G L A S G O W  U N I V E R S I T Y

CHEMISTRY  DEPARTMENT

A thesis entitled

# "Mass Spectrometry of some Organic Compounds"

which is submitted in fulfillment of the

regulations for the degree of Doctor of Philosophy

in the University of Glasgow

By

WILLIAM KENNETH REID, B.Sc. (Hons.)

June, 1962.

# S U M M A R Y.

A thesis entitled

"Mass spectrometry of some organic compounds"

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The thesis discusses the aspects of mass spectrometry related to organic chemistry. It is primarily concerned with involatile substances which cannot be studied by conventional mass spectrometry.

Chapter I is a brief introduction and deals with the development of mass spectrometry from the early positive beam studies to its use in organic analysis.

A study of furan (Chapter IIA) and benzfuran (Chapter IIB) systems is then discussed in an attempt to predict fragmentation patterns of the furan ring system in simple and complex structures. The cracking pattern of simple furans is considered along with the mass spectra obtained from some naturally occurring compounds, such as marrubiin and columbin, which contain a substituted furan ring. Many of these natural products are involatile substances and a direct inlet system is

used to obtain results. Some conclusions are drawn with reference to the identification of the furan system in a molecular structure and tentative structures are proposed for some of the abundant ions produced by electron impact.

Chapter III is devoted to a series of naturally occurring tetracyclic antibiotics (the pyrromycinones and rhodomycinones) which include a polyhydroxyanthraquinone system in their structure. Correlation studies of the series of mass spectra obtained have been found useful in attempts to postulate structures for some related compounds which have been studied unsuccessfully by classical organic chemists.

No worker has yet been able to predict the detailed stereochemical relationships in a compound from mass spectral data alone. Chapter IV discusses the limitations of mass spectrometry in this respect and demonstrates the use of the mass spectrometer to decide the overall "crowding" in a molecule. The chapter comments on the columbin-iso-columbin isomerism, the stereochemistry of $\xi$-rhodomycinone and its isomer and the positional isomerism which occurs in the chlorogriseophenones.

Unsatisfactory results are usually obtained from compounds which are thermally unstable or which have a highly branched structure. However, although part of the

cracking pattern obtained from derivatives of malonic acid may arise by thermal decomposition, it has been found possible to determine the molecular weight of such compounds by use of ions occurring at one mass unit greater than the parent ion. Correlation of the mass spectra of these compounds is again useful in determining structural features of some compounds which contain one or more quaternary centres.

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I hereby declare that this thesis has been composed by myself and that it has not been submitted in whole or in part, for any degree at any other University.

Signed

on the 20th. day of June, 1962.

University of Glasgow.

TABLE OF CONTENTS.



Tables of spectra are included
at end of each corresponding chapter.

# A C K N O W L E D G E M E N T S

The author wishes to express his sincere thanks to Dr. R. I. Reed for his advice, direction and stimulating encouragement which he gave during the course of these investigations.

Also, the author acknowledges the provision of synthetic samples of organic compounds from various colleagues who are named in the appropriate chapters.

Sincere gratitude is due to Miss Jean Wilkie (Glasgow University, Chemistry Department) for her expert technical assistance, and to the technical staff of the Department workshops.

The author also wishes to thank the Institute of Petroleum for a maintenance allowance during the course of this work.

Foreword.

> "It is recognised that every attempt at improvement in scientific exposition must have a limited range and the chieff critical interest will soon be trans-:ferred from what can be explained by any new formulation to what it has not shown itself competent to include".
>
> Sir Joseph Larimer, "Aether and Matter".

The fundamental concept of mass has fascinated scientists since man first attempted to rationalise his universe. Both alchemists and nuclear physicists have attempted to explain the phenomenon but each have found limitations in their expositions. The atomic theory laid waste the early concepts of "destructible" mass and the equilibration of mass and energy has stimulated vast research projects.

Chemists have not been slow to utilise the findings of the physicist since they realised the importance of atomic and molecular weight even from the era of Boyle and Dalton. Modern chemistry, with its yardstick of molecular weight, has found limitations in accurate mass measurements. Mass spectro-:metry is the one technique which is competent to record molecular mass, swiftly and automatically, and only in recent years has it been given the place that is undoubtedly its due.

# CHAPTER I.

## INTRODUCTION.

Positive ions are produced when a chemical compound, usually in the vapour phase, is bombarded with low energy electrons (50 - 70eV). Since the number and type of such ions is determined by the structure of the compound, the positive ion spectrum (the "mass spectrum") is unique for each chemical structure and thus is valuable in the analysis of chemical substances.

In 1910, Thomson [1] passed a beam of positive ions through combined electrostatic and magnetic fields. A separation of ions of different mass/charge ratio (M/e) was achieved, since each different M/e ratio corresponded to a different parabolic path in the deflecting fields. By this method, Thomson obtained the first proof of the existence of isotopes by ionizing the element neon and observing the ions which appeared at an M/e ratio of 20 and 22. Aston [2] extended this work using an instrument with consecutive electric and magnetic fields which focused all ions of the same M/e ratio, although of different velocities, on to a photographic plate. Aston's instrument was known as a "mass spectrograph" from its similarity to an optical spectograph. The term

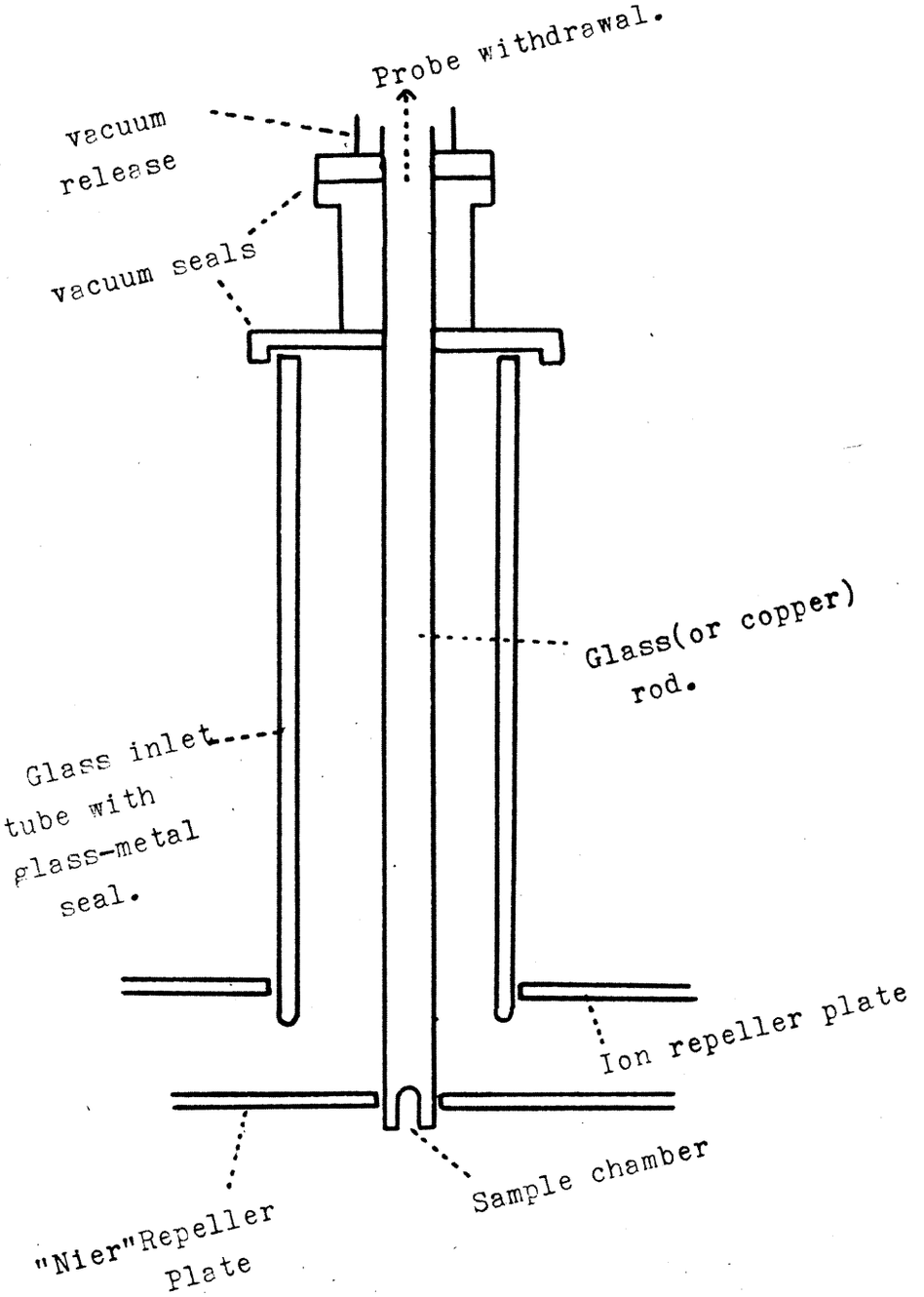
"mass spectrometer" is commonly used for modern instruments in which electrical recording of the ion beam is employed. In 1919, Dempster [3] developed an instrument in which ions of the same M/e ratio had approximately the same kinetic energy; this meant that a magnetic field alone was sufficient to focus the ion beams. In their early stages of development, these instruments were used for identification of isotopes and measurement of their natural abundance.

Instrumental advances led, about 1940, to the first important use of mass spectrometry in analysis of petroleum products. Development of heated inlet systems by O'Neal [4] and Caldecourt [5] extended the range of compounds which could be analysed in the vapour phase. Modern single-focusing machines are mainly developments of Dempster's original concept of magnetic focusing.

The sample is ionized by a beam of electrons emitted from an electrically heated tungsten filament and a mixture of positive, negative and neutral fragments is produced. The positive ions are repelled by a plate at a positive potential, and then are accelerated into the analyser tube, producing an effectively mono-energetic beam. The beam is deflected by a magnetic field at either $60^{\circ}$, $90^{\circ}$ or $180^{\circ}$ angle of deflection. The focused beam is collected on a negatively charged plate and the current produced is amplified and

recorded. The mass/charge ratio is "scanned" either by varying the magnetic field or the accelerating voltage. Modern advances include the development of double-focusing instruments [6] [7] in which mono-energetic ions are produced by primary deflection through an electrostatic field followed by conventional magnetic focusing; this method provides much greater resolving power and it appears that future advances in mass spectrometry will be derived from extensive use of such instruments.

The greatest limitation of the types of samples that can be analysed in conventional mass spectrometers is the requirement that the sample is best analysed in the vapour state. This means that it must also have sufficient stability to be heated to a temperature where it can produce a vapour pressure of approximately 50 microns. However, variations of methods of sample handling, including rapid scanning of the spectrum with the sample in the ion source [8] [9] and direct electron bombardment of the solid material [10], have provided encouraging results. To determine the molecular weight and cracking pattern of involatile materials, Reed [11] [12] has used the direct probe method in which the sample is inserted on a glass or metal probe adjacent to the repeller plate (diagram (I)). This method is useful in correlation work but suffers from the disadvantage that no pressure measurement


Probe withdrawal.
vacuum release
vacuum seals
Glass(or copper) rod.
Glass inlet tube with glass-metal seal.
Ion repeller plate
Sample chamber
"Nier"Repeller Plate

(1).

is possible. However, useful data can be obtained from a study of a series of compounds and this method has been employed in the present work.

Mass spectrometry can be generally applied to a wide range of compounds by the use of different methods of sample handling. The high sensitivity, giving abundant discrete information from a small sample (0.1 - 1.0mgms.), confirms the view that mass spectrometry, either alone or combined with other physical techniques, is a powerful analytical tool.

Since the removal of an electron from a molecule requires approximately 8-15 electron volts, mass spectra which are obtained at higher energies consist of positive ions corresponding not only to the molecular ion but also to fragment ions of the molecular structure. However, the fundamental understanding of the relationship of these fragments to chemical structure is still in its very early stages despite some fine theoretical studies [13] [14]. Empirical correlations have been used to give some valuable results without consideration of the complexities of ion formation. Even these correlations have been hindered by the uncertainty arising in rearrangement processes which occur in the ionization and fragmentation of organic molecules. McLafferty [15] has suggested that such rearrangements can be assessed in terms of current physico-organic mechanisms.

The probability of occurrence of a rearrangement reaction is dependent on the stability of the product ion, the stability of the product neutral fragment and the ease of formation of the transition state of the reaction. In some cases, the presence of the rearranged ion is difficult to confirm but, in others, the occurrence of such an ion is immediately obvious. For example, an ion at M/e=43 occurs in the spectrum of neohexane $(CH_3)_3C.CH_2.CH_3$ and can only arise by migration of a hydrogen atom and rupture of two carbon-carbon bonds.

Random rearrangements can also occur by exchange of atoms in a fragment ion. The classic example of this is the highly stable tropylium ion which has been postulated as the structure of the $C_7H_7^+$ ion by Rylander, Meyerson and Grubb (16). This ion can be derived from benzyl compounds since it acts as a stable ionic intermediate.

The factors producing stability in organic molecules have been postulated as applicable to discussions of positive ions in the mass spectrometer. Thus, ions containing aromatic or conjugated cyclic systems, are preferentially stabilized.

# CHAPTER II.

## THE MASS SPECTRA OF FURAN COMPOUNDS.

### (A) SIMPLE SUBSTITUTED FURANS.

#### (1) Introduction.

Previous studies of oxygen heterocyclic systems have been confined, until recently, to those on furan [17], tetrahydrofuran [18], 2:5-dimethylfuran [19], furfuryl alcohol [20], dibenz(o)furan [21] and some simple cyclic ethers [22]. Friedel and his collaborators [23] have also listed some mass spectra of compounds such as 1:3-trioxolane.

Reports on some furan compounds and oxygen heterocycles have recently been published in a series of papers by Collin [24] [25] [26]. These give an account of substituted furan compounds [24], furan alcohols [24] and oxygen heterocyclic compounds [26]. As an introduction to the present investigation, Collin's work will be discussed.

This author has commented on the aromatic nature of the furan nucleus and has explained many of his results in terms of the inherent stability of the corresponding ion. Comparisons have been drawn with some tetrahydrofuran derivatives [24] [25] which are not stabilized by resonance and which, consequently,

do not show abundant molecular ions.

The results obtained demonstrate that the initial major fragmentation occurs at the bond adjacent to the hetero-atom in most of these compounds (II) (III) (IV). Collin suggests that the ring opens and breakdown then occurs β- to the terminal hetero-atom. The resulting fragment ions then arise from the fissions expected from a non-cyclic oxygen compound.

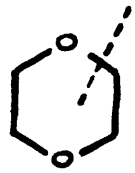
Rearrangements occur in the fragmentation of these compounds and Collin [24] assigns the large M/e=81 peak in α- furfuryl alcohol ( V ) to the stabilized pyran ion ( VI). The abundant doubly charged ion, corresponding to the peak at M/e=40.5, supports this view.

The aromaticity of the furan ring [27] is the major factor in producing a stable molecular ion under electron impact. This has observed generally for most aromatic compounds [28] [29]; other aromatic compounds such as pyridine [30] and the indoles [31] also show abundant molecular ions.

The fragment ions associated with the furan nucleus can be expected to provide evidence for its presence in other chemical structures. This is generally true, provided other fragment ions from the same structure do not give corr-:espondingly abundant peaks at the same M/e ratio. Positive

(II)

(III)



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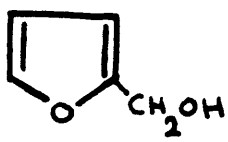

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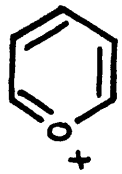
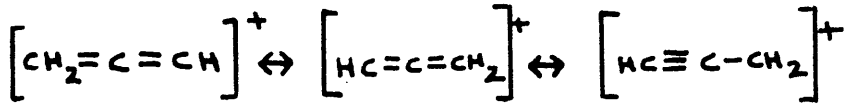


(VI)

(VII)

(VIII)



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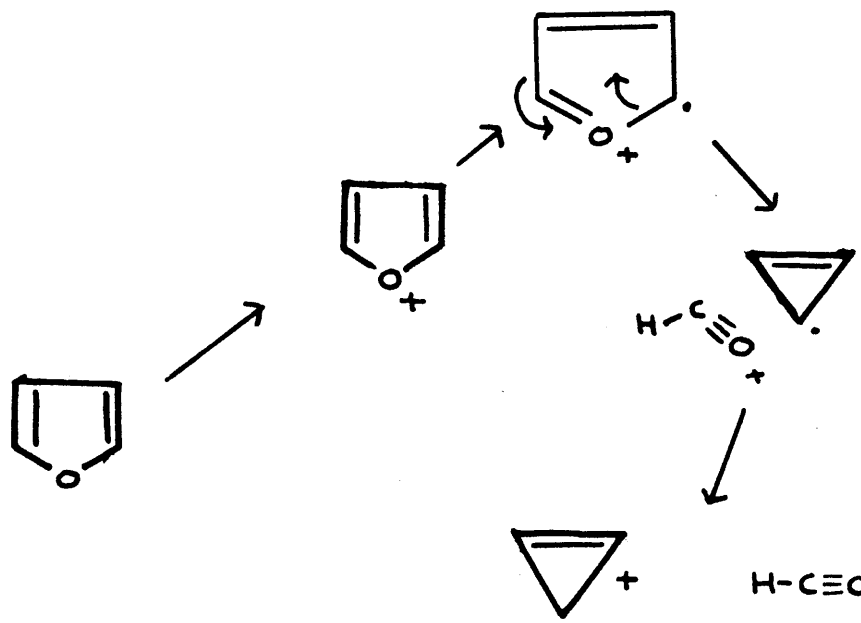


(X)

mle 39

$H-C\equiv O^+$

mle 29.

evidence for the source of these ions in any chemical structure can only come from improved instrumentation with double-focusing machines of high resolving power.

Discussion of Chapter II(A) is in five parts - (1) introduction, (2) published mass spectra, (3) substituted furans, (4) furan carboxylic acids and (5) the furan nucleus in complex structures.

(2) Published mass spectra of furans.

Consideration of the collected information on some simple furan systems is valuable and, for convenience, the published data is included in tabular form. This includes the mass spectra of furan, tetrahydrofuran, 2:5-dimethylfuran and $\alpha$-furfuryl alcohol.

The compounds containing the aromatic furan nucleus each have relative ion abundances greater than 70% of the base peak and, indeed, the largest peak in the alcohol spectrum is that of the molecular ion. On the other hand, tetrahydrofuran with no inherent aromatic stabilization has a small parent ion abundance.

The abundance of the furan ion (M/e 67 or 68) is not particularly large in these spectra and it seems that such a peak would be of little diagnostic value in identifying the presence of such a grouping in a compound. In fact, as

later results show, derivatives containing a 2-substituted furan ring give rise to more stable ions.

A small M/e=39 peak is well known in aromatic and aliphatic fragmentation patterns but the fact that it is the base peak in the furan spectrum requires comment. The only possible breakdown pattern to form this ion is as follows:-

$$68^{+} \rightarrow 39^{+} + 29^{\cdot}$$
$$C_4H_4O^{+} \rightarrow C_3H_3^{+} + CHO^{\cdot}$$

The very large abundance of this ion suggests that it has a specially stable structure.

Rylander and Meyerson[32] have proposed a cationated cyclopropane system for the $C_3H_7^{+}$ ion which occurs in nearly all aliphatic hydrocarbons and state that the "cation" may be a phenyl group. Formulation of the propyl ion as a protonated cyclopropane ring resolves many anomalies associated with this ion and the structure has been shown by these authors to be consistent in appearance potential and labelling experiments. Breslaw[33] observes that theoretical predictions[34] suggesting that certain systems are specially stable or 'aromatic' can be applied to three-membered ring systems containing two electrons, i.e. a cyclopropenyl cation has aromatic character (VII).

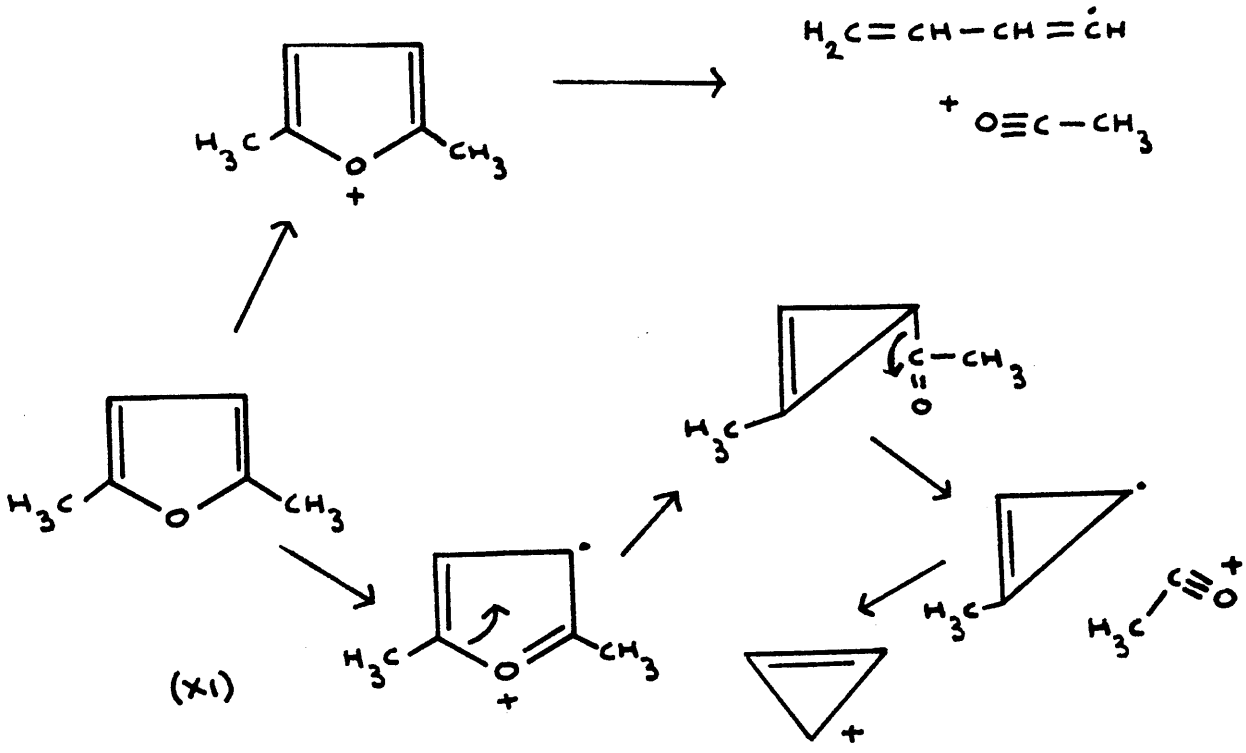
McLafferty[35] [36] has recently proposed that

the $C_3H_3^+$ ion derived from compounds such as $CH_2=C=CH_2$, $CH_3C\equiv CH$ and $CH_2=CH-CH=CH_2$ has the structure of a cyclopropenyl ion ( VII ). Such a structure would also appear to be reasonable for the $C_3H_3^+$ ion from furan itself. The fact that this M/e=39 peak is very abundant and that a peak occurs at M/e=19.5, corresponding to the doubly charged ion ( VIII ), supports this postulate. However, Collin [24] [25] assigns the $C_3H_3^+$ ion from furan to the non-cyclic mesomerically stabilized structures shown in ( IX ).

Assuming the postulate of a cyclopropenyl system for the $C_3H_3^+$ ion, a scheme can be written to explain the pre-:dominant cracking pattern for the furan system. This is shown in ( X ).

The $C_3H_3^+$ ion also occurs in the spectrum of 2:5-dimethylfuran; it has small abundance and the main fragment-:ation appears to be the loss of a $CH_3CO$ fragment giving the base peak. The low abundance of the $C_3H_3^+$ ion in this spectrum suggests that there is a larger contribution from non-cyclic forms, taking into account the presence of the two methyl groups; however, the scheme devised for furan can be extended to the dimethyl derivative although there is more than one possibility (XI).

The spectrum of 2:5-dimethylfuran, although having no peak of high abundance at M/e=19.5, has a doubly charged ion corresponding to (XII) at M/e=26.5. This doubly charged ion



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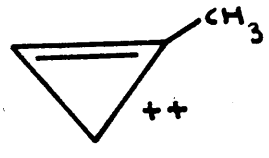

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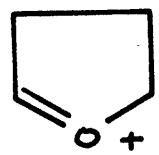

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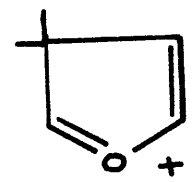

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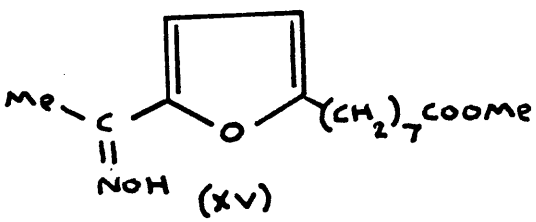

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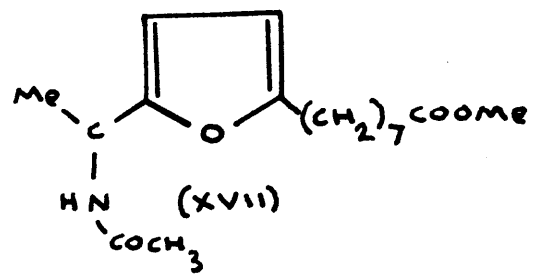

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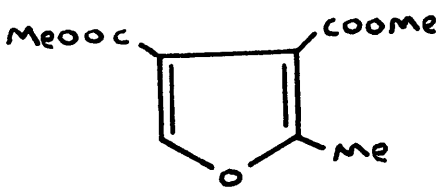

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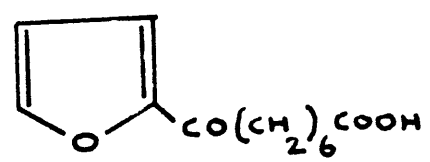


(XVIII)

can conceivably arise from the doubly charged non-cyclic ion stabilized by mesomerism. However, the cyclic system is particularly favoured when considering the driving forces for ion rearrangement (36).

There is a marked similarity between the spectra of furan and tetrahydrofuran except that the ring of the sat-:urated compound is more easily fragmented. This has been studied in detail by Collin (24) (25). The large abundance of the P - 1 peak compared to the moderate abundance of the parent in tetrahydrofuran is perhaps due to preferential formation of unsaturated ions such as (XIII) and (XIV). The peaks at M/e=42 (100%), 41(51.71%) and 43(22.18%) can be assigned to bond rupture adjacent to the oxygen atom and loss of the groupings from the ion formed by ring opening.

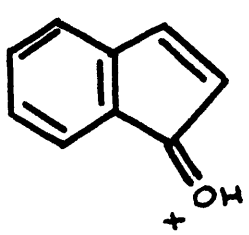
(3) Substituted furans.

The mass spectra of some substituted furans were obtained to enable identification of common features of general furan spectra. The derivatives used were mainly the $\alpha$ -substituted derivatives.

The compounds studied were (XV) methyl 8-[5-(1'-oximinoethyl)-2-furan] caprylate, (XVI) dimethyl-2-methyl-3:4-furan dicarboxylate, (XVII) methyl 8-[5-(1' acetimidoethyl)-2-furan] caprylate and (XVIII) 8-oxo-8-furan caprylic acid.

Mass spectrometric studies on esters [37], including aromatic esters [38], dibasic esters [39], long-chain aliphatic esters [40] [41] [42] and higher methyl esters [40] show the consistent loss of an -OR grouping to be the most important fragmentation. Happ and Stewart [43] have observed that in a series of aliphatic acids structural diagnosis is dependent on the fragmentation of the carboxyl group, resulting in loss of -OH and -COOH from the parent ion. However, McLafferty [44] in his study of stearic acid, $C_{17}H_{35}COOH$, notes that loss of OH and COOH is not typical in long-chain compounds. In aromatic esters, Gohlke and McLafferty [45] have observed the increased intensity of the parent molecular ion and that the base peak results from loss of -OR. Extending these results to $\omega$-phenyl fatty acid esters, Benyon [46] has observed that cyclizations and rearrange-:ments are possible and he has postulated the ion (XIX) as due to fragmentation of (XX) with loss of $-OC_2H_5$. In the compound (XXI), the same author postulates that the ion fragment (XXII) arises by an internal cyclization after removal of $-OC_2H_5$ from the molecular ion.

Since furan derivatives are derivatives of an aromatic system, some of these results will apply to the spectra of the furan derivatives (XV), (XVI), (XVII) and (XVIII).



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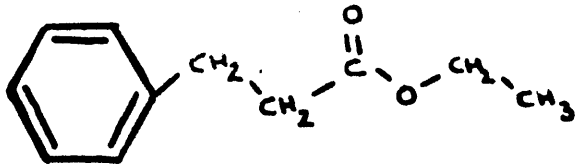

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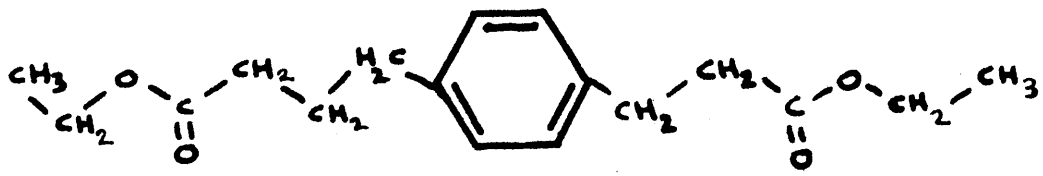

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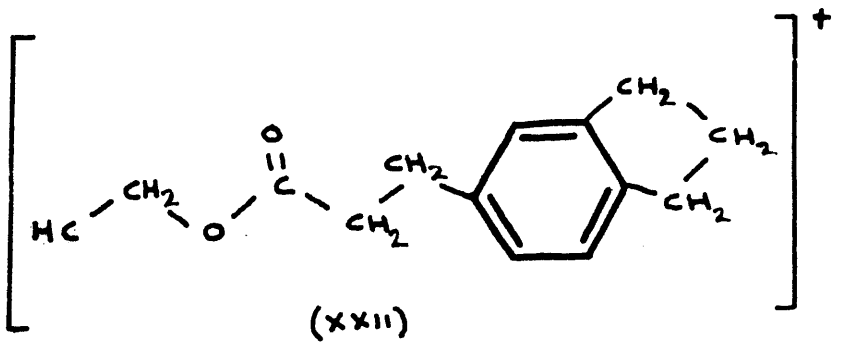

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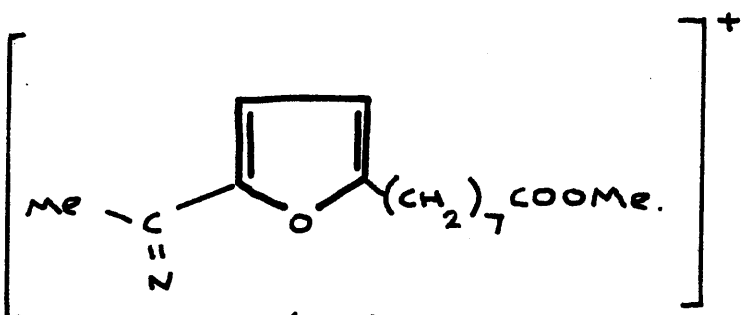
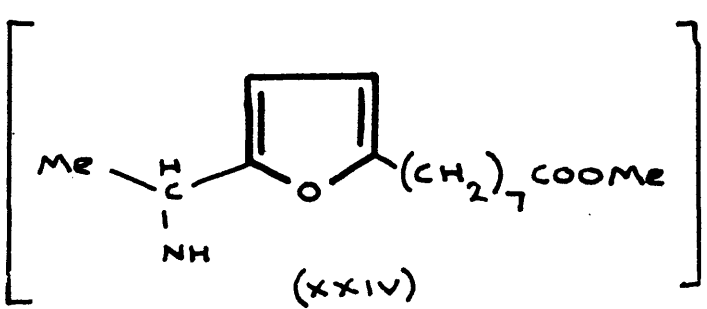


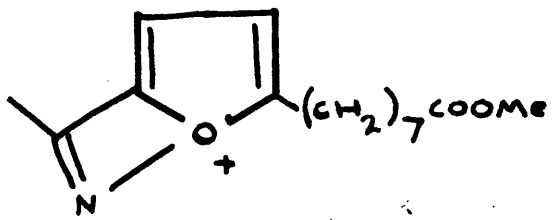
m/e 264

(XXIII)



m/e 266

(XXIV)

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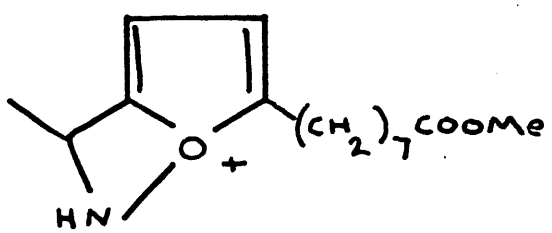


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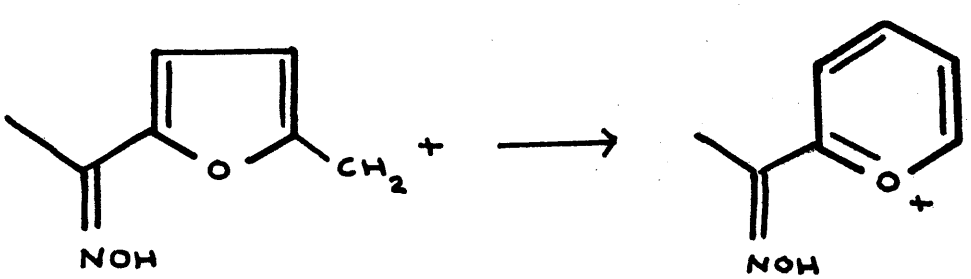


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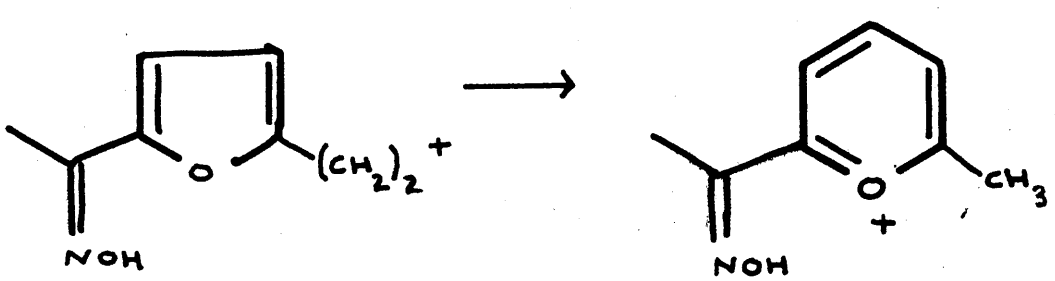



(XXVIII)

EXPERIMENTAL.

The spectra of the four compounds (XV), (XVI), (XVII) and (XVIII) were obtained on a Metropolitan-Vickers MS 2 machine using the direct probe method [47]. The electron energy was 50eV with an accelerating voltage of 2KV. Magnetic scanning was employed. Only with sample (XVI) was external heat applied.

The samples were obtained from Dr. N. McCorkindale (Glasgow University) and were synthesised by standard methods[48].

Mass spectra of these compounds are included in tabular form at the end of this chapter.

DISCUSSION.

As previously described, the peaks corresponding to the furan ion (M/e=67 or 68) are not abundant and consequently are unlikely to be of diagnostic value. The major pattern of fragmentation appears to be elision of groups which are either stable themselves or which produce stabilized ion systems. It is perhaps surprising that many of the very abundant peaks correspond to retention of the long-chain $\alpha$-substituents; however, complex cyclizations and rearrangements are possible, and some are proposed below.

The oxime (XV) and the oxime derivative (XVII) form stable ions (XXIII) and (XXIV) respectively with loss of

an -OH group and a $-COCH_3$ group. The ions (XXIII) and (XXIV) yield the base peak and an abundant peak (35%) in the mass spectrum of (XV) and (XVII) respectively and consequently must have preferentially stabilized structures. Tentative structures (XXV) and (XXVI) can be proposed for these ions but since these structures involve four-membered rings, they are unlikely.

Most of the major peaks in the spectrum of (XV) can be assigned to the ions produced without fragmentation of the oxime portion. Fragmentation of the $\alpha$-substituted side chain of (XV) produces high abundance peaks which may be due to cyclization or rearrangement processes described by Benyon[46] and McLafferty[49]. For example, the abundant M/e=138 ion in the spectrum of (XV) may be due to the ion of structure (XXVII). This proposal can be extended to the ion at M/e=152 which may result from structure (XXVIII). The possible fragmentation pattern of (XV) is shown in (XXIX).

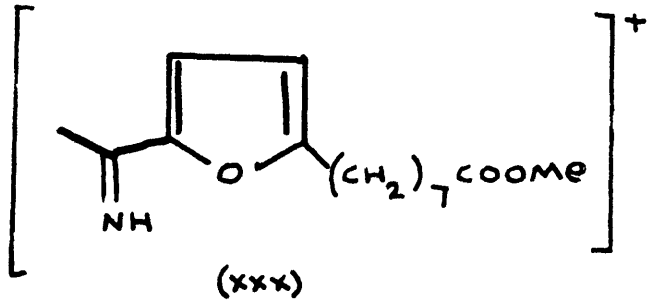
The base peak of (XVII) occurs at M/e=265 and must arise by the loss of 44 mass units from the parent ion; this can only result by the loss of the $COCH_3$ group with hydrogen transfer to give a stabilized ion (XXX).

Thus it is possible that a furan ring system with a side chain may ring expand to produce a stabilized aromatic ion; this will also be considered when complex furan systems are discussed.

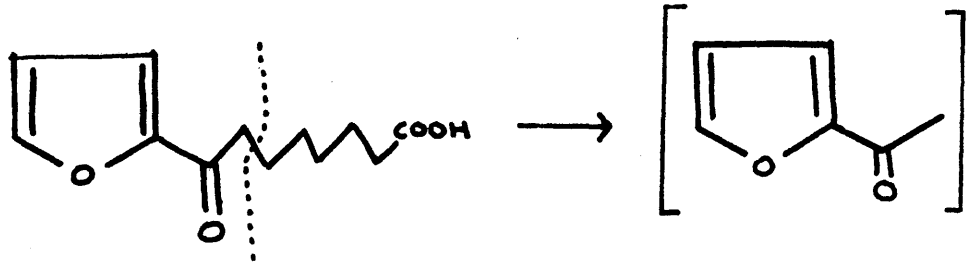
Compound (XVIII) has a weak spectrum with few prominent peaks. The abundant peaks occur at M/e=81(10.3%), 95(73%) and 110, which is the base peak. The remainder of the peaks are relatively small in abundance; the parent peak at M/e=224 has an intensity of 1.67%. Major fragmentation occurs β- to the carbonyl linkage in the side chain with hydrogen transfer giving the base peak. Although α-cleavage predominates only for low molecular weight aldehydes [50] and some ketones [51] it has been noted [51] that β- bond cleavage with hydrogen abstraction is common. However, the fragment corresponding to M/e 95 can only arise by α- cleavage producing (XXXII).

One possible assignment of the M/e=81 ion can be made by considering the reaction path (XXXIII). This is only a tentative scheme but it is difficult to explain the production of it in any other way.

