SYNTHESIS AND MASS SPECTROMETRY OF PHENYLBORONATE ESTERS OF POLYHYDRIC ALCOHOLS.

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Abstract.

1. Phenylboronates of acyclic diols, triols and polyhydric alcohols have been synthesised.

2. Mass spectrometry of phenylboronates of acyclic diols has revealed that the following four processes occur as a result of ionisation by electron impact:-

   (a) Elimination of exocyclic groups by cleavage of C-C bonds.

   (b) Skeletal rearrangement giving rise to highly unsaturated hydrocarbon ions containing 7-10 carbon atoms.

   (c) Elimination of oxo molecules.

   (d) A double elimination exclusive to six-membered phenylboronate rings, which provides a means of detecting this structural unit in compounds of hitherto unknown structure.

3. The mass spectra of phenylboronates of triols, tetritols, pentitols and hexitols were interpreted on the grounds of the processes outlined above, and structures assigned accordingly.

4. The hitherto unsuccessful methylation of hydroxyl groups in phenylboronates has been achieved using diazomethane and boron trifluoride etherate as reagents.

5. Methylation of phenylboronates followed by hydrolysis of the ester, acetylation and analysis of the product by gas-liquid chromatography combined with mass spectrometry revealed that the phenylboronates of triols are, in fact, mixtures of different boronate ring modifications. The compositions of such mixtures have been compared and rationalised in terms of the structures.

To my parents in grateful appreciation for so much.

Acknowledgement.

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Contents.

Synthesis and Mass Spectrometry of Phenylboronate Esters of Polyhydric Alcohols.

I Introduction

In this thesis, "phenylboronate" will be used to denote a cyclic ester of phenylboronic acid and a diol (Fig. I-1). A compound which contains more than one such ring system will be termed a "bis-phenylboronate","tris-phenylboronate", etc.

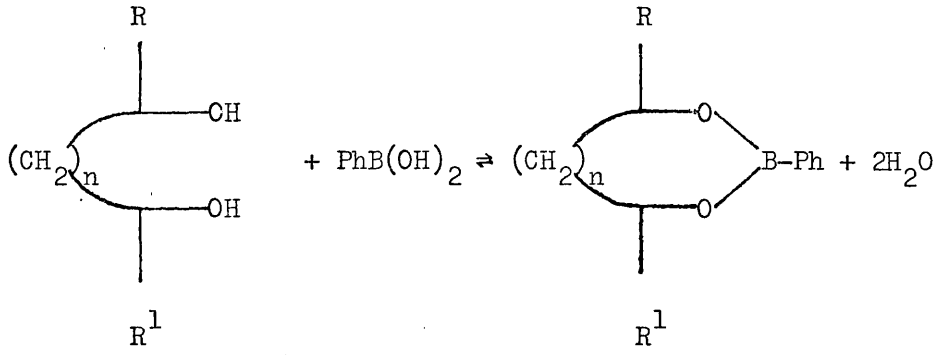


Fig. I-1

"Phenylboronic acid" is the name given in the Ring Index of the American Chemical Society[1] to the compound of formula $C_6H_5B(OH)_2$ first prepared in 1880 by Michaelis and Becker[2]. It is also known as benzeneboronic acid and phenylboric acid. Phenylboronic acid, its substituted analogues and its esters have been widely used for both commercial and analytical purposes.

In the pharmaceutical industry, the acid's anti-convulsant properties have been utilised to produce an anti-epileptic agent[3]; it is also known to enhance the effect of known hypnotics[4]. The property of neutron capture shown by substituted boronic acids shows great promise in the treatment of brain tumours[5]; substituted boronic acids have also been used as selective weed-killers[6] and as curing agents for epoxy resins[7]. Organo-boron compounds have found use in fuel technology and phenylboronic acid is no exception. The acid has been used as an anti-knock additive to petrol[8] and found to stabilise kerosine jet fuel[9,10] while easily hydrolysable

acyclic esters prevent icing of such fuels[11]. Phenylboronate esters have been used as photodevelopers[12].

The formation of cyclic boronates is common in the field of natural products when derivatives of increased thermal stability are required for gas - liquid chromatography (g.l.c.). The parent compounds may be aminoalcohols or diols belonging to the terpenoid[13], steroid[13], alkaloid[14] or carbohydrate groups[15,16].

The separation of monosaccharides as acetates and trimethylsilyl ethers by g.l.c. is complicated by formation of multiple derivatives, representing anomeric forms, with overlapping peaks. For this reason these sugars are first reduced to glycitols which are then acetylated. The ease of formation and stereospecific nature in which the boronate reacts with hydroxyl groups in pairs has led to the development of a rapid method of separation of these glycitols replacing the procedure of acetylation. A butyl substituent rather than phenyl attached to boron lends greater volatility to the derivative, hence the former are preferred for g.l.c. However the greater strength of the B-Ph bond simplifies mass spectrometry and phenylboronate derivatives have recently been used to sequence nucleotides[17].

The paper chromatographic mobilities of certain sugars are increased when phenylboronic acid is incorporated into the solvent. The compounds affected were aldoses and cyclitols having in their most stable conformation a 1(ax), 3(ax)-diol grouping[18,19]. Acyclic polyhydroxy compounds have, in general, much higher R_F values in the solvent containing phenylboronic acid than the aldoses or ketoses from which they derive, thus providing a rapid method for the separation

of pairs of such compounds. It was found that re - chromatography in a solvent containing water separated phenylboronic acid from the polyhydroxy compounds.

Trans-esterification to an added diol compound is also readily effected. Propane-1,3-diol is commonly used for this purpose and enables the phenylboronate grouping to be used for blocking pairs of hydroxyl groups in the synthesis of disaccharides[20] and vitamin B_{15}, pangamic acid, derivatives[21].

This is a little of the work which has been published on phenylboronates since their discovery reported in 1954 by Kuivila et.al.[22]. Subsequently the chemistry has developed in a haphazard manner and it has been decided to disregard the chronological order in favour of more ordered presentation.

Formation of the cyclic esters has been accomplished in many, widely differing ways. Phenylboronates are commonly prepared using phenylboronic anhydride which reacts with a diol system as shown in Fig. I-2.

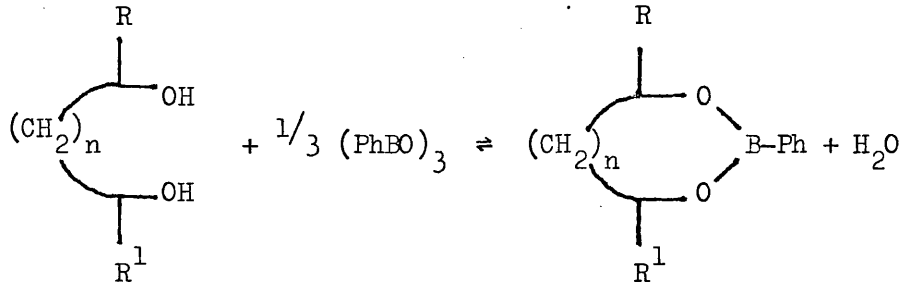


Fig. I-2

No catalyst is required and equilibrium is reached rapidly[23,24]. Methods of preparation have all been concerned with forcing the equilibrium to the right by one of the following methods:-

(i) Use of a large excess of one reagent e.g. glycerol for glycerol phenylboronate[25].

(ii) Precipitation of the ester from an aqueous reaction medium e.g. D-glucitol tris-phenylboronate[22]. This method is only applicable when the ester is resistant to hydrolysis. Monosaccharides have been shown to form stable anionic complexes in solution of the type shown in Fig. I-3 in addition to neutral complexes[26,27].

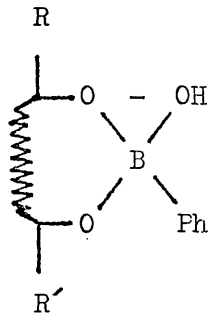


Fig. I-3

(iii) Removal of the water produced. This may be achieved by azeotropic distillation from benzene[28], dioxan[29], toluene[30], or pyridine[17]; by evaporation of an acetone[31] or a 2-methoxy-ethanol solution[21]; by extraction of the ester with a hydrocarbon solvent[32] or simply mechanically[23].

The esters so formed contain only five-, six- or seven- membered rings. Polymeric phenylboronates containing boron bridges are thought to be formed from pentane -1,5-diol[31], hexane -1,6-diol[33] and trans - cyclohexane -1,4-diol[34] (Fig. I-4). Cyclic boronates are more often encountered however.

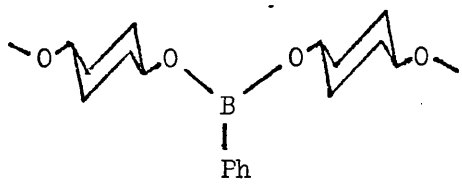


Fig. I-4

Complete substitution occurs such that a polyol with an even number, 2n, of free hydroxyl groups reacts with n/3 moles of anhydride to form an ester with n boronate rings, e.g. erythritol bis-phenylboronate, (Fig. I-5).

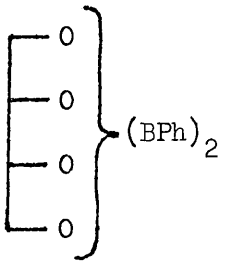


Fig. I-5

A polyol with an odd number, 2n + 1, of hydroxyl groups similarly reacts with n/3 moles of anhydride to produce an ester with one free hydroxyl group, e.g. glycerol phenylboronate, (Fig. I-6).

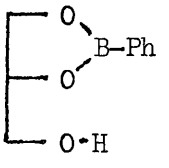


Fig. I-6

In a few cases, larger molar ratios than these may be necessary to form a stoichiometric product due to the formation of rings containing two boron atoms. Such a ring is capable of spanning a large O – O distance and an example occurs in methyl α – D – glucopyranoside 2,3 – (diphenylpyroboronate) 4,6–phenylboronate, (Fig. I-7).

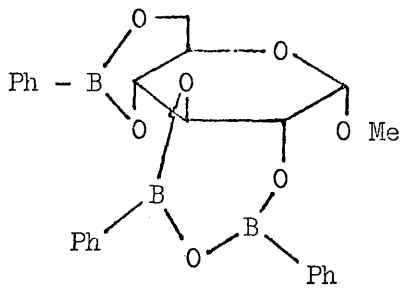


Fig. I-7

Use of smaller molar ratios than n/3 usually results in residual polyol but galactitol forms a bis-phenylboronate (Fig. I-8), which is prepared in aqueous methanol[35]. Dissolution in benzene causes disproportionation to the tris-ester and galactitol. The tris-ester is usually prepared in acetone.

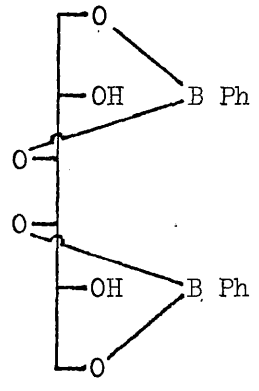


Fig. I-8

This type of behaviour has been observed for this one polyol only but xylitol bis-phenylboronate exhibits polymorphism[36]. The various forms may be interconverted by crystallising from different solvents.

The mechanism of formation has been deduced to occur by cleavage of two B-O bonds. The alternative would involve cleavage of a C-O bond and no change in configuration of an optically active carbon atom has been observed[29].

Due to the electron deficient nature of boron, determination of the structure of phenylboronates is quite complex. The possibility of intermolecular association immediately arises. However, measurements of molecular weights of phenylboronates of diols by depression of freezing point indicates that association in solution of the type shown in Fig. I-9 is negligible[37]. This is unexpected since intermolecular association has been observed to occur in several boronates, but it has been suggested that this is a steric effect of the phenyl group. It has also been observed that the boiling points increase in a normal sequence[24] indicating that association does not occur in the vapour phase. No intermolecular association has been reported of a polyol phenylboronate; they are hence assumed to be monomeric.

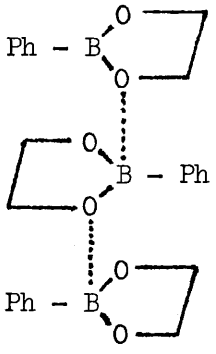
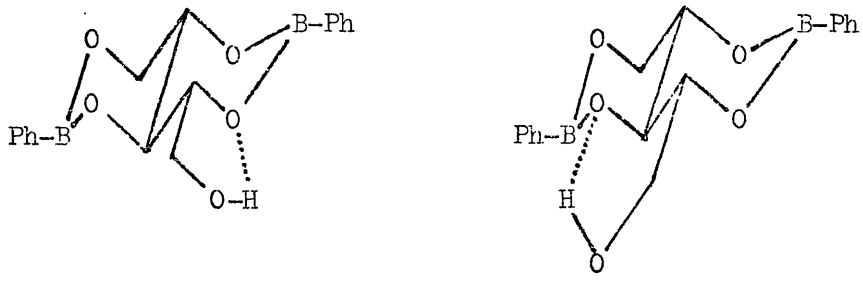


Fig. I-9

Infrared spectral studies in the region 3700 - 3400 cm^{-1} (O H stretching vibration) of phenylboronates in dilute carbon tetrachloride solution (0.005 M; a concentration sufficiently low that intermolecular hydrogen bonding may be disregarded) provide information concerning the nature of intramolecular hydrogen bonding and conformation. Phenylboronates having free hydroxyl

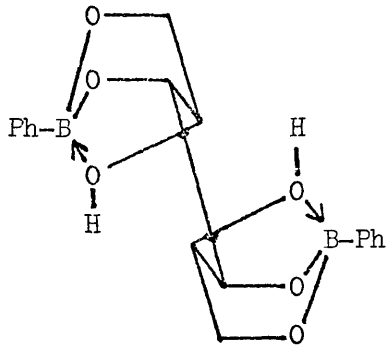
groups generally absorb at a frequency of 3638 ± 2 cm^{-1} if the hydroxyl group is primary, while if it is a secondary hydroxyl group it absorbs at 3628 ± 2 cm^{-1}. Hydrogen bonding to an oxygen atom of the boronate ring may take place shifting the frequency down by $\Delta\nu$ cm^{-1} proportional to the strength of the hydrogen bond, (Fig. I-10).



Ribitol bis - phenylboronate

Fig. I-10

Recognition of configurational groups is effected by comparison with spectra of known compounds such as partially substituted monosaccharides[19] and cyclohexane diols[38]. Absence of hydrogen bonding may indicate co-ordination of the oxygen atom of the hydroxyl group to boron[35], (Fig. I-11).



Galactitol bis - phenylboronate

Fig. I-11

The boronate ring size has been deduced from this information leading, for the first time, to an assignment of a complete structure to a bicyclic boronate which can be made only by this method.

The infrared spectra of phenylboronates are characterised by strong absorptions at 1350-1310 cm^{-1} which have been attributed to the B-O stretching frequency and much sharper ones at 1440 cm^{-1} arising from the B-aryl system. No correlation has been made between absorption frequency and ring size. Structure determinations, necessary for all phenylboronates, save those of diols, are therefore performed from a knowledge of the position of the free hydroxyl group(s). Structures of bicyclic and tricyclic esters without a free hydroxyl group remain unknown.

Structures are determined by formation of a derivative, removal of the boronate followed by either aqueous periodate oxidation or comparison with a known compound. The free hydroxyl group of a phenylboronate may be converted to an ester by treatment with an acid chloride, e.g. acetyl, benzoyl or toluene-p-sulphonyl chlorides, or an anhydride, e.g. acetic or benzoic anhydrides. All five reagents have been successfully employed in various cases and no rearrangements have been observed. Tosylates may afterwards be converted to benzoates or azides[39]. Esterification with an acid in the presence of a dehydrating agent may be performed in some cases[40]. Oxidation with dimethylsulfoxide/acetic anhydride has been used to convert a secondary hydroxyl group into a carbonyl function[41]. However, if the oxygen atom of the free hydroxyl group is co-ordinated to boron as in methyl 6-deoxy-α-D-allopyranoside 2,4-phenylboronate (Fig. I-12) the reactivity is greatly reduced[42,43].

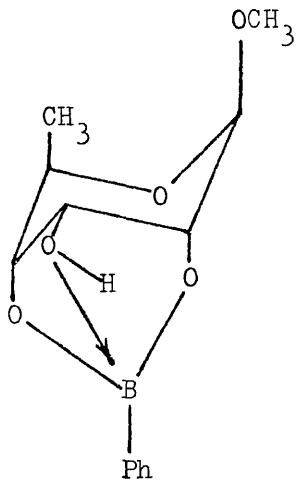


Fig. I-12

However, no difficulty has ever been experienced in producing a phenylcarbamate ester. Methylation, on the other hand, has in the past been unsuccessful[43,44] and it has been suggested[25] that, during methylation by the Purdie method[45], water produced by the reaction cleaves the phenylboronate ring.

Hydrolysis and trans-esterification are the common facile methods of cleaving a phenylboronate ring. Hydrolysis, prior to periodate oxidation, is effected by addition of a large volume of water to a solution of the boronate in N,N-dimethylformamide. Trans-esterification owes its success to the ready formation of propane-1,3-diol phenylboronate in aprotic solvents with the result that phenylboronate rings are often cleaved from carbohydrate esters with propane-1,3-diol[46]. In a small number of cases, e.g. methyl β-D-xylofuranoside[47] cleavage by this method proved unsuccessful and aqueous hydrolysis followed by removal of the phenylboronic acid produced with a strongly basic ion exchange resin was substituted[39]. Other methods of removing

the acid include separation by paper chromatography[35] and extraction with an organic solvent e.g. chloroform[41] or ether[32].

Partial hydrolysis has been observed to occur in one case only - that of methyl α-D-glucopyranoside 2,3 -(diphenylpyroboronate) 4,6-phenylboronate[29]. The pyroboronate ring was cleaved by treatment with benzene saturated with water. In other cases, the course of the reaction proceeds to free polyol e.g. D- mannitol[25]. It is hence not possible to deduce structures of multicyclic boronates from the structures of their hydrolysis products as is customary in the field of cyclic acetal and ketal chemistry.

Phenylboronate esters of furanoid and pyranoid rings have been well documented[29,39,43,44,46,47,48] and it now remains for structures of the esters of acyclic polyols to be similarly assigned and compared with them. In this way, data concerning the size, position and stability of the favoured ring form will be provided. With this type of information, a set of rules was formulated for cyclic acetals and ketals which predicted structures of such derivatives of polyhydric alcohols[49]. However the chemistry of phenylboronates is such that this task is more difficult and two immediate problems present themselves.

The ability of boron to act as an electron acceptor, reducing the reactivity of hydroxyl groups in the molecule, requires that long reaction times in boiling solvents be used to form derivatives. At least one boronate is known to be unstable under these conditions, hence a method which can be used at ambient temperature should be developed. Though the phenylboronates of glycosides have surprisingly never given mixed products, it is quite likely that

mixed esters may be obtained from an acyclic polyol since the O-O distance may vary continuously as a result of free rotation about the carbon skeleton.

An improved method of determining ring size is also required. Structures assigned by observation of hydrogen bonding through infrared spectroscopy must now be viewed with suspicion since it has been shown recently that the oxygen atoms of five- and six- membered boronate rings are non-equivalent[50]. Back donation of electrons from oxygen to boron occurs to a greater extent in a six- than in a five- membered ring resulting in a reduced electron density around the oxygen atoms of a six-membered boronate ring. As the strength of a hydrogen bond varies according to both distance and the electron density of the oxygen atom, the spectral shift, $\Delta\nu$, is no longer directly related to the length of the hydrogen bond, a necessity for the successful application of the method.

Structural studies have previously been restricted to molecules with a free hydroxyl group(s). Acyclic polyols possessing an even number of hydroxyl groups esterify completely with phenylboronic anhydride and a substitution technique is no longer applicable, hence the structures of many alditol phenylboronates remain unknown. Mass spectrometry appeared to have potential in distinguishing between possible ring sizes and to this end, a study of the mass spectra of a series of phenylboronates of diols was undertaken.

II Aspects of Mass Spectrometry.

Before the commencement of this work, only one publication[13] had appeared concerning mass spectrometry of phenylboronates. The compounds were mainly steroidal derivatives and no detailed information was supplied. Since then however, numerous papers have appeared and these will be discussed, in context, in the next chapter. The literature is surveyed to December, 1971. First, it will be useful to review the techniques used in assembling a fragmentation pattern of the phenylboronates of diols.

II-A Instruments - the general design.

In a mass spectrometer, ions are produced from a volatilised sample, separated according to their mass to charge ratio, and their relative abundances are determined. The basic units are therefore a sample introduction system, an ionisation chamber, a mass analyser, and a detection and display system. The chamber in which ionisation of the sample takes place is often referred to as the "ion source ". A mass spectrum may be regarded as a partial product analysis (neutral molecules which are produced are not analysed) of species formed in the "ion source ".

Involatile liquids and some solids can be introduced via a leak from a hot storage vessel, but thermal decomposition of the sample may occur in some cases. Solids are usually introduced on a ceramic direct insertion probe which can be heated so that any solid having a vapour pressure of 10^{-6} torr at a temperature below 360° will give a mass spectrum.

The excessive heat required to volatilise a substance for introduction into the "ion source" is the most common cause of artifact production and it is important to differentiate between

thermal and metal-catalysed effects prior to ionisation and an authentic electron impact promoted phenomenon. One of the most common and typical problems is that encountered in the mass spectra of alcohols which frequently display a $M-H_2O$ peak. This may be an authentic fragment peak or due to the molecular ion of the olefin produced by thermal dehydration prior to ionisation. Clearly, this is of crucial importance to the proper interpretation of a mass spectrum, because the fragmentation pattern of the alcohol is usually quite different from that of the olefin.

Not surprisingly, it was observed that phenylboronates having one free hydroxyl group in the molecule were decomposed by introduction through a heated inlet system and no molecular ion was observed. The spectrum after direct insertion was quite satisfactory however, and dehydration induced by ionisation was observed.

The volatilised sample is ionised by bombardment with a beam of electrons: in order to achieve maximum sensitivity and stability, the energy of the electrons is usually 70 e.v. In some instruments, ionisation is effected using a light source or electric field, but the most common "ion source" employs electron bombardment. All ions move out of the "ion source" under the influence of the ion repeller and pass through an electric accelerating field (V volts) into the mass analyser with a translational energy of Ve.

Mass analysis is usually effected by passing the ions through a magnetic field, H, when they describe different trajectories of radius r .

$$Hev = \frac{mv^2}{r}$$

where v is the velocity of the ion.

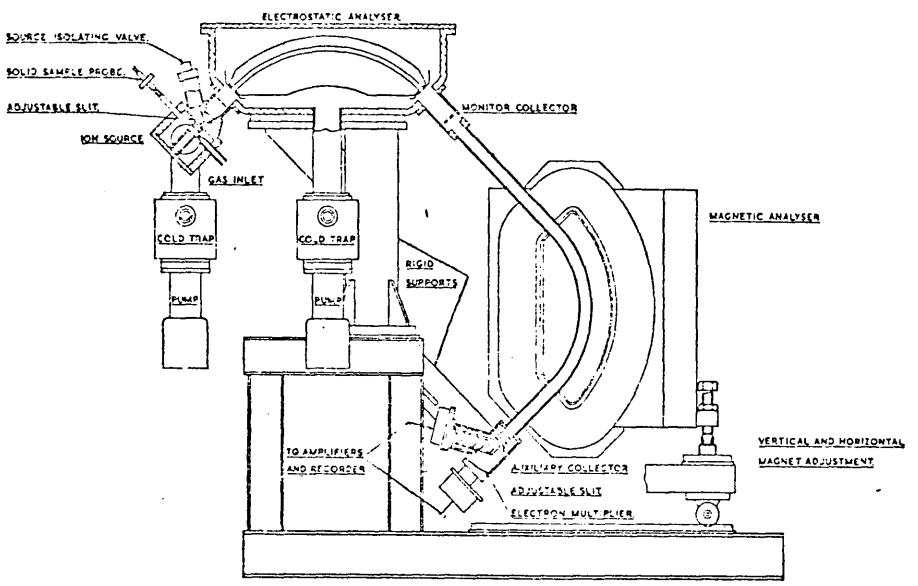
Therefore $r = \frac{mv}{He}$, but $Ve = \frac{mv^2}{2}$,

therefore $v^2 = \frac{2eV}{m}$,

and $r = \left(\frac{2mV}{H^2e}\right)^{\frac{1}{2}}$ or $\frac{m}{e} = \frac{r^2 H^2}{2V}$

By using an electromagnet, H may be increased steadily causing ions of increasing mass to charge ratio to be focussed successively onto a collector slit. An electron-multiplier is positioned behind this slit, and the output fed into a galvanometer recorder. The mass spectrum obtained is a partial product analysis of the reactions occurring in the "ion source ".

An important characteristic of a mass spectrometer is the resolving power, which is a measure of the ability of the instrument to separate ions of different mass to charge ratio. It is usually defined as the highest mass at which there is a "10% valley" between adjacent peaks of equal intensity. For a single focussing instrument of the type described above, such as the Hitachi RMS-4, a typical resolving power is about 5000, the value being limited by energy spread in the ion beam. In a double focussing spectrometer, such as the A.E.I. M.S. 902, with which all the spectra of phenyl-boronates investigated by the author were recorded, this is considerably reduced by placing an electrostatic analyser between the "ion source" and the magnetic analyser, (Fig. II-1). In this way, a resolving power of over 50,000 can be achieved.



TUBE ASSEMBLY MASS SPECTROMETER M.S.902

Fig. II-1

II-B Low resolution.

Ionisation of the sample molecule is achieved by bombardment with electrons of 70 e.v. energy, the most probable amount to be transferred being between 15 and 20 e.v. Typically, about 10 e.v. is required to remove an electron from a molecule to form a ground state molecular ion so that an electronically excited species is formed, having an average energy of excitation of 5-6 e.v. This is not a large amount for a large molecule which may have 2-3 e.v. of zero point energy. Thus, if excited ions can revert rapidly to the ground electronic state by radiationless transitions, ions undergoing decomposition will be ground electronic state, vibrationally excited ions and some of the organic chemist's experience of ions in solution is likely to be applicable. On this premise, the concept of charge localisation is invoked to explain the unimolecular fragmentation which the molecular ion undergoes in the "ion source" as a result of its excess energy.

Ions with a rate constant for decomposition $k > 10^{6}$ sec^{-1} will decompose in the "ion source" and only the fragments will be recorded on the spectrum. As the sample pressure in the instrument never exceeds 10^{-4} torr, ion molecule reactions are so rare as to be negligible and the fragments always have a lower mass than the molecular ion. The spectrum produced by a single focussing spectrometer, such as the Hitachi RMS-4, used by the author to determine the mass spectra of methyl ethers (see Chapter IV), may be simply represented by a bar graph, the mass values of the ions being assumed integral. Examples may be found in the appendix. Any attempt at explaining the spectrum must account for the ions of

greatest abundance. (The heights of the peaks are expressed as a percentage of the total ion current $\%\Sigma$). These may be characterised by precise mass measurement and their origins determined from metastable ions. The information is assembled to form a fragmentation pattern from which the molecule is identified.

II-C High resolution.

The mass values have been assumed in the above to be integral, but a double focussing instrument of higher resolving power such as the M.S. 902 would show that the masses have a decimal part. This may be employed to assign a formula to an ion. For example, the most abundant ion in the spectrum of propane-1,2-diol phenyl-boronate (3) occurs at the nominal mass of $^{m}/_{e}$ 147. If this ion has a formula $C_8 H_8 BO_2$, it should have a precise mass of 147.0617.

8 C = 8 x	12.00000
8 H = 8 x	1.00783
B =	11.00931
2 O = 2 x	15.99491
calc. $C_8 H_8 BO_2$ =	147.0617

Use of this high resolution technique and comparison with an ion of precisely known mass shows the mass to be 147.0614, confirming this formula.

The technique is of immense value when large fragments have been lost from the molecular ion. The peak at $^{m}/_{e}$ 105, again in the spectrum of (3), is an example. The ion may have formula $C_8 H_9$ or $C_6 H_6 BO$ of masses 105.0704 and 105.0512 respectively. By using a high resolving power, both these ions were found to be present and their abundances determined.

Elemental masses relative to carbon 12 are never integers, hence measurement of an ion's mass to one part per million usually results in the assignment of an unambiguous formula. Most of the fragmentation processes which are mentioned in the next chapter are supported by metastable ions, the parent and daughter ions of which have satisfactory precise masses.

II-D Metastable ions.

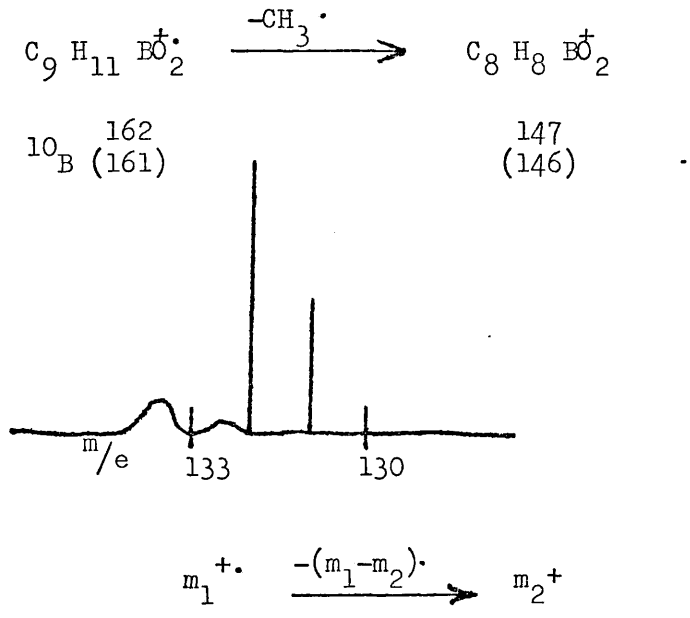
The rate at which ions decompose is a function of their internal energy. Hence ions with a range of rate constants (k) for decomposition are formed in the "ion source ". In a typical instrument, ions spend about 10^{-6} sec in the "ion source ", so that if k exceeds 10^{6} sec^{-1}, a fragment is collected. Ions typically take ca. 20 micro-seconds to reach the collector, so that if k is less than 10^{5} sec^{-1}, a parent ion is collected before decomposition can occur. If k lies between 10^{5} sec^{-1} and 10^{6} sec^{-1}, decomposition might occur whilst the ion is in the analyser tube, thereby giving rise to a metastable transition. If more than one fragmentation process can occur from the same parent ion, the lower energy process usually gives rise to the more intense metastable ion.

Ions of mass m_1 with a small excess energy (k between 10^{5} and 10^{6} sec^{-1}) decompose in the analyser tube of the spectrometer to ions of mass m_2 and, as a result of their reduced kinetic energy, produce a diffuse metastable ion in the spectrum at a position lower than either m_1 or m_2. Such ions m_1 are said to be metastable and an example of a metastable ion appears at $^{m}/_{e}$ 133.4 in the spectrum of (3) reproduced in Fig. II-2. The position at which the metastable ion appears in the spectrum is given by the equation

$$m^* = \frac{m_2^2}{m_1}$$

This metastable ion is therefore caused by the molecular ion losing a methyl radical. Two metastable ions occur because boron occurs naturally as two isotopes of masses 10 and 11 in an abundance ratio of 1:4, the ratio varying slightly with the natural source.

Metastable ion for the process



$$m_1^{+\cdot} \xrightarrow{-(m_1-m_2)\cdot} m_2^{+}$$

$$\frac{m_2^2}{m_1} = m^*$$

$$\frac{147^2}{162} = 133.39 \qquad m^* \text{ found} = 133.4$$

$$\frac{146^2}{161} = 132.40 \qquad = 132.4$$

Fig. II-2

This may be used to advantage when the nature of the daughter ion m_2 is in doubt. Such a case arises when two ions of the same integral mass are present at mass m_2. For example, in the spectrum of pentane-2,4-diol phenylboronate, the identity of the ion

at $^{m}/_{e}$ 105 may be $C_6 H_6 BO$ or $C_8 H_9$. Precise mass measurements have shown both present. The metastable ion at $^{m}/_{e}$ 63.0 ($= 105^2/175$) could result from either of the processes shown in Fig. II-3. The corresponding metastable ions for ^{10}B isotopes would appear at $^{m}/_{e}$ 63.4 and $^{m}/_{e}$ 62.2. The presence of a metastable ion at the former and absence of one at the latter position, indicates the production of a hydrocarbon ion.

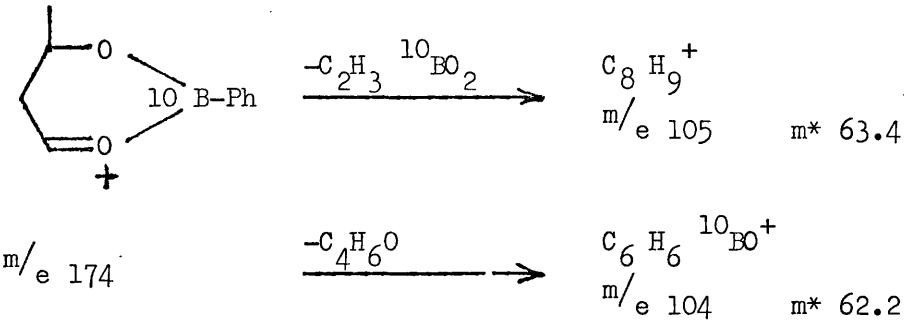


Fig. II-3

Observation of metastable ions in a normal spectrum may sometimes be difficult as a result of their low intensity compared with normal ions. Detection of ^{10}B metastable ions is of increased difficulty as they are only one quarter of the abundance of the corresponding ^{11}B ions. Suppression of the normal ions, using the scintillator device shown in Fig. II-4 simplifies the mass spectrum and by using a higher sensitivity the metastable ions may be enhanced. Observation of a weak ^{10}B metastable ion at $^{m}/_{e}$ 61.8 together with a ^{11}B metastable ion at $^{m}/_{e}$ 61.5 in a ratio of 1:4 in such a spectrum of butane -2,3-diol phenylboronate revealed that the hydrocarbon ion $C_8 H_8$ ($^{m}/_{e}$ 104) rather than $C_6 H_5 BO$ ($^{m}/_{e}$ 104) is produced directly from the molecular ion. The spectrum of the deuterated analogue 2,3-d_2-butane-2,3-diol phenylboronate confirmed this.

$C_{10}H_{13}{}^{11}BO_2^{+\cdot}$ ($^m/_e$ 176) $\longrightarrow$ $C_8H_8^+$ ($^m/_e$ 104) m* 61.5

$C_{10}H_{13}{}^{10}BO_2^{+\cdot}$ ($^m/_e$ 175) $\longrightarrow$ $C_8H_8^+$ ($^m/_e$ 104) m* 61.8

$C_{10}H_{11}D_2{}^{11}BO_2^{+\cdot}$ ($^m/_e$ 178) $\longrightarrow$ $C_8H_7D^+$ ($^m/_e$ 105) m* 61.9

Metastable ions increase the ease of interpretation and assembly of a fragmentation pattern as they are direct proof of a decomposition occurring as a result of ionisation. In cases where the positions of two metastable ions resulting from two possible processes are coincident, the parent of the metastable ion may be determined by accurately measuring the kinetic energy of the ion at the collector. This may be done both directly and indirectly.

The direct method involves replacing the electron-multiplier by the scintillator device shown in Fig. II-4. In so doing, the normal mass spectrum is removed facilitating observation of metastable ions, especially those at integral mass values. Parent ions decomposing in the field free region between the electrostatic and magnetic analysers are studied. If a parent of mass m_1 of kinetic energy Ve electron volts undergoes a metastable transition, then the daughter ion of mass m_2 will arrive at the collector having only $\frac{m_2}{m_1}$ Ve electron volts of kinetic energy. Adjustment of the magnet to bring the metastable ion into focus causes this daughter ion to fall on the scintillator. By careful adjustment of the scintillator voltage, a point is reached when a particular daughter ion is just not detected and a sharp fall occurs in the current produced by the photomultiplier. This cut-off voltage V_c is a direct measure of the kinetic energy of the ion. Hence

$$eV_c = \frac{m_2}{m_1} Ve,$$

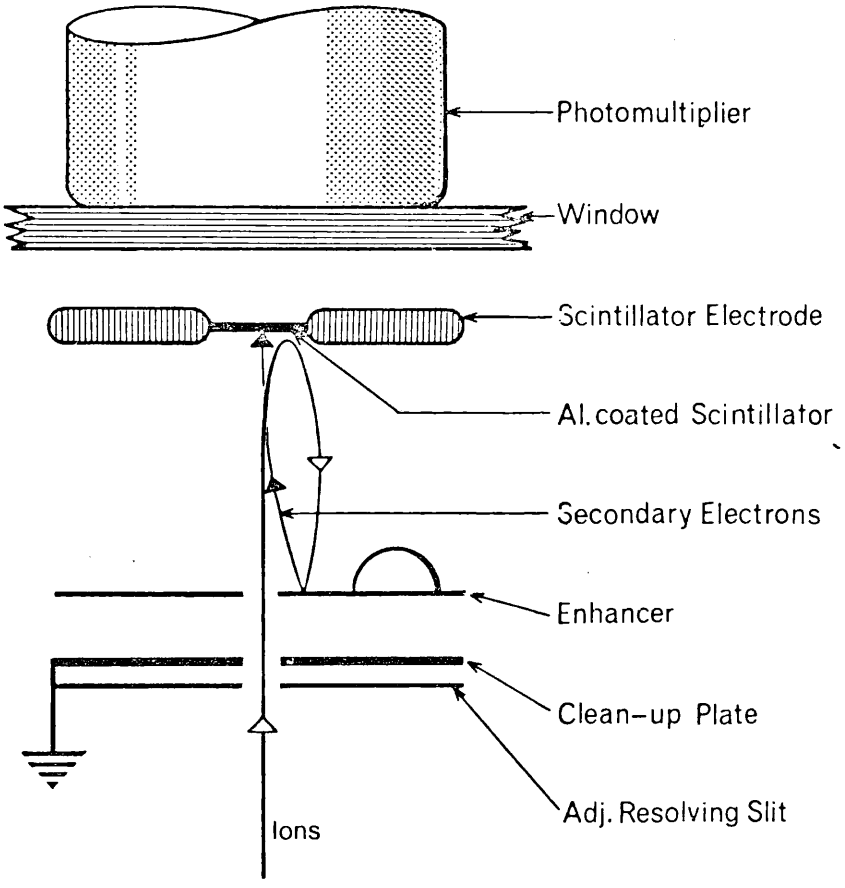

Photomultiplier
Window
Scintillator Electrode
Al. coated Scintillator
Secondary Electrons
Enhancer
Clean-up Plate
Adj. Resolving Slit
Ions

Fig. II-4

where V is the accelerating voltage, and

$$\frac{V_c}{V} = \frac{m_2}{m_1} = \frac{m^*}{m_2}$$

By this method, the metastable ion at $^{m}/_{e}$ 56.3 in the spectrum of butane -1,2,4-triol phenylboronate was assigned the transition

$^{m_1}/_{e}$ 147 $\longrightarrow$ $^{m_2}/_{e}$ 91 (m* calc. = 56.3), since the

accelerating voltage V = 7896 volts,

the cut-off voltage V_c = 4900 volts,

and $m_2 = \frac{V}{V_c} \times m^* = 90.7$

Non-integral masses are attributable to instrumental error and have no significance. An alternative origin of this metastable ion could also have been the transition $^{m_1}/_{e}$ 192 $\longrightarrow$ $^{m_2}/_{e}$ 104 (m* calc. = 56.3).

The indirect method is more time consuming though capable of higher sensitivity. In fact this method showed the transition $^{m_1}/_{e}$ 192 $\longrightarrow$ $^{m_2}/_{e}$ 104 also occurred to a smaller extent. The defocussing technique[51] observes metastable ions decomposing in the field free region between the "ion source" and electrostatic analyser.

A parent ion of mass m_1 having been accelerated by a potential V (volts) after leaving the "ion source" would have a kinetic energy of Ve electron volts. But this would be reduced in a metastable transition

$$m_1^+ \longrightarrow m_2^+ + (m_1 - m_2)$$

to $\frac{m_2}{m_1}$ Ve electron volts and the ion would not be transmitted by the

electrostatic analyser under normal operating conditions.
If the parent ion were given a greater kinetic energy initially by raising the accelerating potential to V_1 volts, then it would be transmitted by an unchanged electrostatic analyser (E volts) if

$$eV = \frac{m_2}{m_1} eV_1$$

$$\text{or} \quad \frac{V_1}{V} = \frac{m_1}{m_2}$$

Normal ions would have a high kinetic energy, collide with the walls of the electrostatic analyser and not be transmitted. The effect would be that only metastable ions would be received by the electron-multiplier, which could consequently be used near its maximum gain.

In practice, the spectrometer must be modified since the ratio V/E is usually fixed. Increasing V, with the electrostatic and magnetic analysers set to collect ions at the normal daughter position, has the effect of showing a series of ions of mass m_2 with decreasing kinetic energies and these have been produced from parents of different masses by metastable transitions. Thus all the precursors of a particular ion may be established by scanning the accelerating potential V and a complete fragmentation pattern assembled.
The following results were obtained in the spectrum of butane -1,2,4-triol phenylboronate.

Daughter ($m/_e$)	$V_1/_V$	Intensity of m*	Parent ($m/_e$)
91	1.616	25	147.1
104	1.830	2	192.1

Thus both processes were found to contribute to the metastable ion at $m/_e$ 56.3.

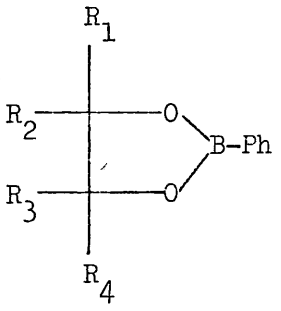
Characterisation of ions in the spectra by precise mass measurement and determination of their immediate precursors from observation of metastable ions led to the formation of a pattern by which the molecular ions fragment. The fragmentation patterns of the phenylboronates of diols were found to be similar and will be compared in the next chapter.

III Electron Impact Induced Fragmentation of Phenylboronates of Diols.

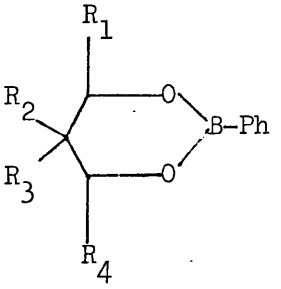
The mass spectra of a series of phenylboronates of known structure were studied in an attempt to elucidate the major fragmentation pathways. The series was commenced with the parent compound, phenylboronic anhydride (1), the spectrum of which has since been published[52].

The most abundant ion in the spectrum (base peak) occurs at the molecular weight $^{m}/_{e}$ 312; hence the presence of anhydride as an impurity in an ester may be discovered easily. The low abundance of fragment ions reflects the stability of its cyclic boronate structure[53], and the great strength of the B-phenyl bond.

2,	R_1 = H,	R_2 = H,	R_3 = H,	R_4 = H
3	H	H	H	CH_3
4	CH_3	H	H	CH_3
4A	CH_3	D	D	CH_3
5	CH_3	CH_3	CH_3	CH_3



6,	R_1 = H,	R_2 = H,	R_3 = H,	R_4 = H
7	H	H	H	CH_3
8	CH_3	H	H	CH_3
9	H	CH_3	CH_3	H



10

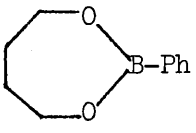


Fig. III-1

The spectra of phenylboronates of a series of diols (2-10) shown in Fig. III-1 were obtained. Three fragmentation processes common to phenylboronates of all the diols which were studied are the following:-

A: Fission of exocyclic C-C bonds,

B: Rearrangement followed by formation of hydrocarbon ions,

C: Elimination of oxo molecules.

These processes are shown in Fig. III-2 for propane-1,2-diol phenylboronate (3).

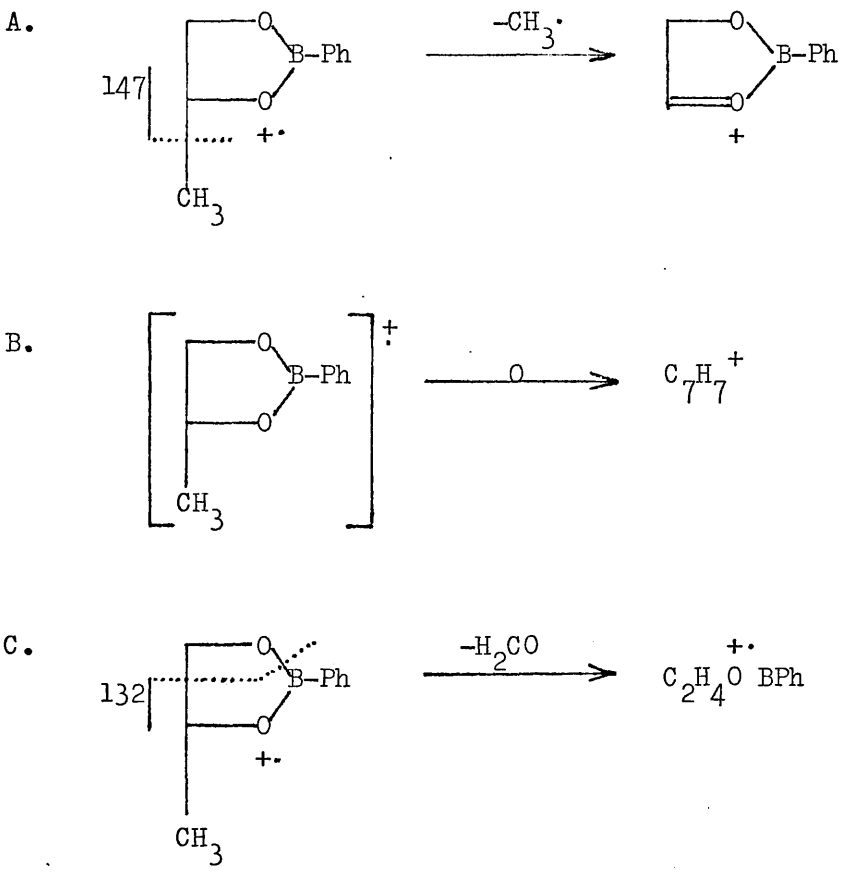


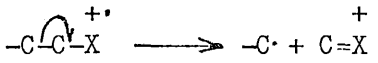
Fig. III-2

The three processes represent the initial manner in which the majority of molecules break up in the "ion source" after ionisation.

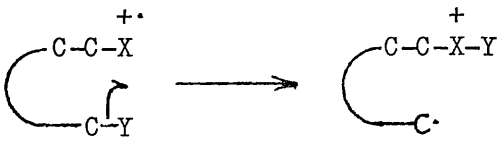
A rationalisation of the bond cleavages involved is most conveniently effected by assuming preferential localisation of charge at specific sites in the molecular ion, and in fragment ions undergoing further decomposition. The localised charged or radical site is then considered to trigger fragmentation and electron book-keeping is effected by using "fish hooks" to describe one electron shifts.

