83. Field-Desorption Mass Spectra of Fern Phloroglucinols Containing Three to Six Ring Constituents[1])

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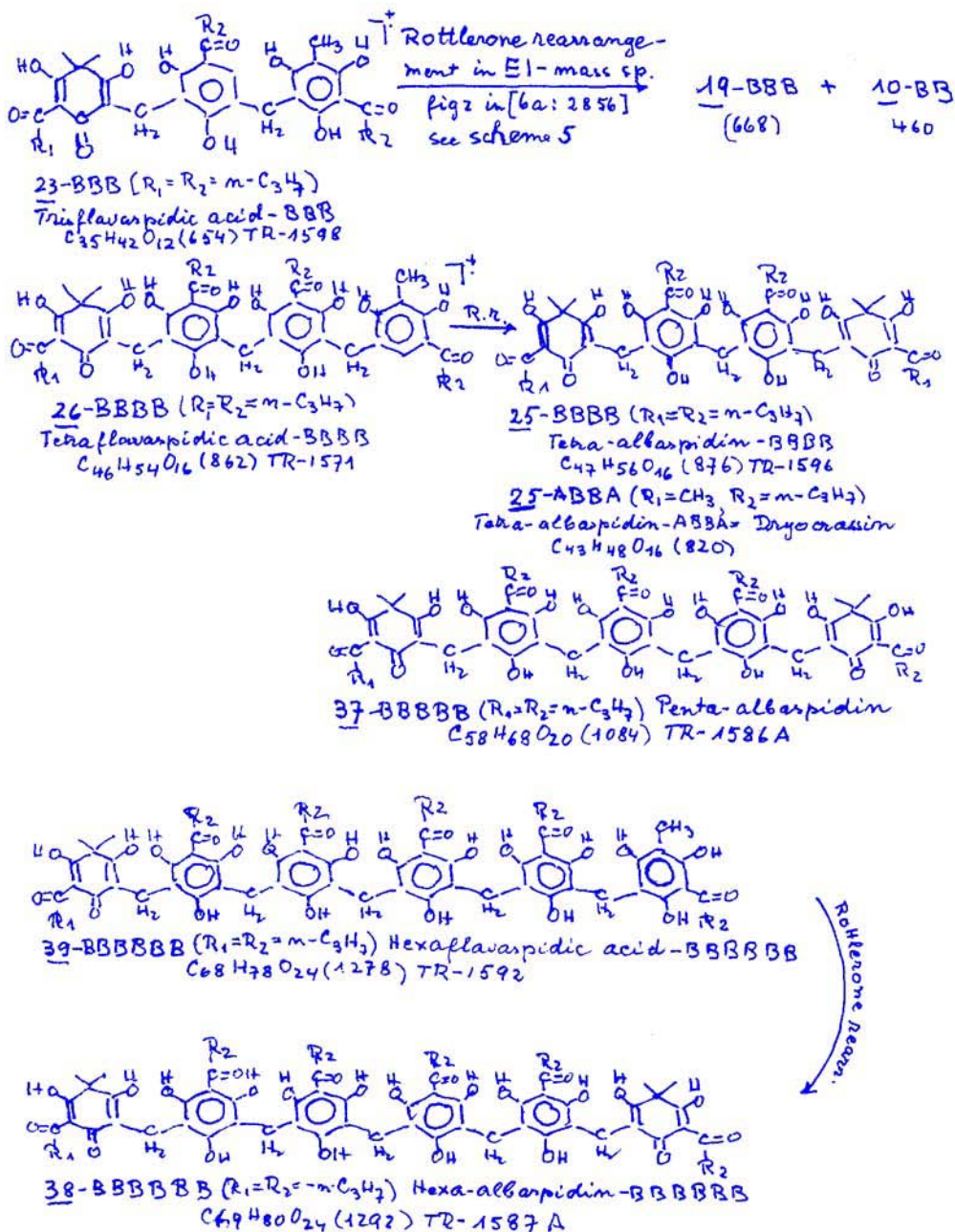Institute of Pharmaceutical Chemistry, University, SF–70101 Kuopio

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It has been previously shown that the structural analysis of the title compounds by electron-impact ionization (EI) mass spectrometry is complicated by extensive, if not complete, thermal rottlerone-type rearrangement and/or fragmentation reactions. The use of a 'softer' ionization technique such as field desorption (FD) is, therefore, required in order that these compounds may be characterized in terms of their molecular size and composition. In this report, the FD mass spectra of typical representatives of this class of compounds are described along with the attempted suppression of undesirable thermal reactions by the optimization of the emitter temperatures.

Introduction. – 'Fern phloroglucinols' and 'acyl-phloroglucinols' are the usual designations (trivial names) for a group of phenolic (or *semi*-phenolic) compounds occurring mainly in the fern genus *Dryopteris* (see reviews by *Berti* and *Bottari* [1], *Penttilä* and *Sundman* [2] and *v. Euw et al.* [3]). *Ca.* 30 basic structures have been found of which only a few are simple phloroglucinol derivatives containing one aromatic (or isomeric 2,5-hexadienone) ring. In most instances, between two and six [4] such rings are linked *via* CH_2 bridges (see the *Formulae* given in *Scheme 1*).

During the past 15 years, electron impact ionization (EI) has been widely employed in the MS analysis of such compounds [5–7]. Under EI conditions, extensive fragmentation is observed which provides useful information on the gross structures of the single ring constituents [5–7]. In the case of unknowns, however, the corresponding low-molecular ion abundances present certain drawbacks such as difficulties in obtaining reliable molecular weights and elemental compositions. Pronounced $M^{+\cdot}$ peaks have only been observed for members of this class, such as albaspidin-BB (**10-BB**, *Scheme 1*) [5], which contain no more than two ring moieties. Compounds with three rings, *e.g.* filixic acid-BBB (**19-BBB**, *Fig. 1a*) or trisflavaspidic acid-BBB (**23-BBB**) already display very weak $M^{+\cdot}$ signals, even when 'mild' ionization conditions, *i.e.* reduced electron energies (12 eV),

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[1]) Dedicated to the late Prof. *Peter Brown* (12.IX.1938–15.III.1981), Dept. of Chemistry, Arizona State University, Tempe, Arizona 08521, U. S. A., whose premature death was a great loss to his friends and collegues. The last letter which we received from him (November 15, 1980) contained the first FD mass spectra of five relatively large fern phloroglucinols which he had successfully analyzed. Two of these spectra, in which no thermal rearrangement and/or fragmentation was observed, are reproduced in this article in *Figs. 1b* and *3*.