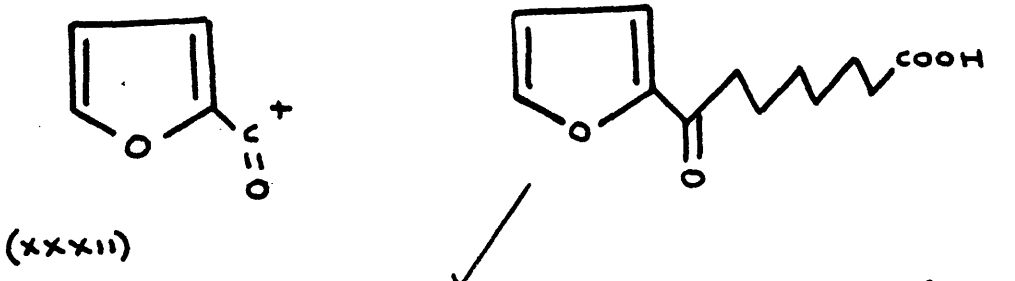
Fragmentation of (XVI) mainly occurs with elim-:ination of the -OMe from the ester groupings. The parent is of low abundance and the usual fragmentation of the furan ring which occurs in the presence of α- methyl substituents produces the base peak at M/e=43. Ring expansion of the α- methyl to the stabilized oxonium system previously discussed appears to be blocked by the β- substituents; this allows ready elision of the $-COCH_3$ group from fragmentation of the furan ring.



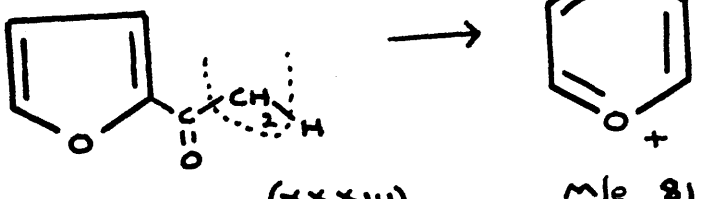
(xxx)



(xxxi)

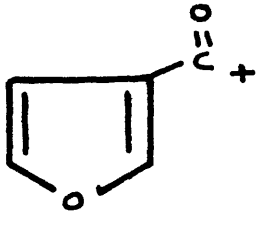


(xxxii)

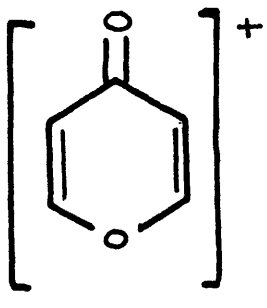


(xxxiii)

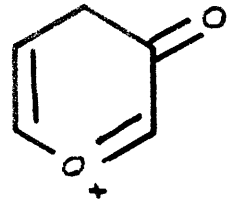
m/e 81



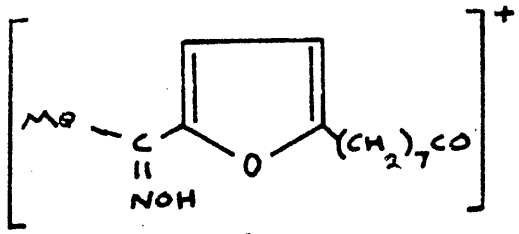
(xxxiv)

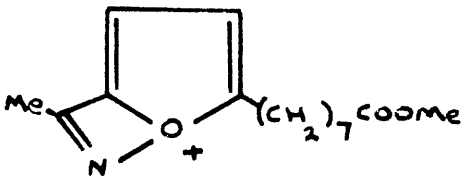


(xxxv)

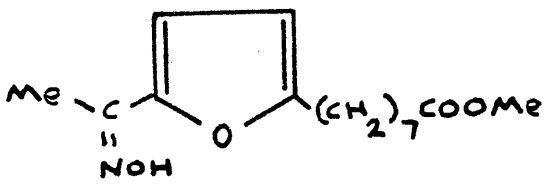


(XXXVI)



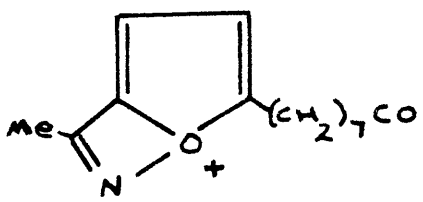


m/e 264 (100%)

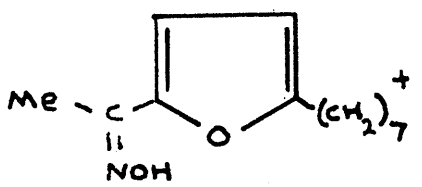


m/e 281.

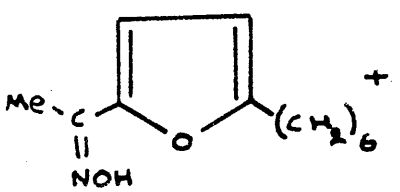
(XXIX)



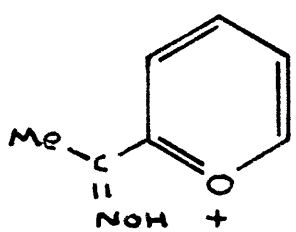
m/e 233.



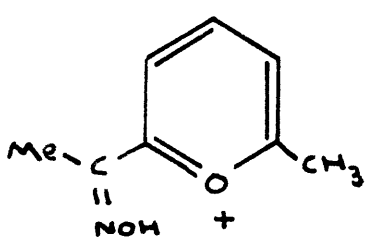
m/e 222.



m/e 208.



m/e 138.



m/e 152.

(4) Furan carboxylic acids.

Introduction.

Although the mass spectrometric techniques usually employed have been found more convenient to apply to ester derivatives rather than acids [39], many spectra of acids are available. Happ and Stewart [43] have studied the mass spectra of a number of simple and long-chain aliphatics including formic, acetic, propionic etc., and have noted the large number of rearrangement peaks; aromatic acids and esters have been examined by McLafferty and Gohlke [38].

In all cases, results are dependent on the volatility of the acids and many authors have observed that it is more convenient to study the more volatile esters. A danger of premature thermal decarboxylation arises in the use of the conventional heated inlet system for involatile acids since the temperature of the inlet is often in excess of the decarboxylation temperature.

The method used to obtain mass spectra of the furan acids [52] was to inject the sample on a long glass probe in close proximity to the electron beam. If possible no external heat was applied, to avoid decomposition before the vapour reached the ionization chamber.

EXPERIMENTAL.

Crude samples of the acids were obtained from

Dr. P. A. Finan (Sheffield University) and standard crystall-:isation procedures using water or water/ethanol mixtures were used for purification.

Approximate temperatures of thermal decarboxyl-:ation were obtained by employing a Stanton thermobalance and noting the decomposition at various temperatures [55]. The results are not discussed in this thesis, but reference is made to earlier work [55].

The mass spectra of these compounds were obtained on the MS 2 instrument using the direct probe method [47]. Slight external heat was used to obtain the spectrum of the tetra-substituted acid.

Results are inserted in tabular form in this chapter.

## DISCUSSION.

The intensity of the parent molecular ion in each of the acids bears an obvious relation to the substitution in the furan nucleus since the 2- and 2:5- substituted acids give less abundant parent peaks than the corresponding 3- and 3:4- substituted compounds. These results reflect the trend occurring in decarboxylation experiments in which a 2- or 2:5- acid is known to be more easily decarboxylated than the corresponding 3- or 3:4- acid [53] [54] [55].

It is not clear whether the spectra recorded for these compounds are those of partially decarboxylated structures. However, the spectra are reproducible and the parent peak is prominent. This leads to the opinion that the temperature of the ionization source itself is insufficient to cause extensive decarboxylation provided the sample is inserted near the electron source. Thus a conventional heated inlet system would appear to be relatively useless for the study of such thermally unstable compounds. (See Chapter V.)

The mono-substituted acids produce high intensity fragments at M/e=39, the base peak, while the disubstituted acids give the base peak at M/e=29. It would thus appear that the dual substitution alters the mechanism whereby the $C_3H_3^+$ ion is preferentially produced. The M/e=29 peak has roughly the same relative intensity for both types of mono-substitution indicating that mono-nuclear substitution has little effect on the loss of a CHO fragment from the ring.

It is well known that carboxylic acids [38] [43] under electron impact can readily lose a mass of 17 as a single fragment and comparison of the relative intensities of the P-17 ions produced for these furan acids is shown. As before, the

| Acid | 2- | 3- | 2:5- | 3:4- |
|---|---|---|---|---|
| P - 17 relative intensity | 36.5% | 92.5% | 10.7% | 39.2% |

substitution has an obvious effect on the formation of this ion and this can only be attributed to preferential stabilization

of (XXXIV) compared to (XXXII). (XXXV) and (XXXVI) are also reasonable structures for these ions and are related to those proposed by Collin [24] for the ion produced from $\alpha$- furfuryl alcohol, although the above structures assume a carbon atom devoid of a hydrogen atom. In all cases, the abundance of such a M/e=95 ion is greater for the 3-carboxy compounds which suggests that (XXXV) is the preferred form. The abundant M/e=96 ion, corresponding to the complete structures (XXXV) and (XXXVI) without hydrogen loss, occurs only in the dicarboxy, and not in the monocarboxy, compounds. The main ion fragments are shown in (XXXVII).

As previously observed, the loss of an -OH group from the dicarboxy acids produces a more stable ion in the case of the 3:4- substituted compounds and this again can be correl-:ated to the relative stability of the substituted forms of (XXXV) and (XXXVI).

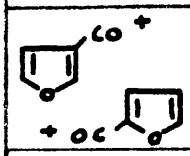
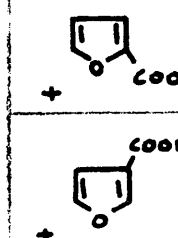
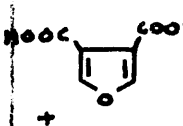
The more prominent ions are tabulated with the values of relative intensity compared to the base peaks of the spectra.

## (5) The furan ring in complex structures.

### (1) Marrubiin.

Marrubiin, the bitter principle of horehound,

Furan carboxylic acids

| Assigned ion. | M/e | 3- | 2- | 2:5- | 3:4- | 2:3:4:5- | 2Me-3:4- |
|---|---|---|---|---|---|---|---|
| P | | 58.2% | 40.7% | 9.0% | 41.2% | 3.3% | 17.7% |
|  | 66 | 15.8% | 7.9% | 50.0% | 32.4% | 38.7% | 10.8% |
| | 67 | 14.2% | 4.9% | 11.3% | 10.8% | 8.8% | 7.6% |
| | 68 | 4.1% | 2.8% | 4.8% | 6.8% | 3.6% | 11.4% |
|  | 29 | 46.3% | 47.7% | 100.0% | 100.0% | 21.6% | - |
|  | 39 | 100.0% | 100.0% | 68.0% | 45.9% | 46.4% | 12.1% |
|  | 84 | 3.2% | 4.4% | 5.9% | 10.1% | 5.9% | - |
|  | 95 | 92.5% | 36.5% | 15.8% | 21.6% | 87.5% | 2.6% |
| | 96 | - | - | 62.8% | 37.7% | 2.2% | - |
|  | 45 | 24.1% | 62.2% | 91.5% | 82.1% | 13.2% | 15.2% |
|  | 44 | 1.8% | 4.8% | 5.1% | 5.4% | 7.0% | 6.2% |
|  | 139 | - | - | 10.7% | 39.2% | - | - |
|  | 112 | 58.2% | 40.7% | 25.6% | 74.0% | 100.0% | 6.5% |
|  | 156 | - | - | 9.0% | 41.2% | 21.9% | - |

(Marrubium vulgare) although first described by Harms in 1842 was not obtained pure until 1932. One of the oxygen functions was found to be unreactive and so was assumed present in an oxide ring. After initial structural work [56] [57] [58], Ghizi [59] [60] [61] found that oxidation of marrubiin with chromic acid in acetic acid gave a loss of three carbon atoms with the inert oxygen. This was confirmed by Cocker and his colleagues [62] [63] [64] who corrected the formula of the product from $C_{17}H_{22}O_4$ to $C_{17}H_{24}O_4$. They concluded that since both double bonds were destroyed, these results were best accomodated by a furan ring and confirmed this by the light absorption characteristics and colour reactions. A structure (XXXVIII) was proposed by Cocker [63] and a later paper was published concerning the stereochemistry [64].

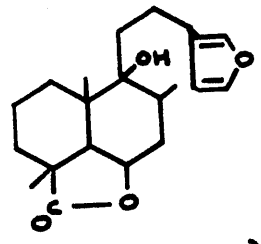
The mass spectrum of marrubiin.

Marrubiin was shown to have the expected molecular weight of 332. Since the compound contains three quaternary centres and since such positions are known to be especially labile in electron impact studies [65] [66] [67], the spectrum is complex with numerous abundant ions. The furan ring is indirectly attached to one such quaternary position and the side chain involved will be easily fragmented.

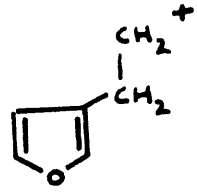
The higher mass portion of the spectrum corresponds

to ions of low abundance formed by loss of the substituent groups e.g. -OH (P - 17),-CO-O-(P - 44) etc., while the medium mass range contains many ions which have obviously been preferentially stabilized. These are produced mainly by complete loss of the substituted furan side chain and successive rupture of the carbon-carbon bonds until the furan ion (M/e 67) is produced. As was observed in part (2) of this chapter, furan rings substituted with alkyl side chains, as well as fragmenting $\alpha$ -to the ring, fragment more often at positions which can give rise to very stable ions, usually by ring closure or ring expansions. Thus the series of peaks at M/e=67,81,95 and possibly 109, separated by a 14 unit mass difference, can be assigned to ions formed by rup-:ture of the quaternary centre linked to the $\beta$- furan ethyl group. The successive peaks can be considered of the form M/e=(67 + 14n) where n is the number of carbon atoms in the effective side chain. Since each such ion is specially abundant, tentative cyclic structures, involving ring expan-:sions, can be written. For example, the peaks at M/e=95 (68.5%) and M/e=81(62%) may be written with structures (XXXIX) and (XL) or (XLI) and (XLII) respectively. The type of ring expansion (XLII) has been postulated by Collin [24] for a similar ion derived from $\alpha$- furfuryl alcohol.

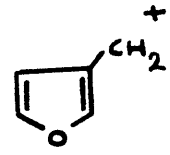
The remaining two quaternary centres can also



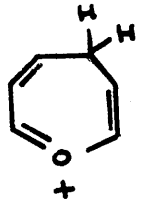

(XXXVIII)




(XXXIX)

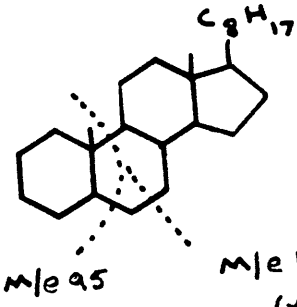



(XL)

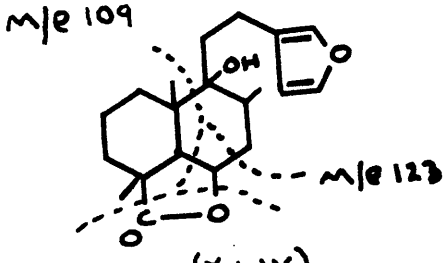



(XLI)

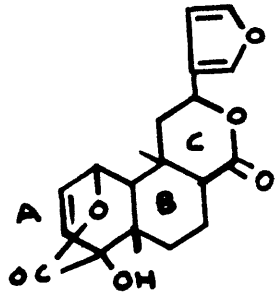

(XLII)



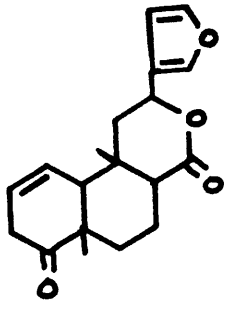

(XLIII)



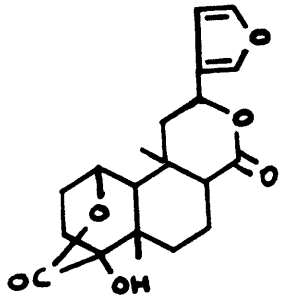

(XLIV)



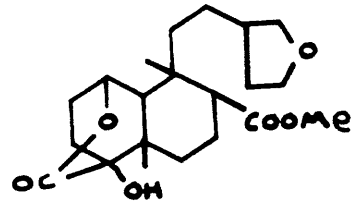

(XLV)




(XLVI)




(XLVII)




(XLVIII)

facilitate bond fission which is similar to the type observed by some authors in steroids [68] [69] [70] and triterpenes[47] and the abundant peaks at M/e=109 and 95 in marrubiin can also be assigned to fragmentation of the type discussed by Friedland [71] and Reed [12] in cholestane. Abundant peaks at M/e=109 and 95 in cholestane can be assigned to the bond rupture in diagram (XLIII).

In marrubiin, fission of ring A can occur with loss of the lactone group to produce ions M/e=109 and 95 with hydrogen migration. However, it is possible that this is an unlikely process as four or five bond fissions are required to produce these ions (XLIV).

Friedel [72] has observed that, in tertiary alcohols, the base peak results from loss of the largest of the three attached alkyl groups. Thus marrubiin, with such a tertiary group, would be expected to give abundant ions corres-:ponding to the loss of the comparatively large β- furan ethyl group. This explains the prominence of the peaks at M/e=81 and 95. The ions occurring at M/e=109 and 123, although possibly arising from this 67,81,95 series, are more likely to owe their origin to the rupture of the ring system. This will be discussed later when considering the related columbin series.

It is difficult to observe in detail the

characteristics of fragmentation of the furan ring. However, it has been observed in this chapter that ready elimination of CO or CHO occurs in simple furan derivatives. In complicated systems such as marrubiin, loss of 28 and 29 mass units occurs but only to a moderate degree (P - 28, 2.5%, P - 29, 5.3%). These results should be compared with those for decarboxycolumbin which shows ready elimination of 28 mass units from the cyclic ketonic group.

The main difficulty in discussing the mass spectrum of marrubiin with respect to the furan grouping is due to the alternative explanations of ion structures. A series of related compounds, the columbins, will now be dis-:cussed in an attempt to resolve this problem.

Columbin.

The structure of columbin, $C_{20}H_{22}O_6$, one of the bitter principles of Colombo root (Jatrorrihiza palmata Miers) has been established [73] [74] as (XLV). One of the oxygen atoms was found to be inert and the two known ethylenic linkages, in addition to a further double bond equivalent, were believed to be combined as a furan ring system; this was supported by ultra-violet and infra-red spectroscopy. Ozonolysis of dihydrocolumbin giving the major product of a $C_{17}$ acid confirmed this. Since only formic acid could be

detected, it was believed that there were no alkyl substituents in the furan ring. The stereochemistry of this compound will be discussed in Chapter IV.

Columbin on melting loses one mole of carbon dioxide [73] [75] [76] to give decarboxycolumbin (XLVI) and it has been shown that this involves destruction of the hydroxyl group although titration demonstrates that one lactone group remains. Barton [73] has proposed structure (XLVI) for decarboxycolumbin.

Columbin, on hydrogenation over palladised calcium carbonate until one mole of hydrogen is absorbed [73], yields dihydrocolumbin for which Barton [73] has postulated the structure (XLVII). Also, columbin can absorb four moles of hydrogen on catalytic hydrogenation to give octahydrocolumbinic acid [74] which can also be obtained by hydrogenation of dihydrocolumbin at atmospheric pressure over 10% of palladium charcoal. The methyl ester of octahydrocolumbinic acid has structure (XLVIII) [74].

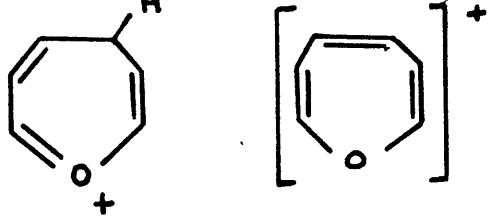
The structure of columbin resembles that of marrubiin which has already been discussed. However, columbin has a dilactone system and one of the lactones is involved in a linkage across a single ring whilst marrubiin has only one lactone group attached across the dicyclic system. The $\beta$-furan ethyl group of marrubiin is now bound into a ring system by a

lactone group.

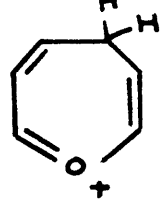
The mass spectrum of columbin.

The ions at M/e=109,95,81 and 67, which are prominent in the mass spectrum of marrubiin, are also of large abundance in the spectrum of columbin, presumably due to the related structures. The ions occurring at M/e=67,81 and 95 are assigned to the elisions of the β-furan ethyl group with loss of the lactone group. Fragments produced by ring rupture in columbin can be assigned to the ions at M/e=109,121,122,123,137, 149 and 161. It should be noted that the rings A in marrubiin and columbin are of comparable mass, and both can produce the same M/e=109 ion by loss of a lactone group and hydrogen migration during the ring rupture.

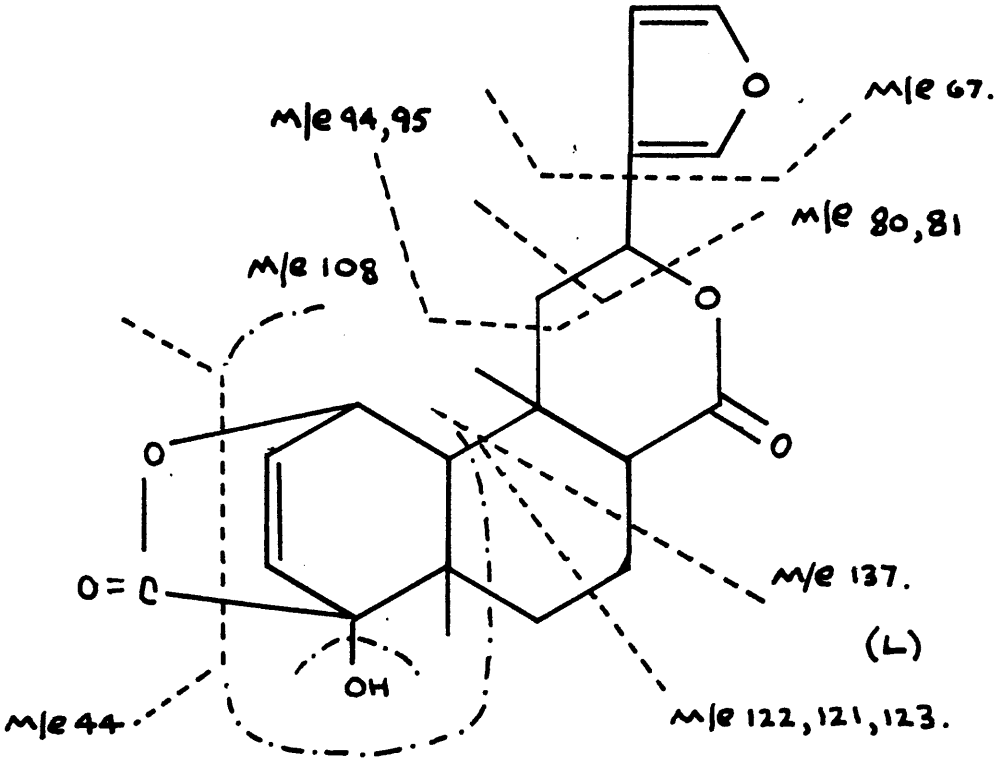
In the spectrum of columbin, M/e=94 is the base peak and this ion is postulated as having the structure (XLIX). Marrubiin, by comparison, has its base peak at M/e=95, which was earlier assigned the structure (XLI). This may be due to the substitution of the lactone ring attached to the β-furan ethyl group with consequently less hydrogen atoms available for formation of (XLI). The ion M/e=67, corresponding to the furan ion, is again only of moderate abundance, even although the furan ring in this case is directly attached to a tertiary carbon atom. This may be due to the lability of the lactone



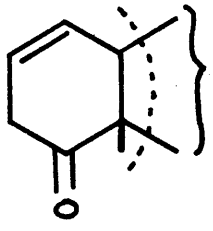
(XLIX)



(XLI)




(L)



$C_7OH_8$

m/e = 108

(LI)

group attached at this position. The envisaged fragmentation pattern for columbin is shown in diagram (L).

Dihydrocolumbin (XLVII).

The compound dihydrocolumbin, with a saturated ring A in the columbin structure, has a very similar spectrum to that of columbin. The base peak occurs at M/e=94 and there are large contributions in the spectrum from the ions at M/e=67,81 and 109 etc., which may be assigned in a similar manner to marrubiin and columbin. However, although the dihydro- compound follows the same pattern as columbin itself, there are moderately abundant peaks at M/e=111 (14.5%) and 125 (10.7%) which suggest that these peaks occur by rupture of the now saturated ring A. The fact that the peak occurring at M/e=109 remains so abundant suggests either that the ring fragment is more stable in the dehydrogenated form or that the M/e=109 peak may arise from further rupture of the β- furan ethyl component around the quaternary carbon. The latter implies that this further rupture may also be possible in the case of marrubiin and columbin. Although such an elision of the quaternary centre with corresponding hydrogen migrations is possible, many bond cleavages and rearrangements must occur to produce the M/e=109 ion which is preferentially stabilized. It may be concluded that the M/e=109 peak and higher mass peaks

in the series originate, for the most part, from rupture of the dicyclic system. There is also a possible contribution arising from fragmentation around the quaternary carbon atom which is substituted by the β- furan ethyl group.

Decarboxycolumbin (XLVI).

Decarboxycolumbin can be regarded as columbin with a modified ring A. This modification arises by removal of the ring lactone and formation of a cyclic ketone. The portion of the mass spectrum which has its origin in rupture of ring A must obviously be different from that of columbin.

The other compounds in this series have shown a small loss of 28 mass units from the parent ion due to the carbonyl group in the lactone. The most prominent peak in the higher mass portion of the decarboxycolumbin spectrum, apart from the molecular ion, is an ion occurring at P - 28. This at once indicates the presence of the ketone group. This cyclic ketonic group is easily lost and it is unlikely that the peaks, which occurred in columbin and which were assigned to ring rupture, would be nearly so abundant in the spectrum of decarboxycolumbin. This is found to be the case even although, by coincidence, the mass of ring A which undergoes fission with loss of a lactone group is exactly 108 mass units as shown in (LI). Thus the peaks at M/e=109 (7.0%),123

(3.7%) and 121 (23.5%) are of low abundance compared to the corresponding peaks of the other compounds. The base peak of the spectrum is M/e=94 and it appears that elision of the β- furan ethyl group is relatively unaffected by the modific-:ations in ring A. However, it should be observed that peak corresponding to the furan ion, M/e=67, has small abundance.

Octahydrocolumbinic acid methyl ester (XLVIII).

Although the methyl ester of octahydrocolumbinic acid gives rise to a similar cracking pattern to that of the other derivatives of columbin, the presence of the tetrahydrofuran ring causes some important modifications in the pattern. Comparison with dihydrocolumbin, which is the nearest related compound to the methyl ester, can be employed to demonstrate this change.

It has been observed earlier [18] that tetrahydrofuran shows a tendency to lose a single hydrogen atom to produce a stable ion. This is also observed in the fragments produced by rupture of the β- tetrahydrofuran ethyl group although abundant ions are observed at two or three mass units below those corresponding to rupture of the saturated β- tetrahydrofuran ethyl substituent. Thus the base peak occurs at M/e=96 and rupture of the β- tetrahydrofuran ethyl group would require a loss of 99 mass units. This is probably indicative of the

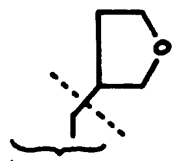
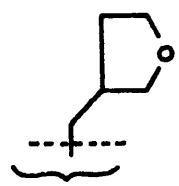
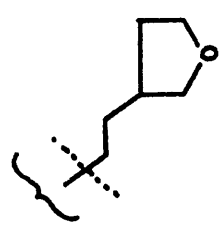
tendency to aromatize to the furan system or ring expand to an unsaturated conjugated ion. A 'spread' of abundant peaks can also be observed around the prominent peaks noted previously in the dihydro- compound as is shown by the values in (LII).

The M/e=99 and 85 peaks are evidence of the pre-:sence of the tetrahydrofuran ring. Other substituents such as lactone [77] and carbomethoxyl are easily lost and their elision results in high abundance peaks. The very abundant P - 31 and P - 32 peaks, as well as arising from rupture of the carbomethoxyl group, can occur by rupture of the tetrahydrofuran ring. [24] [25] Fragmentation of this ring would also produce P - 44, P - 45 and P - 46 peaks. These peaks are observed in the spectrum. The P - 46 peak, although possibly arising from rupture of the lactone ring with hydrogen migration, can also occur by (LIII) with hydrogen migration.

The iso-columbin series.

Columbin is easily isomerised by mild treatment with alkali to iso-columbin and, by the methods for obtaining the columbin derivatives discussed above, a series of iso-columbin derivatives [73] can be obtained. Barton [73] explains this change as epimerisation $\alpha$- to one of the lactone groups and suggests that the lactone group attached to the $\beta$- furan ethyl substituent is involved.

A mass spectrometric study of the iso-columbin

| Peaks corresponding to rupture of the β-tetrahydrofuran ethyl group. | Assignment | Related peaks. |
|---|---|---|
| M/e 71(10.2%) |  (or dicyclic ring rupture) | M/e 67(21.4%)<br>68(7.7%)<br>69(27.5%)<br>70(10.7%) |
| M/e 85(18.9%) |  (or dicyclic ring rupture.) | M/e 79(32.1%)<br>81(37.2%)<br>83(44.4%)<br>82(16.3%)<br>84(7.7%) |
| M/e 99 (10.7%) |  (or dicyclic ring rupture) | M/e 91(21.9%)<br>93(34.2%)<br>94(41.3%)<br>95(52.0%)<br>96(100%)<br>97(29.1%)<br>98(18.9%) |

(LII).

(LIII).

series is included in Chapter IV and some conclusions are drawn concerning the stereochemical factors involved.

## EXPERIMENTAL.

Pure samples of marrubiin and the series of columbin and iso-columbin compounds were obtained from Dr. K. Overton (Glasgow University).

The mass spectra were obtained using an accel-:erating voltage of 2KV with an electron energy of 50eV. The direct inlet method was employed with no external heating.

The results for both the columbin and iso-columbin series are included in tabular form.

## (B) THE BENZFURANS.

Published mass spectra produced by some research organizations [78] include the mass spectra of benzfuran [79], 2-methylbenzfuran [80], 7-methylbenzfuran [81], dibenzfuran [82], and 4-methyldibenzfuran [83]. Enhanced stabilization of the aromatic furan ring in a benzfuran would be expected and, in fact, all these benzfuran compounds give very abundant molecular ions which in many cases are the base peaks. In general, the spectra are not intense but have a number of individual abundant peaks with corresponding doubly charged ions occurring at half

mass units.

The base peak of benzfuran (LIV) is the parent molecular ion (M/e=118) and the only other major peaks occur at P - 28 (M/e=90,36.36%) and P - 29 (M/e=89,37.34%). Thus the characteristic of simple furans, that is the ability to lose a fragment CO or CHO, is continued in the benzfuran series.

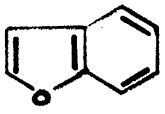
In furans, it was noted that a cyclopropenyl ion seemed a likely structure for the $C_3H_3^+$ ion. This structure can also be adopted in benzfuran and the fragmentation considered as (LV). The fact that the intensity of the doubly charged ion is so large reflects the inherent stability of the $C_7H_5^+$ ion which allows removal of a second electron without further fragmentation.

One notable feature of the spectrum of the 7-methyl derivative of benzfuran (LVI) is the large abundance of the P - 1 ion (M/e=131,91.49%) compared to the parent ion (M/e=132,100%). Since the methyl group is substituted on the benzene ring, it is reasonable to suggest that the large stab-:ilization of the P - 1 ion is due to ring expansion of the benzene ring to a cyclo-heptatriene system [32]. This is supported by the large doubly charged peak at M/e=65.5(2.66%). The ion $C_9H_7O^+$ is aromatically stabilized in some way and one possible structure is shown (LVII).

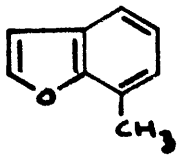
When methyl substitution occurs in the furan ring, as in 2-methylbenzfuran (LVIII), expansion of the benzene ring can no longer occur unless there is drastic bond migration. The large P - 1 peak (the base peak) is suggested to have the structure (LIX). Ring expansion has occurred giving the stable oxonium ion (LIX). This ion is analogous to the structure of the ion postulated by Collin [24] in his study of methylfuran compounds.

The structure of the dibenzfurans is related to that of diphenyl ethers for which an elegant discussion of fragmentation and rearrangement has been given by Beynon, Lester and Williams [84]. An extension of this has been employed by Wilson [85] in the study of diaryl ethers. These authors suggest that the fragmentation (LX) of diphenyl ether involves the loss of CO or CHO from the parent ion. The radical ion can then cyclise to benzcycloheptatriene.

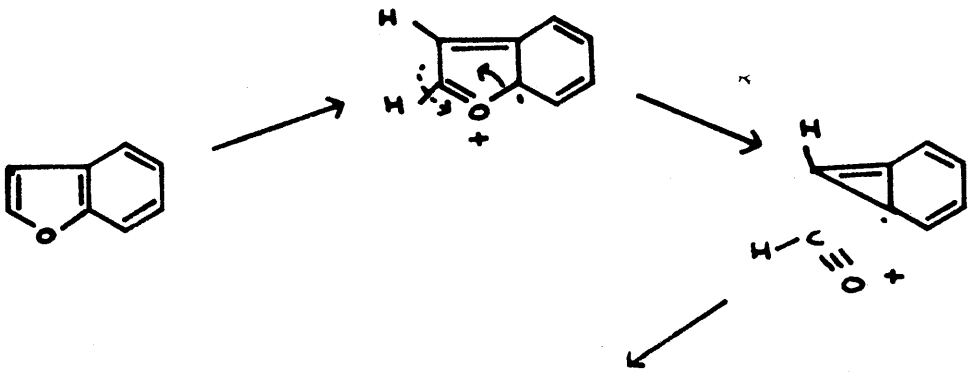
As expected, the parent ion in dibenzfuran itself is the base peak (M/e=168) with a small P - 1 ion. The only other major fragmentation ion occurs at M/e=139 corresponding to loss of CHO from the parent. Now Beynon [86] has proposed that the M/e=139 ion in the spectra of monohydroxyanthraquinones is due to the structure (LXI). A doubly charged ion at M/e=69.5 also occurs. It is possible to postulate the same structure for the ion derived from dibenzfuran by means of the mechanism (LXII).



(LIV)



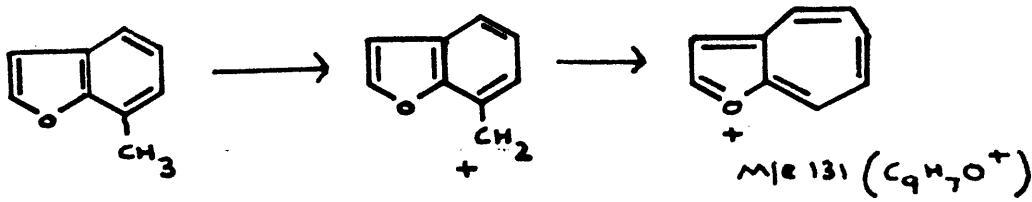
(LVI)



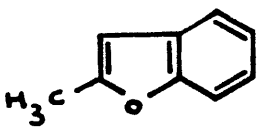
(LV)

m/e 89

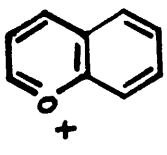
m/e 44·5.



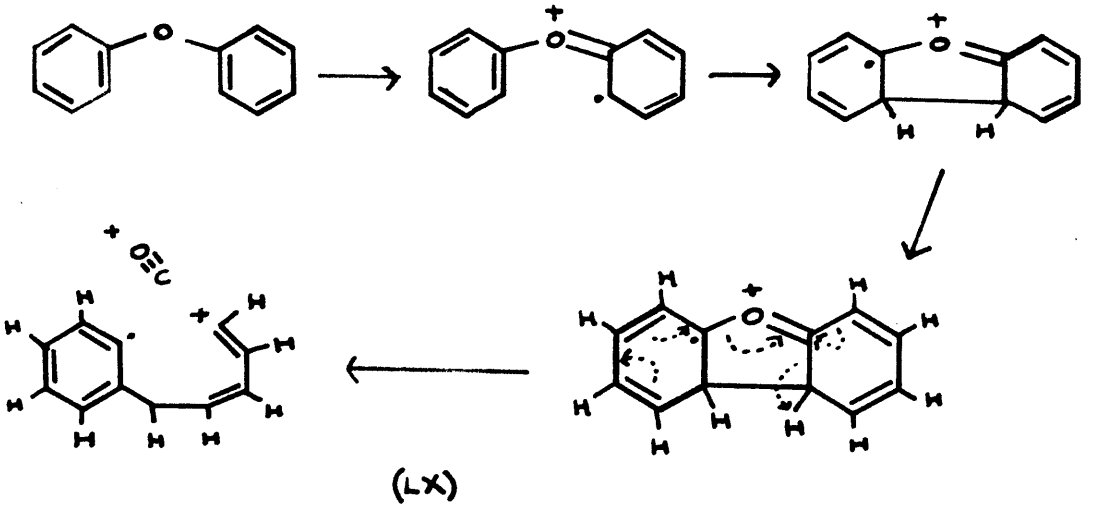
(LVII)



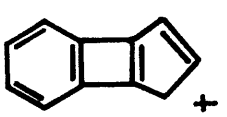
(LVIII)



(LIX)

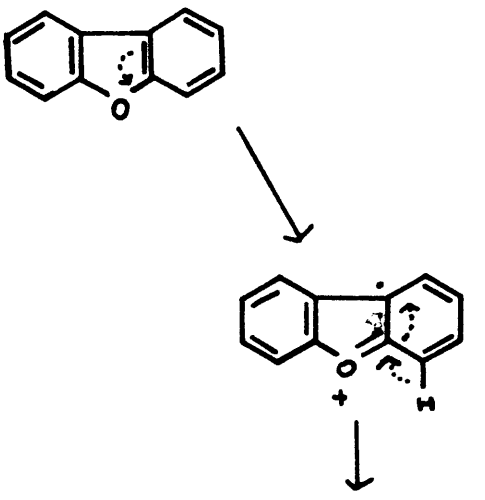


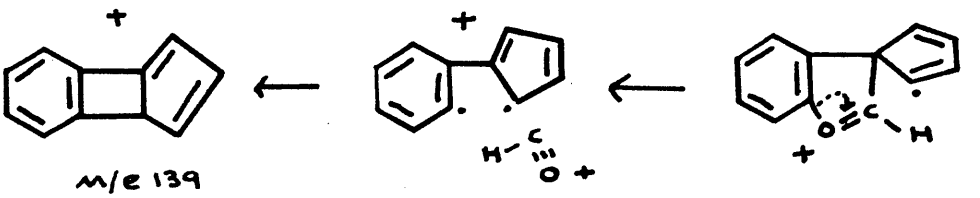
(LX)



$C_{11}H_7^+$

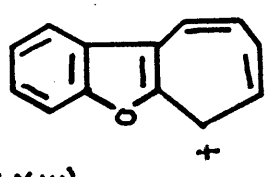
(LXI)



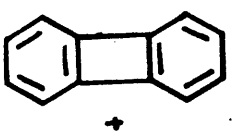


m/e 139

(LXII)



(LXIII)



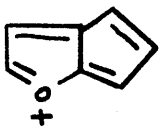
(LXIV)

Similarly to the methylbenzfurans, 4-methyldibenzfuran has an abundant P - 1 peak (M/e=181) and this ion, $C_{13}H_9O^+$, can have the structure (LXIII) with the corresponding doubly charged ion at M/e=90.5. Loss of 29 mass units from this ion produces a stable ion at M/e=152. With an analogous mechanism to (LXII) this ion can reasonably be written as (LXIV) and the very abundant M/e=76 ion can be postulated as arising from the doubly charged peak. Beynon[87] has previously postulated the diphenylene structure (LXIV) for the ion derived from anthraquinone at M/e=152.

