Evidence for the Electron Impact Induced Formation of Prominent Cyclic Acetal Ions from Aliphatic Ester Lipids[1]

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Under electron impact complex ester lipids derived from glycerol and other polyhydric alcohols produce ions $[M - X]^+$ and $[M - XH]^+$ in great abundance (X = RCOO, RO, RCH=CHO, HO). High-resolution mass measurements and specific deuterium labeling confirmed that both types of ions formally retain at least one acyl function and the polyol moiety. Simple homolytic cleavage does not suffice to explain the structural requirements of ion formation and the ion intensities from long-chain diesters of a series of α,ω-diols. A detailed study of the mass spectral fragmentation patterns, ions, and ion intensities of representative long-chain cyclic acetals, and especially of a series of α,ω-diol acetals, has now provided strong evidence that ions $[M - X]^+$ and $[M - XH]^+$ from a great variety of aliphatic ester lipids are cyclic in structure. Mechanisms of ion formation are proposed.

Electron-impact induced expulsion of a long-chain acyloxy group X or elimination of a carboxylic acid XH from triglycerides[2-5] is known to lead to prominent ions $[M - X]^+$ and $[M - XH]^+$. Ions $[M - X]^+$ often give rise to the base peak. Other studies in our laboratories have revealed that the same types of fragments are abundantly produced from diesters,[6] alk-1-enyl ether esters[7,8] (X = RCH=CHO), and alkyl ether esters[8] (X = RO) of short-chain diols. Alkyl ether diesters of glycerol,[9] glycerophosphatides,[10] [X = $R_3N(CH_2)_2OPO_3$], and trimethylsilyl derivatives of diglycerides[11] (X = RCOO) also form the ion pair to a significant extent. In the spectra of diglycerides,[12] ions $[M - X]^+$ and $[M - XH]^+$ appear as major contributors to the total ion current (X = HO or RCOO). However, spectra of simple wax esters[13] display the ion pair only in minute intensity. A systematic investigation of the structural parameters required for the formation of these ions, or of the ion structures, has not been undertaken previously.

The present report is based on a detailed study of the mass spectral patterns of a variety of polysubstituted aliphatic ester lipids, including those bearing additional alkoxy and alk-1-enyloxy functions linked to glycerol or to diol backbones. It will be shown that ions $[M - X]^+$ and $[M - XH]^+$, independent of their origin, formally retain the structural elements of at least one acyl grouping and the complete polyol moiety. High-resolution mass measurements and deuterium labeling served to confirm this proposition. Evidence can now be provided for a mechanism that involves *cyclization* of the acyl function with the short-chain backbone leading to resonance-stabilized "cyclic acetal" structures. Scope and limitations of these findings constitute the subject of this report.

Results and Discussion

Under electron impact triglycerides predominantly lose acyloxy groups.[2-5] The intensity of ion $[M - RCOO]^+$ increases with the chain length of the substituent lost, but is largely independent of the location on the glycerol moiety.[4] The intensity is particularly high for monoacid triglycerides, as abstraction of any of the acyloxy functions contributes to the same ion current. Loss of a hexadecanoyloxy group from tripalmitin (**1a**), *e.g.*, gives rise to the base peak at *m/e 551* (6.85%)[14] (Table I). The same ion is produced from the analogous alkoxy lipids in which one of the ester functions of **1a** is replaced by a long-chain alkyl or alk-1-enyl ether grouping. Loss of the alk-1-enyloxy moiety from 1-*O*-hexadec-1′-enyl-2,3-di-*O*-hexadecanoyl-*sn*-glycerol (**1b**)[15] constitutes the major fragmentation pathway leading to ion $[M - RCH=CHO]^+$ at *m/e 551* (4.75%). Smaller amounts of $[M - RO]^+$ are formed from 1-*O*-alkyl diglycerides and 1,2-di-*O*-alkyl glycerides **1c** (0.54%) and **1d** (0.58%), respectively.

In context with the structural and mechanistic aspects which are to be considered (*vide infra*), it is significant that the intensities of ions $[M - X]^+$ from diesters, alk-1-enyl ether esters, and alkyl ether esters of ethanediol are similarly dependent upon the substituent lost, as are the ion intensities of the corresponding glycerol derivatives (Table I). $[M - X]^+$ gives rise to the base peak at *m/e 283* in the spectra of di-*O*-hexadecanoylethanediol (**2a**) (12.24%, X = RCOO) and octadec-1-enylhexadecanoylethanediol (**2f**) (28.38%, X = RCH=CHO), whereas expulsion of OR from octadecylhexadecanoylethanediol (**2g**) is

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(14) Abundances of ions are given throughout the manuscript as percentages of total ion current; *m/e* values of base peaks are printed in *italics*.