Scheme 1. *Structures of Compounds*[a]*) Discussed in this Work* (including reactions according to *Schemes 4* and *5*)

Rottlerone rearrangement in EI-mass sp. fig 2 in [6a: 2856] see scheme 5

19-BBB + 10-BB
(668)   460

23-BBB (R$_1$ = R$_2$ = n-C$_3$H$_7$)
Triflavaspidic acid – BBB
C$_{35}$H$_{42}$O$_{12}$ (654) TR-1598

26-BBBB (R$_1$ = R$_2$ = n-C$_3$H$_7$)
Tetraflavaspidic acid – BBBB
C$_{46}$H$_{54}$O$_{16}$ (862) TR-1571

R.r.

25-BBBB (R$_1$ = R$_2$ = n-C$_3$H$_7$)
Tetra-albaspidin – BBBB
C$_{47}$H$_{56}$O$_{16}$ (876) TR-1596

25-ABBA (R$_1$ = CH$_3$, R$_2$ = n-C$_3$H$_7$)
Tetra-albaspidin-ABBA – Dryocrassin
C$_{43}$H$_{48}$O$_{16}$ (820)

37-BBBBB (R$_1$ = R$_2$ = n-C$_3$H$_7$) Penta-albaspidin
C$_{58}$H$_{68}$O$_{20}$ (1084) TR-1586 A

39-BBBBBB (R$_1$ = R$_2$ = n-C$_3$H$_7$) Hexaflavaspidic acid – BBBBBB
C$_{68}$H$_{78}$O$_{24}$ (1278) TR-1592

Rottlerone reaon.

38-BBBBBB (R$_1$ = R$_2$ = -n-C$_3$H$_7$) Hexa-albaspidin – BBBBBB
C$_{69}$H$_{80}$O$_{24}$ (1292) TR-1587 A

[a]) For the systematic IUPAC names, *cf.* [4]; compound numbers are the same as in [3] [4].

are used [6a]. Not unexpectedly, *'dryocrassin'* (tetra-albaspidin-ABBA or methylene-bis-norflavaspidic acid-ABBA; **25-ABBA**), which is the only four-ring system to be successfully analyzed by EI, gave no measurable molecular-ion current [8] [9].

Another, more serious disadvantage of employing EI is due to the fact that thermal reactions may occur, which lead to decomposition of the neutral substrate molecules (with or without rearrangement) prior to ionization. These reactions are especially likely to interfere, when the required vaporization temperatures become relatively high owing to the size of the molecule. The most important thermal reaction is the so-called *rottlerone rearrangement,* which was originally encountered in solution chemistry. When this process occurs under the conditions of EI analysis, it can easily lead to misinterpretation of spectra by an inexperienced worker.

Rottlerone rearrangements typically occur in asymmetric polyhydroxy-diacyl-diphenylmethanes. For two-ring systems, they follow *Scheme 2* in which X and Y represent acyl-resorcinol or acyl-phloroglucinol moieties:

Scheme 2. *A Rottlerone Rearrangement in a Two-Ring-System*

$$a \qquad b \qquad\quad a \qquad b$$

$$X\text{--}CH_2\text{--}Y + X\text{--}CH_2\text{--}Y \longrightarrow X\text{--}CH_2\text{--}X + Y\text{--}CH_2\text{--}Y$$

$$\textbf{I} \qquad\qquad\qquad \textbf{I} \qquad\qquad\qquad \textbf{II} \qquad\qquad \textbf{III}$$

When X differs from Y a disproportionation reaction can be observed in which two molecules of asymmetric **I** produce symmetric **II** and **III**. The reaction proceeds most efficiently by warming the substrate in aqueous AcOH or, according to *McGookin et al.* [10], in alkaline solution. It was shown that, under these conditions, hydrolytic cleavage of **I** occurs at the CH$_2$ bridge in both possible ways (*a* and *b*), giving the four monocyclic intermediates **IV, V, VI,** and **VII**. The postulated benzyl-alcohol derivatives **V** and **VI** are highly reactive and promptly condense with XH and YH to re-form the dimeric species. While the combination **IV + V** and **VI + VII** both regenerate the initial educt **I**, their alternatives **IV + VI** and **V + VII** lead to the symmetrical rearrangement products **II** and **III**.

$$XH + HOCH_2Y + XCH_2OH + HY$$

$$\textbf{IV} \qquad \textbf{V} \qquad\quad \textbf{VI} \qquad \textbf{VII}$$

Amongst the fern phloroglucinols, para-aspidin-BB (**7-BB**) has been studied extensively with respect to such rearrangements. Under hydrolytic conditions, for example, **7-BB** yields **36-B, 41-B, 42-B,** and **43-B** according to *Scheme 3,* from which the expected dimeric products, albaspidin-BB (**10-BB**) and methylene-bis-aspidinol-BB (**18-BB**), are formed *via* the condensation of the benzyl-alcohol derivatives **41-B** and **42-B** with the phenols **43-B** and **36-B**, respectively. When solid samples are heated, the same (or equivalent) products are obtained [11] [12], which is of special relevance to the interpretation of EI spectra [6] [7]. In this particular case, the educt **7-BB** and its two rearrangement products **10-B** and **18-B** have the same empirical formula ($C_{25}H_{32}O_8$, $M = 460$). Rottlerone rearrangement is, therefore, not directly reflected in the molecular-

ion region, but corresponding changes in the fragmentation pattern indicate its occurrence. In the absence of H_2O, benzyl alcohols cannot be formed, *i.e.* benzylium cations or radicals and/or quinoid neutrals take the place of the reactive single-ring intermediates.

