Mass spectrometric analysis of long-chain esters of diols

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ABSTRACT Homologous series of synthetic long-chain monoesters and diesters of 1,2-ethanediol were analyzed by mass spectrometry, and the patterns of fragmentation were studied. Under electron impact saturated ethanediol monoesters yielded prominent ions characteristic of the short-chain diol, such as the rearranged ion formed by 2,3-cleavage (m/e 104) and the ion caused by 3,4-cleavage (m/e 117). Fragments characteristic of the constituent long-chain moieties were the acylium ions [RCO]+, [RCO – 1]+, and the ions [RC(OH)]+ of the mass spectra of ethanediol diesters exhibited very intense peaks due to the ions formed by loss of the acyloxy group, [M – RCOO]+, or one carboxylic acid, [M – RCOOH]+. These ions are distinctive for diol diesters. Precise mass measurements by high resolution mass spectrometry verified the composition of the ion fragments.

Spectral studies of some monoesters and diesters of 1,3-propanediol, 1,4-butanediol, 2,3-butanediol, and also of some monounsaturated homologues, demonstrated that mass spectrometry is very suitable for the identification, distinction, and analysis of diol lipids.

SUPPLEMENTARY KEY WORDS diol lipids · diol monoesters · diol diesters · 1,2-ethanediol · 1,3-propanediol · 1,4-butanediol · 2,3-butanediol

LIPIDS in which the short-chain moiety consists of diols rather than of glycerol occur as minor constituents in a large variety of plant and animal tissues, and also in microorganisms (2). Ethanediol, propanediol, butanediols, and other dihydric alcohols were detected in hydrolysates of neutral lipid fractions and were shown to be derived from long-chain monoesters (3, 4), diesters (4–7), and alk-1-enyl ether esters (6). The physical characteristics of these diol lipids (1, 8, 9) are very similar to those of the corresponding glycerol-derived lipids. Methods are needed for the identification, distinction, and analysis of naturally-occurring diol lipids.

The present study was undertaken to evaluate mass spectrometry as a means for identifying and characterizing individual monoesters and diesters of various short-chain diols, for identifying pure classes of these compounds independent of chain length and degree of unsaturation of their aliphatic moieties, and for analyzing mixtures of diol lipids derived from different diols. Mass spectra of monoesters and diesters of ethanediol, 1,3-propanediol, 1,4-butanediol, and 2,3-butanediol are described and interpreted. In the case of monoesters and diesters of ethanediol, mass spectrometric data of homologous series of compounds are reported and general patterns of fragmentation are established. Precise mass measurements of the ions formed from ethanediol octa-decanoate served to ascertain and refine interpretation of the low-resolution spectra.

MATERIALS AND METHODS

Long-chain monoesters and diesters of ethanediol and propanediol were prepared as described previously (8). Esters of butanediols were synthesized by analogous procedures. The compounds used in the present study were pure as judged by thin-layer adsorption chromatography (10), reversed-phase partition chromatography (8), and gas–liquid chromatography (11).

Low-resolution mass spectra were recorded on a Hitachi Perkin-Elmer instrument RMU-6D, using the direct insertion system. Spectra were taken at ionization potentials of 70 and approximately 6–12 ev. Simultaneous scanning of perfluorokerosene, which was introduced through the inlet for liquid samples, permitted accurate counting of peaks. Abundances of ions are given as percentages relative to the most prominent peak.
High-resolution mass spectra were recorded on an AEI MS-9 instrument at the Purdue Mass Spectrometry Center, Department of Chemistry, Purdue University, Lafayette, Ind.

RESULTS

Many of the peaks observed in the mass spectra of diol esters correspond to ions formed by modes of fragmentation or rearrangements previously described for the more common esters of long-chain carboxylic acids, such as methyl esters (12-16), wax esters (14, 17), monoglycerides (18), or triglycerides (19-21).

The spectra measured at low ionization potentials, although not quantitatively reproducible, exhibited major modes of fragmentation. They yielded proportionately more ions of higher mass and accordingly were helpful in interpreting the more complex spectra taken at high ionization potentials. However, only the latter spectra were used for semiquantitative comparisons between spectra of different compounds.