(15) Alk-1-enyldiacylglycerol (**1b**) was prepared from beef heart plasmalogens and contained approximately 60% C_{16}-enol isomer: W. J. Baumann, H. H. O. Schmid, J. K. G. Kramer, and H. K. Mangold, *Z. Physiol. Chem.*, **349**, 1677 (1968).

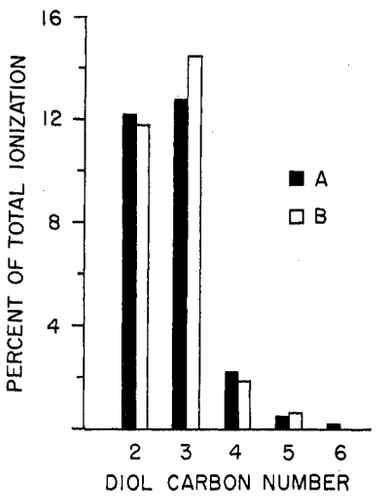


Figure 1.—Cyclic ions from diesters and acetals of α,ω-diols: A, abundances of ions $[M - C_{15}H_{31}COO]^+$ from di-*O*-hexadecanoyldiols (**2a–e**); B, abundances (× 10) of ions $[M - H]^+$ from cyclic acetals of hexadecanal and α,ω-diols (**11a–d**).

TABLE I

ABUNDANCES OF $[M - X]^+$ AND $[M - XH]^+$ FROM LONG-CHAIN ESTERS AND ETHER ESTERS OF POLYHYDRIC ALCOHOLS[a]

Ester lipid	*m/e* (abundance) structure $[M - X]^+$	*m/e* (abundance) structure $[M - XH]^+$
1a	*551* (6.85) **3b**, **4b**[b]	550 (3.74) **6a**, **7a**[b]
1b	*551* (4.75) **3b**, **4b**[c]	550 (0.28) **6a**, **7a**[c]
1c[d]	551 (0.54) **3b**, **4b**[e]	550 (0.23) **6a**, **7a**[e]
	537 (2.84) **3d**, **4d**[b]	536 (1.77) **6b**, **7b**[b]
1d[f]	537 (0.58) **3d**, **4d**[e]	536 (0.25) **6b**, **7b**[e]
2a	*283* (12.24) **5b**[b]	282 (3.55) **8a**[b]
2a-d_4	*287* (11.22) **5b-d_4**[b]	286 (3.55) **8a-d_4**[b]
2b	*297* (12.70) **5d**[b]	296 (4.61) **8b**[b]
2c[g]	311 (2.23) **5f**[b]	310 (1.76) **8c**[b]
2d[h]	325 (0.50) **5h**[b]	324 (0.61) **8d**[b]
2e[i]	339 (0.24) **5j**[b]	338 (0.24) **8e**[b]
2f	*283* (28.38) **5b**[j]	282 (0.54) **8a**[j]
2f-d_4	*287* (33.11) **5b-d_4**[j]	286 (1.66) **8a-d_4**[j]
2g[k]	283 (1.81) **5b**[l]	282 (0.20) **8a**[l]
2g-d_4[m]	287 (2.79) **5b-d_4**[l]	286 (0.35) **8a-d_4**[l]

[a] Abundances in per cent of total ionization; see also ref 14. Molecular and ion structures are given in Schemes I and II. [b] X = $C_{15}H_{31}COO$. [c] X = alk-1-enyloxy, containing approximately 60% of $C_{14}H_{29}CH{=}CHO$; peaks for $[M - RCOO]^+$ and $[M - RCOOH]^+$ are virtually absent. [d] Base peak *m/e* *57* (7.45). [e] X = $C_{16}H_{33}O$. [f] Base peak *m/e* *523* (15.35). [g] Base peak *m/e* *73* (6.58). [h] Base peak *m/e* *69* (7.37). [i] Base peak *m/e* *82* (7.25). [j] X = $C_{16}H_{33}CH{=}CHO$. [k] Base peak *m/e* *57* (8.68). [l] X = $C_{15}H_{37}O$. [m] Base peak *m/e* *57* (6.51).

less likely to occur (1.81%). The abundance of ion $[M - X]^+$ is particularly high for symmetrical diol diesters[6] and also increases with increasing chain length of the acyloxy function lost.[6,8] Moreover, the intensities of $[M - X]^+$ in the spectra of diesters, of α,ω-diols **2a–e** (Table I) are extremely dependent upon the chain length of the constituent diol. Ions $[M - RCOO]^+$ are of maximal abundance for the dihexadecanoates of 1,2-ethanediol (**2a**, 12.24%) and 1,3-propanediol (**2b**, 12.70%); however, their intensities are drastically reduced in magnitude for the diesters of longer chain diols **2c–e** (2.23, 0.50, 0.24%).