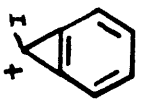
Some nitro- and acetylamino derivatives of benzfuran.

In order to provide additional information on the fragmentation of benzfuran compounds, some simple nitro- and acetylamino- derivatives were studied. The results obtained confirmed the proposal that modifications do occur in cracking patterns according to the substituent groups.

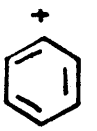
As previously noted, parent ions of the benzfuran system are relatively abundant due to the aromatic character of benzfuran. However the presence of the acetylamino- group tends to lower this abundance, and presumably is due to the preferred rupture of the $-NHCOCH_3$ group. Similarly, peaks corresponding to simple rupture of the furan ring (i.e. loss of 29 mass units from the parent ion) are of low abundance but



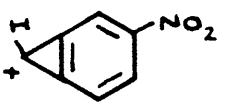
(LXV)



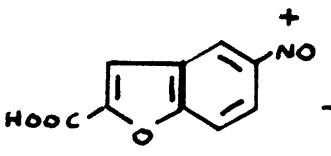
(LXVI)



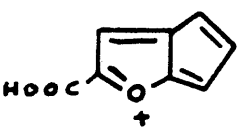
(LXVII)



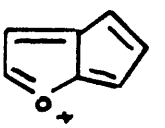
(LXVIII)



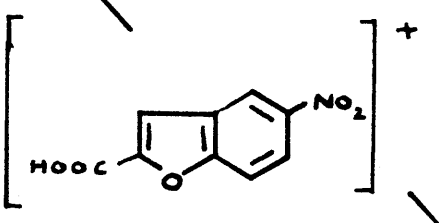
P-16 (5%).



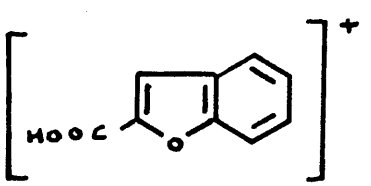
P-58 (4%).



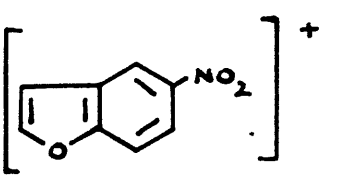
m/e 106 (11%)



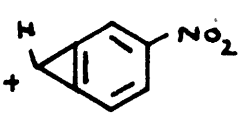
P (100%)



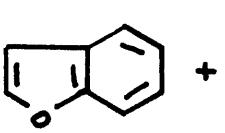
P-46 (38%)



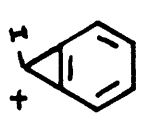
P-44 (7.4%).
P-45 (5.7%).



P-74 (5.7%).



P-90 (3%)



m/e 89 (17.2%)

(LXX)

combinations of the 29 mass units loss with the elision of substituents are more common. When 5-nitro groups are present, the loss of 29 mass units occurs much more readily.

Nitro groups substituted on the benzene ring of benzfuran compounds fragment in a similar manner to aromatic nitro compounds [46] [88]. The cracking pattern involves abundant P - 30 and P - 46 ions (i.e. P - NO and P - $NO_2$ ions). The P - 30 ion, which has a direct C - O linkage, can fragment further by loss of a neutral CO molecule from the aromatic system. This rupture of the benzene ring with elision of a CO group has also been studied in the fragmentation of phenols [46] [89] and aromatic ethers [84]. The ion produced by loss of 28 mass units from the P - 30 ion could have the structure (LXV). However, it is possible that a contribution of this loss of 28 mass units comes from the previously described rupture of the furan ring. Certain groups promote rupture of the benzene ring in benzfuran although this is an inherent property of the groups when substituted in an aromatic system.

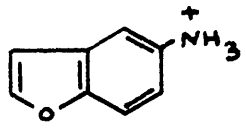
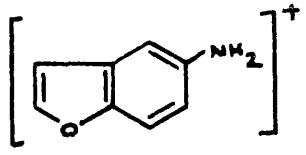
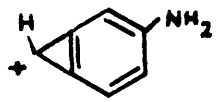
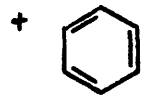
In all cases, the ions occurring at M/e=77,89,105 and 133 are abundant although the presence of the $-NHCOCH_3$ group appears to restrict formation of the ions at M/e=89 and 105. The ion M/e=89 has already been observed in the spectra of other benzfuran compounds and was assigned the structure (LXVI). The phenyl ion (LXVII) is also abundant. The M/e=105 peak is

prominent and can be assigned to the ion which is formed by the loss of CO from the P - 30 ion observed in the spectra of nitro compounds. Using the earlier correlations, the ion at M/e=133 may be assigned structure (LXVIII) less one hydrogen atom.

The stability of the benzfuran system is shown by the facile loss of $-COCH_2-$ from the acetylamino group with hydrogen migration to form an $NH_2$ substituent on the benzene ring.

The compound 5-acetylaminobenzfuran has abundant ions at the M/e values shown in diagram (LXIX) with possible assigned structures shown. It is possible that the ion P - 98, $C_6H_5^+$, is obtained directly from the P - 71 ion by a rearrangement process with elision of an HCN molecule and ring rupture. This is a characteristic fragmentation of aromatic amines [90]. The P - 1 peak in the spectrum is very abundant and the loss of one hydrogen atom from the molecular ion must involve some stabilizing rearrangement such as cyclisation of the $-NHCOCH_2$ group to the benzene ring, assuming that the acetylamino group is involved in the hydrogen loss.

The possible cracking pattern of 2-carboxy-5-nitrobenzfuran is shown in diagram (LXX). The main ion fragments are shown with their tentatively proposed structures; the reaction paths are only included for convenience since

| | M/e | % | Possible assignment. |
|---|---|---|---|
| P - 41 | 134 | 21.0 |  |
| P - 42 | 133 | 100.0 |  |
| P - 71 | 104 | 13.9 |  |
| P - 98 | 77 | 7.3 |  |

(LXIX).

some ions may result from more than one such path.

The generalizations stated at the beginning of this section apply to the remaining two mono-substituted compounds - 5-nitrobenzfuran and 5-acetylaminobenzfuran.

## EXPERIMENTAL.

Pure samples of the benzfuran derivatives were obtained from Dr. Martin-Smith and Dr. S. T. Reid (Glasgow University, Pharmacology Department).

Mass spectra were obtained, as previously, using the direct probe method and no external heating. The energy of the electrons was 50eV with an accelerating voltage of 2KV.

## Results.

The mass spectra are attached in tabular form.

II. Furan (gas) A.P.I. published spectra No. 508

Temperature of inlet 226° C,
50eV, voltage scanning.

| M/e | % | M/e | % |
|---|---|---|---|
| 12 | 1.31 | 41 | 1.51 |
| 13 | 2.56 | 42 | 7.64 |
| 14 | 4.04 | 43 | 0.15 |
| 15 | 0.21 | 44 | 0.04 |
| 16 | 0.09 | 48 | 0.13 |
| 17 | 0.12 | 49 | 0.68 |
| 18 | 0.11 | 50 | 0.80 |
| 19 | 0.18 | 51 | 0.19 |
| 19.5 | 0.06 | 52 | 0.08 |
| 20 | 0.03 | 53 | 0.28 |
| 24 | 0.40 | 54 | 0.04 |
| 25 | 1.70 | 55 | 0.07 |
| 25.5 | 0.02 | 65 | 0.04 |
| 26 | 3.70 | 66 | 0.24 |
| 27 | 0.85 | 67 | 0.54 |
| 28 | 0.92 | 68 | 71.0 p |
| 29 | 16.1 | 69 | 3.05 |
| 30 | 0.20 | 70 | 0.21 |
| 31 | 0.04 | | |
| 32.5 | 0.03 | | |
| 33 | 0.11 | | |
| 33.5 | 0.06 | | |
| 34 | 2.55 | | |
| 34.5 | 0.11 | | |
| 35.3 | 0.09 | | |
| 36 | 1.79 | | |
| 37 | 11.2 | | |
| 38 | 17.9 | | |
| 39 | 100.0 | | |
| 40 | 13.2 | | |

Tetrahydrofuran (gas) A.P.I. published spectra No. 780
Temperature of ion chamber 250°C.
70eV, voltage scanning.

| M/e | % | M/e | % |
|---|---|---|---|
| 12 | 0.89 | 43 | 22.18 |
| 13 | 1.77 | 44 | 4.98 |
| 14 | 5.47 | 45 | 3.25 |
| 15 | 9.64 | 46 | 0.07 |
| 16 | 0.77 | 47 | 0.01 |
| 17 | 0.45 | 48 | 0.02 |
| 18 | 1.32 | 49 | 0.19 |
| 19 | 0.50 | 50 | 0.40 |
| 19.5 | 0.06 | 51 | 0.24 |
| 20 | 0.16 | 52 | 0.05 |
| 24 | 0.20 | 53 | 0.42 |
| 25 | 1.14 | 54 | 0.07 |
| 25.5 | 0.04 | 55 | 0.19 |
| 26 | 8.07 | 56 | 0.05 |
| 27 | 32.59 | 57 | 0.19 |
| 28 | 5.66 | 58 | 0.04 |
| 29 | 21.87 | 59 | 0.09 |
| 30 | 2.11 | 66 | 0.01 |
| 31 | 4.17 | 67 | 0.01 |
| 32 | 0.07 | 68 | 0.07 |
| 33 | 0.04 | 69 | 0.34 |
| 34 | 0.21 | 70 | 0.48 |
| 34.5 | 0.05 | 71 | 26.73 |
| 35 | 0.14 | 72 | 29.16P |
| 36 | 0.38 | 73 | 1.43 |
| 37 | 3.02 | 74 | 0.07 |
| 38 | 5.31 | | |
| 39 | 24.55 | | |
| 40 | 12.52 | | |
| 41 | 51.71 | | |
| 42 | 100.0 | | |

(XI) 2:5-Dimethylfuran (gas) A.P.I. published spectra No. 815

Temperature of ion chamber 250°C.
70eV, voltage scanning.

| M/e | % | M/e | % | M/e | % |
|---|---|---|---|---|---|
| 12 | 1.27 | 43 | 100.0 | 74 | 0.29 |
| 13 | 2.58 | 44 | 2.49 | 75 | 0.10 |
| 14 | 7.33 | 45 | 0.47 | 76 | 0.09 |
| 15 | 25.88 | 46 | 0.10 | 77 | 1.19 |
| 16 | 0.45 | 47 | 0.78 | 78 | 0.42 |
| 17 | 0.07 | 47.5 | 0.50 | 79 | 3.17 |
| 18 | 0.08 | 48 | 0.85 | 80 | 1.49 |
| 19 | 0.09 | 49 | 3.27 | 81 | 37.38 |
| 24 | 0.24 | 50 | 16.68 | 82 | 2.00 |
| 25 | 1.50 | 51 | 19.91 | 83 | 0.12 |
| 25.5 | 0.32 | 52 | 10.62 | 86 | 16.72 |
| 26 | 10.36 | 53 | 56.48 | 87 | 0.10 |
| 26.5 | 0.03 | 54 | 4.01 | 94 | 3.14 |
| 27 | 29.57 | 55 | 1.63 | 95 | 73.99 |
| 28 | 3.14 | 56 | 0.20 | 96 | 87.64 P |
| 29 | 3.25 | 57 | 0.29 | 97 | 5.73 |
| 30 | 0.09 | 58 | 0.48 | 98 | 0.30 |
| 31 | 1.05 | 59 | 0.03 | | |
| 31.5 | 0.19 | 60 | 0.21 | | |
| 32 | 0.45 | 61 | 0.85 | | |
| 32.5 | 0.10 | 62 | 1.10 | | |
| 33 | 0.16 | 63 | 1.36 | | |
| 33.5 | 0.04 | 64 | 0.20 | | |
| 35 | 0.25 | 65 | 2.73 | | |
| 36 | 0.49 | 66 | 1.46 | | |
| 37 | 3.99 | 67 | 7.02 | | |
| 38 | 5.44 | 68 | 1.00 | | |
| 39 | 14.78 | 69 | 0.53 | | |
| 39.5 | 0.07 | 70 | 0.04 | | |
| 40 | 2.60 | 71 | 0.79 | | |
| 40.5 | 0.02 | 72 | 0.07 | | |
| 41 | 12.05 | 73 | 0.14 | | |
| 42 | 6.96 | | | | |

(V) α -Furfuryl alcohol (gas) A.P.I. published spectra No.397.

Temperature of ion chamber 225°C.
70eV, voltage scanning.

| M/e | % | M/e | % |
|---|---|---|---|
| 24 | 0.88 | 52 | 17.8 |
| 25 | 4.19 | 53 | 65.85 |
| 25.5 | 0.53 | 54 | 6.43 |
| 26 | 3.70 | 55 | 3.35 |
| 27 | 47.95 | 56 | 2.07 |
| 28 | 8.23 | 57 | 1.85 |
| 29 | 59.45 | 58 | 1.19 |
| 30 | 4.89 | 59 | 1.32 |
| 31 | 28.58 | 60 | 0.35 |
| 32 | 0.53 | 61 | 0.57 |
| 33 | 0.18 | 62 | 0.44 |
| 33.5 | 5.27 | 63 | 0.22 |
| 34 | 0.04 | 65 | 0.22 |
| 34.5 | 0.13 | 66 | 1.85 |
| 35 | 2.02 | 67 | 1.76 |
| 35.1 | 0.35 | 68 | 4.01 |
| 36 | 3.04 | 69 | 33.77 |
| 37 | 20.60 | 70 | 34.35 |
| 37.1 | 0.66 | 71 | 3.79 |
| 38 | 32.20 | 72 | 0.26 |
| 39 | 96.75 | 79 | 1.45 |
| 40 | 11.99 | 80 | 1.41 |
| 40.5 | 0.22 | 81 | 65.65 |
| 41 | 97.75 | 82 | 13.52 |
| 42 | 77.28 | 83 | 0.92 |
| 43 | 21.49 | 84 | 0.09 |
| 44 | 12.81 | 85 | 0.13 |
| 45 | 0.84 | 94.2 | 0.18 |
| 48 | 0.92 | 95 | 7.93 |
| 48.5 | 4.01 | 96 | 3.26 |
| 49 | 5.29 | 97 | 55.09 |
| 50 | 3.08 | 98 | 100.0 P |
| 51 | 23.13 | 99 | 5.72 |
| | | 100 | 0.57 |

(XV) 2KV, 50eV.

| M/e | % | M/e | % | M/e | % | M/e | % |
|---|---|---|---|---|---|---|---|
| 28 | 16.1 | 78 | 2.3 | 139 | 12.6 | 246 | 2.0 |
| 29 | 7.3 | 79 | 8.5 | 140 | 2.3 | 248 | 6.1 |
| 30 | 1.4 | 80 | 11.6 | 148 | 3.4 | 249 | 6.0 |
| 31 | 9.8 | 81 | 8.9 | 149 | 5.1 | 250 | 10.0 |
| 32 | 4.4 | 82 | 3.3 | 150 | 5.2 | 262 | 2.0 |
| 33 | 3.7 | 83 | 3.6 | 151 | 8.1 | 264 | 100.0 |
| 39 | 5.5 | 91 | 3.5 | 152 | 11.5 | 281 | 26.0 P |
| 40 | 1.9 | 93 | 8.9 | 153 | 1.9 | 282 | 8.9 |
| 41 | 11.1 | 94 | 8.5 | 161 | 1.6 | | |
| 42 | 6.7 | 95 | 6.2 | 162 | 7.2 | | |
| 43 | 9.4 | 96 | 2.3 | 163 | 3.5 | | |
| 44 | 6.3 | 97 | 11.6 | 164 | 5.6 | | |
| 51 | 2.3 | 99 | 2.8 | 165 | 1.7 | | |
| 52 | 7.2 | 105 | 2.3 | 176 | 1.9 | | |
| 53 | 5.4 | 106 | 4.8 | 178 | 2.9 | | |
| 55 | 11.2 | 107 | 7.9 | 179 | 1.5 | | |
| 56 | 2.4 | 108 | 4.1 | 190 | 2.4 | | |
| 57 | 5.0 | 109 | 3.8 | 191 | 1.9 | | |
| 58 | 2.7 | 110 | 3.6 | 192 | 2.2 | | |
| 59 | 6.1 | 111 | 2.3 | 193 | 1.9 | | |
| 60 | 9.6 | 119 | 3.6 | 204 | 7.0 | | |
| 65 | 6.2 | 120 | 6.0 | 205 | 2.3 | | |
| 66 | 5.2 | 121 | 7.6 | 206 | 1.7 | | |
| 67 | 5.3 | 122 | 14.7 | 207 | 1.6 | | |
| 68 | 2.3 | 123 | 8.1 | 208 | 3.7 | | |
| 69 | 8.9 | 133 | 2.0 | 209 | 1.4 | | |
| 70 | 1.9 | 134 | 5.8 | 221 | 1.2 | | |
| 71 | 3.2 | 135 | 5.8 | 222 | 1.7 | | |
| 73 | 9.6 | 136 | 11.5 | 232 | 7.1 | | |
| 74 | 2.2 | 137 | 3.9 | 233 | 1.9 | | |
| 77 | 4.1 | 138 | 58.0 | 234 | 1.5 | | |

2KV, 50eV.

| M/e | % | M/e | % | M/e | % |
|---|---|---|---|---|---|
| 26 | 10.2 | 66 | 11.1 | 196 | 9.3 |
| 27 | 22.2 | 67 | 12.9 | 197 | 6.5 |
| 28 | 17.6 | 68 | 10.2 | 198 | 5.5 P |
| 29 | 32.4 | 69 | 12.9 | | |
| 30 | 10.7 | 77 | 10.2 | | |
| 31 | 16.2 | 78 | 5.5 | | |
| 32 | 5.1 | 79 | 27.8 | | |
| 33 | 2.8 | 80 | 34.3 | | |
| 37 | 9.3 | 81 | 18.5 | | |
| 38 | 10.3 | 82 | 5.4 | | |
| 39 | 33.3 | 83 | 15.7 | | |
| 40 | 10.2 | 93 | 5.4 | | |
| 41 | 19.5 | 94 | 3.7 | | |
| 43 | 100.0 | 95 | 5.4 | | |
| 44 | 9.3 | 107 | 16.6 | | |
| 45 | 8.3 | 108 | 50.0 | | |
| 46 | 6.5 | 109 | 20.4 | | |
| 47 | 3.7 | 110 | 7.4 | | |
| 49 | 5.5 | 111 | 10.2 | | |
| 50 | 22.2 | 112 | 2.8 | | |
| 51 | 53.5 | 123 | 6.6 | | |
| 52 | 38.0 | 124 | 2.8 | | |
| 53 | 46.4 | 137 | 25.0 | | |
| 54 | 8.3 | 138 | 13.9 | | |
| 55 | 7.4 | 139 | 8.3 | | |
| 59 | 40.8 | 140 | 3.7 | | |
| 60 | 17.6 | 153 | 7.4 | | |
| 61 | 4.6 | 166 | 60.2 | | |
| 65 | 10.2 | 167 | 72.1 | | |

2KV, 50eV.

| M/e | % | M/e | % | M/e | % | M/e | % |
|---|---|---|---|---|---|---|---|
| 41 | 25.5 | 87 | 20.1 | 135 | 10.9 | 207 | 8.4 |
| 42 | 14.1 | 91 | 9.1 | 136 | 9.6 | 211 | 16.5 |
| 43 | 56.0 | 93 | 10.4 | 137 | 16.6 | 212 | 5.7 |
| 44 | 42.0 | 94 | 10.4 | 141 | 5.5 | 219 | 16.8 |
| 45 | 10.7 | 95 | 18.7 | 147 | 6.8 | 220 | 13.2 |
| 53 | 4.7 | 96 | 11.1 | 148 | 4.8 | 221 | 10.2 |
| 54 | 8.9 | 97 | 15.5 | 149 | 15.0 | 227 | 17.7 |
| 55 | 32.0 | 98 | 12.9 | 150 | 8.0 | 228 | 4.6 |
| 56 | 11.4 | 99 | 5.9 | 151 | 10.2 | 234 | 8.2 |
| 57 | 20.3 | 101 | 4.5 | 152 | 8.3 | 235 | 4.4 |
| 58 | 7.3 | 105 | 9.6 | 159 | 8.7 | 236 | 9.1 |
| 59 | 17.8 | 106 | 5.0 | 162 | 10.2 | 237 | 9.1 |
| 60 | 8.7 | 107 | 18.2 | 163 | 9.5 | 238 | 5.7 |
| 65 | 3.9 | 108 | 12.3 | 164 | 10.4 | 243 | 6.6 |
| 66 | 3.6 | 109 | 24.1 | 165 | 13.9 | 248 | 19.1 |
| 67 | 14.6 | 110 | 25.4 | 166 | 8.2 | 249 | 24.2 |
| 68 | 7.5 | 111 | 16.8 | 169 | 12.0 | 250 | 12.3 |
| 69 | 20.9 | 112 | 6.8 | 175 | 3.9 | 251 | 44.5 |
| 70 | 9.1 | 113 | 5.5 | 176 | 4.6 | 252 | 11.8 |
| 71 | 11.6 | 115 | 4.3 | 177 | 16.8 | 253 | 6.2 |
| 72 | 4.6 | 117 | 3.6 | 178 | 10.5 | 265 | 100.0 |
| 73 | 6.4 | 119 | 5.2 | 179 | 7.1 | 266 | 35.0 |
| 74 | 21.8 | 120 | 4.8 | 180 | 4.6 | 267 | 14.5 |
| 77 | 14.2 | 121 | 12.2 | 182 | 9.1 | 268 | 6.4 |
| 79 | 8.4 | 122 | 13.2 | 185 | 5.7 | 280 | 10.0 |
| 80 | 4.7 | 123 | 18.9 | 190 | 4.8 | 294 | 8.3 |
| 81 | 21.7 | 124 | 20.6 | 191 | 5.7 | 309 | 32.2 P |
| 82 | 14.5 | 125 | 12.8 | 192 | 9.1 | 310 | 10.9 |
| 83 | 18.8 | 127 | 8.4 | 193 | 9.1 | 311 | 10.2 |
| 84 | 8.7 | 133 | 8.3 | 196 | 20.0 | 312 | 7.3 |
| 85 | 28.1 | 134 | 6.6 | 197 | 5.5 | | |
| 86 | 10.2 | | | 206 | 12.9 | | |

2KV, 50eV.

| M/e | % | M/e | % | M/e | % |
|---|---|---|---|---|---|
| 27 | 9.4 | 81 | 10.3 | 134 | 1.4 |
| 28 | 30.7 | 82 | 5.0 | 135 | 1.5 |
| 29 | 10.6 | 83 | 3.2 | 137 | 1.4 |
| 32 | 6.7 | 84 | 1.6 | 145 | 1.7 |
| 39 | 20.4 | 85 | 1.5 | 146 | 1.0 |
| 40 | 5.8 | 86 | 2.1 | 147 | 3.5 |
| 41 | 16.9 | 91 | 4.2 | 148 | 1.6 |
| 42 | 5.2 | 92 | 1.1 | 149 | 1.3 |
| 43 | 10.3 | 93 | 4.1 | 151 | 1.0 |
| 44 | 7.3 | 94 | 11.3 | 153 | 1.5 |
| 45 | 6.2 | 95 | 73.0 | 159 | 1.0 |
| 50 | 0.8 | 96 | 7.0 | 161 | 1.2 |
| 51 | 1.9 | 97 | 4.1 | 163 | 1.4 |
| 53 | 6.2 | 105 | 2.8 | 165 | 1.7 |
| 54 | 4.5 | 106 | 1.2 | 173 | 1.0 |
| 55 | 17.2 | 107 | 3.7 | 175 | 1.0 |
| 56 | 1.7 | 108 | 2.1 | 177 | 0.8 |
| 57 | 2.4 | 109 | 2.9 | 178 | 1.4 |
| 58 | 3.1 | 110 | 100.0 | 179 | 0.7 |
| 59 | 2.0 | 111 | 12.2 | 191 | 0.8 |
| 60 | 0.9 | 112 | 1.6 | 192 | 0.7 |
| 61 | 3.1 | 114 | 1.0 | 193 | 0.5 |
| 66 | 2.3 | 115 | 1.0 | 206 | 0.8 |
| 67 | 2.1 | 117 | 1.0 | 207 | 0.6 |
| 68 | 7.9 | 119 | 2.7 | 208 | 0.7 |
| 69 | 7.7 | 120 | 1.2 | 224 | 1.7 P |
| 70 | 1.3 | 121 | 3.9 | 225 | 0.6 |
| 71 | 2.6 | 122 | 1.4 | | |
| 73 | 1.3 | 123 | 13.8 | | |
| 77 | 3.3 | 124 | 2.3 | | |
| 79 | 4.1 | 131 | 1.2 | | |
| 80 | 1.6 | 133 | 2.7 | | |

Mass spectra of some furancarboxylic acids.

| M/e | 2- | 3- | 2:5 | 3:4- | 2:3:4:5- | 2-Me-3:4- |
|---|---|---|---|---|---|---|
| 25 | 3.5 | 4.3 | 5.1 | 5.4 | | |
| 26 | 9.0 | 8.0 | 8.2 | 10.1 | 2.9 | |
| 27 | 6.4 | 10.3 | 22.1 | 18.9 | 11.4 | |
| 28 | 8.8 | 6.0 | 8.4 | 10.8 | 11.0 | |
| 29 | 47.7 | 46.3 | 100.0 | 100.0 | 21.6 | |
| 30 | 2.8 | 16.1 | 4.0 | 6.7 | 1.8 | |
| 31 | | | 9.6 | 16.9 | 17.3 | 3.2 |
| 32 | | | | | 2.9 | |
| 33 | | | 1.1 | | 7.4 | 1.2 |
| 36 | 4.4 | 6.9 | 6.5 | 8.1 | 2.2 | 1.3 |
| 37 | 45.0 | 47.0 | 55.2 | 45.2 | 5.9 | 7.0 |
| 38 | 51.1 | 68.5 | 90.0 | 60.1 | 33.1 | 5.4 |
| 39 | 100.0 | 100.0 | 68.0 | 45.9 | 46.4 | 12.1 |
| 40 | 8.6 | 8.4 | 6.2 | 5.4 | 4.4 | 3.6 |
| 41 | 10.3 | 8.6 | 6.2 | 8.1 | 2.6 | 6.4 |
| 42 | 6.1 | 4.4 | 4.4 | 5.4 | 2.9 | 6.1 |
| 43 | 3.5 | 3.7 | 4.0 | 6.8 | 3.7 | 34.1 |
| 44 | 4.8 | 1.8 | 5.1 | 5.4 | 7.0 | 6.2 |
| 45 | 62.2 | 24.1 | 91.5 | 82.1 | 13.2 | 15.2 |
| 46 | 1.7 | | 3.4 | 6.8 | 1.2 | |
| 47 | | | 2.6 | | 1.8 | |
| 48 | | | | | | 1.9 |
| 49 | 3.2 | 3.0 | 3.4 | | | 7.0 |
| 50 | 3.2 | 3.7 | 5.1 | 5.4 | 2.0 | 20.4 |
| 51 | 1.7 | 1.3 | | | | 31.6 |
| 52 | 1.5 | 1.6 | 5.4 | 4.7 | | 26.6 |
| 53 | 9.5 | 12.8 | | 33.7 | 6.9 | 21.6 |
| 54 | 3.0 | 1.9 | 7.6 | 7.4 | 3.8 | |
| 55 | 12.2 | 19.9 | 30.0 | 25.7 | 14.3 | 7.0 |
| 56 | | 4.2 | 4.5 | | 1.2 | |
| 61 | | | | | 1.0 | |
| 62 | | | | | 1.2 | 1.1 |
| 64 | | | 2.0 | | | |
| 65 | 1.9 | 2.8 | 22.4 | 16.2 | 23.6 | 3.8 |
| 66 | 7.9 | 15.8 | 50.0 | 32.4 | 38.7 | 10.8 |
| 67 | 4.9 | 14.2 | 11.3 | 10.8 | 8.8 | 7.6 |
| 68 | 2.8 | 4.1 | 4.8 | 6.8 | 3.6 | 11.4 |
| 69 | 1.0 | | 3.4 | 5.4 | 2.8 | 8.3 |
| 70 | | | | | | 1.8 |
| 71 | | | 4.3 | 6.8 | 1.5 | 1.3 |
| 77 | | | 1.4 | 5.4 | | 9.5 |
| 78 | | | | | | 8.9 |
| 79 | | | 1.4 | 8.1 | | 17.8 |
| 80 | | | | | 6.1 | 15.2 |
| 81 | | 2.4 | 1.7 | | 5.2 | 8.3 |
| 82 | | | 1.7 | | 3.7 | 3.2 |
| 83 | 2.55 | | 11.3 | 11.2 | 6.3 | 1.9 |

(Contd. over)

Mass spectra of some furancarboxylic acids. (contd.)

| M/e | 2- | 3- | 2:5- | 3:4- | 2:3:4:5- | 2-Me-3:4- |
|---|---|---|---|---|---|---|
| 84 | 4.4 | 3.2 | 5.9 | 10.1 | 5.9 | |
| 85 | | | | | 1.4 | |
| 86 | | | | | 1.0 | |
| 91 | | 3.5 | | | | |
| 92 | 2.2 | | 1.1 | 8.8 | | 2.1 |
| 93 | | | | | 2.6 | |
| 94 | | | 2.6 | 10.8 | 15.8 | |
| 95 | 36.5 | 92.5 | 15.8 | 21.6 | 87.5 | 2.6 |
| 96 | | | 62.8 | 37.7 | 2.2 | |
| 97 | | | | | 2.0 | |
| 98 | | | | | | 36.9 |
| 104 | | | | | | 3.8 |
| 106 | | | | 8.1 | | |
| 108 | | | | 12.8 | | |
| 109 | | | | 13.5 | | |
| 110 | | | | | 1.8 | 10.2 |
| 111 | | | | | 4.8 | 8.3 |
| 112 | 40.7p | 58.2p | 25.6 | 74.0 | 100.0 | 6.5 |
| 113 | | | | | 7.8 | |
| 114 | | | | | 3.3 | |
| 115 | | | | | | 3.2 |
| 122 | | | | | 1.0 | |
| 123 | | | | | 1.63 | |
| 126 | | | | | | 26.7 |
| 137 | | | | | | 6.9 |
| 139 | | | 10.7 | 39.2 | 54.0 | |
| 140 | | | | | 7.4 | 1.5 |
| 155 | | | | | 9.0 | 100.0 |
| 156 | | | 9.0p | 41.2p | 21.9 | |
| 157 | | | | | 4.6 | |
| 170 | | | | | | 17.7p |
| 244 | | | | | 3.3p | |

(XXXVIII) The mass spectrum of Marrubiin.

$C_{20}H_{28}O_4$.

| M/e | % | M/e | % | M/e | % |
|---|---|---|---|---|---|
| 28 | 35.5 | 110 | 18.5 | 249 | 17.4 |
| 29 | 5.9 | 111 | 17.3 | 250 | 14.9 |
| 30 | 2.5 | 119 | 18.1 | 251 | 9.9 |
| 31 | 4.9 | 120 | 5.7 | 271 | 4.1 |
| 32 | 6.6 | 121 | 33.0 | 286 | 9.2 |
| 33 | 1.8 | 122 | 14.8 | 287 | 6.1 |
| 36 | 1.8 | 123 | 44.7 | 303 | 5.3 |
| 38 | 1.2 | 124 | 14 | 304 | 2.5 |
| 39 | 4.9 | 125 | 9.8 | 311 | 4.1 |
| 40 | 2.9 | 131 | 7.8 | 312 | 2.1 |
| 41 | 13.3 | 132 | 4.1 | 314 | 5.4 |
| 42 | 6.6 | 133 | 14.5 | 315 | 2.9 |
| 43 | 19.0 | 134 | 31.4 | 332 | 54.5 P |
| 44 | 16.5 | 135 | 77.5 | | |
| 53 | 4.5 | 136 | 39.0 | | |
| 54 | 2.9 | 137 | 25.0 | | |
| 55 | 16.5 | 139 | 15.7 | | |
| 56 | 8.6 | 147 | 14.0 | | |
| 57 | 14.9 | 148 | 6.6 | | |
| 65 | 4.1 | 149 | 39.0 | | |
| 66 | 2.9 | 150 | 39.0 | | |
| 67 | 14.9 | 151 | 25.0 | | |
| 68 | 5.9 | 152 | 79.5 | | |
| 69 | 14.9 | 153 | 17.4 | | |
| 70 | 7.4 | 159 | 7.3 | | |
| 71 | 10.8 | 161 | 9.2 | | |
| 72 | 2.5 | 163 | 49.9 | | |
| 77 | 5.4 | 164 | 20.5 | | |
| 78 | 2.5 | 165 | 49.5 | | |
| 79 | 11.2 | 173 | 17.8 | | |
| 80 | 3.3 | 174 | 7.4 | | |
| 81 | 62.0 | 175 | 18.6 | | |
| 82 | 20.5 | 176 | 13.2 | | |
| 83 | 10.6 | 177 | 33 | | |
| 84 | 7.5 | 178 | 11.2 | | |
| 85 | 5.8 | 179 | 6.6 | | |
| 91 | 11.6 | 180 | 13.1 | | |
| 92 | 3.7 | 181 | 22.1 | | |
| 93 | 19.8 | 189 | 20.0 | | |
| 94 | 22.1 | 190 | 34.0 | | |

(Contd. over)

(XXXVIII) (Contd.)

The mass spectrum of Marrubiin.