Scheme 3. *The Rottlerone Rearrangement in Para-aspidin-BB* (7-BB) *under Hydrolytic Conditions*
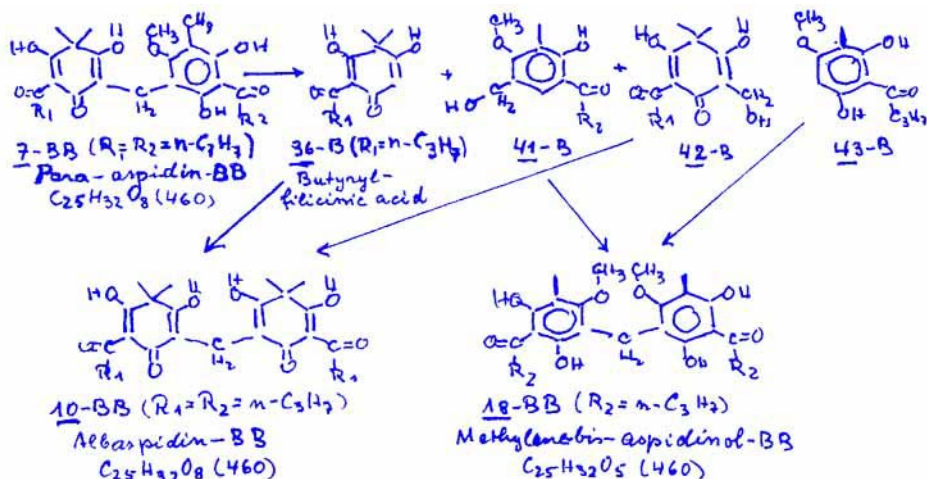
In asymmetric compounds with three or more rings, analogous disproportionation with exchange of the terminal rings may also occur *(Scheme 4)*. Frequently, however, only one of the possible rearrangement products can be detected in the EI spectrum. This may occur owing to the fact that $M^{+\cdot}$ ion currents are generally low. In the spectra of trisflavaspidic acid-BBB (23-BBB) and trisdesaspidin-BBB (21-BBB), for example (both have the formula $C_{35}H_{42}O_{12}$, $M = 654$, *Figs. 2* and *3* in [6a]), the $M^{+\cdot}$ peak of filixic acid-BBB (19-BBB) is clearly recognizable as the common rottlerone-rearrangement product at m/z 668.

Scheme 4. *The Rottlerone Rearrangement in Asymmetric Three-Ring Systems*

$$2\,X-CH_2-Y-CH_2-Z \longrightarrow X-CH_2-Y-CH_2-X + Z-CH_2-Y-CH_2-Z$$

A related fragmentation reaction, which can be observed in symmetrical compounds with three or more rings, is even more puzzling. When filixic acid-BBB (19-BBB) is heated, for example, it is known to produce the two-ring compound albaspidin-BB (10-BB) along with the above rottlerone-rearrangement products [10] [11] [13]. This thermal degradation product is formed owing to the expulsion of a central portion of the molecule, with new bond formation occurring between the terminal, *i.e.* non-linked, moieties. A similar product can also be detected in the EI spectrum of 19-BBB *(Fig. 1a)*, as is evident from an intense peak at m/z 460 (base peak at low ionization energies) corresponding to $M^{+\cdot}$ of
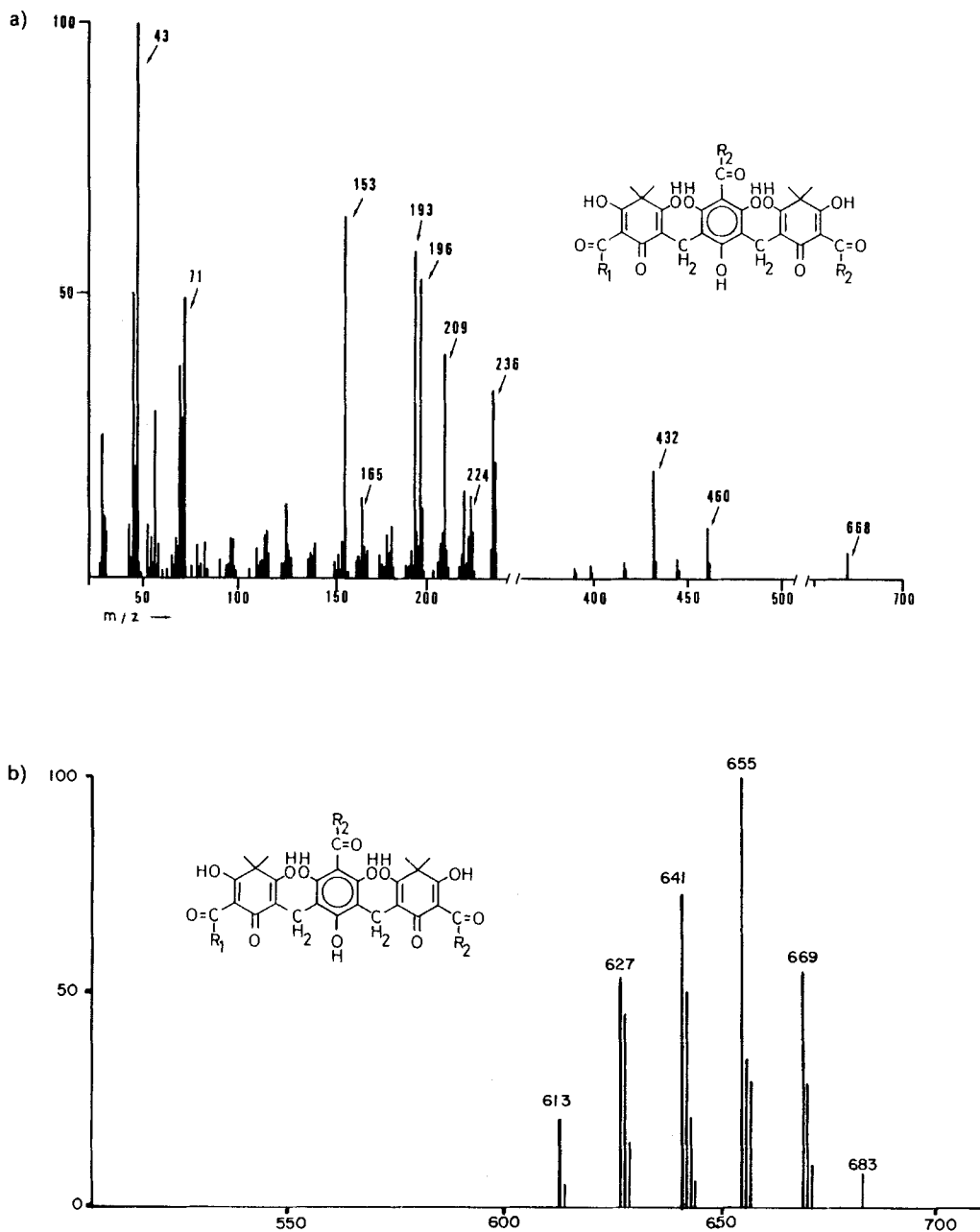
Fig. 1. a) *EI-MS of filixic acid-BBB* (**19-BBB**, $M = 668$; preparation *TR-1459*; ionization energy 75 eV). b) *FD-MS[3]) of filixic acid* (**19**, natural mixture of homologues $M = 612, 626, 640, 654, 668$, and 682; preparation *TR-1570*; emitter current 15 mA).