In contrast to $[M - X]^+$, ions $[M - XH]^+$ are produced in high abundance only when the elimination involves loss of fatty acid (X = RCOO) from triglyceride (**1a**, 3.74%) or from alkyl diglyceride (**1c**, 1.77%). Elimination of long-chain alk-1-enol from **1b** and **2f**, or of alkanol from **1c**, **1d**, and **2g**, is less likely to occur (0.2–0.5%). In analogy to $[M - X]^+$, ions $[M - XH]^+$ are produced from diesters of the shorter chain diols **2a–c** in significant abundances (4.6–1.8%) and in smaller amounts from the longer chain homologs **2d** and **2e** (0.6, 0.2%).

The elemental compositions of ions $[M - X]^+$ and $[M - XH]^+$ were confirmed by high-resolution mass spectrometry of representative compounds.[16] The compositions of both types of ions were also compatible with the results of deuteration studies. Spectra of triacyl derivatives of perdeuterated glycerol display both ions shifted by 5 amu.[17] Similarly, the spectra of the three classes of hexadecanoates of 1,1,2,2-tetradeuterioethanediol[8] (**2a-d_4**, **2f-d_4**, **2g-d_4**) exhibit $[M - X]^+$ and $[M - XH]^+$ at *m/e* 287 and 286, respectively, with intensities very similar to those at *m/e* 283 and 282 in the spectra of the corresponding nondeuterated diol lipids (Table I). The mass shift observed is consistent with the concept that $[M - X]^+$ as well as $[M - XH]^+$ retain the intact alcoholic moiety.

Favored formation of the ion pair $[M - X]^+$ and $[M - XH]^+$ from polysubstituted ester lipids is indicative of a low-energy pathway leading to highly stable ion structures. Therefore, we have previously postulated formation of cyclic ions from triglycerides[4] and from a number of ethanediol-derived lipids,[7,8] as have other investigators,[10,12] without being able to substantiate such structures. On the basis of the present study, it is clear that a mechanism involving merely simply homolytic single bond cleavage at an acyloxy, alk-1-enyloxy, or alkoxy function with charge retention on the polyol-containing fragment does not suffice to explain the intensity of $[M - X]^+$ in the spectra of a large number of glycerol- and diol-derived ester lipids (Table I) and, for example, the virtual absence of the ion in the spectra of wax esters.[13] Figure 1 (bars A) depicts the high intensities of ions $[M - X]^+$ derived from the diesters of C_2 and C_3 α,ω-diols (**2a**, **2b**) and the abrupt intensity decline for these ions originating from diesters of longer chain diols (**2c–e**). This phenomenon can satisfactorily be explained by the formation of cyclic ions which would be most favored, of course, for the five- and six-membered ring structures derived from the C_2 and C_3 diol diesters, respectively.

In the series of diol diesters **2a–e** ions $[M - XH]^+$ display an intensity pattern similar to that of $[M - X]^+$ (Table I), indicating cyclic ion formation as well. However, elimination of a fatty acid from diol diesters is not so drastically dependent upon the diol carbon number as is the extrusion of the acyloxy function.

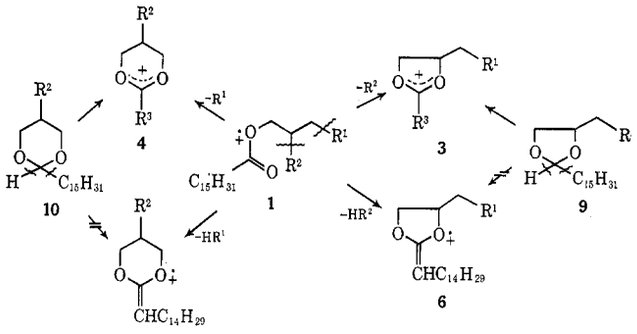
In summary, a great number of glycerol-derived (**1**) and diol-derived (**2**) ester lipids, varying in several structural parameters, produce under electron impact ions $[M - X]^+$ (**3–5**) and $[M - XH]^+$ (**6–8**). We propose that both types of ions possess resonance-

(16) 1,3-Di-*O*-hexadecanoylpropanediol (**2b**): ion **5d**, $C_{19}H_{37}O_2$ (calcd for *m/e*, 297.2794; found, 297.2798); ion **8b**, $C_{19}H_{36}O_2$ (calcd for *m/e*, 296.2715; found, 296.2739). 1,5-Di-*O*-hexadecanoylpentanediol (**2d**): ion **5h**, $C_{21}H_{41}O_2$ (calcd for *m/e*, 325.3106; found, 325.3090); ion **8d**, $C_{21}H_{40}O_2$ (calcd for *m/e*, 324.3028; found, 324.2998). 1,3-Di-*O*-octadecanoylglycerol:[12] ion $[M - RCOO]^+$, $C_{21}H_{41}O_3$ (calcd for *m/e*, 341.3056; found, 341.3055).