This is not to imply that the positive charge is localised totally on one atom, nor is the concept of triggering necessary to explain the phenomenon of fragmentation. In fact, the electron deficiency in the ion makes itself felt over all bonds leading to changes in bond strengths, and product stability also determines the course of the decomposition.

The real significance of the localised charge concept becomes evident only when one considers the most important aspect of rationalising electron impact induced fragmentation, namely the ability to predict which bonds are most likely to break in a given molecule. The molecular ion is, by definition, an odd-electron species (ion radical) and, as has already been emphasised by McLafferty[54], even-electron ions are frequently favoured energetically over their odd-electron counterparts. Hence we may assume that a reaction of relatively low activation energy is associated with pairing the electron at the radical site. In the absence of experimental evidence about the nature of the bond cleavages, it is assumed that they are of homolytic character. The methods of satisfying the electron deficiency in the molecular ion are thus homolysis of the adjacent linkage to produce a double bond,



or reaction with another radical (Y·) to form a new bond. Since ion molecule reactions are rare, Y must be attached to the original molecule and Y· would have to be generated by homolytic fission. Most frequently Y is a hydrogen atom situated within an optimal distance from the electron deficient centre.



Both these methods are used in the three processes A,B and C to satisfy the electron deficiency of the molecular ion of phenylboronates of diols.

III-A. Fission of exocyclic C-C bonds.

The molecular ion(M^+) may lose an exocyclic methyl group, as a methyl radical, from a position α to an oxygen atom by cleavage of a C-C bond producing a resonance stabilised oxonium ion. In all cases, a metastable ion is formed by this process. For example, the molecular ion of propane-1,2-diol phenylboronate (3) forms an oxonium ion I, $^{m}/_{e}$ 147, $C_8H_8BO_2$, together with a metastable ion $^{m}/_{e}$ 133.4 (Fig. III-3). Formation of an oxonium ion is the driving force for this reaction. Thus 2,2-dimethylpropane-1,3-diol phenylboronate (9) does not form an appreciable $M-CH_3$ ion, (see Table III-1). The oxonium ions are stable; often their production is the dominant reaction and they are the base peak of the spectrum. They often become doubly charged and give rise to peaks at half integral mass values, for example $^{m}/_{e}$ 73.5 in the spectrum of (3)

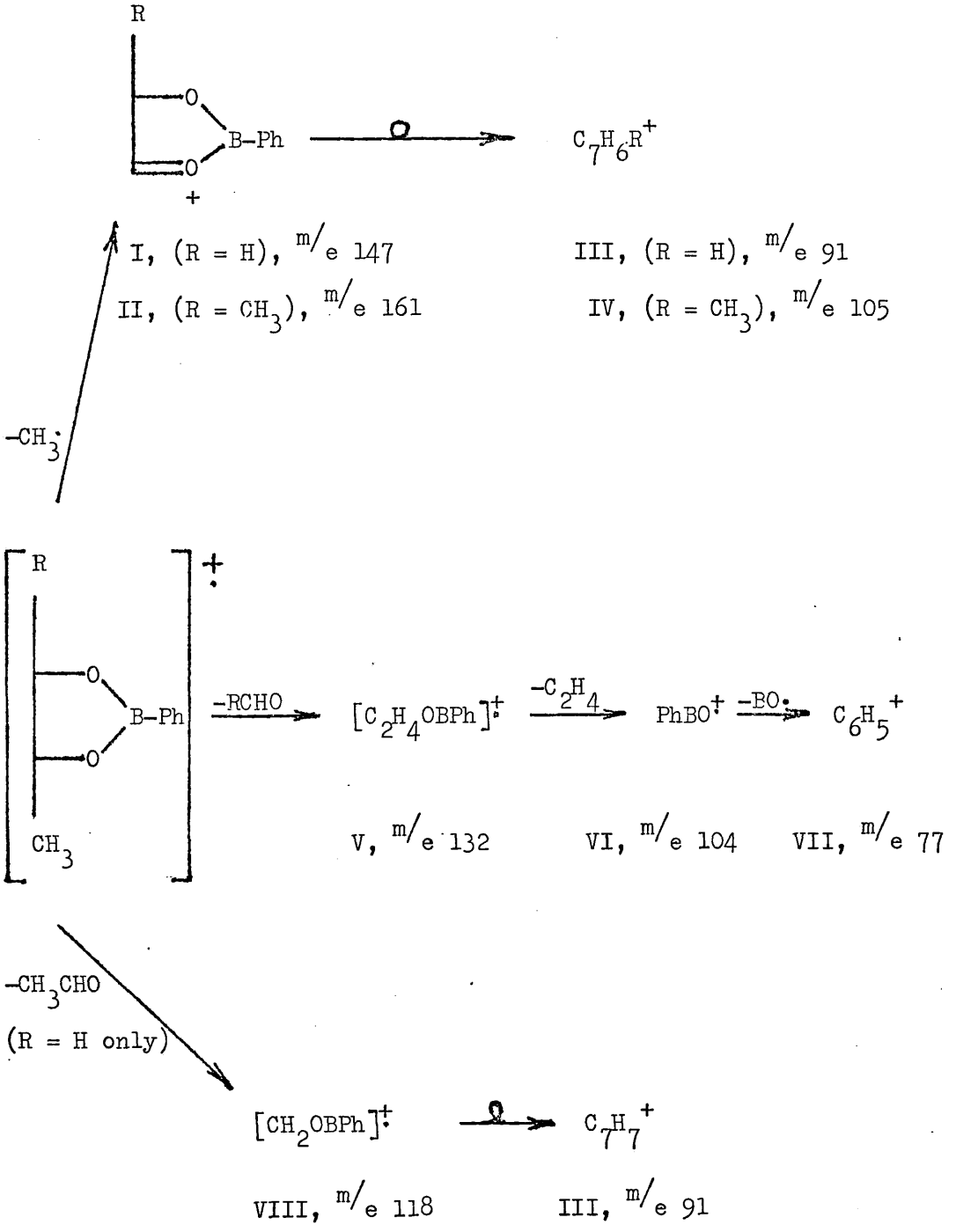


Fig. III-3

Mass numbers refer to ^{11}B isotope only.

Table III-1. Principal peaks in the mass spectra of phenylboronates of diols.

Abundances of ions $(\%\Sigma_{25})^{\neq}$

Ester	M^+	$(M-CH_3)^+$	$C_6H_6BO^+$	$C_6H_5BO^+$
2	31.7	-	0.5	1.1
3	15.1	25.1	5.8	5.0
4	13.4	21.0	14.4	10.4
5	9.5	12.8	26.7	3.3
6	27.9	-	8.0	36.0
7	18.8	13.6	13.3	20.5
8	16.8	10.2	29.4	0.4
9	12.2	0.0	9.5	2.7
10	22.6	-	32.4	5.3

$\neq$ sum of all isotopic species

and $^{m}/_{e}$ 80.5 in the spectra of (4) and (7).

In general, esters having only hydrogen atom substituents form the most abundant molecular ions as removal of a hydrogen radical to produce an oxonium ion is an energetically unfavourable process, e.g. (2), (6) and (10). The spectra hence appear more simple, (see appendix).

Except in the case of pinacol phenylboronate (5), the oxonium ions rearrange and decompose to give hydrocarbon ions. An example is the ion II, $^{m}/_{e}$ 161, $C_9H_{10}BO_2$, (Fig. III-3) produced from butane -2,3-diol phenylboronate (4) which forms IV, $^{m}/_{e}$ 105, C_8H_9. In the mass spectrum of the deuterated analogue 2,3-d_2-butane-2,3-diol phenylboronate (4A), the oxonium ion appears at $^{m}/_{e}$ 163, $C_9H_8D_2BO_2$,

while the hydrocarbon ion incorporates one deuterium atom and appears at $^{m}/_{e}$ 106, C_8H_8D. Similarly the oxonium ion IX, $^{m}/_{e}$ 161, $C_9H_{10}BO_2$, produced from butane-1,3-diol phenylboronate (7) forms the hydrocarbon ion III, $^{m}/_{e}$ 91, C_7H_7 ,(Fig. III-4).

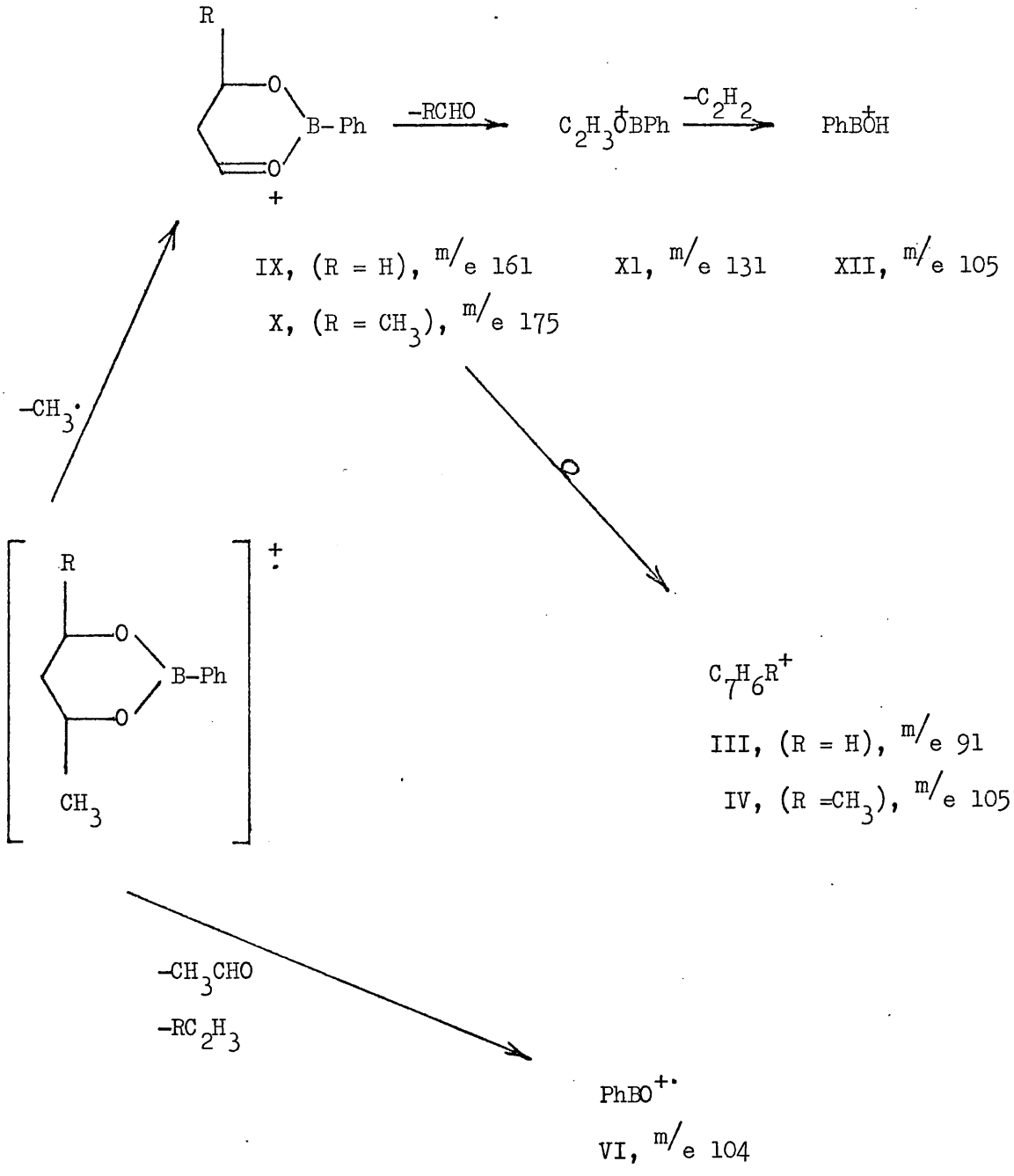


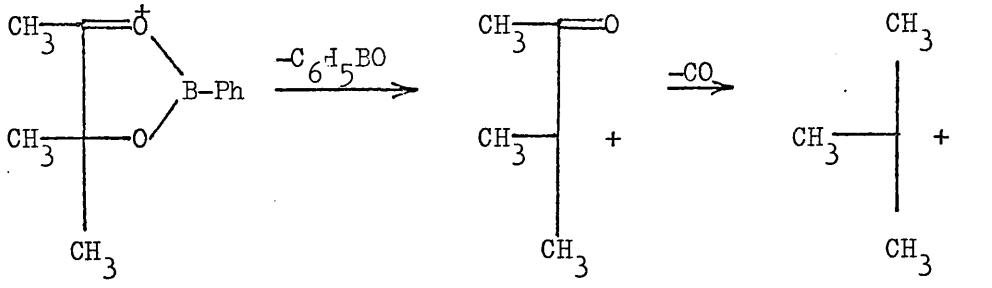
Fig. III-4

Mass numbers refer to ^{11}B isotope only.

A metastable ion at $^{m}/_{e}$ 51.4 supports this rearrangement (Table III-2). Thus it appears that the phenyl group migrates in the oxonium ion to the carbon atom which still bears its substituent.

The oxonium ions IX, $^{m}/_{e}$ 161, $C_9H_{10}BO_2$, and X, $^{m}/_{e}$ 175, $C_{10}H_{12}BO_2$, also undergo an elimination analogous to a Retro Diels Alder fragmentation to eliminate an aldehyde molecule giving XI, $^{m}/_{e}$ 131, C_8H_8BO, evidenced by a metastable ion at $^{m}/_{e}$ 106.6 in the spectrum of (7). Ion XI eliminates acetylene, by migration of a hydrogen atom, to give XII, $^{m}/_{e}$ 105, C_6H_6BO, producing a metastable ion at $^{m}/_{e}$ 84.2 in the spectra of both (7) and (8).

The oxonium ion which is formed from pinacol phenylboronate (5) by removal of a methyl radical (metastable ion $^{m}/_{e}$ 175.1) eliminates C_6H_5BO and forms an ion XIII, $^{m}/_{e}$ 85, C_5H_9O,(Fig. III-5). This process produces a metastable ion at $^{m}/_{e}$ 38.2. By performing defocussing experiments, it was established that the decomposition of XIII by elimination of carbon monoxide to give the hydrocarbon ion XIV, $^{m}/_{e}$ 57, C_4H_9, also produced a metastable ion at $^{m}/_{e}$ 38.2.



$^{m}/_{e}$ 189 XIII, $^{m}/_{e}$ 85 XIV, $^{m}/_{e}$ 57

Fig. III-5

III-B Hydrocarbon ions produced by rearrangement processes

Highly unsaturated hydrocarbon ions containing 7,8, 9 and/or 10 carbon atoms have been observed in the spectra of phenylboronates of diols[55] by precise mass measurements. Their abundances are summarised in Table III-2. From metastable ions present in the spectra, it is deduced that hydrocarbon ions arise from rearrangements of

(i) the molecular ions,

(ii) the oxonium ions,

and(iii) the ion VIII, $^{m}/_{e}$ 118, C_7H_7BO.

Specific examples are as follows.

(i) The molecular ion of butane-1,4-diol phenylboronate (10) rearranges to produce XV, $^{m}/_{e}$ 104, C_8H_8, directly (Fig. III-6).

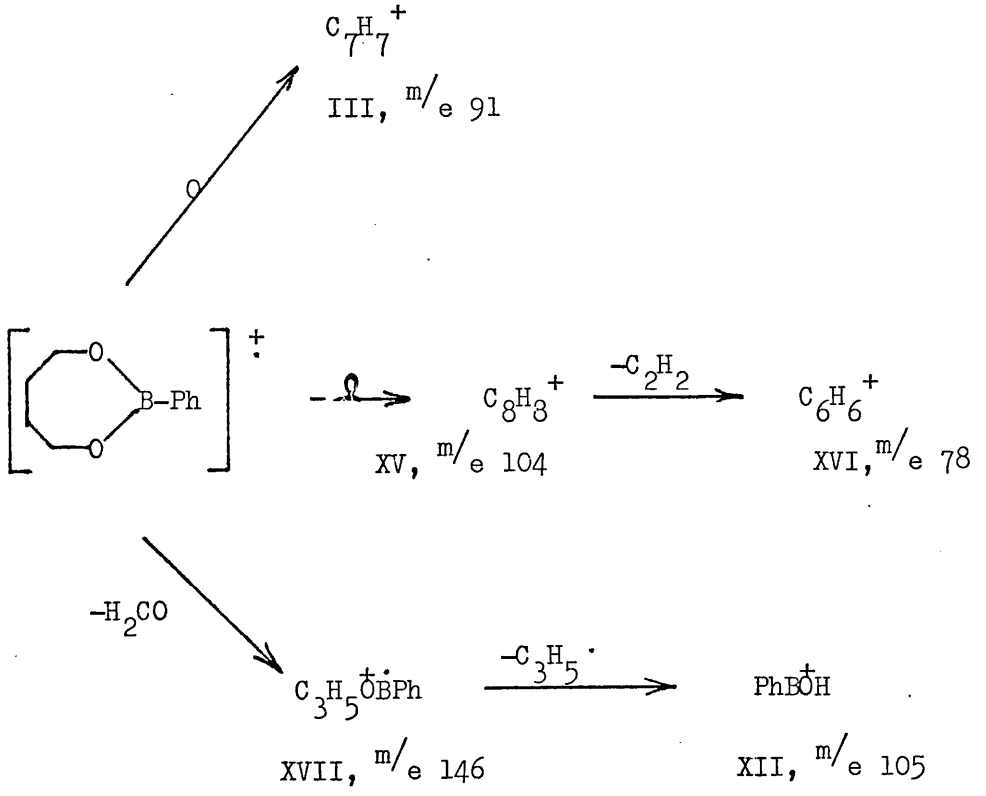


Fig. III-6

Table III-2. Hydrocarbon ions formed from diol phenylboronates.

Ester	Abundance of hydrocarbon ions ($\%\Sigma_{25}$)≠						Metastable ions	
	$C_7H_7^+$ m/e 91	$C_8H_8^+$ m/e 104	$C_8H_9^+$ m/e 105	$C_9H_{10}^+$ m/e 118	$C_9H_{11}^+$ m/e 119	$C_{10}H_{12}^+$ m/e 132	Obs. (m/e)	Assignment ≠
2	14.5	-	-	-	-	-	56.1	$M^+ \rightarrow C_7H_7^+$
							70.2	VIII $\rightarrow C_7H_7^+$
3	6.5	1.9	2.2	-	-	-	56.3	I $\rightarrow C_7H_7^+$
							70.2	VIII $\rightarrow C_7H_7^+$
4	1.5	5.8	2.6	-	-	-	61.5	$M^+ \rightarrow C_8H_8^+$
							51.5	II $\rightarrow C_7H_7^+$
							68.6	II $\rightarrow C_8H_9^+$
5	0.2	-	-	11.4	-	-	68.2	$M^+ \rightarrow C_9H_{10}^+$
6	4.6	-	-	-	-	-	51.1	$M^+ \rightarrow C_7H_7^+$
7	6.6	1.0	1.3	-	-	-	51.4	IX $\rightarrow C_7H_7^+$
8	1.0	2.7	11.3	-	-	-	63.1	X $\rightarrow C_8H_9^+$
9	2.3	-	-	-	1.3	0.9	91.8	$M^+ \rightarrow C_{10}H_{12}^+$
							70.2	VIII $\rightarrow C_7H_7^+$
10	2.0	3.5	-	-	-	-	47.1	$M^+ \rightarrow C_7H_7^+$
							61.5	$M^+ \rightarrow C_8H_8^+$

≠ ^{12}C isotope only

≠ Calculated using ^{11}B.

That $^{m}/_{e}$ 104 is XV, C_8H_8, and not the isobaric ion VI, C_6H_5BO, was established by precise mass measurement and two metastable ions at $^{m}/_{e}$ 61.5 and $^{m}/_{e}$ 61.8 in an abundance ratio of 4:1. This has already been discussed in the preceding chapter for butane-2,3-diol phenylboronate (4).

(ii) The oxonium ion X, $^{m}/_{e}$ 175, $C_{10}H_{12}BO_2$, produced from pentane-2,4-diol phenylboronate (8) rearranges and gives IV, $^{m}/_{e}$ 105, C_8H_9, evidenced by two metastable ions at $^{m}/_{e}$ 63.0 and $^{m}/_{e}$ 63.4 in an abundance ratio of 4:1.

(iii) The ion VIII, $^{m}/_{e}$ 118, C_7H_7BO, produced from ethane-1,2-diol phenylboronate by elimination of formaldehyde rearranges giving III, $^{m}/_{e}$ 91, C_7H_7, and a metastable ion at $^{m}/_{e}$ 70.2.

It has been suggested that III, $^{m}/_{e}$ 91, C_7H_7, in the spectrum of (2) is the tropylium ion [56,57]. The formation of such a highly stable species would explain the unusual cleavage of the strong B-phenyl bond. It has also been suggested[58] that the distribution of hydrocarbon fragments at low mass indicates that III is the tropylium ion. In particular $^{m}/_{e}$ 65, attributed to the cyclopentadienyl cation or more likely an acyclic isomer[59,60], is produced by elimination of acetylene and gives rise to a metastable ion at $^{m}/_{e}$ 46.4. However, the structure of III may only be decided by appearance potential measurements.

A mechanism has been proposed[58] recently for the formation of the tropylium ion from ethane-1,2-diol phenylboronate (2) and propane-1,3-diol phenylboronate (6). This involves α-cleavage in the molecular ion and attack at the ortho position of the aromatic ring by a cationic site mechanism in the resultant oxonium ion (Fig. III-7). Extension of this proposal to the cases of butane-2,3-diol phenylboronate

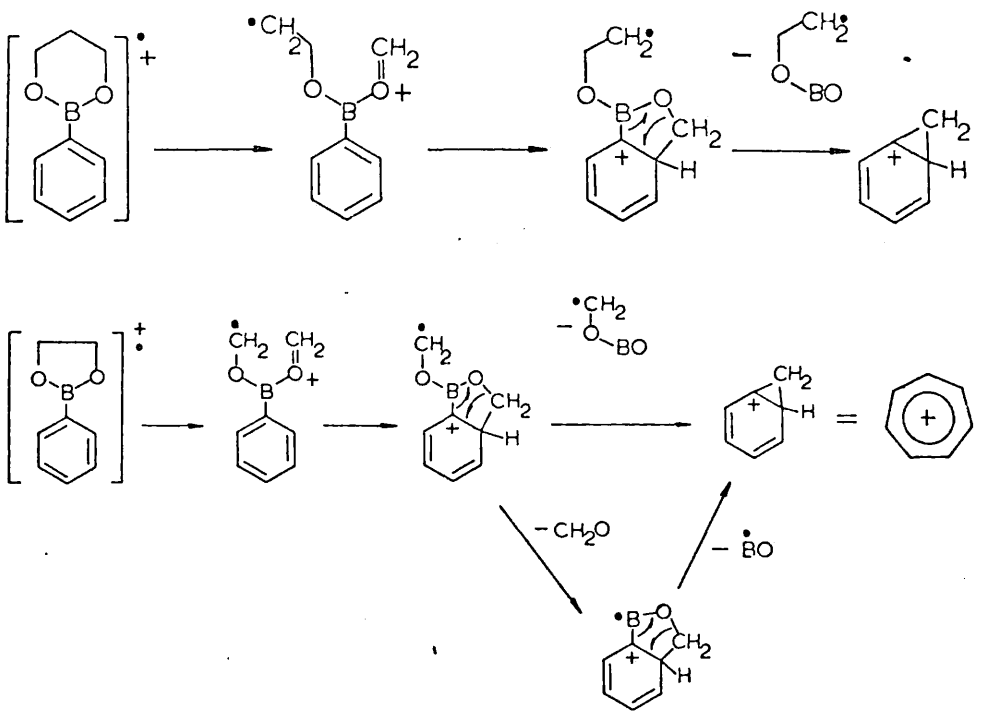


Fig. III-7

Fig. III-8

(4) and pentane-2,4-diol phenylboronate (8) would predict rearrangement of the molecular ions to give $^{m}/_{e}$ 105, C_8H_9, directly (Fig. III-8). The parent ions of IV, $^{m}/_{e}$ 105, C_8H_9, are difficult to determine due to the presence of an isobaric ion C_6H_6BO but metastable ions indicate that these are the oxonium ions II, $^{m}/_{e}$ 161, $C_9H_{10}BO_2$, and X, $^{m}/_{e}$ 175, $C_{10}H_{12}BO_2$. No mechanism has been put forward for the formation of XV, $^{m}/_{e}$ 104, C_8H_8. Indeed its structure is unknown. Thus, the author has been unable to provide evidence that the mechanism of Fig. III-7 is a general one. It might indeed be doubtful whether III, C_7H_7, is produced from (2) and (6) by this mechanism. Such hydrocarbon ions have also been observed in the spectrum of a borate ester[61]. The compound 4,6-dimethyl-2-phenoxy-1,3,2-dioxaborinan was found to produce hydrocarbon ions of formula C_7H_7, C_8H_8, and C_8H_9 on electron impact. Recently, it has been discovered that tropylium ions occur also in the mass spectra of acyclic esters of phenylboronic acid[62].

III-C. Elimination of oxo molecules.

A molecule containing a carbonyl function is eliminated from the molecular ion by cleavage of two bonds of the boronate ring. In the case of propane-1,2-diol phenylboronate (3), formaldehyde is eliminated forming V, $^{m}/_{e}$ 132, C_8H_9BO, which is also formed from (4) by elimination of acetaldehyde (Fig. III-3). Acetaldehyde may also be eliminated from (3) to form VIII, $^{m}/_{e}$ 118, C_7H_7BO, which may be formed from (2) by elimination of formaldehyde. The ion VIII rearranges to III, $^{m}/_{e}$ 91, C_7H_7. Elimination of ethylene from V, $^{m}/_{e}$ 132, C_8H_9BO, to form VI, $^{m}/_{e}$ 104, C_6H_5BO, produces a metastable ion at $^{m}/_{e}$ 81.9. Decomposition of VI occurs giving a phenyl ion

VII, $^{m}/_{e}$ 77, C_6H_5, and a metastable ion at $^{m}/_{e}$ 57.0.

Absence of fragments M-104 and absence of metastable ions at mass values $104^2/M$ suggest that VI is not produced directly from the molecular ion of five-membered boronate rings. This would seem to imply that epoxide molecules are not formed, in keeping with similar observations on the mass spectra of cyclic sulphites and carbonates[63]. However ions M-104 of formula C_2H_4S have been found in high abundance in the spectra of dithioborolane[57].

The molecular ion of pinacol phenylboronate (5) eliminates acetone forming an ion $^{m}/_{e}$ 146, $C_9H_{11}BO$. This is probably not of the same structure as XVII, $^{m}/_{e}$ 146, $C_9H_{11}BO$ (Fig. III-6) formed from the molecular ion of (10) by elimination of formaldehyde, since XVII rearranges to produce XII, $^{m}/_{e}$ 105, C_6H_6BO and a metastable ion at $^{m}/_{e}$ 75.5.

III-D. Double elimination - a fragmentation exclusive to a six-membered boronate ring.

In contrast to the five- and seven-membered boronate rings, metastable ions occur in the spectra of all the 1,3-diol phenylboronates studied, which indicate that VI, $^{m}/_{e}$ 104, C_6H_5BO, is produced directly from the molecular ion. This fragmentation has been interpreted in the case of propane-1,3-diol phenylboronate as proceeding by elimination of trimethylene oxide from the molecular ion[58] but it is more likely to proceed by a double elimination. Such an elimination has been observed to occur in the mass spectrum of toluene[60]. This process is shown in Fig. III-4 for compounds (7) and (8).

Evidence for the double elimination is quite substantial. Propane-1,3-diol phenylboronate (6) produces a metastable ion at $^{m}/_{e}$ 107.6 corresponding to the molecular ion eliminating formaldehyde to form V, $^{m}/_{e}$ 132, C_8H_9BO, (Fig. III-9). Another metastable ion at $^{m}/_{e}$ 81.9 corresponds to V subsequently eliminating ethylene to form VI, $^{m}/_{e}$ 104, C_6H_5BO. A third metastable ion at $^{m}/_{e}$ 66.8 corresponds to the molecular ion producing VI directly. Hence this process corresponds to the double elimination of formaldehyde and ethylene.

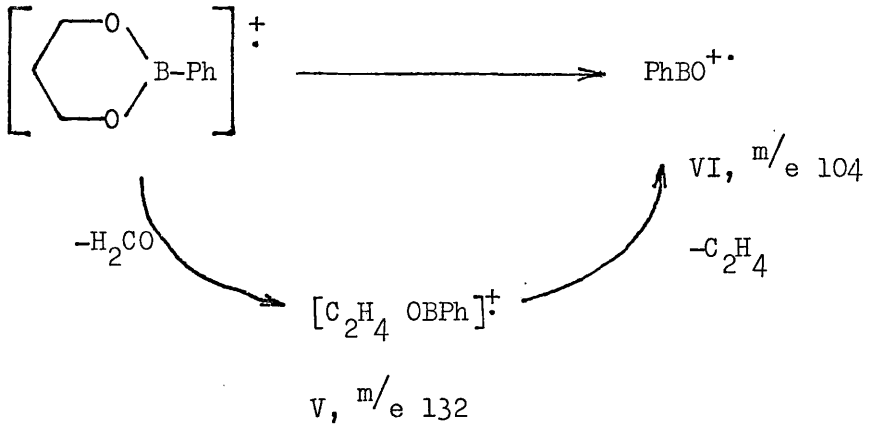


Fig. III-9

When the boronate ring becomes more highly substituted as in 2,2-dimethylpropane-1,3-diol phenylboronate (9), the ionisation potential of the olefin which is produced is reduced to approximately equal that of VI, $^{m}/_{e}$ 104, and both fragments appear in the spectrum. This is equivalent to delocalisation of the positive charge over the whole molecule, (Fig. III-10). The ions VI, $^{m}/_{e}$ 104, C_6H_5BO, and XVIII, $^{m}/_{e}$ 56, C_4H_8, (base peak) were both found by defocussing experiments to be produced directly from the molecular ion. Other metastable ions were recorded at $^{m}/_{e}$ 134.7,

formed when the molecular ion eliminates formaldehyde, and $^{m}/_{e}$ 56.9 corresponding to the formation of VI, $^{m}/_{e}$ 104. The occurrence of a fragmentation exclusive to six-membered boronate rings has thus been established.

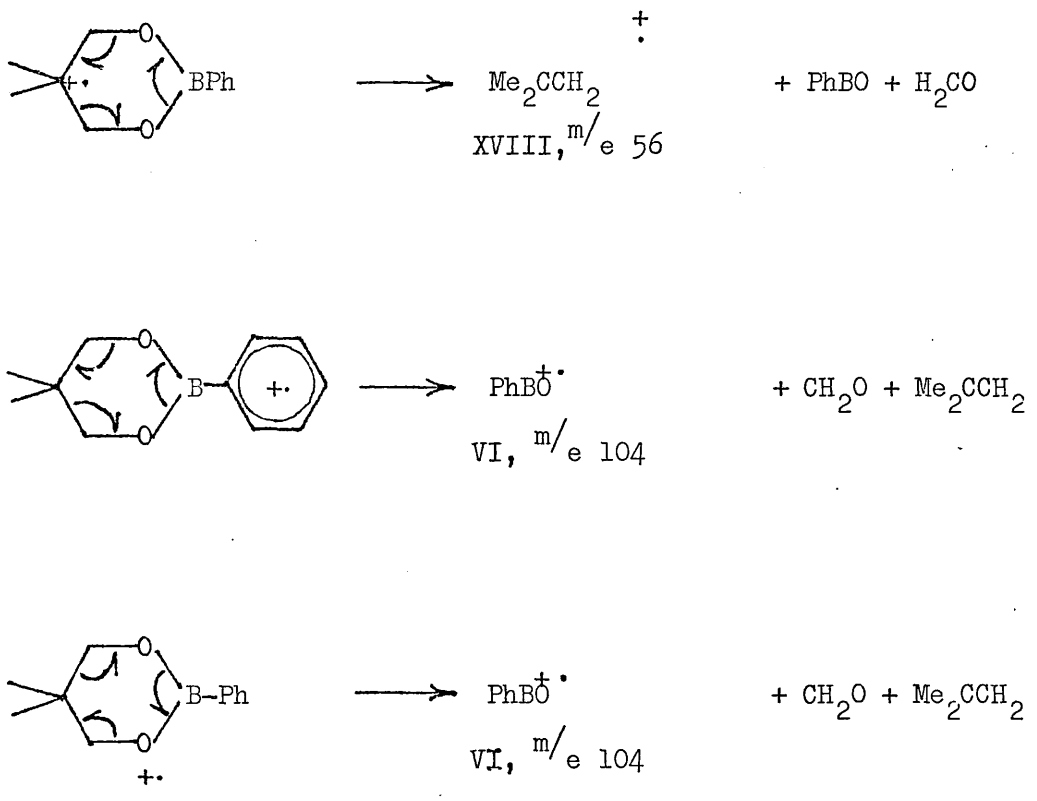


Fig. III-10

It now remains for the general fragmentation pattern which has been uncovered to be applied to the problem of interpreting the spectra of phenylboronates whose structures are ambiguous. The phenylboronate of an acyclic trihydric alcohol may at most have three different structures. The correct structure may be immediately obvious from its mass spectrum.

IV Synthesis and Structure of Phenylboronates of Triols.

Structures of phenylboronates derived from only two unsubstituted acyclic polyols[35] are known with certainty, although more than a dozen have been prepared. This is because a reliable method has not yet been developed for determining the structures of bi- and tricyclic esters. Phenylboronates of acyclic trihydric alcohols obviate this problem since formation and characterisation of a derivative is alone sufficient to assign a reliable structure.

With this view in mind, phenylboronates of the two commercially available triols (glycerol and butane-1,2,4-triol) were prepared in toluene. Glycerol phenylboronate had previously been prepared under different conditions[35].

A review of previous work shows that in all cases except that of galactitol bis-phenylboronate, a primary hydroxyl group forms the derivative. This has happened in glycerol[35], ribitol, L-lyxitol and xylitol phenylboronates[38], possibly for stereochemical reasons because a primary hydroxyl group can co-ordinate to boron most easily. Triols without primary hydroxyl groups should form phenylboronates which will yield information concerning the favoured ring size for formation of the esters. Hence, the syntnesis of four triols having terminal methyl groups was undertaken. These were L-erythro-butane-1,2,3-triol; ribo-, L-arabino-, and xylo-pentane-2,3,4-triols. The preparation of L-arabino-pentane-2,3,4-triol[64] and xylo-pentane-2,3,4-triol[65] have been previously reported but by different synthetic routes to those used by the author. After the completion of this work, the synthesis of L-erythro-butane-1,2,3-triol[66] was reported, but again using a different route.

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IV-A Synthesis of deoxy compounds.

Formation of terminal methyl groups was attempted by the following methods:-

Reduction of toluene-p-sulphonylhydrazones

Desulphurisation of thioacetals by Raney nickel

Reduction of toluene-p-sulphonate esters.

(i) Reduction of toluene-p-sulphonylhydrazones.

The derivatives of toluene-p- sulphonylhydrazide can be grouped into two categories: the toluene-p-sulphonylhydrazones (derivatives of aldehydes and ketones: general formula $Ts-NH-N=CR_1R_2$) and the substituted toluene-p-sulphonylhydrazides (acyl, aryl or alkyl-toluene-p- sulphonylhydrazides: general formula Ts-NH-NH-R). The reduction sequence involves formation of a toluene-p- sulphonyl-hydrazone of the aldehyde or ketone and reduction of the C=N double bond to form an alkyl toluene-p-sulphonylhydrazide as an intermediate. This decomposes on heating to give nitrogen, toluene-p-sulphinic acid and the hydrocarbon derived from the aldehyde or ketone. The method thus effects an overall conversion from a carbonyl function to a methylene function.

The reaction has been employed in steroid[67] and carbohydrate synthesis[68]. In the latter case, 1-deoxy-D-glucitol was prepared in a 42% yield. Repetition of the reaction under near identical conditions (Expt. 5) produced variable yields but none higher than this figure. It was considered that a closer examination might improve the reaction, increasing the yield, and ultimately render unnecessary chromatography on a cellulose column required to separate the biproduct.

The identity of the biproduct, though not established with certainty, is most probably the reduced form of the sugar. In the case of D-glucose toluene-p-sulphonylhydrazone, the biproduct could not be differentiated from D-glucitol.

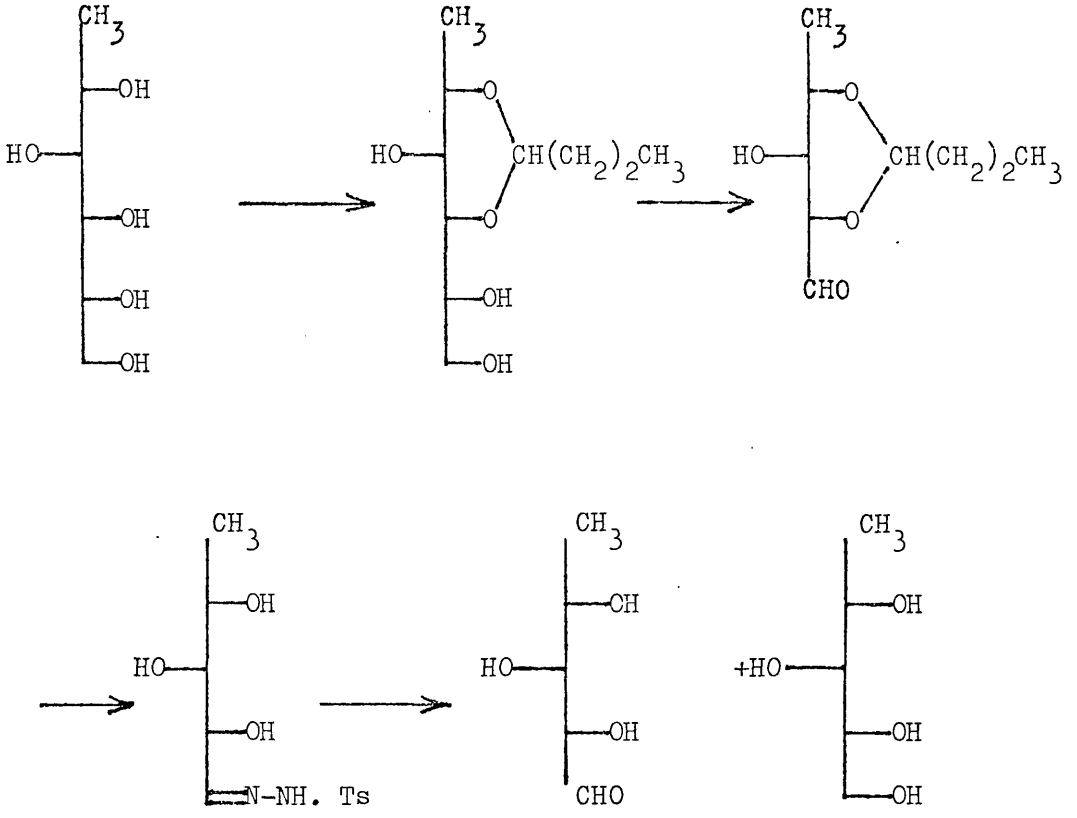
It is well known that alkyl toluene-p-sulphonylhydrazones decompose on heating under alkaline conditions to yield olefins, the Bamford-Stevens reaction[69]. It has been demonstrated[70,71] that the decomposition proceeds by formation of a diazo compound which may undergo either proton transfer from proton donor solvents with subsequent cationic decomposition, or carbenic decomposition in aprotic solvents. In some cases it has been observed that alcohols are formed[72] and a mechanism has been proposed for their formation from the parent hydrazones in the presence of base. It was concluded that protonation of nitrogen led to the formation of toluene-p-sulphinate esters which were converted smoothly to alcohols. An aprotic reaction mixture prevented formation of the alcohols.

Comparison with the required formation of 1-deoxy-D-glucitol indicated that reduction of D-glucose toluene-p-sulphonylhydrazone was probaly slow and that premature increase of the reaction temperature was causing decomposition of the starting material in a similar fashion to that observed by Wilt et.al.[72]. In addition, water present in the solvent may have caused slight hydrolysis of D-glucose toluene-p-sulphonylhydrazone forming D-glucose which would be reduced rapidly to D-glucitol displacing the equilibrium further.

The last mentioned possibility was simply overcome by freeing the solvent, methanol, of water. Change of solvent to an aprotic system, used by Wilt et.al. to prevent formation of alcohols, would

have rendered the starting material totally insoluble. In any case, D-glucose toluene-p-sulphonylhydrazone was itself a source of protons. Potassium borohydride reacts slowly with methanol hence a large excess (7 moles) was required to effect complete reduction of the hydrazone over a long period. Boiling of the reaction mixture was delayed for 48 hours to effect complete reduction at ambient temperature. Potassium borohydride was added slowly throughout this period. Decomposition of the toluene-p-sulphonylhydrazide by boiling and work up of the reaction mixture in the previous manner consistently yielded 85% conversion to 1-deoxy-D-glucitol (Expt. 6). Similar success was achieved in improving the preparation of 1-deoxy-D-xylitol (Expt. 8).

The preparation of 1-deoxy-D-glucitol was the first step in the synthesis of xylo-pentane-2,3,4-triol by a series of reactions (Fig. IV-1) involving the intermediates 1-deoxy-2,4-O-butylidene-D-glucitol (Expt. 9), which upon oxidation with sodium periodate yielded 2,4-O-butylidene-5-deoxy-L-xylose. On hydrolysis, 5-deoxy-L-xylose (Expt. 10) was produced as a syrup from which a toluene-p-sulphonylhydrazone was prepared (Expt. 11). However, reduction of this derivative with potassium borohydride produced 5-deoxy-L-xylose, 1-deoxy-D-xylitol and trace amounts of a triol (Expt. 12).



Ts = $-SO_2C_6H_4.CH_3$

Fig. IV-1

A possible explanation of this obtuse behaviour may involve an equilibrium between furanoid and acyclic forms of 5-deoxy-L-xylose toluene-p-sulphonylhydrazone. The equilibrium may lie well in favour of the furanoid form which would not be reduced. This proposal would require that other toluene-p-sulphonylhydrazones derived from pentoses and hexoses exist in a pyranoid ring form and that this is convertible to the acyclic form, illustrated in Fig. IV-2 for D-ribose toluene-p-sulphonylhydrazone.

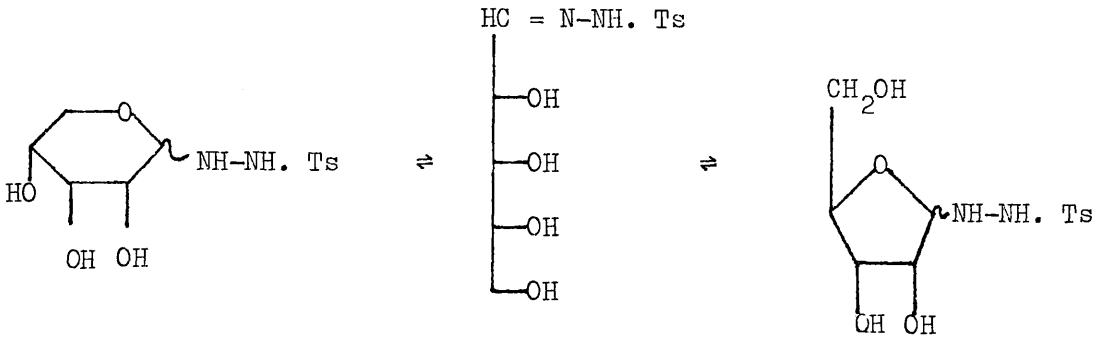


Fig. IV-2

(ii) Reductive desulphurisation of dialkyldithioacetals with Raney nickel.

Reductive desulphurisation of aldose dialkyldithioacetals[73,74,75] using an excess of Raney nickel catalyst provides a simple method of preparing 1-deoxy sugar alcohols (Fig. IV-3). In a

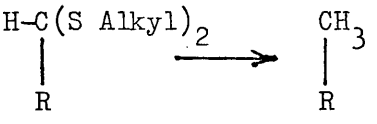


Fig. IV-3

review, Fletcher and Richtmyer[76] questioned the value of using as high catalyst ratios as have been reported in the literature. They tabulate examples of ratios from 9:1 to 15:1 (g. of Raney nickel catalyst to g. of thioacetal derivative). Generally, the yield of 1-deoxy-polyol varied inversely with the catalyst ratio. The decrease in yield was probably due to adsorption of product on the catalyst. Too low a ratio, however, results in incomplete reduction and formation of 1-deoxy-1-S-alkyl polyols[77].

Conversion of 5-deoxy-L-arabinose diethyldithioacetal to L-arabino-pentane-2,3,4-triol was effected successfully by reductive desulphurisation[64] (Fig. IV-4) (Expt. 19).

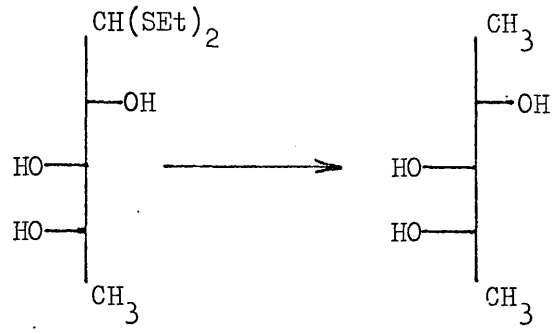


Fig. IV-4

Similar treatment of D-erythrose diethyldithioacetal (Expt. 21) caused formation of a small amount of a diol in addition to the expected product L-erythro-butane-1,2,3-triol (Fig. IV-5).

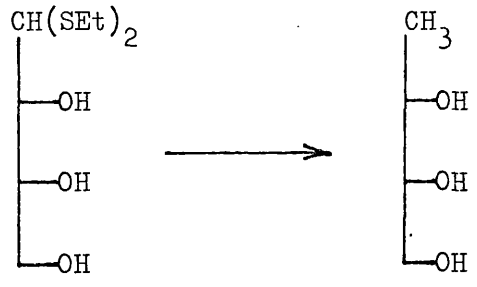


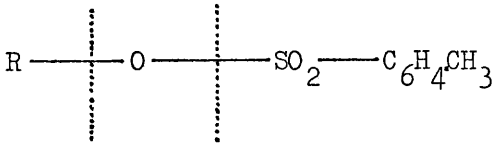
Fig. IV-5

Epimerisation at C2 occurred to a small extent when 2,3,4-tri-O-acetyl-5-deoxy-L-xylose diethyldithioacetal was treated with Raney nickel (Expt. 22). The desired xylo-pentane-2,3,4-triol was thus contaminated with a small amount of L-arabino-pentane-2,3,4-triol, the amount increasing with time spent in contact with the nickel, and at this stage the method was abandoned.

(iii) Reduction of toluene-p-sulphonic esters.

The most common procedure for the sulphonylation of sugars entails the use of toluene-p-sulphonyl chloride in pyridine. The desired sulphonic ester may be contaminated with products containing chlorine; unfortunately the alternative reagent, toluene-p-sulphonic anhydride, is not readily available. Pyridine is used as solvent because of its well-known catalytic effect on esterification of alcohols. A discussion of such reactions has been presented[78] in which the possibility is considered that complexes of pyridine with sulphonyl chlorides are responsible for the catalytic effect of pyridine.

