	4.7	78	1.0	110	0.6		
57	0.9	79	0.9	111	0.6		
58	2.1	81	1.1	125	7.2		
59	1.1	82	1.6	126	49.0		
60	0.4	84	3.3	127	4.0		
61	1.1	85	1.2	128	2.9		

BENZYL 2-HYDROXYPHENYL SULPHIDE.

m/e	%Abund.	m/e	%Abund.
39	5.1	90	0.8
40	0.8	91	100.0
41	1.1	92	9.1
44	1.0	93	0.5
45	2.5	94	4.3
50	1.5	95	0.7
51	2.5	96	0.7
52	1.0	97	3.2
53	2.1	98	0.5
62	0.9	121	0.6
63	3.2	125	1.1
64	1.1	126	1.0
65	11.8	216	21.0M
66	2.0	217	3.5
69	1.2	218	1.3
70	1.0		
71	0.6		
77	0.9		
78	0.6		
89	1.9		

2-HYDROXYPHENYL 1-PHENYLETHYL SULPHIDE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
39	2.3	79	7.7	231	1.5
44	0.6	80	0.6	232	0.5
45	1.4	89	0.6		
50	1.8	91	4.1		
51	3.8	94	3.6		
52	1.4	95	0.5		
53	2.2	96	0.5		
62	0.6	97	4.3		
63	1.9	98	1.0		
64	0.6	102	1.3		
65	2.0	103	8.7		
66	1.1	104	9.4		
69	1.0	105	100.0		
70	0.7	106	9.5		
71	0.5	107	0.5		
74	0.8	125	1.6		
75	0.6	126	6.3		
76	0.8	127	0.6		
77	10.0	213	0.5		
78	5.1	230	8.7M		

2-HYDROXYPHENYL METHYL SULPHONE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
39	31.5	62	6.9	85	0.6	158	4.7
40	2.8	63	22.5	91	1.1	159	3.3
41	1.5	64	14.0	92	6.7	172	100.0M
42	0.6	65	66.5	93	53.5	173	8.3
43	0.7	66	7.9	94	13.5	174	5.2
44	0.7	67	1.1	95	1.8		
45	5.7	69	2.7	96	3.1		
46	1.2	70	2.1	97	2.2		
47	2.2	71	0.5	98	0.5		
48	2.7	73	0.5	107	2.3		
49	0.9	74	2.1	108	0.5		
50	5.4	75	1.6	109	80.0		
51	5.9	76	0.9	110	7.3		
52	5.6	77	4.2	111	0.7		
53	8.5	78	2.1	113	3.3		
54	0.8	79	2.0	125	0.8		
55	2.0	80	2.2	126	0.5		
57	0.5	81	15.0	140	1.2		
58	1.1	82	1.2	141	2.5		
61	2.2	84	0.9	157	57.5		

ETHYL 2-HYDROXYPHENYL SULPHONE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
39	33.3	65	45.0	92	35.0	140	100.0
41	0.8	66	5.0	93	28.3	141	10.8
42	0.5	67	0.6	94	13.5	142	5.2
43	0.8	69	2.4	95	2.4	143	0.6
44	4.5	70	2.8	96	7.3	157	35.0
45	4.0	71	0.6	97	1.9	158	3.3
46	0.5	74	1.6	98	0.6	159	2.0
47	0.5	75	1.3	103	0.7	186	88.3M
48	2.5	76	4.3	107	3.7	187	8.5
49	0.7	77	3.5	109	35.0	188	4.5
51	3.8	78	1.5	110	4.7		
52	3.3	79	1.1	111	1.1		
53	6.7	80	1.0	112	9.5		
54	0.6	81	4.5	113	5.3		
55	1.7	82	0.6	114	0.8		
59	0.9	83	0.5	121	1.3		
61	1.4	84	7.3	123	0.6		
62	4.0	85	0.9	124	0.7		
63	15.8	86	0.5	125	0.7		
64	10.3	91	1.1	126	0.6		