(17) Trioctadecanoylglycerol produced $[M - RCOO]^+$ at *m/e* 607 (2.29), $[M - RCOOH]^+$ at *m/e* 606 (2.04). Perdeuteration in the glycerol moiety shifted the ion pair to *m/e* 612 (2.37) and 611 (1.86); *m/e* 610 (0.37).[5]

stabilized cyclic structures such as those depicted in Schemes I and II.

SCHEME I



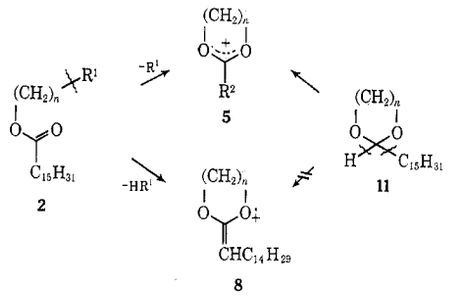
1a, $R^1 = R^2 = C_{15}H_{31}COO$ (m/e 806)
b, $R^1 = C_{14}H_{29}CH{=}CHO$; $R^2 = C_{15}H_{31}COO$ (m/e 790)
c, $R^1 = C_{16}H_{33}O$; $R^2 = C_{15}H_{31}COO$ (m/e 792)
d, $R^1 = R^2 = C_{16}H_{33}O$ (m/e 778)
e, $R^1 = H_3N(CH_2)_2OPO_3$; $R^2 = C_{15}H_{31}COO$
f, $R^1 = (CH_3)_3N(CH_2)_2OPO_3$; $R^2 = C_{15}H_{31}COO$

3a, 4a, $R^1 = R^2 = C_{15}H_{31}COO$; $R^3 = H$ (m/e 341)
3b, 4b, $R^1 = R^2 = C_{15}H_{31}COO$; $R^3 = C_{15}H_{31}$ (m/e 551)
3c, 4c, $R^1 = R^2 = C_{16}H_{33}O$; $R^3 = H$ (m/e 327)
3d, 4d, $R^1 = R^2 = C_{16}H_{33}O$; $R^3 = C_{15}H_{31}$ (m/e 537)
3e, 4e, $R^1 = R^2 = CH_3COO$; $R^3 = H$ (m/e 145)
3f, 4f, $R^1 = R^2 = CH_3COO$; $R^3 = C_{15}H_{31}$ (m/e 355)

6a, 7a, $R^1 = R^2 = C_{15}H_{31}COO$ (m/e 550)
6b, 7b, $R^1 = R^2 = C_{16}H_{33}O$ (m/e 536)

9a, 10a, $R^1 = R^2 = C_{15}H_{31}COO$ (m/e 552)
9b, 10b, $R^1 = R^2 = C_{16}H_{33}O$ (m/e 538)
9c, 10c, $R^1 = R^2 = CH_3COO$ (m/e 356)

SCHEME II



2a, $R^1 = C_{15}H_{31}COO$; $n = 2$ (m/e 538)
b, $R^1 = C_{15}H_{31}COO$; $n = 3$ (m/e 552)
c, $R^1 = C_{15}H_{31}COO$; $n = 4$ (m/e 566)
d, $R^1 = C_{15}H_{31}COO$; $n = 5$ (m/e 580)
e, $R^1 = C_{15}H_{31}COO$; $n = 6$ (m/e 594)
f, $R^1 = C_{16}H_{33}CH{=}CHO$; $n = 2$ (m/e 550)
g, $R^1 = C_{18}H_{37}O$; $n = 2$ (m/e 552)

5a, $R^2 = H$; $n = 2$ (m/e 73)
b, $R^2 = C_{15}H_{31}$; $n = 2$ (m/e 283)
c, $R^2 = H$; $n = 3$ (m/e 87)
d, $R^2 = C_{15}H_{31}$; $n = 3$ (m/e 297)
e, $R^2 = H$; $n = 4$ (m/e 101)
f, $R^2 = C_{15}H_{31}$; $n = 4$ (m/e 311)
g, $R^2 = H$; $n = 5$ (m/e 115)
h, $R^2 = C_{15}H_{31}$; $n = 5$ (m/e 325)
i, $R^2 = H$; $n = 6$ (m/e 129)
j, $R^2 = C_{15}H_{31}$; $n = 6$ (m/e 339)

8a, $n = 2$ (m/e 282)
b, $n = 3$ (m/e 296)
c, $n = 4$ (m/e 310)
d, $n = 5$ (m/e 324)
e, $n = 6$ (m/e 338)

11a, $n = 2$ (m/e 284)
b, $n = 3$ (m/e 298)
c, $n = 4$ (m/e 312)
d, $n = 5$ (m/e 326)

Cyclic ions of comparable structures must be expected from cyclic acetals, similar to those previously postulated for the fragments from aliphatic[18] and steroidal[19] ketals and acetals. Therefore, we synthesized model compounds and studied the fragmentation patterns and ions produced from these representative long-chain cyclic acetals.