Monoesters of Diols

In the spectra of the monoesters of diols recorded at an ionization potential of 70 ev, the intensities of the molecular peaks at M are smaller than 10% of the base peak. Ions formed by the loss of a hydroxy group (M-17) or water (M-18) from the diol monoesters are of very low abundance.

Ions Characteristic of the Diol Moieties. The spectra of all saturated monoesters of 1,2-ethanediol (see Table 1), recorded at low electron voltage, exhibit the base peak at m/e 104. This peak, which is also of high intensity in high voltage spectra, is due exclusively to an ion (I) formed by 2,3-cleavage of the ethanediol monoester and cyclic rearrangement of one hydrogen originating from the C-4 methylene group (22). Precise mass measurements of the fragment I are in agreement with an ion [C₆H₁₀O₄]⁺ having the following structure:

\[
\text{OH} \quad [\text{HO-CH₂-CH₂-O-C=CH₂}]^+ \quad \text{I}
\]

In the mass spectra of 1,3-propanediol octadecanoate (see Fig. 1) the peak corresponding to ion I from ethanediol monoesters occurs at m/e 118. The spectra of the monoesters of 1,4-butanediol and 2,3-butanediol exhibit the strong peak at m/e 132. These ions produced by 2,3-cleavage are analogous to those formed from methyl esters (m/e 74) (15) and also from ethyl esters (m/e 88) (17) of long-chain carboxylic acids. The spectra of unsaturated diol monoesters show weak peaks corresponding to these types of ions.

Another ion containing the intact diol moiety is m/e 117, formed by 3,4-cleavage of the monoesters of ethanediol. It is produced from saturated esters in about 40% abundance, and the following structure is suggested:

\[
\text{O} \quad [\text{HO-CH₂-CH₂-O-C=CH₂}]^+ \quad \text{II}
\]

Ions formed by 3,4-cleavage of the monoesters of 1,3-propanediol, 1,4-butanediol, and 2,3-butanediol are usually less abundant; they occur at m/e 131 and 145,

<table>
<thead>
<tr>
<th>TABLE I</th>
<th>RELATIVE ABUNDANCES OF THE MORE CHARACTERISTIC IONS FROM 1,2-ETHANEDIOL MONOESTERS</th>
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respectively. These ions must be produced by the same mode of fragmentation that leads to ion m/e 87 in the spectra of long-chain methyl esters (14). The spectra of the cis-9-octadecenoates of ethanediol and propanediol (see Fig. 2) show peaks of significantly lower intensities at m/e 117 and 131, respectively, than do the corresponding saturated monoesters. Ion II from ethanediol monoesters (m/e 117) is the most abundant fragment of the homologous series of ions $C_nH_{2n-1}O_2$. The peak intensities within this series are generally low and therefore not listed in the tables (with the exception of M-43).

Loss of the acyl group from diol monoesters yields ions which identify also the constituent diol moieties. For example, fragmentation of monoesters of ethanediol yields ion m/e 61 (4-34%) having the structure:

$$[\text{HO-CH}_2-\text{CH}_2-\text{O}]^+$$

The ions derived from 1,3-propanediol monoesters...
(m/e 75) and from 1,4-butanediol and 2,3-butanediol monoesters (m/e 89) are significantly more abundant than those from the corresponding ethanediol derivatives (see Fig. 1). The spectra of unsaturated diol monoesters show only weak peaks associated with ion III.

Ions Characteristic of the Acyl Moieties. Most of the peaks in the mass spectra of diol monoesters are caused by fragments from the long-chain moieties, and thus do not identify the constituent diols. Prominent peaks of this type are caused by the acylium ions,

$$[R-CO]^+$$

They occur at M−61 in the spectra of monoesters of 1,2-ethanediol. The peak intensities within this series of ions IV are rather high and decrease slightly with increasing chain lengths (see Table 1). The acylium ion from 1,3-propanediol octadecanoate (m/e 267) occurs at M−75, and those from the corresponding esters of 1,4-butanediol and 2,3-butanediol are found at M−89. Under electron impact unsaturated diol monoesters produce acylium ions in an abundance comparable with that of the saturated compounds. Acylium fragment IV was reported to be formed similarly from many other types of ester lipids (12–21).

