The Mass Spectra of Phrymarolins, 1,2-Dioxygenated-3,7-dioxabicyclo[3.3.0]octane Lignans\textsuperscript{1}

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The mass spectra of phrymarolins, which were isolated from Phryma leptostachya L. as novel lignans, have been investigated. The most predominant fragmentation was the splitting of the acetal linkage. The fragment ions (m) and (n), at m/e 141 and m/e 99 respectively, are considered to be characteristic to the lignans. The accurate molecular weight measurements of important ions provided a further evidence for the structure of phrymarolin-I.

Recently the mass spectrometry of lignans has been reported by Duffield,\textsuperscript{1} Pelter,\textsuperscript{2} and Takahashi \textit{et al.}\textsuperscript{3} for naphthalene lactone- and perhydrofurofuran-type lignans.

With respect to the mass spectrometry of 1-hydroxy-3, 7-dioxabicyclo[3. 3. 0]octane lignans such as gmelinol, the fragmentations were simplified due to the lack of random splitting, though more fragments were produced for each process than symmetric lignans such as sesamin; the hydroxy group stabilizes an adjacent radical and thus favours its production. Stereochemical differences within the same group of lignans did not cause any major differences to their spectra.

In this paper the mass spectra, which provided supporting evidences for the previously reported structures of phrymarolin-I and -II,\textsuperscript{4} will be described.

In the following discussion the term Ar stands for 2-methoxy-4, 5-methylenedioxyphenyl, and the stereochemistry is not implied in the formulae, unless otherwise illustrated.

The most predominant fragmentation of phrymarolins (Ia, IIa) and their derivatives (IV, V, VI) is the splitting of the acetal linkage as it was reported for sesamolin,\textsuperscript{5} except the compound (III) which possesses an acetal-methoxyl instead of an acetal-phenoxy1 and shows the molecular ion as the base peak.

Phrymarolins show very similar spectra as expected on the ground of their structures. The electron impact on phrymarolin-I(Ia) and phrymarolin-II(IIa) results in the production

\begin{figure}
\centering
\includegraphics[width=\textwidth]{mass_spectra.png}
\caption{Fig. 1.}
\end{figure}

\textsuperscript{1} This paper had been presented at the 6th Federation Meeting of Chemical Societies in Western Japan (Fukuoka) on July 12, 1969.
of the ion (a) at m/e 321 as the base peak, and after proton capture, the phenol ion (b) at m/e 168 and the corresponding ion (c) at m/e 138 from Ia and IIa, respectively. Another major difference between the spectra is an ion peak at m/e 153 which is not found in the spectrum of phrymarolin-II (Fig. 8).

With respect to the desacetyl derivatives, a remarkable difference was found (Fig. 9). Desacetyl phrymarolin-I (Ib) produced the phenol ion b as the base peak along with less intensive peaks at m/e 279 (d) and its deprotonized ion of m/e 278 (e), while desacetyl phrymarolin-II (Iib) gave again ion, d, which corresponds to a from phrymarolin-II, as the ion b along with a neutral fragment (d')

**FIG. 2.**

On argument of the stereochemistry of the aroxy group, it is noticeable that the tetrahydrofuran-3-ol (IV), in which the aroxy and the hydroxyl are in cis-relationship, gave an abundant ion peak at m/e 138, while the sesamol ion was less intensive in the spectrum of dihydrodesacetylphrymarolin-II (V), which has trans-relationship between the aroxy and the hydroxy group (Fig. 6, 9, 10).

However, this assumption on the production of the phenol ions is much subject to uncertainty, being referred to the spectrum of the ketone (VI) which gave an abundant ion at m/e 168 with the ion (f) as the base peak, nevertheless it has no hydroxy group. It is indicated by a metastable ion peak that ion f is arisen from ion b. This is also supported by the fact that ion f is not recogniz-

**FIG. 3.**

most abundant ion along with the phenol ion c with a less intensity.

This difference may be caused by the following intramolecular rearrangement in desacetyl phrymarolin-I*1 to produce the stable phenol

*1 The absorption band due to the tertiary hydroxy group was shown at $\nu_{\text{max}}$ 3520 cm$^{-1}$ at a concentration below $5 \times 10^{-3}$ M in CCl$_4$. This may suggest an interaction between the hydroxy and the o-methoxy groups.

*2 The $\lambda_{\text{max}}$ (EtOH) of 2-methoxysesamol (304 nm) and sesamol (296 nm) may be referred for their ionization potentials.
ed in the spectra of phrymarolin-II and its derivatives. Furthermore, the electron impact on 1-ethoxy-2-methoxy-4,5-methylene-dioxybenzene (VII) results in the production of the ion at m/e 153 as the base peak along with abundant ion b in an expected fashion (Fig. 4, 10).

A characteristic ion peak for phrymarolins is found at m/e 141 and assigned to such a structure (n). The corresponding ion (m) is observed in the spectra of desacetyl derivatives such as Ib, IIb, and III. Ion m may be assignable to a pyrone or a protonized diketone species (Fig. 7).

Many other fragment ions from phrymarolins essentially correspond to those of perhy-
A metastable ion peak indicates that the ion at m/e 191 (g) is arisen from the fragment ion at m/e 250 (h), and in turn which may break down to the ion at m/e 161 (i) by the loss of CH$_2$O grouping (Fig. 5).

The ion peak at m/e 165, which corresponds to ArCH$_2^+$ (j) and an important fragment ion in the spectra of perhydrofurofuran lignans, is readily recognized.

The ion peak at m/e 180, which corresponds to ArCHO$^+$ (k), is only observed in the spectra of such compounds as I incorporating a 3,7-dioxabicyclo[3.3.0]octane ring.

The ion at m/e 181 corresponds to ArCHOH (l), which is an abundant ion in the spectra.
of 1-hydroxy-perhydrofurofuran lignans and their derivatives such as gmelinol, dihydrogmelinol and di-O-methyl olivil. This ion is also an important ion of Ib, IIb and III, even of the acetates Ia and IIa, but again it has never been observed in the spectra of dihydro derivatives of them.

With respect to the degradation products, IV, V and VI, the spectra are much simple (Fig. 9, 10).

The splitting of the acetal linkage produces the ions (o) at m/e 250, (p) at m/e 280, and (q) at m/e 248 from IV, V, and VI, respectively (Fig. 6).
Accurate molecular weight measurements were carried out on the major fragment ions of phrymarolin-I and its desacetyl derivative in accordance with the expected structures (Table).

The mass spectra of phrymarolins and their degradation products are shown in the figures (Fig. 8〜10).

EXPERIMENTAL

The spectra were measured on a JMS-01SG spectrometer using the direct inlet procedure at 75 eV. The
samples were prepared as described in previous papers.\textsuperscript{4)} Accurate molecular weight determinations were carried out by a photographic method.

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\textbf{REFERENCES}