Acetals **9–11** (Table II) show the expected parent ion peaks. The spectra display fewer ions, reflecting the exceptional stability afforded by $[M - C_{15}H_{31}]^+$ and $[M - H]^+$ (**3–5**). It appears reasonable to assume that formation of fragments **3–5** merely involves single-bond fission with charge retention in the ring system, leading to resonance-stabilized cyclic ion structures (Schemes I and II). Favored formation of such ions is indicative of the stability of such structures in general.

TABLE II

PROMINENT IONS IN THE MASS SPECTRA OF CYCLIC ACETALS DERIVED FROM HEXADECANAL[a]

	m/e (abundance) structure		
Cyclic acetal	M^+	$[M - H]^+$	$[M - C_{15}H_{31}]^+$
9a	552 (0.13)	551 (0.29) **3b**	*341* (33.26) **3a**
cis-**10a**	552 (0.21)	551 (0.48) **4b**	*341* (22.34) **4a**
trans-**10a**	552 (0.19)	551 (0.39) **4b**	*341* (22.27) **4a**
9b	538 (0.10)	537 (0.17) **3d**	*327* (18.56) **3c**
cis-**10b**	538 (0.15)	537 (0.26) **4d**	*327* (15.09) **4c**
trans-**10b**	538 (0.06)	537 (0.24) **4d**	*327* (14.61) **4c**
cis-**9c**	356 (0.07)	355 (0.25) **3f**	*145* (33.95) **3e**
trans-**9c**	356 (0.07)	355 (0.22) **3f**	*145* (38.36) **3e**
9c-d_1	357 (0.03)	355 (0.20) **3f**	*146* (47.36) **3e**-d_1
cis-**10c**	356 (0.12)	355 (0.44) **4f**	*145* (23.30) **4e**
cis-**10c**-d_1	357 (0.05)	355 (0.22) **4f**	*146* (19.96) **4e**-d_1
trans-**10c**	356 (0.09)	355 (0.29) **4f**	*145* (20.89) **4e**
trans-**10c**-d_1	357 (0.07)	355 (0.32) **4f**	*146* (28.16) **4e**-d_1
11a	284 (0.28)	283 (1.18) **5b**	*73* (65.00) **5a**
11a-d_1	285 (0.08)	283 (0.29) **5b**	*74* (57.79) **5a**-d_1
11a-d_4	288 (0.08)	287 (0.19) **5b**-d_4	*77* (30.37) **5a**-d_4
11b	298 (0.42)	297 (1.45) **5d**	*87* (45.29) **5c**
11b-d_1	299 (0.05)	297 (0.13) **5d**	*88* (20.15) **5c**-d_1
11c	312 (0.09)	311 (0.18) **5f**	*101* (39.20) **5e**
11c-d_1	313 (0.01)	311 (0.01) **5f**	102 (7.87) **5e**-d_1[b]
11d	326 (0.04)	325 (0.06) **5h**	*115* (16.22) **5g**

[a] Abundances in per cent of total ionization; see also ref 14. Molecular and ion structures are given in Schemes I and II. [b] Base peak *m/e 41* (10.37).

Prominent ions $[M - C_{15}H_{31}]^+$ from 2-pentadecyl-substituted cyclic acetals (**9–11**) give rise to the base peak in the spectra of the isomeric acyl- (**9a**, **10a**), alkyl- (**9b**, **10b**), and acetyl-substituted (**9c**, **10c**) glycerol acetals producing *m/e 341*, *327*, and *145*, respectively (Table II). For all three lipid classes formation of $[M - C_{15}H_{31}]^+$ bearing 1,3-dioxolane structures (**3a**, **3c**, **3e**) is favored over those having the 1,3-dioxane skeleton (**4a**, **4c**, **4e**). Cis dioxanes produce the ion in slightly greater abundance than do trans isomers, while for the isomeric dioxolanes the situation is reversed. The long-chain cyclic acetals of α,ω-diols (**11a–d**) display $[M - C_{15}H_{31}]^+$ (**5a**, **5c**, **5e**, **5g**) with significantly decreasing intensities as the ring

(18) R. A. Friedel and A. G. Sharkey, Jr., *Anal. Chem.*, **28**, 940 (1956); H. Audier, M. Fétizon, J.-C. Gramain, J. Schalbar, and B. Waegel, *Bull. Soc. Chim. Fr.*, 1880 (1964); R. E. Wolff, G. Wolff, and J. A. McCloskey, *Tetrahedron*, **22**, 3093 (1966); J. T. B. Marshall and D. H. Williams, *ibid.*, **23**, 321 (1967).