2-HYDROXYPHENYL n-PROPYL SULPHONE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
39	17.3	69	0.8	111	0.5
40	2.0	70	1.2	112	5.4
41	15.9	74	0.7	113	2.3
42	2.5	75	0.6	120	0.5
43	22.7	76	1.7	123	0.7
44	2.0	77	1.2	125	0.8
45	1.8	78	0.5	133	1.8
48	1.0	81	1.4	134	0.6
50	1.7	84	3.0	140	100.0
51	1.5	91	0.6	141	9.1
52	1.4	92	14.9	142	5.1
53	2.7	93	6.6	143	0.5
55	0.8	94	14.1	157	3.7
57	0.7	95	1.4	158	2.9
58	0.9	96	3.4	185	2.3
62	1.3	97	1.1	200	41.5M
63	6.3	107	4.1	201	4.4
64	4.4	108	0.5	202	2.3
65	15.4	109	4.9		
66	2.7	110	1.5		

2-HYDROXYPHENYL ISOPROPYL SULPHONE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
39	25.5	64	5.0	93	5.0	142	5.9
40	5.0	65	17.7	94	12.5	157	0.9
41	22.6	66	5.9	95	1.5	158	13.6
42	6.8	67	1.5	96	5.5	159	1.1
43	26.8	68	0.6	97	2.5	160	0.7
44	3.9	69	1.3	98	0.9	168	1.7
45	2.6	70	1.6	103	0.5	200	24.1M
47	0.5	75	0.9	107	0.5	201	3.0
48	2.6	76	0.8	109	1.9	202	1.5
50	2.6	77	2.0	110	1.6		
51	2.6	78	1.9	111	0.6		
52	1.8	79	1.1	112	6.5		
53	2.8	80	0.5	113	2.5		
54	0.7	81	1.0	114	0.5		
55	1.1	82	0.7	120	0.7		
58	1.1	83	0.5	124	1.2		
60	0.6	84	4.1	125	0.5		
61	0.8	85	0.5	126	3.7		
62	1.8	91	1.1	140	100.0		
63	6.4	92	16.6	141	8.8		

2-HYDROXYPHENYL n-BUTYL SULPHONE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
39	30.7	63	9.6	94	21.5	142	5.6
40	3.1	64	6.7	95	1.8	143	0.9
41	36.3	65	28.9	96	5.6	147	4.3
42	1.9	66	4.9	97	1.5	148	1.2
43	1.1	67	0.5	98	0.5	149	0.7
44	2.8	69	1.3	103	0.5	157	4.0
45	2.9	70	1.7	107	5.9	158	6.4
48	2.0	74	1.0	108	1.1	159	1.6
49	0.7	75	1.0	110	1.4	172	4.0
50	3.2	76	1.8	111	0.6	185	3.2
51	3.3	77	1.9	112	5.2	196	0.5
52	2.5	78	0.7	113	4.5	197	0.5
53	4.4	79	0.5	114	0.5	214	26.7M
54	0.7	80	0.6	121	7.8	215	3.4
55	6.7	81	2.2	122	1.0	216	1.6
56	4.8	84	4.6	124	0.9		
57	21.1	85	0.7	126	0.7		
58	1.6	91	0.8	133	0.6		
61	0.7	92	15.2	140	100.0		
62	2.2	93	9.6	141	14.8		

2-HYDROXYPHENYL s-BUTYL SULPHONE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
39	23.9	63	5.0	95	1.3	214	20.5M
40	4.0	64	4.2	96	4.6	215	2.7
41	3.5	65	17.1	97	1.3	216	1.2
42	2.8	66	6.3	103	0.5		
43	1.8	67	0.9	107	0.7		
45	1.7	69	0.9	109	1.6		
47	0.5	70	1.2	110	1.3		
48	2.0	74	0.8	112	4.8		
49	0.7	75	0.6	113	3.1		
50	3.1	76	1.3	121	0.7		
51	3.2	77	0.5	124	0.8		
52	1.8	78	0.9	126	1.0		
53	3.4	79	0.6	140	100.0		
54	1.0	81	1.1	141	17.8		
55	6.2	84	3.0	142	5.8		
56	8.2	85	0.5	143	1.0		
57	26.8	91	2.9	157	1.0		
58	1.5	92	12.5	158	17.1		
61	0.7	93	5.1	159	4.8		
62	1.5	94	12.5	160	1.3		