$C_{20}H_{28}O_4$.

| M/e | % | M/e | % | M/e | % |
|---|---|---|---|---|---|
| 95 | 68.5 | 191 | 32.5 | | |
| 96 | 20.6 | 192 | 7.3 | | |
| 97 | 13.3 | 205 | 10.6 | | |
| 98 | 5.8 | 209 | 20.1 | | |
| 99 | 8.3 | 210 | 18.2 | | |
| 105 | 14.0 | 219 | 14.5 | | |
| 106 | 7.4 | 220 | 20.5 | | |
| 107 | 28.1 | 221 | 7.4 | | |
| 108 | 24.5 | 237 | 9.9 | | |
| 109 | 100.0 | 246 | 5.8 | | |

| | (XLV) | | (XLVI) | | (XLVII) | |
|---|---|---|---|---|---|---|
| M/e | Columbin | ISO-Columbin | Decarboxy-Columbin | Decarboxy-ISO-Columbin | Dihydro-Columbin | Dihydro ISO-Columbin |
| 27 | 9.5 | 5.6 | 18.7 | | 7.3 | 18.2 |
| 28 | 15.8 | 25.4 | 30.1 | 18.8 | 57.1 | 75.5 |
| 29 | 9.1 | 8.8 | 12.1 | 5.8 | 16.5 | 33.6 |
| 30 | 1.2 | | | | | 3.7 |
| 31 | 7.3 | 7.7 | 8.8 | 12.6 | 34.5 | 5.5 |
| 32 | | | 1.8 | | 11.2 | 46.5 |
| 33 | | | | | 10.7 | |
| 37 | 5.2 | | | | | 4.6 |
| 38 | 1.4 | | | | | 5.9 |
| 39 | 17.5 | 9.6 | 38.7 | 7.8 | | 39.0 |
| 40 | 6.0 | 4.0 | 13.2 | | 5.1 | 18.2 |
| 41 | 29.8 | 26.7 | 85.5 | 16.8 | 19.6 | 78.0 |
| 42 | 3.5 | | 7.7 | | 7.3 | 19.1 |
| 43 | 27.0 | 23.3 | 35.7 | 11.4 | 35.5 | 54.5 |
| 44 | 62.5 | 67.0 | 12.1 | 7.1 | 19.6 | 53.5 |
| 45 | 15.1 | | | | 6.7 | |
| 50 | | | | | | |
| 51 | | | 4.4 | | | 6.8 |
| 52 | | | 2.6 | | | 4.1 |
| 53 | 8.4 | 12.2 | 11.1 | 7.3 | 7.9 | 14.6 |
| 54 | 4.6 | | 6.3 | | | 5.9 |
| 55 | 8.1 | 35.4 | 33.5 | 18.0 | 31.0 | 59.9 |
| 56 | | | 3.7 | | 9.0 | 16.4 |
| 57 | | | | 3.7 | 20.7 | 37.0 |
| 58 | | | | | 14.0 | 16.0 |
| 59 | | | | | | 3.6 |
| 60 | | | | | 7.3 | 2.7 |
| 63 | | | | | | 5.5 |
| 65 | | 8.2 | 1.8 | 4.7 | 6.2 | |
| 66 | | 6.5 | 1.8 | | 5.1 | 9.1 |
| 67 | 14.8 | 18.2 | 3.4 | 12.0 | 16.2 | 26.4 |
| 68 | 4.7 | 20.3 | 2.8 | 31.2 | 23.0 | 11.8 |
| 69 | 10.5 | 21.0 | 2.9 | 14.4 | 25.8 | 32.3 |
| 70 | | | 2.6 | | 6.7 | 12.7 |
| 71 | 5.6 | 6.6 | | | 15.7 | 18.2 |
| 73 | | | | | 23.0 | |
| 76 | | | | | | 5.5 |
| 77 | 19.2 | 25.1 | | 15.6 | 14.6 | 25.5 |
| 78 | 4.2 | | 3.3 | | | 8.2 |
| 79 | 36.5 | 52.0 | | 36.0 | 30.8 | 25.5 |
| 80 | 11.9 | 16.1 | 22.0 | 28.9 | 11.2 | 8.2 |
| 81 | 51.0 | 69.0 | 4.1 | 36.0 | 53.8 | 41.4 |
| 82 | 22.6 | 25.0 | 9.9 | 13.2 | 18.5 | 22.7 |
| 83 | 11.3 | 6.8 | 4.1 | 8.4 | 16.2 | 19.1 |

(Contd. over)

| M/e | (XLV) Columbin | ISO-Columbin | (XLVI) Decarboxy-Columbin | Decarboxy-ISO-Columbin | (XLVII) Dihydro-Columbin | Dihydro-ISO-Columbin |
|---|---|---|---|---|---|---|
| 84 | 14.5 | 10.8 | | | 7.9 | 10.0 |
| 85 | 3.8 | | | 5.2 | 11.7 | 13.6 |
| 86 | | | | | 14.6 | 11.8 |
| 91 | 38.0 | 38.0 | 6.6 | 28.2 | 29.1 | 35.5 |
| 92 | 11.1 | 11.9 | 4.4 | 8.4 | 7.9 | 10.0 |
| 93 | 44.3 | 40.5 | 12.5 | 32.4 | 36.0 | 30.0 |
| 94 | 100.0 | 100.0 | 100.0 | 84.0 | 100.0 | 77.7 |
| 95 | 80.1 | 44.6 | 58.0 | 39.5 | 66.0 | 49.0 |
| 96 | 11.1 | 9.5 | 4.8 | 11.4 | 13.4 | 17.3 |
| 97 | 14.8 | 12.2 | 4.1 | | 22.5 | 19.0 |
| 100 | 6.0 | | | | | |
| 103 | 5.2 | | 3.4 | 6.1 | | 5.9 |
| 104 | 3.4 | | | | | 9.2 |
| 105 | 32.5 | 16.8 | 5.9 | 33.0 | 31.5 | 30.0 |
| 106 | 15.4 | 14.3 | 3.4 | 14.4 | 14.0 | 10.9 |
| 107 | 41.4 | 4.6 | 5.3 | 52.1 | 49.2 | 18.2 |
| 108 | 26.0 | 58.5 | 3.8 | 60.1 | 43.2 | 16.4 |
| 109 | 36.5 | 77.0 | 7.0 | 83.5 | 66.0 | 21.9 |
| 110 | 8.1 | 23.0 | 2.6 | 29.4 | 21.7 | 14.6 |
| 111 | | | | | 14.5 | 10.9 |
| 112 | 5.4 | 18.2 | | | | |
| 114 | | | | | | 7.3 |
| 115 | 2.7 | 5.1 | 3.7 | 9.0 | | 11.4 |
| 116 | 7.0 | 3.5 | 2.6 | | | 6.4 |
| 117 | 6.0 | 9.6 | 6.6 | 15.6 | | 12.7 |
| 118 | 5.7 | 6.0 | 6.3 | 10.8 | | 5.9 |
| 119 | 7.6 | 37.3 | 15.8 | 37.2 | 33.5 | 38.0 |
| 120 | 3.2 | 12.2 | 7.4 | 20.4 | 13.4 | 14.5 |
| 121 | 40.5 | 64.5 | 23.5 | 100.0 | 65.1 | 33.6 |
| 122 | 9.5 | 23.0 | 5.5 | 27.6 | 15.7 | 11.8 |
| 123 | 3.5 | 8.2 | 3.7 | 11.4 | 16.2 | 12.7 |
| 124 | 2.7 | | | | | 11.8 |
| 125 | 1.6 | | | | 10.7 | 19.1 |
| 126 | | | | | | 11.4 |
| 127 | 2.7 | | | 7.2 | | 24.0 |
| 128 | 2.4 | | | 7.2 | | 31.8 |
| 129 | 2.6 | 5.6 | 5.9 | 9.0 | | 44.5 |
| 130 | | 3.5 | 4.1 | | | 18.2 |
| 131 | 6.1 | 16.9 | 22.7 | 22.7 | 17.9 | 52.0 |
| 132 | 3.5 | 8.8 | 7.0 | 11.4 | 11.2 | 25.5 |
| 133 | 8.7 | 32.5 | 23.5 | 44.5 | 36.0 | 73.0 |
| 134 | 5.7 | 17.7 | 9.6 | 23.4 | 17.9 | 26.4 |
| 135 | | 13.6 | 5.2 | 28.8 | 22.9 | 25.5 |
| 136 | | 4.6 | 2.9 | 10.8 | | 7.7 |
| 137 | 7.6 | 5.1 | | | 12.9 | 10.0 |
| 138 | | 3.7 | | 6.6 | | |

(Contd. over)

| M/e | (XLV) Columbin | (XLV) ISO-Columbin | (XLVI) Decarboxy-Columbin | (XLVI) Decarboxy-ISO-Columbin | (XLVII) Dihydro-Columbin | (XLVII) Dihydro ISO-Columbin |
|---|---|---|---|---|---|---|
| 141 | 2.3 | | | | | 6.4 |
| 142 | 1.9 | | | | | |
| 143 | 2.6 | 4.5 | 4.1 | 7.2 | | |
| 145 | 5.0 | 11.9 | 6.3 | 15.1 | 17.4 | 14.5 |
| 146 | | 6.5 | 6.3 | | 6.7 | 9.1 |
| 147 | 9.6 | 25.5 | 19.8 | 24.6 | 28.5 | 32.7 |
| 148 | 5.3 | 15.0 | 13.2 | 16.8 | 16.2 | 17.3 |
| 149 | 37.1 | 6.8 | 4.1 | 13.2 | 15.1 | 10.9 |
| 150 | | 3.5 | | | | 4.6 |
| 151 | | 3.0 | | | 10.1 | |
| 152 | 6.8 | 7.7 | | 9.6 | 17.3 | 15.0 |
| 153 | 7.8 | 16.8 | | | 20.7 | |
| 158 | | 2.6 | | | | |
| 159 | 8.1 | 8.8 | 2.2 | 12.6 | 19.6 | 12.3 |
| 160 | 4.9 | 12.6 | 8.1 | 21.6 | 15.7 | 9.1 |
| 161 | 16.0 | 14.0 | 8.5 | 25.3 | 22.4 | 11.8 |
| 162 | 6.7 | 3.5 | 2.9 | | | 7.3 |
| 163 | | 3.7 | | | 11.8 | 16.8 |
| 164 | | 3.5 | | | | |
| 165 | | 2.5 | | | | |
| 166 | | 4.6 | | 9.0 | | |
| 171 | 2.4 | 3.9 | | | 9.0 | 7.3 |
| 172 | 3.4 | | | | | |
| 173 | 3.6 | 5.9 | | 7.8 | 13.4 | 12.7 |
| 174 | | | | | | 9.1 |
| 175 | | 5.6 | | 9.4 | 12.9 | 10.5 |
| 176 | 3.9 | 4.6 | | 9.6 | | 7.3 |
| 177 | 7.3 | 3.7 | 4.8 | 6.2 | | 8.2 |
| 178 | 7.8 | 3.3 | | | 14.5 | 6.4 |
| 179 | 7.0 | 2.8 | | | | 8.2 |
| 181 | 4.7 | | | | | |
| 183 | | 3.7 | | | | 5.9 |
| 185 | | 3.1 | 7.0 | 5.2 | | 5.5 |
| 186 | | 2.5 | 6.3 | | | |
| 187 | | 5.4 | | 7.4 | | 6.4 |
| 188 | | 10.2 | | 14.4 | | |
| 189 | 3.5 | 7.0 | | 11.1 | 13.4 | 5.5 |
| 190 | | 3.9 | | 7.9 | 16.5 | |
| 191 | | 6.3 | 3.7 | 8.9 | 20.3 | 9.6 |
| 192 | | | | 6.5 | | |
| 201 | | | 11.0 | | | |
| 202 | | | | 6.2 | | |
| 203 | 3.0 | | 16.5 | 6.1 | 15.7 | 7.3 |
| 204 | 7.8 | 8.1 | 5.3 | 10.8 | 17.9 | 5.9 |
| 205 | 3.8 | 11.5 | 4.4 | 26.4 | 24.7 | |
| 206 | | 4.7 | | 10.8 | 10.1 | |
| 207 | | | | | | |
| 208 | | | | | | 7.7 |

(Contd. over)

| | (XLV) | | (XLVI) | | (XLVII) | |
|---|---|---|---|---|---|---|
| M/e | Columbin | ISO-Columbin | Decarboxy-Columbin | Decarboxy-ISO-Columbin | Dihydro-Columbin | Dihydro-ISO-Columbin |
| 218 | | | | 6.4 | | |
| 219 | | | 17.7 | 5.0 | | |
| 220 | 3.0 | | 3.7 | 4.9 | | |
| 222 | | | | | | 7.7 |
| 231 | 15.1 | | | 5.4 | 8.4 | |
| 232 | | | | 4.4 | | |
| 236 | | | | | | 15.2 |
| 237 | | | | | | 5.9 |
| 239 | | 2.4 | | | | |
| 245 | 4.9 | 3.7 | 3.7 | | | |
| 246 | 2.4 | 2.4 | | 4.6 | | |
| 247 | | | | | 7.7 | 5.9 |
| 249 | | | | | | 10.5 |
| 252 | 1.6 | 2.8 | 4.1 | 5.4 | | |
| 253 | 1.9 | | 3.7 | 6.6 | | |
| 257 | 3.8 | | | | | |
| 258 | 6.0 | | | | | |
| 259 | 6.8 | | | | 9.5 | |
| 260 | 3.5 | | | | | |
| 261 | 3.0 | | | | | |
| 262 | | 1.6 | | | | |
| 264 | | | | | | 9.2 |
| 268 | 2.2 | | 5.2 | 5.0 | | |
| 269 | | 1.8 | 3.7 | 3.5 | | |
| 270 | | 1.8 | | 4.4 | | |
| 271 | 1.6 | | 4.4 | 3.8 | | |
| 272 | | | | | 8.4 | 6.8 |
| 273 | | | | | | 5.5 |
| 275 | 6.5 | | | | | |
| 276 | 3.5 | | | | | |
| 279 | | | 3.7 | | | 5.5 |
| 281 | | | 2.9 | | | |
| 286 | 8.5 | | 11.4 | 6.0 | | 5.9 |
| 287 | | | 4.4 | | | |
| 295 | 4.7 | 1.6 | | | | |
| 296 | | | 8.6 | 4.0 | | |
| 297 | | | 2.9 | | | |
| 298 | | 1.7 | | | | |
| 299 | | | 2.6 | 5.8 | | |
| 301 | | | | | | 7.3 |
| 310 | | 1.6 | | | | |
| 311 | | | | | 22.4 | |
| 312 | | | | | 9.0 | |
| 313 | 12.2 | 17.5 | | | | |
| 314 | | 5.6 | 29.5 p | 50.5 p | 21.8 | 12.7 |
| 315 | | | 9.6 | 14.4 | 8.4 | 6.4 |

(Contd. over)

| | (XLV) | | (XLVI) | | (XLVII) | |
|---|---|---|---|---|---|---|
| M/e | Columbin | ISO-Columbin | Decarboxy-Columbin | Decarboxy-ISO-Columbin | Dihydro-Columbin | Dihydro-ISO-Columbin |
| 316 | | | | 4.0 | | 9.6 |
| 317 | | | | | | 9.2 |
| 332 | | | | | 6.7 | 23.6 |
| 333 | | | | | | 8.7 |
| 338 | | | | | | 4.6 |
| 342 | | | | | 3.9 | 9.1 |
| 343 | 0.7 | | | | | 5.5 |
| 345 | | | | | 3.4 | |
| 358 | 1.35 p | 4.2 p | | | | |
| 360 | | | | | 28.6 p | 100.0 |
| 361 | | | | | 8.4 | 30.1 |

(XLVIII) Octahydrocolumbinic acid methyl ester. M.Wt. 380.

2 KV. 50eV, slight heat.

| M/e | % | M/e | % | M/e | % | M/e | % | M/e | % |
|---|---|---|---|---|---|---|---|---|---|
| 40 | 56.4 | 86 | 14.8 | 119 | 24.5 | 151 | 11.7 | 183 | 3.6 |
| 41 | 27.0 | 87 | 9,7 | 120 | 10.2 | 152 | 6.1 | 184 | 2.0 |
| 42 | 6.7 | 88 | 3.6 | 121 | 29.6 | 153 | 6.6 | 185 | 7.1 |
| 43 | 35.8 | 89 | 3.1 | 122 | 10.7 | 154 | 4.1 | 186 | 4.1 |
| 44 | 27.5 | 91 | 21.9 | 123 | 25.0 | 155 | 4.1 | 187 | 11.2 |
| 45 | 7.1 | 92 | 6.6 | 124 | 13.8 | 156 | 3.1 | 188 | 5.6 |
| 53 | 9.2 | 93 | 34.2 | 125 | 14.8 | 157 | 16.3 | 189 | 10.7 |
| 54 | 4.4 | 94 | 41.3 | 126 | 7.1 | 158 | 6.1 | 190 | 5.1 |
| 55 | 46.0 | 95 | 52.0 | 127 | 7.7 | 159 | 18.4 | 191 | 9.2 |
| 56 | 7.7 | 96 | 100.0 | 128 | 5.6 | 160 | 6.6 | 192 | 6.1 |
| 57 | 15.8 | 97 | 29.1 | 129 | 6.1 | 161 | 19.9 | 193 | 46.4 |
| 58 | 12.2 | 98 | 18.9 | 130 | 3.6 | 162 | 7.7 | 194 | 19.9 |
| 59 | 10.7 | 99 | 10.7 | 131 | 10.2 | 163 | 15.3 | 195 | 9.2 |
| 65 | 5.1 | 100 | 3.6 | 132 | 6.6 | 164 | 7.1 | 196 | 5.1 |
| 66 | 4.1 | 101 | 3.6 | 133 | 42.1 | 165 | 10.7 | 197 | 6.1 |
| 67 | 21.4 | 102 | 2.0 | 134 | 13.3 | 166 | 9.7 | 198 | 5.1 |
| 68 | 7.7 | 103 | 3.6 | 135 | 21.9 | 167 | 11.2 | 199 | 8.2 |
| 69 | 27.5 | 104 | 3.1 | 136 | 10.2 | 168 | 4.1 | 200 | 3.6 |
| 70 | 10.7 | 105 | 25.0 | 137 | 15.3 | 169 | 3.6 | 201 | 6.1 |
| 71 | 10.2 | 106 | 11.7 | 138 | 9.7 | 170 | 2.0 | 202 | 4.1 |
| 72 | 2.6 | 107 | 43.4 | 139 | 8.2 | 171 | 4.6 | 203 | 32.6 |
| 73 | 3.1 | 108 | 19.9 | 140 | 3.6 | 172 | 2.6 | 204 | 12.2 |
| 74 | 2.6 | 109 | 28.1 | 141 | 4.1 | 173 | 8.7 | 205 | 12.8 |
| 77 | 10.2 | 110 | 16.3 | 142 | 3.6 | 174 | 4.1 | 206 | 8.7 |
| 78 | 4.6 | 111 | 11.7 | 143 | 6.6 | 175 | 32.1 | 207 | 14.8 |
| 79 | 32.1 | 112 | 3.6 | 144 | 4.1 | 176 | 6.6 | 208 | 7.7 |
| 80 | 9.2 | 113 | 3.5 | 145 | 13.8 | 177 | 13.3 | 209 | 12.8 |
| 81 | 37.2 | 114 | 9.2 | 146 | 6.1 | 178 | 6.6 | 210 | 5.1 |
| 82 | 16.3 | 115 | 7.7 | 147 | 19.4 | 179 | 8.2 | 211 | 4.1 |
| 83 | 44.4 | 116 | 4.1 | 148 | 8.2 | 180 | 5.1 | 212 | 2.6 |
| 84 | 7.7 | 117 | 7.7 | 149 | 14.3 | 181 | 5.6 | 213 | 4.6 |
| 85 | 18.9 | 118 | 5.1 | 150 | 7.1 | 182 | 3.1 | 214 | 3.1 |

(Contd. over)

(XLVIII) (Contd.) Octahydrocolumbinic acid methyl ester M.Wt. 380.

2KV, 50eV, slight heat.

| M/E | % | M/e | % | M/e | % | M/e | % |
|---|---|---|---|---|---|---|---|
| 215 | 6.1 | 247 | 16.8 | 279 | 32.1 | 320 | 20.4 |
| 216 | 5.1 | 248 | 13.8 | 280 | 10.2 | 321 | 16.8 |
| 217 | 19.9 | 249 | 64.8 | 281 | 45.4 | 322 | 6.1 |
| 218 | 8.2 | 250 | 20.9 | 282 | 14.8 | 323 | 3.1 |
| 219 | 11.2 | 251 | 7.7 | 283 | 4.6 | 324 | 2.6 |
| 220 | 9.2 | 252 | 3.6 | 284 | 6.6 | 329 | 3.1 |
| 221 | 25.6 | 253 | 4.6 | 285 | 5.1 | 330 | 7.7 |
| 222 | 17.3 | 254 | 3.1 | 286 | 4.6 | 331 | 6.6 |
| 223 | 10.2 | 255 | 2.6 | 287 | 4.6 | 332 | 3.6 |
| 224 | 5.6 | 256 | 3.6 | 288 | 3.1 | 333 | 5.6 |
| 225 | 3.6 | 257 | 6.1 | 289 | 3.1 | 334 | 10.2 |
| 226 | 3.1 | 258 | 4.1 | 290 | 3.1 | 335 | 4.9 |
| 227 | 3.6 | 259 | 6.1 | 291 | 4.6 | 336 | 2.6 |
| 228 | 5.6 | 260 | 17.3 | 292 | 29.1 | 337 | 2.6 |
| 229 | 6.6 | 261 | 12.2 | 293 | 12.8 | 344 | 16.8 |
| 230 | 4.6 | 262 | 7.1 | 294 | 5.1 | 345 | 7.1 |
| 231 | 14.8 | 263 | 40.8 | 295 | 4.1 | 346 | 3.9 |
| 232 | 16.3 | 264 | 14.8 | 296 | 3.1 | 347 | 4.6 |
| 233 | 14.2 | 265 | 6.1 | 297 | 3.1 | 348 | 50.0 |
| 234 | 8.7 | 266 | 4.1 | 301 | 3.1 | 349 | 27.5 |
| 235 | 35.2 | 267 | 10.7 | 302 | 9.0 | 350 | 9.7 |
| 236 | 12.8 | 268 | 4.6 | 303 | 7.7 | 351 | 3.6 |
| 237 | 6.6 | 269 | 3.6 | 304 | 4.6 | 352 | 5.6 |
| 238 | 3.6 | 270 | 2.0 | 305 | 5.1 | 362 | 5.1 |
| 239 | 3.6 | 271 | 2.0 | 306 | 9.7 | 363 | 3.1 |
| 240 | 2.6 | 272 | 2.0 | 307 | 4.1 | 364 | 2.0 |
| 241 | 3.1 | 273 | 3.6 | 308 | 2.6 | 365 | 3.6 |
| 242 | 3.1 | 274 | 9.7 | 309 | 2.6 | 380 | 60.7 P |
| 243 | 3.6 | 275 | 8.7 | 312 | 4.6 | 381 | 23.5 |
| 244 | 3.1 | 276 | 8.0 | 316 | 5.1 | | |
| 245 | 21.4 | 277 | 8.7 | 317 | 3.1 | | |
| 246 | 14.8 | 278 | 5.6 | 318 | 5.1 | | |
| | | | | 319 | 8.2 | | |

(XLVIII) Octahydroisocolumbinic acid methyl ester.

2KV, 50eV, slight heat.

| M/e | % | M/e | % | M/e | % | M/e | % | M/e | % |
|---|---|---|---|---|---|---|---|---|---|
| 40 | 31.6 | 84 | 12.6 | 117 | 10.7 | 150 | 12.1 | 183 | 6.3 |
| 41 | 33.5 | 85 | 37.0 | 118 | 6.8 | 151 | 17.0 | 184 | 4.9 |
| 42 | 7.3 | 86 | 21.4 | 119 | 37.9 | 152 | 8.7 | 185 | 10.2 |
| 43 | 37.9 | 87 | 14.1 | 120 | 17.0 | 153 | 9.7 | 186 | 6.3 |
| 44 | 16.5 | 88 | 3.4 | 121 | 55.3 | 154 | 6.8 | 187 | 16.5 |
| 45 | 16.0 | 89 | 2.9 | 122 | 19.4 | 155 | 5.8 | 188 | 8.7 |
| 46 | 6.3 | 90 | 1.9 | 123 | 41.3 | 156 | 3.9 | 189 | 17.0 |
| 51 | 4.9 | 91 | 34.5 | 124 | 29.6 | 157 | 25.2 | 190 | 7.8 |
| 52 | 3.9 | 92 | 1017 | 125 | 24.8 | 158 | 11.2 | 191 | 14.1 |
| 53 | 18.7 | 93 | 58.7 | 126 | 12.1 | 159 | 35.4 | 192 | 8.7 |
| 54 | 6.8 | 94 | 68.4 | 127 | 10.7 | 160 | 13.1 | 193 | 46.6 |
| 55 | 74.9 | 95 | 100.0 | 128 | 7.3 | 161 | 37.4 | 194 | 26.2 |
| 56 | 10.2 | 96 | 55.3 | 129 | 8.3 | 162 | 13.1 | 195 | 13.1 |
| 57 | 21.4 | 97 | 32.0 | 130 | 4.4 | 163 | 25.2 | 196 | 7.8 |
| 58 | 17.5 | 98 | 9.2 | 131 | 19.4 | 164 | 13.1 | 197 | 8.3 |
| 59 | 18.0 | 99 | 8.7 | 132 | 9.7 | 165 | 18.0 | 198 | 8.7 |
| 65 | 7.3 | 100 | 5.0 | 133 | 47.6 | 166 | 16.0 | 199 | 11.7 |
| 66 | 5.8 | 101 | 5.8 | 134 | 18.4 | 167 | 23.3 | 200 | 6.8 |
| 67 | 36.4 | 102 | 1.9 | 135 | 36.9 | 168 | 8.3 | 201 | 10.2 |
| 68 | 11.7 | 103 | 4.4 | 136 | 14.1 | 169 | 6.8 | 202 | 5.3 |
| 69 | 43.2 | 104 | 3.4 | 137 | 25.2 | 170 | 3.9 | 203 | 29.6 |
| 70 | 17.7 | 105 | 38.3 | 138 | 14.6 | 171 | 8.7 | 204 | 31.6 |
| 71 | 14.6 | 106 | 15.0 | 139 | 12.1 | 172 | 4.9 | 205 | 19.9 |
| 72 | 2.9 | 107 | 74.8 | 140 | 5.3 | 173 | 14.6 | 206 | 12.1 |
| 73 | 3.9 | 108 | 40.3 | 141 | 5.3 | 174 | 6.8 | 207 | 35.4 |
| 74 | 3.4 | 109 | 47.6 | 142 | 4.9 | 175 | 30.6 | 208 | 19.4 |
| 77 | 16.5 | 110 | 43.2 | 143 | 9.2 | 176 | 12.6 | 209 | 26.7 |
| 78 | 6.3 | 111 | 18.4 | 144 | 5.3 | 177 | 22.8 | 210 | 10.7 |
| 79 | 50.5 | 112 | 5.3 | 145 | 20.9 | 178 | 11.2 | 211 | 8.3 |
| 80 | 14.1 | 113 | 4.9 | 146 | 8.7 | 179 | 15.5 | 212 | 4.9 |
| 81 | 81.1 | 114 | 13.6 | 147 | 33.0 | 180 | 9.7 | 213 | 7.8 |
| 82 | 34.0 | 115 | 10.2 | 148 | 13.6 | 181 | 14.7 | 214 | 6.3 |
| 83 | 72.9 | 116 | 4.9 | 149 | 25.7 | 182 | 6.8 | | |

(Contd. over)

(XLVIII) (Contd.) Octahydroisocolumbinic acid methyl ester.

2KV, 50eV. slight heat.

| M/e | % | M/e | % | M/e | % | M/e | % | |
|---|---|---|---|---|---|---|---|---|
| 215 | 9.2 | 248 | 13.1 | 282 | 39.3 | 316 | 18.4 | |
| 216 | 5.3 | 249 | 85.0 | 283 | 13.1 | 317 | 10.7 | |
| 217 | 25.2 | 250 | 35.4 | 284 | 9.2 | 318 | 12.1 | |
| 218 | 11.7 | 251 | 14.1 | 285 | 7.3 | 319 | 18.4 | |
| 219 | 17.0 | 252 | 5.3 | 286 | 6.3 | 320 | 36.0 | |
| 220 | 13.6 | 253 | 13.6 | 287 | 6.3 | 321 | 25.2 | |
| 221 | 37.4 | 254 | 7.8 | 288 | 9.2 | 322 | 8.7 | |
| 222 | 43.2 | 255 | 5.8 | 289 | 6.8 | 323 | 4.4 | |
| 223 | 22.8 | 256 | 5.3 | 290 | 5.8 | 324 | 3.9 | |
| 224 | 8.7 | 257 | 8.9 | 291 | 7.3 | 329 | 3.9 | |
| 225 | 6.8 | 258 | 5.8 | 292 | 43.2 | 330 | 14.1 | |
| 226 | 3.9 | 259 | 8.7 | 293 | 20.4 | 331 | 6.8 | |
| 227 | 4.9 | 260 | 21.8 | 294 | 9.2 | 332 | 3.4 | |
| 228 | 4.9 | 261 | 15.5 | 295 | 7.3 | 333 | 7.3 | |
| 229 | 6.8 | 262 | 8.7 | 296 | 5.9 | 334 | 10.2 | |
| 230 | 4.9 | 263 | 20.9 | 297 | 4.4 | 335 | 5.8 | |
| 231 | 16.5 | 264 | 11.7 | 298 | 3.4 | 336 | 3.4 | |
| 232 | 35.9 | 265 | 6.8 | 299 | 3.9 | 337 | 4.9 | |
| 233 | 17.0 | 266 | 4.4 | 300 | 3.4 | 338 | 2.9 | |
| 234 | 10.7 | 267 | 26.2 | 301 | 3.9 | 344 | 11.2 | |
| 235 | 46.1 | 268 | 9.2 | 302 | 19.4 | 345 | 8.3 | |
| 236 | 19.9 | 269 | 4.4 | 303 | 18.4 | 346 | 5.3 | |
| 237 | 10.7 | 270 | 2.9 | 304 | 9.2 | 347 | 5.8 | |
| 238 | 4.9 | 271 | 3.4 | 305 | 7.3 | 348 | 91.3 | |
| 239 | 4.9 | 272 | 2.9 | 306 | 21.4 | 349 | 40.8 | |
| 240 | 2.9 | 273 | 7.8 | 307 | 8.3 | 350 | 13.1 | |
| 241 | 4.4 | 274 | 18.4 | 308 | 4.9 | 352 | 19.4 | |
| 242 | 3.9 | 275 | 15.0 | 309 | 3.4 | 353 | 7.8 | |
| 243 | 5.8 | 276 | 9.7 | 310 | 2.4 | 358 | 2.4 | |
| 244 | 3.6 | 277 | 11.2 | 311 | 2.4 | 362 | 11.2 | |
| 245 | 16.0 | 278 | 8.3 | 312 | 5.3 | 363 | 5.8 | |
| 246 | 15.5 | 279 | 8.3 | 313 | 4.4 | 376 | 5.0 | imp. |
| 247 | 16.0 | 280 | 4.9 | 314 | 2.4 | 380 | 93.7P | |
| | | 281 | 21.8 | 315 | 4.9 | 381 | 39.8 | |

Benzfuran. 70 ev.

(Manufacturing Chemists Association Research Project No. 86).

| M/e | % | M/e | % |
|---|---|---|---|
| 25 | 1.19 | 64 | 7.60 |
| 26 | 4.83 | 65 | 1.06 |
| 27 | 4.16 | | |
| 28 | 1.15 | 69.0m | 0.73 |
| 29 | 4.42 | | |
| | | 73 | 0.61 |
| 31 | 0.45 | 74 | 1.69 |
| | | 75 | 1.23 |
| 36 | 0.93 | | |
| 37 | 6.34 | 77 | 0.80 |
| 38 | 8.99 | | |
| 39 | 14.07 | 84 | 0.52 |
| 40 | 1.92 | 85 | 1.60 |
| 41 | 0.60 | 86 | 2.63 |
| | | 87 | 2.39 |
| 43 | 3.15 | 88 | 4.69 |
| 43.5 | 0.83 | 89 | 37.34 |
| 44 | 1.45 | 90 | 36.36 |
| 44.5 | 1.56 | 91 | 3.54 |
| 45 | 1.43 | 92 | 0.46 |
| 49 | 2.17 | 103 | 0.50 |
| 50 | 7.16 | | |
| 51 | 7.01 | 105 | 3.50 |
| 52 | 0.78 | | |
| 53 | 1.42 | 115 | 3.11 |
| | | 116 | 3.31 |
| 57.5 | 0.55 | 117 | 3.61 |
| 58 | 0.68 | 118 | 100.00P |
| 59 | 5.23 | 119 | 8.95 |
| 59.5 | 0.47 | 120 | 2.41 |
| 60 | 1.01 | | |
| 61 | 5.97 | | |
| 62 | 12.53 | | |
| 63 | 26.04 | | |

2-Methylbenzfuran. 70 ev.

(Manufacturing Chemists Association Research Project No. 89).

| M/e | % | M/e | % | |
|---|---|---|---|---|
| 25 | 0.75 | 74 | 4.60 | |
| 26 | 4.80 | 75 | 3.74 | |
| 27 | 7.25 | 76 | 3.86 | |
| 28 | 1.59 | 77 | 17.12 | |
| 29 | 1.29 | 78 | 10.54 | |
| | | 79 | 0.87 | |
| 37 | 3.75 | | | |
| 38 | 6.86 | 85 | 0.58 | |
| 39 | 13.42 | 86 | 1.06 | |
| 40 | 0.89 | 87 | 1.38 | |
| 41 | 1.12 | 88 | 0.79 | |
| 42 | 0.56 | 89 | 2.46 | |
| 43 | 5.24 | | | |
| | | 91 | 0.46 | |
| 49 | 2.04 | | | |
| 49.5 | 0.55 | 98 | 0.65 | |
| 50 | 12.01 | | | |
| 50.5 | 1.01 | 100 | 0.45 | |
| 51 | 22.46 | 101 | 1.34 | |
| 51.5 | 1.73 | 102 | 5.27 | |
| 52 | 5.26 | 103 | 13.29 | |
| 53 | 2.48 | 104 | 5.48 | |
| | | 105 | 1.24 | |
| 55 | 0.76 | | | |
| | | 115 | 0.45 | |
| 61 | 2.70 | | | |
| 62 | 5.88 | 130 | 7.35 | |
| 63 | 10.61 | 131 | 100.00 | P-1 |
| 64 | 2.18 | 132 | 78.81 | P |
| 65 | 3.29 | 133 | 7.88 | |
| 65.5 | 2.86 | 134 | 1.41 | |
| 66 | 6.62 | | | |
| 66.5 | 0.68 | | | |
| 73 | 0.89 | | | |

4-Methyldibenzofuran. 70 ev.

(Manufacturing Chemists Association Research Project No. 102).

| M/e | % | M/e | % | M/e | % | M/e | % | M/e | % |
|---|---|---|---|---|---|---|---|---|---|
| 28 | 0.55 | 55.5 | 0.12 | 75 | 5.77 | 105 | 0.24 | 140 | 0.22 |
| 29 | 0.57 | 56 | 0.17 | 75.5 | 2.40 | 106 | 0.06 | 141 | 0.05 |
| | | 56.5 | 0.13 | 76 | 12.28 | 107 | 0.03 | 142 | 0.15 |
| 31 | 0.04 | 57 | 0.08 | 76.5 | 2.05 | 108 | 0.04 | 143 | 0.05 |
| | | 57.5 | 0.07 | 77 | 3.77 | 109 | 0.20 | 144 | 0.03 |
| 36 | 0.07 | 58 | 0.04 | 77.5 | 1.71 | 110 | 0.50 | 145 | 0.03 |
| 37 | 1.21 | 58.5 | 0.01 | 78 | 0.99 | 111 | 0.52 | 146 | 0.05 |
| 37.5 | 0.03 | 59 | 0.03 | 79 | 0.14 | 112 | 0.21 | 147 | 0.07 |
| 38 | 3.00 | 60 | 0.11 | 80 | 0.05 | 113 | 0.21 | 148 | 0.18 |
| 38.5 | 0.03 | 60.7 | 0.16 | 81 | 0.07 | 114 | 0.53 | 149 | 0.67 |
| 39 | 7.43 | 61 | 1.42 | 81.5 | 0.09 | 115 | 1.25 | 150 | 2.62 |
| 40 | 0.47 | 61.5 | 0.26 | 82 | 0.20 | 116 | 0.15 | 151 | 5.77 |
| 40.7 | 0.04 | 62 | 3.87 | 82.5 | 0.05 | 117 | 0.02 | 152 | 15.95 |
| 41 | 0.31 | 62.5 | 0.59 | 83 | 0.05 | 118 | 0.04 | 153 | 5.81 |
| 42 | 0.10 | 63 | 8.62 | 84 | 0.11 | 119 | 0.01 | 154 | 1.29 |
| 43 | 0.16 | 63.5 | 1.52 | 85 | 0.71 | 120 | 0.03 | 155 | 1.12 |
| 43.5 | 0.05 | 64 | 3.92 | 86 | 2.12 | 121 | 0.06 | 156 | 0.15 |
| 44 | 0.07 | 64.5 | 0.61 | 87 | 2.87 | 122 | 0.25 | | |
| 44.5 | 0.04 | 65 | 0.90 | 88 | 1.04 | 123 | 0.14 | 162 | 0.02 |
| 45 | 0.02 | 65.5 | 0.14 | 89 | 1.66 | 124 | 0.13 | 163 | 0.09 |
| 46 | 0.02 | 66 | 0.21 | 90 | 1.52 | 125 | 0.76 | 164 | 0.18 |
| | | 66.5 | 0.14 | 90.5 | 5.90 | 126 | 3.20 | 165 | 0.23 |
| 48 | 0.05 | 67 | 0.22 | 91 | 9.63 | 127 | 4.37 | 166 | 0.10 |
| 48.5 | 0.02 | 67.5 | 0.09 | 91.5 | 1.35 | 128 | 1.53 | 167 | 0.04 |
| 49 | 0.51 | 68 | 0.10 | 92 | 0.15 | 129 | 0.55 | 168 | 0.05 |
| 49.5 | 0.18 | 68.5 | 0.10 | | | 130 | 0.35 | 169 | 0.05 |
| 50 | 4.96 | 69 | 0.14 | 96 | 0.02 | 131 | 0.45 | | |
| 50.6m | 0.19 | 69.5 | 0.34 | 97 | 0.23 | 132 | 0.20 | 173 | 0.02 |
| 51 | 7.01 | 70 | 0.08 | 98 | 1.58 | 133 | 0.14 | 174 | 0.03 |
| 51.5 | 0,09 | 70.5 | 0.03 | 99 | 1.14 | 134 | 0.13 | 175 | 0.06 |
| 52 | 1.75 | 71 | 0.04 | 100 | 0.57 | 135 | 0.09 | 176 | 0.08 |
| 53 | 1.42 | 71.5 | 0.03 | 101 | 1.57 | 136 | 0.10 | 177 | 0.10 |
| 54 | 0.14 | 72 | 0.06 | 102 | 1.53 | 137 | 0.38 | 178 | 0.16 |
| 54.5 | 0.03 | 73 | 0.52 | 103 | 0.39 | 138 | 0.39 | 179 | 0.99 |
| 55 | 0.45 | 74 | 4.59 | 104 | 0.11 | 139 | 1.51 | 180 | 8.66 |
| | | | | | | | | 181 | 78.85 |
| | | | | | | | | 182 | 100.0P |
| | | | | | | | | 183 | 96.85 |
| | | | | | | | | 184 | 13.03 |
| | | | | | | | | 185 | 0.92 |
| | | | | | | | | 186 | 0.05 |

7-Methylbenzfuran. 70 ev.

(Manufacturing Chemists Association Research Project No. 90).

| M/e | % | M/e | % |
|---|---|---|---|
| 25 | 0.75 | 75 | 5.28 |
| 26 | 4.67 | 76 | 5.12 |
| 27 | 8.70 | 77 | 22.86 |
| 28 | 2.42 | 78 | 14.16 |
| 29 | 5.50 | 79 | 1.00 |
| 37 | 4.39 | 82m | 0.61 |
| 38 | 6.62 | | |
| 39 | 11.67 | 84 | 0.46 |
| 40 | 0.87 | 85 | 0.66 |
| 41 | 0.70 | 86 | 1.10 |
| | | 87 | 1.45 |
| 43 | 0.70 | 88 | 0.50 |
| | | 89 | 2.48 |
| 49 | 2.37 | 90 | 0.86 |
| 49.5 | 0.59 | | |
| 50 | 15.35 | 98 | 1.03 |
| 50.5 | 1.73 | 99 | 0.61 |
| 51 | 31.52 | 100 | 0.60 |
| 51.5 | 2.86 | 101 | 1.93 |
| 52 | 3.19 | 102 | 8.36 |
| 53 | 4.07 | 103 | 19.03 |
| | | 104 | 18.09 |
| 60 | 0.52 | 105 | 1.84 |
| 61 | 3.07 | | |
| 62 | 6.39 | 119 | 1.73 |
| 63 | 12.71 | | |
| 64 | 2.04 | 130 | 6.08 |
| 65 | 2.27 | 131 | 91.49 |
| 65.5 | 2.66 | 132 | 100.00 P |
| 66 | 5.08 | 133 | 9.82 |
| 66.5 | 0.54 | 134 | 0.55 |
| 73 | 1.24 | | |
| 74 | 6.29 | | |

Dibenzofuran. 70 ev.

(Manufacturing Chemists Association Research Project No. 101.)

| M/e | % | M/e | % | M/e | % | M/e | % | M/e | % |
|---|---|---|---|---|---|---|---|---|---|
| 28 | 0.19 | 53 | 0.64 | 77 | 0.40 | 111 | 0.79 | 161 | 0.01 |
| 29 | 0.47 | 54 | 0.10 | 78 | 0.06 | 112 | 0.50 | 162 | 0.03 |
| | | 54.5 | 0.11 | 79 | 0.05 | 113 | 4.06 | 163 | 0.03 |
| 31 | 0.08 | 55 | 1.00 | 80 | 0.01 | 114 | 3.80 | 164 | 0.08 |
| 31.5 | 0.02 | 55.5 | 0.36 | 81 | 0.02 | 115 | 0.94 | 165 | 0.16 |
| | | 56 | 0.70 | 82 | 0.03 | 116 | 0.61 | 166 | 0.29 |
| 35 | 0.02 | 56.5 | 0.60 | 83 | 0.15 | 117 | 0.53 | 167 | 0.75 |
| 36 | 0.17 | 57 | 0.79 | 83.5 | 0.12 | 118 | 0.51 | 168 | 100.0P |
| 37 | 1.86 | 57.5 | 0.13 | 84 | 9.80 | 119 | 0.24 | 169 | 13.27 |
| 37.5 | 0.05 | | | 84.5 | 1.36 | 120 | 0.12 | 170 | 0.95 |
| 38 | 3.41 | 58.5 | 0.26 | 85 | 1.17 | 121 | 0.08 | 171 | 0.03 |
| 38.5 | 0.01 | | | 86 | 2.84 | 122 | 0.09 | | |
| 39 | 6.27 | 60 | 0.20 | 87 | 3.76 | 123 | 0.04 | | |
| 40 | 0.30 | 61 | 1.74 | 88 | 2.07 | 124 | 0.33 | | |
| 41 | 0.16 | 62 | 4.30 | 89 | 2.53 | 125 | 0.07 | | |
| 42 | 0.08 | 63 | 6.87 | 90 | 0.40 | 126 | 0.07 | | |
| 42.5 | 0.02 | 64 | 1.21 | 91 | 0.06 | 127 | 0.04 | | |
| 43 | 0.30 | 65 | 0,66 | 92 | 0.23 | 128 | 0.03 | | |
| 43.5 | 0.07 | 65.5 | 0.02 | 93 | 0.06 | 129 | 0.21 | | |
| 44 | 0.11 | 66 | 0.17 | 94 | 0.04 | 130 | 0.04 | | |
| 44.5 | 0.05 | 66.5 | 0.06 | | | 131 | 0.03 | | |
| 45 | 0.04 | 67 | 0.29 | 96 | 0.02 | 132 | 0.06 | | |
| 45.7 | 0.02 | 67.5 | 0.13 | 97 | 0.19 | 133 | 0.07 | | |
| 46 | 0.04 | 68 | 0.63 | 98 | 1.11 | 134 | 0.12 | | |
| 46.3 | 0.02 | 69 | 3.40 | 99 | 0.67 | 135 | 0.10 | | |
| 46.7 | 0.03 | 69.5 | 5.34 | 100 | 0.28 | 136 | 0.28 | | |
| | | 70 | 2.29 | 101 | 0.58 | 137 | 1.39 | | |
| 48 | 0.06 | 70.5 | 0.25 | 102 | 0.26 | 138 | 2.95 | | |
| 48.5 | 0.01 | 71 | 0.37 | 103 | 0.03 | 139 | 28.92 | | |
| 49 | 0.60 | 71.5 | 0.04 | 104 | 0.01 | 140 | 4.25 | | |
| 49.5 | 0.07 | 72 | 0.07 | 105 | 0.01 | 141 | 0.25 | | |
| 50 | 3.79 | 73 | 0.60 | | | 142 | 0.17 | | |
| 50.5 | 0.04 | 74 | 4.06 | 108 | 0.06 | 143 | 0.02 | | |
| 51 | 3.50 | 75 | 3.41 | 109 | 0.36 | | | | |
| 52 | 0.46 | 76 | 0.68 | 110 | 0.74 | 150 | 0.02 | | |

5-Nitrobenzfuran.