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size increases (65–16%). Ions corresponding to $[M - C_{15}H_{31}]^+$ are not produced from the ester lipids **1** and **2**.

In contrast, ions $[M - H]^+$ from acetals **9–11** actually correspond to $[M - X]^+$ from the ester lipids (Schemes I and II). Ions $[M - H]^+$ are consistently more intense than the parent acetal ions. Specific C-2 deuteration in the ring of a number of representative acetals (**9c**, **10c**, **11a–c**) or perdeuteration of the alcoholic backbone (**11a**) demonstrated that in the formation of $[M - H]^+$ the hydrogen is predominantly lost from the ring C-2, not from the polyol or the alkyl chain (Table II). The isomeric acyl- (**9a**, **10a**), alkyl- (**9b**, **10b**), and acetyl-substituted (**9c**, **10c**) glycerol acetals produce $[M - H]^+$ at *m/e* 551 (**3b**, **4b**, corresponding to $[M - RCOO]^+$ from triglycerides), 537 (**3d**, **4d**, corresponding to $[M - RCOO]^+$ from alkyl diacyl glycerols), and 355, respectively. In contrast to loss of the long alkyl group, expulsion of H-2 from the molecular acetal ion is more favored for the 1,3-dioxanes than it is for the 1,3-dioxolanes, probably because fragmentation of the former involves loss of an axial hydrogen,[20,21] and it is more likely to occur with the cis isomers.

Ions $[M - H]^+$ from diol acetals **11a–d** are identical in composition with ions $[M - RCOO]^+$ produced from diol diesters **2a–d** (see Scheme II and Tables I and II). Hence, the question arises whether they are identical in structure as well. If these ions possess cyclic structures **5b**, **5d**, **5f**, and **5h** postulated in Scheme II, their stabilities are a function of ring size and should be expressed by similar ion-intensity patterns. Although the absolute intensities[14] of both ions differ by a factor of approximately 10, the relative intensity of $[M - H]^+$ as a function of the carbon number of the constituent diol (Figure 1, B) matches almost perfectly that found for $[M - RCOO]^+$ (Figure 1, A). Both show a maximum for the ions having the 1,3-dioxane skeleton, and both exhibit a sharp intensity decline for the ions of larger ring size. Hence, the cyclic structures formulated for $[M - X]^+$ from ester lipids **1** and **2** appear established.

Formation of ions $[M - X]^+$ from esters and ether esters probably takes place by a mechanism involving (a) fragmentation, *i.e.*, extrusion of an acyloxy, alk-1-enyloxy, or alkoxy group from the molecular ion, followed by (b) cyclization of a residual ester radical with the short-chain moiety. All relevant information obtained by specific deuterations in the alcohol moiety (Tables I and II) or at C-2 through C-6 of the acyl functions of triglycerides[5] is consistent with such a mechanism. Hence, the ease of initial cleavage is a contributing factor to the intensity of $[M - X]^+$, as is the stability of the cyclic ion structure. Abstraction of an alk-1-enyloxy group is favored over that of an acyloxy or alkoxy function, while the stability of $[M - X]^+$ is largely a function of ring size. The fragmentation pathways are summarized in Schemes I and II.

The cyclic structures of ions $[M - XH]^+$ from ester lipids cannot be deduced by the same reasoning as for ions $[M - X]^+$ because the corresponding ions are not produced from cyclic acetals. However, the general dependence of ion intensities upon diol carbon numbers in the spectra of diol diesters **2a–e**, as well as the results of deuteration studies (*vide infra*), strongly advocates structures such as **6–8** given in Schemes I and II.

Formation of ions $[M - XH]^+$ proceeds by a pathway independent of that leading to $[M - X]^+$. The fact that $[M - XH]^+$ contributes significantly to the total ion current only for loss of a fatty acid, not alk-1-enol or alkanol, gives credence to an activation mechanism involving hydrogen transfer to the acyloxy carbonyl prior to RCOOH elimination. Complete retention of deuterium in ions $[M - XH]^+$ from the respective esters of perdeuterated glycerol[17] or ethanediol (**2a**-d_4, see Table I) clearly excludes abstraction of hydrogen from the polyol moieties. To define more precisely the origin of the activated hydrogen, the spectra of a series of triglycerides specifically dideuterated in one of the methylene groups at C-2 through C-6 of all three acyl functions were reexamined.[5] In this series, the highest intensity of $[M - RCOOD]^+$ was clearly displayed by the tri-2,2-dideuterioacylglycerol,[22] lending additional support to structures **6–8** proposed in Schemes I and II.