The reduction of toluene-p-sulphonic esters has been studied using lithium aluminium hydride[79] and also Raney nickel[80]. It was concluded that there are two distinct reactions with lithium aluminium hydride, namely hydrogenolysis with fission of either S-O bonds (1) or C-O bonds (2) viz:



(2) (1)

From the examples studied, it appeared that, although aryl toluene-p-sulphonates reacted according to scheme (1), alkyl toluene-p-sulphonates (including esters of carbohydrates) reacted according to either scheme.

The whole field of sulphonic ester derivatives of carbohydrates has been the subject of a review[81] and in general toluene-p-sulphonic esters of secondary alcohols react according to scheme (1) with

lithium aluminium hydride to yield an alcohol. On the other hand, sulphonic esters of primary alcohols react according to scheme (2) to yield terminal deoxy compounds. Many such examples have been reported. Reduction of 5-O-toluene-p-sulphonyl-D-arabinose dithioacetals derived from, methane-, ethane-, 2-propane-, 2-butane- or α-toluene thiols[82] gave the corresponding 5-deoxy-D-arabinose dithioacetal in 40-56% yield. It is interesting to note that the corresponding ribo- and xylo-dithioacetals probably form 5-O-toluene-p-sulphonic esters upon treatment with toluene-p-sulphonyl chloride, but these spontaneously form 2,5-anhydro-dithioacetals[83].

ribo- and xylo-Pentane-2,3,4-triols were hence synthesised by reduction of toluene-p-sulphonic esters. The synthetic route involved formation from the respective pentitols of 1,5-di-O-trityl-2,3,4-tri-O-benzoyl-pentitols (Expts. 23, 26) and 1,5-di-O-toluene-p-sulphonyl-2,3,4-tri-O-benzoyl-pentitols (Expts. 24, 27). The required triols were obtained by reduction with lithium aluminium hydride in boiling tetrahydrofuran (Expts. 25, 28). The reaction sequence is illustrated for the ribo-isomer in Fig. IV-6.

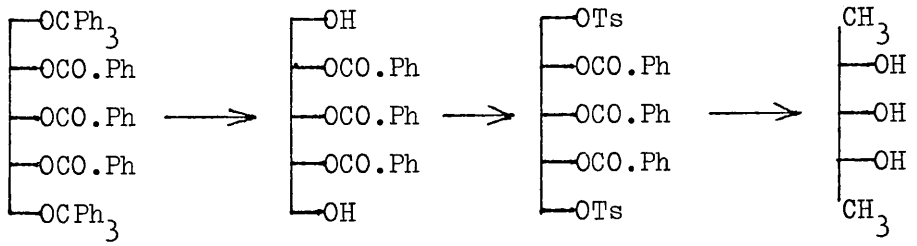


Fig. IV-6

Purity of the prepared triols was established by paper and gas-liquid chromatography. A small quantity was oxidised with

aqueous sodium metaperiodate to effect a structure determination[84]. The periodate uptake was estimated by the arsenite method[85] (Expt. 29), the formic acid produced by titration with alkali, and the formaldehyde produced by the chromotropic acid method[86,87]. The results, shown in Table IV-1, are in agreement with expectations.

Table IV-1. Periodate oxidation of triols.

Triol	Periodate uptake	Formic acid produced	Formaldehyde produced
L-erythro-Butane-1,2,3-triol	1.98 mol.	0.92 mol.	0.97 mol.
ribo-Pentane-2,3,4-triol	2.03 mol.	1.07 mol.	
L-arabino-Pentane-2,3,4-triol	2.03 mol.	1.06 mol.	
xylo-Pentane-2,3,4-triol	2.07 mol.	1.06 mol.	

IV-B Preparation of phenylboronates of triols.

The chosen method for the preparation of the phenylboronates of triols (Expt. 31) was similar to that successfully employed previously for phenylboronates of diols viz. azeotropic distillation of water and toluene from an equimolar mixture of the triol and phenylboronic anhydride. The distillation allows the preparation of esters with a small equilibrium constant for formation, by constant removal of water from the reaction vessel.

The method suffers from the effects of pyrolysis of the triol, which as a result of its lyophobic nature, adheres to the surface of the vessel. Agitation of the flask aids dissolution in the phenylboronic anhydride solution, and use of benzene as solvent[28]

lowers the temperature required to carry out the reaction.

A homogeneous reaction mixture may be achieved by using 2-methoxyethanol as solvent[21] instead of benzene. Both the triol and anhydride are soluble in this solvent at 90°. Reaction time is reduced but the conditions in no way force the equilibrium in favour of the ester. This method proved satisfactory for the preparation of L-arabino-pentane-2,3,4-triol phenylboronate producing an ester identical with that obtained using benzene as solvent. Isolation of the phenylboronate was effected by evaporation of solvents under reduced pressure.

In two cases, this led to the formation of a crystalline solid. One of these was glycerol phenylboronate which had been prepared previously[35] in aqueous methanol. The other was L-erythro-butane-1,2,3-triol phenylboronate. The other reaction mixtures produced viscous liquids, only one of which distilled completely; the remainder formed various amounts of involatile material. Products are shown in Table IV-2. The quantity of residue formed from butane-1,2,4-triol increased with increasing residence time in boiling solvent and on changing from benzene to toluene i.e. increasing temperature.

Retention of configuration during formation of a phenylboronate from L-arabino-pentane-2,3,4-triol was established by hydrolysis, (Expt. 33). Retention of configuration is in agreement with findings of Ferrier et.al.[29] concerning methyl α-D-glucopyranoside.

Table IV-2. Phenylboronates of triols

Parent triol	Solvent used for preparation	Product	m.p.	b.p.	%B found	%B calc.
Glycerol	toluene	(11)	76-78°		6.10	6.10
Butane-1,2,4-triol	benzene, toluene	Distillate (12) Residue (12A)		100-103°/0.05 m m.	5.55 5.72	5.62
L-erythro-Butane-1,2,3-triol	benzene	(13)	75-76°		5.60	5.62
ribo-Pentane-2,3,4-triol	benzene	Distillate (14) Residue (14A)	150-158°	116-120°/1.0 m m.	4.85[a] 6.36[b]	5.24
L-arabino-Pentane-2,3,4-triol	benzene 2-methoxyethanol	Distillate (15) Residue (15A)		90-94°/0.2 m m.	5.25 5.33	5.24
xylo-Pentane-2,3,4-triol	benzene	Distillate (16) Residue (16A)		82-84°/0.1 m m.	4.88[a] 6.47[b]	5.24
Pentane-1,3,5-triol	toluene	(17)		125-128°/0.03 m m.	5.20	5.24

a. It is likely that the low boron content arises as a result of contamination by unreacted triol. The retention volume of its tri-O-methyl ether would have been too low to allow its detection by g.l.c. (see p.77).

b. The high boron content might be due to contamination by phenylboronic acid or its anhydride.

IV-C Methods for determination of structure.

(i) Mass spectrometry.

The mass spectra of the phenylboronates of triols may be found in the appendix. Low resolution spectra were obtained by inserting samples directly into the "ion source"; high resolution mass measurements and defocussing experiments were performed using an all glass heated inlet system which produced a more steady sample pressure. It is appreciated that the latter measurements were taken under very different conditions from the low resolution spectra.

All the phenylboronates of triols formed molecular ions which were sufficiently stable to be recorded in the mass spectra, though they were of reduced abundance compared with the phenylboronates of diols. In two cases, those with high boron content, ions of mass greater than the molecular weight of a mono-phenylboronate were present. The residue (14A) obtained on distillation of ribo-pentane-2,3,4-triol phenylboronate may contain diphenylpyroboronate rings and will not be considered further here.

Glycerol phenylboronate (11) has been assigned a 1,2 structure[35] by characterisation of its phenylcarbamate derivative. The mass spectrum of (11) exhibits an abundant molecular ion at $^{m}/_{e}$ 178, $C_9H_{11}BO_3$, and the base peak corresponds to I, $^{m}/_{e}$ 147, $C_8H_8BO_2$, in agreement with the observation made on phenylboronates of diols concerning cleavage of exocyclic C-C bonds. An ion XIX, $^{m}/_{e}$ 31, CH_3O, is also formed (Fig. IV-7) which is very characteristic of primary alcohols.

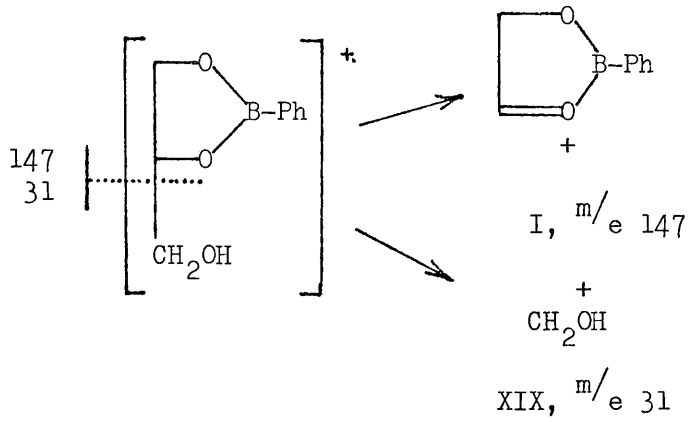


Fig. IV-7

The other two paths of fragmentation of the molecular ion, viz. elimination of formaldehyde and rearrangement to produce hydrocarbon ions also occur with the result that the spectrum generally resembles that of propane-1,2-diol phenylboronate (see p31). Thus a metastable ion at $^{m}/_{e}$ 56.3 corresponds to the oxonium ion I, $^{m}/_{e}$ 147, $C_8H_8BO_2$, rearranging to produce the hydrocarbon ion III, $^{m}/_{e}$ 91, C_7H_7, and another metastable ion at $^{m}/_{e}$ 46.5 possibly corresponds to III, $^{m}/_{e}$ 91, eliminating acetylene to form $^{m}/_{e}$ 65, C_5H_5.

It is profitable to construct a hypothetical spectrum of glycerol-1,3-phenylboronate in order that a six-membered ester ring may be recognised. A mass spectrum similar to that of 2,2-dimethylpropane-1,3-diol phenylboronate would be expected, in which VI, $^{m}/_{e}$ 104, C_6H_5BO, is produced from the molecular ion by a double elimination (Fig. IV-8). An ion XX, $^{m}/_{e}$ 44, C_2H_4O, should also be formed, whose structure would conventionally be that of the enolic form of acetaldehyde. In fact,

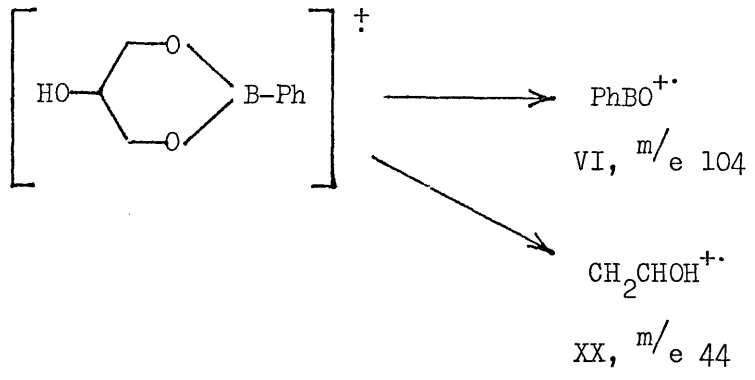
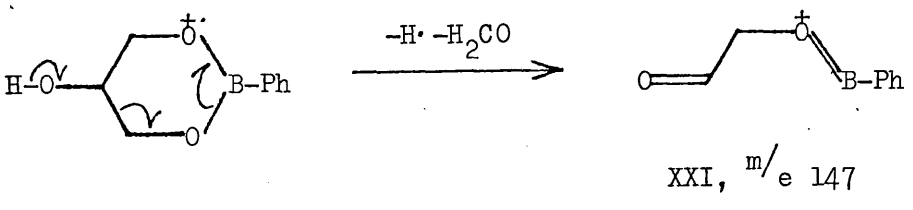


Fig. IV-8

these two fragments are present in the spectrum. A very small metastable ion at $^{m}/_{e}$ 60.7 indicates that VI, $^{m}/_{e}$ 104, is produced directly from the molecular ion. It would appear therefore that a small amount of the 1,3 isomer is present in glycerol phenylboronate.

Indeed, were it not for the low abundance of VI, $^{m}/_{e}$ 104, and XX, $^{m}/_{e}$ 44, and the high abundance of I, $^{m}/_{e}$ 147, it could be concluded that glycerol largely forms a 1,3-phenylboronate. This observation stems from a study of the mass spectrum of glycerol-1,3-benzylidene acetal[88] in which it was observed that the molecular ion eliminated a hydrogen radical and formaldehyde to produce M-31 to an extent of 15% of the abundance of the molecular ion. If this process occurs in six-membered boronate rings, an ion XXI, $^{m}/_{e}$ 147, $C_8H_8BO_2$, would be produced from glycerol-1,3-phenylboronate (Fig. IV-9). Clearly great caution is required

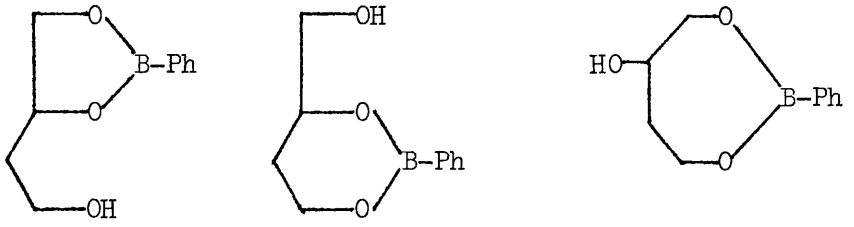


XXI, $^{m}/_{e}$ 147

Fig. IV-9

in the interpretation of the mass spectra of phenylboronates of triols in view of the similarity of the fragment ions which may be produced and the mixtures of isomers which the sample may contain.

Butane-1,2,4-triol forms a phenylboronate whose structure may contain a five-, six- or seven-membered ester ring. The three possible structures are shown in Fig. IV-10.



(12a) (12b) (12c)

Fig. IV-10

It has been suggested, on the basis of hydrolysis studies that the structure is butane-1,2,4-triol 1,2-phenylboronate[33], (12a). Distillation of the ester divided it into two portions; the distillate and residue had almost identical low resolution spectra. Only the spectrum of the distillate (12) was studied further and using this, a defocussing experiment showed that the parent ions of VI, $^{m}/_{e}$ 104, C_6H_5BO, included the molecular ion $^{m}/_{e}$ 192, $C_{10}H_{13}BO_3$. This implies that double elimination is occurring from a six-membered boronate ring. Further evidence of double elimination is provided by a fragment $^{m}/_{e}$ 58, C_3H_6O, the molecular ion of allyl alcohol, which eliminates a hydrogen radical forming $^{m}/_{e}$ 57, C_3H_5O[89].

The conclusion that this is the spectrum of the 1,3-phenylboronate (12b) is strengthened by the high abundance of the oxonium ion

IX, $^{m}/_{e}$ 161, $C_9H_{10}BO_2$, and XIX, $^{m}/_{e}$ 31, CH_3O. The mass spectrum resembles that of butane-1,3-diol phenylboronate (see p.33) with a metastable ion at $^{m}/_{e}$ 84.2 corresponding to XI, $^{m}/_{e}$ 131, C_8H_8BO, eliminating acetylene to form XII, $^{m}/_{e}$ 105, C_6H_6BO. A metastable ion at $^{m}/_{e}$ 51.4 results from rearrangement of the oxonium ion IX, $^{m}/_{e}$ 161, $C_9H_{10}BO_2$, to III, $^{m}/_{e}$ 91, C_7H_7.

Yet another metastable ion appears in the spectrum at $^{m}/_{e}$ 157.8 as a result of electron impact induced elimination of water from the molecular ion, rather than thermal dehydration. Deuterium labelling experiments have shown[90,91] that electron impact induced dehydration occurs predominantly by a 1,4-elimination through a six-membered transition state, in marked contrast to 1,2-elimination in thermal dehydrations. Thus the molecular ion of butane-1,2,4-triol 1,2-phenylboronate (12a) would readily eliminate water producing an abundant M-18 ion (Fig. IV-11).

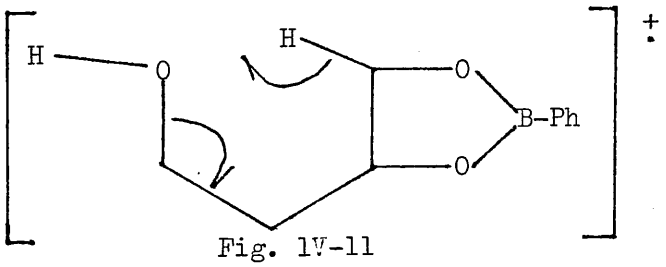
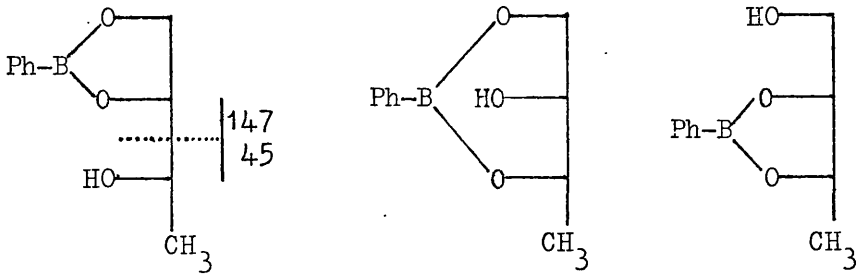


Fig. IV-11

Stereochemical reasons prevent dehydration of the 1,3-phenylboronate (12b) by 1,4-elimination, hence the small M-H_2O peak is probably produced from a small quantity of the 1,2-phenylboronate present in the sample. Such an impurity would account for the presence of I, $^{m}/_{e}$ 147, $C_8H_8BO_2$, which is unlikely to be produced from the 1,3-phenylboronate.

The presence of the 1,4-phenylboronate (12c) isomer cannot be discounted as its fragmentation pattern is unknown. The residue (12A) remaining after distillation is monomeric, determined both by measurements of depression of freezing point in benzene and mass spectrometry. It may be concluded that the two fractions are isomers (12b) and (12c).

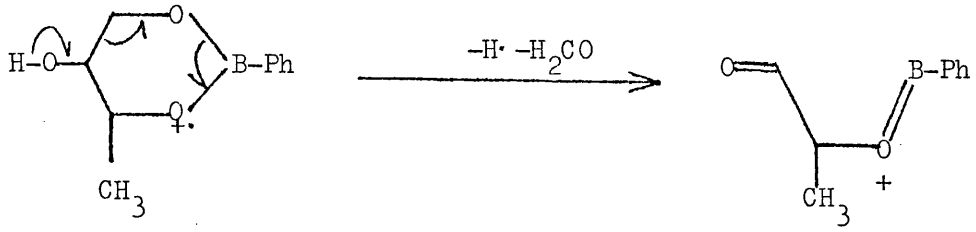
The three possible structures of L-erythro-butane-1,2,3-triol phenylboronate are shown in Fig. IV-12.



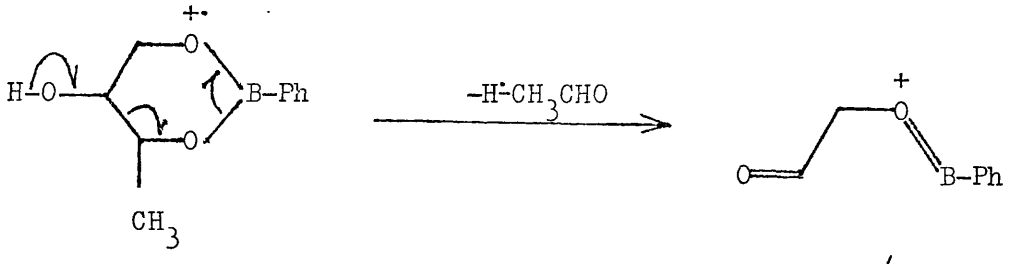
(13a) (13b) (13c)

Fig. IV-12

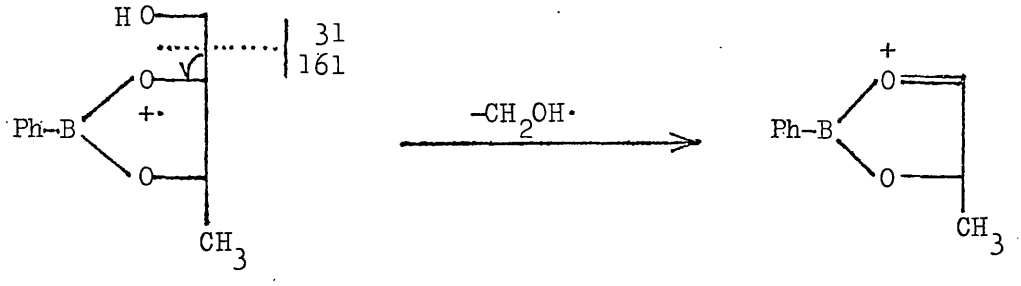
Ions $^{m}/_{e}$ 45, C_2H_4O, and $^{m}/_{e}$ 147, $C_8H_8BO_2$, immediately suggest that the structure is a 1,2-phenylboronate (13a). However it is unlikely that fragments $^{m}/_{e}$ 161, $C_9H_{10}BO_2$, and $^{m}/_{e}$ 148, $C_8H_9BO_2$, would be formed from such a structure; it is more likely that they are produced from the other two possible isomers (13b) and (13c). Ion $^{m}/_{e}$ 161 would then have the structure II or XXII. (Fig. IV-13). Ion $^{m}/_{e}$ 148, $C_8H_9BO_2$, is



XXII, $^{m}/_{e}$ 161



XXI, $^{m}/_{e}$ 147



II, $^{m}/_{e}$ 161

Fig. IV-13

produced by elimination of acetaldehyde from the molecular ion of (13b) and (13c). Double elimination of an aldehyde and C_6H_5BO does not appear to be a major fragmentation. L-erythro-Butane-1,2,3-triol phenylboronate thus appears to be a mixture of isomers.

The mass spectra of the phenylboronates 14, 15, 15A and 16 of the three isomeric pentane-2,3,4-triols will be considered together as they are very similar. All contain a molecular ion $^{m}/_{e}$ 206, $C_{11}H_{15}BO_3$, showing the boronates are monomeric. Each triol may form a five- or six-membered ring phenylboronate; both would be expected to fragment under electron impact to produce $^{m}/_{e}$ 161, $C_9H_{10}BO_2$, which may have the structure II or XXII (Fig. IV-14). The ion is in such high

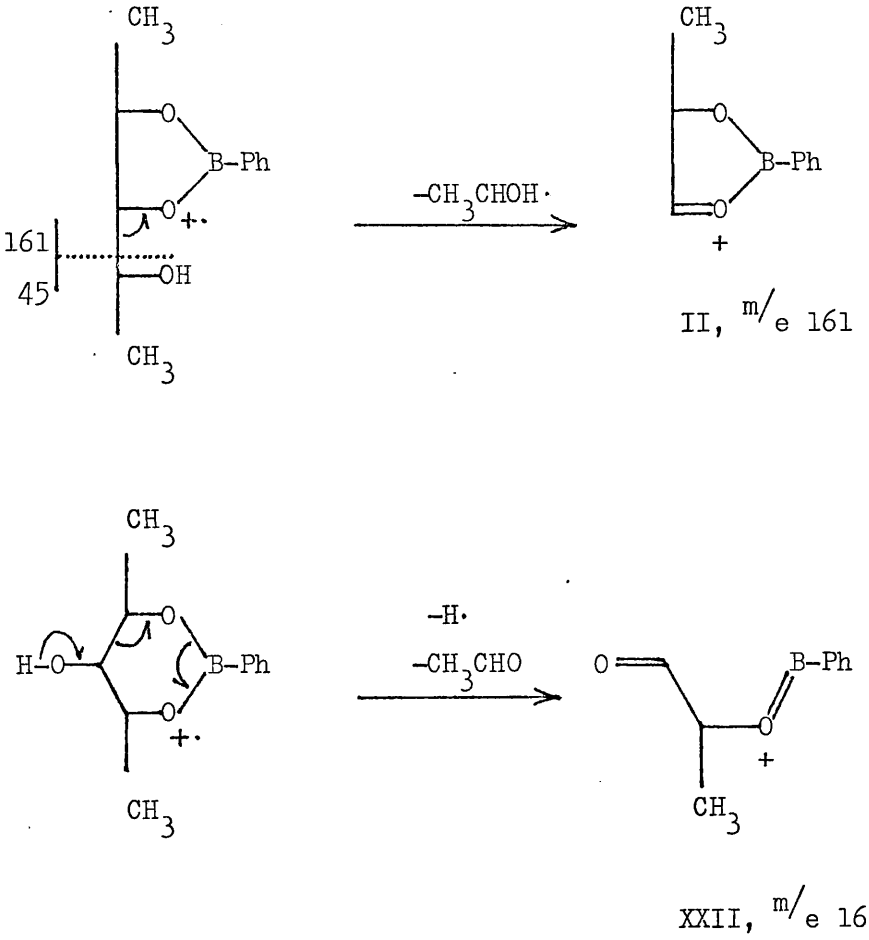
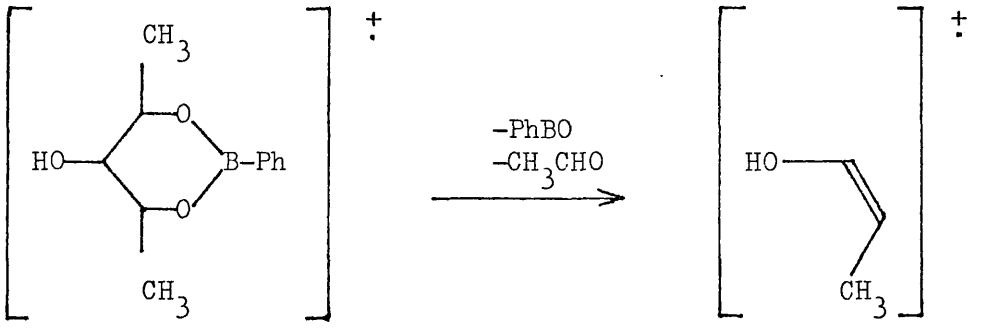


Fig. IV-14

abundance that it is likely to be II (see p.57) and suggests a five-membered ester ring. Also in high abundance is $^{m}/_{e}$ 118, C_9H_{10}. The ion produced by the double elimination fragmentation

(Fig. IV-15) XXIII, $^{m}/_{e}$ 58, C_3H_6O, is abundant and it may be inferred that the phenylboronate rings are six-membered. However, VI, $^{m}/_{e}$, C_6H_5BO, is in quite low abundance. Also, a defocussing



XXII, $^{m}/_{e}$ 58

Fig. IV-15

experiment performed using xylo-pentane-2,3,4-triol phenylboronate (16) showed that the parent ion of XXII, $^{m}/_{e}$ 58, C_3H_6O, was not the molecular ion but mainly II, $^{m}/_{e}$ 161, $C_9H_{10}BO_2$. The ion XXIII, $^{m}/_{e}$ 58, C_3H_6O, therefore, is not produced by a double elimination reaction but by a rearrangement and its presence in the spectra of these pentane-triol phenylboronates does not necessarily indicate a six-membered boronate ring. Thus the structures of the pentane-2,3,4-triol phenylboronates cannot be determined with certainty from their mass spectra alone.

Pentane-1,3,5-triol phenylboronate (17) may have, in its structure, a six- or eight-membered boronate ring. Discovery of an eight-membered ring would be novel since it has been reported that pentane-1,5-diol forms a polymeric boronate[31]. In fact, (17) is readily shown to be a primary alcohol because the mass spectrum contains ions XIX, $^{m}/_{e}$ 31, CH_3O, and IX, $^{m}/_{e}$ 161, $C_9H_{10}BO_2$, (Fig. IV-16).

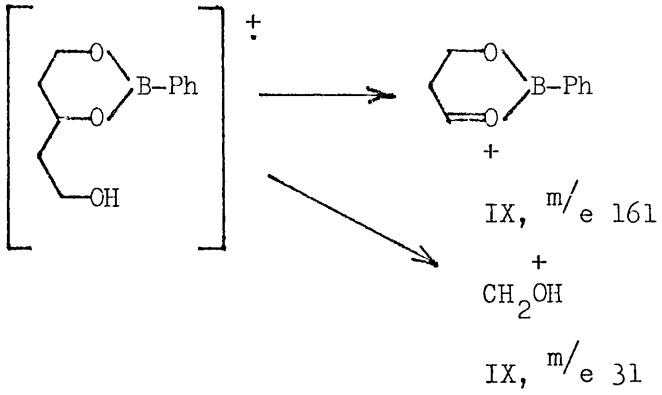


Fig. IV-16

The oxonium ion IX, $^{m}/_{e}$ 161 is similar to that produced from butane-1,3-diol phenylboronate (see p.33) and fragments in a similar manner. Thus rearrangement to III, $^{m}/_{e}$ 91, C_7H_7, (base peak) occurs, evidenced by a metastable ion at $^{m}/_{e}$ 51.5 and also consecutive elimination of formaldehyde and acetylene to give XI, $^{m}/_{e}$ 131, C_8H_8BO, and XII, $^{m}/_{e}$ 105, C_6H_6BO.

A feature, not previously encountered, is the extensive dehydration of the molecular ion $^{m}/_{e}$ 206, $C_{11}H_{15}BO_3$, which occurs producing XXIV, $^{m}/_{e}$ 188, $C_{11}H_{13}BO_2$, and a metastable ion at $^{m}/_{e}$ 171.5 (Fig. IV-17). The fragment XXIV, $^{m}/_{e}$ 188, may break up to give VI, $^{m}/_{e}$ 104, C_6H_5BO, or XXV, $^{m}/_{e}$ 84, C_5H_8O, and metastable ions at $^{m}/_{e}$ 57.5 and $^{m}/_{e}$ 37.4 respectively. Simultaneous

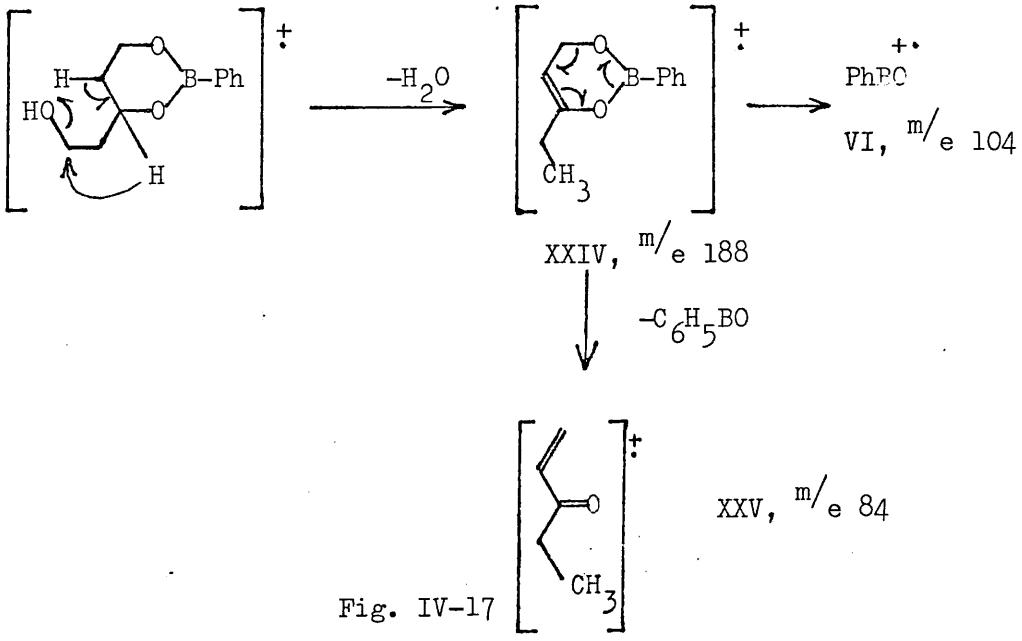


Fig. IV-17

explusion of water and C_6H_5BO may occur from the molecular ion to form XXV, $^{m}/_{e}$ 84, C_5H_8O, evidenced by a metastable ion at $^{m}/_{e}$ 34.3. The parent ions of VI, $^{m}/_{e}$ 104, and XXV, $^{m}/_{e}$ 84, were determined by defocussing experiments and confirm the metastable ion assignments.

The molecular ion also produces XXVI, $^{m}/_{e}$ 178, $C_9H_{11}BO_3$ by elimination of ethylene supported by a metastable ion $^{m}/_{e}$ 153.8. Ion XXVI, $^{m}/_{e}$ 178, expels a hydrogen atom to form XXVII, $^{m}/_{e}$ 177, $C_9H_{10}BO_3$, and a metastable ion at $^{m}/_{e}$ 176.0. Ion XXVII, $^{m}/_{e}$ 177, decomposes in a most unusual way by cleavage of the B-Ph bond and elimination of a phenyl radical to produce XXVIII, $^{m}/_{e}$ 100, $C_3H_5BO_3$, and a metastable ion at $^{m}/_{e}$ 56.7, (Fig. IV-18).

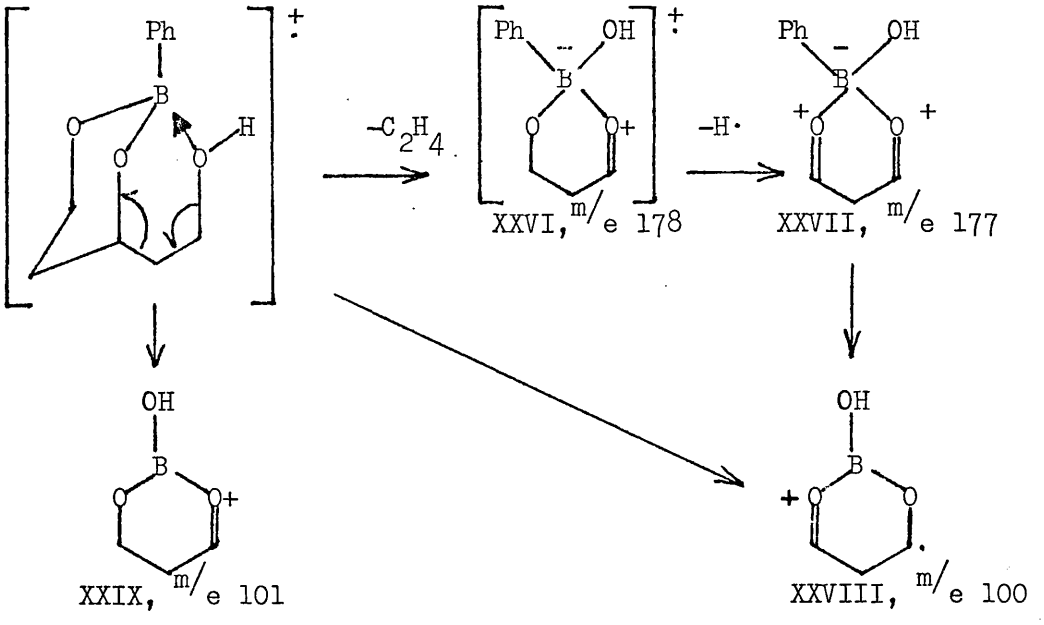


Fig. IV-18

Cleavage of this bond has previously been observed to occur only in connection with formation of hydrocarbon ions. It is suggested that in this compound the bond is weakened by donation of electrons from the oxygen atom of the free hydroxyl group to boron forming a

dative bond. Formation of such a fused tricyclic structure has been observed when cyclitols form borate complexes[92]. Further evidence is supplied by defocussing experiments which show that XXVIII, $^{m}/_{e}$ 100, is produced both from the molecular ion $^{m}/_{e}$ 206, and from XXVII, $^{m}/_{e}$ 177. A metastable ion at $^{m}/_{e}$ 49.3 suggests that the molecular ion also produces XXIX, $^{m}/_{e}$ 101, $C_3H_6BO_3$, directly confirming the presence of a boron-oxygen dative bond in the structure.

Use of mass spectrometry has proved to be successful in determining structures of phenylboronates of triols in only a limited number of cases. In fact, it has been shown later (p.79) that most of these compounds are mixtures of isomeric modifications of boronate ring sizes. Hence, it is not surprising that experimental data presented in this section cannot be satisfactorily rationalised and used for structural determination.

(ii) Infrared spectroscopy

Alcohols absorb in the frequency range 3500-3700 cm^{-1} which occurs in the infrared region. This absorption corresponds to the O-H stretching frequency. Hydrogen bonding, which occurs in concentrated solution, broadens the absorption, but at a concentration below 0.005 M, intermolecular hydrogen bonding is reduced to a negligible degree and only intramolecular hydrogen bonding occurs. The previously broad hydroxyl absorption becomes resolved into sharp absorption bands, the frequency of which can be measured easily.

Absorption between 3644 and 3605 cm^{-1} corresponds to the free hydroxyl group frequency in an alcohol or phenol[93]. Within any single class of compounds the overall range of absorption is smaller

still and the free hydroxyl group band of a large number of 1,2-diols occurs at 3630 ± 5 cm^{-1} [94]. Primary alcohols have been found to absorb near 3642 cm^{-1} and secondary alcohols near 3629 cm^{-1} [95]. This is true for simple alcohols but benzyl alcohol absorbs at 3614 cm^{-1} and the conclusion may be drawn that it is unwise to apply the generalisation too far[96].

Indeed, the infrared spectra of the phenylboronates of triols (Table IV-3) also lie outside this generalisation. Thus the free hydroxyl groups in the three isomeric pentane-2,3,4-triol phenylboronates, which should absorb near 3629 cm^{-1}, actually absorb in the range 3638-3630 cm^{-1}. At this stage,

Parent triol	Product	Frequencies of absorption (cm^{-1}) ±1cm^{-1}		
Glycerol			3640	3613
Butane-1,2,4-triol	distillate		3641	3606
" "	residue	3669	3636	3606
L-erythro-Butane-1,2,3-triol			3632	3605
ribo -Pentane-2,3,4-triol	distillate	3707	3638	3595
" "	residue	3669	3637	3594
L-arabino-Pentane-2,3,4-triol	distillate	3670	3634	3606
" "	residue	3670	3634	3606
xylo -Pentane-2,3,4-triol	distillate		3630	3597
" "	residue	3668	3632	3597
Pentane-1,3,5-triol			3725	3640	3578

Table IV-3. Infrared spectra of phenylboronates of triols.

attention should be drawn to the frequency of absorption of ribo-pentane-2,3,4-triol phenylboronate (14A), an ester which has a high boron content. This compound absorbs strongly at 3637 cm^{-1} and it seems likely therefore, that the structure contains a free hydroxyl group and a diphenylpyroboronate ring.

Absorptions occurring to the low frequency side 3613 - 3594 cm^{-1} are caused by a weakened O-H bond. The weakening is probably caused by intramolecular hydrogen bonding to an oxygen atom of the boronate ring. Intramolecular hydrogen bonding has been the subject of a review[97]. In simple cases, e.g. mono-O-methyl ethers of diols[98], the shift $\Delta\nu$ to low frequency has been correlated with the length of the hydrogen bond and has become a powerful tool in conformational analysis[99]. The formulation of such a correlation for phenylboronates would be unwise in view of the report[50] that oxygen to boron back donation is greater in six-than in five-membered boronate rings.

This report is supported by the ^{13}C nuclear magnetic resonance spectra of simple phenylboronates obtained by the author, (see Experimental section). It may be seen that carbon nuclei situated at equivalent positions in compounds containing five- and six-membered boronate rings resonate with different chemical shifts and are hence surrounded by different electronic environments.

(iii) Periodate oxidation of phenylcarbamate derivatives.

It has already been stated in Chapter I that a phenylcarbamate ester may be made of most phenylboronates possessing a free hydroxyl group. Such derivatives are crystalline and have the added advantage that under conditions of aqueous periodate oxidation the

phenylcarbamoyl moiety is not cleaved[38]. Preparation of these derivatives suffers from the disadvantage that the reaction mixture must be heated for long periods as the reaction is sluggish and in some cases it is necessary to add a catalyst. The reaction is known to be base catalysed[100], and triethylamine is often added to increase the rate of reaction.

Triethylamine, although a strong electron donor, is sterically hindered and does not form stable amine complexes with phenylboronates of diols[23]. Nevertheless, it was considered possible that triethylamine might catalyse an isomerisation of the phenylboronate in addition to its known catalytic effect on phenylcarbamate formation. This possibility was discounted when the phenylboronates of glycerol and L-erythro-butane-1,2,3-triol were refluxed with triethylamine and recovered unchanged, (Expt. 34).

Phenylcarbamate esters were prepared (Expt. 35) from all the phenylboronates of triols except four (12A, 15A, 16, 16A). In these four cases, it may be assumed that the reactivity of the free hydroxyl group was reduced by its co-ordination to the boron atom[42,43,44]. In two cases, (14 and 16), the phenylboronate was impure, containing free triol. Fractionation was achieved by allowing the reaction to proceed at first at 25°, removing the triol tri-phenylcarbamate and continuing the reaction at the refluxing temperature of toluene to produce a triol phenylboronate mono-phenylcarbamate.

It is known that when phenylboronates are dissolved in aqueous organic solvents, hydrolysis occurs, leaving in solution the polyol and phenylboronic acid[18]. Oxidation of the polyol with sodium metaperiodate has been successfully accomplished in the presence of phenylboronic acid[38]. This method was successfully employed for the

oxidation of the triol phenylboronate phenylcarbamates (Expt. 36), the periodate uptake being estimated by the arsenite method[85] and the formaldehyde produced with chromotropic acid[86,87]. The results are shown in Table IV-4.

Table IV-4. Periodate oxidation of phenylboronate phenylcarbamates of triols.

Phenylboronate phenylcarbamate of parent triol		Periodate consumed after 40 min.	Formaldehyde produced after 5 hr.
Glycerol	(11)	0.94 mol.	
Butane-1,2,4-triol	(12)	0.02 "	
L-erythro-Butane-1,2,3-triol	(13)	0.55 "	0.32 mol.
ribo-Pentane-2,3,4-triol	(14)	0.13 "	
" "	(14A)	0.38 "	
L-arabino-Pentane-2,3,4-triol	(15)	0.87 "	
" "	(15A)	0.86 "	

A triol phenylboronate phenylcarbamate produces a mono-O-carbamoyl-triol and phenylboronic acid on hydrolysis. The structure of the mono-substituted triol contains a diol system previously occupied by the phenylboronate moiety. If the boronate ring is five-membered, a 1,2-diol is produced which consumes one molar ratio of periodate and when one of the hydroxyl groups is primary, formaldehyde (1 mol.) is produced.

Consumption of periodate and formation of formaldehyde in amounts corresponding to fractions of a molar ratio must indicate that the phenylboronate phenylcarbamates are mixtures of isomers. If the phenylboronates of triols too are isomeric mixtures, it is desirable not only to know which isomers they contain but also in what proportions. This information is not deducable from the results of periodate oxidations, since a quantity of the phenylcarbamate remains in the mother liquor on recrystallisation and yields seldom exceed 60%. In addition, impurities such as tri-O-phenylcarbamoyl triols must be removed during recrystallisation and this is often difficult due to similarity of solubilities. The result is that the percent nitrogen analysis figures are high in some cases (e.g. ribo-pentane-2,3,4-triol phenylboronate phenylcarbamate) due to the presence in the sample of a small amount of a compound which is resistant to periodate oxidation. It is thus desirable to develop more reliable chemical methods for assignments of structures to these phenylboronates.

(iv) Methylation of hydroxyl groups of phenylboronates.

Formation of thermally stable, volatile derivatives is required in order that gas-liquid chromatography may be performed. The isomers may then be separated and their proportions determined. Preparation of the derivative under conditions (e.g. ambient temperature or below) which reduce the possibility of isomerisation of the phenylboronate would be an asset.

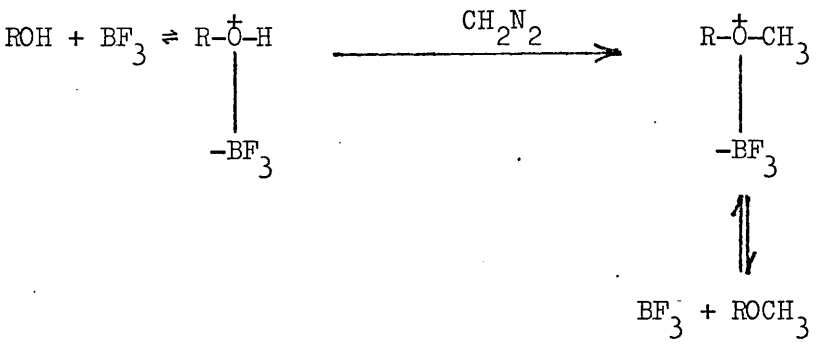
Methyl ethers exhibit the properties of volatility and thermal stability required for gas-liquid chromatography and hence methoxyl derivatives of carbohydrates have been used successfully for analysis

of sugars over a period of many years. Attempts at forming methyl ethers of hydroxyl groups of phenylboronates[25,29,43,44] using silver oxide and methyl iodide (the method of Purdie and Irvine[45]) in N,N-dimethylformamide[101] have so far been unsuccessful. Water is produced as the reaction proceeds, and it has been postulated[25], that this cleaves the phenylboronate ring.

$$ROH + CH_3I = ROCH_3 + HI$$

$$2HI + Ag_2O = 2AgI + H_2O$$

A procedure which affords methyl ethers without producing water uses diazomethane with boron trifluoride etherate as a catalyst. The method has been applied successfully to pentanols[102] and acetylated carbohydrates[103,104]. It has been suggested[102] that the reaction mechanism is similar to that originally proposed by Meerwein and Hintz[105] for catalysis by alkoxides, viz:



A competing reaction, the boron trifluoride catalysed polymerisation of diazomethane to give polymethylene[106], also occurs.

Using similar reaction conditions to those used by Gros et.al.[103,104], D-glucose bis-phenylboronate was methylated (Expt. 39) by the author and upon cleavage of the boronate ring and removal of phenylboronic acid, 6-O-methyl-D-glucose was obtained in a 36% yield, from D-glucose.

The claim that the structure of the boronate is α-D-glucofuranose 1,2; 3,5-bis-phenylboronate[21] (Fig. IV-19) was thus supported. Other methods of preparation had obtained 6-O-methyl-D-glucose in a 14% yield via three intermediates from D-glucose[104].