50eV, 2KV.

| M/e | % | M/e | % |
|---|---|---|---|
| 39 | 5.6 | 89 | 49.8 |
| 40 | 1.3 | 90 | 5.9 |
| 41 | 2.3 | 95 | 2.7 |
| 42 | 2.0 | 96 | 1.3 |
| 43 | 5.9 | 97 | 2,3 |
| 44 | 6.3 | 104 | 2.0 |
| 45 | 2.3 | 105 | 14.0 |
| 49 | 2.4 | 106 | 2.6 |
| 50 | 2.3 | 111 | 1.7 |
| 51 | 2.1 | 115 | 3.3 |
| 52 | 2.2 | 117 | 41.6 |
| 53 | 2.2 | 118 | 8.6 |
| 55 | 3.3 | 119 | 4.4 |
| 57 | 4.0 | 133 | 19.6 |
| 62 | 5.3 | 134 | 25.0 |
| 63 | 26.4 | 162 | 11.1 |
| 64 | 2.7 | 163 | 100.0 P |
| 67 | 1.7 | 164 | 13.9 |
| 68 | 1.3 | | |
| 69 | 3.6 | | |
| 70 | 2.3 | | |
| 71 | 3.0 | | |
| 75 | 2.0 | | |
| 76 | 2.3 | | |
| 77 | 14.1 | | |
| 78 | 7.3 | | |
| 79 | 2.3 | | |
| 80 | 2.3 | | |
| 81 | 3.0 | | |
| 82 | 2.0 | | |
| 83 | 2.3 | | |
| 87 | 2.6 | | |
| 88 | 3.6 | | |

(LXX) 2-carboxy-5-nitrobenzfuran.

2KV, 50eV.

| M/e | % | M/e | % | M/e | % |
|---|---|---|---|---|---|
| 29 | 0.7 | 79 | 1.7 | 134 | 4.1 |
| 30 | 1.1 | 80 | 0.4 | 135 | 0.7 |
| 31 | 3.3 | 81 | 5.3 | 143 | 1.3 |
| 32 | 0.8 | 82 | 0.4 | 144 | 3.4 |
| 33 | 1.1 | 83 | 0.5 | 145 | 0.8 |
| 36 | 0.5 | 85 | 0.4 | 147 | 0.7 |
| 38 | 0.3 | 87 | 2.2 | 149 | 4.0 |
| 39 | 1.9 | 88 | 7.3 | 150 | 0.6 |
| 43 | 1.4 | 89 | 17.2 | 159 | 0.7 |
| 44 | 3.9 | 90 | 1.7 | 160 | 2.5 |
| 45 | 1.8 | 91. | 0.5 | 161 | 38.8 |
| 50 | 0.7 | 93 | 0.9 | 162 | 5.7 |
| 51 | 0.5 | 95 | 0.6 | 163 | 7.4 |
| 52 | 0.7 | 97 | 0.4 | 164 | 0.7 |
| 53 | 1.1 | 102 | 0.4 | 175 | 0.5 |
| 55 | 0.7 | 103 | 0.7 | 176 | 0.5 |
| 57 | 0.7 | 104 | 0.6 | 177 | 15.4 |
| 60 | 0.7 | 105 | 11.0 | 178 | 3.5 |
| 62 | 3.1 | 106 | 1.4 | 179 | 0.9 |
| 63 | 7.8 | 107 | 2.4 | 190 | 3.9 |
| 64 | 0.7 | 108 | 0.4 | 191 | 5.7 |
| 65 | 2.8 | 109 | 0.5 | 192 | 1.0 |
| 66 | 0.7 | 116 | 3.3 | 206 | 7.6 |
| 67 | 0.6 | 117 | 3.7 | 207 | 100.0 P |
| 68 | 0.3 | 118 | 0.6 | 208 | 18.1 |
| 69 | 4.0 | 119 | 2.1 | | |
| 70 | 0.4 | 121 | 1.1 | | |
| 71 | 0.5 | 123 | 0.4 | | |
| 75 | 1.0 | 130 | 0.6 | | |
| 76 | 2.2 | 131 | 1.4 | | |
| 77 | 11.1 | 132 | 1.1 | | |
| 78 | 1.7 | 133 | 5.7 | | |

5-Acetylaminobenzfuran.

2KV, 50eV.

| M/e | % | M/e | % | M/e | % |
|---|---|---|---|---|---|
| 27 | 0.9 | 79 | 2.0 | 120 | 0.9 |
| 28 | 2.8 | 80 | 1.6 | 121 | 1.7 |
| 29 | 1.8 | 81 | 2.7 | 122 | 0.7 |
| 31 | 3.4 | 82 | 1.4 | 123 | 0.9 |
| 32 | 0.6 | 83 | 1.4 | 128 | 0.7 |
| 33 | 0.9 | 84 | 0.7 | 129 | 0.6 |
| 39 | 4.2 | 85 | 1.3 | 130 | 0.6 |
| 40 | 1.1 | 86 | 0.9 | 131 | 2.4 |
| 41 | 1.6 | 87 | 1.7 | 132 | 11.3 |
| 42 | 0.7 | 88 | 0.5 | 133 | 100.0 |
| 43 | 9.1 | 90 | 0.5 | 134 | 21.0 |
| 44 | 1.3 | 91 | 1.7 | 135 | 3.0 |
| 45 | 0.6 | 92 | 0.5 | 137 | 0.9 |
| 51 | 3.3 | 93 | 1.5 | 144 | 0.9 |
| 52 | 1.1 | 94 | 5.8 | 145 | 2.3 |
| 53 | 1.0 | 95 | 3.4 | 146 | 2.0 |
| 55 | 2.5 | 96 | 1.0 | 147 | 1.0 |
| 56 | 1.1 | 97 | 1.6 | 148 | 1.0 |
| 57 | 2.5 | 98 | 0.6 | 152 | 1.1 |
| 58 | 1.1 | 99 | 0.3 | 158 | 2.1 |
| 62 | 0.4 | 102 | 0.8 | 159 | 1.0 |
| 63 | 1.0 | 103 | 3.4 | 160 | 0.9 |
| 64 | 0.3 | 104 | 13.9 | 161 | 0.6 |
| 65 | 0.8 | 105 | 8.4 | 162 | 0.7 |
| 66 | 0.6 | 106 | 2.3 | 170 | 0.5 |
| 67 | 1.1 | 107 | 2.2 | 172 | 0.7 |
| 68 | 0.7 | 108 | 1.6 | 173 | 1.0 |
| 69 | 2.1 | 109 | 1.8 | 174 | 52.1 |
| 70 | 1.0 | 110 | 1.0 | 175 | 10.4 P |
| 71 | 1.6 | 111 | 0.9 | | |
| 75 | 0.4 | 112 | 0.7 | | |
| 76 | 1.9 | 117 | 1.3 | | |
| 77 | 7.3 | 118 | 1.0 | | |
| 78 | 5.2 | 119 | 2.0 | | |

4-Nitro-5-acetylamino-benzfuran.

2KV, 50eV.

| M/e | % | M/e | % | M/e | % |
|---|---|---|---|---|---|
| 28 | 5.0 | 91 | 1.1 | 162 | 4.9 |
| 31 | 2.4 | 92 | 5.3 | 163 | 0.7 |
| 32 | 0.7 | 95 | 7.9 | 171 | 1.0 |
| 33 | 0.8 | 97 | 0.7 | 172 | 2.0 |
| 39 | 0.4 | 102 | 1.5 | 173 | 2.9 |
| 40 | 0.2 | 103 | 2.2 | 174 | 63.9 |
| 41 | 1.1 | 104 | 2.7 | 175 | 7.6 |
| 42 | 6.3 | 105 | 6.9 | 176 | 1.5 |
| 43 | 7.4 | 106 | 1.5 | 177 | 1.7 |
| 44 | 1.5 | 109 | 7.9 | 178 | 100.0 |
| 51 | 0.8 | 111 | 0.7 | 179 | 21.4 |
| 55 | 1.5 | 115 | 0.9 | 188 | 1.9 |
| 56 | 0.8 | 116 | 0.9 | 190 | 0.9 |
| 57 | 2.2 | 117 | 2.0 | 204 | 1.1 |
| 58 | 0.4 | 118 | 1.6 | 205 | 0.9 |
| 62 | 0.3 | 119 | 1.6 | 220 | 63.0 P |
| 63 | 0.6 | 120 | 4.6 | 221 | 13.1 |
| 64 | 0.4 | 121 | 7.9 | | |
| 65 | 0.6 | 130 | 4.0 | | |
| 68 | 0.5 | 131 | 2.7 | | |
| 69 | 1.2 | 132 | 46.6 | | |
| 70 | 0.6 | 133 | 11.8 | | |
| 71 | 1.1 | 134 | 1.5 | | |
| 75 | 0.5 | 144 | 13.0 | | |
| 76 | 2.4 | 145 | 3.6 | | |
| 77 | 3.7 | 146 | 1.9 | | |
| 78 | 1.1 | 147 | 2.2 | | |
| 79 | 0.4 | 148 | 29.8 | | |
| 80 | 0.9 | 149 | 3.9 | | |
| 85 | 0.7 | 159 | 1.1 | | |
| 89 | 0.7 | 160 | 2.2 | | |
| 90 | 0.9 | 161 | 4.8 | | |

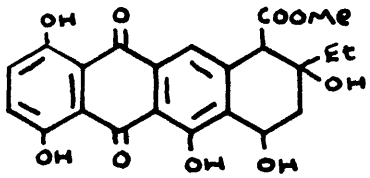
# CHAPTER III.

## RHODOMYCINONES AND PYRROMYCINONES.

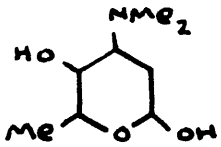
### Introduction.

The mould metabolite actinomycete A 220 produces a mixture of antibiotics, rutilantins A, B and C, which yield a red crystalline aglycone, rutilantinone, and nitrogen containing carbohydrates on mild acid hydrolysis. Ollis [91], using a combination of ultra-violet and infra-red spectroscopy with chemical evidence, suggested that rutilantinone had the structure (LXXI). Simultaneously, Prelog [92] and Brockman [93] [94] were conducting researches on a number of substances obviously related to rutilantinone. These authors showed that a particular strain of Streptomyces produced four metabolites, $\epsilon$-pyrromycinone, $C_{22}H_{20}O_9$, $\xi$-pyrromycinone, $C_{22}H_{20}O_8$, $\eta$-pyrromycinone, $C_{22}H_{16}O_7$ and pyrromycin, $C_{30}H_{35}NO_{11}$. Pyrromycin was shown to be composed of $\epsilon$-pyrromycinone and a nitrogenous sugar, rhodosamine, with possible structure (LXXII).

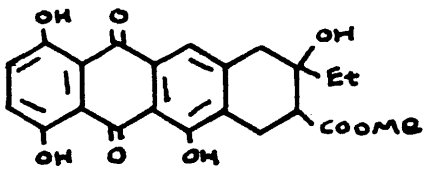
Prelog [92] and Brockman [93] conducted independent investigations on the structure of $\epsilon$-pyrromycinone and concluded that it had the structure (LXXIII). However, after collaboration with Ollis had shown that $\epsilon$-pyrromycinone was



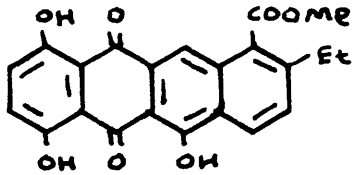
(LXXI)



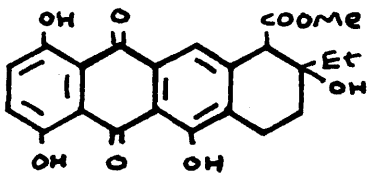
(LXXII)



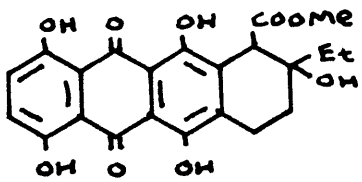
(LXXIII)



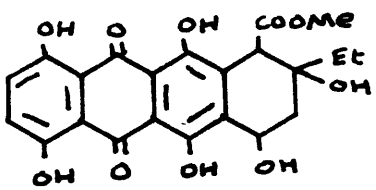
(LXXIV)



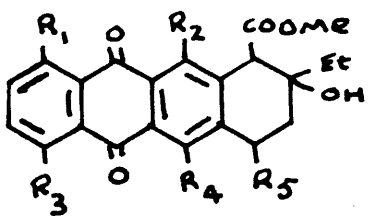
(LXXV)



(LXXVI)



(LXXVII)



| | $R_1$ | $R_2$ | $R_3$ | $R_4$ | $R_5$ |
|---|---|---|---|---|---|
| ζ-Py. | OH | H | OH | OH | H |
| ζ-Rh. | H | OH | OH | OH | H |
| ε-Rh. | H | OH | OH | OH | OH |
| ζ-iso-Rh. | OH | OH | OH | OH | H |
| ε-iso-Rh. | OH | OH | OH | OH | OH |

(LXXVIII)

identical with rutilantinone, this structure was later modified to (LXXI). $\eta$ -Pyrromycinone was found identical to bisanhydro-rutilantinone and was assigned the structure (LXXIV). A structure (LXXV) was also proposed for $\zeta$ -pyrromycinone.

For some years, Brockman and his colleagues [95]-[102] have shown interest in the mould products from Streptomyces purpurascens which include $\beta$ -rhodomycinone, $\gamma$ -rhodomycinone, $\delta$ -rhodomycinone, $\epsilon$ -rhodomycinone, $\zeta$ -isorhodomycinone, $\epsilon$ -isorhodomycinone and the rhodomycins (nitrogenous glycosides). These workers proposed structures (LXXVI) for $\zeta$ -isorhodomycinone [101] and (LXXVII) for $\epsilon$ -isorhodomycinone [101].

A considerable amount of attention has been devoted to the other mould products of Streptomyces purpurascens, particularly $\beta$ -rhodomycinone. However, although tentative structures have been proposed for $\beta$ -rhodomycinone [100][103], it has not been possible to make complete structural proposals for $\beta$ -, $\gamma$ - and $\delta$ - rhodomycinones. From the ultra-violet spectra, all that can be said with certainty is that these compounds are derivatives of 1:4:5:-trihydroxyanthraquinone.

Some doubt has arisen concerning the molecular weight of $\beta$ -rhodomycinone which will be considered in the appropriate section in this chapter.

The structural relationships of the series of compounds are shown in diagram (LXXVIII).

## DISCUSSION.

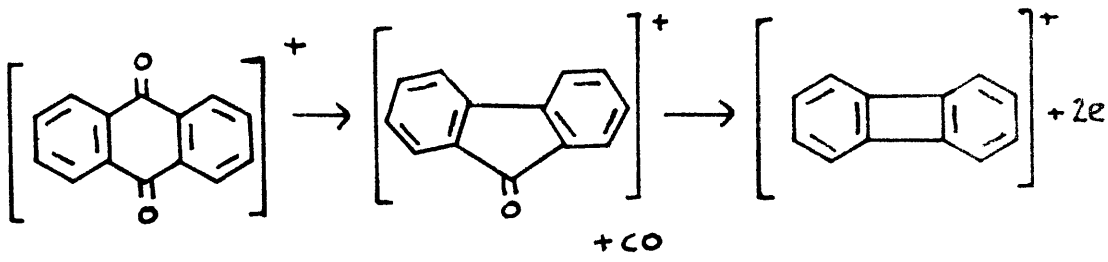
### (a) The mass spectra of hydroxyanthraquinones.

Beynon and Williams [86] have studied the mass spectra of hydroxyanthraquinones and anthraquinone itself in detail and have shown that anthraquinone gives a simple spectrum corresponding to the loss of CO , $C_2O_2$ , $C_2O_2H$ and $C_2O_2H_2$. The fragmentation is considered to be of the type (LXXIX).

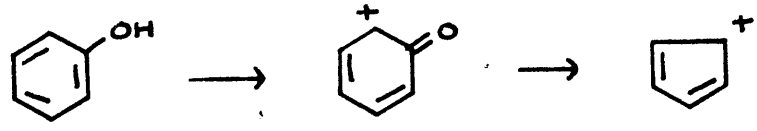
The mass spectra of some phenols have also been recorded [89] and the parent ion of phenol is thought to behave as (LXXX) [104]. Tracer experiments by Momigny [89] using deuterated phenol have confirmed this result and the author has shown that migration of deuterium atoms into the ring under electron impact is possible.

The combination of these systems into the hydroxyanthraquinones has led Beynon [86] to comment on their behaviour in the mass spectrometer.

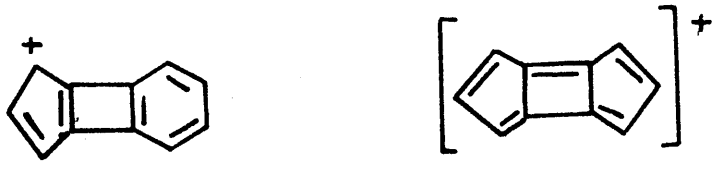
Monohydroxyanthraquinones readily lose one or more molecules of CO and show metastable peaks at M/e 171.6 and M/e 144.0 corresponding to this facile loss. As expected



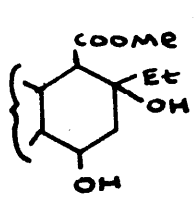

(LXXIX)



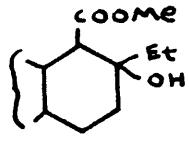

(LXXX)



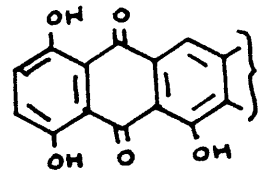

(LXXXI) (LXXXII)



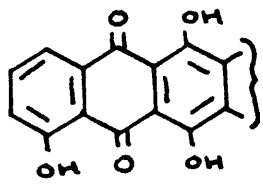

ε-



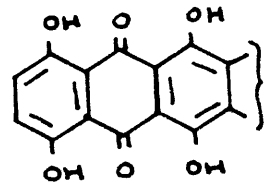

ζ-




Py.




Rh.




iso-Rh.

(LXXXIII)

from earlier work on phenols, peaks also occur at P - OH. However, it is possible to distinguish 2-hydroxyanthraquinones from 1-hydroxyanthraquinones because the probability of loss of -OH is much greater in the 2-hydroxyl compound since, in the 1-hydroxyl compound, the -OH is intramolecularly hydrogen bonded to the quinone system. Beynon (86) postulates that the peak corresponding to M/e=139 in the spectra of the monohydroxyanthraquinones results from the loss of $C_3O_3H$ which can give rise to the ion (LXXXI). The exceptional stability of this ion is shown by the presence of a peak at M/e=69.5 (3.8%) caused by removal of an electron without further fragmentation.

The mass spectra of the dihydroxyanthraquinones show that where a hydroxyl group is substituted on each ring, a large P - OH peak is produced whereas a smaller peak results when both hydroxyls are on the same ring. The loss of an -OH group, as in the mono-hydroxy compound, appears to be related to internal hydrogen bonding. This is reflected in the abundance of P - OH peaks which is found to be greatest for the 2:6-isomer in which there is a minimum of intramolecular bonding. The dihydroxyl compounds all show an ion corresponding to the loss of $C_4O_4$ and Beynon (86) has suggested that the structure of the associated ion is (LXXXII).

It is found that loss of substituted OH and CO

groups in 1:4:5:8-tetrahydroxyanthraquinone is an improbable process (P -CO,2.4%, P -$C_2O_2$,1.1%) and the spectrum is rather weak in its fragmentation pattern below the molecular ion which is the base peak. In fact, the tetra-substituted hydroxyls adjacent to the carbonyl groups of a quinonoid system seem to have a stabilizing effect on the fragmentation pattern. In general, the mass spectrometer cannot detect the orientation in the anthraquinone system.

(b) General comments and correlations.

The nomenclature of these compounds is based on two structural factors - the polyhydroxyanthraquinone system and the substitution in the unsaturated ring. The Greek prefix is related to this substitution ( $\epsilon$- and $\zeta$- ) and the iso- or normal rhodomycinone nomenclature to the substitution in the anthraquinone structure. The nomenclature system is shown in diagram (LXXXIII).

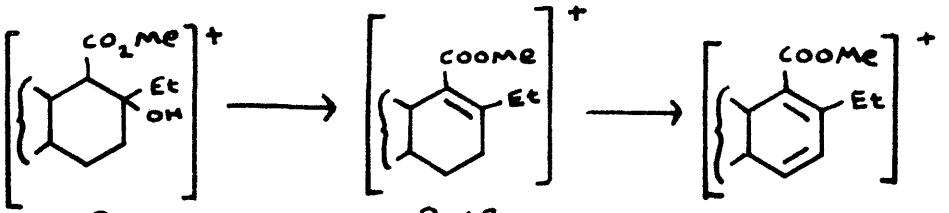
In general, the parent molecular ion is prominent although is never the base peak. The spectra fall into two parts - the higher, and more useful, diagnostic portion corres-:ponding to loss of substituted groupings and fragmentation of the non-aromatic ring, and the lower mass region corresponding to fragmentation of the anthraquinone system. As Beynon has shown, the hydroxyanthraquinone structure, especially with

1:4:5:8- substitution, is stable in the mass spectrometer and fragmentation peaks are of low abundance for such a system. Fortunately, ultra-violet spectra of these compounds [105] can easily pinpoint the position of the hydroxyls in the anthraquinone system.

As expected, the $\epsilon$- and $\zeta$- series have many peaks in common. All these compounds tend to lose a molecule of water from the unsaturated ring to give moderately abundant P - 18 ions. However, in the spectrum of $\zeta$ -pyrromycinone, as well as in this P - 18 ion, there also occurs a larger ion at P - 20 (55.0%). Now, it is a feature of the thermal degradation of organic vapours in a mass spectrometer [106] that successive loss of pairs of hydrogen atoms occurs accompanied by ring formation. Double bond formation then takes place in the ring. In the case of alcohols, the first step is probably the loss of a molecule of water; this results in an abundant P - 20 fragment ion. Certainly, difficulty was found in obtaining the spectrum of $\zeta$ -pyrromycinone and considerable heating was necessary to obtain a spectrum. This step is shown in (LXXXIV).

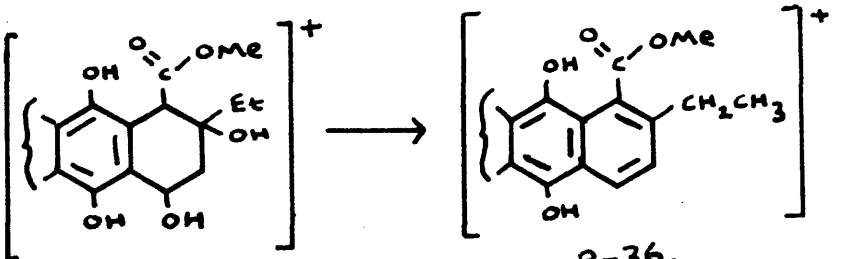
The presence of the carbomethoxyl group in the unsaturated ring gives rise to prominent ions at P - OMe, P - HOMe, P - $CO_2Me$ and P - $HCO_2Me$; this is the standard fragmentation expected from ester groupings [45] [40].

The main driving force in all these compounds



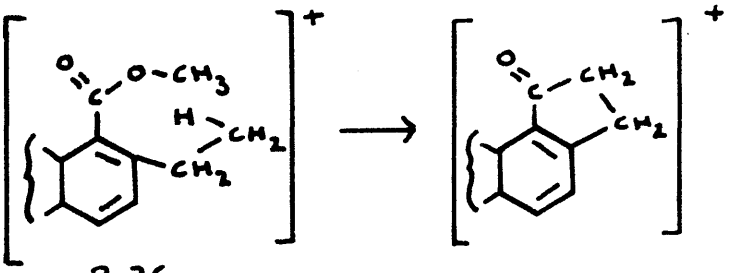

P (82·5%) P-18 (43·8%). P-20 (55%).

(LXXXIV).



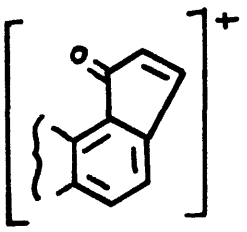

P P-36.

(LXXXV).




P-36. P-68.

(LXXXVI)




(LXXXVII)

appears to be the aromatization of the unsaturated ring and most ions of high mass can be explained as resulting from the loss of substituents from this ring without ring rupture. Thus the following ions are well pronounced.

P - 89), P - 88) — P - ($HCO_2Me$ + Et)

P - 76), P - 77), P - 78) — P - ($HCO_2Me$ + $H_2O$) or P - ($CO_2Me$ + $H_2O$) etc.

P - 107), P - 106), P - 105) — P - ($HCO_2Me$ + $H_2O$ + Et)

The main difference arises from the fact that the $\epsilon$ -series contains two hydroxyls in the unsaturated ring and loss of two molecules of water from this will produce aromaticity in it. Thus, the $\epsilon$ -series is characterized by an abundant P - 36 ion. The same ion is not evident in the $\varsigma$ -series. Also, the most abundant ions in the two $\epsilon$ -rhodomycinones studied were at P - 68 (the base peaks) which are absent in the $\varsigma$ -series. Since this ion is so abundant, it must arise from the inherent structure of the unsaturated ring in the $\epsilon$ -rhodomycinones. It is postulated that the P -68 ion is

actually P - ($2H_2O$ + HOMe). The loss of two molecules of water means that the unsaturated ring is now aromatized and that we are now dealing with an aromatic ester with an alkyl side chain in the adjacent position (LXXXV). In particular, interesting rearrangement ions have been noted in certain aromatic esters, especially in the esters of phenyl fatty acids.[46] The rearrangement involves loss of the OMe or HOMe from the ester grouping with subsequent ring formation. This may be extended to the present problem and the rearrangement can be considered as (LXXXVI).

Although the mechanism is plausible, a much more stable ion would be formed, for example, by resonance stabilization (LXXXVII). There is in fact no abundant ion corresponding to (LXXXVII).

(c) Ketone derived from ζ-pyrromycinone.

When ζ-pyrromycinone is heated, an isomeric keto-ester and an anhydro compound are formed[107]. The keto-ester is transformed back to ζ-pyrromycinone by heating with ethylamine-pyridine mixture. The reaction is related to one of the steps envisaged in the biosynthesis[108] [109] of the pyrromycinones and the keto-ester product[110] is believed to have a structure in which the unsaturated terminal ring in the pyrromycinones is no longer present.

By mass spectrometry, the molecular weight of the compound was found to be 412 which demonstrates that it is isomeric with ζ-pyrromycinone. Abundant ions occurred at the following M/e ratios.

| | | |
|---|---|---|
| P 100% (M/e=412) | P - 30 3.7%(M/e=382) | P - 57 28.4%(M/e=355) |
| P - 17 5.1%(M/e=395) | P - 31 11.3%(M/e=381) | P - 77 10.7%(M/e=335) |
| P - 18 13.2%(M/e=394) | P - 55 22.6%(M/e=357) | P - 88 16.4 (M/e=324) |
| P - 29 6.3%(M/e=383) | P - 56 74.1%(M/e=356) | P - 89 26.5 (M/e=323) |

Although, chemically, the sample is known to be an ester, there is no abundant P - 59 (or 60) ion which would indicate this. However, there is an ion at P - 31 which means either that an OMe group is present in an ester grouping, although not directly linked to a ring system, or that a hydroxymethyl group ($-CH_2OH$) occurs in the structure. There is no chemical evidence for the presence of the hydroxymethyl component. An abundant P - 59 (or 60) ion would result, as in the other compounds of this series, if the -COOMe group was attached directly to a ring system.

The large P - 29 ion, which does not appear in the spectra of the other rhodomycinones or pyrromycinones to any great extent (even although there are potential sources of such ions from both the phenolic hydroxyls and the quinone carbonyls) demonstrates that there must be a free carbonyl

group. Linked to this fact are the abundant P - 56,57 ions which indicate the presence of a $-COCH_2CH_3$ component since keto groups may rupture $\alpha$- to the carbonyl.

The abundant P -88,89 ions may be due to the combined loss of HOMe and $-COCH_2CH_3$ (or -OMe and $HCO.CH_2CH_3$) which have been previously described. Assuming the position of the -COOMe group as unaltered, from biosynthetic arguments, the structure (LXXXVIII) can be postulated for the keto ester. The prominent P -88,89 ions can then be assigned tentatively to the rearrangement (LXXXIX).

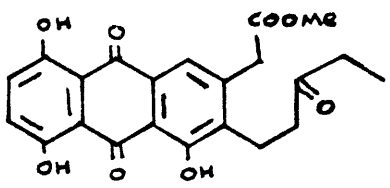
It may be observed that correlation of the overall fragmentation pattern of this compound with those of the tetra-cyclic system already described demonstrates the possibility of the unsaturated ring being no longer present.

(d) The isomer at $C_9$ and $C_{10}$ of $\zeta$-pyrromycinone.

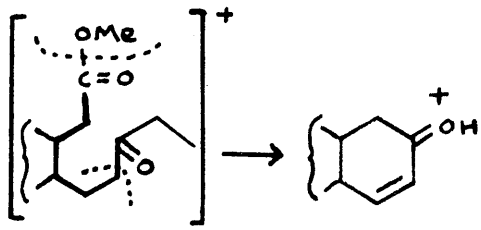
A detailed discussion of $\zeta$-pyrromycinone and its isomer at $C_9$ and $C_{10}$ will be given in Chapter IV. It can be mentioned that the two mass spectra are very similar.

(e) The structures of $\beta$-, $\gamma$-, and $\delta$-rhodomycinones.

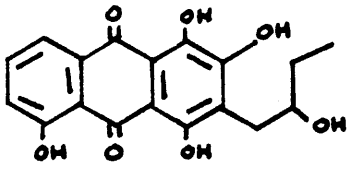
Other rhodomycinones have been reported from Streptomyces purpurascens cultures and for convenience individ-



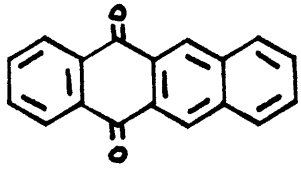

(LXXXVIII).



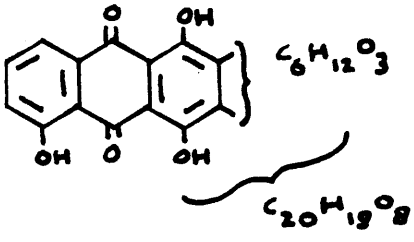

(LXXXIX).



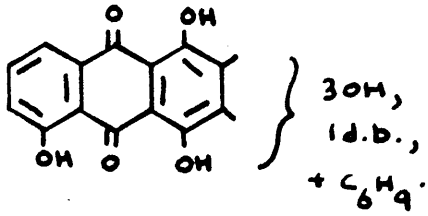

(XC).



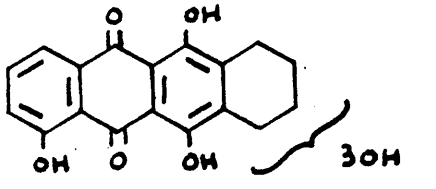

(XCI)



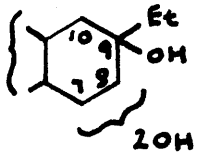

(XCII)



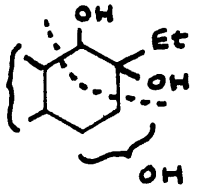

(XCIII)



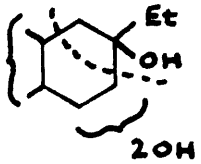

(XCIV)




(XCV)




(XCVI)




(XCVII)

:ual members are distinguished by Greek letters. These are arranged in alphabetical order corresponding to the order of their $R_F$ value in chromatographic separation [99]. Thus $\alpha$-rhodomycinone is the rhodomycinone with the smallest $R_F$ value. However, the $R_F$ values of the two series (normal and iso) run parallel and it is not possible to separate the corr-:esponding rhodomycinones and iso-rhodomycinones by paper chromatography.

Among the products obtained from chromatograms are $\beta$- , $\gamma$- , and $\delta$-rhodomycinones and a large amount of information has been collected about these compounds, mostly by Brockman and his school [95] - [102]. However, all that can be said with certainty at the present time is that these three rhodomycinones are derivatives of 1:4:5-trihydroxyanthraquinone from their ultra-violet absorption spectra [99].

(1) $\beta$-Rhodomycinone.

A structure of $\beta$-rhodomycinone has been proposed by Brockman and Franck [99] as (XC). This compound has molecular formula $C_{18}H_{16}O_7$ corresponding to a calculated molecular weight of 344 and calculated analysis of C 62.79%, H 4.68%, O 32.53%. However, some confusion has arisen about the molecular weight of $\beta$-rhodomycinone. A Rast molecular

weight determination in phenol by Brockman [99] gave a value of 320. This value did not appear to correspond closely to the analytical figures and the three reasonable molecular formulae which appeared to fit approximately to molecular weight 320 were $C_{18}H_{16}O_7$, $C_{16}H_{14}O_6$ and $C_{20}H_{20}O_8$.

After consideration of all the evidence, Brockman [99] decided to postulate a structure (XC) with the formula $C_{18}H_{16}O_7$. The U.V. spectrumobtained by this author showed that the four nuclear positions were chelated. He also obtained a penta-acetate and concluded that there were five hydroxy groups present, four of which were involved in substitution in the aromatic rings of the anthraquinone system. Evidence for the side-chain was obtained by Kuhn-Roth oxidation which produced only volatile propionic acid.

Zinc dust distillations were performed to confirm this structure. Although Brockman admitted that naphthacene and 9:10-dihydronaphthacene were formed and although it was well known that such compounds were produced from (XCI) and its hydroxy derivatives, neither the analysis figures nor the molecular weight would fit a tetracyclic system. Moreover, Kuhn-Roth oxidation seemed to indicate an alkyl side chain.

Some years later, Brockman and Boldt [100] reconsidered the whole question of β-rhodomycinone and discovered by reaction with hydriodic acid that the proposed

formula lacked some carbon atoms. Treatment of β-rhodomycinone with hydriodic acid yielded a compound which, on oxidation and analysis of the product, gave β-rhodomycinone as $C_{20}H_{16-18}O_8$ or $C_{23}H_{20-22}O_9$. Thus until a mass spectrometric study of β-rhodomycinone could be undertaken, some doubt existed not only about the final structure but also concerning such fundamental facts as molecular weight and molecular formula.

The mass spectrum of β-rhodomycinone showed an accurate molecular weight of 386 and, combined with the analytical figures of Brockman, this gave the true formula of β-rhodomycinone as $C_{20}H_{18}O_8$. The mass spectrum also showed the following abundant ions.

| | | | |
|---|---|---|---|
| P | 3.8% | P - 53 | 8.4% |
| P - 16 | 8.3% | P - 66 | 10.0% |
| P - 17 | 7.5% | P - 67 | 21.6% |
| P - 18 | 22.1% | P - 71 | 11.2% |
| P - 34 | 12.1% | P - 72 | 34.1% |
| P - 35 | 25.8% | P - 73 | 15.0% |
| P - 36 | 70.1% | P - 74 | 32.5% |
| P - 50 | 16.7% | P - 75 | 33.4% |
| P - 51 | 59.9% | P - 90 | 35.5% |
| P - 52 | 100.0% | P -103 | 12.0% |

The mass spectrum of β-rhodomycinone may be used to show that there can be no -COOMe group in the molecule since there are no abundant P - 59, P - 60 or P - 31 ions.

Using Brockman's ultra-violet absorption data, a partial structure (XCII) can now be written assuming the accuracy of the molecular weight determined by mass spectrometry.

Since there is an abundant ion at P - 36, it may be noted that the $C_6H_{12}O_3$ fragment, in diagram (XCII), must contain at least two hydroxyls. From the general pattern of the mass spectrum, $\beta$ -rhodomycinone is closely related to the other rhodomycinones. The formula $C_{20}H_{18}O_8$ is satisfied by twelve double bond equivalents and eleven of these occur in the substituted anthraquinone system. Although a consideration of structure (XC) along with Brockman's chemical evidence seems to indicate that the remaining double bond equivalent can only be accommodated as an ethylenic double bond in an alkyl side chain, there is no evidence for such an isolated double bond either chemically or from the mass spectrum of $\beta$ -rhodomycinone. The base peak in the spectrum occurs at P - 52 with abundant ions at P - 53 and P - 51. If it is assumed that a major con-:tribution to this ion is made by the loss of two molecules of water (P - 36), it can be proposed that there are in fact three hydroxy groups in the undetermined part of the molecule since P - 52 or P - 53 corresponds to the loss of a third hydroxyl from this portion. Another partial structure (XCIII) may now be written at this point.

The abundant P - 36 ions, which occurred in the

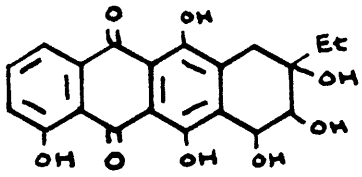
mass spectra of the $\epsilon$ -rhodomycinones, suggests the possibility of an unsaturated ring which becomes aromatized with loss of two molecules of water under electron impact. Also, the P - 52 and P - 53 ions can be considered as resulting from loss of a further -OH or -O- from an aromatic ring. A tentative structure with an unsaturated ring may now be proposed (XCIV). The presence of an ethyl group in the other rhodomycinones is not easily correlated to the mass spectrum of these compounds as this group appears to fragment after the loss of either the ring hydroxyls or the carbomethoxyl group.

An unsaturated ring system with substituent hydroxyls attached to an aromatic system will fragment in two ways under electron impact. Either it will become aromatic if the hydroxyl positions facilitate this or it will fragment adjacent to tertiary or quaternary centres. This can be shown to be so by correlation of the cracking patterns of the other rhodomycinones where the prominent peaks correspond both to aromatization of the unsaturated ring and fragmentation of the remaining substituent groups. $\beta$ -rhodomycinone shows both types of fragmentation. The P - 51, P - 52, P - 53 and P - 36 ions correspond to aromatization and loss of a further -OH group, while those at P - 72, P - 73 etc., P - 90 and P - 103 correspond to fragmentation of the unsaturated ring system.

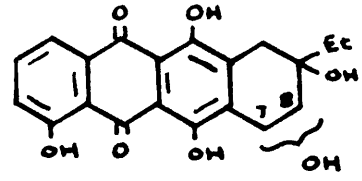
Assuming that hydroxyls substituted on the same carbon are unlikely and that the 9-position of the rhodomycinones remains unchanged since the spectra are similar, it may be tentatively proposed that the remaining two hydroxyls are either on the 7- or 8- positions as shown in diagram (XCV). Now if fragmentation of the ring occurred adjacent to the quat-:ernary centre (9-), an ion should be observed either at (XCVI) P - 88 or (XCVII) P - 71, P - 72.