10-BB (see also *Fig.* 1 in [6a][2]). In [6a], the genesis of this ion has been tentatively formulated according to *Scheme 5*. The $M^{+\cdot}$ ion of its counterpart **44-B** could, however, not be detected, whereas an ion corresponding to its protonated form was clearly visible (m/z 209).

Scheme 5. *The Fragmentation of Filixic Acid-BBB* (**19**-BBB) *into Albaspidin-BB* (**10**-BB), *Formulated as an EI-Induced Expulsion Reaction According to* Lounasmaa et al. [6a]
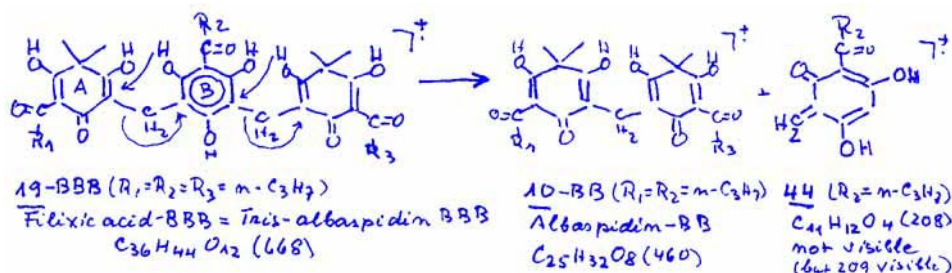
Results and Discussion. – In the course of a recent study, several new oligophloroglucinols were isolated from *Dryopteris aitoniana* which contain four, five, and six ring constituents [4]. To determine their structures, it was essential to find reliable MS methods for unambiguous molecular-weight assignment. For the above reasons, EI methods had proven inadequate and, therefore, 'softer' methods of ionization were obvious candidates for further investigation. Although field ionization (FI) [14] and chemical ionization (CI) [15], which also require vaporization of the thermally labile molecules prior to ionization, seemed promising (particularly as the former had given good results with other polar substrates [16]), both methods failed in the present case. Condensed phase ionization by field desorption (FD) [17] and fast atom bombardment (FAB) [18] did, however, prove successful. Application of this latter technique in conjunction with two-dimensional mass spectrometry (MS/MS) [19] will be reported elsewhere [20].

Using FD, 'preformed' M-like ions such as $M^{+\cdot}$ and/or $[M + H]^+$ (or, in the presence of Na^+, also $[M + Na]^+$ attachment ions) are desorbed directly from the surface of an activated emitter, when a strong electrical field gradient is applied (together with slow heating when necessary). As it is not necessary to evaporate the sample prior to ionization, it was expected that the interference of thermal reactions will be greatly reduced.

In *Figs. 1b, 2–7*, a selection of FD mass spectra of the above fern phloroglucinols, which contain three to six rings, is presented. The spectra were recorded at minimum emitter heating currents in order that the proportion of unrearranged/undecomposed molecular species should be maximized. At successively higher emitter currents (higher emitter temperatures) $M^{+\cdot}$ and/or $[M + H]^+$ ions of rottlerone-rearrangement products and various fragment ions become visible. *Scheme 1* summarizes the structural formulae of the phloroglucinol substrates which were analyzed in this fashion.

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[2])　In this particular case, it is uncertain as to whether the ion observed at m/z 460 originates from a thermal process occurring prior to EI or from a genuine EI-induced process, as previously formulated in [6a].