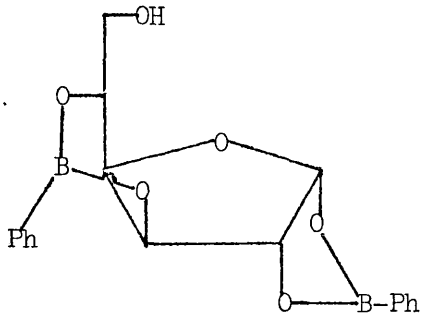


Fig. IV-19

The phenylboronates of triols were similarly treated with diazomethane in dichloromethane at -5° (Expt. 40). Reaction times were short, (30 min.) and monomethyl ethers of triol phenylboronates were formed in excellent yield (83-100%). The compounds were hydrolysed with water, and phenylboronic acid converted to bromobenzene by addition of bromine water[107]. The resulting triol monomethyl ethers were acetylated and analysed by gas-liquid chromatography, (P.P.E. 110-150°). Relative proportions and retention volumes of components are shown in Table IV-5. Tri-O-acetyl triols are products of unreacted phenylboronates. Unreacted material will contain an excessive amount of a secondary alcohol compared with a primary alcohol since the latter reacts slightly faster with diazomethane than the former[102]. For catalysis by boron trifluoride in ether[102] (isomeric pentanols) the relative rates of methylation were in the order primary; secondary = 1.09 : 1 indicating low

selectively of the reagent. Hence, it is unlikely that converted and unconverted material will have widely differing isomeric compositions.

In some cases, all possible monomethyl ethers of the triol had been formed, e.g. L-erythro-butane-1,2,3-triol phenylboronate had formed a methyl ether of the hydroxyl groups at positions 1,2 and 3. The identity of each component was established by coupling the gas-liquid chromatograph to a mass spectrometer.

(v) Combined gas-liquid chromatography - mass spectrometry of methyl ethers derived from phenylboronates of triols.

Characterisation of an unknown compound by gas-liquid chromatography is effected by comparison of its retention volume (RV) with that of a compound believed to belong to the same group (e.g. alditol acetates). This procedure requires synthesis of the suspected compound for comparative analysis.

Addition of a mass spectrometer to the detection system of a gas-liquid chromatograph obviates this necessity. A mixture may be separated into components and a mass spectrum of each obtained. If the mass spectra can be analysed successfully, the identities of components which have never been previously prepared may be established.

Combined gas-liquid chromatography - mass spectrometry of acetates of partially methylated alditols has been pioneered by Lindberg and co-workers [108,109]. By analysis of a large number of mass spectra of such compounds, the electron impact induced fragmentation pattern by which all molecular ions of alditol acetates fragment has been deduced. The processes involved are now understood and the fragments which will be produced by a particular structure can be predicted.

The fragmentation of alditol acetates, e.g. D-glucitol hexaacetate, is easily interpreted, as demonstrated by Chizhov et.al.[110,111]. The main peaks of the mass spectrum correspond to ions formed by primary fission between two adjacent carbon atoms in the chain and to those arising by elimination of acetic acid ($^{m}/_{e}$ 60) or ketene ($^{m}/_{e}$ 42) from these primary fragments. The intensities of the fragments decrease with increasing mass number. A deoxy group inhibits the cleavage of the neighbouring bonds, as exemplified by tri-O-acetyl-butane-1,2,4-triol (Fig. IV-20).

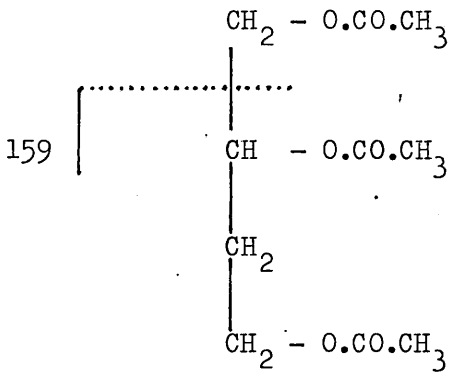


Fig. IV-20

Mass spectra of isomeric alditol acetates having the same structure but different configurations are practically indistinguishable e.g. ribo-, L-arabino- and xylo-pentane-2,3,4-triol acetates. A systematic investigation of mass spectra of partially methylated alditol acetates has led to the following generalisations:

1. Derivatives with the same substitution pattern give very similar mass spectra, typical of that substitution pattern. The small differences that may be observed in the relative intensities of peaks for stereoisomers are insufficient for unambiguous identification.

2. The base peak of the spectrum is usually $^{m}/_{e}$ 43, C_2H_3O.

3. Primary fragments are formed by fission between carbon atoms in the chain. Fission between a methoxylated and an acetoxylated carbon is preferred over fission between two acetoxylated carbons. The fragment with the methoxyl group carries the positive charge. The alditol acetates derived from 1-O-methyl, 2-O-methyl and 3-O-methyl-butane-1,2,3-triol may be used as examples, Fig. IV-21. The

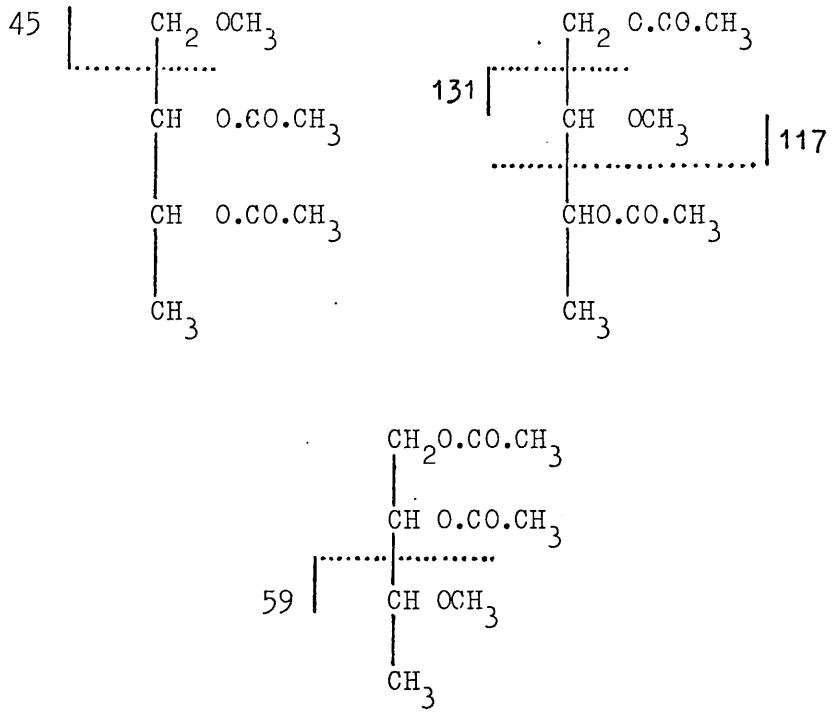


Fig. IV-21

ions formed by other substitution patterns may be found in Table IV-6.

4. Secondary fragments are formed from the primary by single or consecutive elimination of acetic acid ($^{m}/_{e}$ 60), ketene ($^{m}/_{e}$ 42), methanol ($^{m}/_{e}$ 32) or formaldehyde ($^{m}/_{e}$ 60).

Table IV-5. Gas-liquid chromatography of methoxyl derivatives of phenylboronates of triols.

Phenylboronate of	Product	Methoxyl substituent (%)				Free triol (%)
		1	2	3	4	
Glycerol		61 (0.31)	38 (0.38)			1 (1.00)
Butane-1,2,4-triol	distillate	87 (0.32)	0		7 (0.29)	6 (0.96)
	residue	88	0		6	6
L-erythro-Butane-1,2,3-triol		8 (0.31)	50 (0.37)	25 (0.35)		17 (0.80)
ribo-Pentane-2,3,4-triol	distillate		24 (0.29)	72 (0.31)		4 (0.65)
	residue		21	70		9
L-arabino-Pentane-2,3,4-triol	distillate		95 (0.32)	0		5 (0.71)
	residue		94	0		6
xylo-Pentane-2,3,4-triol	distillate		100 (0.40)	0		0
	residue		100	0		0
Pentane-1,3,5-triol		100 (0.46)		0		0

Retention volumes (RV), P.P.E. 110-150°, glycerol standard, are shown in parentheses.

Table IV-6. Primary fragments (>10% of the base peak) in the mass spectra of acetates of partially methylated triols.

Parent alcohol	Primary fragments m/e45	m/e59	m/e87	m/e117	m/e131	m/e145	m/e159
glycerol						X	
1-O-methyl- "	X						
2-O-methyl- "				X			
butane-1,2,4-triol							X
1-O-methyl- "	X						
2-O-methyl- "				X	X		
4-O-methyl- "	X				X		
butane-1,2,3-triol			X			X	
1-O-methyl- "	X						
2-O-methyl- "				X	X		
3-O-methyl- "		X					
pentane-2,3,4-triol			X				X
2-O-methyl- "		X					
3-O-methyl- "					X		
pentane-1,3,5-triol							X
1-O-methyl- "	X						
3-O-methyl- "					X		

The validity of the rules stated above, when applied to mono-O-methyl-di-O-acetyl triols, was substantiated by preparing 1-O-methyl-glycerol diacetate and 2-O-methyl-glycerol diacetate. Inspection of their mass spectra revealed that the primary fragments

formed were $^{m}/_{e}$ 45 and $^{m}/_{e}$ 117, respectively (Table IV-6). It was thus possible to determine the substitution pattern of mono-O-methyl-di-O-acetyl triols by analysing their mass spectra according to the principles outlined above.

The isomeric modifications of boronate ring sizes which exist in phenylboronates of triols were deduced from the structures of the mono-O-methyl-di-O-acetyl triols. Compositions of the mixtures of isomers were estimated from the gas-liquid chromatograms (Table IV-5), and were found to be very similar for the distilled and residual boronates. These figures were thus combined in the total products (Table IV-7).

Table IV-7. Structures of phenylboronates of triols.

Structures assigned to phenylboronates of triols			Isomer ratio in product
Glycerol	1,2-	phenylboronate	8/5
"	1,3-	"	
Butane-1,2,4-triol	1,2-	"	1/13
" "	2,4-	"	
L-erythro-Butane-1,2,3-triol	1,2-	"	3/6/1
" " "	1,3-	"	
" " "	2,3-	"	
ribo-Pentane-2,3,4-triol	2,3-	"	1/3
" " "	2,4-	"	
L-arabino-Pentane-2,3,4-triol	2,3- and/or 3,4-	"	
xylo-Pentane-2,3,4-triol	2,3-	"	
Pentane-1,3,5-triol	1,3-	"	

IV-D Structural assignments

The results which each method has produced are complementary. Mass spectrometry (i) proved to be moderately successful in determining the structure of the major component of each phenylboronate. Periodate oxidation of phenylcarbamate derivatives (iii) was a more reliable method, but in some cases e.g. butane-1,2,4-triol phenylboronate, was unable to decide the structure in favour of the 1,3- or 1,4-phenylboronate. The method was able, however, to indicate a mixture of isomeric phenylboronates by non-integral consumption of periodate.

Both methods produced evidence which established the presence of a dative bond in the structure of certain compounds. Such a bond was discovered to exist in pentane-1,3,5-triol 1,3-phenylboronate by analysis of its mass spectrum (Fig. IV-18). An inability to form a phenylcarbamate derivative of xylo-pentane-2,3,4-triol 2,3-phenylboronate may indicate the presence of a dative bond in the structure of this ester also (Fig. IV-22). Similar

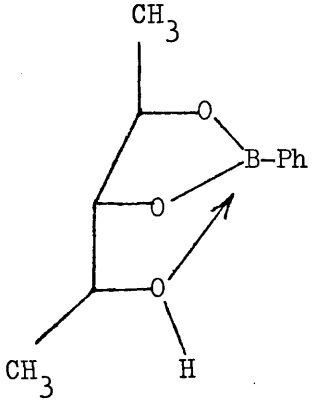


Fig. IV-22

structures have been proposed previously for cis, cis-1,2,3-triol systems[43,112] but formation of a trans-annular O——B dative bond across a six-membered boronate ring was proposed.

Combined gas-liquid chromatography - mass spectrometry (v) of methoxyl derivatives was unable to provide information concerning dative bonding. However, structures of all components of a mixture of isomeric phenylboronates and composition of the mixture were determined for all the phenylboronates of triols by this method. Results obtained by other methods support those obtained by this method (v). The results obtained with residues of distillation were almost identical with those obtained using phenylboronates which distilled. Consequently, the ratio of isomeric phenylboronates in the product (Table IV-8) is a weighted mean of the results obtained using phenylboronates which distilled. In the cases of the residues of butane-1,2,4-triol phenylboronate (12A) and L-arabino-pentane-2,3,4-triol phenylboronate (15A) the mass spectra showed no ions of mass greater than $^{m}/_{e}$ 192 and $^{m}/_{e}$ 206 respectively. It is possible that thermal degradation of a polymer to monomer is occurring. The mass spectrum of the residue of xylo-pentane-2,3,4-triol phenylboronate contains ions at high mass and this compound must be also polymeric.

An inspection of Table IV-8 reveals that triols containing a deoxy function preferentially form six-membered phenylboronate rings if all substituents on the heterocycle are equatorial. Thus butane-1,2,4-triol, L-erythro-butane-1,2,3-triol, ribo-pentane-2,3,4-triol and pentane-1,3,5-triol largely from six-membered phenylboronate rings. It is interesting to note that a change of configuration

from ribo- to L-arabino- or xylo-pentane-2,3,4-triol destabilises the system, presumably by introduction of an axial substituent and this is sufficient to entirely prevent formation of a six-membered boronate ring. Five-membered rings are formed in substantial amounts by L-erythro-butane-1,2,3-triol, L-arabino- and xylo-pentane-2,3,4-triols. Among this series, it may be observed that heterocycles with two bulky substituents in a cis-configuration are destabilised. As a result, L-erythro-butane-1,2,3-triol forms a 1,2-phenylboronate (25%) to a larger extent than a 2,3-phenylboronate (8%). This observation may only be completed by determination of the structure of L-arabino-pentane-2,3,4-triol phenylboronate.

None of the methods (i), (iii), (v) is capable of deciding the structure of L-arabino-pentane-2,3,4-triol phenylboronate in favour of the 2,3- or 3,4-phenylboronate. The isomers are likely to have identical mass spectra, form phenylcarbamate derivatives which consume 1 mol. of sodium periodate and produce mono-O-methyl-di-O-acetyl triols with identical mass spectra. The ambiguity may be removed by synthesis of 1-d_1-L-lyxo-pentane-2,3,4-triol phenylboronate from L-arabinose (Fig. IV-23) via the intermediates:-

L-arabinose diethyldithioacetal;

5-O-toluene-p-sulphonyl-L-arabinose diethyldithioacetal, and

5-d_1-5-deoxy-L-arabinose diethyldithioacetal .

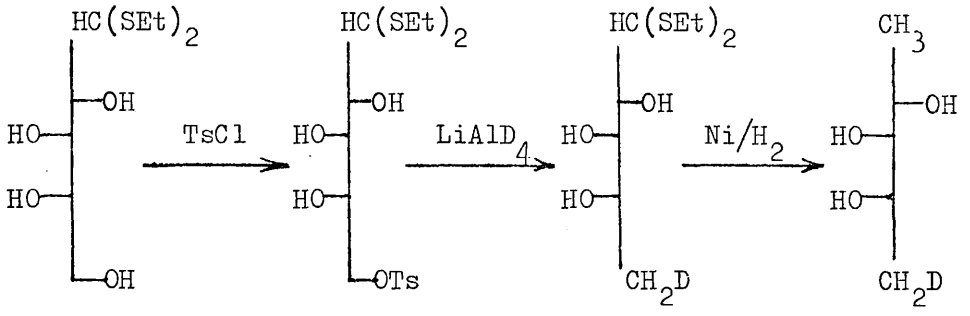


Fig. IV-23

Conversion of the phenylboronate to a monomethyl triol diacetate, as described on p.73, followed by observation of ions at either $^{m}/_{e}$ 59, C_3H_7O, or $^{m}/_{e}$ 60, C_3H_6DO, would indicate that L-arabino-pentane-2,3,4-triol formed a 3,4- or 2,3-phenylboronate respectively, (Fig. IV-24).

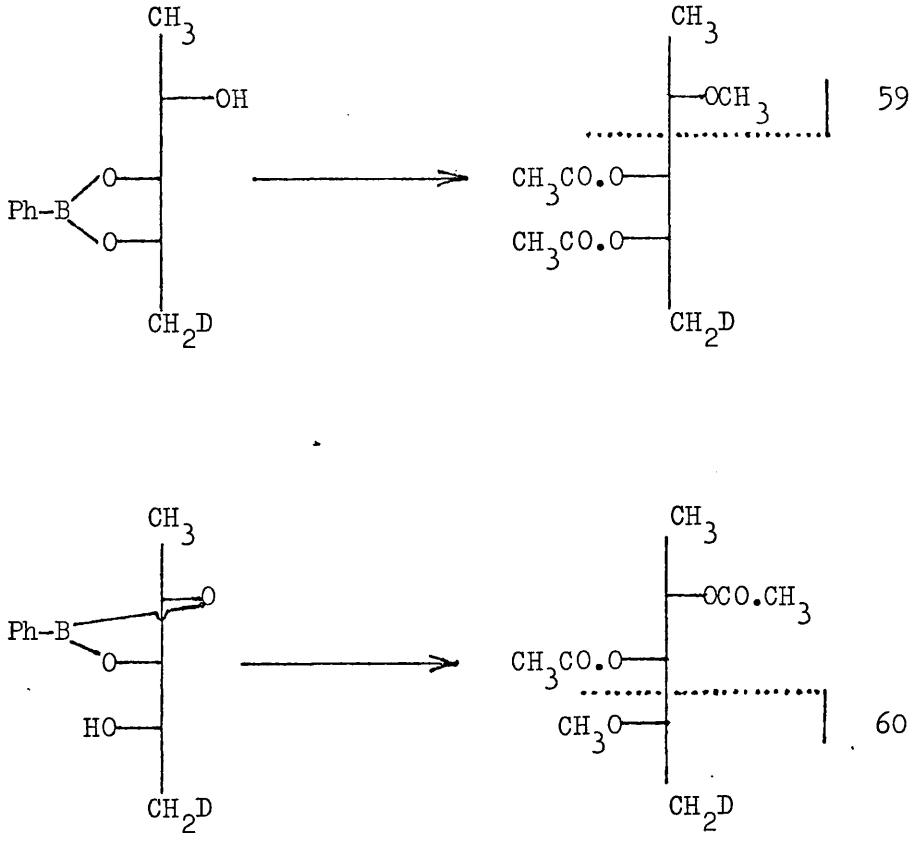
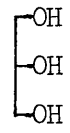
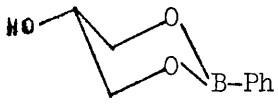
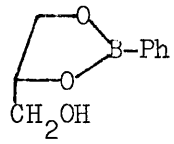
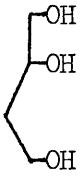
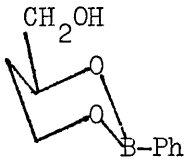
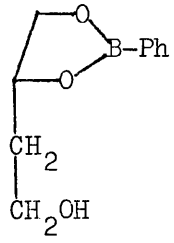
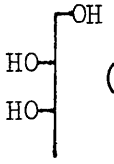
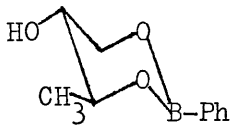
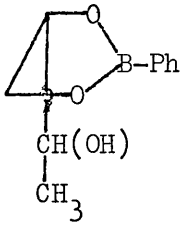
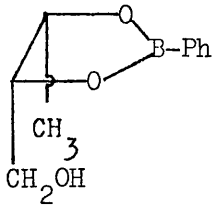
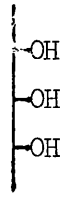
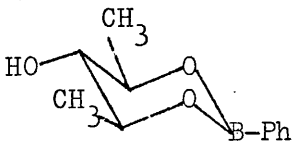
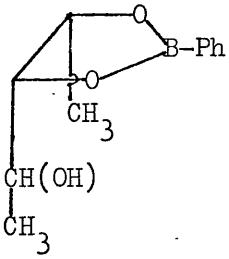
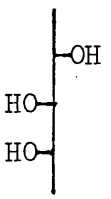
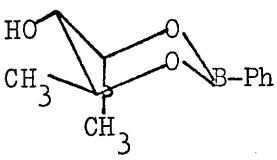
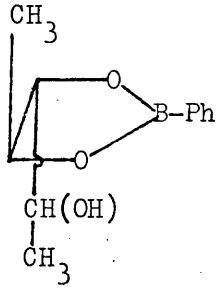
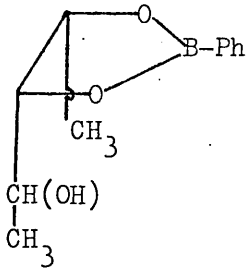
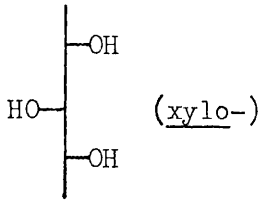


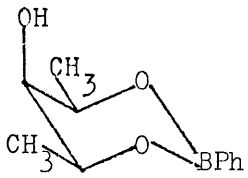
Fig. IV-24

Table IV-8.

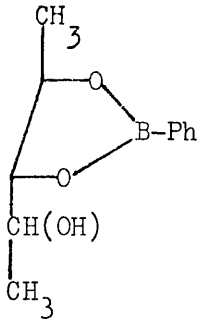
Parent triol	Possible structures of phenylboronates ≠		
	 (5)	 (8)	
	 (13)	 (1)	
 (L-erythro-)	 (6)	 (3)	 (1)
 (ribo-)	 (3)		 (1)
 (L-arabino-)	 (0)		

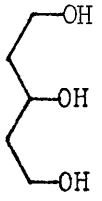


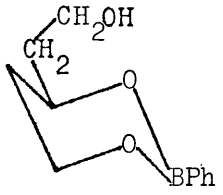
(xylo-)



(o)







≠ Figures in parentheses are ratios of isomers in total product.

V Structures of Phenylboronates of Tetritols, Pentitols and Hexitols.

Structural studies on phenylboronate esters have previously been confined to suitable substitution of free hydroxyl groups in the molecule. This method can provide an unambiguous structure only for a monocyclic system. Since partial hydrolysis of alditol bis- and tris-phenylboronates has proved unsuccessful[25], many of their structures remain unknown.

It was considered that partial alcoholysis using propane-1,3-diol might generate mono- and bis-phenylboronates from the tris-phenylboronates of hexitols. Indeed, when a reaction mixture obtained from one mole of propane-1,3-diol and one mole of galactitol tris-phenylboronate in pyridine was analysed by g.l.c. (trimethylsilyl ether, S.E.30, 186°), it was found that cleavage of one boronate ring had occurred, producing essentially a galactitol bis-phenylboronate (Expt. 43). Use of two moles of propane-1,3-diol cleaved two boronate rings to produce essentially a galactitol mono-phenylboronate.

Structures of the partial alcoholysis products could not be determined but if the reaction is successful in removing boronate rings selectively, a modified technique may be used to determine complete structures. The structures of the intermediate galactitol bis- and mono-phenylboronates may be deduced by a sequence of reactions which would convert them to partially methylated alditol acetates. These may then be analysed, as in the previous chapter, by a combination of gas-liquid chromatography and mass spectrometry and a structure indirectly assigned to the hexitol tris-phenylboronate.

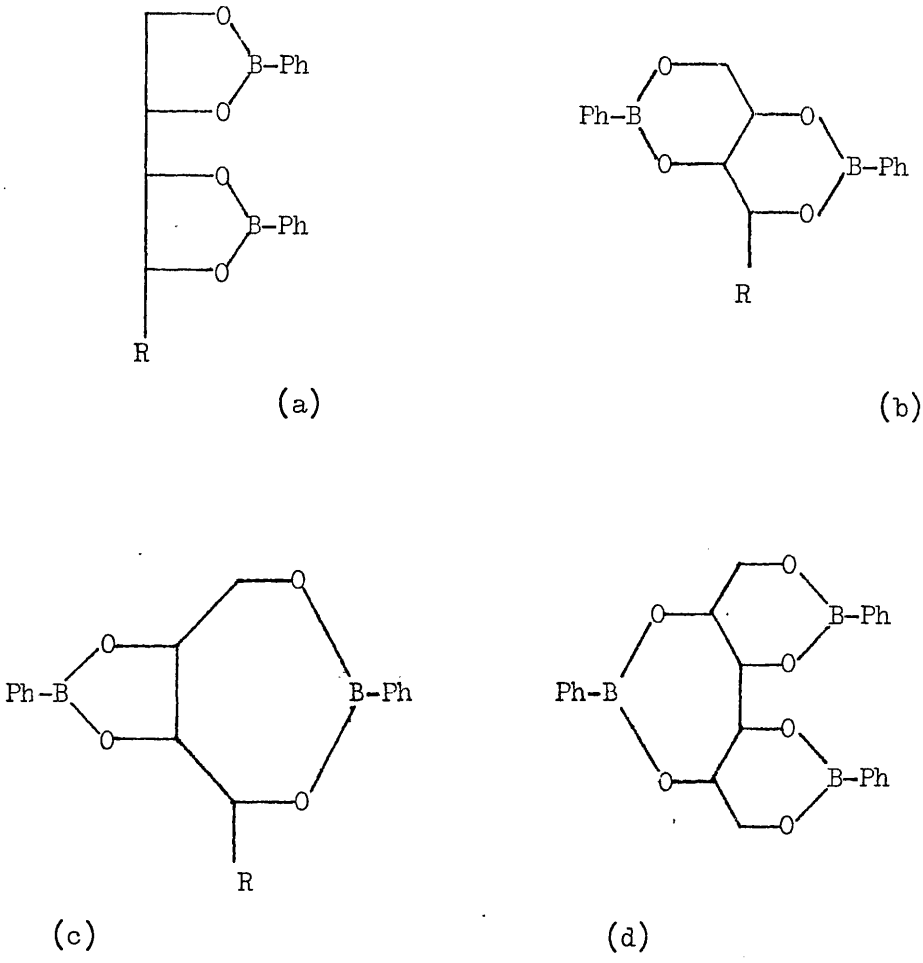


Fig. V-1

Four structures for phenylboronates of alditols are most worthy of attention (Fig. V-1). Selection of these four is based on two observations. Firstly, a primary hydroxyl group always remains free when a pentitol forms a bis-phenylboronate[38]. Secondly, mono-phenylboronate rings larger than seven-membered have never been prepared.

It was with the aim of directly correlating structure with fragmentation pattern under electron impact that the mass spectra of the following phenylboronates of alditols were studied:-

Erythritol bis-phenylboronate (18),

L-Threitol bis-phenylboronate (19),

1-Deoxy-D-xylitol bis-phenylboronate (20),

Ribitol bis-phenylboronate (21),

D-Arabitol bis-phenylboronate (22),

Xylitol bis-phenylboronate (23),

D-Glucitol tris-phenylboronate (24),

1-d_1-D-Glucitol tris-phenylboronate (24A),

Galactitol tris-phenylboronate (25), and

D-Mannitol tris-phenylboronate (26).

V-A Mass spectrometry.

Mass spectra were obtained by inserting the sample directly into the "ion source". Abundant molecular ions indicated that all the compounds studied were monomeric. Mass spectra may be found in the appendix.

(i) Half rupture.

In the spectra of all the compounds studied, the base peak occurred at $^{m}/_{e}$ 147, $C_8H_8BO_2$, which can be interpreted as arising from a 4,4'-bis-1,3-dioxaborolan type structure, Fig. V-1a. Based on previous experience of monocyclic systems (Chapter III), fragmentation would be expected to proceed by cleavage of the bond linking the two dioxaborolan rings (Fig. V-2). Fragments I, $^{m}/_{e}$ 147, $C_8H_8BO_2$, and XXX, $^{m}/_{e}$ (146 + R) would then be formed.

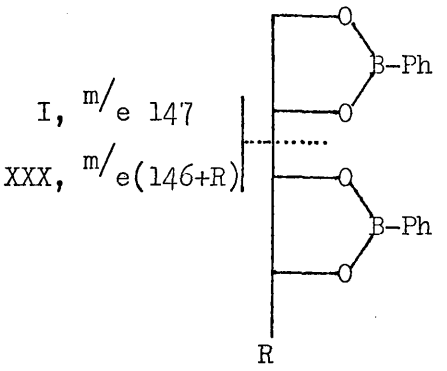
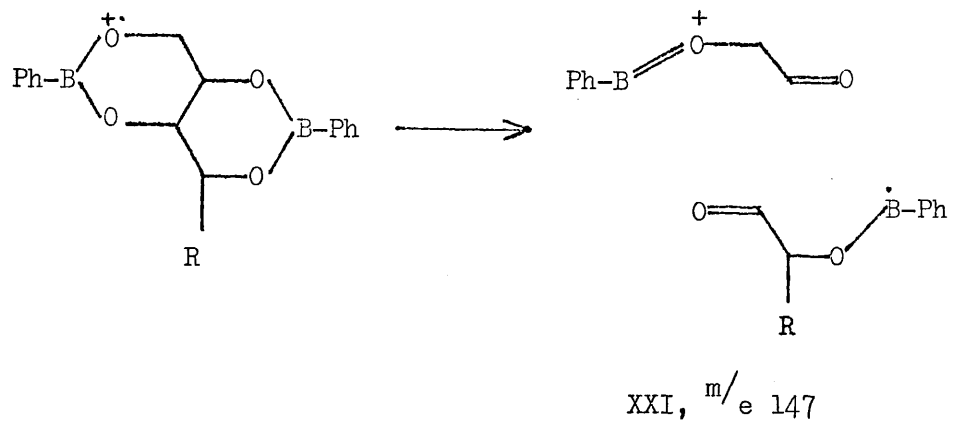
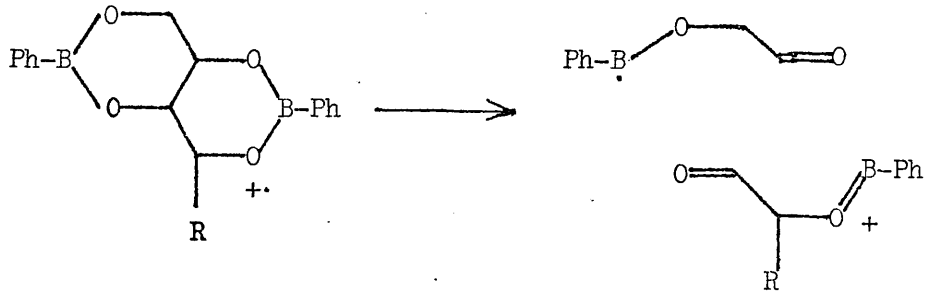


Fig. V-2

However, fragments $^{m}/_{e}$ 147, $C_8H_8BO_2$, may also be formed by a multiple fission of bonds. Studies of cyclic benzylidene acetals[88] of known structure have shown that a process called "half rupture" occurs under electron impact in 1,3, 6,8-tetra-oxabicyclo [4.4.0] decanes, causing the molecular ion to break into halves by cleavage of three bonds. If this process also operates in fused ring cyclic boronates, structures of type (b) (Fig. V-1) would produce ions XXI, $^{m}/_{e}$ 147, $C_8H_8BO_2$, and XXXI, $^{m}/_{e}$ (146 + R). The fragmentation may be considered to be triggered by localising the positive charge on an oxygen atom attached to C1 or C4 (Fig. V-3). Hence ions $^{m}/_{e}$ 147 and $^{m}/_{e}$ (146 + R) may be produced from both structures (a) and (b) and would quite probably be produced from structures (c) and (d) also. These ions are hence not necessarily key fragments for elucidation of structure.



XXI, $^{m}/_{e}$ 147

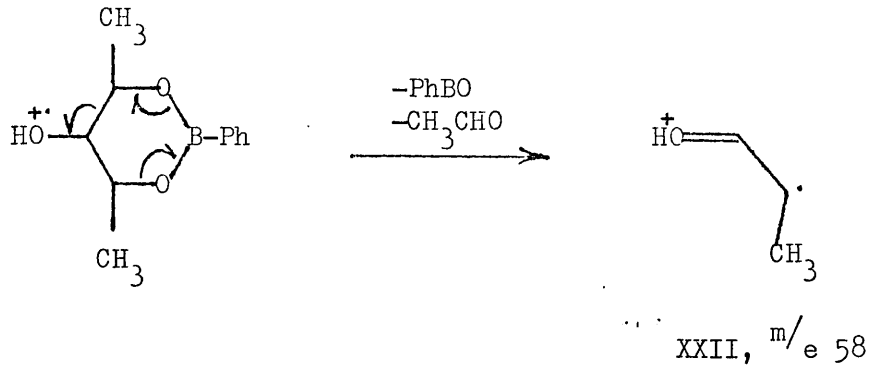


XXXI, $^{m}/_{e}$ (146 + R)

Fig. V-3

(ii) Double elimination.

It has been observed (Chapter III) that six-membered boronate rings fragment by double elimination of an aldehyde and an olefin to produce VI, $^{m}/_{e}$ 104, C_6H_5BO, cf. propane-1,3-diol phenylboronate. Alternatively, double elimination of an aldehyde and C_6H_5BO may yield an ionised olefin cf. 2,2-dimethylpropane-1,3-diol phenylboronate. The latter fragmentation is illustrated for ribo-pentane-2,3,4-triol phenylboronate (Fig. V-4).

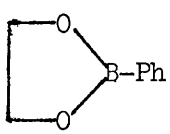


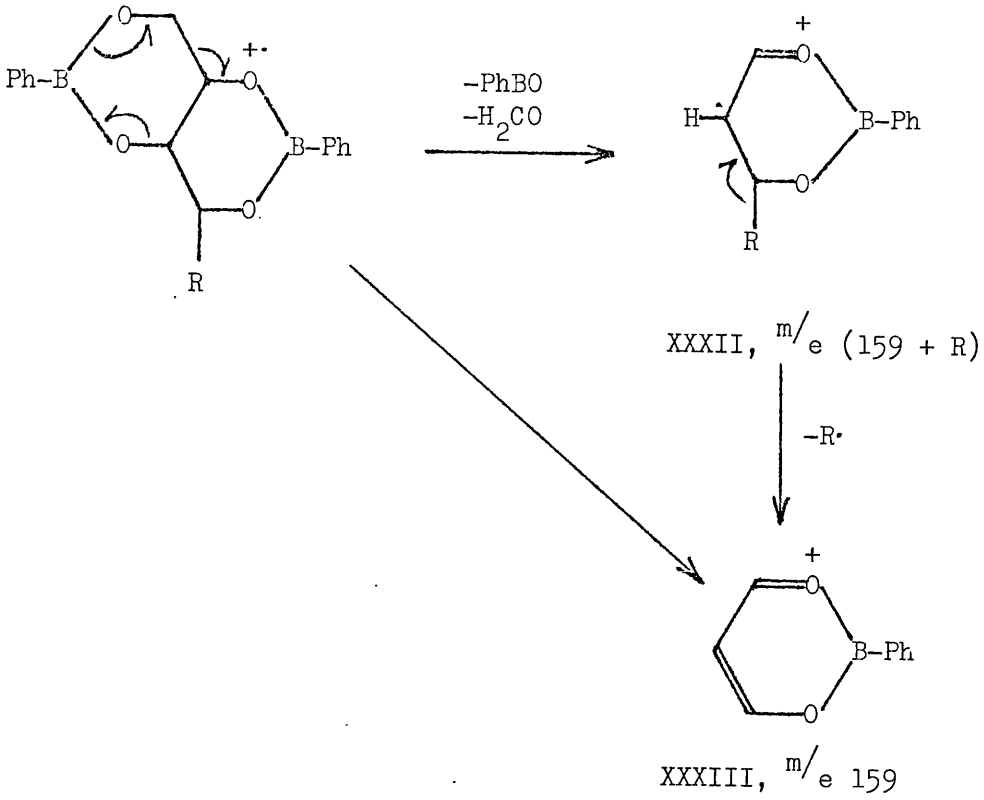
XXII, $^{m}/_{e}$ 58

Fig.V-4

It is likely that double elimination also occurs in bicyclic esters, in which case the fragments expected from compounds possessing two fused six-membered rings are XXXII, $^{m}/_{e}$ (159 + R); XXXIII, $^{m}/_{e}$ 159, $C_9H_8BO_2$ and XXXIV, $^{m}/_{e}$ 160, $C_9H_9BO_2$ depending on the localisation of charge. Indeed, the compounds studied do give rise to such ions (Table V-1). It is thus proposed that they fragment according to the schemes of Fig. V-5.

Table V-1. Major fragments in the mass spectra of alditol phenylboronates (18-25).

		Major fragments ($^{m}/_{e}$)				
Ester	R	XXI	XXXI	XXXII	XXXIII	XXXIV
18,19,	H	147	147	160	159	160
20,	CH_3	147	161	174	159	160
21,22,23,	CH_2OH	147	177	190	159	160
24,25,26.		147	293	306	159	160


Ph–B
B–Ph
R
-PhBO
-H2CO
H
B–Ph
R
XXXII, m/e (159 + R)
-R·
B–Ph
XXXIII, m/e 159

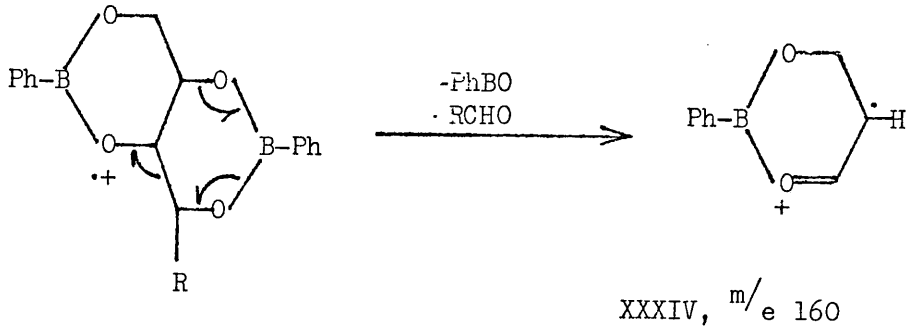

Ph–B
B–Ph
R
-PhBO
· RCHO
Ph–B
H
XXXIV, m/e 160

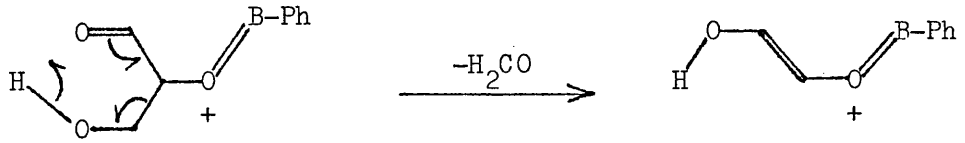
Fig. V-5

In some cases, metastable ions (see appendix)provided evidence that the ions XXXII, $^{m}/_{e}$ (159 + R); XXXIII, $^{m}/_{e}$ 159, and XXXIV, $^{m}/_{e}$ 160, were produced directly from the molecular ions. In the spectra of the pentitol and hexitol phenylboronates (21-26) studied, the abundances of the fragment XXXII, $^{m}/_{e}$ (159 + R), were low. It is proposed that double elimination and elimination of the radical R may take place together and produce XXXIII, $^{m}/_{e}$ 159, directly from the molecular ion. This proposal is supported in the cases of the pentitol bis-phenylboronates (21-23), by metastable ions at $^{m}/_{e}$ 78.0. Defocussing experiments supported this assignment to the metastable ion. These experiments also proved that XXXIV, $^{m}/_{e}$ 160, was produced directly from the molecular ion giving rise to a metastable ion at $^{m}/_{e}$ 79.0. This evidence is particularly valuable in the cases of the pentitol bis-phenylboronates as it demonstrates that the products of double elimination are not produced from an oxonium ion, which was found to occur in the cases of phenylboronates of triols (Chapter IV).

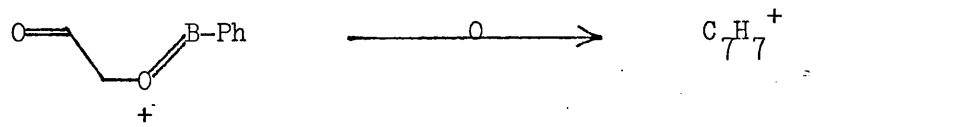
Thus, the criterion that an alditol phenylboronate which undergoes double elimination on electron impact possesses two fused six-membered boronate rings may confidently be used to assign structures. The presence of fragments XXXII, $^{m}/_{e}$ (159 + R); XXXIII, $^{m}/_{e}$ 159, $C_9H_8BO_2$, and XXXIV, $^{m}/_{e}$ 160, $C_9H_9BO_2$, in the mass spectrum of such an ester is sufficient evidence to assign a structure of type (b) (Fig. V-1) rather than structures (a), (c) or (d). These fragments were identified in the spectra of the phenylboronates of alditols by precise mass measurements and their abundances are shown in Table V-2. If these ions were absent or in low abundance (the sum of abundances $\%\Sigma_{40}$ of XXXII + XXXIII + XXXIV $< 10\%$), it was not

possible to infer any structural information from the mass spectrum. Thus the esters (18-25) were assigned structures containing two fused six-membered phenylboronate rings. Double elimination appears to be a general fragmentation process for molecules possessing two fused six-membered heterocycles since a similar fragmentation has been observed to occur in 1,3,6,8-tetraoxabicyclo [4.4.0] decanes[88].

Fragments $^{m}/_{e}$ 147, $C_8H_8BO_2$, and $^{m}/_{e}$ (146 + R), which appear in the spectra of esters (18-25) must therefore be produced by "half rupture". Metastable ions at $^{m}/_{e}$ 73.5 indicate that XXI, $^{m}/_{e}$ 147, $C_8H_8BO_2$, is produced directly from the molecular ions of tetritol bis-phenylboronates, (Fig. V-3). When R = CH_2OH (pentitol bis-phenylboronates) the ion XXXI, $^{m}/_{e}$ 177, $C_9H_{10}BO_3$, may rearrange and eliminate formaldehyde to give the ion XXXV, $^{m}/_{e}$ 147, $C_8H_8BO_2$, (Fig. V-6). This process gives rise to a metastable ion at $^{m}/_{e}$ 122.1 for the cases of the pentitol bis-phenylboronates (21,22 and 23). The ion XXI, $^{m}/_{e}$ 147 may rearrange to give the hydrocarbon ion III, $^{m}/_{e}$ 91, C_7H_7, and produces a metastable ion at $^{m}/_{e}$ 56.3 (Fig. V-6).



XXXI, $^{m}/_{e}$ 177 XXXV, $^{m}/_{e}$ 147



XXI, $^{m}/_{e}$ 147 III, $^{m}/_{e}$ 91

Fig. V-6

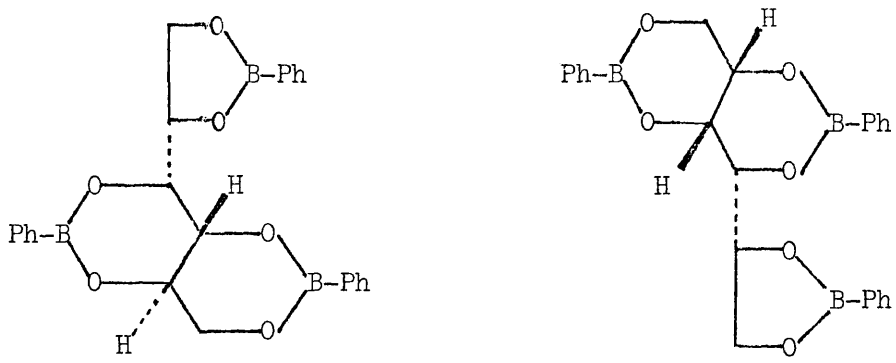
Table V-2. Abundances of major fragments in the mass spectra of alditol phenylboronates (18-26).

Parent alditol	Compound	Sum of abundances of all istopic species % Σ_{40} $C_8H_8BO_2^{\neq}$	XXXI	XXXII	XXXIII	XXXIV	M^+
Erythritol	18	15.9	-	-	6.1	8.9	13.0
L-Threitol	19	21.8	-	-	10.7	9.7	10.8
1-Deoxy-D-xylitol	20	4.0	16.8	0.2	6.5	18.0	14.4
Ribitol	21	28.0	2.9	0.0	7.7	8.7	8.9
D-Arabitol	22	33.0	5.4	0.0	6.8	7.1	9.8
Xylitol	23	35.6	6.9	0.0	11.9	5.8	8.0
D-Glucitol	24	28.2	4.2	0.2	11.5	2.0	8.6
Galactitol	25	27.7	2.3	0.2	12.1	3.7	13.6
D-Mannitol	26	61.3	3.6	0.0	2.3	0.0	6.4

$\neq$ sum of ions I, XXI and XXXV.

V-B Structural assignments.

It has been established by mass spectrometry that the phenylboronates of eight of the alditols studied (18-25) possess structures which contain two fused six-membered boronate rings. In most cases, this is sufficient to determine the structure completely. However, in the case of D-glucitol tris-phenylboronate, two possible structures arise. The position to which the rings are attached may be 1,2; 3,5; 4,6 or 1,3; 2,4; 5,6 (Fig. V-7).



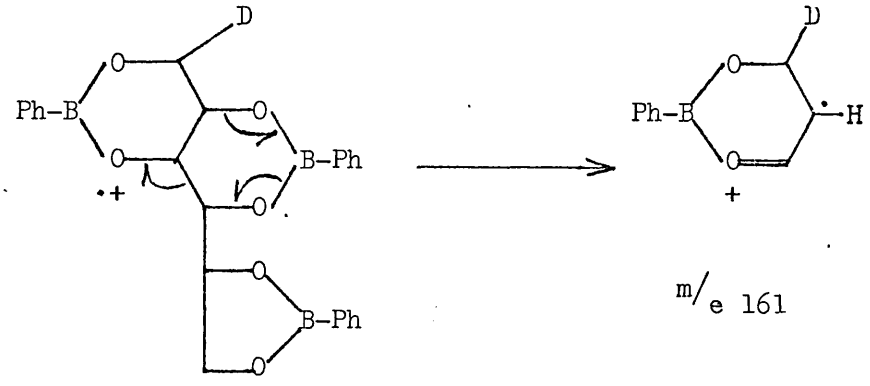
D-Glucitol

1,2; 3,5; 4,6 tris-phenylboronates

1,3; 2,4; 5,6 tris-phenylboronates

Fig. V-7

The ambiguity in structure was resolved in favour of the latter by obtaining the mass spectrum of 1-d_1-D-glucitol tris-phenylboronate (24A). The fragment XXXIV ($^{m}/_{e}$ 160, $C_9H_9BO_2$, in the spectrum of D-glucitol tris-phenylboronate) had incorporated one deuterium atom and in the spectrum of 24A occurred at $^{m}/_{e}$ 161, $C_9H_8DBO_2$, (Fig. V-8). The fragments XXXII, $^{m}/_{e}$ 306, $C_{18}H_{16}B_2O_4$, and XXXIII, $^{m}/_{e}$ 159, $C_9H_8BO_2$, were also present in the spectrum.