Experimental Section

Low-resolution mass spectra were recorded using a Hitachi Perkin-Elmer instrument RMU-6D. Samples were introduced through the direct inlet system. The source temperature was approximately 250°, the ionizing energy was 70 eV, and the ionizing current was 80 μA. Simultaneous scanning of perfluorokerosene, which was introduced through the inlet for liquid samples, ensured accurate counting of peaks.[14] High-resolution mass spectra were recorded on CEC-21-110B and AEI MS-9 instruments.

All compounds used in the present study were pure as judged by adsorption tlc and/or glc. Triglycerides (**1a**) were purchased from The Hormel Institute Lipids Preparation Laboratory; the synthesis of triglycerides specifically dideuterated in one of the C-2 through C-6 methylene groups of all three acyl functions was previously reported.[5] Alk-1-enyldiacylglycerols (**1b**),[15] alkyldiacylglycerols (**1c**),[23] and dialkylacylglycerols (**1d**),[23] as well as diesters (**2a–e**),[24] alk-1-enyl ether esters (**2f**),[7] and alkyl ether esters (**2g**)[24] of diols, were synthesized as described previously. Long-chain cyclic acetals of glycerol (**9**, **10**) were prepared by acid-catalyzed condensation of hexadecanal and glycerol.[20] Individual stereoisomers were obtained by repeated fractionation of the glycerol acetal acetates (**9c**, **10c**) by adsorption tlc and/or preparative glc. $LiAlH_4$ reduction of the isomeric individual acetates afforded the corresponding hydroxy compounds, which served for the preparation of the alkoxy derivatives (**9b**,**10b**)[20] and for the synthesis of the long-chain esters (**9a**, **10a**) by standard acylation with hexadecanoyl chloride in benzene–pyridine medium. Characteristic data of the acylated glycerol acetals **9a**, and **10a** are as follows.

2-Pentadecyl-4-hexadecanoyloxymethyl-1,3-dioxolanes (9a) had mp 79–80°; R_f 0.39;[25] ir (CS_2, C_2Cl_4)[26] 1736 (s), 1418, 1387 (sh), 1368 (m), 1355 (sh), 1234, 1163 (m), 1141 (s), 1123 (s), 1047 (m),

(20) W. J. Baumann, *J. Org. Chem.*, **36**, 2743 (1971).

(21) W. J. Baumann, T. H. Madson, and B. J. Weseman, *J. Lipid Res.*, **13**, 640 (1972).

(22) Tri-2,2-dideuteriotetradecanoyl glycerol[5] produced $[M - RCOO]^+$ at *m/e* 499 (3.38). The intensity of $[M - RCOOD]^+$ at *m/e* 497 (1.07) was somewhat low, as can be expected for labile C-2 deuteriums.

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(25) Thin layer adsorption chromatography was done on layers of silica gel H (Merck), 0.3 mm thick, in tanks lined with filter paper, using hexane–Et_2O (90:10, v/v) as developing solvent.

(26) Infrared spectra were taken with a Perkin-Elmer Model 21 spectrophotometer. Carbon disulfide served as solvent, except in the ranges 2400–2000 and 1650–1400 cm^{-1}, where tetrachloroethylene was used. Relative intensities are given as s, strong; m, medium; sh, shoulder; weak bands are without designation. Bands associated with vibrations of the aliphatic chains are not listed.

990, 958 cm^{-1}. *Anal.* Calcd for $C_{35}H_{68}O_4$: C, 76.03; H, 12.40. Found:[27] C, 76.26; H, 12.76.

cis-**2-Pentadecyl-5-hexadecanoyloxy-1,3-dioxane** (**10a**) had mp 95–96°; R_f 0.32;[25] ir (CS_2, C_2Cl_4)[26] 1732 (s), 1408, 1340, 1244 (m), 1170, 1152 (s), 1104 (m), 1073 (m), 1008 (m), 950, 902, 791 cm^{-1}. *Anal.* Calcd for $C_{35}H_{68}O_4$: C, 76.03; H, 12.40. Found:[27] C, 76.30; H, 12.70.

trans-**2-Pentadecyl-5-hexadecanoyloxy-1,3-dioxane** (**10a**) had mp 87–89°; R_f 0.65;[25] ir (CS_2, C_2Cl_4)[26] 1740 (s), 1420, 1350 (sh), 1215, 1150 (s), 1115 (m), 1095 (sh), 1075 (sh), 1043 (m), 960, 900 cm^{-1}. *Anal.* Calcd for $C_{35}H_{68}O_4$: C, 76.03; H, 12.40. Found:[27] C, 75.90; H, 12.63.