The spectra of all diol monoesters studied exhibit another series of intense peaks which are characteristic of the constituent fatty acids of the compounds. The peaks are due to fragments V formally produced by loss of the diol HO-(CH₂)₄-OH. The mechanism involved is probably similar to that leading to ion M−32 from mono-unsaturated long-chain methyl esters (19). In the spectra of ethanediol monoesters the peaks due to ion V occur at M−62. Propanediol octadecanoate forms ion M−76 (m/e 266), and correspondingly butanediol octadecanoates produce fragment M−90. The spectra of the octadecanoates of ethanediol and propanediol exhibit very prominent peaks at m/e 264, which in some instances represent the base peak (see Table 1 and Fig. 2).

Intense peaks in the spectra of long-chain esters at M−43 have been shown to be formed by loss of a C₆H₁₄ fragment. Elimination of a terminal propyl group appears to take place, however, only to a small extent (16). A cyclic mechanism for elimination of the C-2 to C-4 methylene groups and capture of a hydrogen from the remaining chain has been suggested (23). Our studies of the low-resolution spectra of the various diol monoesters strongly indicated that the ions M−43 were preferentially formed through a different mechanism; peak intensities for M−43 decrease very significantly in the series of ethanediol monoesters as the molecular weight increases (see Table 1); furthermore, we have not observed significant peaks at M−43 in the spectra of the derivatives of 1,3-propanediol or the butanediols. The spectra can be explained by occurrence of the rearrangement ion VI which has been observed previously as a fragment from other long-chain esters (24). Thus, the M−43 ion produced from ethanediol octadecanoate

$$\begin{array}{c}
R-C \quad \text{OH} \\
\text{OH} \\
\end{array}$$

and giving rise to the peak at m/e 285 (15%) is identical with ion VI (m/e 285) formed from the octadecanoates
of 1,3-propanediol (26%), 1,4-butanediol (54%), and 2,3-butanediol (5%). Formation of the ion VI is greatly favored in the case of the 1,4-butanediol monoester, whereas 2,3-butanediol monoester preferably forms an acylium ion. Precise mass measurements of the ions with a mass of 285, derived from ethanediol octadecanoate, show that approximately two-thirds of the intensity of ion M−43 is due to [R-C(OH)2]+, the remaining one third to [M−C2H5]+. The peaks at m/e 283 in the spectra of the cis-9-octadecenoates of 1,2-ethanediol and 1,3-propanediol, corresponding to ion V, are extremely weak.

The spectra of the saturated and unsaturated monoesters of all the diols studied show peaks of medium to high intensities corresponding to the fragments C6H12−3O and (or) C5H11O. We could show by high-resolution mass spectrometry that both types of ions are indeed responsible for the mass peaks at m/e 56, 70, 84, 98, 112, etc., the contribution of C5H11O to the individual intensities being somewhat higher than that of the olefinic hydrocarbons C6H12. The same series of peaks was previously found in the spectra of esters of dibasic acids (25) and was assigned to ions having cycloalkenol structures. In our case, formation of the cycloalkenols C5H11O could be explained by loss of the diol moiety and part of the aliphatic chain. For example, 5,6-cleavage of the acyl group and rearrangement of one hydrogen would yield an ion m/e 84 corresponding to a five-membered ring structure (VIIa); 6,7-cleavage would produce an ion m/e 98 corresponding to a six-membered ring structure (VIIb); and 7,8-cleavage would form an ion m/e 112 corresponding to a seven-membered cycloalkenol (VIIc).

$$\left[ \begin{array}{c} \text{H}_2\text{C}\vdash \text{O} \vdash (\text{CH}_2)_x \\ \text{H}_2\text{C} \vdash \text{CH} \\ \text{OH} \end{array} \right]^+$$

The postulated cyclic structure is substantiated by the finding that in all spectra of diol monoesters the most intense peak in the series of ions VII occurs at m/e 98, which would represent a six-membered cycloalkenol. However, the possibility should not be ruled out that in the series C5H11O the signals, especially those at low and high mass numbers, are caused by ions other than cycloalkenols.