$^{m}/_{e}$ 161

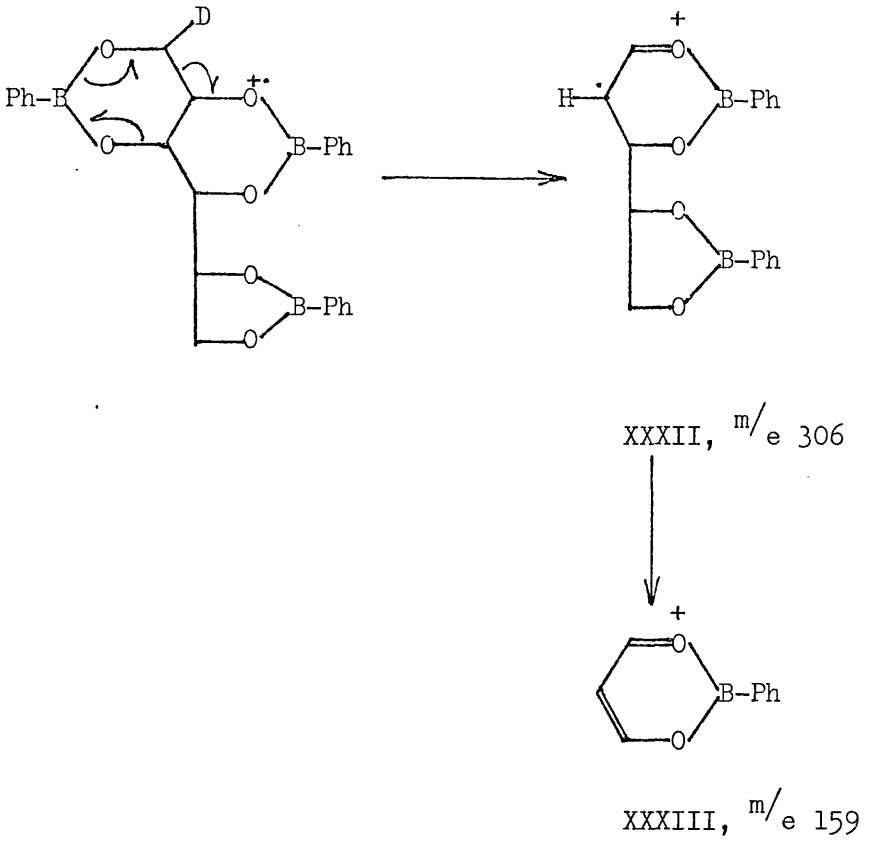


Fig. V-8

The structure of the bis-phenylboronate formed by D-arabitol cannot be assigned solely using mass spectrometry. The positions of attachment of the boronate rings may be 1,3; 2,4 or 2,4; 3,5. Fortunately, it has already been established[38] that L-lyxitol forms a bis-phenylboronate in which the hydroxyl group at C 5 is free. The structure must be therefore L-lyxitol 1,3; 2,4-bis-phenylboronate. The structures of the phenylboronates (18-25) are illustrated in Fig. V-9.

The abundances of fragments XXXII, XXXIII and XXXIV in the mass spectrum of D-mannitol tris-phenylboronate are quite low and total only 2.3%, hence it is unlikely that its structure contains two fused six-membered boronate rings. Such a structure is unlikely

for conformational reasons also. Rotation about the C2-C3 bond in such a structure would be restricted by interaction between the hydrogen atoms attached to C1 and C5 (Fig. V-10).

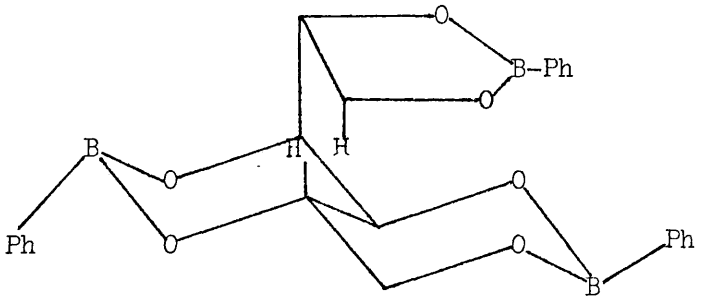
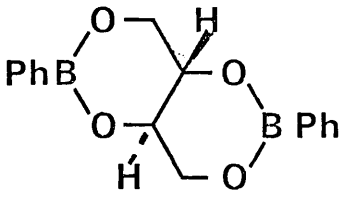


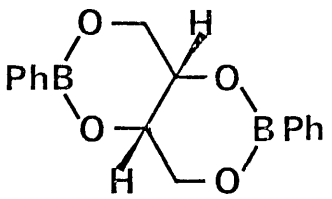
Fig. V-10

It is possible that the structure of this compound may yet be determined using a combination of the techniques of partial alcoholysis and methylation, as discussed on p. 86.

Thus, a simple mass-spectrometric method has been developed which is capable of detecting, in the structure of a multicyclic phenylboronate, a system containing two fused six-membered boronate rings. This information proved sufficient to enable assignment of complete structures to eight alditol phenylboronates of previously unknown structure.

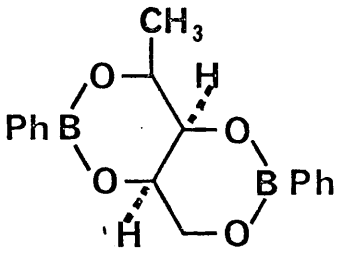


Erythritol (18)



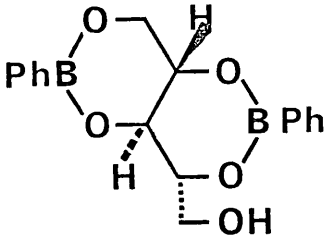
L-Threitol (19)

1,3; 2,4-bis-phenylboronates

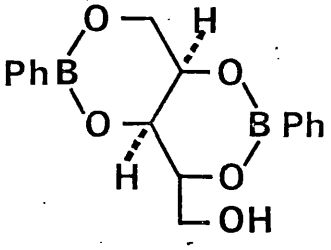


1-Deoxy-D-xylitol (20)

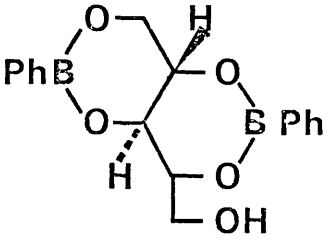
2,4; 3,5-bis-phenylboronate



D-Ribitol (21)

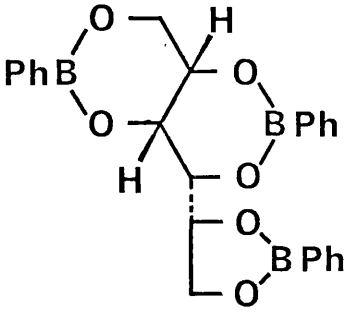


L-Xylitol (22)

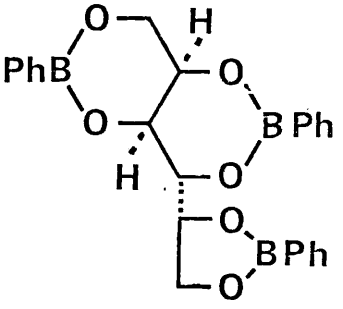


L-Lyxitol (23)

1,3; 2,4-bis-phenylboronates



D-Glucitol (24)



L-Galactitol (25)

1,3; 2,4; 5,6-tris-phenylboronates

Fig. V-9

VI Experimental.

Paper Chromatography.

Whatman No.1 chromatography paper was used, with the following solvent systems, for descending chromatography.

Solvent system (a): n-butanol, ethanol, water; 40 : 11 : 19 v/v.

Solvent system (b): ethyl acetate, acetic acid, formic acid, water; 18 : 3 : 1 : 4 v/v.

Solvent system (c): n-butanol, pyridine, water; 6 : 4 : 3 v/v.

Electrophoresis.

The Shandon High Voltage Electrophoresis apparatus was used. Whatman No.3 MM paper, width 11 cm, was employed.

Sodium borate electrolyte.

A 0.2 M solution of sodium borate in water was adjusted to pH 10.0 with sodium hydroxide. Electrophoresis was carried out at 2,500 volts for 1.5 hr. The non-migrating marker, used to correct for electroendosmosis, was 2,3,4,6-tetra-O-methyl-D-glucose[113].

Sodium molybdate and tungstate electrolytes.

A 0.1 M solution of sodium molybdate dihydrate or sodium tungstate dihydrate in water was adjusted to pH 5.0 by dropwise addition of concentrated sulphuric acid. Electrophoresis was carried out at 1,500 volts for 2.5 hr. The non-migrating marker was glycerol. The paper was dried at 120-130° and treated with a staining reagent.

Staining Reagents.

Reagent 1. : A freshly prepared 0.2% solution of potassium permanganate in acetone. Sugars and polyols appear as yellow spots on a purple background which fades rapidly[114].

Reagent 2. : Three solutions through which the paper is dipped successively.

a) Saturated aqueous silver nitrate solution (2.5 ml) and water (10 ml) in acetone (500 ml).

b) Sodium hydroxide (10 g) and water (50 ml) in ethanol (500 ml).

c) 5% aqueous sodium thiosulphate. Sugars and polyols appear as brown spots on a white background.

Gas-liquid chromatography.

A Perkin-Elmer F-11 chromatograph, with flame ionisation detector and glass columns (2 m x 4 mm) was used, with nitrogen as the carrier gas. When coupled to a mass spectrometer, helium carrier gas was used and a reduced flow rate was obtained using glass columns of 1 mm internal diameter. The following stationary phases were employed:-

P.P.E. - 10% w/w m-bis (m-phenoxyphenoxy) benzene on silane-treated Chromosorb W (100-120 mesh) [115].

S.E.-30 (a methyl silicone) 3% w/w on Gas Chrom P.

Mass spectrometry.

The gas-liquid chromatograph was coupled via a Watson-Biemann separator to a Hitachi RMS-4 mass spectrometer. Mass spectra of partially methylated triol acetates were obtained by operating the "ion source" at 200°, 50 e.v. and 80 μ.a. target current.

Mass spectra of phenylboronates were obtained using a A.E.I. M.S. 902 mass spectrometer operating at 70 e.v. and 100 μ.a. trap current.

Infrared spectroscopy.

Infrared spectra of phenylboronates of triols were obtained in dilute carbon tetrachloride solution using glass cells of 4 cm path length. The spectra were recorded using a Perkin-Elmer 325 grating spectrometer.

Nuclear magnetic resonance spectroscopy.

Carbon-13 nuclear magnetic resonance spectra were obtained using a Bruker HFX-90 spectrometer operating at 22.63 MHz. locked to hexafluorobenzene. Samples were examined, at normal working temperature, as neat liquids with tetramethylsilane added as the internal reference.

Carbon-13 nuclear magnetic resonance spectra of phenylboronates of diols.

Phenylboronate of	Chemical Shift (δ) relative to tetramethylsilane (p.p.m.) ± 0.1 p.p.m.
Ethane-1,2-diol	-135.4
	-131.7
	-128.1
	- 66.0
Propane-1,2-diol	-135.5
	-131.6
	-128.1
	- 74.0
	- 72.7
	- 21.9
Butane-2,3-diol	-135.3
	-131.6
	-128.1
	- 80.8
	- 76.0
	- 21.1
	- 16.8

Phenylboronate of	Chemical Shift (δ) relative to tetramethylsilane (p.p.m.) ± 0.1 p.p.m.
Propane-1,3-diol	-134.4
	-130.8
	-127.6
	- 62.0
	- 27.7
Butane-1,3-diol	-134.3
	-130.8
	-127.9
	- 67.9
	- 61.5
	- 34.5
	- 23.2
Pentane-2,4-diol	-134.5
	-130.7
	-127.8
	- 68.3
	- 64.8
	- 42.7
	- 39.5
	- 23.5
	- 23.0

Expt. 1. Phenylboronic anhydride.

The preparation of phenylboron dichloride is essentially the same as that used by Burch et.al.[116]. Boron trichloride (50 g) was cooled in a cardice/acetone mixture and poured onto tetraphenyltin (45 g). The boron trichloride was refluxed using a cold finger, and, when the reaction had subsided, the mixture was heated at 50° for 35 min. The mixture was distilled using a short fractionating column and a fraction boiling in the range 172-178° collected.

An equal volume of carbon tetrachloride (30 ml) was added and the solution added dropwise to cracked ice (300 ml) with stirring. The ice was allowed to melt and the white acid filtered off. It was recrystallised from water (100 ml) after hot filtration. Heating at 110° for 6 hr. converted it to phenylboronic anhydride (16.0 g, 33%), m.p. 218-219°, lit.[117] m.p. 209-214°.

Expt. 2. Preparation of phenylboronates of diols.

An equimolar mixture of the diol and phenylboronic anhydride was heated in refluxing toluene for 8 hr. using a Dean and Stark head. The resulting solution was evaporated under reduced pressure and the residual liquid distilled in vacuo. Purity was established by elemental analysis and gas-liquid chromatography.

Expt. 3. 2,3-d_2-Butane-2,3-diol.

Lithium aluminium deuteride (1.0 g) was added to a solution of biacetyl (3.7 g) in dry ether (50 ml) and the mixture allowed to stand 16 hr. The reaction mixture was worked up with a saturated aqueous solution of sodium sulphate, and the solvent removed under reduced pressure. The crude product was isolated by continuous

extraction with dichloromethane. The extract was distilled under reduced pressure yielding 2,3-d_2-butane-2,3-diol (1.48 g, 40%) as a fraction boiling between 52-56°/3 mm, n_D^{20} = 1.431.

Expt. 4. D-Glucose toluene-p-sulphonylhydrazone.

Toluene-p-sulphonylhydrazide (25.1 g) dissolved in hot ethanol (200 ml) was added to D-glucose (24.3 g) dissolved in a hot mixture of water (30 ml) and acetic acid (30 ml). The mixture was allowed to cool at 20° for 12 hr. White crystals of D-glucose toluene-p-sulphonylhydrazone (43.4 g, 88%) were filtered off, washed with ethanol and ether and dried, m.p. 168-170°, lit.[118] m.p. 170°.

Expt. 5. 1-Deoxy-D-glucitol.

This preparation is essentially the same as that used by de Belder and Weigel[68]. To a suspension of D-glucose toluene-p-sulphonylhydrazone (25.0 g) in methanol (700 ml) was added gradually potassium borohydride (15.0 g) and the mixture refluxed 12 hr. Methanol was removed by distillation under reduced pressure and the residue dissolved in water (500 ml). The solution was treated with Amberlite IR-120 (H^+) resin until a positive test for potassium was no longer obtained, the resin filtered off and water removed by distillation under reduced pressure. Boric acid was removed by repeated dissolution in methanol and evaporation. The residue was a yellow syrup, which on paper chromatography in solvent (a) revealed two components [R_G 2.1 (1-deoxy-D-glucitol) and R_G 1.0 (D-glucitol)].

The syrup was dissolved in n-butanol saturated with water (70 ml) and applied to a cellulose column (7.5 cm x 80 cm) which was eluted with the same solvent. Fractions (25 ml) were collected. Fractions 209-290 were combined and evaporated to give a white solid on trituration with ethanol. Recrystallisation from ethyl acetate yielded

1-deoxy-D-glucitol (4.8 g, 41%), m.p. 128-129°, lit.[68] m.p. 128-129°.

Expt. 6. Improved preparation of 1-deoxy-D-glucitol.

To a suspension of D-glucose toluene-p-sulphonylhydrazone (29.0 g) in dry methanol (800 ml) was added potassium borohydride (19.0 g) in small portions over a period of 48 hr. The mixture was then refluxed for 24 hr. and worked up in the same manner as in the previous experiment. The required compound, 1-deoxy-D-glucitol (11.8 g, 86%), m.p. 128-129°, was obtained.

Expt. 7. D-Xylose toluene-p-sulphonylhydrazone.

Toluene-p-sulphonylhydrazide (10.0 g) was dissolved in hot ethanol (80 ml) and added to a solution of D-xylose (8.0 g) in a hot mixture of water (10 ml) and acetic acid (10 ml). The mixture was allowed to cool for 12 hr. The crystals which formed, were filtered off, washed with ethanol and ether and dried to yield D-xylose toluene-p-sulphonylhydrazone (16.5 g, 92%), m.p. 149-150°, lit.[119] m.p. 149°.

Expt. 8. 1-Deoxy-D-xylitol.

To a suspension of D-xylose toluene-p-sulphonylhydrazone (8.0 g) in dry methanol (160 ml) was added potassium borohydride (8.0 g) in small portions over a period of 24 hr . The mixture was heated at 50° for 14 hr. and then worked up as in Experiment 6. The required compound, 1-deoxy-D-xylitol (3.0 g, 77%), $[\alpha]_D^{20}$ + 3.5° (c 1.0 in methanol) was obtained as a pale yellow viscous syrup which could not be induced to crystallise. On acetylation, a tetra-acetate m.p. 62-63° was obtained, lit.[75] m.p. 62-63°.

Expt. 9. 1-Deoxy-2,4-O-butylidene-D-glucitol.

n-Butyraldehyde (3.5 g) and 1-deoxy-D-glucitol (8.0 g) were dissolved in water (160 ml) and 5N-aqueous hydrochloric acid (40 ml) was added. After allowing to stand for 24 hr. at room temperature, the reaction mixture was neutralised with aqueous sodium hydroxide and evaporated under reduced pressure. The solid residue thus produced was triturated with warm ethanol (200 ml), insoluble material filtered off and the filtrate evaporated to a solid residue. This residue was leached with boiling benzene (100 ml) and the hot solution decanted into another vessel and allowed to cool, whereupon a crystalline deposit separated. The crude product was filtered off and recrystallised twice from benzene to yield 1-deoxy-2,4-O-butylidene-D-glucitol (4.0 g, 36%), m.p. 128-130°, $[\alpha]^{20}_{5461}$ -1.2° (c 1.0 in water), lit.[120] m.p. 128-130°, $[\alpha]^{25}_{5461}$ -1.2° (c 0.8 in water).

Expt. 10. 5-Deoxy-L-xylose.

To a solution of 1-deoxy-2,4-O-butylidene-D-glucitol (11.5 g) in sodium phosphate buffer (250 ml, 0.1 M, pH 7.4) was added, at 0° with stirring, sodium metaperiodate (12.0 g). After 5 hr. at 0°, the solution was freeze-dried. The residue was extracted with cold chloroform (4 x 100 ml) and the extracts evaporated under reduced pressure.

The resulting colourless syrup was dissolved in water (200 ml) and boiled with Amberlite IR 120 (H^+) resin (20 ml) for 2 hr. The mixture was allowed to cool, the resin filtered off, and the filtrate evaporated to a colourless syrup of 5-deoxy-L-xylose (6.9 g, 99%), R_G 2.26 solvent (a).

On reduction with sodium borohydride, a product was obtained which could not be distinguished from 1-deoxy-D-xylitol, M_3 (Mo) 1.09. On acetylation, an acetate was formed m.p. and mixed m.p. 62-63°, lit.[75] m.p. 62-63°.

Expt. 11. 5-Deoxy-L-xylose toluene-p-sulphonylhydrazone.

Toluene-p-sulphonylhydrazide (0.93 g) and 5-deoxy-L-xylose (0.67 g) were dissolved in dry methanol (15 ml) and the mixture refluxed for 30 min. Evaporation under reduced pressure afforded 5-deoxy-L-xylose toluene-p-sulphonylhydrazone, R_G 4.50 solvent (a), as a syrup.

Expt. 12. Reduction of 5-deoxy-L-xylose toluene-p-sulphonylhydrazone.

To a solution of 5-deoxy-L-xylose toluene-p-sulphonylhydrazone (0.52 g) in dry methanol (15 ml) was added potassium borohydride (0.52 g) in portions over a period of 14 hr. The mixture was refluxed for 12 hr. and worked up in a similar manner to that described in Experiment 5. The resulting syrup was chromatographed on paper using solvent (a). The major components of the mixture appeared to be 1-deoxy-D-xylitol, R_G 2.15, and 5-deoxy-L-xylose, R_G 2.27. A trace amount of xylo-pentane-2,3,4-triol, R_G 3.01, was also formed.

Expt. 13. L-Rhamnitol.

To a solution of L-rhamnose monohydrate (25.0 g) in water (100 ml) was added potassium borohydride (3.8 g). The mixture was allowed to stand 14 hr. and then potassium ions were removed with Amberlite IR 120 (H^+) resin. The resin was filtered off, washed with water and the aqueous solution evaporated under reduced pressure to yield a colourless syrup. The syrup was dissolved in methanol (50 ml)

and evaporated to give the crude product containing some boric acid. Treatment with methanol was repeated five times to produce a colourless syrup which was boiled with acetone (300 ml) and crystallised on cooling. The crystals were filtered off and dried. Recrystallisation from methanol-chloroform afforded L-rhamnitol (17.2 g, 76%), m.p. 119-121°, $[\alpha]_D^{20}$ + 12.5° (c 1.0 in water), lit.[74] m.p. 121°, $[\alpha]_D$ + 10.7° in water.

Expt. 14. 1,2; 3,4-Di-O-isopropylidene-L-rhamnitol.

A mixture of L-rhamnitol (9.0 g), anhydrous copper sulphate (6.0 g), concentrated sulphuric acid (10 ml), and acetone (165 ml) was shaken at room temperature for 16 hr., then basified with concentrated aqueous ammonia (5.0 ml). The filtered solution was concentrated and the solid residue was recrystallised from benzene, to yield 1,2; 3,4-di-O-isopropylidene-L-rhamnitol (8.1 g, 61%) m.p. 64-66°, $[\alpha]_D^{20}$ -16° (c 1.5 in methanol), lit.[121] m.p. 64-66°, $[\alpha]_D$ -16° (c 1.5 in methanol).

Expt. 15. 3,4-O-Isopropylidene-L-rhamnitol.

1,2; 3,4-Di-O-isopropylidene-L-rhamnitol (8.2 g) was finely powdered and shaken vigorously with dilute hydrochloric acid (200 ml ; pH 1.0) until an almost clear solution was obtained (ca. 7 min.). The solution was neutralised with aqueous sodium carbonate solution. Extraction of the mixture with chloroform (100 ml) removed starting material (4.0 g) and subsequent continuous extraction with ether removed the mono-O-isopropylidene compound. The recovered starting material was rehydrolysed and the process repeated until recovered starting material was reduced to ca. 0.5 g. The combined ether extracts afforded crude product (6.9 g) from which was obtained , by recrystallisation from benzene, pure 3,4-O-isopropylidene-L-rhamnitol (4.0 g, 58%), m.p. 79-80°, $[\alpha]_D^{20}$ -24° (c 2.0 in water), lit.[121] m.p. 77-78°, $[\alpha]_D$ -24° (c 2.2 in water).

Expt. 16. 5-Deoxy-L-arabinose.

To a solution of 3,4-O-isopropylidene-L-rhamnitol (3.3 g) in phosphate buffer (70 ml; 0.1 M, pH 7.4) was added, with stirring at 0°, sodium metaperiodate (3.6 g). After 5 hr., the solution was freeze-dried and the residue extracted with cold chloroform (4 x 40 ml). The extracts were combined and evaporated under reduced pressure.

The residual syrup was dissolved in water (50 ml) and Amberlite IR 120 (H^+) resin (5 ml) added. The mixture was boiled for 2 hr. cooled, and filtered. The aqueous solution was concentrated to yield 5-deoxy-L-arabinose (2.0 g, 94%), R_G 2.32 solvent (a), M_G (B) 0.76.

Expt. 17. 5-Deoxy-L-arabinose diethyldithioacetal.

A solution of 5-deoxy-L-arabinose (1.0 g) in concentrated hydrochloric acid (1.35 ml) was cooled to 0° and ethanethiol (1.35 ml) added. The mixture was shaken at room temperature for 40 min. at which time it became solid. After cooling to 0°, water (13 ml) was added and the crystals filtered off. Recrystallisation from water afforded 5-deoxy-L-arabinose diethyldithioacetal (1.4 g, 78%), m.p. 108-109°, $[\alpha]_D^{20}$ +27° (c 1.0 in methanol); R_G 3.82 solvent (a), lit.[82] m.p. 108-109° for D-isomer.

Expt. 18. Raney nickel.[122]

To a solution of sodium hydroxide (190 g) in water (750 ml) cooled to 10° was added, with stirring, nickel-aluminium alloy (150 g) at such a rate that the temperature of the mixture remained below 25°. The mixture was heated at 80° for 1 hr., then allowed to cool. The supernatant liquid was decanted and the black deposit washed with water until the pH of the washings reached 6.0. The product was

washed with ethanol (3 x 100 ml) to yield Raney nickel (120 ml).

Expt. 19. L-arabino-Pentane-2,3,4-triol.

To a solution of 5-deoxy-L-arabinose diethyldithioacetal (14.1 g) in warm ethanol (1400 ml) was added Raney nickel (200 ml) and the mixture refluxed for 3 hr. After allowing to cool, the ethanolic solution was decanted and the residue refluxed with ethanol (1l.) for 30 min. The ethanolic solutions were combined and distilled under reduced pressure yielding L-arabino-pentane-2,3,4-triol (3.8 g, 54%), b.p. 88-92°/0.3 mm., $[\alpha]_D^{25}$+6.0° (c 1.0 in water). (Found: C, 46.84; H, 10.03. $C_5H_{12}O_3$ requires C, 50.00; H, 10.00%). R_G 3.33 solvent (a), R_G 2.95 solvent (b), M_G (B) 0.60, M_s (Mo) 0.05, M_s (W) 0.00. RV 0.71, acetate derivative, P.P.E. at 145°, glycerol standard.

Expt. 20. D-Erythrose diethyldithioacetal.

D-Erythrose (7.0 g), separated from D-glucose by cellulose column chromatography, was disssolved in concentrated hydrochloric acid (10.5 ml) and cooled to 0°. Ethanethiol (10.5 ml) was added and the mixture shaken at room temperature for 3 hr. The mixture was again cooled to 0° and water (100 ml) added. The resulting emulsion was neutralised with sodium carbonate and extracted with dichloromethane (2 x 100 ml). The combined extracts were dried with sodium sulphate, filtered, and the filtrate evaporated to yield a syrup of D-erythrose diethyldithioacetal (10.2 g, 78%), R_G 3.91 solvent (a).

Expt. 21. 1-Deoxy-D-erythritol.

To a solution of D-erythrose diethyldithioacetal (10.2 g) in ethanol (400 ml) was added Raney nickel (180 ml) and the mixture allowed to stand 1 hr. and then refluxed for 2 hr. After allowing to cool, the supernatant liquid was decanted and the black residue

extracted with boiling ethanol (400 ml) for 30 min. The ethanol extracts were distilled *in vacuo* and yielded a small amount of a mixture of butane-1,2-diol and butane-2,3-diol, b.p. 85-90°/2.5 mm and 1-deoxy-D-erythritol (2.11 g, 46%), b.p. 125-128°/1.0 mm, $[\alpha]_D^{22}$+17.3° (c 2.5 in water), R_G 1.83 solvent (c), M_G (B) 0.65, M_S (Mo) 0.00, M_S (W) 0.00, RV 0.80, acetate derivative, P.P.E. at 140°, glycerol standard.

Expt. 22. Attempted preparation of 2,3,4-tri-O-acetyl-xylo-pentane-2,3,4-triol.

A solution of 5-deoxy-L-xylose (7.0 g) in concentrated hydrochloric acid (10.0 ml) was cooled to 0° and ethanethiol (10.0 ml) added. The mixture was shaken for 40 min., cooled to 0° and ice-cold water (50 ml) added. The resulting emulsion was neutralised with sodium carbonate, and extracted with dichloromethane (2 x 100 ml). The extracts were dried with sodium sulphate, filtered and evaporated to yield 5-deoxy-L-xylose diethyldithioacetal (10.3 g, 82%) as a syrup, RV 1.60, trimethylsilyl derivative, A.P.K. at 178°, D-glucitol standard.

The product (10.0 g) was dissolved in dry pyridine (100 ml) and acetic anhydride (100 ml) added. The mixture was allowed to stand for 14 hr. at room temperature, then poured into a mixture of ice-water (1l.) and the ice allowed to melt. The crude product was formed as a syrup which adhered to the vessel. The aqueous solution was decanted and replaced by water (1l.). This procedure was repeated several times. The water was finally decanted and the residue recrystallised from ethanol to yield 2,3,4-tri-O-acetyl-5-deoxy-L-xylose diethyldithioacetal (12.0 g, 80%), m.p. 154-156°.

To a solution of 2,3,4-tri-O-acetyl-5-deoxy-L-xylose diethyldithioacetal (12.0 g) in ethanol (250 ml) was added Raney nickel (100 ml) and the mixture refluxed for 4 hr. The ethanol was decanted and the nickel extracted with boiling ethanol (3 x 200 ml).. The ethanolic solutions were combined and evaporated to a volume of 50 ml. On cooling, crystals separated of 2,3,4-tri-O-acetyl-pentane-2,3,4-triol (5.0 g, 62%), m.p. 121-124°, (lit.[65] m.p. 123-124°). Found C, 53.62; H, 7.13; S, 0.00, $C_{11}H_{18}O_6$ requires C, 53.66; H, 7.32; S. 0.00%. Gas-liquid chromatography showed the presence of two components (RV 0.71 and 0.89), acetate derivative, P.P.E. at 140°, glycerol standard. It must be assumed that the compound was not optically pure and that both L-arabino- and xylo- isomers were present.

Expt. 23. 1,5-Di-O-trityl-2,3,4-tri-O-benzoyl-ribitol.

Ribitol (27.5g) was dried at 90° under reduced pressure over phosphorus pentoxide and dissolved in pyridine (250 ml) which had been distilled from phosphorus pentoxide immediately before use. Trityl chloride (102.0 g) was added, the mixture shaken until a solution was obtained and allowed to stand 72 hr. at room temperature. Dry pyridine (400 ml) was added, the solution cooled to 0° and benzoyl chloride (81 ml) added. The mixture was allowed to stand for 48 hr. at room temperature, water (2 ml) was added and the mixture agitated. After 30 min., the reaction mixture was poured into ice-water (5 l.), and the ice allowed to melt. The precipitate was filtered off, dissolved in dichloromethane (1l.) and washed successively with aqueous sodium hydrogen sulphate (3 x 60 ml; 20%), aqueous sodium hydrogen carbonate (4 x 40 ml; 10%) and water

(2 x 10 ml). The solution was dried with sodium sulphate and evaporated to a thin syrup containing pyridine and the required product, which was stirred with methanol (400 ml) for 14 hr. The precipitate was filtered off and recrystallised from ethanol-dichloromethane yielding 1,5-di-O-trityl-2,3,4-tri-O-benzoyl-ribitol (155 g, 90%), m.p. 159-161°, lit.[123] m.p. 161°.

Expt. 24. 1,5-Di-O-toluene-p-sulphonyl-2,3,4-tri-O-benzoyl-ribitol.

To a solution of 1,5-di-O-trityl-2,3,4-tri-O-benzoyl-ribitol (16.0 g) in dichloromethane (200 ml) was added acetic acid (50 ml) and a solution of hydrogen bromide in acetic acid (10 ml; 45%). After 1 min. the solution was poured into aqueous potassium hydrogen carbonate solution (750 ml; 20%) and the dichloromethane layer removed. The aqueous layer was extracted with dichloromethane (2 x 200 ml), the three extracts combined, dried with sodium sulphate, filtered and evaporated. The resulting syrup was dissolved in benzene (50 ml) and the solution evaporated.

The syrup was dissolved in dry pyridine (100 ml), toluene-p-sulphonylchloride (18.0 g) added and the mixture shaken to form a solution. After 40 hr. at room temperature, methanol (2 ml) was added and after a further 30 min., methanol (500 ml) at 0° was added. A precipitate formed which was filtered off after 1 hr. It was washed well with methanol and dried to yield 1,5-di-O- toluene--p-sulphonyl-2,3,4-tri-O-benzoyl-ribitol (7.2 g, 55%), m.p. 163-164°, lit.[123] m.p. 160-161°.

Expt. 25. ribo-Pentane-2,3,4-triol.

A suspension of 1,5-di-O-toluene-p-sulphonyl-2,3,4-tri-O-benzoyl-ribitol (50.0 g) in dry tetrahydrofuran (800 ml) was cooled in an ice bath and lithium aluminium hydride (9.0 g) added. When the

reaction had subsided, the mixture was refluxed and stirred for 4 hr., then allowed to cool. Water (10.0 ml), aqueous sodium hydroxide (10.0 ml; 15%) and water (30 ml) were added successively while sitrring continued. The precipitate which formed was filtered off and extracted with boiling methanol (1l.) for 5 hr. The extract was evaporated and the residue dissolved in water (100 ml). Insoluble material was filtered off and the filtrate treated with Amberlite IR 120 (H^+) resin to remove sodium ions. The tetrahydrofuran solution was evaporated and the residue dissolved in water (100 ml). This aqueous solution was extracted with toluene (100 ml) and sodium ions removed with Amberlite IR 120 (H^+) resin. The aqueous solutions were combined and treated with Amberlite IR 45 (OH^-) resin until neutral. The aqueous solution was distilled under reduced pressure yielding ribo-pentane-2,3,4-triol (3.5 g, 45%) b.p. 146-150°/1.0 mm, R_G 2.96 solvent (a), R_G 5.25 solvent (b), R_G 2.03 solvent (c), M_G (B) 0.51, M_s (Mo) 0.00, M_s (W) 0.00, RV 0.65, acetate derivative, P.P.E. at 140°, glycerol standard.

Expt. 26. 1,5-Di-O-trityl-2,3,4-tri-O-benzoyl-xylitol.

Xylitol (27.5 g) was treated as in Experiment 23 to yield 1,5-di-O-trityl-2,3,4-tri-O-benzoyl-xylitol (141 g, 80%), m.p. 197-199°, lit.[124] m.p. 197-198°.

Expt. 27. 1,5-Di-O-toluene-p-sulphonyl-2,3,4-tri-O-benzoyl-xylitol.

1,5-Di-O-trityl-2,3,4-tri-O-benzoyl-xylitol (16.0 g) was treated as in Experiment 24 to yield 1,5-di-O-toluene-p-sulphonyl-2,3,4-tri-O-benzoyl-xylitol (7.5 g, 58%), m.p. 163-167°, lit.[123] m.p. 165-168°.

Expt. 28. xylo-Pentane-2,3,4-triol.

1,5-Di-O-toluene-p-sulphonyl-2,3,4-tri-O-benzoyl-xylitol (50.0 g) was treated as in Experiment 25 to yield xylo-pentane-2,3,4-triol (2.8 g, 36%), b.p. 88-92°/0.5 mm, R_G 2.96 solvent (a), R_G 5.10 solvent (b), R_G 1.82 solvent (c), M_G (B) 0.66, M_S (Mo) 0.08, M_S (W) 0.07, RV 0.89, acetate derivative, P.P.E. at 140°, glycerol standard.

Expt. 29. Periodate oxidation of triols.

The four triols which had been prepared were oxidised with aqueous sodium periodate solution.

1. Periodate uptake.

Sodium metaperiodate (2.140 g) was dissolved in water (100.0 ml). A portion of this solution (10.0 ml) was added to a solution of the triol (0.030-0.040 g) in water and made up to 100.0 ml with water. A second portion (10.0 ml) was made up to 100.0 ml with water to form a blank solution.

After various times, aliquots (10.0 ml) were withdrawn and added to sodium arsenite solution (25.0 ml; 0.01N). Aqueous sodium hydrogen carbonate (10 ml; 7%) and aqueous potassium iodide (5ml; 20%) were added and after 20 min. excess sodium arsenite was back-titrated with iodine solution (0.02N), using sodium starch glycollate indicator. The uptake of periodate increased very little after 30 min. reaction time. The results are shown in Table IV-1, p.52.

2. Formic acid produced.

An aliquot (5.0 ml) of the above reaction mixture was treated with aqueous ethylene glycol (1 ml; 5%), the solution sealed and allowed to stand for 20 min. The formic acid was then titrated with 0.01N-sodium hydroxide using phenolphthalein indicator.

The amount of formic acid produced increased very little after 30 min. reaction time. The results are shown in Table IV-1, p. 52.

3. Formaldehyde produced.[86,87]

A solution containing glycerol (0.030 g) in aqueous sodium periodate (100.0 ml; 0.01 M) was allowed to stand 5 hr. in the dark. Aliquots (1.0 ml) were withdrawn and accurately diluted with water to 10, 25 and 50 ml. An aliquot (1.0 ml), from the above reaction mixture containing L-erythro-butane-1,2,3-triol, was withdrawn and diluted with water to 10.0 ml.

From these diluted solutions, aliquots (1.0 ml) were treated with aqueous sodium sulphate solution (0.10 ml; 20%) and chromotropic acid reagent (8.40 ml). [The chromotropic acid solution was prepared by dissolving the sodium salt (0.20 g) in water (20.0 ml) and adding sulphuric acid (80 ml; 12.5 M)]. A blank was formed using water (1.0 ml). The mixtures were heated at 100° for 1 hr. during which times colourations developed. After cooling, aqueous thiourea solution (0.50 ml; 0.40%) was added and the optical densities of the solutions measured at 570 mμ.

Results.

moles formaldehyde	absorbance
6.5×10^{-4} M	1.21
1.3×10^{-4} M	0.48
1.3×10^{-4} M	0.24
Formaldehyde solution from reaction mixture	0.41 (0.97 mol.)

The results are shown in Table IV-1, p. 52.

Expt. 30. Pentane-1,3,5-triol.

To a stirred suspension of lithium aluminium hydride (27.0 g) in dry ether (850 ml) was added slowly a solution of 3-hydroxy-diethylglutarate (76.0 g) in dry ether (180 ml). The mixture was refluxed and stirred for 2 hr. then cooled in ice. Water (180 ml) was added slowly, the resultant precipitate filtered off and extracted with ethanol (3 x 1l.). The extracts were combined with the ethereal layer and saturated with carbon dioxide. Insoluble material was filtered off and the filtrate distilled in vacuo to yield pentane-1,3,5-triol (22.4 g, 50%), b.p. 152-154°/1.5 mm, lit.[125] 147-151°/2 mm.

Expt. 31. Preparation of phenylboronates of triols.

The triol (ca. 2 g) was refluxed in benzene or toluene (75 ml) with one equivalent of phenylboronic anhydride. Water was removed over a period 5-14 hr., as an azeotrope, using a Dean and Stark head. Evaporation of solvent produced either a solid, which was recrystallised from hexane, or an oil, which was distilled in vacuo. Physical properties and analysis figures are shown in Table IV-2, p. 54.

Expt. 32. Boron analysis.

A calibration graph was obtained in the following manner. Phenylboronic anhydride (0.121 g) was dissolved in 50% ethanol (100.0 ml) and a portion (10.0 ml) removed and diluted to 100.0 ml. A portion (5.0 ml) of this solution was diluted to 100.0 ml. A second portion (10.0 ml) was removed and diluted to 100.0 ml from which were taken portions of volume 10.0, 20.0 and 30.0 ml, and each diluted to 100.0 ml. In this way, solutions containing concentrations of boron shown on the next page were obtained. Absorbances of the solutions were determined at 219 mμ. A blank

was formed using 50% ethanol.

Results.

g. boron/100 ml.	absorbance
1.25×10^{-5}	0.104
2.50×10^{-5}	0.209
3.76×10^{-5}	0.309
6.27×10^{-5}	0.518

Boron content of samples was determined by dissolving the sample (0.03-0.05 g) in 50% ethanol (100.0 ml) and diluting the solution twice by factors of ten, as above, before determining the absorbance. Boron content was established using the calibration graph.

Expt. 33. Hydrolysis of L-arabino-pentane-2,3,4-triol phenylboronate.

The residue remaining after distillation of L-arabino-pentane-2,3,4-triol phenylboronate (0.02 g) was dissolved in warm water (2 ml) and the phenylboronic acid destroyed with bromine water (0.6 ml; 3%). After 10 min., the solution was evaporated and the residue treated with methanol (4 x 2 ml). Methanol was evaporated and the residue acetylated using acetic anhydride (4 ml) and pyridine (4 ml). After 10 min. at 90°, the solution was evaporated and the residue dissolved in chloroform (0.3 ml). This solution (3 μl.) was introduced into a gas-liquid chromatograph which showed that only 2,3,4-tri-O-acetyl-L-arabino-pentane-2,3,4-triol had been formed (RV 0.71, P.P.E. at 150°, glycerol standard).

Expt. 34. Attempted isomerisations of phenylboronates of triols.

Glycerol phenylboronate (0.15 g) and triethylamine (0.10 ml) were refluxed together in toluene (20 ml) for 14 hr. Evaporation of solvent yielded a crystalline residue m.p. 76-78°, mixed m.p. 76-78°.

A similar procedure using L-erythro-butane-1,2,3-triol phenylboronate also produced the boronate unchanged, m.p. 75-76°, mixed m.p. 75-76°.

Expt. 35. Preparation of triol phenylboronate mono-phenylcarbamates.

Triol phenylboronate was refluxed with phenyl isocyanate (1.1 mol.) in dry toluene for 8-24 hr. If the reaction was sluggish, triethylamine (1.0 mol.) was added and refluxing continued 8 hr. Solvents were evaporated and the residue recrystallised from benzene-hexane or hexane. Results are shown below.

The phenylboronates of ribo- and xylo-pentane-2,3,4-triols contained free triol. This was removed by allowing to stand with triethylamine and excess phenyl isocyanate in toluene at room temperature for 2 hr. Crystals of the triol tri-phenylcarbamate were filtered off and the filtrate refluxed to obtain the triol phenylboronate mono-phenylcarbamate.

Glycerol phenylboronate mono-phenylcarbamate, $C_{16}H_{16}BNO_4$ requires C, 66.49; H, 5.42; N, 4.72%. A butane-triol phenylboronate mono-phenylcarbamate, $C_{17}H_{18}BNO_4$ requires C, 66.59; H, 5.79; N, 4.50%. A pentane-triol phenylboronate mono-phenylcarbamate, $C_{18}H_{20}BNO_4$, requires C, 66.46; H, 6.20; N, 4.31%.

Phenylboronate phenylcarbamates of triols.

Triol of phenylboronate		Catalyst	m.p.	yield (%)	Found C (%)	Found H (%)	Found N (%)
Glycerol			116-117°	60	64.51	5.30	4.88
Butane-1,2,4-triol							
	distillate	$(C_2H_5)_3N$	85-87°	54	65.70	5.89	4.63
	residue	$(C_2H_5)_3N$	no reaction				
L-erythro-	Butane-1,2,3-triol		89-91°	65	65.30	6.06	4.69
ribo-	Pentane-2,3,4-triol						
	distillate	$(C_2H_5)_3N$	163-164°	55	65.80	5.83	4.46
	residue	$(C_2H_5)_3N$	163-164°	20	65.58	5.64	
L-arabino-	Pentane-2,3,4-triol						
	distillate		103-104°	60	66.56	6.14	4.38
	distillate	$(C_2H_5)_3N$	103-104°	40	66.43	6.20	4.32
	residue	$(C_2H_5)_3N$	no reaction				
xylo-	Pentane-2,3,4-triol						
	distillate	$(C_2H_5)_3N$	no reaction				
	residue	$(C_2H_5)_3N$	no reaction				

Expt. 36. Periodate oxidation of phenylboronate phenylcarbamates of triols.

1. Periodate uptake.

The phenylboronate phenylcarbamate of a triol (ca. 0.10 g) was dissolved in N,N-dimethylformamide (25.0 ml), water (25 ml) added, aqueous sodium metaperiodate (10.0 ml; 0.1 M) added and the volume made up to 100.0 ml with water. This reaction mixture was stored in the dark. A blank was formed using an equivalent weight of phenylboronic anhydride in place of the phenylboronate phenylcarbamate of the triol. Periodate uptake was determined as in Experiment 29.1. The results are shown in Table IV-4, p.70.

2. Formaldehyde produced.

The quantity of formaldehyde produced on oxidation of L-erythro-butane-1,2,3-triol phenylboronate phenylcarbamate was measured as in Experiment 29.3.

Expt. 37. α-D-glucofuranose-1,2; 3,5-bis-phenylboronate.

D-Glucose (1.0 g) and phenylboronic anhydride (1.16 g) were dissolved in 2-methoxyethanol by heating at 90° for 30 min. The solvent was evaporated and the residue recrystallised from toluene to yield α-D-glucose-1,2; 3,5-bis-phenylboronate (1.76 g, 90%), m.p. 161-162°, lit.[21] m.p. 161-162°.

Expt. 38. Diazomethane.[126]

A solution of toluene-p-sulphonylmethylnitrosamide (21.5 g) in dichloromethane (125 ml) was slowly added to a stirred mixture of potassium hydroxide (6.0 g), water (10 ml), 2-(2-ethoxyethoxy) ethanol (35 ml) and dichloromethane (10 ml). The reaction mixture was heated by an oil both at 70-75° which ensured that diazomethane

and dichloromethane distilled together. A solution of diazomethane (2.7-2.9 g, 64-69%) in dichloromethane (125 ml) was obtained, which was dried over sodium hydroxide pellets and stored at 0°.

Expt. 39. 6-O-Methyl-D-glucose.

A solution of α-D-glucofuranose-1,2; 3,5-bis-phenylboronate (1.2 g) in dichloromethane (20 ml) was cooled to -5° and boron trifluoride etherate (0.04 ml) added. A solution of diazomethane (0.5 g) in dichloromethane was added slowly. After 30 min. at -5°, a white precipitate of polymethylene had formed and was filtered off. Dichloromethane was evaporated, the residue dissolved in n-butanol saturated with water (10 ml) and applied to the top of a cellulose powder column (3cm x 30 cm). The column was eluted with the same solvent, fractions (25 ml) collected, fractions 15-19 combined and evaporated. The residue was twice recrystallised from ethanol yielding 6-O-methyl-D-glucose (0.27 g, 40%), m.p. 143-144°, R_G 1.92 solvent (a), R_G 1.37 solvent (c), M_G (B) 0.88, $[\alpha]_D^{20}$ + 95° → + 61° (c 1.0 in water), lit.[127] m.p. 142-144°, $[\alpha]_D^{20}$ + 95.2° → + 61.0° (c 1.2 in water).

Expt. 40. Methylation of phenylboronates of triols.

The phenylboronate of a triol (0.02 g) was dissolved in a solution of boron trifluoride etherate in dichloromethane (0.16%; 1 ml) and cooled to -5°. Diazomethane in dichloromethane (5 ml) was added and after 3 min., a further 5 ml was added. After 30 min. at -5° solvent was evaporated and the residue hydrolysed with boiling water (2 ml). The phenylboronic acid thus produced was converted to bromobenzene by addition of bromine water (3%; 0.6 ml) and after allowing to stand 15 min. at 20°, the solution was evaporated.

Boric acid was removed by repeated distillation of the residue with methanol as in Experiment 33 to produce a monomethyl ether of a triol (83-100%). The residue was acetylated using acetic anhydride (4 ml) and pyridine (4 ml). After 10 min. at 90°, the solution was evaporated and the residue dissolved in chloroform (0.3 ml). This solution (3 µl.) was applied to a gas-liquid chromatography column (2m x 1mm) containing P.P.E. stationary phase. By this means, the components of the mixture were separated and analysed, on line, by a flame ionisation detector and mass spectrometer. Retention volumes (RV), structures of components and relative proportions are shown in Table IV-5 (p.77).

Expt. 41. Preparation of polyol bis- and tris-phenylboronates.