The fact that ions (XCVII) are abundant suggests that position 10- is unsubstituted and that the two remaining hydroxyls are substituted at positions 7 and 8. After frag-:mentation (XCVII) has occurred, there is the further possibility of loss of an -OH or $H_2O$ group from the acyclic system to give an ion at P - 90. This ion is moderately abundant (35.5%). Also there is the possibility of further fragmentation of the remaining $-CH(OH).CH_2OH$ group to produce an ion at P - 103 (P - (72 + 31)) which is moderately abundant (12.0%).

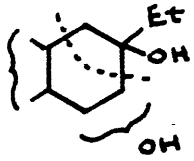
A tentative structure (XCVIII) can now be pro-:posed for β -rhodomycinone which assumes (i) that the ultra-violet absorption data indicates a 1:4:5:-trihydroxyanthraquinone system, (ii) that two hydroxyl substituents on the same carbon atom are unlikely and (iii) that correlations of mass spectra in a series of closely related compounds are valid. The structure (XCVIII) is supported by molecular weight, analysis figures, ultra-violet spectra and mass spectra correlations. Most of



(XCVIII).

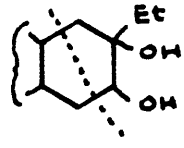


(XCIX).

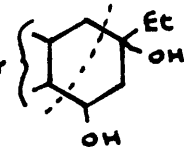


P-72.

(C).

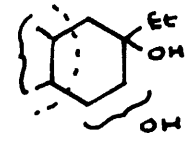


or



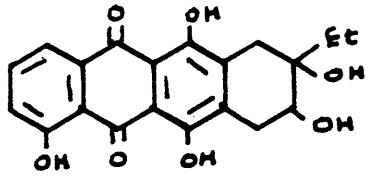
P-99, P-100.

(CI).

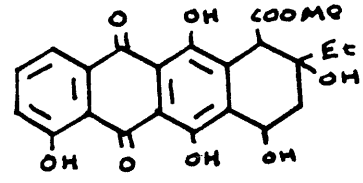


P-115.

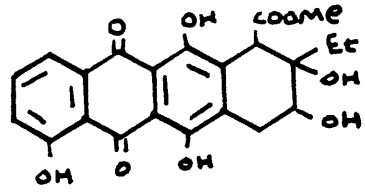
(CII).



(CIII).



(CIV).



(CV).

Brockman's earlier chemical findings, including the zinc dust distillation experiments, can be re-interpreted to fit this structure [107].

(II) γ-Rhodomycinone.

γ-Rhodomycinone is another metabolite isolated from Streptomyces purpurascens [100] and ultra-violet spectra [107] have shown it to be a derivative of 1:4:5-trihydroxyanthraquinone. Brockman [111] has noted that the structure of γ-rhodomycinone appears to be related to both β- and δ-rhodomycinones and that δ-rhodomycinone takes an intermediate position in the three structures.

The mass spectrum of γ-rhodomycinone has abundant ions at the following M/e ratios and the molecular ion occurs at M/e=370 (51.8%).

P, P-15, P-16, P-17, P-18, P-33, P-34, P-35, P-36, P-46, P-47, P-51, P-63
P-71, P-72, P-73, P-74, P-75, P-85, P-99, P-100, P-115.

Using the arguments applied to the structural diagnosis of β-rhodomycinone, γ-rhodomycinone has no $-CO_2Me$ group present and has at least two hydroxyls in the non-aromatic portion of its structure. The presence of an abundant P - 72 ion suggests that 10- position is again unsubstituted and also that the quaternary centre, found in

all rhodomycinones, is present at position 9-. Thus, a partial structure for γ-rhodomycinone can be written (XCIX), assuming that an unsaturated ring is present, by correlation with previous spectra. The placing of the second hydroxyl group in this ring must be at the 7- or 8- position. If the 7- position was correct, the mass spectrum should resemble more closely the mass spectrum of compounds in the ε-pyrromycinone series. However, the structure of β-rhodomycinone, with a hydroxyl in the 8- position, shows signs of facile ring fragmentation. The same pattern is repeated in γ-rhodomycinone and the ring fragmentation can be assigned to the abundant ions (C), (CI) and (CII).

Thus a possible structure of γ-rhodomycinone is (CIII) since the general pattern of the mass spectrum does not resemble closely that of the ε-rhodomycinone series.

(III) δ-Rhodomycinone.

The molecular weight of this compound by a mass spectrometric analysis is 428 and by a procedure similar to that used for the previous compounds, some structural features can be deducted. Firstly, there are two, and only two, hydroxyls in the part of the molecule not involving the anthraquinone system. This follows from the abundant P - 36 ion and the absence of abundant ions at P - 52 or P - 53.

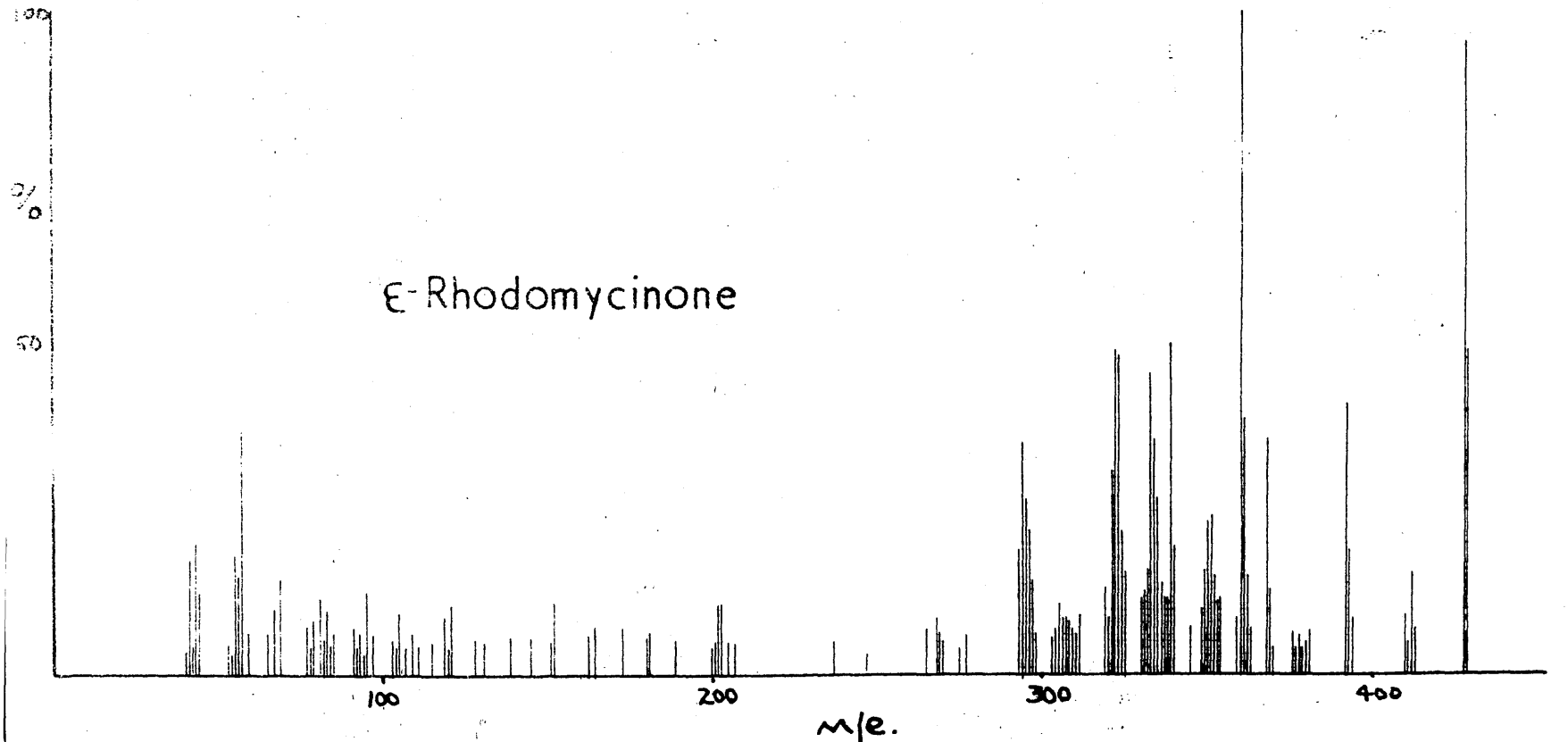
Secondly, there is a carbomethoxy group present since the P - 60 ion is abundant.

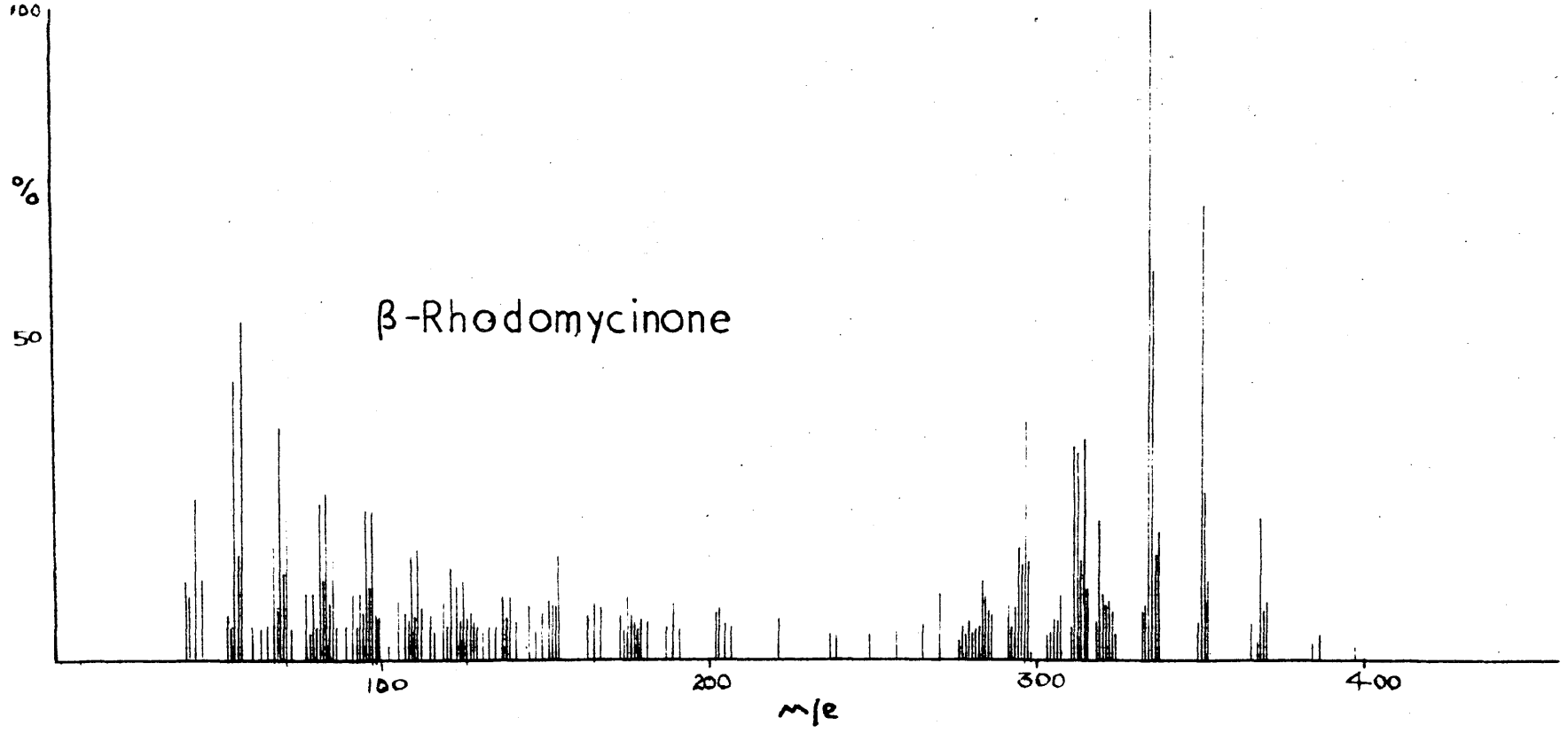
The spectrum shows abundant peaks at the following masses -

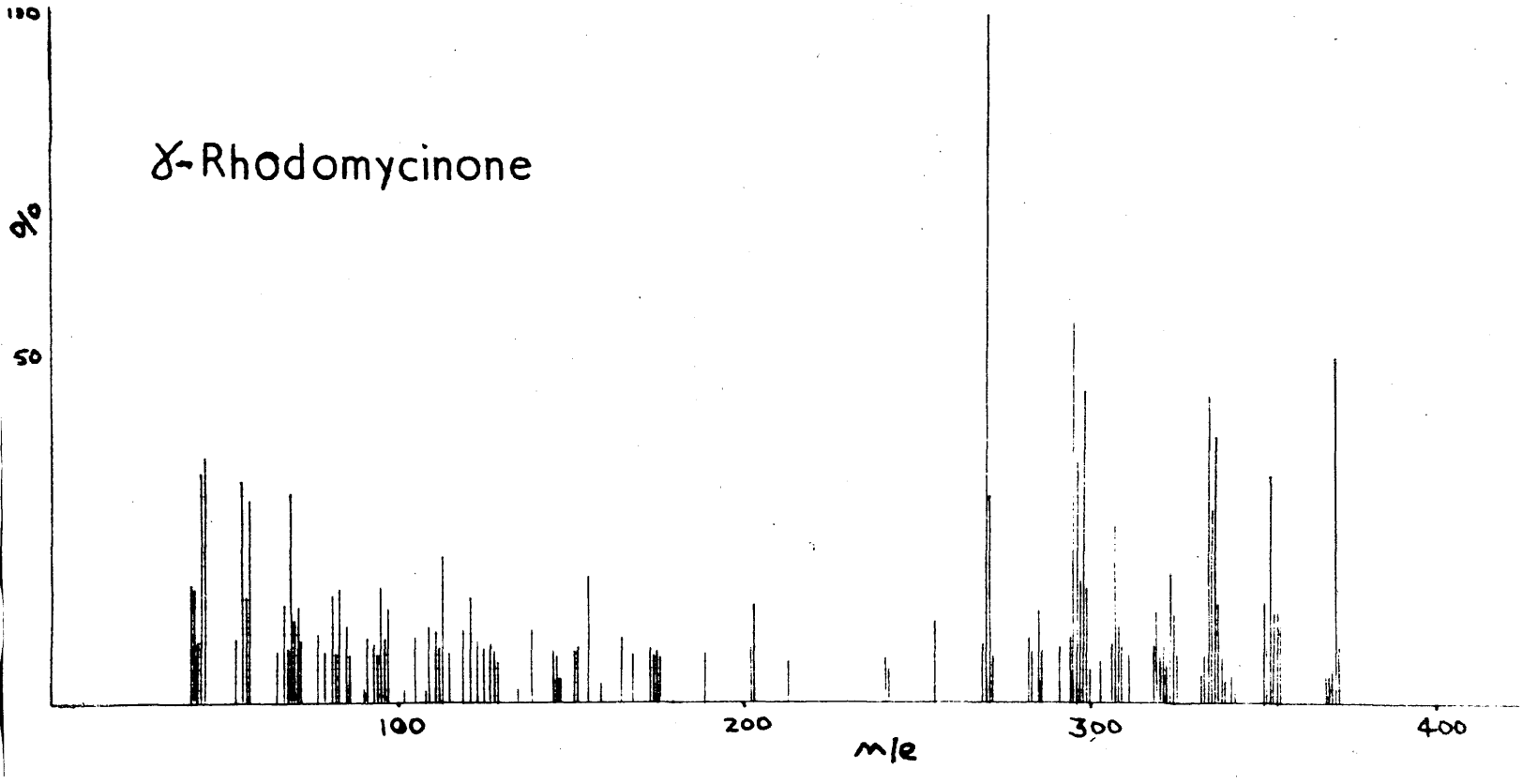
P, P-16, P-17, P-18, P-19, P-20, P-35, P-36, P-48, P-60, P-68, P-67, P-66, P-65, P-76, P-77, P-78, P-88, P-89, P-95, P-105, P-106, P-107.

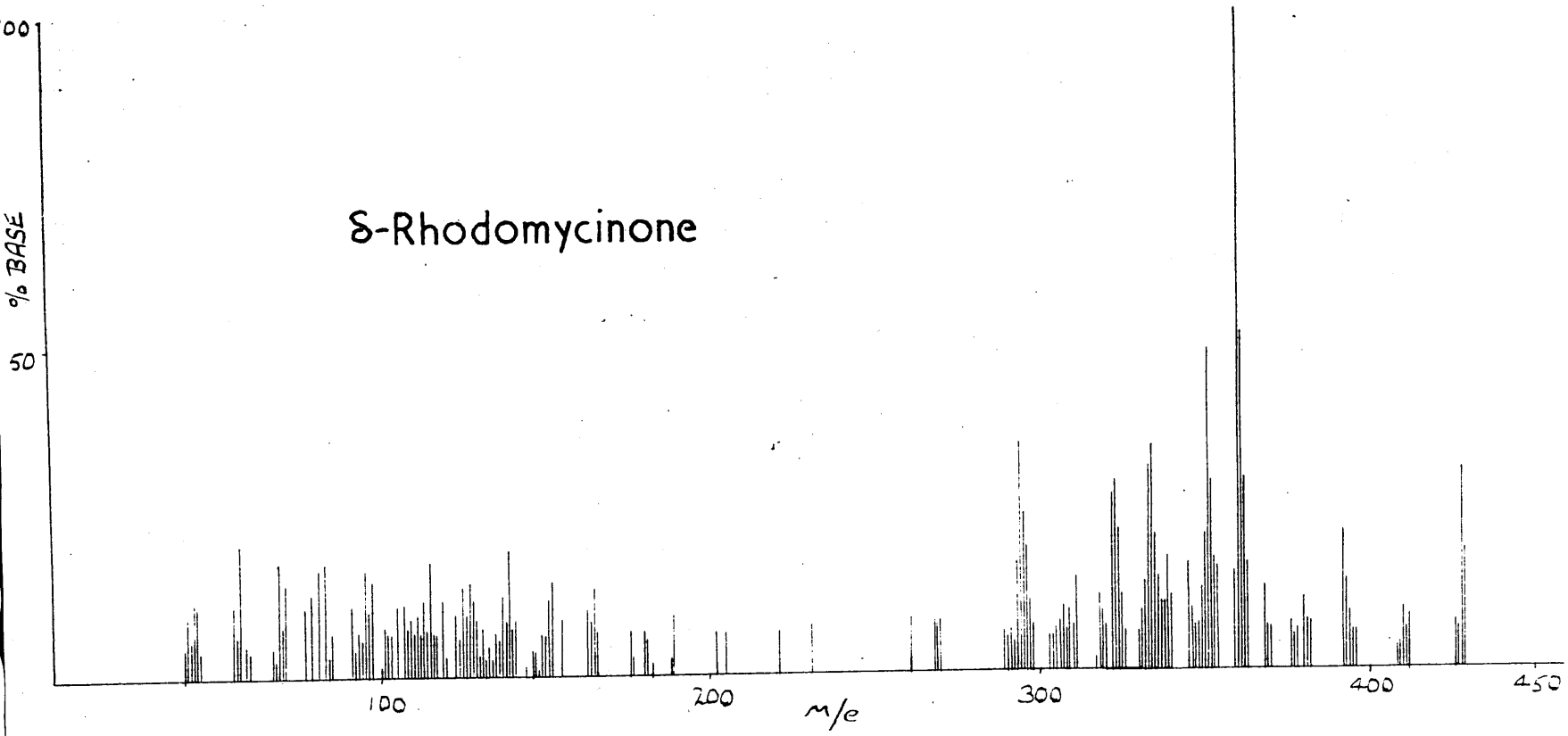
This pattern of fragmentation resembles that of other spectra in the rhodomycinone series, principally the P - 36 and P - 68 (the base peak) ions, and it can be concluded that there is a tetracyclic system present. Again the ultra-violet absorption evidence points to a 1:4:5-trihydroxyanthraquinone system in the first three rings. It can be postulated that $\delta$-rhodomycinone has either the structure (CIV) or, less likely, (CV).

Structure (CV) is unlikely since the cracking pattern does not display any prominent ring fission, but rather is related to the breakdown of $\epsilon$-rhodomycinone which has the identical structural formula (CIV). It is postulated that $\delta$-rhodomycinone has the structure (CIV) and it must be a stereoisomer of $\epsilon$-rhodomycinone. This relationship between $\delta$- and $\epsilon$-rhodomycinones has been noted by Brockman (111). The close similarity in the two mass spectra is shown in attached histograms.


100
%
50
ε-Rhodomycinone
100
200
300
400
m/e.


100
%
50
β-Rhodomycinone
100
200
300
400
m/e


γ-Rhodomycinone
100
%
50
100
200
300
400
m/e


8-Rhodomycinone
% BASE
100
50
100
200
300
400
450
m/e

(f) Conclusions and Summary.

This chapter has mainly been concerned with the usefulness of correlations of mass spectra of a known series of compounds and application of these findings to some unknown compounds of similar structure. Structural formulae have been assigned to $\beta$-, $\gamma$- and $\delta$-rhodomycinone, the elucidation of which has defied the classical chemist's approach. This has been due to the inaccurate molecular weights assumed. Not only does the mass spectrometer clarify immediately the molecular formula but it is of undoubted use in assigning the main structural features.

(g) Experimental.

Pure samples of the compounds studied in the mass spectrometer were obtained from Dr. W. D. Ollis (Bristol University). The samples were purified and prepared by Dr. H. Brockman (Göttingen).

The samples are involatile and in most cases, spectra were obtained using a long glass probe with very slight external heating of the ion chamber.

$\epsilon$-iso-Rhodomycinone gave a very weak spectrum even under drastic conditions and the spectrum obtained possibly is due in part to thermal decomposition.

Tables of the mass spectra obtained are included. Owing to the involatility of the samples, and therefore to the low abundance of the ions, peak abundances were only measured to 0.1% of the base peak.

(LXXXVIII) Ketone derived from ς -pyrromycinone.

2KV, 50eV. M.Wt. 412.

| M/e | % | M/e | % | M/e | % |
|---|---|---|---|---|---|
| 40 | 1.3 | 235 | 3.7 | 335 | 10.7 |
| 41 | 13.8 | 239 | 3.7 | 339 | 3.7 |
| 42 | 3.9 | 249 | 4.4 | 352 | 3.7 |
| 44 | 8.8 | 253 | 5.0 | 353 | 4.4 |
| 51 | 6.3 | 255 | 5.0 | 354 | 6.3 |
| 53 | 3.7 | 265 | 2.5 | 355 | 28.4 |
| 54 | 2.5 | 267 | 5.7 | 356 | 74.1 |
| 55 | 8.2 | 277 | 4.4 | 357 | 22.6 |
| 56 | 5.0 | 278 | 3.9 | 358 | 6.3 |
| 57 | 17.6 | 279 | 4.4 | 365 | 6.9 |
| 59 | 3.7 | 280 | 3.9 | 376 | 3.7 |
| 67 | 8.8 | 281 | 14.5 | 380 | 7.5 |
| 69 | 13.8 | 282 | 8.2 | 381 | 11.3 |
| 71 | 9.4 | 283 | 9.5 | 382 | 3.7 |
| 81 | 9.5 | 284 | 4.4 | 383 | 6.3 |
| 83 | 8.8 | 293 | 3.9 | 393 | 2.5 |
| 85 | 5.7 | 294 | 6.3 | 394 | 13.2 |
| 91 | 5.0 | 295 | 42.7 | 395 | 5.1 |
| 95 | 9.4 | 296 | 22.5 | 412 | 100.0 P |
| 96 | 5.7 | 297 | 10.1 | 413 | 15.5 |
| 97 | 7.5 | 298 | 4.4 | | |
| 105 | 5.7 | 306 | 3.9 | | |
| 109 | 6.3 | 307 | 4.4 | | |
| 110 | 3.7 | 308 | 3.9 | | |
| 119 | 5.0 | 309 | 12.6 | | |
| 123 | 3.7 | 310 | 5.0 | | |
| 149 | 3.7 | 321 | 8.2 | | |
| 165 | 4.4 | 322 | 5.0 | | |
| 197 | 3.7 | 323 | 26.5 | | |
| 207 | 5.1 | 324 | 16.4 | | |
| 221 | 3.7 | 325 | 5.7 | | |
| 225 | 3.2 | 334 | 5.1 | | |

(CIV) ∈ -rhodomycinone. M.Wt. 428.

2KV, 50eV, slight heat.

| M/e | % | M/e | % | M/e | % | M/e | % | M/e | % |
|---|---|---|---|---|---|---|---|---|---|
| 40 | 3.3 | 103 | 5.3 | 237 | 4.9 | 325 | 15.7 | 377 | 4.0 |
| 41 | 17.7 | 104 | 4.0 | 247 | 3.3 | 330 | 12.1 | 378 | 6.0 |
| 42 | 4.9 | 105 | 9.3 | 265 | 7.3 | 331 | 12.9 | 379 | 3.7 |
| 43 | 20.0 | 107 | 4.0 | 268 | 8.5 | 332 | 16.5 | 380 | 4.9 |
| 44 | 12.1 | 109 | 6.5 | 269 | 5.7 | 333 | 46.0 | 381 | 7.3 |
| 53 | 4.1 | 111 | 4.5 | 270 | 4.9 | 334 | 35.5 | 392 | 41.0 |
| 54 | 2.8 | 115 | 4.9 | 275 | 4.0 | 335 | 27.4 | 393 | 17.8 |
| 55 | 18.2 | 119 | 8.9 | 277 | 6.5 | 336 | 13.7 | 394 | 8.1 |
| 56 | 14.5 | 120 | 3.6 | 293 | 19.0 | 337 | 12.2 | 410 | 9.3 |
| 57 | 37.0 | 121 | 10.5 | 294 | 35.5 | 338 | 12.2 | 411 | 4.9 |
| 59 | 6.0 | 128 | 5.3 | 295 | 27.0 | 339 | 49.8 | 412 | 14.9 |
| 65 | 5.7 | 131 | 4.9 | 296 | 22.1 | 340 | 18.6 | 413 | 7.3 |
| 67 | 9.7 | 139 | 5.7 | 297 | 14.5 | 345 | 6.9 | 428 | 95.5P |
| 69 | 14.5 | 145 | 5.3 | 298 | 6.1 | 348 | 9.7 | 429 | 49.2 |
| 69.5 | 4.8 | 147.5 | 2.4 | 303 | 5.7 | 349 | 15.7 | | |
| 77 | 7.3 | 151 | 4.8 | 304 | 6.8 | 350 | 23.0 | | |
| 78 | 4.0 | 152 | 10.9 | 305 | 10.9 | 351 | 24.1 | | |
| 79 | 6.8 | 163 | 5.7 | 306 | 8.9 | 352 | 14.9 | | |
| 81 | 11.7 | 165 | 7.7 | 307 | 8.9 | 353 | 11.3 | | |
| 82 | 5.3 | 173 | 7.3 | 308 | 8.5 | 354 | 12.2 | | |
| 83 | 9.7 | 180 | 5.3 | 309 | 7.3 | 359 | 8.5 | | |
| 84 | 4.5 | 180.5 | 4.0 | 310 | 6.1 | 360 | 100.0 | | |
| 85 | 6.1 | 181 | 6.9 | 311 | 9.3 | 361 | 38.8 | | |
| 91 | 7.3 | 189 | 5.7 | 319 | 13.7 | 362 | 14.9 | | |
| 92 | 4.0 | 200 | 4.0 | 320 | 9.3 | 363 | 7.3 | | |
| 93 | 6.5 | 201 | 5.3 | 321 | 31.0 | 368 | 36.0 | | |
| 94 | 2.4 | 202 | 11.3 | 322 | 49.1 | 369 | 12.5 | | |
| 95 | 12.5 | 203 | 11.7 | 323 | 48.5 | 370 | 4.0 | | |
| 97 | 6.0 | 235 | 4.9 | 324 | 22.3 | 376 | 6.5 | | |

(LXXVII). $\epsilon$ -isorhodomycinone. M. Wt. 444.

2KV, 50eV.

(Spectrum very weak even under drastic conditions).

| M/e | % | M/e | % | M/e | % | M/e | % | M/e | % |
|---|---|---|---|---|---|---|---|---|---|
| 40 | 21.6 | 95 | 33.1 | 295 | 17.9 | 353 | 14.0 | 428 | 52.1 |
| 41 | 30.0 | 96 | 14.0 | 296 | 18.0 | 354 | 7.7 | 429 | 20.5 |
| 42 | 29.2 | 97 | 7.7 | 297 | 12.7 | 355 | 20.5 | 444 | 42.0P |
| 43 | 46.1 | 98 | 14.0 | 309 | 22.6 | 360 | 8.9 | 445 | 19.2 |
| 44 | 45.0 | 105 | 2.5 | 310 | 30.5 | 366 | 11.4 | | |
| 45 | 16.6 | 107 | 29.2 | 311 | 46.0 | 367 | 15.4 | | |
| 53 | 16.6 | 109 | 59.0 | 312 | 29.2 | 368 | 25.1 | | |
| 55 | 95.0 | 111 | 40.8 | 313 | 15.3 | 369 | 14.0 | | |
| 56 | 34.6 | 119 | 53.5 | 319 | 12.7 | 370 | 7.7 | | |
| 57 | 91.0 | 123 | 44.5 | 320 | 10.1 | 376 | 100.0 | | |
| 65 | 28.0 | 185 | 30.0 | 321 | 16.6 | 377 | 46.1 | | |
| 66 | 10.1 | 186 | 15.3 | 322 | 19.9 | 378 | 40.8 | | |
| 67 | 71.5 | 189 | 23.0 | 323 | 21.6 | 384 | 17.9 | | |
| 68 | 14.0 | 191 | 16.6 | 324 | 25.6 | 385 | 7.7 | | |
| 69 | 97.0 | 203 | 17.9 | 325 | 10.1 | 392 | 16.6 | | |
| 70 | 20.5 | 213 | 19.2 | 334 | 23.0 | 393 | 7.7 | | |
| 71 | 41.0 | 217 | 15.3 | 335 | 25.6 | 394 | 12.7 | | |
| 77 | 20.5 | 218 | 16.6 | 336 | 15.3 | 395 | 7.7 | | |
| 79 | 17.9 | 219 | 25.6 | 337 | 39.5 | 396 | 17.9 | | |
| 81 | 34.6 | 235 | 48.5 | 338 | 43.2 | 408 | 24.2 | | |
| 82 | 67.5 | 236 | 22.6 | 339 | 68.6 | 409 | 10.2 | | |
| 83 | 40.9 | 237 | 15.3 | 340 | 34.5 | 410 | 11.4 | | |
| 84 | 19.2 | 256 | 19.2 | 349 | 94.5 | 411 | 5.1 | | |
| 85 | 41.0 | 277 | 20.5 | 350 | 71.5 | 412 | 16.6 | | |
| 91 | 5.0 | 293 | 14.0 | 351 | 75.0 | 426 | 10.1 | | |
| 94 | 10.1 | 294 | 12.8 | 352 | 29.2 | 427 | 7.7 | | |

(LXXVIII) ζ -rhodomycinone. M. Wt. 412.

2KV, 50eV.

| M/e | % | M/e | % | M/e | % | M/e | % | M/e | % |
|---|---|---|---|---|---|---|---|---|---|
| 40 | 1.7 | 97 | 18.7 | 146 | 6.8 | 294 | 10.2 | 338 | 6.8 |
| 41 | 18.7 | 103 | 7.7 | 147 | 8.5 | 295 | 48.5 | 339 | 8.5 |
| 42 | 3.4 | 105 | 17.8 | 147.5 | 6.8 | 296 | 34.0 | 340 | 6.8 |
| 43 | 17.4 | 107 | 11.1 | 149 | 8.5 | 297 | 10.2 | 349 | 5.9 |
| 44 | 13.6 | 109 | 18.7 | 151 | 10.2 | 298 | 5.9 | 350 | 10.2 |
| 45 | 3.4 | 110 | 10.1 | 152 | 10.2 | 303 | 5.1 | 351 | 15.3 |
| 55 | 5.1 | 111 | 13.6 | 153 | 6.8 | 304 | 5.1 | 352 | 34.0 |
| 56 | 2.6 | 115 | 11.9 | 161.5 | 3.4 | 305 | 6.8 | 353 | 17.0 |
| 57 | 23.8 | 117 | 8.5 | 163 | 9.4 | 306 | 17.8 | 354 | 6.8 |
| 59 | 6.8 | 118 | 6.8 | 165 | 17.0 | 307 | 16.2 | 356 | 5.1 |
| 65 | 4.3 | 119 | 17.9 | 173 | 9.4 | 308 | 20.4 | 360 | 32.5 |
| 67 | 10.2 | 120 | 9.4 | 175 | 9.4 | 309 | 15.3 | 361 | 11.9 |
| 69 | 8.5 | 121 | 18.7 | 189 | 7.7 | 310 | 8.5 | 362 | 16.8 |
| 70 | 4.0 | 123 | 11.9 | 201 | 5.1 | 317 | 5.1 | 363 | 5.9 |
| 71 | 5.1 | 124 | 6.8 | 202 | 8.5 | 318 | 5.1 | 368 | 5.1 |
| 77 | 3.4 | 125 | 10.2 | 203 | 21.0 | 319 | 7.7 | 376 | 5.1 |
| 79 | 5.1 | 126 | 7.7 | 204 | 7.7 | 320 | 6.8 | 380 | 16.5 |
| 81 | 8.5 | 127 | 8.5 | 205 | 5.1 | 321 | 10.2 | 381 | 11.2 |
| 82 | 3.4 | 128 | 10.2 | 221 | 7.7 | 322 | 15.3 | 383 | 5.1 |
| 83 | 7.7 | 129 | 7.7 | 249 | 7.6 | 323 | 100.0 | 392 | 7.7 |
| 85 | 3.4 | 131 | 9.4 | 277 | 6.8 | 324 | 54.5 | 394 | 11.1 |
| 89 | 6.8 | 133 | 10.2 | 278 | 7.7 | 325 | 16.2 | 395 | 5.1 |
| 90 | 3.4 | 135 | 7.7 | 279 | 6.8 | 326 | 5.1 | 410 | 5.1 |
| 91 | 14.5 | 137 | 9.4 | 280 | 9.4 | 332 | 6.8 | 412 | 63.8P |
| 92 | 6.8 | 138 | 6.8 | 281 | 9.0 | 333 | 13.6 | 413 | 24.6 |
| 93 | 11.1 | 139 | 11.1 | 282 | 9.4 | 334 | 44.1 | 426 | 4.3 imp |
| 93.5 | 5.1 | 140 | 6.8 | 283 | 5.1 | 335 | 88.5 | 428 | 10.4 imp |
| 95 | 25.5 | 141 | 10.2 | 291 | 5.1 | 336 | 31.5 | 429 | 6.8 imp |
| 96 | 11.9 | 145 | 9.4 | 293 | 7.7 | 337 | 11.9 | | |

(LXXV) ς-pyrromycinone. M.Wt. 412.

2KV, 50eV.

| M/e | % | M/e | % | M/e | % | M/e | % | M/e | % |
|---|---|---|---|---|---|---|---|---|---|
| 41 | 11.0 | 105 | 43.9 | 145 | 13.8 | 307 | 26.3 | 378 | 12.5 |
| 43 | 15.1 | 106 | 15.0 | 147 | 13.8 | 308 | 25.0 | 379 | 7.5 |
| 44 | 12.1 | 107 | 25.0 | 147.5 | 13.5 | 309 | 20.0 | 380 | 27.5 |
| 55 | 27.5 | 108 | 17.5 | 148 | 13.8 | 319 | 13.8 | 381 | 12.5 |
| 56 | 20.1 | 109 | 47.5 | 149 | 44.0 | 320 | 10.0 | 382 | 7.5 |
| 57 | 35.2 | 110 | 23.8 | 152 | 17.5 | 321 | 15.0 | 383 | 10.0 |
| 59 | 13.5 | 111 | 35.0 | 163 | 13.7 | 322 | 11.3 | 392 | 55.1 |
| 67 | 10.1 | 112 | 17.5 | 165 | 27.5 | 323 | 82.5 | 393 | 22.5 |
| 69 | 13.4 | 113 | 13.8 | 166 | 17.5 | 324 | 41.2 | 394 | 43.8 |
| 71 | 6.4 | 115 | 27.5 | 167 | 15.0 | 325 | 12.5 | 395 | 12.5 |
| 77 | 13.1 | 117 | 15.0 | 179 | 13.5 | 332 | 12.5 | 396 | 7.5 |
| 79 | 7.5 | 119 | 40.0 | 180 | 12.5 | 333 | 17.5 | 412 | 82.5 P |
| 81 | 7.5 | 121 | 20.0 | 221 | 12.5 | 334 | 42.5 | 413 | 32.5 |
| 82 | 6.5 | 122 | 12.5 | 235 | 13.7 | 335 | 100.0 | | |
| 83 | 6.5 | 123 | 32.5 | 249 | 12.5 | 336 | 38.8 | | |
| 84 | 7.5 | 124 | 17.5 | 277 | 15.0 | 337 | 15.0 | | |
| 85 | 5.2 | 125 | 23.6 | 278 | 10.0 | 338 | 8.8 | | |
| 91 | 4.6 | 126 | 15.0 | 279 | 11.3 | 351 | 10.0 | | |
| 92 | 5.5 | 127 | 17.5 | 280 | 20.0 | 355 | 13.7 | | |
| 93 | 28.7 | 128 | 22.5 | 281 | 21.2 | 356 | 40.0 | | |
| 94 | 25.0 | 129 | 22.5 | 282 | 10.0 | 357 | 13.8 | | |
| 95 | 72.5 | 131 | 20.0 | 283 | 10.0 | 360 | 10.0 | | |
| 96 | 37.5 | 133 | 25.0 | 294 | 15.0 | 361 | 13.8 | | |
| 97 | 55.0 | 135 | 20.0 | 295 | 86.5 | 362 | 17.5 | | |
| 98 | 25.0 | 137 | 25.0 | 296 | 41.2 | 363 | 10.0 | | |
| 99 | 17.5 | 138 | 15.0 | 297 | 16.3 | 365 | 12.5 | | |
| 103 | 12.5 | 139 | 20.0 | 305 | 11.2 | 376 | 5.0 | | |
| 104 | 12.5 | 141 | 20.0 | 306 | 26.3 | 377 | 12.5 | | |

(LXXVI) ζ -isorhodomycinone. M.Wt. 428.