2-HYDROXYPHENYL ISOBUTYL SULPHONE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
39	28.5	64	4.4	97	1.2
40	3.2	65	20.6	107	3.5
41	43.8	66	3.1	108	0.5
42	3.8	69	0.9	109	3.6
43	2.3	70	1.2	110	1.1
44	3.7	74	0.8	112	4.0
45	2.0	75	0.6	113	3.2
48	1.7	76	1.4	124	0.8
49	0.6	77	1.6	126	0.5
50	2.3	78	0.6	140	100.0
51	2.4	79	0.5	141	16.7
52	1.8	81	1.3	142	5.4
53	2.4	84	2.6	143	0.9
54	0.5	85	0.5	157	4.2
55	4.8	91	0.5	158	6.5
56	4.8	92	12.2	159	2.3
57	63.5	93	6.5	160	0.5
58	2.4	94	34.9	214	34.9M
62	1.5	95	2.2	215	4.0
63	6.4	96	4.6	216	1.9

2-HYDROXYPHENYL t-BUTYL SULPHONE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
39	24.5	65	15.2	126	0.7
40	3.7	66	3.8	140	45.3
41	41.5	69	0.8	141	7.0
42	1.8	70	1.0	142	2.8
44	2.2	75	0.5	158	18.7
45	1.4	76	1.3	159	2.1
48	1.3	77	0.5	160	1.0
49	0.5	81	0.5	214	6.8M
50	2.2	83	1.7	215	0.9
51	2.2	92	5.7	216	0.5
52	1.3	93	4.1		
53	2.6	94	9.4		
54	0.6	95	0.8		
55	4.5	96	2.8		
56	7.7	97	1.1		
57	100.0	107	0.5		
58	4.2	109	1.1		
62	1.1	110	0.6		
63	4.6	112	2.2		
64	3.2	113	2.4		

2-HYDROXYPHENYL ISOPENTYL SULPHONE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
39	47.7	59	0.5	81	2.0	124	0.8
40	6.2	61	1.0	84	4.0	125	0.8
41	40.0	62	3.4	85	0.8	126	1.8
42	9.2	63	12.3	91	1.1	135	3.7
43	100.0	64	7.7	92	10.8	136	0.5
44	3.8	65	36.9	93	11.5	137	0.5
45	3.2	66	7.7	94	23.8	140	51.5
46	0.5	67	1.7	95	2.5	141	29.2
47	0.6	68	0.6	96	5.2	142	5.5
48	3.4	69	6.2	97	2.1	143	1.8
49	0.9	70	24.6	98	0.5	157	4.6
50	4.3	71	19.2	103	0.5	158	12.3
51	4.8	72	1.4	107	3.2	159	16.9
52	3.1	74	1.2	108	0.8	160	1.9
53	7.2	75	1.2	109	5.1	161	1.1
54	1.4	76	1.7	110	1.2	162	0.5
55	29.2	77	2.3	112	3.7	172	3.4
56	2.3	78	1.0	113	5.7	185	2.8
57	2.3	79	0.8	114	0.7	186	0.6
58	1.4	80	0.6	121	1.3	213	0.5

2-HYDROXYPHENYL ISOPENTYL SULPHONE (Contd.)

m/e	%Abund.
228	23.8M
229	3.4
230	1.5

BUT-2-ENYL 2-HYDROXYPHENYL SULPHONE.

m/e	%Abund.	m/e	%Abund.	m/e	%Abund.	m/e	%Abund.
39	34.3	65	23.6	103	0.5	212	7.5M
40	2.5	66	3.6	105	2.1	213	1.1
41	1.9	69	1.5	107	1.0	214	0.5
44	1.4	70	1.5	109	1.5		
45	2.0	74	0.8	110	0.5		
48	1.9	75	0.8	112	2.2		
49	0.6	76	0.9	113	2.0		
50	3.6	77	1.3	115	2.2		
51	4.2	78	0.8	126	0.5		
52	2.5	79	0.7	131	0.5		
53	7.2	81	0.9	133	1.8		
54	3.3	84	2.1	140	32.5		
55	100.0	85	0.5	141	3.0		
56	4.2	91	1.4	142	1.9		
57	0.5	92	6.3	147	0.9		
58	1.0	93	4.9	148	3.6		
61	0.6	94	4.6	157	1.1		
62	2.2	95	1.2	158	14.8		
63	8.6	96	3.3	159	1.4		
64	5.4	97	1.2	160	0.7		