Two methods were used to prepare polyol phenylboronates.

i) A solution of phenylboronic anhydride was added to a solution of the polyol in water. A precipitate formed which was filtered off, washed with water and methanol and dried.

ii) To a solution of the polyol in 2-methoxyethanol was added phenylboronic anhydride. The mixture was warmed at 90° for 30 min. and evaporated forming a crystalline residue.

The esters were recrystallised from toluene-hexane and their physical data are shown below. Phenylboronates not listed were available from previous work.

Phenylboronate	Method of preparation	m.p.
1-Deoxy-D-xylitol bis-	(ii)	164-165°
D-Glucitol tris-	(i) (ii)	188-189° lit.[22] m.p. 187-190°
1-d_1-D-Glucitol tris-	(ii)	187-189°
D-Mannitol tris-	(i)	136-137° lit.[22] m.p. 134-135°

Expt. 42. 1-d_1-D-Glucitol.

To a solution of D-glucose (0.10 g) in water (5 ml) was added sodium borodeuteride (0.014 g). After 4 hr. the solution was treated with Amberlite IR 120 (H^+) resin, the resin filtered off and the filtrate evaporated. The residue was treated with methanol (4 x 4 ml) and recrystallised from ethanol-water to yield 1-d_1-D-glucitol (0.095 g, 94%), m.p. 95-100°, M_s (Mo) 1.00.

Expt. 43. Partial trans-esterification of galactitol tris-phenylboronate.

To a solution of galactitol tris-phenylboronate (0.100 g) in pyridine (5 ml) was added a solution of propane-1,3-diol (0.017 g) in pyridine (5 ml). The mixture was briefly shaken and a portion (1 ml) removed. To this portion were added hexamethyldisilazane (0.2 ml) and trimethylsilylchloride (0.1 ml), the mixture was shaken for 30 sec. and allowed to stand 5 min. A white precipitate of ammonium chloride formed. The supenatant liquid was decanted and evaporated. The residue was dissolved in dry ether (0.5 ml) and a small portion analysed by gas-liquid chromatography. The procedure was repeated using propane-1,3-diol (0.034 g, 2 mol.).

Galactitol tris-phenylboronate was involatile under the chromatographic conditions used (S.E.-30 186°) and only the trimethylsilyl ethers of galactitol bis-phenylboronate (RV 11.0), galactitol mono-phenylboronate (RV 2.65) and galactitol (RV 1.0) could be detected. Propane-1,3-diol phenylboronate (RV 0.50) also appeared in the chromatograms.

Results showed that use of 1 mol. of propane-1,3-diol produced

galactitol bis-phenylboronate (1720) and

galactitol mono-phenylboronate(200).

Use of 2 mol. of propane diol gave

galactitol bis-phenylboronate (700),

galactitol mono-phenylboronate (1330) and

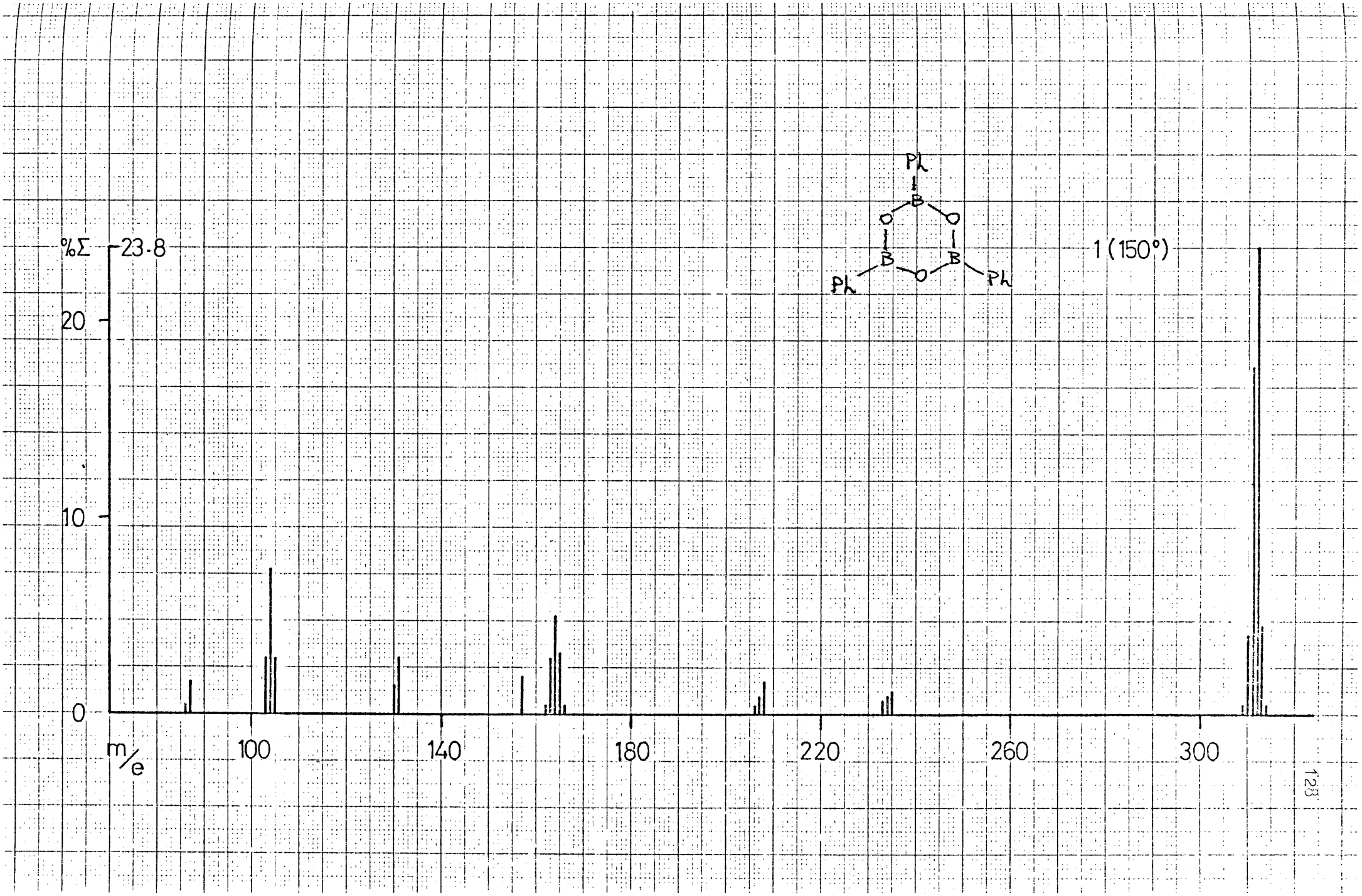
galactitol (trace).

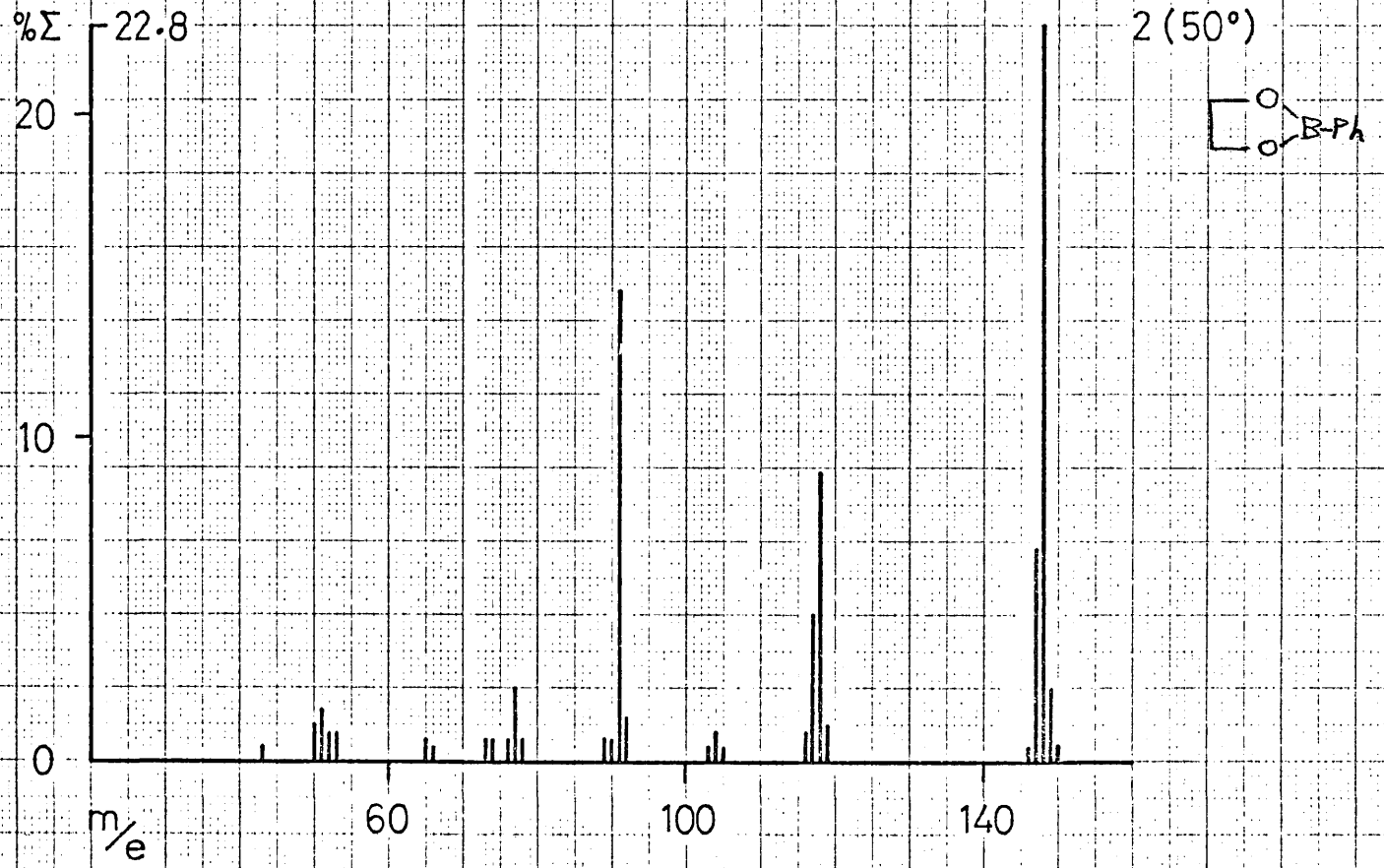
Numbers in parentheses are peak areas and thus are not directly proportional to quantities.

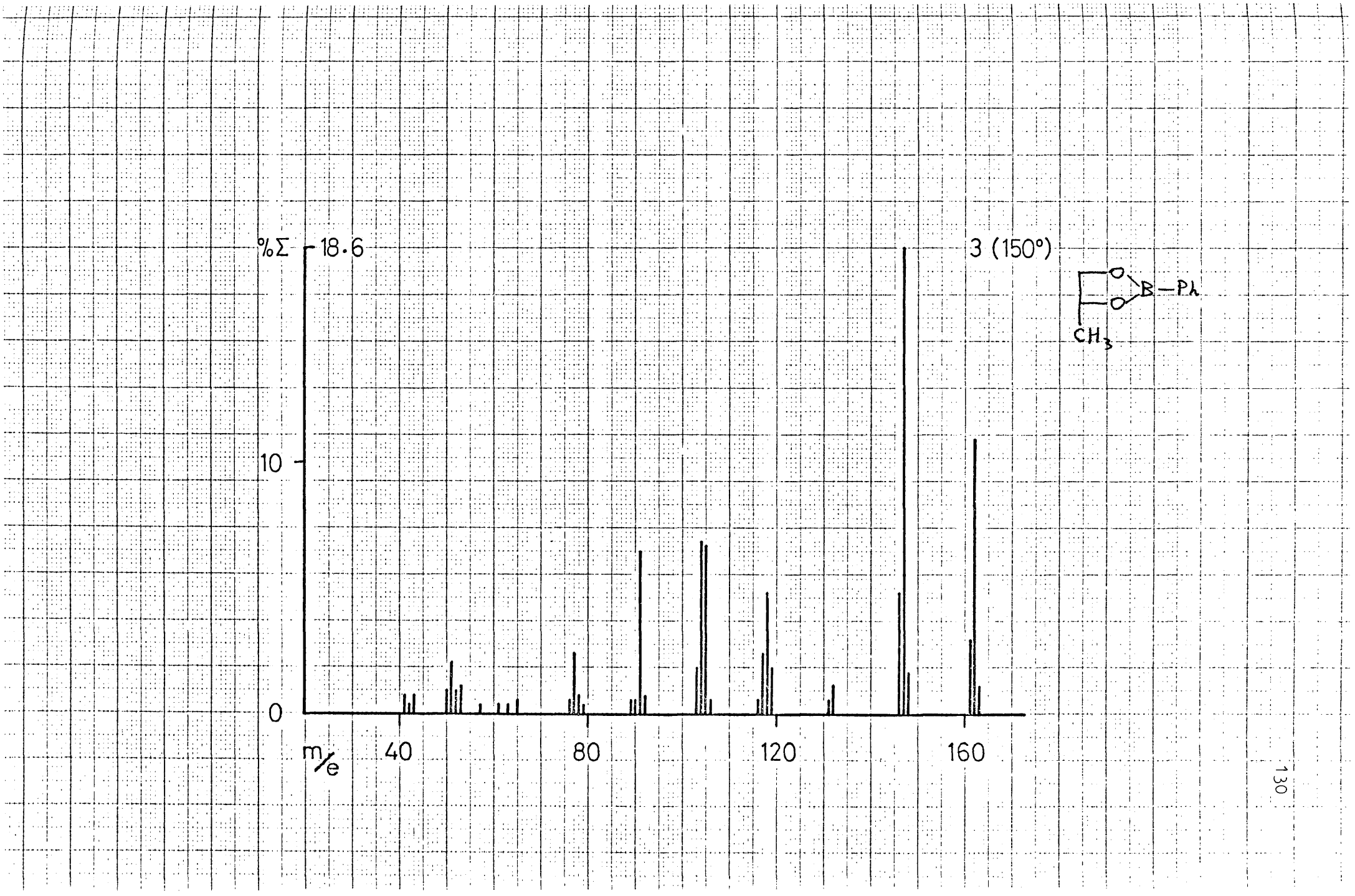
Appendix - Mass Spectra of Phenylboronates of Diols, Triols, Tetritols, Pentitols and Hexitols.

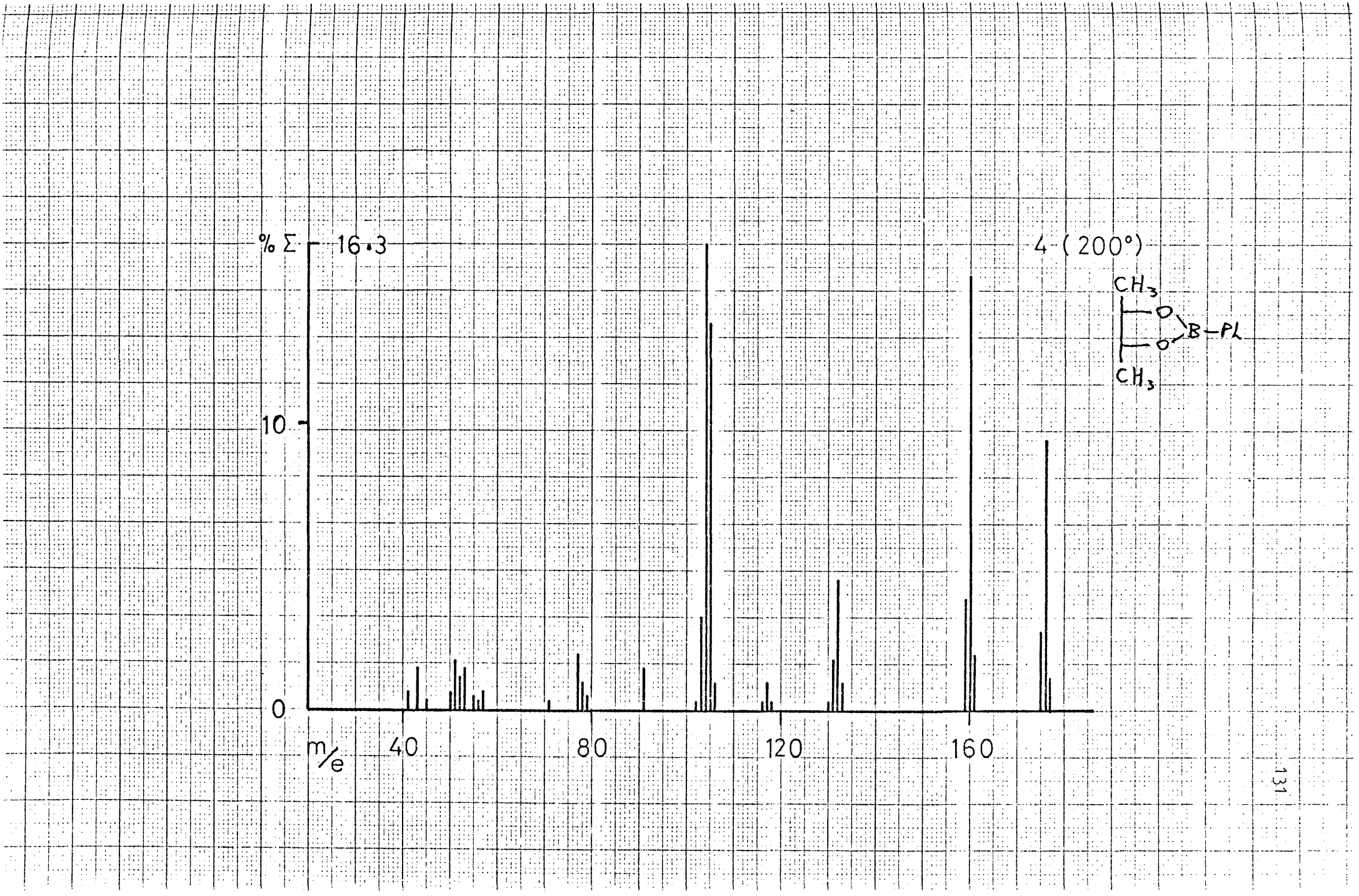
The data listed in the following pages is divided into three parts. Part A contains the low resolution mass spectra of the phenylboronates studied. Numbers in parentheses refer to the temperature of the "ion source". Abundances of ions are quoted as a percentage of the total ion current. Part B contains precise mass measurements and formulae of ions. In Part C, metastable ions which appear in the low resolution spectra are tabulated together with metastable transitions in which they may have been produced. Experimental measurements to determine parent and daughter ions which produce metastable ions are also reproduced.

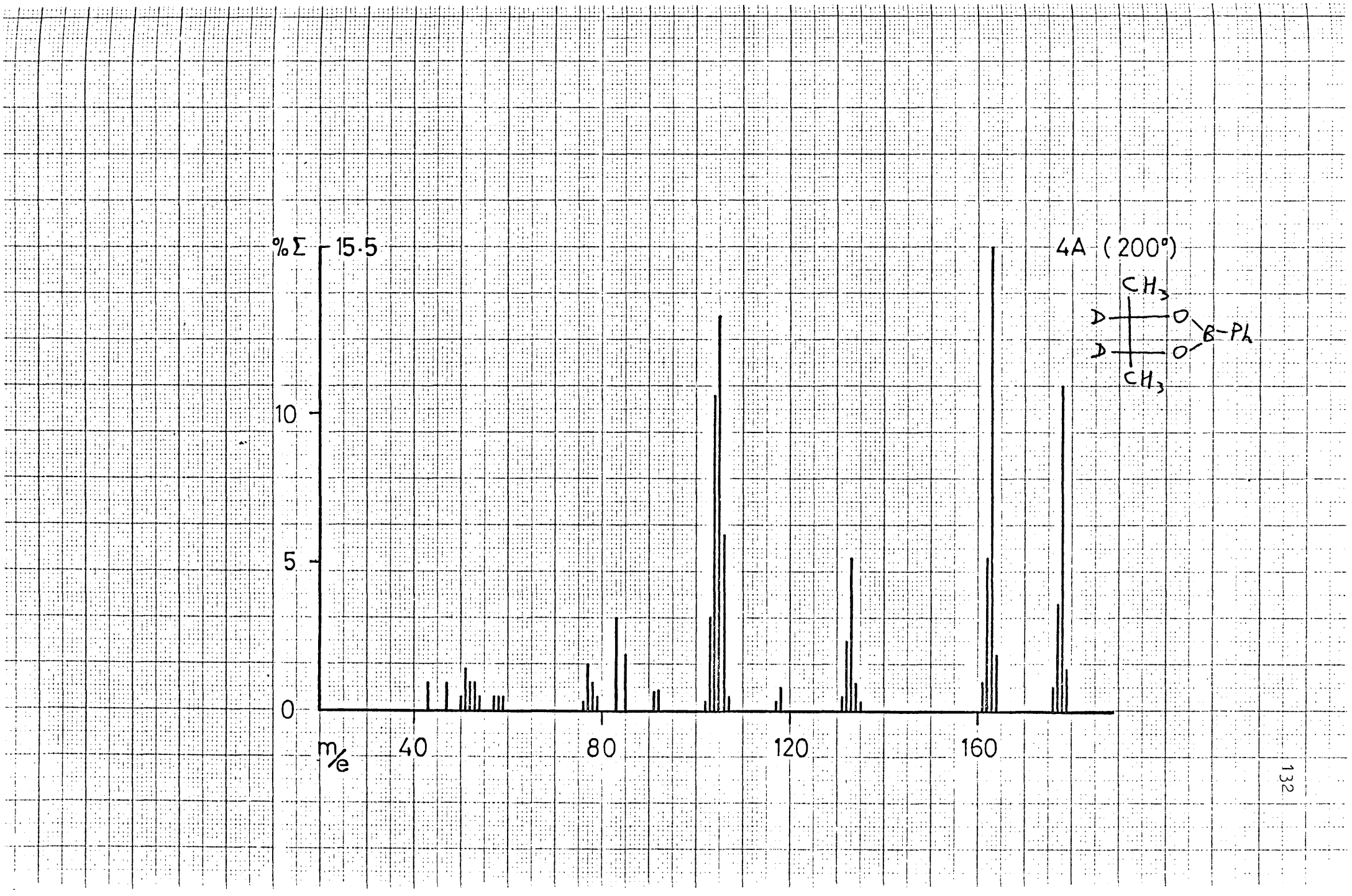
Part A - Low resolution mass spectra of phenylboronates.