Fig. 1b shows a typical FD spectrum (upper mass range)[3] of a natural mixture of various homologues of filixic acid (**19**) which was isolated from *Dryopteris filix-mas* (L.) SCHOTT. Such mixtures are very difficult to separate, but the nature of their constituents can be deduced from degradation experiments [21], and to some extent, from the fragments present in EI-MS. The six $[M + H]^+$ signals observed in the FD spectra can be assigned to a number of species which contain combinations of acetyl (A; R = CH_3), propionyl (P; R = C_2H_5), butyryl (B; R = C_3H_7), and valeroyl (V; R = C_4H_9) substituents. The peaks at m/z 613, 627, 641, 655, 669, and 683 are, therefore, likely to correspond mainly to **19-ABA**, **19-ABP**, **19-ABB**, **19-PBB**, **19-BBB**, and **19-BBV**, respectively. The practically exclusive formation of intact *M*-like ions, owing to the low thermal exposure and low transfer of excess internal energy, facilitates qualitative and (when calibration is made) quantitative mixture analysis. In the case of **19-BBB**, the EI-MS *(Fig. 1a)* is dominated by fragmentation with and without preceding rottlerone rearrangement.

Fig. 2a shows the (15 mA) FD-MS[4] of trisflavaspidic acid-BBB (**23-BBB**, preparation *TR 1598,* m.p. 171–172°) which was isolated as a pure compound from *Dryopteris aitoniana* [4]. In this case, the spectrum is dominated by the $M^{+\cdot}$ species at m/z 654, rather than the $[M + H]^+$ species. While this ion represents a large proportion of the intact molecular species, the low-abundance peak which appears at m/z 446 is most likely to reflect incipient fragmentation according to *Scheme 5* ($X-CH_2-Z$ from $X-CH_2-Y-CH_2-Z$).

The EI behavior of this compound, however, reflects excessive thermal and/or EI-induced fragmentation even under low-energy conditions (12 eV). Besides the low-intensity $M^{+\cdot}$ peak of the intact molecule (about 1% rel. int.), a rottlerone product ($M^{+\cdot}$ at m/z 668, also about 1% rel. int.) is obtained according to *Scheme 4*. For the rest, thermal and/or EI-induced fragmentation to two- and mainly one-ring moieties dominate the spectrum (Fig. 2 in [6a]).

It can also be seen, however, that, if the emitter current is raised beyond 15 mA, thermal reactions quickly become significant. At 18 mA *(Fig. 2b)*[4], the $M^{+\cdot}$ ion at m/z 654 is still the base peak (M^{++} at m/z 327), but the above type-*c* rottlerone-rearrangement product is conspicuous ($M^{+\cdot}$ at m/z 668, ca. 12% rel. int., M^{++} at m/z 334) along with the various two-ring species such as that at m/z 446 (already visible at 15 mA and now close to 40% rel. int.) and the four less important species at m/z 460, 444, 432, and 418 (up to 30% rel. int.). Within this last group, it is probable that at least two peaks (m/z 460, $X-CH_2-X$ and m/z 446, $X-CH_2-Z$) represent thermal artefacts which originate from the recombination of single-ring degradation products, according to *Scheme 5*. A thermal genesis is likely, as new intra- and intermolecular linkages have been formed between constituents which were originally unconnected (2 residues X) or quite distant (X and Z). It is interesting to note that the dominant type-*d* product $X-CH_2-Z$ (formally arising from expulsion of the central Y moiety) is of no importance in the EI spectrum of **23-BBB**, whereas a corresponding $X-CH_2-X$ species represents the major rearrangement product *(cf. Scheme 5)* of the symmetrical counterpart **19-BBB** *(Fig. 1a)*. Under

Fig. 2 a) *FD-MS*[4]*) of Trisflavaspidic Acid-BBB* (**23**-BBB, $M = 654$; preparation *TR-1598*; emitter current 15 mA).
b) *FD-MS*[4]*) of Trisflavaspidic Acid-BBB* (**23**-BBB, $M = 654$; preparation *TR-1598*; emitter current 18 mA).
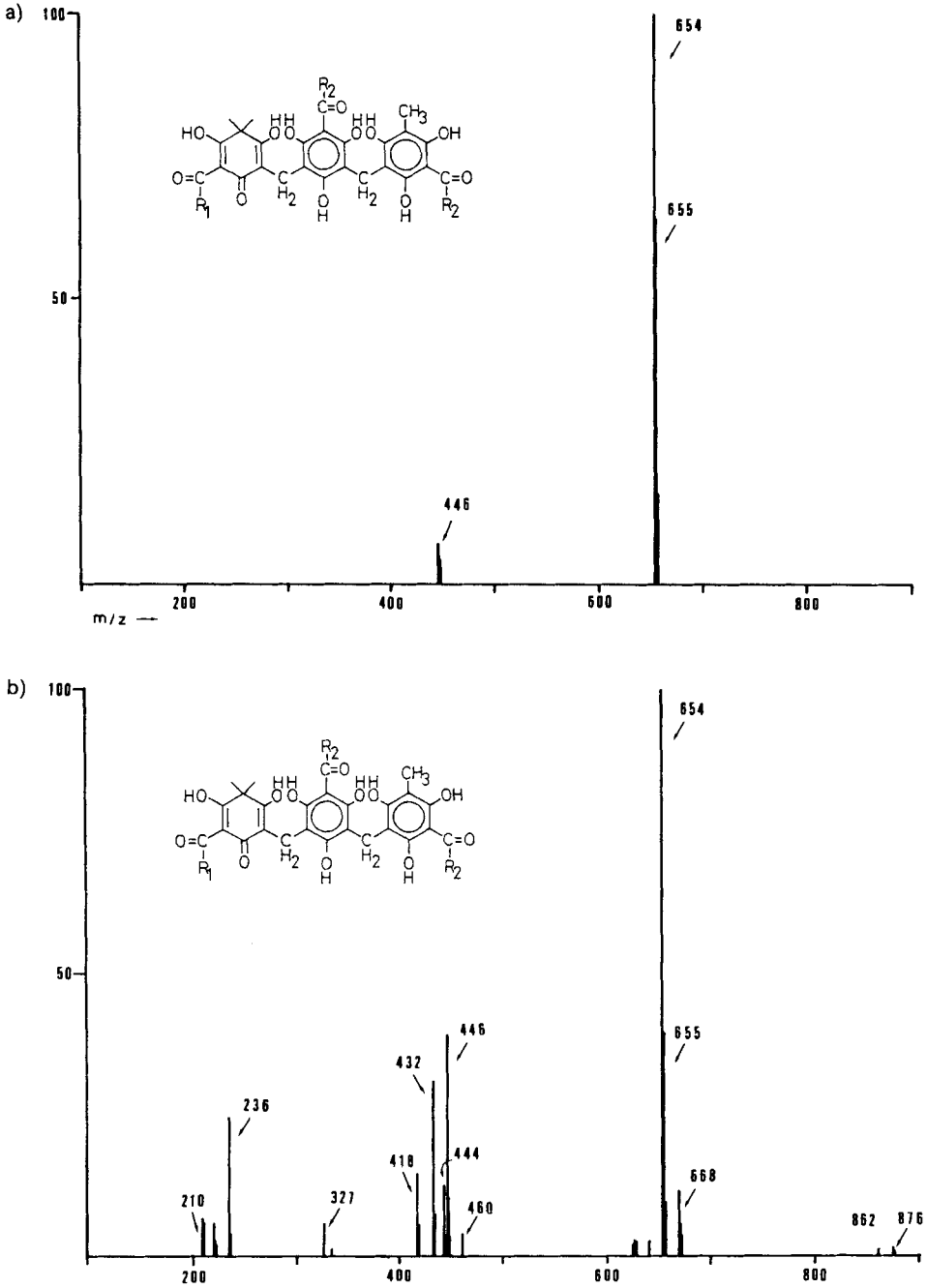
the chosen FD conditions, the three other ions representing [(X–CH$_2$–Y–CH$_2$) – H] (m/z 444), X–CH$_2$–Y–H (m/z 432), and H–Y–CH$_2$–Z (m/z 418) are also more likely to be thermal recombination products than genuine EI fragments of intact (or rearranged) 'trimeric' molecular ions. The apparent formation of the low-yield 'second-order' recombination products of the dimeric ions (i.e. species formally corresponding to X–CH$_2$–Y–CH$_2$–Y–CH$_2$–X (m/z 876) and X–CH$_2$–Y–CH$_2$–Y–CH$_2$–Z (m/z 862)) is also of interest. To date, such products have not been reported, although they can be readily rationalized by extending *Scheme 5*.