2KV, 50eV.

| M/e | % | M/e | % | M/e | % | M/e | % | M/e | % |
|---|---|---|---|---|---|---|---|---|---|
| 41 | 24.5 | 111 | 9.4 | 201 | 3.6 | 309 | 13.8 | 355 | 6.0 |
| 43 | 18.0 | 115 | 79.5 | 202 | 7.2 | 310 | 8.4 | 356 | 7.2 |
| 44 | 13.2 | 119 | 11.3 | 203 | 25.2 | 311 | 14.4 | 359 | 2.0 |
| 55 | 21.5 | 121 | 13.9 | 204 | 6.0 | 312 | 8.4 | 360 | 10.2 |
| 56 | 4.2 | 123 | 7.8 | 205 | 3.6 | 319 | 6.0 | 361 | 6.0 |
| 57 | 36.0 | 125 | 6.0 | 219 | 5.4 | 320 | 5.4 | 362 | 16.8 |
| 67 | 10.2 | 128 | 5.4 | 221 | 5.4 | 321 | 9.6 | 363 | 6.6 |
| 69 | 18.6 | 129 | 3.6 | 249 | 6.0 | 322 | 20.5 | 364 | 2.4 |
| 70 | 4.8 | 131 | 5.4 | 250 | 2.4 | 323 | 100.0 | 368 | 9.6 |
| 71 | 10.8 | 133 | 6.0 | 267 | 3.6 | 324 | 60.1 | 369 | 6.6 |
| 77 | 4.8 | 137 | 6.6 | 268 | 3.0 | 325 | 22.1 | 376 | 5.4 |
| 79 | 4.8 | 139 | 7.2 | 277 | 3.6 | 326 | 7.2 | 377 | 2.4 |
| 81 | 1.4 | 141 | 6.0 | 278 | 3.6 | 332 | 4.8 | 378 | 6.0 |
| 82 | 3.6 | 145 | 6.6 | 279 | 6.6 | 333 | 10.8 | 379 | 4.8 |
| 83 | 8.4 | 147 | 6.0 | 280 | 8.4 | 334 | 32.5 | 380 | 16.8 |
| 85 | 2.4 | 147.5 | 5.4 | 281 | 9.6 | 335 | 84.0 | 381 | 11.4 |
| 91 | 9.6 | 149 | 6.0 | 282 | 6.6 | 336 | 32.5 | 382 | 4.8 |
| 92 | 4.2 | 150 | 4.2 | 283 | 3.6 | 337 | 13.2 | 394 | 9.6 |
| 93 | 7.3 | 151 | 7.2 | 285 | 4.8 | 338 | 7.2 | 395 | 4.2 |
| 95 | 18.6 | 152 | 6.6 | 293 | 6.6 | 339 | 24.6 | 396 | 7.8 |
| 96 | 7.8 | 163 | 6.6 | 294 | 15.6 | 340 | 15.6 | 397 | 3.6 |
| 97 | 12.6 | 165 | 12.0 | 295 | 46.2 | 347 | 3.6 | 410 | 6.0 |
| 98 | 4.2 | 166 | 5.4 | 296 | 31.2 | 348 | 4.2 | 411 | 21.6 |
| 103 | 3.6 | 168 | 4.8 | 297 | 13.2 | 349 | 6.6 | 412 | 70.5 |
| 104 | 3.6 | 173 | 7.2 | 298 | 5.4 | 350 | 15.6 | 413 | 28.1 |
| 105 | 10.8 | 175 | 7.8 | 305 | 4.8 | 351 | 44.5 | 424 | 2.4 |
| 107 | 7.2 | 176 | 5.4 | 306 | 13.8 | 352 | 21.6 | 426 | 1.8 |
| 109 | 13.2 | 189 | 6.6 | 307 | 13.2 | 353 | 8.4 | 428 | 21.2P |
| 110 | 6.0 | 191 | 5.4 | 308 | 18.0 | 354 | 8.4 | 429 | 9.6 |

β - RHODOMYCINONE. UNKNOWN. M.Wt. (found) 386.

2KV, 50eV.

| M/e | % | M/e | % | M/e | % | M/e | % | M/e | % |
|---|---|---|---|---|---|---|---|---|---|
| 40 | 12.5 | 94 | 6.6 | 139 | 9.6 | 265 | 5.4 | 319 | 21.6 |
| 41 | 10.0 | 94.5 | 3.3 | 141 | 5.4 | 270 | 10.0 | 320 | 10.0 |
| 43 | 25.0 | 95 | 23.4 | 145 | 6.7 | 276 | 2.5 | 321 | 7.9 |
| 44 | 23.3 | 96 | 11.2 | 145.5 | 2.5 | 277 | 5.0 | 322 | 8.3 |
| 45 | 11.9 | 97 | 22.9 | 147 | 5.0 | 278 | 4.6 | 323 | 7.5 |
| 53 | 6.7 | 98 | 6.7 | 149 | 7.1 | 279 | 6.3 | 324 | 4.2 |
| 54 | 5.4 | 99 | 5.8 | 151 | 9.6 | 280 | 4.2 | 332 | 7.5 |
| 55 | 42.9 | 102.5 | 1.7 | 152 | 9.2 | 281 | 4.6 | 333 | 8.4 |
| 56 | 15.8 | 105 | 8.8 | 153 | 7.9 | 282 | 5.4 | 334 | 100.0 |
| 57 | 52.2 | 107 | 6.7 | 155 | 15.8 | 283 | 12.0 | 335 | 59.9 |
| 60 | 5.6 | 108 | 6.3 | 154.5 | 3.3 | 284 | 10.4 | 336 | 16.7 |
| 63 | 4.5 | 108.5 | 2.5 | 163 | 7.5 | 285 | 7.5 | 337 | 20.0 |
| 65 | 5.8 | 109 | 15.8 | 165 | 9.6 | 286 | 7.5 | 349 | 5.8 |
| 67 | 17.9 | 110 | 7.5 | 167 | 8.3 | 291 | 8.8 | 350 | 70.1 |
| 68 | 7.9 | 111 | 17.1 | 173 | 7.5 | 292 | 5.0 | 351 | 25.8 |
| 69 | 36.1 | 112 | 8.3 | 174 | 4.6 | 293 | 8.4 | 352 | 12.1 |
| 70 | 13.3 | 115 | 6.7 | 175 | 8.8 | 294 | 16.7 | 365 | 5.4 |
| 71 | 22.1 | 117 | 4.2 | 176 | 6.7 | 295 | 14.6 | 367 | 2.5 |
| 72 | 5.4 | 119 | 8.3 | 177 | 5.8 | 296 | 35.5 | 368 | 22.1 |
| 77 | 9.6 | 120 | 5.4 | 178 | 5.0 | 297 | 15.8 | 369 | 7.5 |
| 78 | 4.2 | 121 | 13.8 | 179 | 6.3 | 298 | 1.0 | 370 | 8.3 |
| 79 | 9.6 | 123 | 11.2 | 181 | 6.3 | 303 | 2.5 | 384 | 2.5 |
| 80 | 4.6 | 124 | 5.8 | 187 | 4.8 | 304 | 4.2 | 386 | 3.8P |
| 81 | 24.1 | 125 | 12.1 | 189 | 9.1 | 305 | 6.3 | 387 | 1.7 |
| 82 | 11.7 | 126 | 6.3 | 191 | 4.2 | 306 | 6.3 | | |
| 83 | 25.0 | 127 | 7.5 | 202 | 7.1 | 307 | 9.6 | | |
| 84 | 8.4 | 128 | 5.8 | 203 | 7.5 | 310 | 5.4 | | |
| 85 | 16.2 | 129 | 5.0 | 205 | 5.4 | 311 | 33.4 | | |
| 86 | 5.4 | 131 | 4.2 | 207 | 5.0 | 312 | 32.5 | | |
| 89 | 5.4 | 133 | 5.0 | 221 | 5.4 | 313 | 15.0 | | |
| 91 | 9.3 | 135 | 5.0 | 237 | 4.6 | 314 | 34.1 | | |
| 92 | 5.0 | 137 | 8.8 | 249 | 4.2 | 315 | 11.2 | | |
| 93 | 9.3 | 138 | 5.4 | 257 | 4.2 | 318 | 6.7 | | |

χ -Rhodomycinone. (UNKNOWN) M.Wt. (found) 370.

2KV, 50eV, slight heat.

| M/e | % | M/e | % | M/e | % | M/e | % | |
|---|---|---|---|---|---|---|---|---|
| 40 | 17.1 | 97 | 13.2 | 175 | 7.3 | 311 | 6.8 | |
| 41 | 16.6 | 102.5 | 1.8 | 176 | 6.7 | 318 | 8.5 | |
| 42 | 8.7 | 105 | 9.5 | 189 | 7.3 | 319 | 13.4 | |
| 43 | 33.1 | 108.5 | 1.8 | 202 | 8.5 | 320 | 7.3 | |
| 44 | 35.2 | 109 | 11.0 | 203 | 14.0 | 321 | 8.5 | |
| 53 | 9.3 | 111 | 10.4 | 213 | 6.2 | 322 | 6.2 | |
| 55 | 32.4 | 112 | 7.9 | 241 | 6.2 | 323 | 18.9 | |
| 56 | 15.3 | 113 | 21.4 | 242 | 4.8 | 324 | 12.9 | |
| 57 | 29.3 | 115 | 7.9 | 255 | 11.6 | 325 | 6.7 | |
| 65 | 7.3 | 119 | 10.3 | 269 | 8.5 | 332 | 4.3 | |
| 67 | 14.0 | 121 | 15.2 | 270 | 100.0 | 333 | 6.1 | |
| 68 | 7.9 | 123 | 9.1 | 271 | 29.9 | 334 | 45.1 | |
| 69 | 30.5 | 125 | 8.5 | 272 | 6.7 | 335 | 27.5 | |
| 70 | 11.6 | 127 | 7.9 | 282 | 9.4 | 336 | 39.5 | |
| 71 | 13.6 | 128 | 7.7 | 283 | 7.3 | 337 | 15.2 | |
| 72 | 9.3 | 129 | 6.0 | 285 | 13.4 | 338 | 6.7 | |
| 77 | 9.8 | 135.5 | 1.8 | 286 | 7.3 | 339 | 3.1 | |
| 79 | 7.3 | 139 | 10.4 | 291 | 7.9 | 341 | 3.6 | |
| 81 | 15.2 | 144.5 | 1.2 | 294 | 9.8 | 342 | 2.4 | |
| 82 | 7.3 | 145 | 7.2 | 295 | 55.1 | 350 | 15.2 | |
| 83 | 16.4 | 146 | 6.7 | 296 | 35.4 | 351 | 7.9 | |
| 85 | 11.6 | 147.5 | 3.1 | 297 | 17.1 | 352 | 33.6 | |
| 86 | 7.3 | 151 | 7.3 | 298 | 45.1 | 353 | 12.8 | |
| 90.5 | 2.4 | 152 | 7.9 | 299 | 16.4 | 354 | 12.8 | |
| 91 | 9.8 | 155 | 18.3 | 300 | 4.8 | 355 | 11.6 | |
| 93 | 8.5 | 159.5 | 2.4 | 303 | 5.5 | 368 | 3.6 | |
| 94 | 6.7 | 165 | 9.5 | 306 | 8.5 | 369 | 3.6 | |
| 94.5 | 3.6 | 168 | 7.3 | 307 | 26.7 | 370 | 51.8 | P |
| 95 | 16.5 | 173 | 7.9 | 308 | 11.0 | 371 | 18.3 | |
| 96 | 9.3 | 174 | 6.7 | 309 | 8.1 | 372 | 7.9 | |

δ-rhodomycinone. M.Wt. (found) 428.

(UNKNOWN).

2KV,50eV, Slight Heat.

| M/e | % | M/e | % | M/e | % | M/e | % | M/e | % | M/e | % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 40 | 4.6 | 102.5 | 2.8 | 135 | 6.5 | 231 | 7.5 | 330 | 5.6 | 382 | 7.0 |
| 41 | 9.4 | 103 | 6.5 | 136 | 5.1 | 261 | 7.9 | 331 | 9.4 | 392 | 21.0 |
| 42 | 5.6 | 105 | 10.3 | 137 | 12.2 | 268 | 7.5 | 332 | 13.1 | 393 | 13.1 |
| 43 | 11.2 | 107 | 10.3 | 138 | 7.9 | 269 | 7.0 | 333 | 31.6 | 394 | 8.9 |
| 44 | 10.3 | 108 | 7.5 | 139 | 18.2 | 270 | 7.5 | 334 | 34.5 | 395 | 5.6 |
| 45 | 3.8 | 109 | 8.4 | 140 | 7.5 | 289 | 6.1 | 335 | 20.5 | 396 | 5.6 |
| 55 | 10.3 | 110 | 6.5 | 141 | 8.4 | 290 | 5.2 | 336 | 14.1 | 408 | 3.3 |
| 56 | 6.1 | 110.5 | 2.8 | 144.5 | 1.4 | 291 | 6.5 | 337 | 10.8 | 409 | 3.8 |
| 57 | 19.7 | 111 | 9.4 | 146 | 4.2 | 292 | 4.7 | 338 | 10.8 | 410 | 9.8 |
| 59 | 4.7 | 112 | 6.5 | 146.5 | 1.8 | 293 | 16.4 | 339 | 17.3 | 411 | 5.6 |
| 60 | 3.8 | 113 | 11.2 | 147 | 4.2 | 294 | 35.0 | 340 | 11.2 | 412 | 7.9 |
| 67 | 4.6 | 114 | 7.0 | 147.5 | 1.9 | 295 | 24.3 | 345 | 16.8 | 426 | 7.0 |
| 68 | 2.8 | 114.5 | 2.8 | 148 | 1.8 | 296 | 18.7 | 346 | 9.4 | 427 | 6.5 |
| 69 | 17.7 | 115 | 17.2 | 148.5 | 1.9 | 297 | 10.7 | 347 | 6.5 | 428 | 30.4P |
| 70 | 7.5 | 116 | 5.6 | 149 | 6.5 | 298 | 7.5 | 348 | 7.0 | 429 | 17.8 |
| 71 | 14.0 | 117 | 5.5 | 150 | 6.5 | 303 | 5.6 | 349 | 12.2 | | |
| 77 | 10.3 | 119 | 11.2 | 151 | 11.2 | 304 | 5.6 | 350 | 20.6 | | |
| 79 | 11.2 | 120.5 | 3.8 | 152 | 14.0 | 305 | 6.5 | 351 | 48.6 | | |
| 81 | 15.9 | 123 | 8.9 | 155 | 8.4 | 306 | 7.5 | 352 | 29.0 | | |
| 83 | 16.8 | 124 | 5.6 | 163 | 9.8 | 307 | 9.4 | 353 | 16.8 | | |
| 84 | 3.8 | 125 | 13.1 | 164 | 7.5 | 308 | 6.4 | 354 | 15.1 | | |
| 85 | 6.5 | 126 | 9.4 | 165 | 13.1 | 309 | 9.4 | 359 | 15.0 | | |
| 91 | 10.3 | 127 | 14.0 | 166 | 6.6 | 310 | 7.5 | 360 | 100.0 | | |
| 92 | 3.7 | 128 | 11.7 | 176 | 6.5 | 311 | 14.1 | 361 | 51.2 | | |
| 93 | 6.4 | 129 | 8.4 | 177.5 | 3.3 | 317 | 2.8 | 362 | 28.1 | | |
| 93.5 | 2.8 | 129.5 | 2.8 | 180 | 6.5 | 318 | 11.2 | 363 | 15.9 | | |
| 94 | 5.6 | 130 | 3.7 | 180.5 | 3.7 | 319 | 9.4 | 368 | 12.6 | | |
| 94.5 | 3.7 | 130.5 | 2.3 | 181 | 5.1 | 320 | 7.0 | 369 | 6.5 | | |
| 95 | 15.9 | 131 | 7.5 | 183.5 | 1.8 | 321 | 10.3 | 370 | 6.1 | | |
| 96 | 9.4 | 131.5 | 2.8 | 188.5 | 2.8 | 322 | 27.1 | 376 | 7.0 | | |
| 97 | 14.0 | 132 | 2.8 | 189 | 8.9 | 323 | 28.9 | 377 | 4.8 | | |
| 100.5 | 1.9 | 132.5 | 0.9 | 202 | 6.5 | 324 | 21.5 | 378 | 5.6 | | |
| 101 | 7.5 | 133 | 4.7 | 205 | 6.4 | 325 | 11.2 | 380 | 10.3 | | |
| 102 | 6.5 | 134 | 3.8 | 221 | 6.5 | 326 | 5.6 | 381 | 7.5 | | |

# CHAPTER IV.

## ISOMERISM IN MASS SPECTROMETRY.

### Introduction.

Differences in the mass spectra of some closely related compounds have been noted by several authors, although so far no theory has been evolved to explain the small but significant changes. Simple geometrical isomerism, as found in dialkylcyclanes and ethylenic substances, gives rise to substantial variation in peak intensity. In general, however, conformational and configurational isomers give very similar fragmentation patterns, the only difference being in the peak abundances of the ion fragments which depend on the geometry of the molecule as a whole.

Mohler and his co-workers [112] [113] have commented briefly on the mass spectra of the cis and trans -decalins (decahydronaphthalenes) and have noted the differences in the two parent ion abundances (cis 71.8%, trans 85.5%) and in the base peak (cis M/e=67, trans M/e68).

An account of the mass spectra of some epimeric alcohols has been published by Biemann and Siebl [114]. For a series of epimers, Biemann observed that the less crowded epimer had the most abundant parent peak but that the P - 18 peak was smaller than in the more crowded epimer which had a

smaller parent peak abundance. The ion abundances were taken as a percentage of the total ionization under the same conditions. This treatment of peak abundances, as a fraction of the total ion current, has been dealt fully by other workers [115] - [120]. Otvos and Stevenson [121] gave a firmer foundation to the use of total ionization in mass spectrometry since they showed that the summation of all ion abundances in the mass spectra of a number of compounds is directly proportional to calculated cross-sections for ionization by electrons. Thus, in fact, total ionization is an important physical property in any molecule.

Total ionization, measured under the same con-:ditions, is independent of structure for structural isomers of the same molecular weight. Friedel, Shultz and Sharkey[72] have suggested that this fact can be used to determine the molecular weight of an unknown alcohol by determining the total ionization. However, it is not possible to determine the absolute total ionization by the instrumental methods used in the present work. The ratio of the abundance of an ion to the total ionization of the spectrum is used for comparison.

Geometrical isomers have been studied by D'Or and his colleagues [122] and they have shown that the parent ion is more abundant in the trans isomer. Earlier, Natalis[123] had considered the mass spectra of six cis and trans cyclohexanes;

his results showed the same pattern - that the ion stability of trans compounds is greater than the cis in the dialkylhexanes. In this case, complications arise from ring conformations and Natalis found the following values for cis-trans related com-:pounds, depending on the axial or equatorial linkages (CVI) of substituent groups.

| Isomer | Parent abundances (% total ionization) | | |
|---|---|---|---|
| | 1:2- | 1:3- | 1:4- |
| cis | 0.10 | 0.28 | 0.40 |
| trans | 0.15 | 0.16 | 0.24 |

These results confirm the view that cis disposed groups in space, or the groups causing crowding in the molecule, produce small parent peaks relative to the corresponding isomer. Interactions across these rings, as well as in adjacent positions, now become important and an attempt will be made here to extend these simple concepts to complicated molecules.

The stereochemistry of manoyl oxide [124] (CVII) has been determined by Hodges and Reed [125] by comparing the P/P - 15 ion abundances and showing that the positions are more congested in manoyl oxide than in epi-manoyl oxide. This method of comparing ion abundances does, in effect, employ the technique of total ionization factors which are cancelled out in the final computation. Reed [52] has further extended

this technique to the inositols (the hexahydroxycyclohexanes) which are known in all isomeric forms.

Previous work has shown that one of the major factors affecting the fragmentation pattern in a molecule is the molecular crowding in the parent ion species. As yet, the fine detail of such a treatment has escaped solution but a general picture of lability of a molecular ion can be obtained from a study of its spectrum. However, as well as the crowd-:ing in the molecular ion, consideration of the stereochemistry of the product ion must be taken into account. This has been done by Biemann (114) in his work on the P - 18 peaks from epimeric alcohols.

As the complexity of the system increases, subtler interactions across rings have to be taken into account. This requires careful consideration of the molecular ring models of the compound. In general, 1:3- interactions across rings are the most severe and will lead to unstable ions in the mass spectrometer as they do in chemical reactions. It is realised that mass spectrometry is not yet at the stage of applying complex physical theories to predict or explain the relative stabilities of ions; however, interesting conclusions can be drawn from careful correlation of a series of compounds.

The isomer of ζ -pyrromycinone.

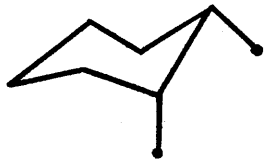
In Chapter III, the mass spectra of a series of pyrromycinones and rhodomycinones have been discussed. Within this series, Ollis [107] has isolated a compound believed to be the isomer at $C_9$ and $C_{10}$ of ζ -pyrromycinone (CVIII).

The mass spectra of the two isomers were obviously very closely related giving fundamentally identical fragmentation patterns. However, there were some differences in ion abundances as shown in the table below.

| M/e | ζ -pyrromycinone (%base peak) | isomer (%base peak) |
|---|---|---|
| 412 | 82.5 | 48.1 |
| 395 | 12.5 | 15.1 |
| 394 | 43.8 | 36.5 |
| 392 | 55.1 | 2.8 |
| 335 | 100.0 | 37.0 |
| 334 | 42.5 | 100.0 |

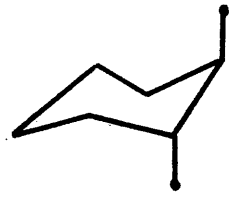
The pyrromycinone system is a particularly useful one for such studies since, for present purposes, the phenolic anthraquinone nucleus is scarcely fragmented by electron impact in the mass spectrometer and the contribution from this portion of the molecule to the general fragmentation of the molecule is negligible. The major breakdown occurs in the substituted alicyclic ring.

Applying Biemann's method [114], the parent P



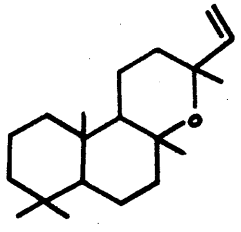
cis-1:2-Equatorial Axial

(a)



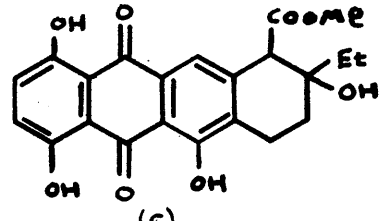
trans-1:2-Diaxial.

(CVI)



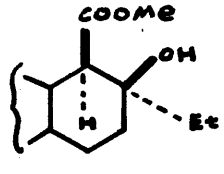
(b)

(CVII)

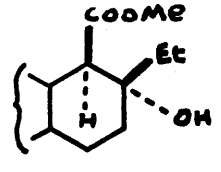



(c)

(CVIII)




ζ-Pyrromycinone




Isomer.

(CIX)

and P - 18 ions can be considered in detail. If $I_p$ is the abundance of the parent ion (fraction of total ion current) in $\zeta$-pyrromycinone and $I_{p-18}$ is the abundance of the P - 18 peak, the ratio of these two, $I_p/I_{p-18}$ depends on the relationship of the substituent groups in the alicyclic ring since the contribution from other sources of the P - 18 peak will either be negligible or constant. Similarly, let $I_p'$ and $I_{p-18}'$ be the corresponding values for the isomer. For these two ratios, $I_p/I_{p-18}$ and $I_p'/I_{p-18}'$, the smaller will apply to the more crowded isomer. Thus, if $I_p/I_{p-18} < I_p'/I_{p-18}'$, then the compound with parent ion P would be the more crowded isomer.

Results.

The results obtained are shown in the following table.

| | Fraction of total ionization | | |
|---|---|---|---|
| | P | P - 18 | P/P - 18 |
| $\zeta$-pyrromycinone | 0.0305 | 0.0162 | 1.88 |
| isomer | 0.0472 | 0.0351 | 1.30 |

Since the isomer gives the smaller ratio, it must be the more crowded molecule and the stereochemistry can be assigned as (CIX) assuming the stability of the remainder of the structure to electron impact and that thermal decomposition,

suggested by the differences in abundance of the P - 20 peaks, is a minimum.

A justification for the use of the peak ratio method has been proposed by Johnsen [126] in his study of hydrocarbon mixtures. This author observes that errors normally associated with pressure measurement of the sample prior to expansion are not present. Temperature fluctuations in the sample handling system affect all components equally and peak ratios are less likely to be affected by electrical fluctuations in the ionization chamber than individual peaks. Consequently, Johnsen suggests that this method can be applied to mixtures of isomers and, in general, for the analysis of mixtures.

Application of this peak abundance ratio method is the best obtained under instrumental conditions used in this work as the direct probe method employed does not allow accurate pressure measurement in the ion chamber or inlet system. It is possible that this expression of peak ratios will cancel the effects of varying pressures or sensitivities. The two isomers were studied as close as possible to stable conditions although the pressure could not be controlled to a constant value. These compounds would be difficult to handle in the conventional inlet system with fitted manometers since they are involatile and spectra could only be obtained in

more drastic, less easily reproducible, conditions.

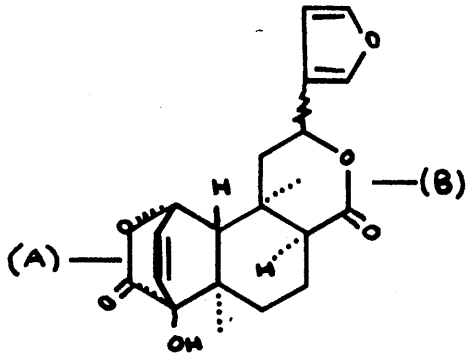
## THE STEREOCHEMISTRY OF THE ISO-COLUMBIN SERIES.

### Introduction.

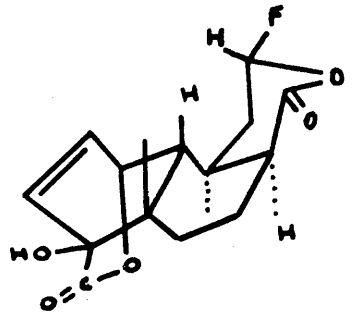
Columbin is easily isomerized by mild treatment with alkali to iso-columbin and Barton [73] explains this change as involving epimerisation $\alpha$- to one of the lactone's carbonyl groups. Interest has been shown concerning the stereochemical relationships of this series of compounds. Cava and his collaborators [127] have proposed the stereochemistry of columbin as (CX) from optical rotary dispersion measurements on octahydrodecarboxycolumbinic acid. These authors make the biogenetic assumption that the A/B ring fusion is trans and this has been shown to be inadmissable by Overton and his co-workers [128] who suggest the stereochemistry (CXI) for columbin with a cis-cis ring fusion and (CXII) for iso-columbin with a cis-trans ring fusion.

### Discussion and Results.

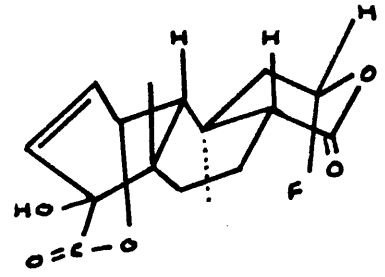
As discussed earlier, mass spectrometric measurements of complex stereoisomers are only useful in determining the overall "crowding" in a molecule and unless

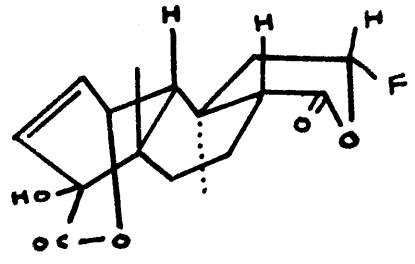



(CX).

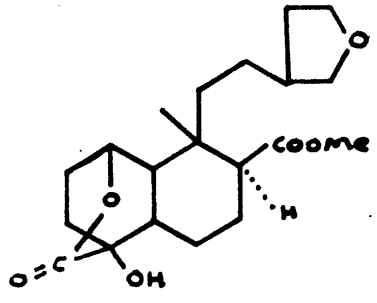



(CXI).




(CXII).




(CXIII).

special conditions arise, they are unable to relate the detailed stereochemistry of substituent groups. However, often the overall "crowding" in a molecular structure can be of value and the results of a mass spectrometric investigation are now discussed.

The information obtained from a study of the peak ratio method applied to complex molecules has already been discussed and applications of this method to the parent molecular ions of the columbin series have led to the following results:-

| Compound | Total Ionizn.T. (sum of % base peaks) | Parent Intensity ($I_p$) (% base peak) | $\frac{I_p}{T^p} \times 100.$ |
|---|---|---|---|
| Columbin | 1317.0 | 1.35 | 0.10 |
| *iso*-Columbin | 1563.7 | 4.20 | 0.27 |
| Decarboxy-columbin | 1018.8 | 29.5 | 2.89 |
| Decarboxy-*iso*-columbin | 1654.8 | 50.5 | 3.05 |
| Dihydrocolumbin | 1926.9 | 28.6 | 1.41 |
| Dihydro-*iso*-columbin | 2438.2 | 100.0 | 4.10 |
| Octahydrocolumbinic acid methyl ester | 3301.5 | 60.7 | 1.84 |
| Octahydro-*iso*-columbinic acid methyl ester | 4906.9 | 93.7 | 1.90 |

It may be noted that in general the fragmentation patterns of the normal and *iso*- series are very closely related. However, there is a noticeable difference in many of the prominent ions suggesting that stereochemical factors are involved.

In all cases, it can be postulated that the iso-compounds with the largest parent ion intensities relative to the total ion current are the less crowded molecules and this can also be seen by consideration of molecular models of the stereochemical structures proposed by Overton (128). The fact that the $I_p/T$ ratio for the octahydrocolumbinic acid methyl ester (CXIII) is very similar to that of the isomer, octahydro-iso-columbinic acid methyl ester, is evidence for the flexible nature of these molecules when the lactone ring (B) in structure (CX) is not present. This means that the isomers have very similar "crowding" and that the main stereochemical differences are present in lactone ring (B).

The similarity of the value of the $I_p/T$ ratio for decarboxycolumbin and decarboxy-iso-columbin shows that the loss of the lactone ring (A) converts the boat conformation of ring (A) into a more flexible structure. This means that there is a smaller difference between the stereochemistry of the decarboxyisomers.

The fact that columbin is easily converted into iso-columbin suggests that the iso- compound is the less crowded isomer. This is confirmed from the mass spectra. However, the structures of the iso-compounds proposed by both Cava and Overton are systematically less crowded and it is not possible to distinguish between these isomers in detail.

No author has been able to use mass spectrometry successfully in such an investigation of complex fused ring systems. This is one of the present limitations of mass spectrometry.

Experimental.

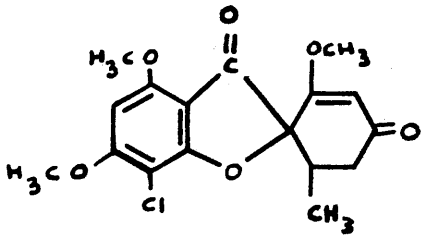
See Chapter II.

## CHLOROGRISEOPHENONES.

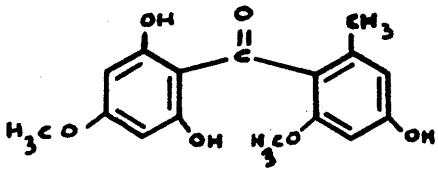
Introduction.

Chlorination is known to be a major process in grieofulvin (CXIV) biosynthesis and chlorination of griseophenone C (CXV) [129] in the course of fermentative production of griseofulvin affords griseophenone B, which has been shown to have the structure (CXVI).

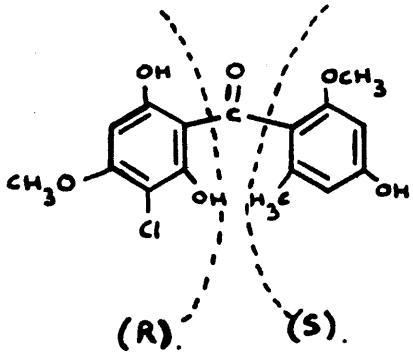
Mono-,di- and tri-chlorogriseophenones may be isolated when the benzophenone (CXV) is treated with the appropriate amount of sulphuryl chloride in ether. However, another sample of monochlorogriseophenone C (monochlorogriseophenone C II), isolated from the preparation of dichlorogriseophenone C, has been found to have an identical infra-red spectrum with that of griseophenone B and produces no depression of melting



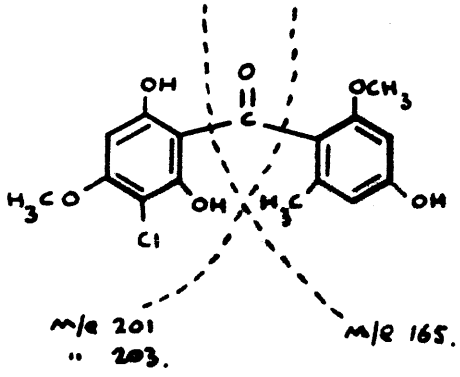
(CXIV).



(CXV)




(CXVI)




(CXVII)

point with that compound [130]. Monochlorogriseophenone C I has been shown not to be identical to griseophenone B since, although the mixed melting point is undepressed and the infra-red spectra in bromoform are identical, there are differences in the infra-red spectra when determined in a nujol mull.

A mass spectrometric examination of these compounds was undertaken to confirm firstly the identical nature of griseophenone B and monochlorogriseophenone C II and secondly the nature of the substitution in the sample of monochlorogriseophenone C I.

The structure of an unknown compound, "Q 5", was determined mainly from mass spectrometric evidence. However, the author has not been permitted to disclose inform-:ation on this study at the request of Dr. G. A. Somerfeld (Glaxo Laboratories). All that can be said is that this compound is a chloro-substituted derivative of griseophenone B and proof of the structure was obtained by correlation of the mass spectra of this series of compounds.

Discussion and Results.

Previous authors have observed the lability of the carbonyl group under electron impact and the chlorogriseophenones discussed above would be expected to fragment at both linkages $\alpha$- to the carbonyl group. If the stable fragment ions

obtained by this fission contain chlorine atoms, these can be detected by a careful examination of the mass/charge ratio at which these fragments appeared.

Although the detection of chlorine substituents in a benzene ring may be possible by consideration of the fragment ions, it is impossible to postulate the different structures of positional isomers in a benzene ring unless special conditions of substitution arise [131]. This is another major limitation in the mass spectrometric method in its present state of development.

The mass spectrum of griseophenone B is identical in all respects with monochlorogriseophenone C II and these compounds must have identical structures. The presence of chlorine is confirmed by certain fragment ions, including the parent ion which has ions corresponding to the chlorine isotopes of mass 35 and 37. The ions in the spectrum of griseophenone B confirm that the chlorine atom is substituted in the phloro-glucinol ring (R) in diagram (CXVI) and the fragmentation pattern is postulated as in diagram (CXVII). This result is obtained swiftly and conclusively from a careful study of the spectrum and demonstrates the application of mass spectrometry to a difficult chemical problem.

The spectrum of Griseophenone B (and monochlorogriseophenone C II) has abundant ions at M/e=165,172,

200,201,202,203,307,309,323 and 338. These ion fragments are produced by the expected fragmentation $\alpha$- to the benzophenone carbonyl group. An abundant ion would have been observed at M/e=199 if the chlorine atom had been substituted in the ring (S) in diagram (CXVI).

Monochlorogriseophenone C I gives a very weak spectrum causing the ion abundances, measured as percentage base peak, to be relatively high. However, prominent ion fragments are again observed at M/e=201 and 203 and the pattern of fragmentation follows approximately, but not exactly, that of Griseophenone B. This means that the chlorine atom is again substituted in ring (R). It will be observed that the two possible positions of substitution in ring (R) are equivalent which suggests that the structure of Griseophenone B is repeated in monochlorogriseophenone C I. However, it is difficult to align this evidence with the infra-red and chemical data obtained [130] and further chemical work on this topic is being continued in other laboratories [130].

Experimental.

Samples of $\xi$-rhodomycinone and its isomer were obtained from Dr. W. D. Ollis (Bristol University). The iso-columbin series were obtained from Dr. K. Overton (Glasgow University) and the chlorogriseophenone samples were sent by

Dr. G. A. Somerfeld (Glaxo Laboratories).

All these samples were involatile and the direct probe method was used in all cases. The spectra were run under the usual conditions and the tables of the mass spectra of these compounds are included in this section or, in the case of the iso-columbins, in Chapter II.

(LXXV) Racemate of ς-pyrromycinone at $C_{10}$ and $C_9$. M.Wt. 412.

| M/e | % | M/e | % | M/e | % | M/e | % | M/e | % | M/e | % | M/e | % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 41 | 2.8 | 127 | 2.4 | 192 | 1.3 | 165 | 1.9 | 318 | 2.8 | 360 | 1.5 | | |
| 43 | 3.1 | 128 | 2.6 | 193 | 1.3 | 266 | 1.9 | 319 | 4.6 | 361. | 2.4 | | |
| 44 | 2.6 | 129 | 1.7 | 197 | 2.4 | 267 | 2.6 | 320 | 6.3 | 362 | 5.7 | | |
| 55 | 3.9 | 133.5 | 1.1 | 205 | 1.5 | 268 | 2.2 | 321 | 9.6 | 363 | 9.3 | | |
| 56 | 2.2 | 137 | 3.1 | 211 | 1.7 | 269 | 3.3 | 322 | 17.4 | 364 | 4.4 | | |
| 57 | 9.8 | 139 | 2.8 | 220 | 1.5 | 270 | 2.8 | 323 | 36.0 | 365 | 9.6 | | |
| 59 | 3.7 | 140.5 | 2.6 | 221 | 3.3 | 277 | 3.9 | 324 | 20.5 | 366 | 3.7 | | |
| 67 | 1.7 | 147.5 | 5.2 | 222 | 1.7 | 278 | 4.2 | 325 | 9.6 | 367 | 1.9 | | |
| 69 | 2.6 | 148 | 3.1 | 223 | 1.9 | 279 | 7.8 | 327 | 2.2 | 276 | 3.9 | | |
| 71 | 1.7 | 150 | 1.5 | 224 | 1.9 | 280 | 9.4 | 328 | 1.8 | 377 | 5.7 | | |
| 77 | 1.7 | 151 | 2.8 | 225 | 4.8 | 281 | 5.8 | 329 | 1.5 | 178 | 3.9 | | |
| 79 | 1.7 | 152 | 2.6 | 237 | 1.9 | 282 | 4.4 | 333 | 36.5 | 379 | 4.0 | | |
| 81 | 1.9 | 153 | 2.4 | 239 | 1.9 | 283 | 2.1 | 334 | 100.0 | 380 | 10.6 | | |
| 82 | 1.3 | 154 | 1.7 | 248 | 2.2 | 289 | 2.1 | 335 | 37.0 | 381 | 9.3 | | |
| 82.5 | 0.7 | 155 | 2.2 | 249 | 3.0 | 290 | 1.9 | 336 | 9.8 | 382 | 4.8 | | |
| 83 | 1.7 | 159 | 1.9 | 250 | 2.2 | 291 | 2.4 | 337 | 3.9 | 383 | 8.5 | | |
| 84 | 1.7 | 161.5 | 1.3 | 251 | 2.4 | 292 | 4.4 | 338 | 3.9 | 384 | 3.5 | | |
| 93.5 | 0.7 | 163 | 2.1 | 252 | 3.7 | 293 | 6.1 | 340 | 4.4 | 391 | 1.7 | | |
| 94.5 | 4.4 | 164 | 1.7 | 253 | 3.3 | 294 | 29.5 | 348 | 3.5 | 392 | 2.8 | | |
| 95 | 1.9 | 165 | 4.1 | 254 | 1.9 | 295 | 34.4 | 349 | 4.8 | 393 | 0.9 | | |
| 97 | 1.5 | 166 | 1.7 | 255 | 2.1 | 296 | 17.4 | 350 | 7.8 | 394 | 36.5 | | |
| 103 | 1.5 | 167 | 1.9 | 256 | 1.3 | 297 | 3.9 | 351 | 10.9 | 395 | 15.2 | | |
| 105 | 1.5 | 168 | 1.7 | 261 | 1.5 | 303 | 2.2 | 352 | 8.3 | 408 | 1.9 | | |
| 107 | 1.7 | 169 | 1.3 | 263 | 1.5 | 304 | 3.1 | 353 | 4.6 | 409 | 1.5 | | |
| 108 | 1.8 | 171 | 1.5 | 265 | 1.9 | 305 | 3.1 | 354 | 5.0 | 412 | 49.1P | | |
| 109 | 1.7 | 175 | 1.7 | 266 | 1.9 | 306 | 14.8 | 355 | 9.8 | 413 | 25.2 | | |
| 110.5 | 0.9 | 176 | 2.2 | 267 | 2.6 | 307 | 13.9 | 356 | 19.4 | | | | |
| 115 | 3.9 | 179 | 1.5 | 268 | 2.2 | 308 | 11.5 | 357 | 12.3 | | | | |
| 116 | 1.5 | 181 | 1.8 | 261 | 3.3 | 309 | 9.3 | 358 | 2.1 | | | | |
| 119 | 1.9 | 189 | 1.8 | 263 | 1.5 | 317 | 2.2 | 359 | 1.3 | | | | |

Monochlorogriseophenone C I. M.Wt. 338.