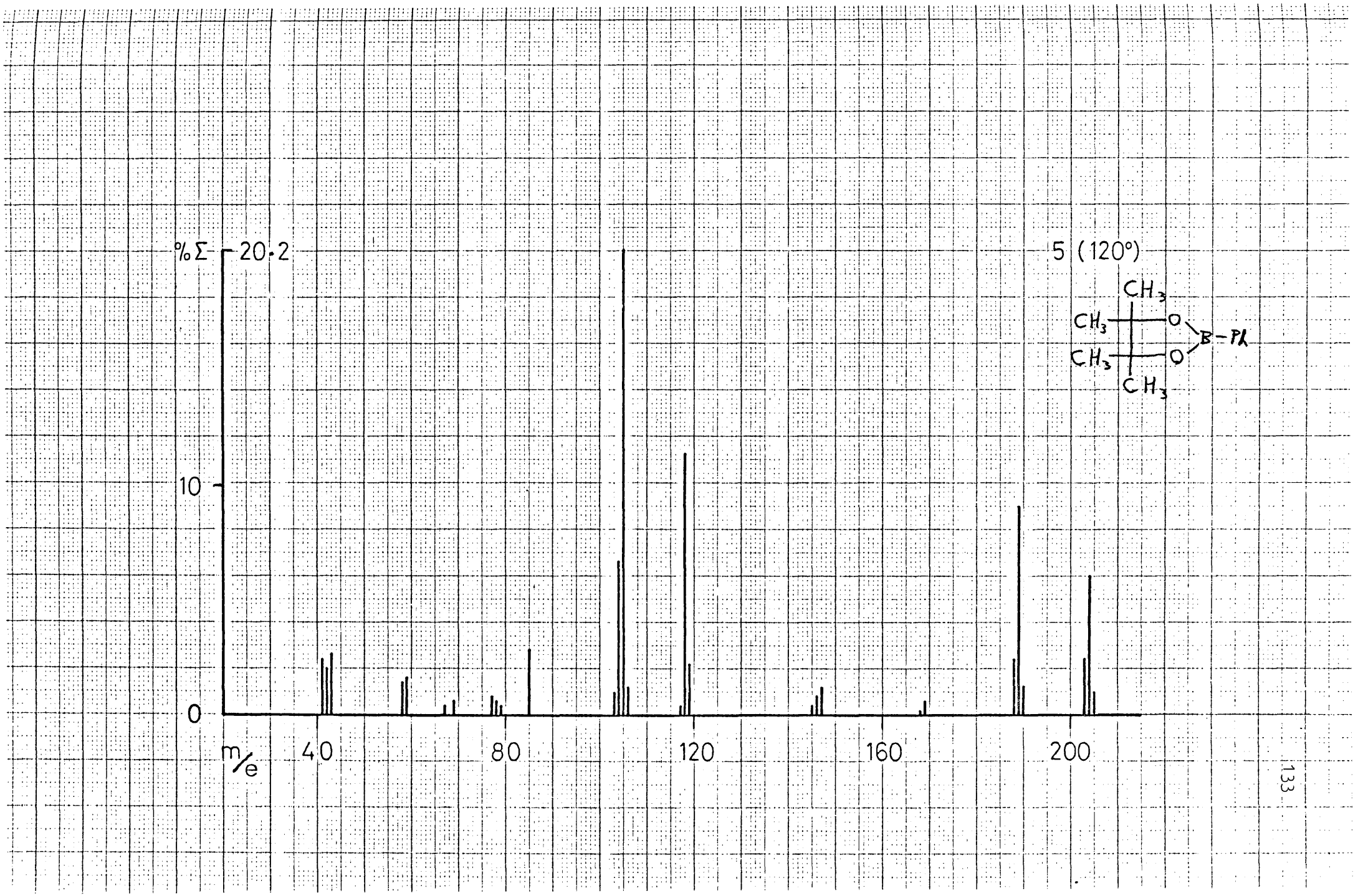

%Σ
23·8
20
10
0
m/e
100
140
180
220
260
300
1 (150°)
Ph
B
O
O
B
B
O
Ph
Ph
123

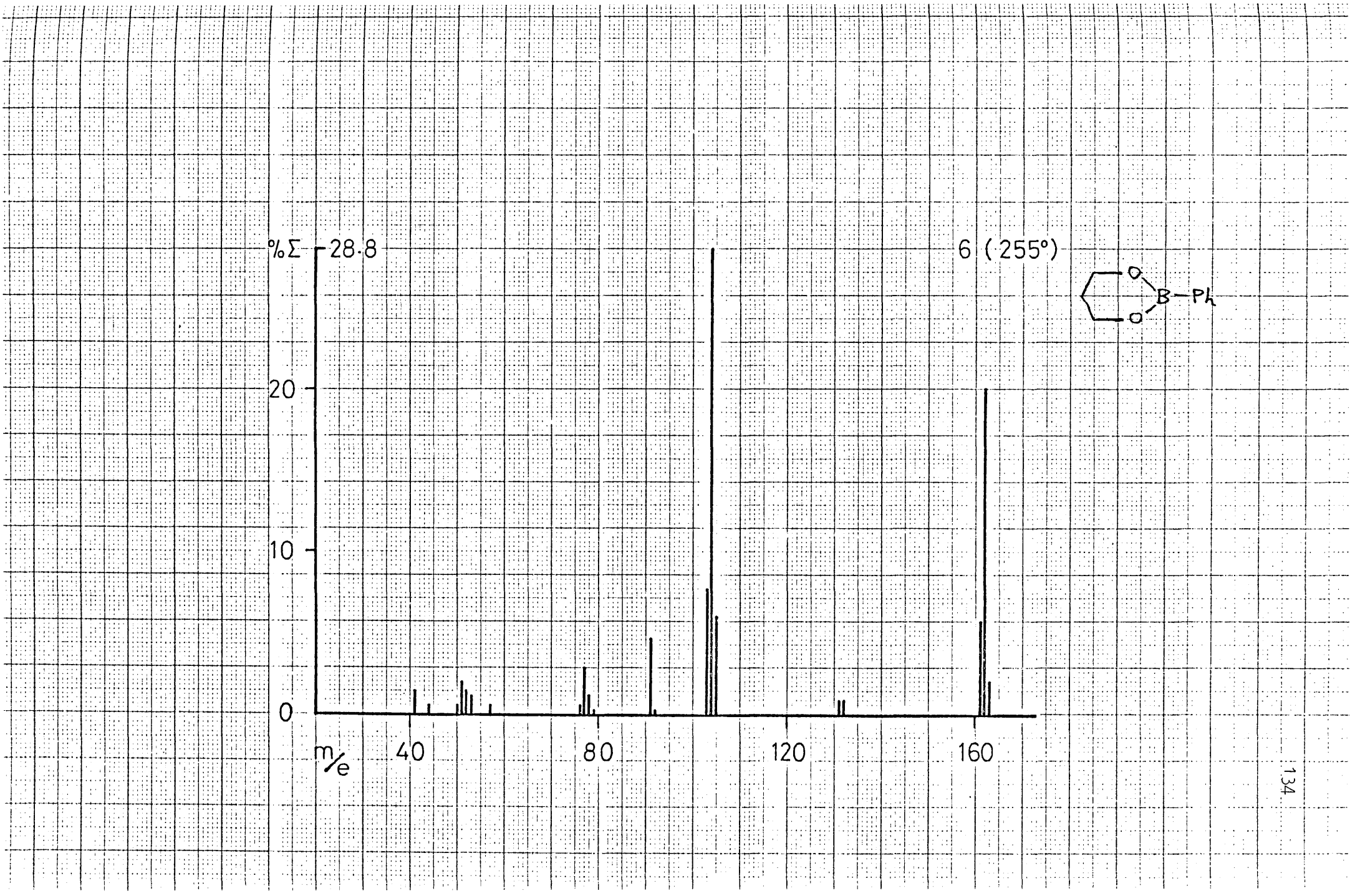

%Σ
22·8
20
10
0
m/e
60
100
140
2 (50°)
B-Ph

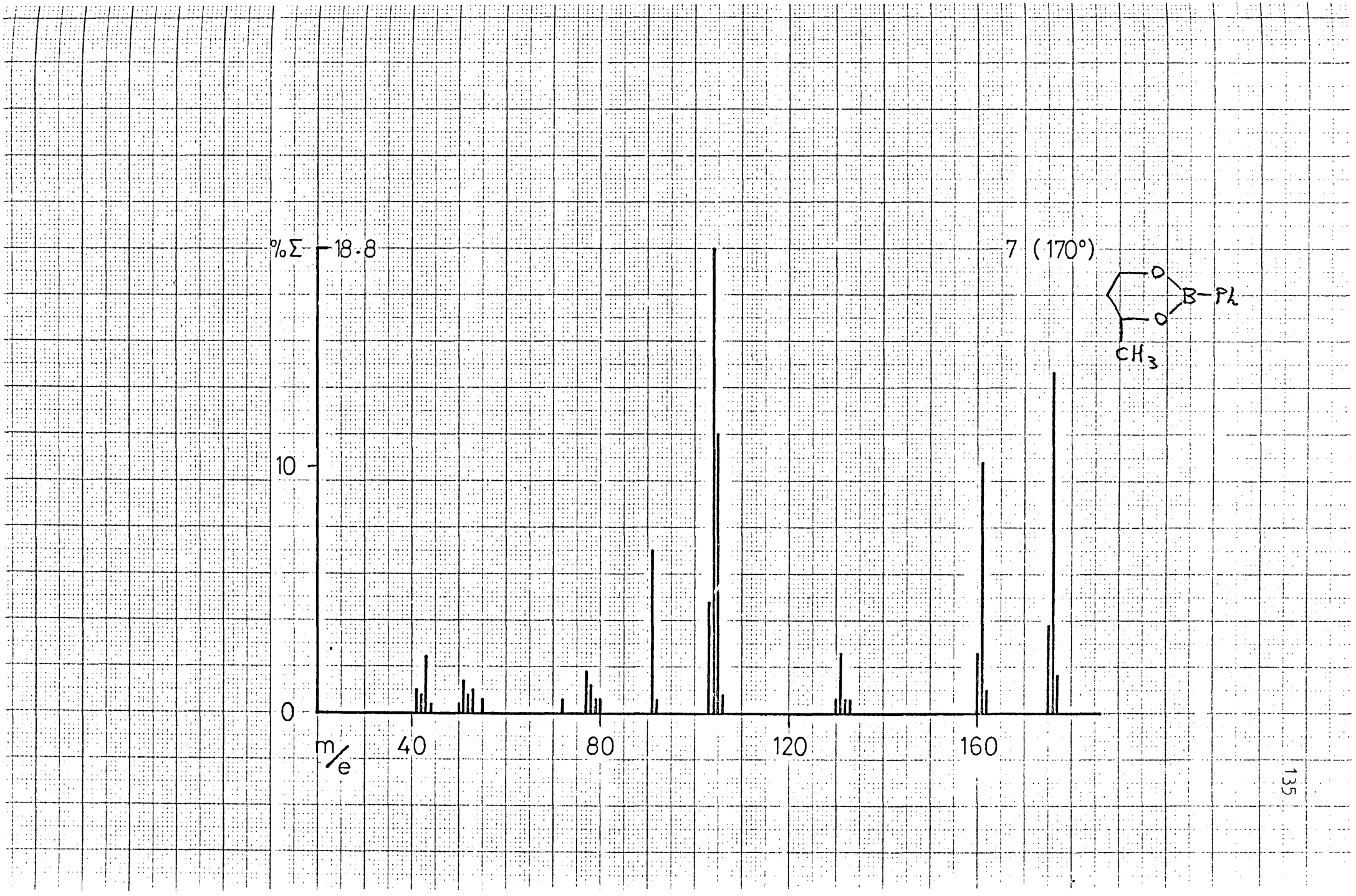

%Σ
18.6
10
0
m/e
40
80
120
160
3 (150°)
B—Ph
CH3

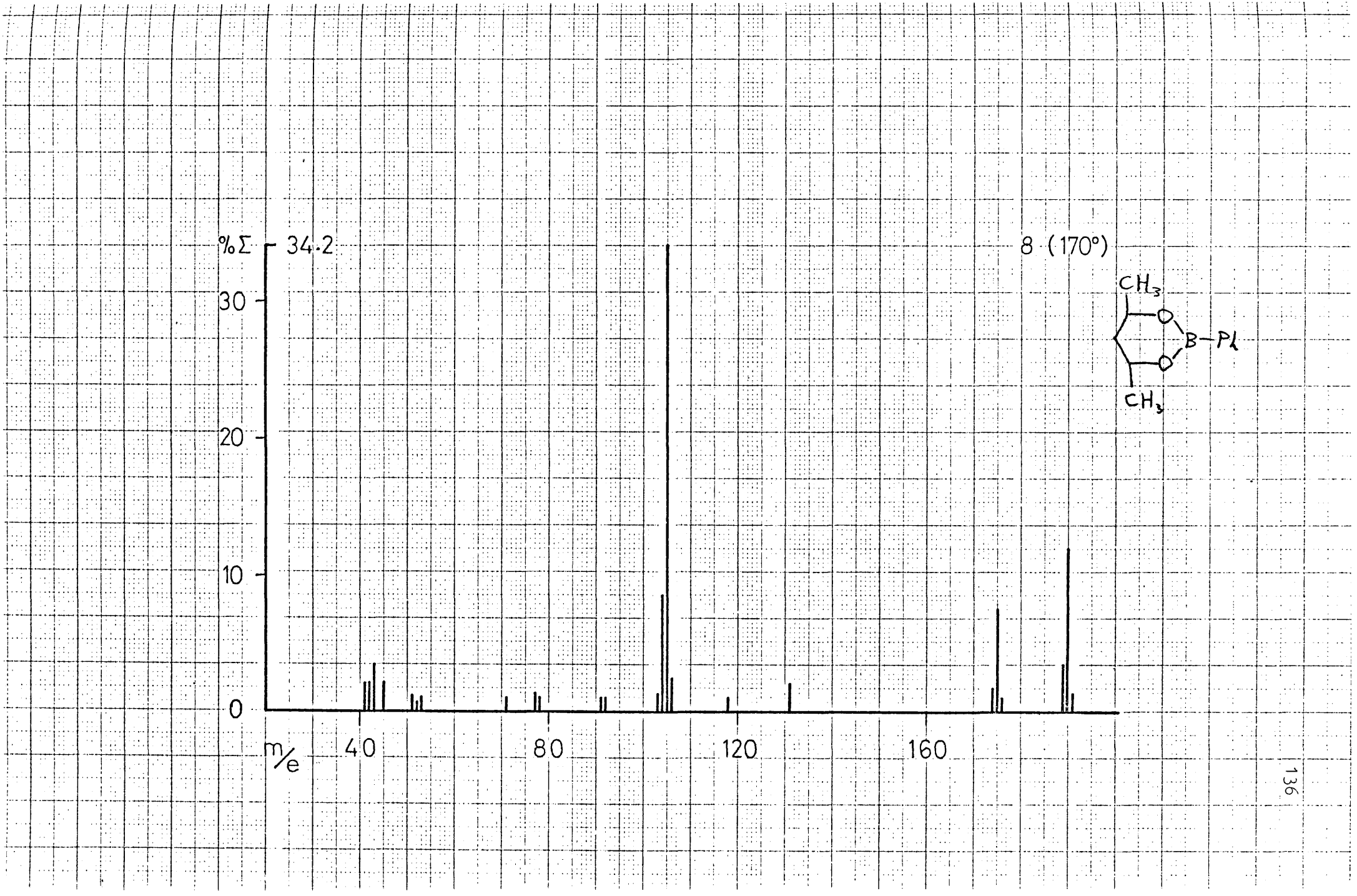

% Σ
16.3
10
0
m/e
40
80
120
160
4 (200°)
CH3
O
B–Pl
O
CH3

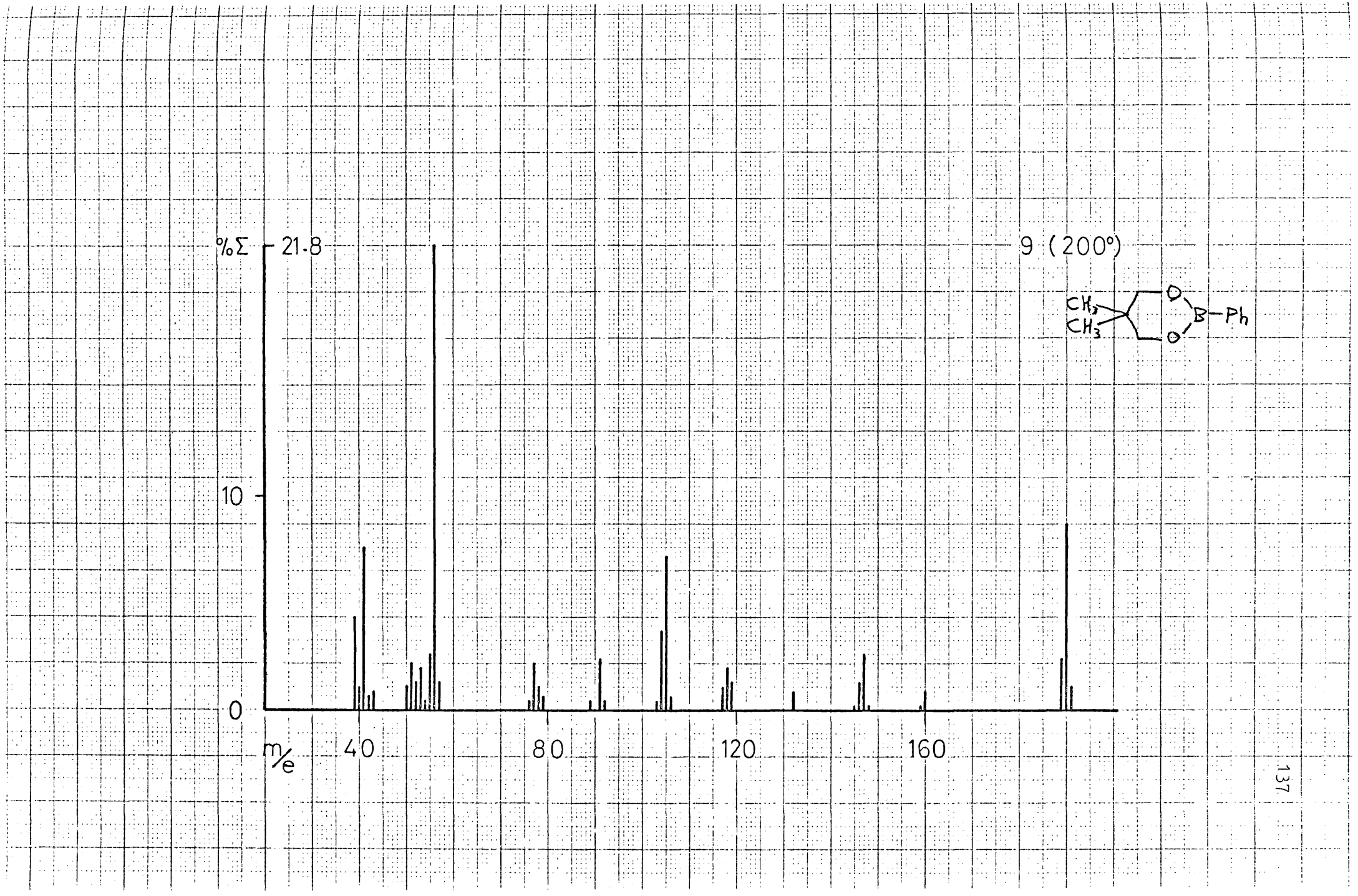

%Σ
15·5
10
5
0
m/e
40
80
120
160
4A (200°)
CH3
D
O
B-Ph
D
O
CH3

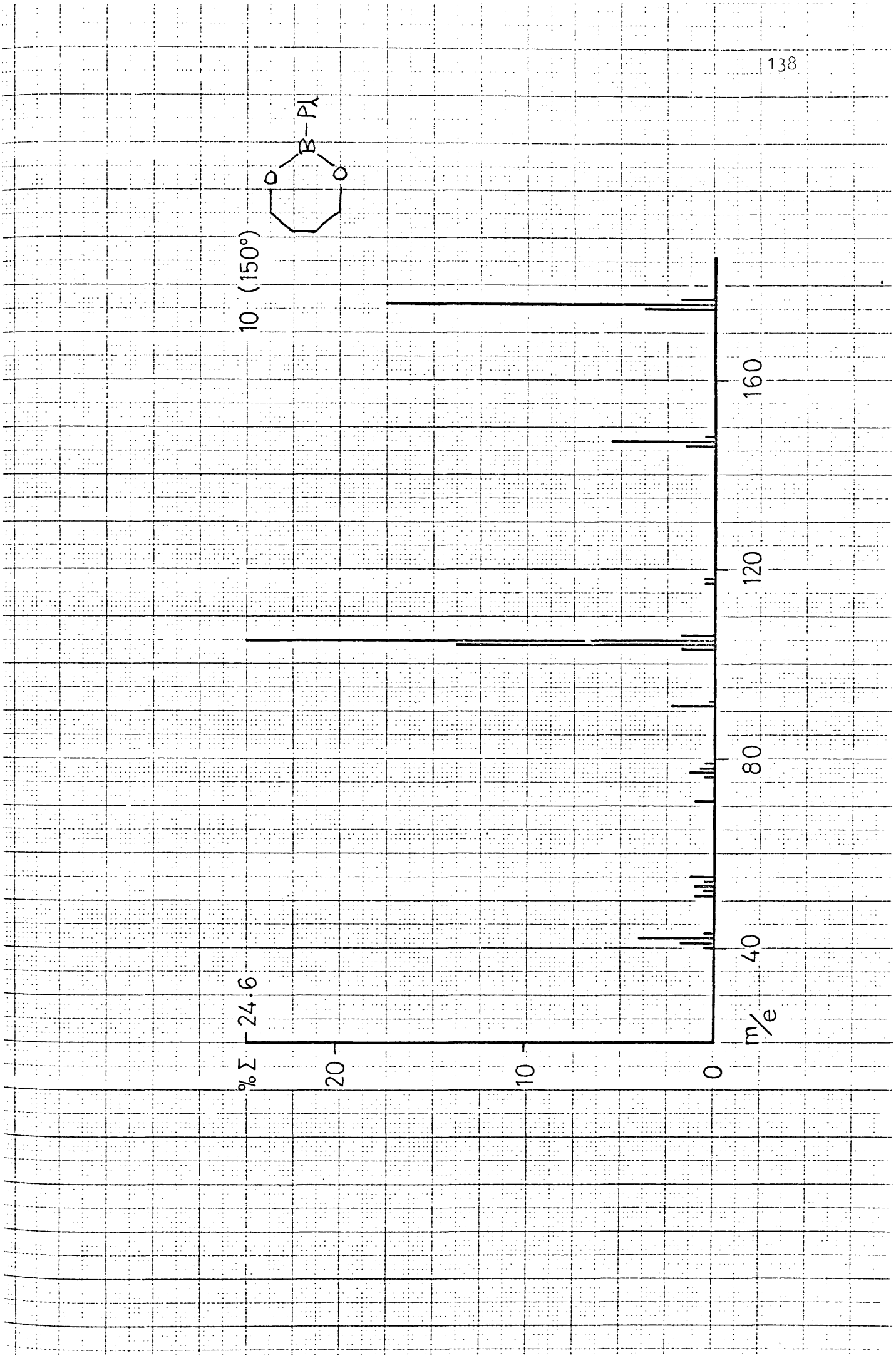

%Σ
20·2
10
0
m/e
40
80
120
160
200
5 (120°)
CH3
CH3
O
B-Ph
CH3
O
CH3

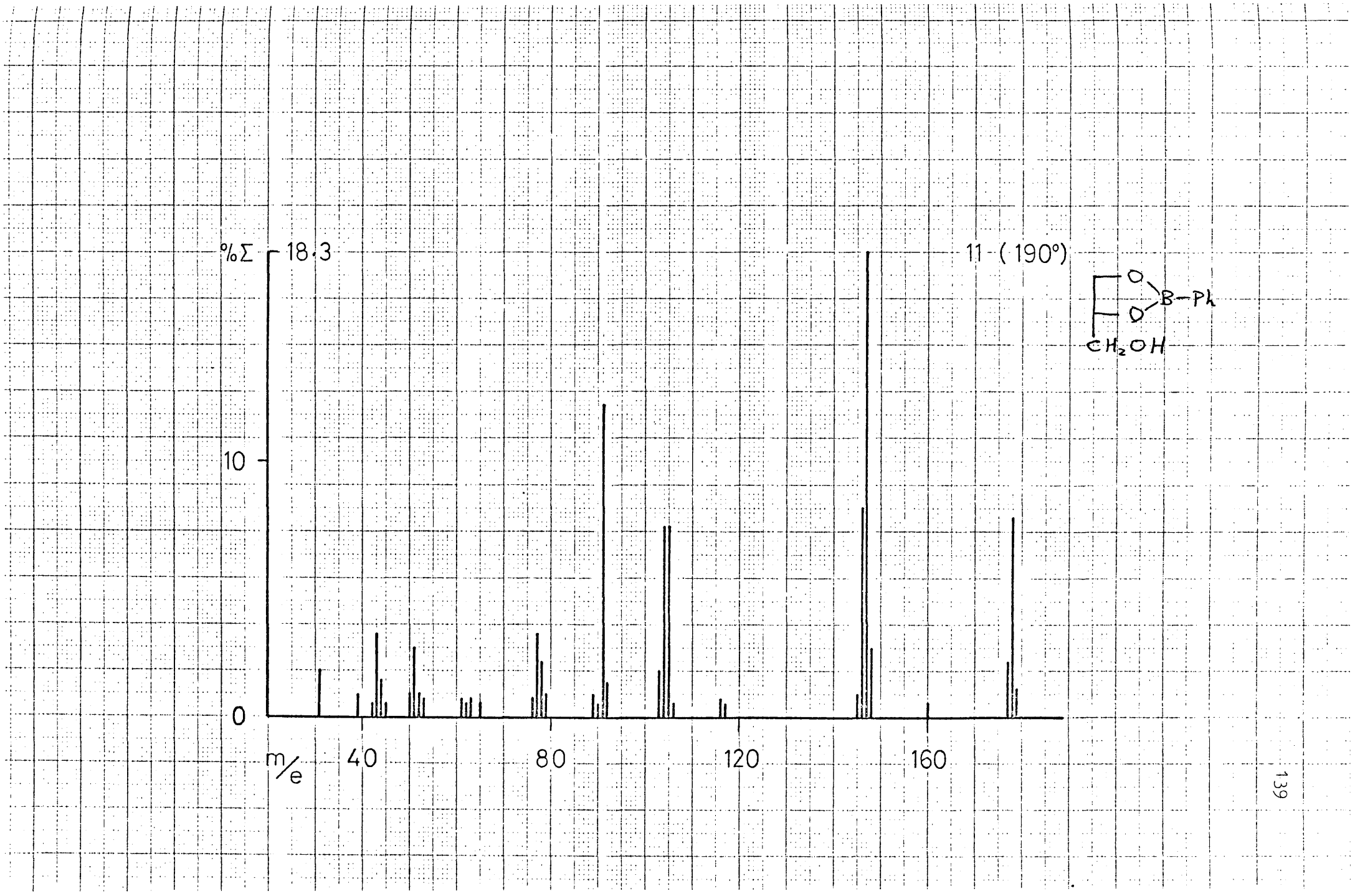

%Σ
28·8
20
10
0
m/e
40
80
120
160
6 (255°)
O
B
Ph
O

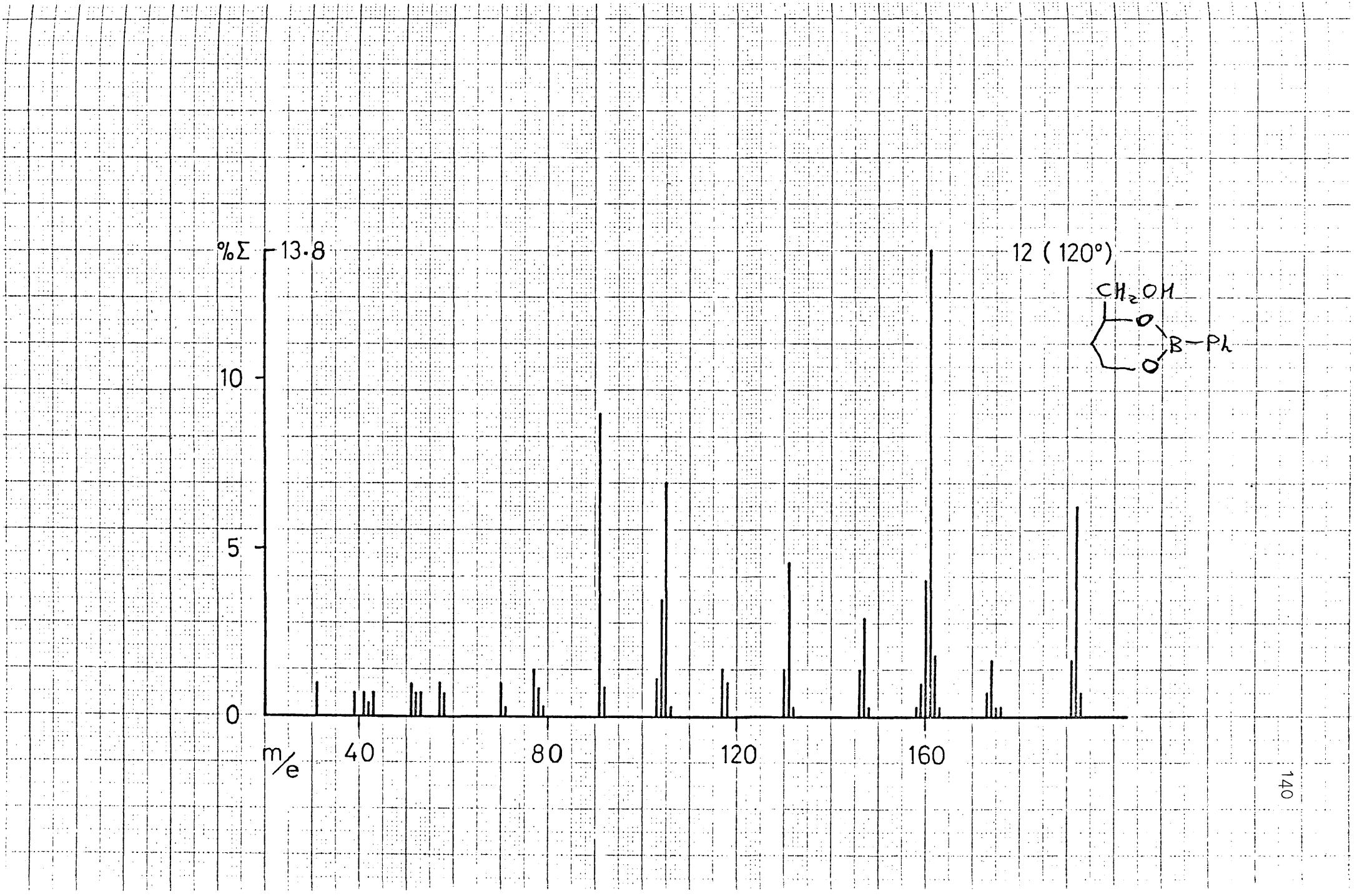

%Σ
18·8
10
0
m/e
40
80
120
160
7 (170°)
O
B–Ph
O
CH3

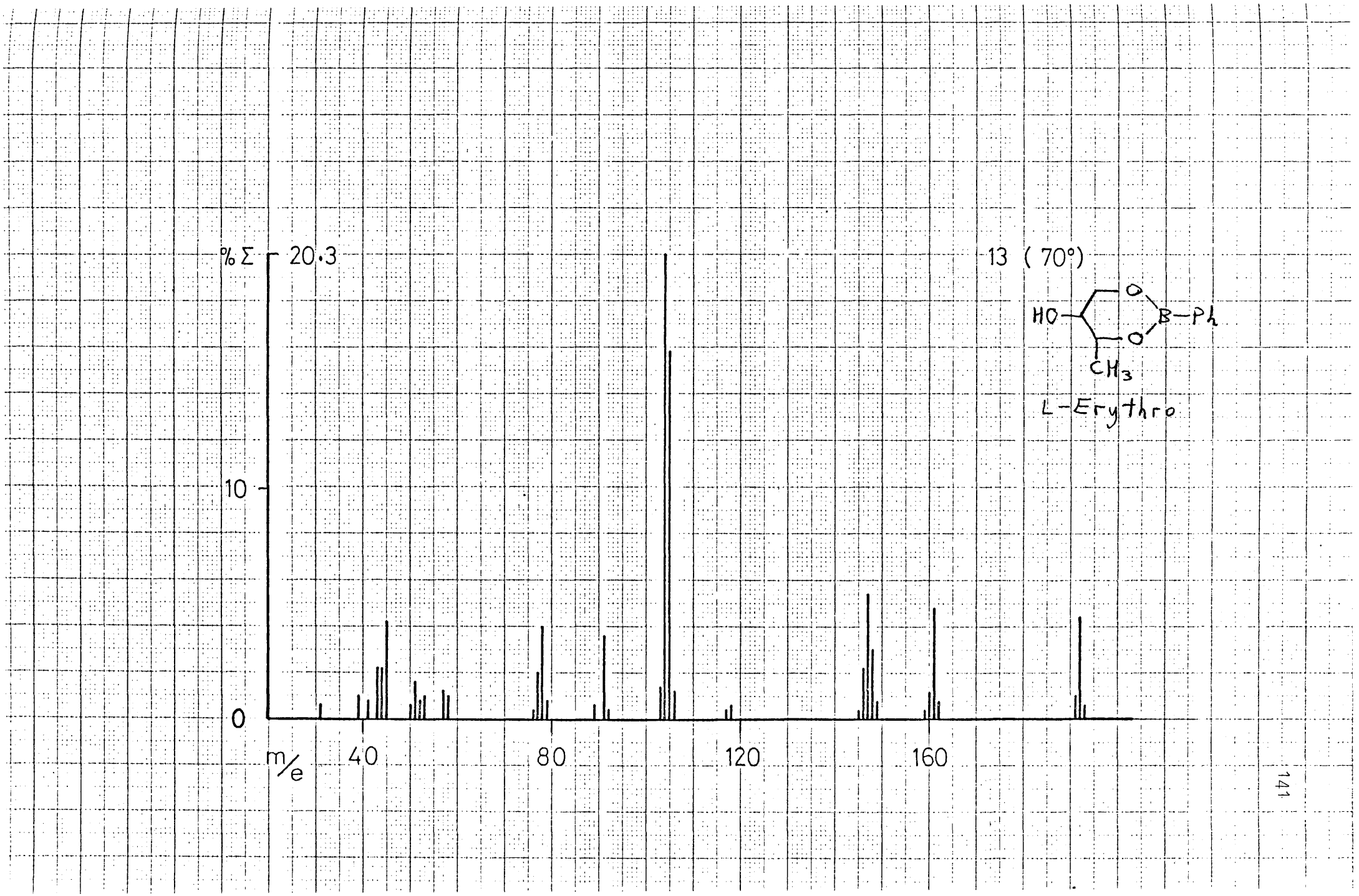

%Σ
34.2
30
20
10
0
m/e
40
80
120
160
8 (170°)
CH3
B
Ph
CH3

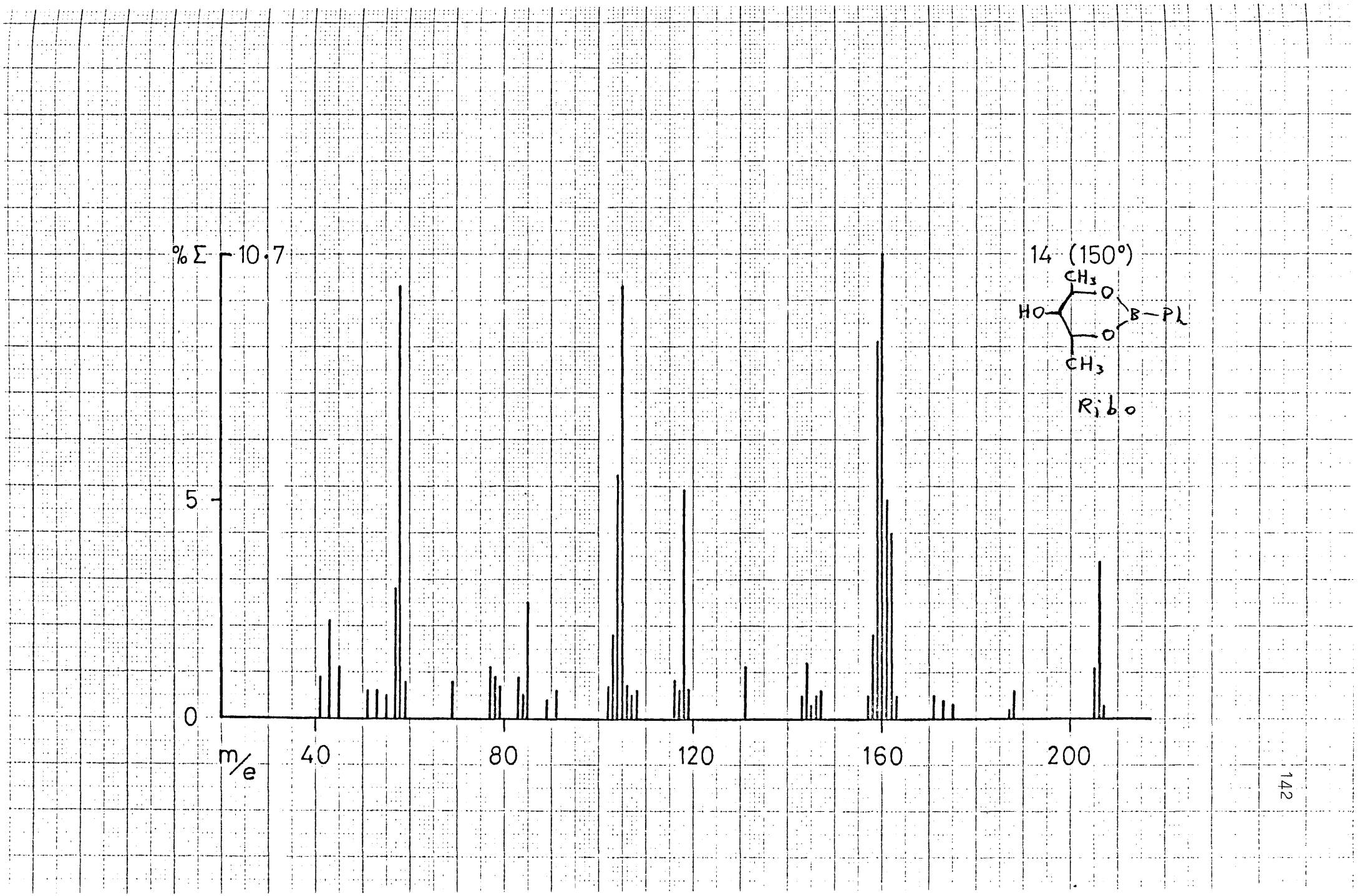

%Σ
21·8
10
0
m/e
40
80
120
160
9 (200°)
CH3
CH3
O
B
Ph
O

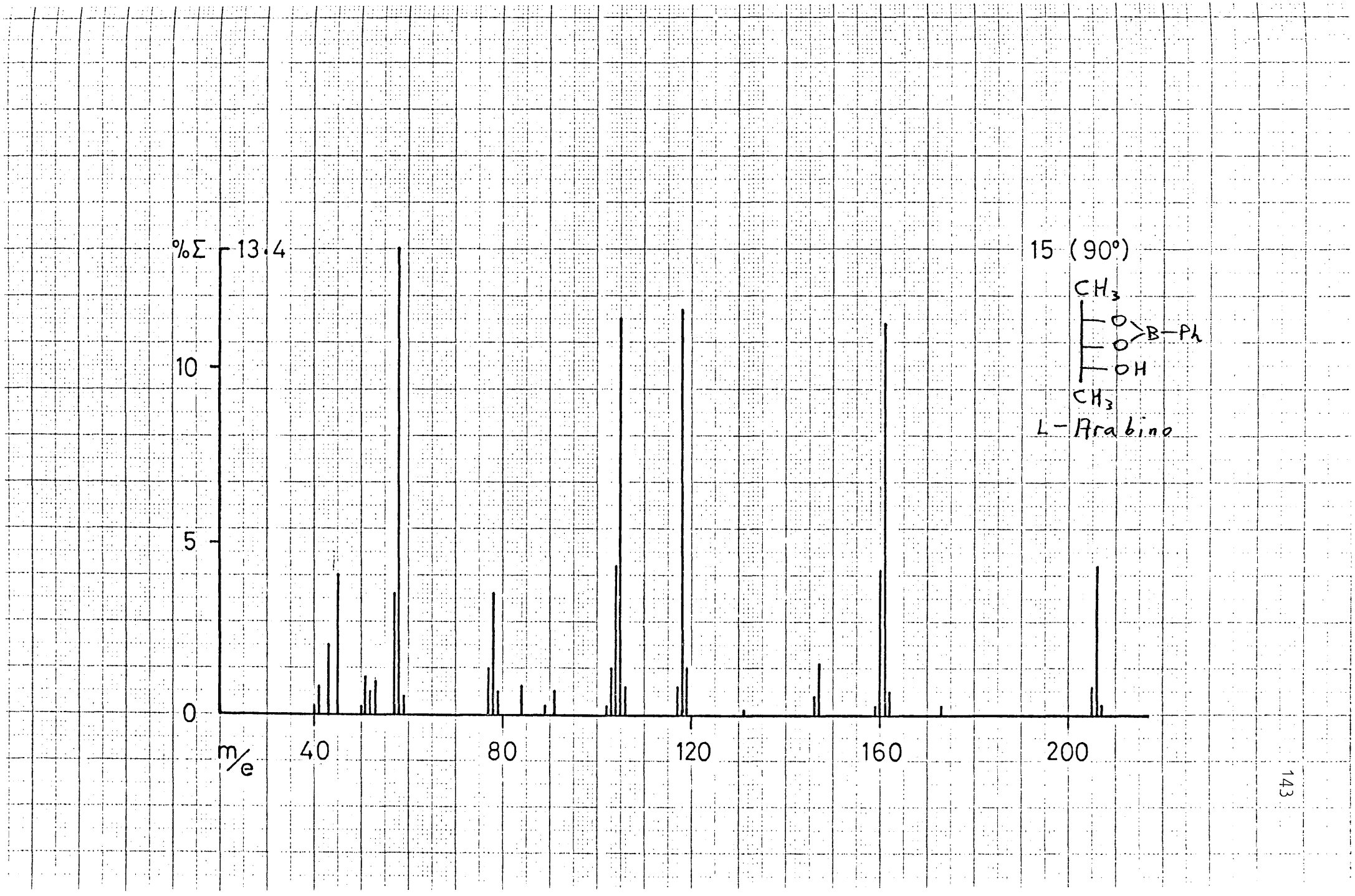

B-Ph
10 (150°)
24.6
% Σ
20
10
0
40
80
120
160
m/e

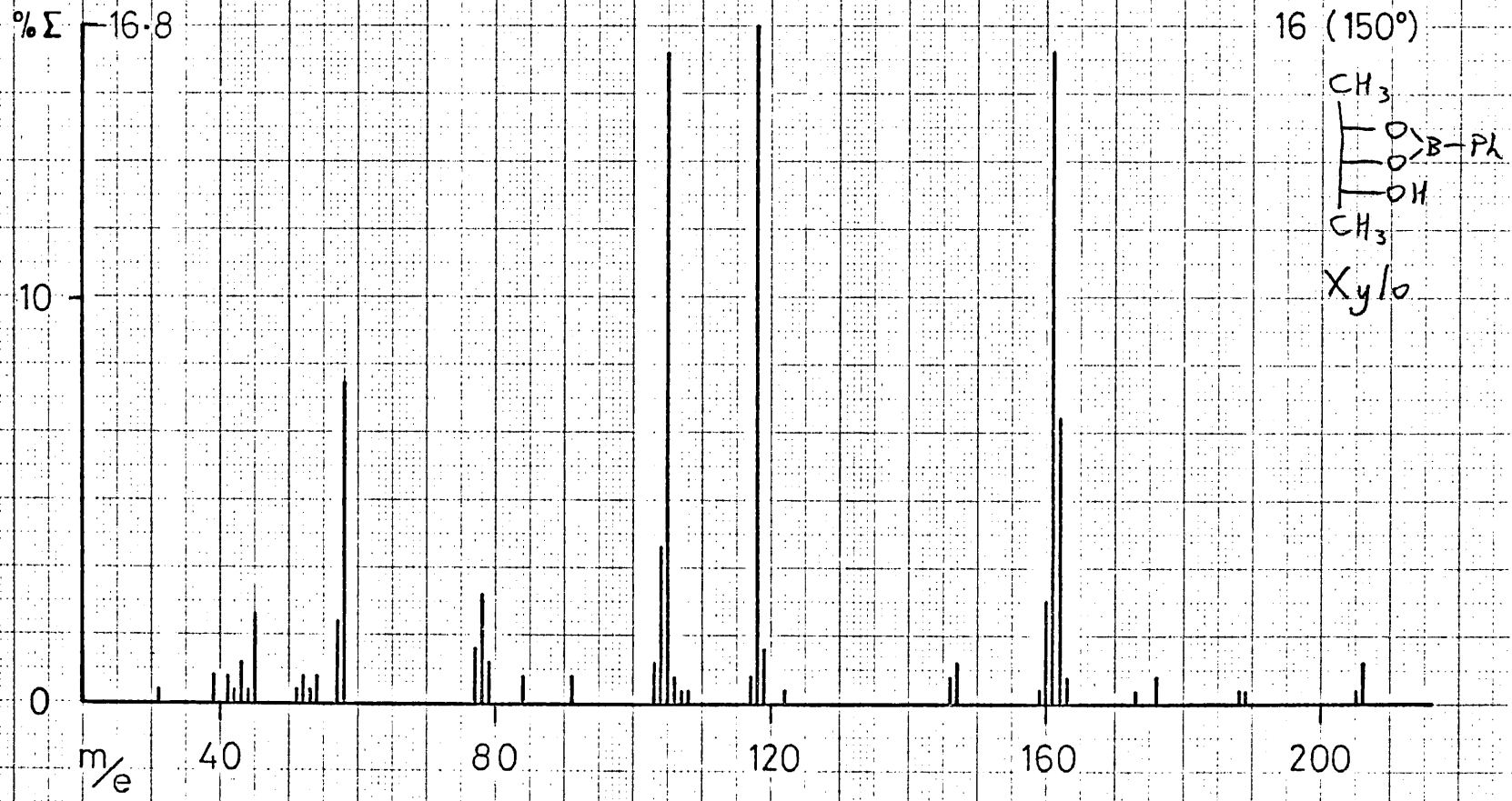

%Σ
18·3
10
0
m/e
40
80
120
160
11 (190°)
O
B–Ph
O
CH₂OH

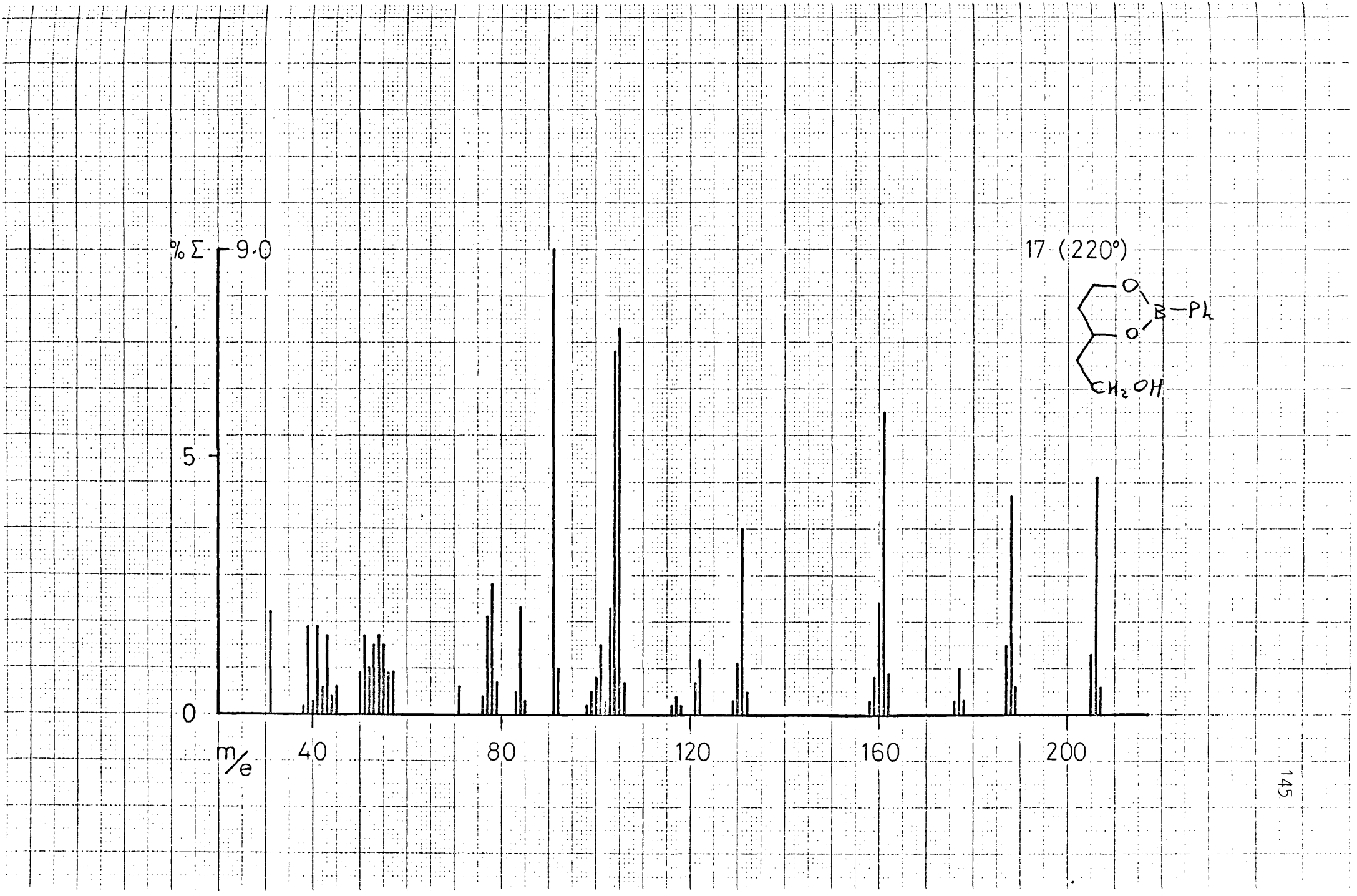

%Σ
13·8
10
5
0
m/e
40
80
120
160
12 (120°)
CH₂OH
O
B—Ph
O

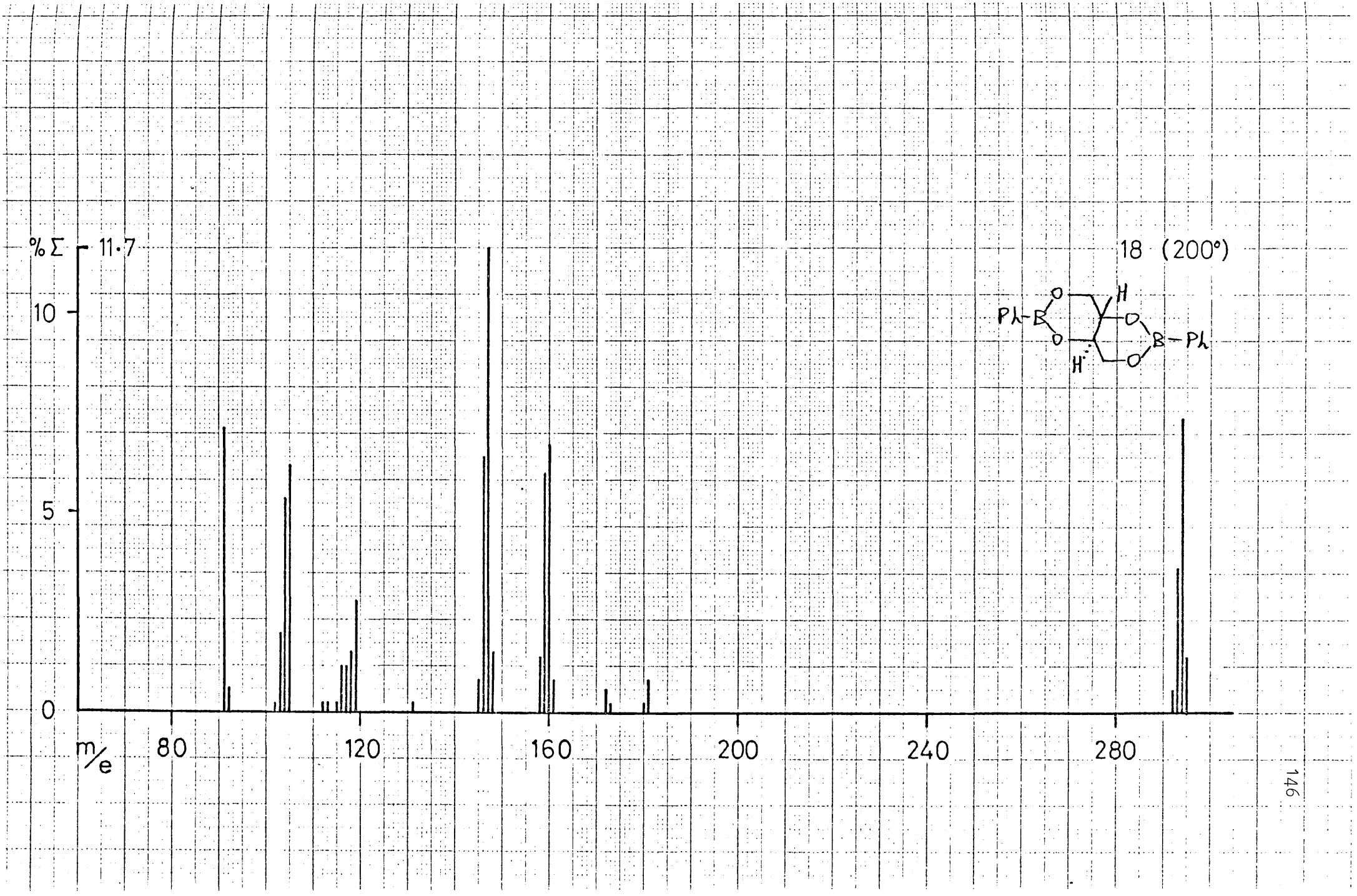

% Σ
20.3
10
0
m/e
40
80
120
160
13 (70°)
HO
O
B–Ph
O
CH3
L-Erythro

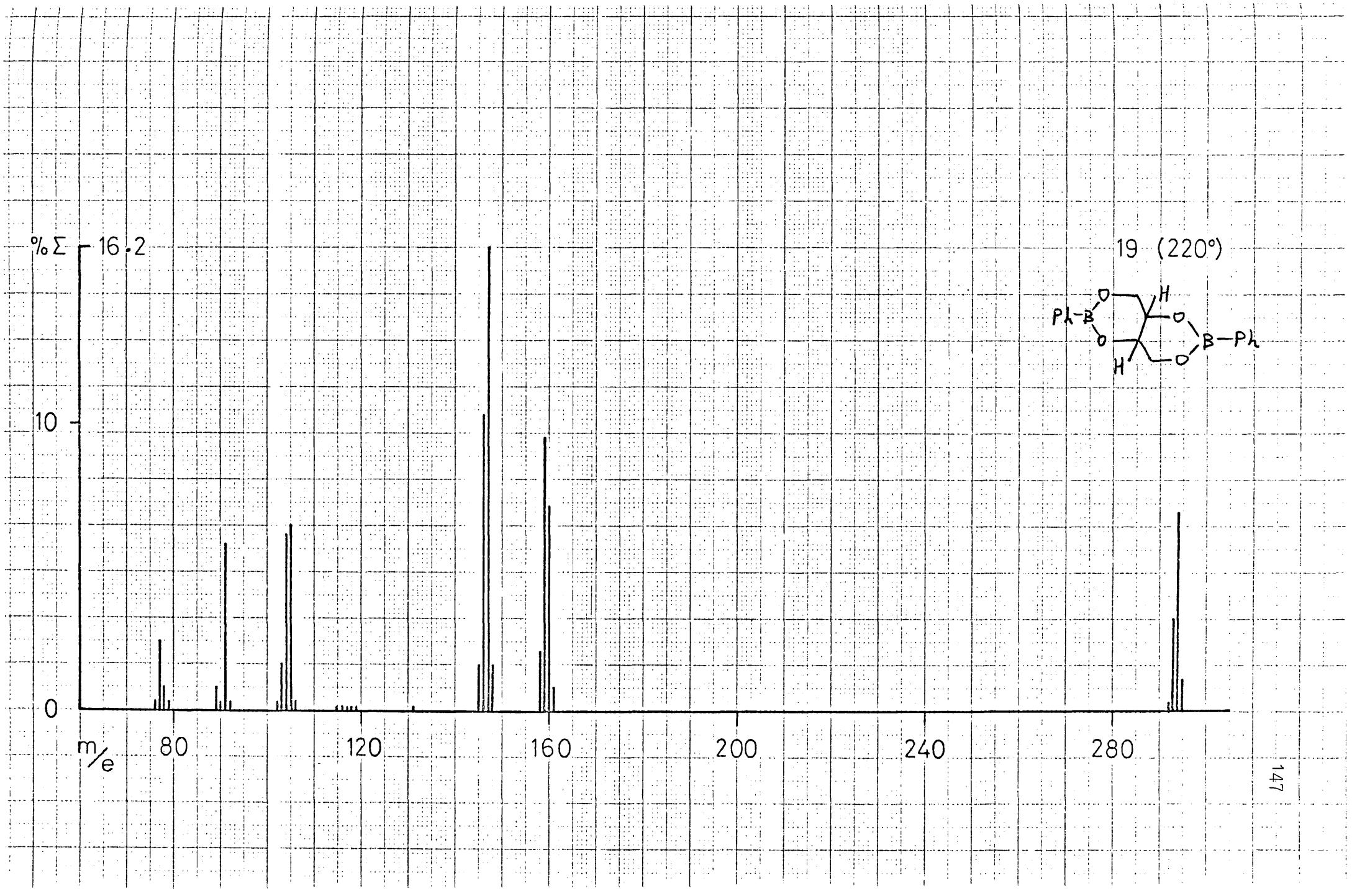

% Σ
10·7
5
0
m/e
40
80
120
160
200
14 (150°)
CH3
O
HO
B—PL
O
CH3
Ribo

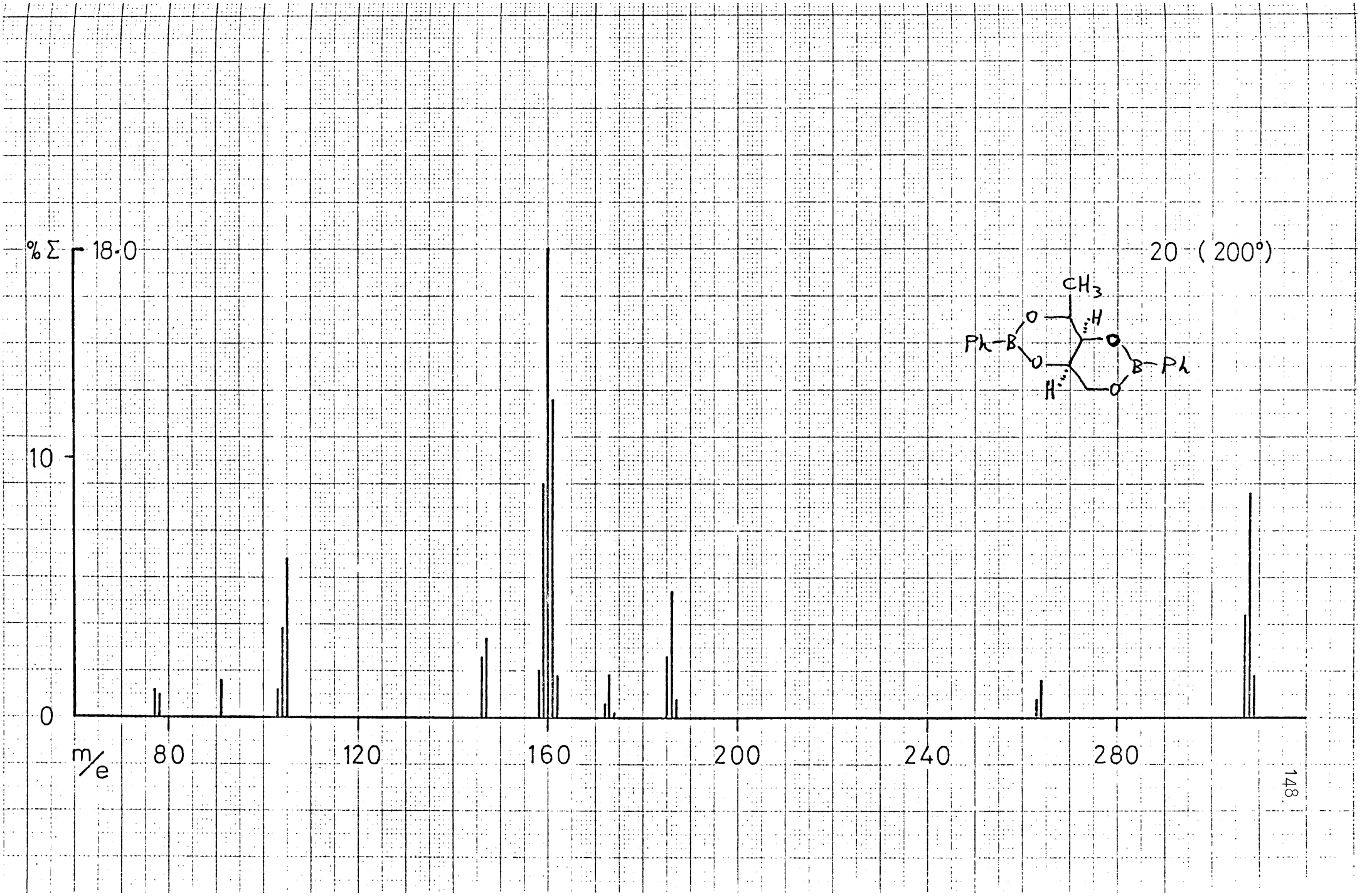

%Σ
13·4
10
5
0
m/e
40
80
120
160
200
15 (90°)
CH3
O
O
B—Ph
OH
CH3
L-Arabino

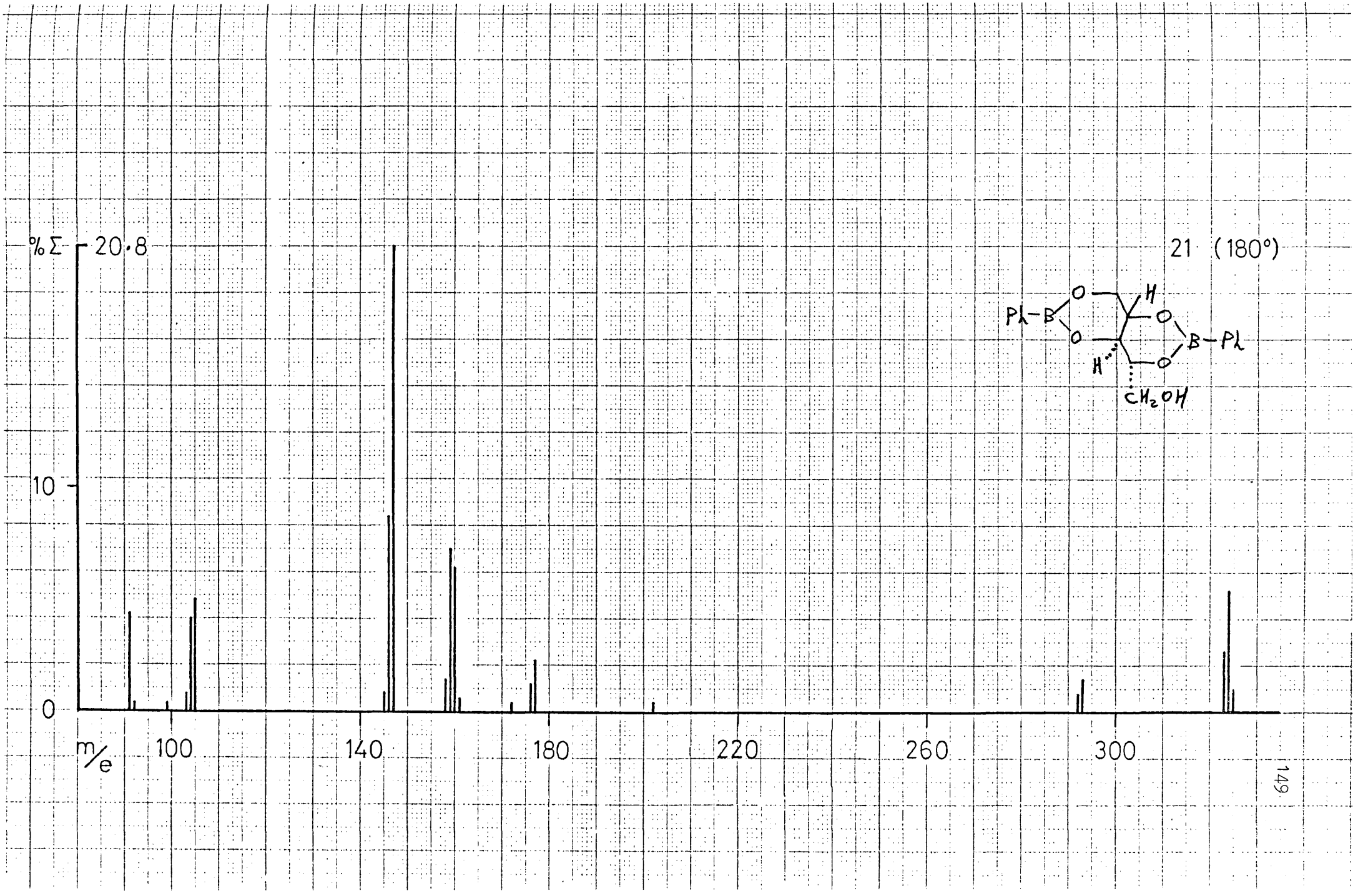

%Σ
16·8
10
0
m/e
40
80
120
160
200
16 (150°)
CH3
O
O
B–Ph
OH
CH3
Xylo

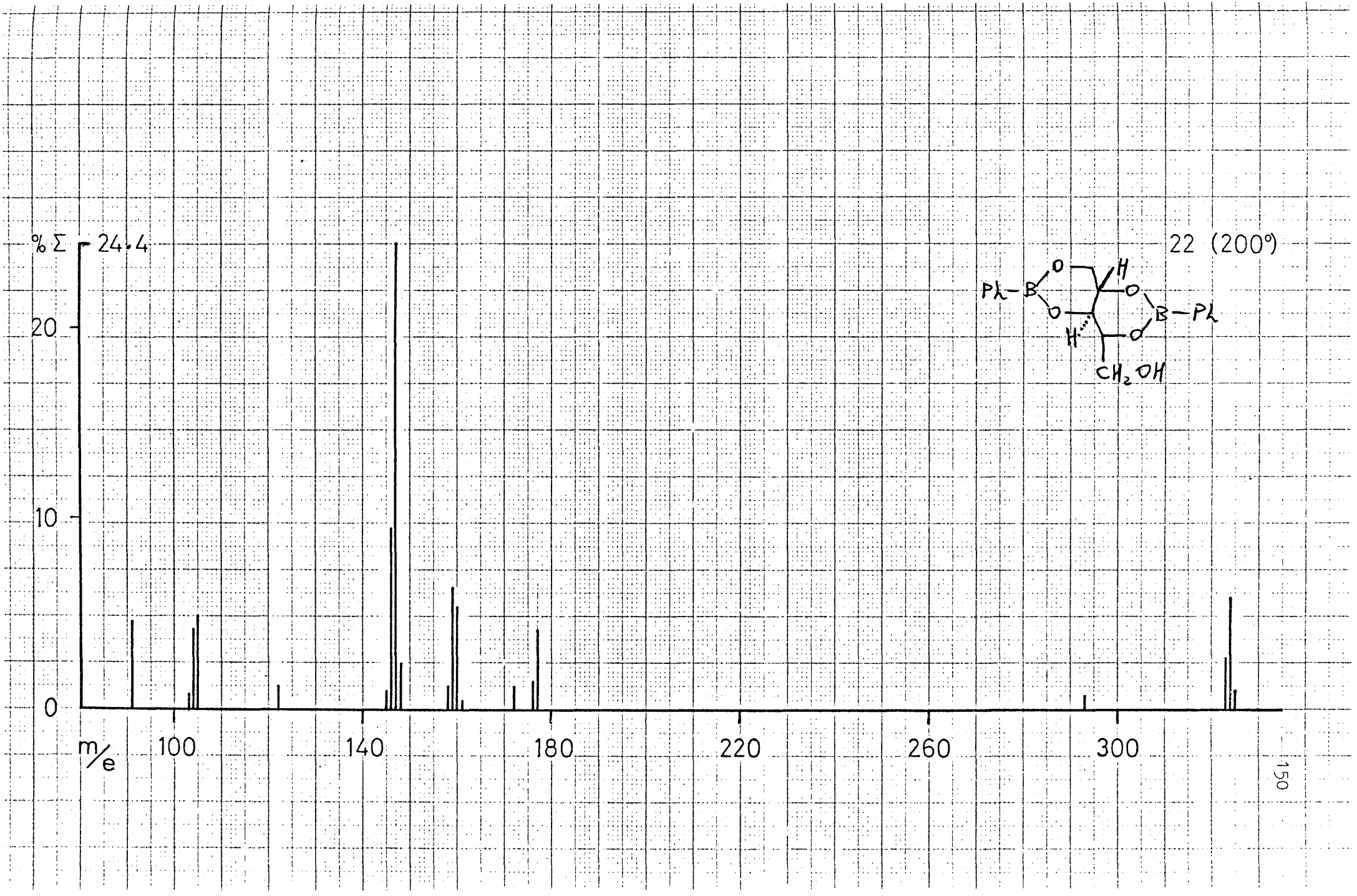

%Σ
9.0
5
0
m/e
40
80
120
160
200
17 (220°)
O
B—Ph
O
CH₂OH

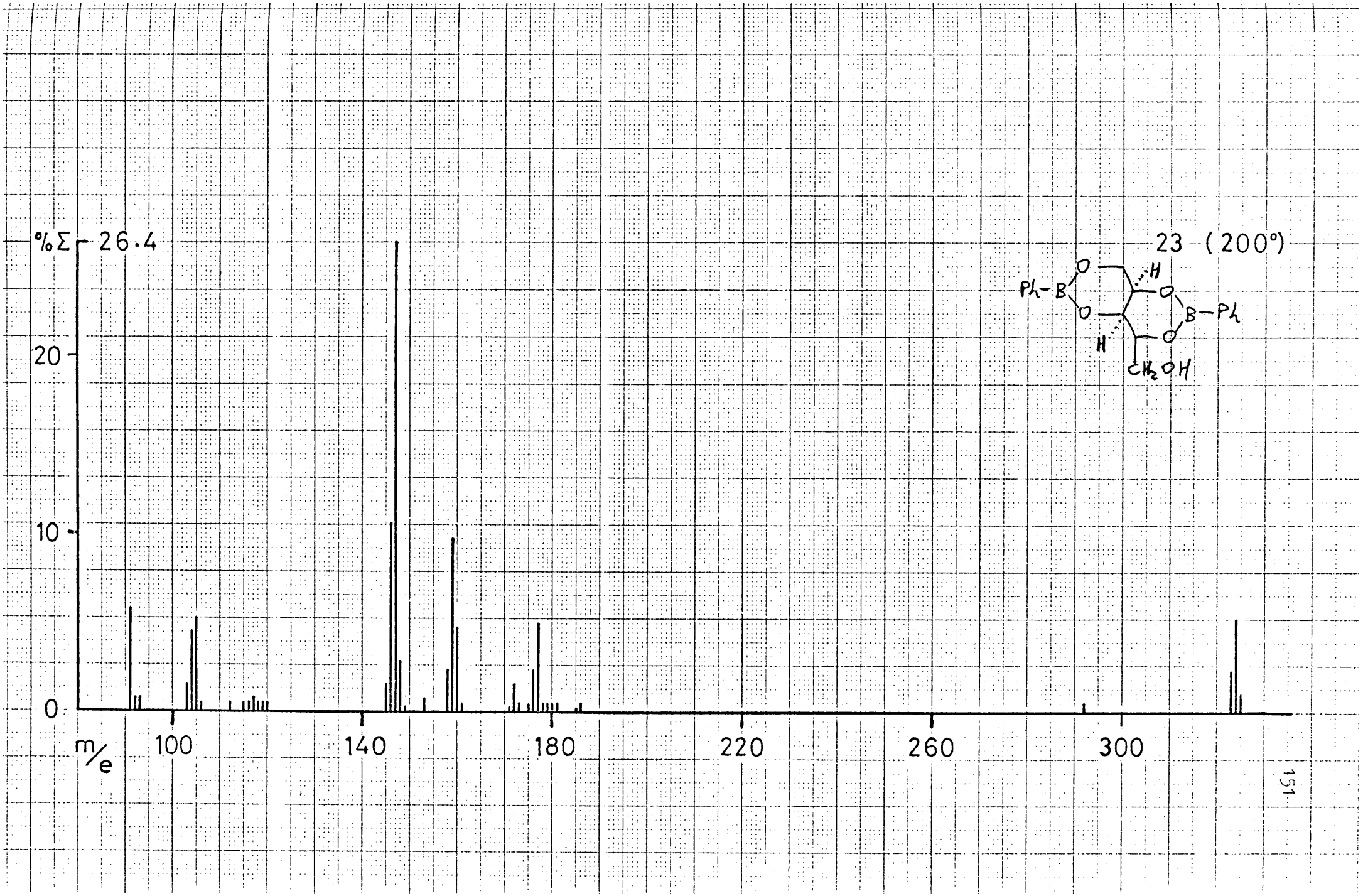

%Σ
11·7
10
5
0
m/e
80
120
160
200
240
280
18 (200°)
Ph
B
O
H
Ph

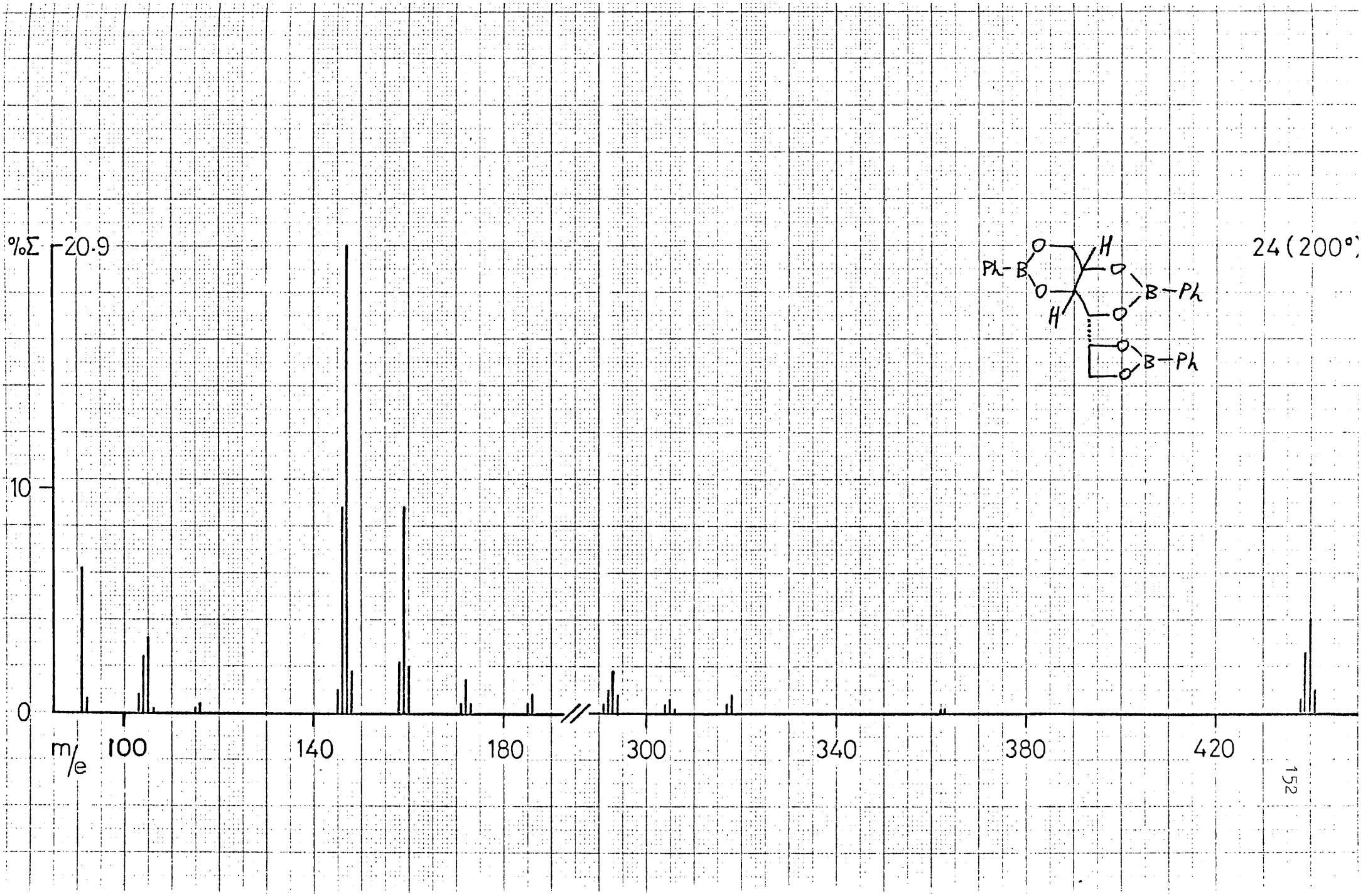

%Σ
16.2
10
0
m/e
80
120
160
200
240
280
19 (220°)
Ph-B
O
O
H
O
B-Ph
O
H

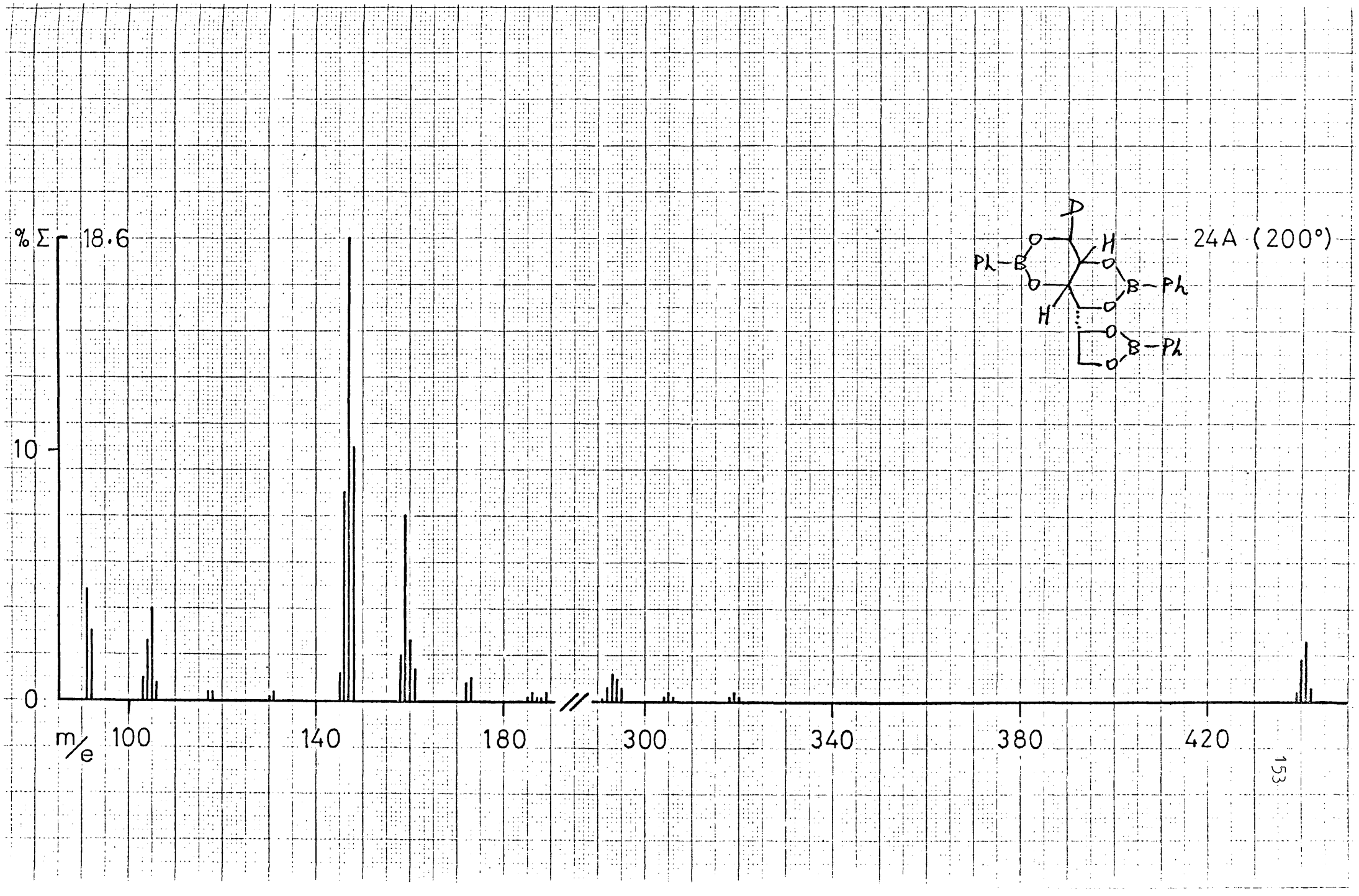

%Σ
18·0
10
0
m/e
80
120
160
200
240
280
20 (200°)
CH3
O
H
Ph–B
O
O
B–Ph
H
O

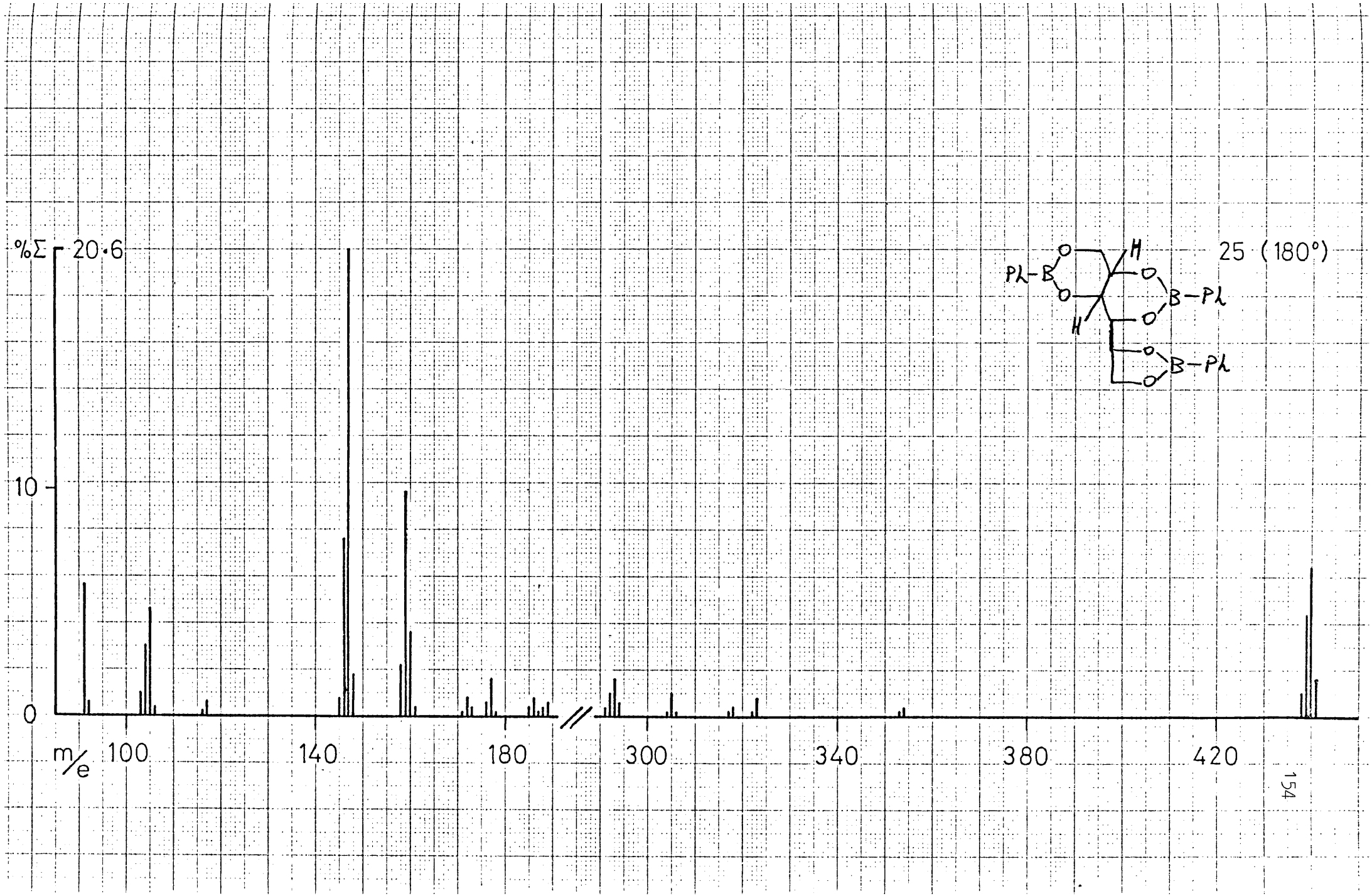

%Σ
20·8
10
0
m/e
100
140
180
220
260
300
21 (180°)
Ph-B
O
H
O
B-Ph
H
O
CH₂OH

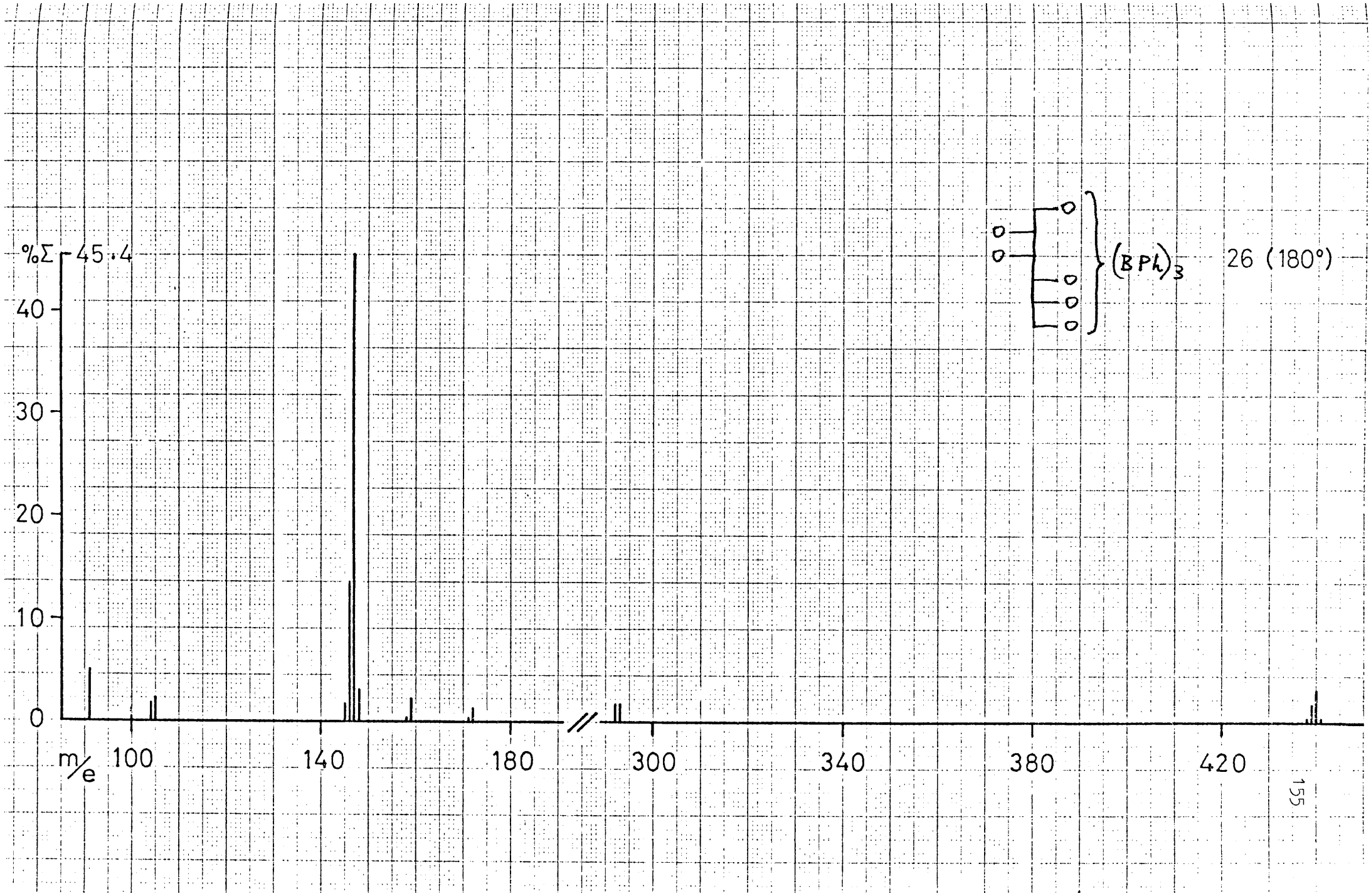

% Σ
24.4
20
10
0
m/e
100
140
180
220
260
300
150
22 (200°)
Ph
B
O
H
CH₂OH


%Σ 26.4
20
10
0
m/e
100
140
180
220
260
300
23 (200°)
Ph-B
B-Ph
H
H
CH₂OH


%Σ
20·9
10
0
m/e
100
140
180
300
340
380
420
24 (200°)
Ph-B
B-Ph
B-Ph
H
H


% Σ
18.6
10
0
m/e
100
140
180
300
340
380
420
24A (200°)
Ph
B
O
H
153


%Σ
20·6
10
0
m/e
100
140
180
300
340
380
420
25 (180°)
Ph-B
B-Ph
B-Ph
H
H


%Σ
45.4
40
30
20
10
0
m/e
100
140
180
300
340
380
420
(BPh)3
26 (180°)
155

Part B - Precise mass measurements of ions produced from phenylboronates.

Ester	Measured mass ($^m/e$)	Possible formulae	Calculated mass ($^m/e$)	Multiplet intensity ratio
2	118.0589	C_7H_7BO	118.0590	
	117.0620	$C_7H_7{}^{10}BO$	117.0624	2/
	117.0510	C_7H_6 BO	117.0512	3
	105.0707	C_8H_9	105.0704	1/3
	105.0512	C_6H_6 BO	105.0512	
3	132.0745	C_8H_9 BO	132.0746	
	119.0665	C_7H_8 BO	119.0668	
	118.0591	C_7H_7 BO	118.0590	
	117.0784	C_9H_9	117.0782	1
	117.0626	$C_7H_7{}^{10}BO$	117.0624	/3
	117.0514	C_7H_6 BO	117.0512	/2
	105.0708	C_8H_9	105.0704	1/2
	105.0515	C_6H_6 BO	105.0512	
	104.0624	C_8H_8	104.0626	1/2
	104.0435	C_6H_5 BO	104.0433	
4	132.0747	C_8H_9 BO	132.0746	
	105.0709	C_8H_9	105.0704	1/4
	105.0514	C_6H_6 BO	105.0512	
	104.0626	C_8H_8	104.0626	3/
	104.0551	$C_6H_6{}^{10}BO$	104.0548	2/
	104.0437	C_6H_5 BO	104.0433	4
	103.046	$C_6H_5{}^{10}BO$	103.0469	2/1
	103.0358	C_6H_4 BO	103.0355	

	91.0546	C_7H_7	91.0548	
4A	133.0812	C_8H_8DBO	133.0809	
	132.0846	$C_8H_8D^{10}BO$	132.0845	
	132.0733	C_8H_7DBO	132.0731	
	118.0573	C_7H_5DBO	118.0574	
	106.0766	C_8H_8D	106.0767	
	106.0569	C_6H_5DBO	106.0574	
	105.0688	C_8H_7D	105.0688	
	105.0510	C_6H_6BO	105.0512	
	104. 0547	$C_6H_6{}^{10}BO$	104.0548	
	104.0433	C_6H_5BO	104.0433	
	103.0468	$C_6H_5{}^{10}BO$	103.0469	
	103.0353	C_6H_4BO	103.0355	
5	147.0978	$C_9H_{12}BO$	147.0981	1/1
	147.0614	$C_8H_8BO_2$	147.0617	
	85.0653	C_5H_9O	85.0653	
	59.0496	C_3H_7O	59.0497	
	58.0419	C_3H_6O	58.0419	
	57.0701	C_4H_9	57.0704	1/1
	57.0341	C_3H_5O	57.0340	
	43.0185	C_2H_3O	43.0184	
6	132.0747	C_8H_9BO	132.0746	
	131.0673	C_8H_8BO	131.0668	
	105.0502	C_6H_6BO	105.0512	
	104.0434	C_6H_5BO	104.0433	
	103.0467	$C_6H_5{}^{10}BO$	103.0469	5/1
	103.0350	C_6H_4BO	103.0355	

7	131.0664	C_8H_8BO	131.0668	
	105.0706	C_8H_9	105.0704	1/8
	105.0513	C_6H_6BO	105.0512	
	104.0627	C_8H_8	104.0626	1/2
	104.0548	$C_6H_6{}^{10}BO$	104.0548	2/14
	104.0432	C_6H_5BO	104.0433	
	103.0470	$C_6H_5{}^{10}BO$	103.0469	3/2
	103.0359	C_6H_4BO	103.0355	
	43.0191	C_2H_3O	43.0184	
8	131.0663	C_8H_8BO	131.0668	
	105.0710	C_8H_9	105.0704	1/2
	105.0520	C_6H_6BO	105.0512	
	104.0550	$C_6H_6{}^{10}BO$	104.0548	
	43.0188	C_2H_3O	43.0184	4/1
	43.0550	C_3H_7	43.0548	
9	147.0617	$C_8H_8BO_2$	147.0617	
	146.0540	$C_8H_7BO_2$	146.0539	
	132.0939	$C_{10}H_{12}$	132.0939	
	119.0859	C_9H_{11}	119.0861	
	118.0590	C_7H_7BO	118.0590	
	117.0618	$C_7H_7{}^{10}BO$	117.0624	
	105.0514	C_6H_6BO	105.0512	
	104.0544	$C_6H_6{}^{10}BO$	104.0548	3/2
	104.0430	C_6H_5BO	104.0433	
	56.0627	C_4H_8	56.0626	
	41.0392	C_3H_5	41.0391	
	39.0235	C_3H_3	39.0235	

10	105.0514	C_6H_6BO	105.0512	
	104.0628	C_8H_8	104.0626	$^3/_5/_3$
	104.0550	$C_6H_6{}^{10}BO$	104.0548	
	104.0434	C_6H_5BO	104.0433	
	42.0467	C_3H_6	42.0469	
11	117.0518	C_7H_6BO	117.0512	
	105.0508	C_6H_6BO	105.0512	
	104.0545	$C_6H_6{}^{10}BO$	104.0548	
	51.0237	C_4H_3	51.0235	
	43.0186	C_2H_3O	43.0184	
12	147.0618	$C_8H_8BO_2$	147.0617	$^{12}/_1$
	147.0444	$C_9H_7O_2$	147.0446	
	146.0653	$C_8H_8{}^{10}BO_2$	146.0653	$^{37}/_{31}$
	146.0540	$C_8H_7BO_2$	146.0539	
	104.0552	$C_6H_6{}^{10}BO$	104.0548	$^{17}/_{12}$
	104.0434	C_6H_5BO	104.0433	
	57.0342	C_3H_5O	57.0340	
	31.0184	CH_3O	31.0184	
13	161.0771	$C_9H_{10}BO_2$	161.0774	
	147.0611	$C_8H_8BO_2$	147.0617	
	133.0465	$C_7H_6BO_2$	133.0461	
	118.0789	$C_4H_{11}BO_3$	118.0801	
		C_9H_{10}	118.0782	
	118.0596	C_7H_7BO	118.0590	
	117.0711	C_9H_9	117.0704	

	117.0519	C_7H_6BO	117.0512	
	105.0711	C_8H_9	105.0704	$^{12}/_{21}$
	105.0520	C_6H_6BO	105.0512	
	104.0632	C_8H_8	104.0626	$^{65}/_{10}/_{9}$
	104.0550	$C_6H_6{}^{10}BO$	104.0548	
	104.0441	C_6H_5BO	104.0433	
	58.0778	C_4H_{10}	58.0783	
	45.0342	C_2H_5O	45.0340	$^{10}/_{1}$
	45.0147	H_2BO_2	45.0148	
	45.0542	C_3H_7	43.0548	
14	162.0850	$C_9H_{11}BO_2$	162.0852	
	161.0769	$C_9H_{10}BO_2$	161.0774	
	160.0700	$C_9H_9BO_2$	160.0696	
	118.0780	C_9H_{10}	118.0782	
	105.0704	C_8H_9	105.0704	$^{1}/_{2}$
	105.0512	C_6H_6BO	105.0512	
	58.0419	C_3H_6O	58.0419	
15	190.1159	$C_{11}H_{15}BO_2$	190.1165	
	162.0847	$C_9H_{11}BO_2$	162.0852	
	161.0776	$C_9H_{10}BO_2$	161.0774	
	147.0615	$C_8H_8BO_2$	147.0617	
	131.0671	C_8H_8BO	131.0668	
	118.0779	C_9H_{10}	118.0782	
	105.0699	C_8H_9	105.0704	$^{1}/_{5}$
	105.0504	C_6H_6BO	105.0512	
	104.0541	$C_6H_6{}^{10}BO$	104.0548	$^{7}/_{9}$
	104.0428	C_6H_5BO	104.0433	

	78.0469	C_6H_6	78.0469	
	58.0419	C_3H_6O	58.0419	
	45.0340	C_2H_5O	45.0340	
	43.0184	C_2H_3O	43.0184	
16	162.0847	$C_9H_{11}BO_2$	162.0852	
	161.0770	$C_9H_{10}BO_2$	161.0774	
	147.0614	$C_8H_8BO_2$	147.0617	
	118.0782	C_9H_{10}	118.0782	
	105.0701	C_8H_9	105.0704	
	105.0512	C_6H_6BO	105.0512	
	58.0419	C_3H_6O	58.0419	
	57.0342	C_3H_5O	57.0340	
17	178.0781	$C_9H_{11}BO_3$	178.0801	
	177.0717	$C_9H_{10}BO_3$	177.0723	
	122.0537	$C_6H_7BO_2$	122.0539	
	121.0574	$C_6H_7{}^{10}BO_2$	121.0575	
	105.0508	C_6H_6BO	105.0512	
	104.0545	$C_6H_6{}^{10}BO$	104.0548	$^1/_3$
	104.0431	C_6H_5BO	104.0433	
	103.0466	$C_6H_5{}^{10}BO$	103.0469	$^2/_1$
	103.0352	C_6H_4BO	103.0355	
	101.0409	$C_3H_6BO_3$	101.0410	
	100.0447	$C_3H_6{}^{10}BO$	100.0448	$^1/_1$
	100.0331	$C_3H_5BO_3$	100.0332	
	84.0574	C_5H_8O	84.0575	
	78.0466	C_6H_6	78.0469	
	78.0273	C_4H_3BO	78.0277	
	54.0467	C_4H_6	54.0469	

18	236.1017	$C_{15}H_{13}BO_2$	236.1010	
	186.0670	$C_9H_8B_2O_3$	186.0660	
	173.0773	$C_{10}H_{10}BO_2$	173.0774	1/2
	173.0590	$C_8H_7B_2O_3$	173.0585	
	172.0698	$C_{10}H_9BO_2$	172.0696	
	160.0690	$C_9H_9BO_2$	160.0696	
	159.0730	$C_9H_9{}^{10}BO_2$	159.0732	1/3
	159.0616	$C_9H_8BO_2$	159.0617	
	147.0614	$C_8H_8BO_2$	147.0617	
	146.0539	$C_8H_7BO_2$	146.0539	
	119.0666	C_7H_8BO	119.0668	
	118.0598	C_7H_7BO	118.0590	
	117.0520	C_7H_6BO	117.0514	
	116.0624	C_9H_8	116.0626	
	105.0340	C_7H_5O	105.0341	
19	160.0699	$C_9H_9BO_2$	160.0696	
	159.0728	$C_9H_9{}^{10}BO_2$	159.0732	
	159.0614	$C_9H_8BO_2$	159.0617	
	147.0619	$C_8H_8BO_2$	147.0617	
20	174.0850	$C_{10}H_{11}BO_2$	174.0852	
	161.0776	$C_9H_{10}BO_2$	161.0774	
	160.0800	$C_9H_{10}{}^{10}BO_2$	160.0810	1/4
	160.0700	$C_9H_9BO_2$	160.0690	
	159.0618	$C_9H_8BO_2$	159.0617	
	147.0614	$C_8H_8BO_2$	147.0617	
	105.0725	C_8H_9	105.0725	1/4
	105.0512	C_6H_6BO	105.0512	

	104.0550	$C_6H_6{}^{10}BO$	104.0548
	104.0437	C_6H_5BO	104.0433
21	293.1164	$C_{16}H_{15}B_2O_4$	293.1156
	177.0720	$C_9H_{10}BO_3$	177.0723
	160.0691	$C_9H_9BO_2$	160.0696
	159.0621	$C_9H_8BO_2$	159.0617
	147.0614	$C_8H_8BO_2$	147.0617
22	293.1163	$C_{16}H_{15}B_2O_4$	293.1156
	177.0722	$C_9H_{10}BO_3$	177.0723
	160.0689	$C_9H_9BO_2$	160.0696
	159.0621	$C_9H_8BO_2$	159.0617
	147.0617	$C_8H_8BO_2$	147.0617
23	293.1158	$C_{16}H_{15}B_2O_4$	293.1156
	177.0720	$C_9H_{10}BO_3$	177.0723
	160.0693	$C_9H_9BO_2$	160.0696
	159.0618	$C_9H_8BO_2$	159.0617
	147.0616	$C_8H_8BO_2$	147.0617
24	160.0672	$C_9H_9BO_2$	160.0696
	159.0611	$C_9H_8BO_2$	159.0617
	147.0612	$C_8H_8BO_2$	147.0617
	105.0510	C_6H_6BO	105.0512
25	160.0680	$C_9H_9BO_2$	160.0696
	159.0618	$C_9H_8BO_2$	159.0617
	147.0612	$C_8H_8BO_2$	147.0617
	105.0515	C_6H_6BO	105.0512

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	104.0626	C_8H_8	104.0626	
	104.0552	$C_6H_6{}^{10}BO$	104.0548	$^4/_5/_6$
	104.0439	C_6H_5BO	104.0433	
26	147.0619	$C_8H_8BO_2$	147.0617	

Part C - Metastable ions produced by phenylboronates.

Ester	Metastable ions ($^{m}/_{e}$) obs.	calc.	Metastable assignment Parent ion	Daughter ion
1	253.0	252.8	282	267
	238.0	237.8	267	252
	129.3	129.3	208	164