Under these conditions, the fragments corresponding to the inferred one-ring precursors of the recombination products, i.e. m/z 210 (H–Z), 222 [(CH$_2$–Z) – H], and 236 [(X–CH$_2$) – H] are still of minor importance. If the emitter current is raised to 20 mA, however, the peak at m/z 210 becomes the base peak, whereas the peaks at m/z 222 and 236 are increased to about 35 and 15% rel. int., respectively. The X–H monomer (m/z 224), which was absent at 18 mA, now appears (about 20% rel. int.), as does the second rottlerone type-c rearrangement product Z–CH$_2$–Y–CH$_2$–Z (m/z 640). At the same time, the intensity of the intact M^+ ion at m/z 654 decreases to about 50% rel. int., while type-c product X–CH$_2$–Y–CH$_2$–X retains most of its previous abundance (ca. 12%). At 21 mA, the peak at m/z 210 dominates the spectrum, as it carries close to 50% of total ion current.

The fern phloroglucinols which contain four, five, and six ring moieties, closely resemble this FD behavior. Oligophloroglucinols of this molecular size do not generally yield EI spectra, which contain sufficient information about the structure of the entire molecule. By contrast, highly useful FD spectra are obtained without difficulty, as long as the emitter temperature is carefully controlled. This is exemplified by *Fig. 3*, which shows the (15 mA) FD spectrum of a sample of *'dryocrassin'* (**25-ABBA**) [8] [9] isolated from
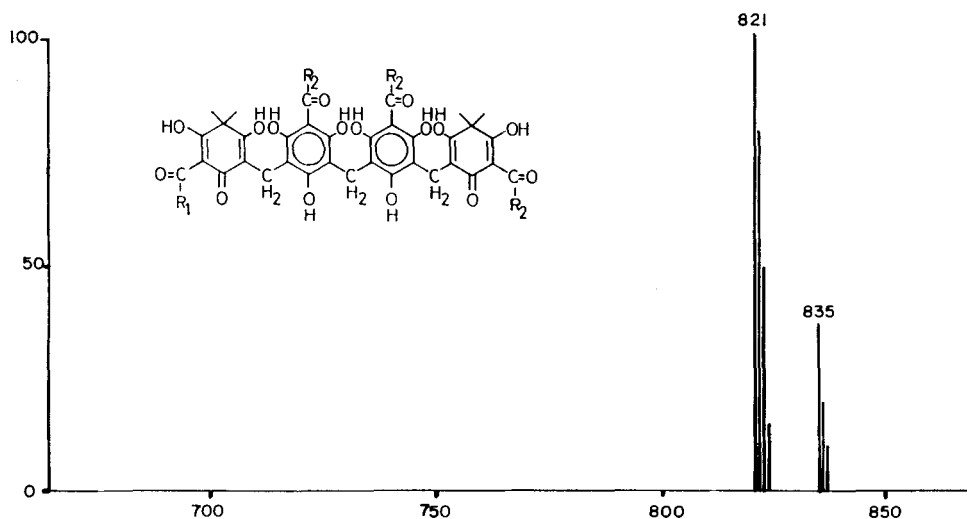

Fig. 3. *FD-MS^3) of 'Dryocrassin'* (**25-ABBA**, *M* = 820; the preparation contained *ca.* 30% of the homologue ABBP, *M* = 834; emitter current 15 mA)