BENZYL 2-HYDROXYPHENYL SULPHONE.

m/e	%Abund.	m/e	%Abund.
39	3.4	90	1.1
40	1.2	91	100.0
41	2.0	92	9.1
48	1.4	93	1.3
50	1.5	94	6.8
51	2.7	95	0.7
52	1.0	97	0.6
53	0.9	105	0.7
62	1.1	106	0.7
63	3.7	107	0.6
64	2.5	165	1.3
65	15.7	183	0.6
66	3.0	184	1.6
67	0.7	248	7.1M
74	0.5	249	1.1
77	1.4	250	0.5
78	1.3		
79	0.9		
81	0.7		
89	2.3		

2-HYDROXYPHENYL 1-PHENYLETHYL SULPHONE.

m/e	%Abund.	m/e	%Abund.
39	3.2	103	7.1
45	0.8	104	5.8
50	1.1	105	100.0
51	3.3	106	9.2
52	1.1	107	0.5
53	0.9	113	0.9
63	1.6	124	1.0
64	0.6	126	0.8
65	3.3	141	0.8
70	0.5	142	2.5
76	0.5	262	0.7M
77	9.6		
78	3.6		
79	9.1		
80	0.6		
91	1.0		
94	0.8		
96	1.8		
97	0.8		
102	0.8		

Appendix to Chapter 3.

ALGOL PROGRAMME.

```
begin
integer  i,j,n,l,s,a,b,M,N,N1,t;real Amax,Bmax,x,Y;
open (20); open (70);
write text (70, [MONTEIRO [cc]]);
N:=read (20); M:=read (20);
begin array H,H1[1:N,1:M], y,A,B[1:N];

integer array  m[1:N];
for i:=1 step 1 until N do
begin m[i] :=read (20);
for j:=1 step 1 until M do
H1[i,j] :=H[i,j] :=read (20);
end;

L5:  begin
writetext (70,[[cc] NUMBER OF*COMPOUNDS*IN*THE*MIXTURE]);
write (70,format ([snd]),M);
newline (70,3);

end;

W1:  for i:= 1 step 1 until N do
W2:  y [i]:= H[i,1]/H[i,2];
W3:  writetext (70,[VALUES*OF*Y [c]]);
x:=Y:=y[2];
for i:= 1 step 1 until N do
begin   if y[i]>Y then Y := y[i];
        if y[i]<x then x := y[i];

end;

s:=0; t:=0;

a:= x;
b:= Y;
for i:=1 step 1 until N do

begin

write (70,format ([s-d.dd10 +nd]),y[i]);
A[i]:= H[i,1]-aXH[i,2];
B[i]:= H[i,2]-1/bXH[i,1];
if A[i]≤-0.5 then s:= s+1;
if B[i]≤-0.5 then t:= t+1;

end;
```

```
newline (70,1);
writetext (70,[[cc] PURE*COMPOUNDS[c]];
if s > 0.25 XN or t > 0.25 XN then

begin

writetext (70,[[c] S*=]);
write (70,format ([nd]),s);
writetext (70,[[c] T*=]);
write (70,format([nd]),t);
newline (70,2);
for i:=1 step 1 until N do

begin  A[i]:= H[i,1]-1/b  XH[i,2];
       B[i]:= H[i,2]-aXH[i,1];

end;

end;

for i:=1 step 1 until N do
write (70,format([4sndd]),m[i]);
newline (70,2);
Amax:=A[1]; Bmax:= B[1];
for i:=2 step 1 until N do

begin

if Amax<A[i] then Amax:= A[i];
if Bmax<B[i] then Bmax:= B[i];

end;

for i:= 1 step 1 until N do

begin

A[i]:= A[i]/Amax X100;
write (70,format([s-ndd.d]),A[i]);

end

newline (70,1);
for i:= 1 step 1 until N do

begin

B[i]:= B[i]/Bmax X100;
write (70,format ([s-ndd.d]),B[i]);

end;
end;

close (70); close (20);

end→
```