	57.7	57.8	103	77
	57.0	57.0	104	77
2	70.2	70.2	118	91
	57.6	57.6	103	77
	57.0	57.0	104	77
	56.1	56.0	148	91
	46.5	46.4	91	65
	33.8	33.8	77	51
3	133.3	133.4	162	147
	132.4	132.4	161	146
	82.0	81.9	132	104
	70.2	70.2	118	91
	57.7	57.6	103	77
	57.0	57.0	104	77
	56.3	56.3	147	91
	46.5	46.4	91	65
	33.8	33.8	77	51
4	147.3	147.3	176	161
	82.0	81.9	132	104
	68.9	68.9	160	105

	68.6	68.5	161	105
	61.8	61.8	175	104
	61.5	61.5	176	104
	57.5	57.6	103	77
	57.0	57.0	104	77
	51.5	51.4	161	91
	33.8	33.8	77	51
4A	149.4	149.3	178	163
	148.3	148.3	177	162
	83.5	83.5	132	105
	82.5	82.6	131	104
	81.3	81.3	133	104
	69.0	68.9	163	106
	62.0	61.9	178	105
5	175.2	175.1	204	189
	116.5	116.7	147	131
	114.5	114.3	189	147
	75.6	75.5	146	105
	68.2	68.3	204	118
	57.6	57.6	103	77
	57.0	57.0	104	77
	38.2	38.2	189	85
		38.2	85	57
6	107.5	107.6	162	132
	106.6	106.6	161	131
	84.3	84.2	131	105
	81.9	81.9	132	104

	66.8	66.8	162	104
	57.0	57.0	104	77
	51.1	51.1	162	91
7	147.3	147.3	176	161
	146.4	146.3	175	160
	106.5	106.6	161	131
	84.2	84.2	131	105
	83.0	83.2	130	104
	61.5	61.5	176	104
	57.0	57.0	104	77
	51.4	51.4	161	91
8	161.3	161.2	190	175
	160.3	160.2	189	174
	84.1	84.2	131	105
	63.4	63.4	174	105
	63.1	63.0	175	105
	57.0	57.0	104	77
		56.9	190	104
9	134.7	134.7	190	160
	131.5	131.4	160	145
	113.8	113.7	190	147
	112.2	112.2	190	146
	103.9	103.7	132	117
	91.8	91.7	190	132
	87.0	87.0	160	118
	70.2	70.2	118	91
	57.6	57.6	103	77

	57.0	57.0	104	77
		56.9	190	104
	56.3	56.3	147	91
	51.1	51.1	119	78
	33.8	33.8	77	51
	30.0	30.0	56	41
10	121.1	121.1	176	146
	75.5	75.5	146	105
	74.6	74.6	145	104
	61.8	61.8	175	104
	61.5	61.5	176	104
	58.5	58.5	104	78
	57.0	57.0	104	77
	47.1	47.1	176	91
11	144.0	143.8	178	160
	121.3	121.4	178	147
	119.7	119.8	178	146
	101.4	101.3	147	122
	88.5	88.5	160	119
	60.7	60.8	178	104
	56.3	56.3	147	91
	46.5	46.5	178	91
		46.4	91	65
12	157.8	157.7	192	174
	145.4	145.3	174	159
	135.0	135.0	192	161
		135.1	160	147

	84.2	84.2	131	105
	56.3	56.3	192	104
		56.3	147	91
	51.4	51.4	161	91
13	114.1	114.1	192	148
	113.1	113.1	191	147
	101.0	101.3	147	122
	75.0	75.0	147	105
	73.6	73.6	147	104
	73.1	73.1	148	104
	68.5	68.5	161	105
	58.5	58.5	104	78
	56.5	56.3	192	104
		56.3	147	91
	41.1	41.1	148	78
	33.8	33.8	77	51
15	171.5	171.6	206	188
	161.1	161.2	190	175
	158.5	158.4	189	173
	136.5	136.4	190	161
	133.4	133.4	162	147
	127.4	127.4	206	162
	116.5	116.7	147	131
	86.0	86.0	162	118
	68.6	68.5	161	105
	57.6	57.6	103	77
	57.0	57.0	104	77
	56.3	56.3	147	91

	51.5	51.5	118	78
	20.2	20.2	161	57
16	171.5	171.6	206	188
	133.4	133.4	162	147
	127.5	127.4	206	162
	126.5	126.4	205	161
	116.6	116.7	147	131
	106.6	106.6	161	131
	86.0	86.0	162	118
	68.6	68.5	161	105
	51.5	51.6	118	78
	20.2	20.2	161	57
17	176.0	176.0	178	177
	171.5	171.6	206	188
	153.8	153.8	206	178
	134.4	134.5	188	159
	84.2	84.2	131	105
		84.1	177	122
	83.2	83.2	176	121
	57.6	57.5	188	101
	57.0	57.0	104	77
	56.7	56.5	177	100
	51.5	51.4	161	91
	49.3	49.5	206	101
	37.4	37.5	188	84
	34.3	34.3	206	84
	33.8	33.8	77	51

18	237.0	237.1	294	264
	189.5	189.4	294	236
	118.0	117.7	204	186
	100.8	100.6	294	172
	87.3	87.1	294	160
	73.5	73.5	294	147
	57.0	57.0	104	77
	56.4	56.3	147	91
	45.9	46.1	172	89
	33.8	33.8	77	51
19	86.0	86.0	294	159
	73.5	73.5	294	147
	72.5	72.7	236	131
	70.2	70.3	118	91
	68.8	69.0	160	105
	56.4	56.3	147	91
	49.1	49.2	172	92
	37.0	36.8	294	104
	33.7	33.8	77	51
20	226.5	226.3	308	264
	131.0	131.1	264	186
	84.3	84.2	308	161
	83.0	83.1	308	160
	68.6	68.5	161	105
	56.3	56.3	147	91
	51.5	51.4	161	91
21	265.0	265.0	324	293
	134.5	134.7	190	160

	133.0	133.1	190	159
	122.1	122.1	177	147
	113.8	113.7	190	147
	96.6	96.7	324	177
	79.0	79.0	324	160
	77.9	78.0	324	159
	73.7	73.8	293	147
	66.8	66.7	324	147
	56.3	56.3	147	91
	46.7	46.8	177	91
22	265.0	265.0	324	293
	122.0	122.1	177	147
	96.8	96.7	324	177
	79.1	79.0	324	160
	78.0	78.0	324	159
	73.7	73.8	293	147
	56.3	56.3	147	91
	46.9	46.8	177	91
23	265.0	265.0	324	293
	122.1	122.1	177	147
	96.8	96.7	324	177
	78.9	79.0	324	160
	77.8	78.0	324	159
	73.7	73.8	293	147
	56.5	56.3	147	91
	47.0	46.8	177	91

24	299.5	299.5	440	363
	230.0	229.8	440	318
	211.5	211.4	440	305
	195.0	195.1	440	293
	73.7	73.8	293	147
	72.7	72.8	293	146
	58.2	58.2	440	160
	57.6	57.5	440	159
	56.5	56.3	147	91
25	230.0	229.8	440	318
	211.4	211.4	440	305
	195.0	195.1	440	293
	73.7	73.8	293	147
	72.6	72.8	293	146
	58.2	58.2	440	160
	57.6	57.5	440	159
	56.3	56.3	147	91
26	299.5	299.5	440	363
	195.2	195.1	440	293
	56.5	56.3	147	91

Precursors of metastable ions determined by defocussing experiments.

Ester	Daughter m_2 (m/e)	Intensity	Voltage ratio	Parent m_1 (m/e)	Intensity
5	85		2.224	189.0	
	57		1.493	85.1	
9	132	1,000	1.213	160.1	8.0
			1.439	189.9	430
	104	1,000	1.019	106.0	4.2
			1.262	131.2	0.5
			1.397	145.3	2.5
			1.645	171.1	0.5
			1.813	188.6	1.3
	77	375	1.015	78.2	4.0
			1.345	103.6	1.0
			1.630	125.5	0.3
	56	10,000	2.863	160.3	1.2
			3.394	190.1	3.0
12	105	10,000	1.251	131.4	120
			1.400	147.0	2
			1.531	160.8	3
			1.656	173.9	2
			1.830	192.2	1
	104	10,000	1.252	130.2	80
			1.421	147.7	7
			1.543	160.5	3
			1.674	174.1	1
			1.830	192.1	2
	91	10,000	1.297	118.0	10

			1.616	147.1	25
			1.769	161.0	150
	77	10,000	1.353	104.2	170
			1.569	120.8	6
			1.673	128.8	1
14	58	10,000	1.474	85.5	1
			1.750	101.5	3
			1.993	115.6	1.5
			2.779	161.2	1
			3.553	206.1	0.6
16	58	10,000	1.480	85.8	0.5
			1.759	102.0	1.5
			2.776	161.0	5
17	122	600	1.690	206.2	4
	105	5,000	1.252	131.1	50
			1.381	145.0	0.6
			1.525	160.1	0.8
			1.789	187.8	1.5
	104	4.300	1.252	130.2	18
			1.804	187.8	0.8
	100	400	1.288	128.8	1
			1.774	177.4	0.5
			2.062	206.2	1
	84	900	1.216	102.1	1
			1.333	112.1	0.6
			1.510	127.0	0.5
			2.236	187.8	12

			2.450	205.8	34
	77	1,800	1.354	104.2	35
			1.576	121.2	0.6
21	177	6,100	1.252	221.6	2
			1.588	281.1	3.4
			1.657	293.3	2.7
			1.831	324.0	122
	160	9,100	1.120	179.2	6.4
			1.189	190.2	2.0
			1.272	203.5	5.5
			1.651	264.2	1.9
			1.915	306.4	1.9
			2.026	324.2	67
	159	8,100	1.102	175.2	10
			1.120	178.1	38
			1.195	190.0	4.4
			1.279	203.4	25
			1.654	263.0	6
			1.768	281.1	4.6
			1.927	306.4	2.0
			2.037	323.9	110
	147	9,700	1.129	166.0	7.4
			1.210	177.9	93
			1.294	190.2	1.6
			1.711	251.5	0.5
			1.995	293.3	27
			2.084	306.3	0.6
			2.206	324.3	4.7

22	177	1,500	1.831	324.1	12
	160	2,500	1.651	264.2	0.5
			1.912	305.9	2
			2.026	324.2	15
	159	2,000	1.282	203.8	1.5
			1.654	263.0	0.5
			1.774	282.1	0.8
			1.924	305.9	0.5
			2.037	323.9	16
	147	5,000	1.210	177.9	55
			1.297	190.7	0.4
			1.990	292.5	6
			2.083	306.2	1
			2.201	323.5	3
23	177		1.834	324.6	
	160		1.915	306.4	3
			2.026	324.2	6
	159		1.654	263.0	1.5
			1.771	281.6	1.5
			1.921	305.4	0.8
			2.038	324.0	9
	147		1.205	177.1	100
			1.993	293.0	3
			2.083	306.2	2
			2.200	323.4	1.5

Precursors of metastable ions determined from measurements of kinetic energies of metastable ions.

Compound	Metastable ion (m/e)	Accelerating voltage (V)	Cut-off voltage (V_c)	V/V_c	Daughter m_1 (m/e)	Parent m_2 (m/e)
12	56.3	7896	7775	1.015	57.1	57.9
			5760	1.370	77.1	105.5
			4900	1.611	90.7	146.6
18	87.1	7481	4070	1.838	160.1	294.1

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Formation of Hydrocarbon Ions from Phenylboronates of Diols under Electron Impact

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Formation of Hydrocarbon Ions from Phenylboronates of Diols under Electron Impact

By I. R. McKINLEY and H. WEIGEL*

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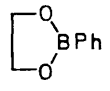
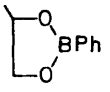
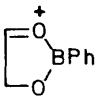
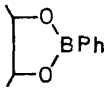
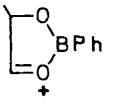
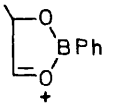
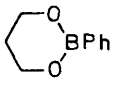
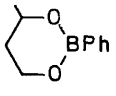
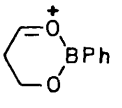
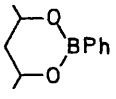
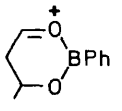
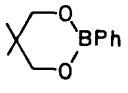
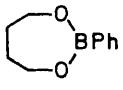
Summary Rearrangement under electron impact seems to be a general property of phenylboronates of diols: depending on the structure of the ester the products of rearrangement are hydrocarbon ions containing 7, 8, 9, and/or 10 carbon atoms.

THE report by Cragg and Todd[1] that the tropylium ion is formed by a rearrangement process from the phenylboronate of ethylene glycol (I) under electron impact prompts us to report that, in our experience, this type of rearrangement seems to be a more general property of cyclic esters of phenylboronic acid.

The Table shows the hydrocarbon ions produced from phenylboronates of diols in an A.E.I. M.S.902 spectrometer

Hydrocarbon ions formed from cyclic esters of phenylboronic acid

	Compound	Abundance of hydrocarbon ions (%Σ 25)					Metastable peaks	
		$C_7H_7^+$ *m/e* 91	$C_8H_8^+$ *m/e* 104	$C_8H_9^+$ *m/e* 105	$C_9H_{11}^+$ *m/e* 119	$C_{10}H_{12}^+$ *m/e* 132	Obs. (*m/e*)	Assignment[a]
(I)		14·5	—	—	—	—	56·1	$(I)^+ \longrightarrow C_7H_7^+$
							70·2	$PhBOCH_2^+ \longrightarrow C_7H_7^+$
(II)		6·5	1·9	2·2	—	—	56·3	
							70·2	$PhBOCH_2^+ \longrightarrow C_7H_7^+$
(III)		1·5	5·8	2·6	—	—	61·5	$(III)^+ \longrightarrow C_8H_8^+$
							51·5	
							68·6	
(IV)		4·6	—	—	—	—	51·1	$(IV)^+ \longrightarrow C_7H_7^+$
(V)		6·6	1·0	1·3	—	—	51·4	
(VI)		1·0	2·7	11·3	—	—	63·1	
(VII)		2·3	—	—	1·3	0·9	91·8	$(VII)^+ \longrightarrow C_{10}H_{12}^+$
							70·2	$PhBOCH_2^+ \longrightarrow C_7H_7^+$
(VIII)		2·0	3·5	—	—	—	47·1	$(VIII)^+ \longrightarrow C_7H_7^+$
							61·5	$(VIII)^+ \longrightarrow C_8H_8^+$

[a] Calculated using ^{11}B.

operating at 70 ev. In each case, assignment of structure was made from precise mass determinations. From the metastable peaks present in the mass spectra it is deduced that the hydrocarbon ions may arise from rearrangements of (i) the molecular ions, (ii) the resonance stabilised oxonium ions produced on removal of alkyl groups attached to the boronate ring system, and (iii) the ion $PhBOCH_2^+$. Details of the mass spectra of the listed phenylboronates and those of polyhydric alcohols will be published elsewhere.

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[1] R. H. Cragg and J. F. J. Todd, *Chem. Comm.*, 1970, 386.