Dryopteris crassirhizoma [9]. The preparation contained about 30% of a higher homologue (probably **25-ABBP**) which is responsible for the peak at m/z 835. Similarly, at 21 mA (minimum) emitter current, the FD spectra *(Fig. 4)*[4]) of the symmetrical compound tetra-albaspidin-BBBB (**25-BBBB**), which was isolated as a pure compound (sample *TR 1596*, m.p. 131–133°), from *Dryopteris aitoniana* [4], consists predominantly of $M^{+ \cdot}$ and $[M + H]^+$ signals at m/z 876 and 877, respectively (in a ratio of *ca.* 2:3). As in the case of **23-BBB**, formation of the formal expulsion product $X–CH_2–Y–CH_2–X$ from the $X–CH_2–Y–CH_2–Y–CH_2–X$ precursor (by recombination of degradation products in analogy to *Scheme 5*) is still of only minor significance ($M^{+ \cdot}$ and $[M + H]^+$ at m/z 668 and 669, respectively, both about 20% rel. int.). At an emitter current of 23 mA, a second degradation product is observed, which formally corresponds to $[(X–CH_2–Y–CH_2–Y) – H]$ ($M^{+ \cdot}$ and $[M + H]^+$ *ca.* 1:1 at m/z 640 and 641).
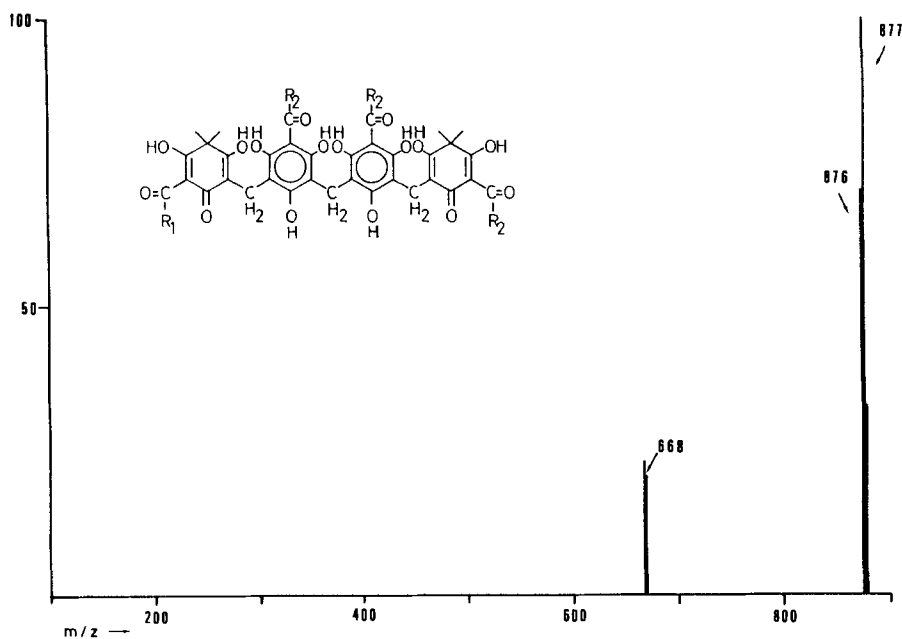
Fig. 4. *FD-MS*[4]) *of Tetra-albaspidin-BBBB*
(**25-BBBB**, $M = 876$; preparation *TR-1596*; emitter current 21 mA)