In the spectra of monoesters of ethanediol, another series of ions is found corresponding to the ions C6−H2n−1O2 and to a smaller extent to C6H2n+2O. The more intense peaks occur at m/e 73, 87, 101, 115, and 129 (see Table 1). Analogous to the structure assigned to fragments obtained from long-chain methyl esters (19) the following formulae VIIIa−e are suggested for Cn−H2n−1O2 derived from ethanediol esters:

$$\begin{align*}
\text{VIIIa: } x &= 1 \quad \text{m/e 73} \\
\text{VIIIb: } x &= 2 \quad \text{m/e 87} \\
\text{VIIIc: } x &= 3 \quad \text{m/e 101} \\
\text{VIID: } x &= 4 \quad \text{m/e 115} \\
\text{VIIe: } x &= 5 \quad \text{m/e 129}
\end{align*}$$

The high-voltage spectra of all diol monoesters studied exhibit two series of intense peaks corresponding to m/e 29 + 14n (series A) and to m/e 41 + 14n (series B) for n > 1. Peaks of both series can form the base peak, e.g., m/e 43 (series A) in the spectra of saturated diol monoesters and m/e 55 (series B) in the spectra of unsaturated monoesters (see Fig. 2). The ions of both series are usually correlated to hydrocarbon fragments which are known to be formed by a variety of mechanisms (26). Our study of the high-resolution mass spectra of ethanediol monoesters revealed, however, that in addition to the hydrocarbon ions C6H2n+1 (series A) and C6H2n−1 (series B) at least two other ions contribute to the peak intensities in series A, namely C6H2n−6O and C6H2n−5O2, and at least one other ion contributes to the intensities in series B, namely C6H2n−2O. It is obvious that these ions, because of their complexity, provide little information of diagnostic value, and, therefore, they are not listed in the tables. Similarly, the spectra of ethanediol monoesters exhibit a peak at m/e 60, which is significantly more intense in high-voltage spectra (see Table 1). This ion (IX) was reported to be formed from other esters of long-chain carboxylic acids,

$$\text{IX}$$

and structure IX was suggested (14).

**Diesters of Diols**

In the mass spectra of the diol diesters studied, parent peaks appear in a magnitude of about 1% of the base peak. The spectra contain the same series of ions VII as described for the monoesters. Again the most intense signal is that at m/e 98, which is at least partially due to a six-membered cycloalkenol. As in the spectra of monoesters, the series of ions VIII (m/e 73, 87, etc.) occurs in the spectra of diesters. Similarly, the two series of peaks at m/e 29 + 14n (series A) and m/e 41 + 14n (series B) are present. The peaks at m/e 43 and m/e 57 can approach the intensity of the base peak.

The diesters of the short-chain diols produce the fragments [M − RCOC]+ which usually give rise to the base peaks. Because an intense peak is obtained by loss of either acyloxy group, diesters of ethanediol having two different acyl moieties produce two major ions X (see Table 2). Ethanediol dihexadecanoate shows one
TABLE 2  RELATIVE ABUNDANCES OF THE MORE CHARACTERISTIC IONS FROM 1,2-ETHANEDIOL DIESTERS

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<tr>
<th>m/e*</th>
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<th>Dihexadecanoate MW 538</th>
<th>Hexadecanoate Octadecanoate MW 566</th>
<th>Dioctadecanoate MW 594</th>
<th>Octadecanoate cis-9-Octadecanoate MW 592</th>
<th>Di-cis-9-Octadecanoate MW 590</th>
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* Less prominent peaks do also occur in some of the spectra of ethanediol diesters at m/e 60, 61, 67, 73, 101, 104, 115, 117, 129, and elsewhere (see Table 1).

Prominent peak for [M − RCOO]⁺ at m/e 283 (Xa), the dioctadecanoate at 311 (Xb), and ethanediol hexadecanoate octadecanoate shows both peaks, the one due to loss of the C₄H₉-moiety being more intense. The [M − acyloxy]⁺ ion of 1,3-propanediol dioctadecanoate is found at m/e 235. Fragmentation of the unsaturated diol diesters yields the corresponding ions having two mass units less. Thus, the base peak of ethanediol di-cis-9-octadecanoate occurs at m/e 309 (Xc), and that of the propanediol derivative at 323.