50ev, 2KV.

| M/e | % | M/e | % | M/e | % | M/e | % |
|---|---|---|---|---|---|---|---|
| 43 | 41.5 | 93 | 15.6 | 150 | 15.0 | 323 | 8.4 |
| 44 | 58.6 | 94 | 25.1 | 151 | 33.1 | 338 | 14.3P |
| 45 | 7.1 | 95 | 47.5 | 163 | 22.1 | 339 | 6.5 |
| 50 | 5.1 | 96 | 17.6 | 165 | 35.0 | 340 | 7.8 |
| 51 | 8.2 | 97 | 41.6 | 166 | 14.3 | | |
| 52 | 5.8 | 98 | 9.1 | 167 | 24.0 | | |
| 53 | 11.8 | 99 | 9.5 | 177 | 13.0 | | |
| 54 | 7.8 | 105 | 13.6 | 179 | 16.9 | | |
| 55 | 58.1 | 108 | 7.1 | 191 | 13.0 | | |
| 56 | 18.7 | 109 | 21.5 | 193 | 13.0 | | |
| 57 | 47.1 | 110 | 15.6 | 200 | 62.1 | | |
| 58 | 5.6 | 115 | 6.5 | 201 | 100.0 | | |
| 59 | 4.3 | 119 | 23.4 | 202 | 29.2 | | |
| 60 | 4.9 | 120 | 11.7 | 203 | 51.5 | | |
| 61 | 4.5 | 121 | 30.0 | 219 | 33.1 | | |
| 63 | 6.5 | 122 | 23.4 | 241 | 18.9 | | |
| 64 | 5.3 | 123 | 47.5 | 242 | 25.6 | | |
| 65 | 8.8 | 124 | 22.6 | 243 | 37.0 | | |
| 66 | 8.7 | 125 | 37.6 | 249 | 8.4 | | |
| 67 | 30.5 | 126 | 14.3 | 251 | 7.8 | | |
| 68 | 11.7 | 127 | 13.0 | | | | |
| 69 | 66.0 | 128 | 12.3 | 263 | 12.3 | | |
| 70 | 18.3 | 129 | 15.6 | 264 | 12.5 | | |
| 71 | 30.2 | 131 | 18.2 | 272 | 20.8 | | |
| 72 | 5.2 | 133 | 18.2 | 273 | 17.5 | | |
| 73 | 5.5 | 135 | 23.4 | 274 | 7.2 | | |
| 77 | 15.7 | 136 | 18.2 | 277 | 11.1 | | |
| 78 | 9.7 | 137 | 17.8 | 278 | 8.4 | | |
| 79 | 19.2 | 138 | 68.2 | 279 | 7.8 | | |
| 80 | 9.5 | 139 | 40.5 | 280 | 5.2 | | |
| 81 | 45.5 | 140 | 15.6 | 292 | 5.2 | | |
| 82 | 35.5 | 141 | 12.3 | 305 | 7.8 | | |
| 83 | 45.0 | 142 | 7.2 | 306 | 47.5 | | |
| 84 | 13.6 | | | 307 | 51.2 | | |
| 85 | 20.8 | 143 | 12.4 | 308 | 28.0 | | |
| 91 | 13.6 | 145 | 18.2 | 309 | 19.5 | | |
| 92 | 5.9 | 149 | 22.1 | 310 | 7.2 | | |

(CXVI) Griseophenone B. M. Wt. 338.
(and Monochlorogriseophenone C II)
2KV, 50eV.

| M/e | % | M/e | % | M/e | % | M/e | % | M/e | % |
|---|---|---|---|---|---|---|---|---|---|
| 43 | 1.5 | 104 | 1.4 | | | 202 | 39.1 | 323 | 17.1 |
| 44 | 1.8 | 105 | 2.1 | | | 203 | 43.6 | 324 | 6.5 |
| 50 | 1.2 | 106 | 2.4 | | | 204 | 8.7 | 325 | 7.2 |
| 51 | 2.3 | 107 | 9.2 | | | 205 | 4.4 | 326 | 2.8 |
| 52 | 1.8 | 108 | 6.7 | | | 213 | 2.2 | 337 | 7.8 |
| 53 | 3.7 | 109 | 9.8 | | | 214 | 2.2 | 338 | 36.0P |
| 55 | 3.4 | 110 | 2.1 | | | 229 | 2.4 | 339 | 13.6 |
| 57 | 1.5 | 111 | 2.1 | | | 242 | 2.1 | 340 | 14.6 |
| 59 | 1.8 | 113 | 1.2 | | | 243 | 2.8 | 341 | 5.6 |
| 65 | 3.1 | 114 | 1.5 | | | 249 | 2.4 | | |
| 66 | 3.7 | 115 | 2.7 | 150 | 4.5 | 251 | 2.4 | | |
| 67 | 3.7 | 119 | 1.8 | 151 | 4.0 | 263 | 3.1 | | |
| 68 | 1.5 | 120 | 2.1 | 153.5 | 1.5 | 264 | 2.8 | | |
| 69 | 7.0 | 121 | 3.4 | 156 | 2.1 | 265 | 2.8 | | |
| 73 | 1.5 | 122 | 8.5 | 157 | 5.9 | 266 | 2.1 | | |
| 75 | 1.7 | 123 | 4.5 | 158 | 3.4 | 267 | 1.8 | | |
| 77 | 6.4 | 124 | 2.4 | 159 | 3.4 | 271 | 2.4 | | |
| 78 | 4.0 | 129 | 6.4 | 160 | 2.4 | 272 | 2.4 | | |
| 79 | 4.9 | 130 | 2.7 | 161.5 | 1.8 | 273 | 3.4 | | |
| 80 | 2.4 | 131 | 4.0 | 164 | 3.1 | 277 | 5.2 | | |
| 81 | 2.7 | 132 | 2.1 | 165 | 18.9 | 278 | 6.5 | | |
| 82 | 1.2 | 133 | 1.8 | 166 | 4.3 | 279 | 8.4 | | |
| 83 | 1.5 | 134 | 2.1 | 167 | 3.4 | 280 | 7.1 | | |
| 84 | 1.2 | 135 | 3.4 | 169 | 3.4 | 281 | 5.6 | | |
| 85 | 1.8 | 136 | 3.4 | 170 | 3.7 | 282 | 3.7 | | |
| 89 | 1.7 | 137 | 5.2 | 171 | 3.9 | 292 | 3.6 | | |
| 90 | 2.1 | 138 | 54.1 | 172 | 10.7 | 293 | 3.4 | | |
| 91 | 2.1 | 139 | 21.4 | 173 | 3.5 | 294 | 3.4 | | |
| 92 | 1.8 | 140 | 4.2 | 174 | 4.7 | 295 | 1.8 | | |
| 93 | 1.8 | 143 | 3.4 | 175 | 1.8 | 305 | 4.2 | | |
| 94 | 4.5 | 144 | 4.5 | 185 | 2.2 | 306 | 11.2 | | |
| 95 | 4.9 | 145 | 3.4 | 186 | 3.7 | 307 | 74.0 | | |
| 96 | 1.5 | 146 | 2.7 | 187 | 2.4 | 308 | 26.3 | | |
| | | 147 | 2.4 | 188 | 2.1 | 309 | 30.0 | | |
| 101 | 1.6 | 149 | 2.1 | 189 | 1.8 | 310 | 9.9 | | |
| 102 | 1.8 | | | 199 | 1.5 | 311 | 3.7 | | |
| 103 | 2.4 | | | 200 | 57.0 | 321 | 7.2 | | |
| | | | | 201 | 100.0 | 322 | 5.9 | | |

# CHAPTER V.

## THE SUBSTITUTED MALONIC ACIDS.

### Introduction.

The presence of certain structural features in a molecule, such as highly branched positions, is known to produce a very weak parent ion. In some cases, the molecular ion may be absent and only fragment ions arising from decomposition of the labile parent ion can be recognised. Various techniques have been developed to determine the molecular weight of such compounds. These methods include effusiometry [132], preparation of derivatives [133], total ionization [72] and the "P + 1" method [134].

At large sample pressures, certain classes of hydrogen containing compounds give rise to "anomalous" peaks at one mass unit above the molecular weight. The abundance of such peaks is proportional to the square of the sample pressure [135] which means that an inter-molecular reaction is occurring. This has been applied to ethers, amines, glycols and nitriles [134]; extensions to this method have been used for the analysis of sulphones [136], esters [136][137], carbonates [136] and amino alcohols [138]. The reaction involved is one of hydrogen abstraction [139] [140] [141] from

a neutral molecule i.e.

$$CH_3OH^+ + CH_3OH \longrightarrow CH_3OH_2^+ + CH_3O.$$

Compounds which are thermally unstable often undergo thermal fragmentation and, for this reason, some authors [39] have recommended the conversion of acids to esters. It is often difficult to decide whether thermal or electron impact fragmentation is occurring, if the compound can undergo both types of breakdown. In both cases the parent ion may be absent but the minimum amount of thermal decomposition can be assured if the direct probe method is used.

In this chapter, a mass spectrometric study of some derivatives of malonic acid has been undertaken. From the above considerations, these compounds are difficult to study in the mass spectrometer since malonic acid and its derivatives are thermally unstable [142] and contain quaternary centres substituted by aliphatic hydrocarbon chains. Normal mass spectrometric study would perhaps be impossible as thermal decomposition would then be a likely process.

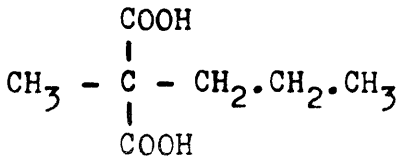
## Discussion and Results.

The derivatives of malonic acid which were studied are shown in attached diagrams as (CXVIII), (CXIX), (CXX), (CXXI), (CXXII), (CXXIII), (CXXIV) and (CXXV).

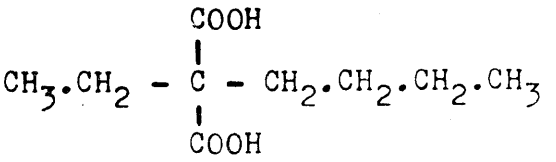
A small parent peak was only observed in the compounds (CXXIII), methyl malonic acid, and (CXXV), the acetylene derivative of n-pentyl malonic acid, together with a variable P + 1 peak. These were the only compounds having a tertiary grouping and the presence of the hydrogen atom attached to this position must, in some way, confer stability on the parent ion. It is known, in general terms, that quaternary centres are more liable to rupture and this is shown in the other compounds with only a quaternary centre present.

A P + 1 peak is also observed in the compounds (CXVIII), (CXIX), (CXX) and (CXXI) but in this case there is no parent ion. This can be accounted for by the presence of quaternary centres which render them labile under electron impact. The fact that a P + 1 ion is present suggests that the compound is undergoing true fragmentation by electron impact.

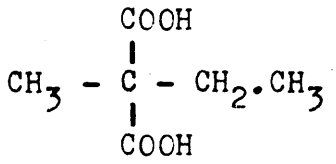
The symmetrically substituted acids (CXXIV) and (CXXII) give neither parent or P + 1 peaks under variable conditions and both appear to be very unstable compounds. (CXXII) gave an unsatisfactory spectrum and it appears to be undergoing drastic decomposition. The spectrum of (CXXIV) is shown on the attached "histogram". In this case, the major peak arises from loss of 44 mass units ($CO_2$) from the non-existent parent ion which suggests that decarboxylation is occurring.



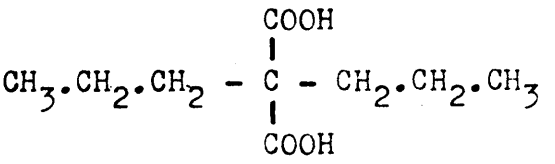
(CXVIII).



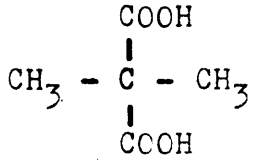
(CXIX).



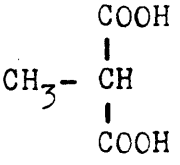
(CXX).



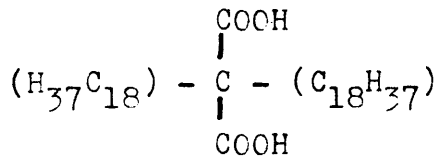
(CXXI).



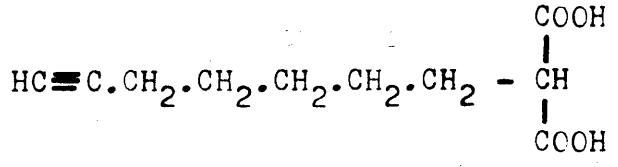
(CXXII).



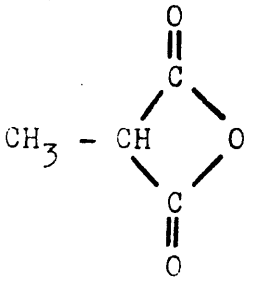
(CXXIII).



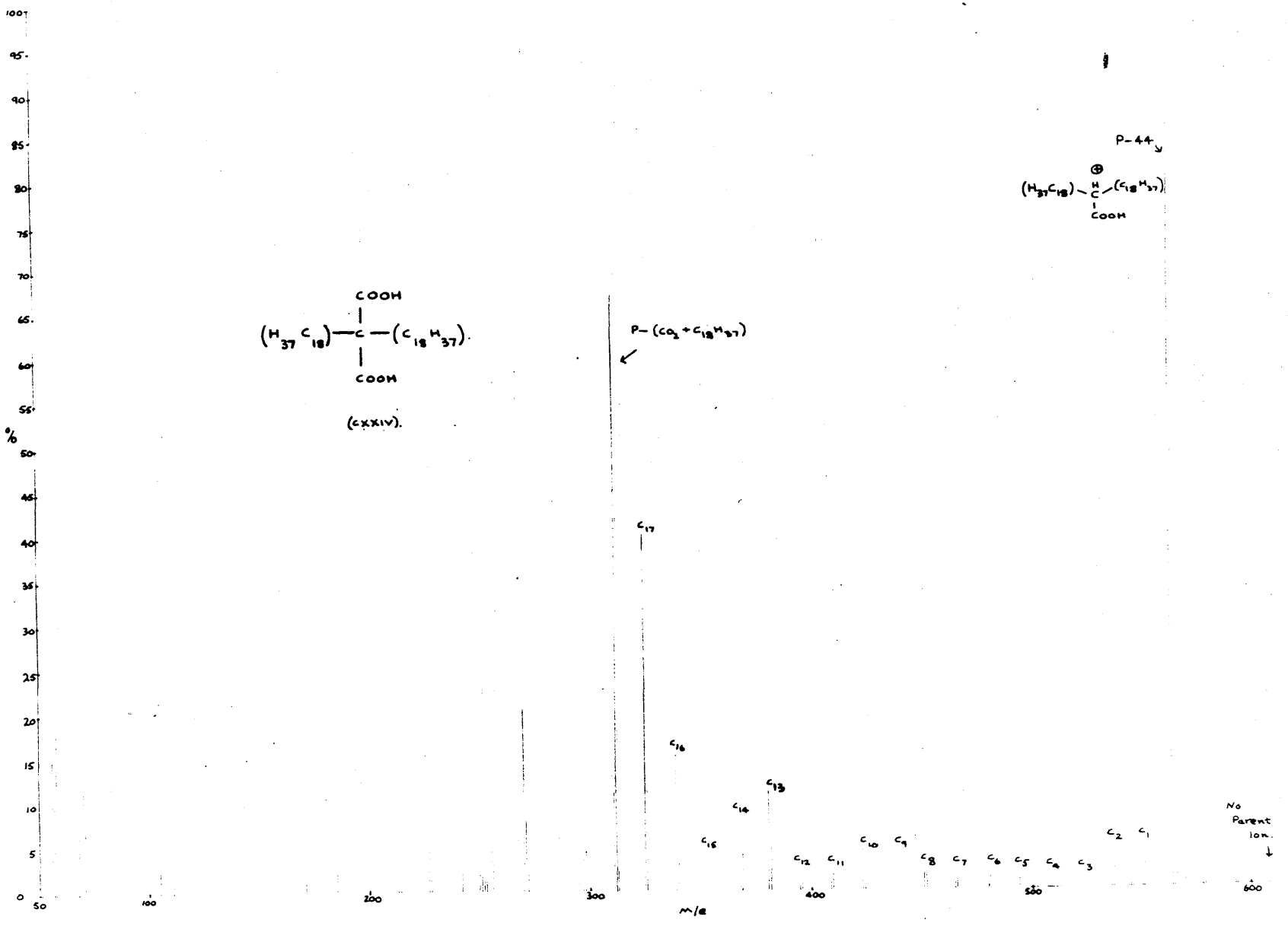
(CXXIV).



(CXXV).



(CXXVI).


100
95
90
85
80
75
70
65
60
55
%
50
45
40
35
30
25
20
15
10
5
0
50
100
200
300
400
500
600
m/e
COOH
(H37 C18)—C—(C18 H37).
COOH
(cxxiv).
P-(CO2+C18H37)
P-44
⊕
(H37C18)—HC—(C18H37)
COOH
C17
C16
C15
C14
C13
C12
C11
C10
C9
C8
C7
C6
C5
C4
C3
C2
C1
No Parent Ion.

At the quaternary centres, fragmentation occurs to produce an ion which has lost the largest substituent in that position. For example, (CXX) produces a peak at M/e=118 corresponding to loss of the ethyl group (with hydrogen migration) while a $C_3H_6$ portion is readily lost from (CXVIII). The histogram of the spectrum of (CXXIV) shows that, following loss of $CO_2$, the $C_{18}H_{37}$ substituent is then lost by successive carbon-carbon ruptures to produce an ion with the remaining $C_{18}H_{37}$ group intact.

Gohlke and McLafferty [45] have observed that, in dibasic aromatic acids, if the two -COOH groups are ortho to each other, a peak is observed corresponding to anhydride formation. In the malonic acids, peaks around M/e=100 are present in most cases and these may be assigned to formation of the ion of methyl malonic anhydride (CXXVI). The abundances of these ions are shown below.

| Compound. | M/e | % |
|---|---|---|
| (CXVIII) | 100 | 100.0% |
| (CXIX) | 101 | 96.2% |
| (CXX) | 100 | 100.0% |
| (CXXI) | 99 | 58.5% |
| | 100 | 14.7% |
| | 102 | 50.9% |
| (CXXII) | - | - |
| (CXXIII) | 100 | 10.0% |
| | 101 | 13.6% |
| (CXXV) | 99 | 27.6% |
| | 100 | 9.2% |

All the compounds readily lose 44,45 or 46 mass

units to produce stable ions. It is uncertain if this is due totally to fragmentation by electron impact, but possibly both the compounds (CXXIV) and (CXXII) undergo decarboxylation processes. All the compounds show abundant ions corresponding to $CH_3CH_2CO_2H^+$ (M/e=74) or the corresponding ion structures produced by hydrogen migration. The ion abundances of these structures are shown:

| Compound | M/e | % |
|---|---|---|
| (CXVIII) | 73 | 16.0 |
| | 74 | 32.0 |
| (CXIX) | 73 | 75.6 |
| | 74 | 7.7 |
| (CXX) | 73 | 66.5 |
| | 74 | 25.6 |
| (CXXI) | 73 | 99.1 |
| | 74 | 7.5 |
| (CXXII) | 73 | 51.0 |
| | 74 | 2.5 |
| (CXIII) | 73 | 51.0 |
| | 74 | 100.0 |
| (CXXIV) | 73 | - |
| | 74 | 7.5 |
| (CXXV) | 73 | 42.3 |
| | 74 | 9.6 |

Loss of both carboxy groups can also occur. For example, (CXVIII) has an abundant ion at M/e=72 corresponding to the hydrocarbon ion $C_5H_{12}^+$ which can only arise by loss of two -COOH groups. Similar ions are observed in the remainder of the series and successive ruptures of carbon-carbon bonds produce ions of the same type.

## CONCLUSIONS.

In general, these compounds fragment primarily at the quaternary or tertiary centres with the formation of preferred ion structures. These are the anhydride ion, the ions of propionic acid and its mono-carboxy analogues and certain hydrocarbon fragments. In most cases, fragmentation is not a thermal process and this method could be of value in determining the structures of such labile acids. However, there is the danger that the weak parent ion will be overlooked and this would jeopardise attempts at structure determination. Assuming the knowledge of the presence of a quaternary centre, the best method would be to vary the conditions used to obtain the spectrum in the hope of observing a P + 1 ion. In most cases, such ions are present unless the compound is exceptionally unstable.

The P + 1 ions, which vary in abundance with the conditions, should not be confused with the isotopic peaks of the parent ion. In all cases, the abundance of the observed P + 1 ion far exceeded that expected from such isotopic peaks.

## EXPERIMENTAL.

The pure samples were obtained from Dr. P.A. Finan (Sheffield University).

Mass spectra were obtained under mild conditions using no external heat. The accelerating voltage was 2KV with an electron energy of 50eV.

In some cases, the size of sample was altered to obtain a P + 1 peak. No pressure control was possible.

Tables of the mass spectra obtained are attached.

## CONCLUSION.

Although mass spectrometry of organic compounds can lead to valuable conclusions, no physical technique alone can answer every query to which the organic chemist seeks an answer. However, a realisation of these limitations can produce scope for development. The present work has attempted to demonstrate the applicability of mass spectrometry in certain cases.

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(CXVIII) 1-Methyl-1-propyl malonic acid. M.Wt. 160.

2KV, 50eV.

| M/e | % | M/e | % | M/e | % | M/e | % |
|---|---|---|---|---|---|---|---|
| 42 | 13.0 | 70 | 13.0 | 96 | 6.1 | 121 | 3.0 |
| 43 | 30.0 | 71 | 11.5 | 97 | 8.0 | 122 | 2.5 |
| 44 | 16.5 | 72 | 40.5 | 98 | 11.2 | 123 | 3.8 |
| 45 | 27.0 | 73 | 16.0 | 99 | 11.0 | 124 | 3.0 |
| 46 | 3.5 | 74 | 32.0 | 100 | 100.0 | 125 | 3.2 |
| 47 | 3.0 | 75 | 3.5 | 101 | 11.6 | 126 | 2.4 |
| 50 | 3.5 | 76 | 3.0 | 102 | 3.4 | 127 | 4.2 |
| 51 | 4.2 | 77 | 5.0 | 103 | 2.3 | 128 | 3.0 |
| 52 | 3.5 | 78 | 3.5 | 104 | 2.2 | 129 | 2.8 |
| 53 | 9.1 | 79 | 5.0 | 105 | 3.6 | 131 | 3.5 |
| 54 | 5.3 | 80 | 3.4 | 106 | 2.4 | 133 | 3.0 |
| 55 | 26.5 | 81 | 8.5 | 107 | 3.0 | 135 | 3.8 |
| 56 | 11.5 | 82 | 5.5 | 108 | 2.9 | 136 | 3.0 |
| 57 | 14.5 | 83 | 9.0 | 109 | 5.4 | 137 | 2.8 |
| 58 | 4.5 | 84 | 4.2 | 110 | 3.2 | 138 | 3.0 |
| 59 | 23.5 | 85 | 7.1 | 111 | 4.0 | 139 | 3.0 |
| 60 | 4.0 | 86 | 7.6 | 112 | 3.5 | 140 | 2.2 |
| 63 | 3.0 | 87 | 90.5 | 113 | 7.0 | 141 | 3.0 |
| 64 | 2.5 | 88 | 11.5 | 114 | 19.5 | 142 | 2.8 |
| 65 | 5.0 | 89 | 3.5 | 115 | 8.5 | 143 | 4.4 |
| 66 | 3.5 | | | 116 | 15.5 | 160 | - P |
| 67 | 11.5 | 91 | 4.5 | | | 161 | 3.9 |
| 68 | 7.8 | 92 | 3.0 | 117 | 5.5 | | |
| 69 | 54.5 | 93 | 3.5 | 118 | 91.3 | | |
| | | 94 | 3.0 | 119 | 11.5 | | |
| | | 95 | 8.0 | 120 | 3.8 | | |

(CXIX) **1-Ethyl-1-butyl malonic acid.** M.Wt. 188.

2KV, 50eV.

| M/e | % | M/E | % | M/e | % | M/E | % |
|---|---|---|---|---|---|---|---|
| 43 | 18.9 | | | 114 | 91.6 | 161 | 1.2 |
| 44 | 41.6 | | | 115 | 22.6 | 165 | 1.5 |
| 45 | 13.0 | | | 116 | 25.9 | 166 | 1.2 |
| 46 | 1.6 | | | 117 | 25.0 | 167 | 1.2 |
| 53 | 6.5 | | | 118 | 2.4 | 168 | 1.2 |
| 54 | 5.2 | | | 119 | 1.6 | 169 | 2.4 |
| 55 | 100.0 | | | 123 | 3.6 | 170 | 2.3 |
| 56 | 28.2 | | | 124 | 12.2 | 171 | 2.6 |
| 57 | 33.6 | 86 | 31.5 | 125 | 4.5 | 172 | 3.6 |
| 58 | 3.2 | 87 | 40.8 | 126 | 37.5 | 173 | 2.0 |
| 59 | 6.4 | 88 | 58.5 | 127 | 20.6 | 189 | 10.5 P + 1 |
| 60 | 3.2 | 89 | 4.7 | 128 | 3.2 | 190 | 1.2 |
| 61 | 3.2 | 90 | 1.2 | 129 | 20.6 | | |
| 64 | 3.1 | 91 | 2.0 | 130 | 2.8 | | |
| 65 | 1.2 | 92 | 1.6 | 131 | 1.6 | | |
| 66 | 2.1 | 93 | 2.4 | 132 | 35.6 | | |
| 67 | 6.1 | 94 | 1.8 | 133 | 3.9 | | |
| 68 | 6.2 | 95 | 5.6 | 134 | 1.2 | | |
| 69 | 33.5 | 96 | 7.3 | 135 | 1.5 | | |
| 70 | 12.5 | 97 | 14.6 | 137 | 1.5 | | |
| 71 | 6.9 | 98 | 42.7 | 138 | 1.5 | | |
| 72 | 2.8 | 99 | 31.9 | 139 | 1.1 | | |
| 73 | 75.6 | 100 | 5.7 | 141 | 10.9 | | |
| 74 | 7.7 | 101 | 96.2 | 142 | 19.5 | | |
| 75 | 1.6 | 102 | 7.3 | 143 | 6.7 | | |
| 76 | 2.0 | 103 | 1.2 | 144 | 11.7 | | |
| 77 | 2.1 | 104 | 1.5 | 145 | 3.2 | | |
| 78 | 1.6 | 105 | 1.7 | 146 | 1.2 | | |
| 79 | 2.8 | 106 | 1.7 | 149 | 1.3 | | |
| 80 | 2.0 | 107 | 1.7 | 154 | 8.5 | | |
| 81 | 8.5 | 108 | 1.6 | 155 | 2.8 | | |
| 82 | 5.7 | 109 | 5.8 | 156 | 1.2 | | |
| 83 | 69.2 | 110 | 5.6 | 157 | 1.6 | | |
| 84 | 8.5 | 111 | 15.3 | 159 | 1.8 | | |
| 85 | 5.3 | 112 | 10.4 | 160 | 6.7 | | |
| | | 113 | 13.7 | | | | |

(CXX) 1-Methyl-1-Ethyl malonic acid. M.Wt. 146.

2KV, 50eV.

| M/e | % | M/e | % |
|---|---|---|---|
| 40 | 6.7 | 82 | 17.5 |
| 41 | 65.0 | 83 | 20.6 |
| 42 | 13.4 | 84 | 40.6 |
| 43 | 32.5 | 85 | 23.1 |
| 44 | 22.4 | 86 | 14.6 |
| 45 | 79.5 | 87 | 94.0 |
| 46 | 5.6 | 88 | 24.2 |
| 47 | 2.5 | 89 | 3.7 |
| 50 | 4.1 | 95 | 3.7 |
| 51 | 7.5 | 99 | 17.9 |
| 52 | 4.1 | 100 | 100.0 |
| 53 | 22.4 | 101 | 37.4 |
| 54 | 14.5 | 102 | 46.6 |
| 55 | 85.0 | 103 | 5.6 |
| 56 | 22.0 | 104 | 5.2 |
| 57 | 17.5 | 113 | 5.9 |
| 58 | 5.9 | 114 | 3.7 |
| 59 | 52.1 | 117 | 3.7 |
| 60 | 4.9 | 118 | 92.0 |
| 67 | 3.4 | 119 | 18.4 |
| 68 | 5.2 | 120 | 3.4 |
| 69 | 76.5 | 128 | 1.9 |
| 70 | 16.0 | 129 | 5.6 |
| 71 | 7.5 | 132 | 2.2 |
| 72 | 78.0 | 135 | 1.5 |
| 73 | 66.5 | 147 | 3.0 P + 1 |
| 74 | 25.6 | | |
| 75 | 1.5 | | |
| 78 | 2.5 | | |
| 81 | 4.1 | | |

(CXXI)

## Dipropyl malonic acid.

50eV, 2KV.

| M/e | % | M/e | % | M/e | % |
|---|---|---|---|---|---|
| 50 | 0.6 | 95 | 7.3 | 148 | 0.7 |
| 51 | 1.1 | 96 | 1.9 | 155 | 0.8 |
| 52 | 1.1 | 97 | 70.1 | 159 | 0.7 |
| 53 | 11.3 | 98 | 7.2 | 169 | 0.6 |
| 54 | 8.5 | 99 | 58.5 | 170 | 0.6 |
| 55 | 68.2 | 100 | 14.7 | 171 | 6.8 |
| 56 | 18.2 | 101 | 15.1 | 172 | 1.3 |
| 57 | 36.7 | 102 | 50.9 | 179 | 0.6 |
| 58 | 3.4 | 103 | 3.9 | 183 | 0.9 |
| 59 | 2.8 | 104 | 0.7 | 189 | 3.7 P + 1 |
| 60 | 3.1 | 108 | 0.7 | 190 | 0.9 |
| 61 | 0.7 | 109 | 4.6 | | |
| 64 | 0.7 | 110 | 34.9 | | |
| 65 | 1.9 | 111 | 3.9 | | |
| 66 | 1.6 | 112 | 1.4 | | |
| 67 | 13.6 | 113 | 16.4 | | |
| 68 | 5.2 | 114 | 3.2 | | |
| 69 | 100.0 | 115 | 91.2 | | |
| 70 | 11.6 | 116 | 9.2 | | |
| 71 | 5.6 | 117 | 72.1 | | |
| 72 | 2.7 | 118 | 5.3 | | |
| 73 | 99.1 | 119 | 1.1 | | |
| 74 | 7.5 | 123 | 0.8 | | |
| 75 | 1.1 | 124 | 1.1 | | |
| 77 | 0.9 | 125 | 1.9 | | |
| 78 | 0.9 | 126 | 49.6 | | |
| 79 | 1.6 | 127 | 11.4 | | |
| 80 | 0.9 | 128 | 45.5 | | |
| 81 | 5.4 | 129 | 4.9 | | |
| 82 | 4.7 | 130 | 0.8 | | |
| 83 | 7.8 | 141 | 5.3 | | |
| 84 | 7.7 | 142 | 9.1 | | |
| 85 | 4.8 | 143 | 5.9 | | |
| 86 | 2.7 | 144 | 9.3 | | |
| 87 | 4.8 | 145 | 4.0 | | |
| 88 | 1.2 | 146 | 26.0 | | |
| 91 | 0.7 | 147 | 2.7 | | |

(CXXII) Dimethylmalonic acid. M.Wt. 132.

50eV, 2 KV.

Spectrum very weak and decomposition appears to be taking place.

| M/e | % | M/e | % |
|---|---|---|---|
| 50 | 2.9 | 63 | 2.1 |
| 51 | 2.1 | 65 | 2.5 |
| 52 | 2.1 | 66 | 2.5 |
| 53 | 10.1 | 67 | 4.5 |
| 54 | 4.9 | 68 | 7.0 |
| 55 | 63.5 | 69 | 17.5 |
| 56 | 7.5 | 70 | 75.5 |
| 57 | 13.0 | 71 | 9.0 |
| 58 | 15.5 | 72 | 2.5 |
| 59 | 100.0 | 73 | 51.0 |
| 60 | 15.0 | 74 | 3.5 |
| 61 | 2.5 | 75 | 2.0 |
| | | 76 | 3.5 |
| | | 77 | 5.0 |
| | | 78 | 8.5 |
| | | - | - |
| | | (No other peaks present.) | |

(CXXIII) 1-Methyl malonic acid. M.Wt. 118.

2KV, 50eV.

| M/e | % | M/e | % | M/e | % | |
|---|---|---|---|---|---|---|
| 40 | 2.6 | 76 | 1.0 | 107 | 1.1 | |
| 41 | 13.3 | 77 | 1.1 | 108 | 1.0 | |
| 42 | 5.1 | 78 | 0.8 | 109 | 1.8 | |
| 43 | 10.5 | 79 | 1.5 | 110 | 1.1 | |
| 44 | 16.7 | 80 | 0.8 | 111 | 1.1 | |
| 45 | 63.3 | 81 | 3.1 | 112 | 0.8 | |
| 46 | 6.8 | 82 | 1.6 | 113 | 0.6 | |
| 47 | 3.3 | 83 | 3.3 | 114 | 0.6 | |
| 52 | 0.8 | 84 | 1.1 | 115 | 1.2 | |
| 53 | 5.3 | 85 | 1.6 | 116 | 0.8 | |
| 54 | 3.5 | 86 | 1.3 | 117 | 0.6 | |
| 55 | 55.6 | 87 | 2.8 | 118 | 3.0 | P |
| 56 | 61.0 | 88 | 3.5 | 119 | 3.5 | P+1 |
| 57 | 10.3 | 91 | 1.6 | | | |
| 58 | 1.5 | 92 | 1.0 | | | |
| 59 | 2.5 | 93 | 1.3 | | | |
| 60 | 1.3 | 94 | 1.0 | | | |
| 63 | 1.0 | 95 | 3.2 | | | |
| 65 | 0.9 | 96 | 2.0 | | | |
| 66 | 0.7 | 97 | 2.3 | | | |
| 67 | 2.5 | 98 | 1.6 | | | |
| 68 | 1.5 | 99 | 1.7 | | | |
| 69 | 6.0 | 100 | 10.0 | | | |
| 70 | 4.3 | 101 | 13.6 | | | |
| 71 | 3.6 | 102 | 2.0 | | | |
| 72 | 11.6 | 103 | 1.0 | | | |
| 73 | 76.0 | 104 | 0.8 | | | |
| 74 | 100.0 | 105 | 1.3 | | | |
| 75 | 7.3 | 106 | 0.8 | | | |

(CXXV) 1-Hept-6-yne malonic acid.

70eV, 2KV.

| M/e | % | M/e | % | M/e | % | M/e | % |
|---|---|---|---|---|---|---|---|
| 43 | 36.1 | 80 | 40.0 | 117 | 23.6 | 154 | 5.2 |
| 44 | 36.0 | 81 | 51.1 | 118 | 4.6 | 155 | 3.8 |
| 45 | 35.2 | 82 | 22.6 | 119 | 9.4 | 156 | 4.1 |
| 46 | 3.4 | 83 | 17.6 | 120 | 4.9 | 157 | 3.3 |
| 47 | 2.1 | 84 | 14.3 | 121 | 9.9 | 158 | 4.2 |
| 48 | 1.7 | 85 | 12.2 | 122 | 9.9 | 159 | 5.8 |
| 49 | 3.5 | 86 | 54.0 | 123 | 34.5 | 160 | 2.6 |
| 50 | 15.2 | 87 | 23.2 | 124 | 16.8 | 161 | 3.1 |
| 51 | 23.0 | 88 | 2.5 | 125 | 11.1 | 162 | 12.3 |
| 52 | 19.3 | 89 | 3.3 | 126 | 8.3 | 163 | 4.5 |
| 53 | 34.4 | 90 | 2.5 | 127 | 8.9 | 164 | 2.8 |
| 54 | 54.0 | 91 | 32.3 | 128 | 7.5 | 165 | 2.9 |
| 55 | 92.5 | 92 | 17.2 | 129 | 4.4 | 166 | 2.9 |
| 56 | 13.8 | 93 | 41.0 | 130 | 3.1 | 167 | 2.4 |
| 57 | 20.5 | 94 | 94.3 | 131 | 3.7 | 168 | 2.5 |
| 58 | 5.8 | 95 | 79.9 | 132 | 2.9 | 169 | 2.3 |
| 59 | 14.2 | 96 | 15.9 | 133 | 6.9 | 170 | 2.6 |
| 60 | 19.2 | 97 | 30.2 | 134 | 39.0 | 171 | 3.8 |
| 61 | 3.8 | 98 | 11.8 | 135 | 19.0 | 172 | 4.2 |
| 62 | 3.5 | 99 | 27.6 | 136 | 8.0 | 173 | 2.9 |
| 63 | 9.2 | 100 | 9.2 | 137 | 16.4 | 174 | 2.5 |
| 64 | 3.4 | 101 | 3.3 | 138 | 9.5 | 179 | 2.9 |
| 65 | 19.3 | 102 | 2.1 | 139 | 8.2 | 180 | 3.4 |
| 66 | 18.6 | 103 | 3.8 | 140 | 7.0 | 181 | 6.5 |
| 67 | 75.1 | 104 | 76.1 | 141 | 9.8 | 184 | 2.5 |
| 68 | 29.6 | 105 | 26.0 | 142 | 3.7 | 190 | 2.6 |
| 69 | 45.2 | 106 | 15.1 | 143 | 2.8 | 198 | 2.4 P |
| 70 | 13.0 | 107 | 31.5 | 144 | 3.5 | 199 | 2.5 |
| 71 | 21.4 | 108 | 21.7 | 145 | 3.7 | | |
| 72 | 58,5 | 109 | 19.4 | 146 | 2.4 | | |
| 73 | 42.3 | 110 | 17.6 | 147 | 6.0 | | |
| 74 | 9.6 | 111 | 18.4 | 148 | 3.5 | | |
| 75 | 4.6 | 112 | 22.7 | 149 | 3.3 | | |
| 76 | 6.4 | 113 | 15.0 | 150 | 2.4 | | |
| 77 | 45.1 | 114 | 8.7 | 151 | 5.3 | | |
| 78 | 89.9 | 115 | 9.3 | 152 | 23.0 | | |
| 79 | 100.0 | 116 | 4.2 | 153 | 11.5 | | |

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