Fig. 5 shows the corresponding (19-mA emitter current) spectrum[4]) of the unsymmetrical analogue, tetraflavaspidic acid-BBBB (**26-BBBB**, preparation *TR 1571*, m.p. 170–171°) isolated from *Dryopteris aitoniana* [4]. Again, the $M^{+ \cdot}$ (m/z 862) and $[M + H]^+$ (m/z 863) are the most intense signals in the spectrum. Minor, but nevertheless significant contributions arise from 'early' degradation to $X–CH_2–Y–CH_2–Z$ ($M^{+ \cdot}$ at m/z 654) and $X–CH_2–Y–CH_2–X$ ($M^{+ \cdot}$ at m/z 668) and are likely to reflect thermal decomposition of the original $X–CH_2–Y–CH_2–Y–CH_2–Z$ species *via* recombination of one- and/or
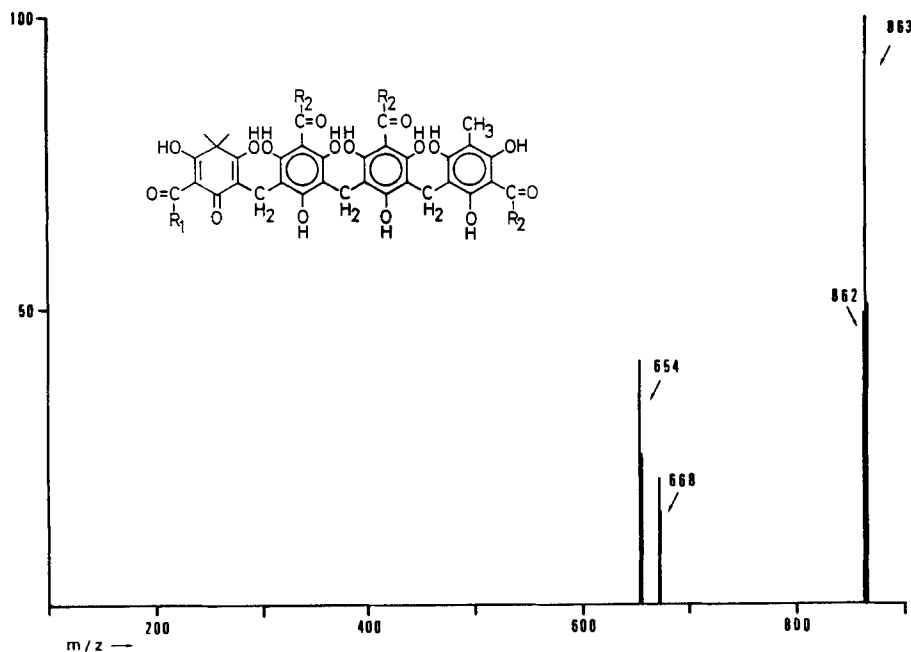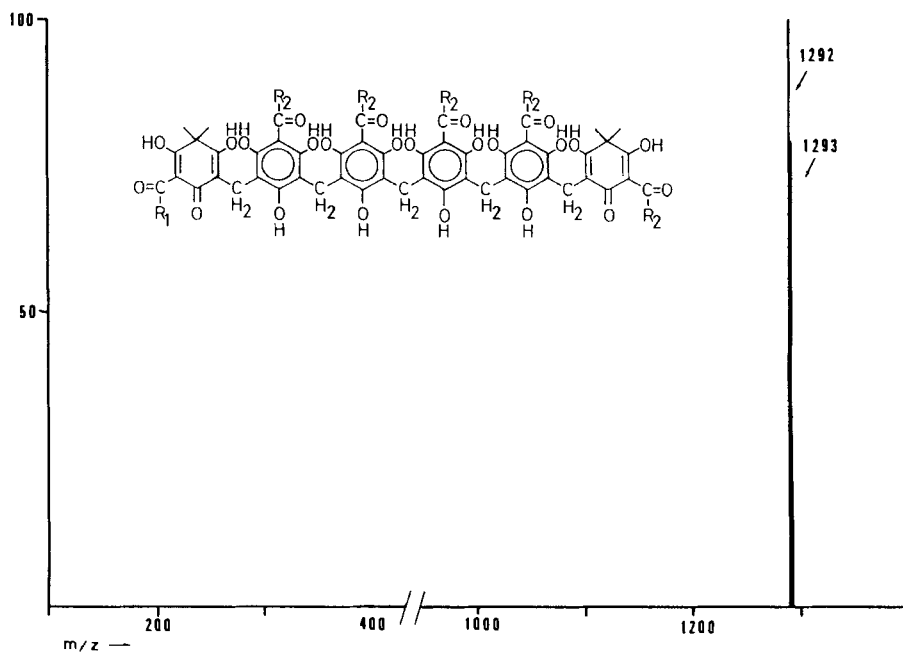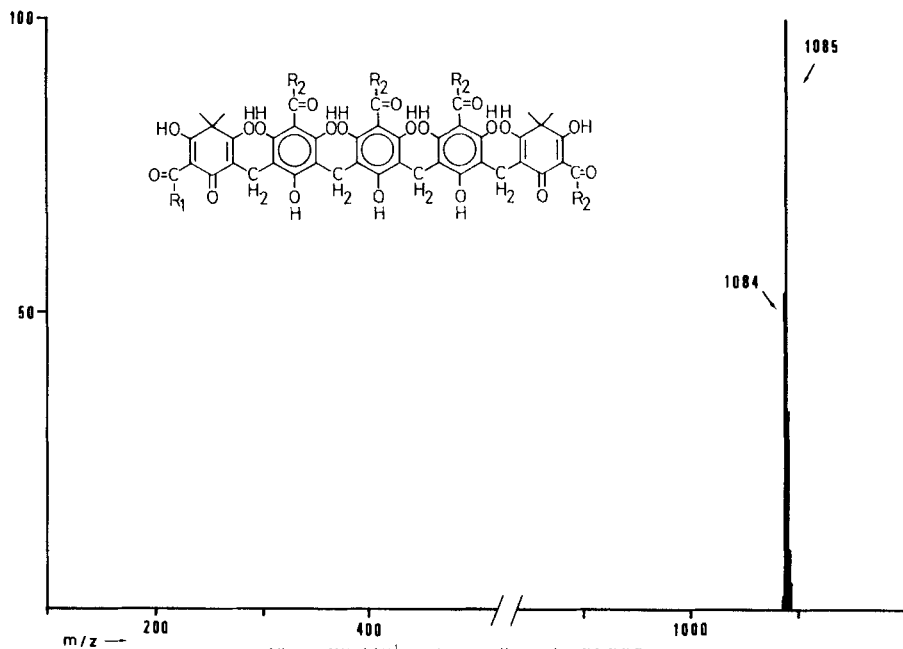
Fig. 5. *FD-MS⁴) of Tetraflavaspidic Acid-BBBB*
(**26-BBBB**, $M = 862$; preparation *TR-1571;* emitter current 19 mA)

two-ring constituents, in analogy to *Scheme 5*. Some rottlerone rearrangement, producing tetra-albaspidine ($X–CH_2–Y–CH_2–Y–CH_2–X$, $M^{+\cdot}$ at m/z 876), was additionally observed at elevated emitter currents (21 mA).

For the largest fern phloroglucinols reported to date, *i.e.* those which incorporate five- and six-ring constituents, the recording of spectra which are free from contributions of rearrangement and/or degradation products, proved straightforward (with the exception of hexaflavaspidic acid-BBBBBB (**39-BBBBBB**; preparation *TR-1592*) which gave no useful spectrum). These findings are illustrated in *Figs. 6* and *7* which show typical FD spectra⁴) of penta-albaspidin-BBBBB (**37-BBBBB**) and hexa-albaspidin-BBBBBB (**38-BBBBBB**). Samples of both these compounds (preparations *TR 1586a*, m.p. 194–196°; and *TR 1587A*, m.p. 168–175°, respectively) were isolated from *Dryopteris aitoniana*. Emitter currents of 20 and 25 mA were required to produce M-like ions of the $M^{+\cdot}$ and $[M + H]^+$ type of these compounds (m/z 1084/1085 and 1292/1293, respectively). In these two cases, sensitivity problems prevented an evaluation of higher emitter currents with respect to rottlerone rearrangement and/or related degradation reactions.

Fig. 6. *FD-MS*[4]) *of Penta-albaspidin-BBBBB*
(37-BBBBB, M = 1084; preparation *TR-1586a;* emitter current 20 mA)

Fig. 7. *FD-MS*[4]) *of Hexa-albaspidin-BBBBBB*
(38-BBBBBB, M = 1292; preparation *TR-1578;* emitter current 25 mA)

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