Peaks of medium intensities are caused by the fragments [M − RCOOH]⁺ (Xa-c) which are formed from saturated and unsaturated diesters of 1,2-ethanediol and 1,3-propanediol. Ions X and XI are distinctive for diol diesters. The mode of fragmentation involved in the formation of [M − RCOO]⁺ and [M − RCOOH]⁺ can be assumed to be similar to that described previously for triglycerides (19-21).

The second most intense peak in the spectra of diol diesters is usually that due to the acyl ion (XII). Specific ions [RCO⁺] occur for each of the acyl groups present in the diesters. The signal of hexadecanoates of diols is found at m/e 239 (XIIa), that of octadecanoates at 267 (XIIb), and that of cis-9-octadecanoates at m/e 265 (XIIc). Peaks due to acyl ions are also present in the spectra of diol monoesters and of other long-chain esters and glycerides.

The mass spectra of diesters of ethanediol and propanediol show peaks of lower intensities corresponding to fragments formed by loss of an acyl group from the intact compounds and capture of two hydrogens. Ethanediol dioctadecanoate produces the ion m/e 301 (XIIia), dioctadecanoate the ion 329 (XIIib), and the hexadecanoate octadecanoate forms both fragments. The dioctadecanoate of 1,3-propanediol shows the corresponding peak at m/e 343. Corresponding peaks also occur in the spectra of unsaturated diol diesters (XIIic).

DISCUSSION

The mass spectrum of each of the diol lipids recorded exhibits a pattern of peaks that is characteristic of the compound investigated. Individual diol monoesters and diol diesters can be described and distinguished unequivocally by their mass spectra.

Furthermore, the results of this study demonstrate that classes of diol monoesters, i.e., mixtures of diol esters containing different long-chain moieties but the same diol, can be identified by their mass spectra. The rearranged ions formed from diol monoesters by 2,3-cleavage (I) and the ions formed by 3,4-cleavage (II) give rise to very intense and characteristic peaks which indicate the constituent diol of the monoester. Ions I and II are less likely to be formed from unsaturated esters; therefore, hydrogenation of natural samples of diol monoesters prior to mass spectrometric analyses is advisable. Peaks characteristic of the acyl moieties of diol monoesters are those due to the ions [RCO⁺] (IV), [RCO − 1]+ (V) and [RC(OH)₂]+ (VI). cis-9-Octadecanoates exhibit very prominent peaks at m/e 264 (V) and 265 (IV) (see Fig. 2).
Fig. 1 shows the low-voltage mass spectra of the mono-
butanoates and diesters of 1,2-ethanediol, 1,3-propanediol, 1,4-
butanediol, and 2,3-butanediol, as well as the spectrum of a mixture of these diol monoesters. It is evident that not only diol monoesters containing different acyl moieties, but also monoesters derived from different diols can be detected in lipid mixtures and distinguished from each other. Recording of low-voltage spectra is advisable when mixtures of diol monoesters, which usually cannot be separated by chromatographic procedures, are to be analyzed. By means of this technique, monoesters of different diols, which can be isolated from natural sources or obtained through specific enzymatic or acidic hydrolysis of natural diol diesters and neutral diol plasmalogens, can be identified in mixtures of these compounds by mass spectrometric analysis. Also, semiquantitative estimates appear to be feasible.

Diol diesters form two major ions, \([M - RCOO]^+ (X)\) and \([M - RCOOH]^+ (XI)\), which are distinctive for these compounds. In addition, the spectra of diol diesters exhibit very prominent peaks due to the acylum ions \([RCO]^+ (XII)\). The latter peaks occur also in the spectra of other long-chain esters, and are thus less suitable for the identification of a given diol lipid. However, knowledge of the acyl functions permits the identification and analysis of the diol moieties through ions X and XI. As diol diesters cannot be separated from triglycerides by the usual chromatographic techniques, mass spectrometry appears to be promising for the identification of diol diesters in natural lipid mixtures.

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