Cyclic diol acetals **11a–d** were prepared by acid-catalyzed condensation[28] of the corresponding diols with hexadecanal followed by tlc purification with toluene as developing solvent.

(27) Elemental analyses were by I. Beetz, Mikroanalytisches Laboratorium, Kronach, Germany.

(28) P. V. Rao, S. Ramachandran, and D. G. Cornwell, *J. Lipid Res.*, **8**, 380 (1967).

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Registry No.—**1a**, 555-44-2; **1b**, 41562-98-5; **1c**, 41562-99-6; **1d**, 6110-59-4; **2a**, 624-03-3; **2a-d_4**, 34083-13-1; **2b**, 818-21-3; **2c**, 26719-63-1; **2d**, 26933-79-9; **2e**, 23130-50-9; **2f**, 34083-10-8; **2f-d_4**, 41563-08-0; **2g**, 29899-13-6; **2g-d_4**, 41563-10-4; **9a**, 41563-11-5; **9b**, 41563-12-6; *cis*-**9c**, 30889-29-3; *trans*-**9c**, 30889-32-8; **9c-d_1**, 41563-15-9; *cis*-**10a**, 41563-16-0; *trans*-**10a**, 41563-17-1; *cis*-**10b**, 34298-21-0; *trans*-**10b**, 34315-34-9; *cis*-**10c**, 30889-23-7; *cis*-**10c-d_1**, 41563-21-7; *trans*-**10c**, 30889-26-0; *trans*-**10c-d_1**, 41563-23-9; **11a**, 4360-57-0; **11a-d_1**, 41563-25-1; **11a-d_4**, 41563-26-2; **11b**, 17352-27-1; **11b-d_1**, 41563-28-4; **11c**, 41563-29-5; **11c-d_1**, 41563-30-8; **11d**, 41583-11-3.

Phenacyl Photosensitive Blocking Groups

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The *p*-methoxyphenacyl group and α-methylphenacyl group have been found useful photosensitive protecting groups for the carboxyl function. Both types of esters are cleavable in ethanol or dioxane solution at 20° by uv light. The reaction has been applied to esters of N-protected alanine, glycine, phenylalanine, tryptophane, glycylglycine, and benzylaspartylserine and to benzoic acid.

Most useful protecting groups are removed by common chemical reactions. In principle, however, it should be possible to design protecting groups which could be removed by photolysis. In accord with the progress of organic photochemistry, several photosensitive blocking groups have been designed. The advantage of photosensitive blocking groups is that they can be removed under completely neutral and mild conditions.

The first photochemical removal of a blocking group was observed in the photolysis of carbobenzoxyglycine.[1] The irradiation of an aqueous solution of the sodium salt of carbobenzoxyglycine with the 2537-Å mercury line gave a small amount of glycine along with a mixture of other products.

$$PhCH_2OCONHCH_2COONa \xrightarrow{h\nu} H_2NCH_2COONa + \text{mixture}$$

The use of *o*-nitrobenzyl derivatives as photosensitive blocking reagents for amino and carboxyl functions has been reported.[2,3] Irradiation of these derivatives at wavelengths longer than 3200 Å cleaves the protecting group without affecting light-sensitive amino acids.

The potential of certain aromatic azides as photosensitive blocking groups has also been explored.[4] The photolysis of alkyl or acyl derivatives of β-(*o*-azidophenyl)ethyl alcohol yields indole and the corresponding alcohol or acid. This reaction is interesting as a photocyclization reaction. However, since the yield is low, it is not attractive as a photoremoval reaction of a protecting group.

Benzoin esters and other desyl compounds yield 2-phenylbenzofuran upon irradiation with uv light.[5]

A preliminary investigation of the application of this furanization reaction in the unmasking of carboxylic acid esters of appropriately substituted benzoins has been reported.[6] The irradiation of the benzoin derivatives of phthaloylglycine by uv light at 3200 Å formed phthaloylglycine and the corresponding furan derivatives.

These photosensitive blocking groups are all unique and interesting. However they are somewhat complicated to use practically in syntheses, and are far from being widely applicable protecting groups. Since the search for a photosensitive blocking group has just begun, more practical and simple blocking groups can be expected.

Discussion

The phenacyl group has low-lying excited states because of the interaction of the electrons between the carbonyl group and the phenyl ring. Therefore the photolysis of substituted phenacyl esters was first attempted. When *p*-methoxyphenacyl benzoate was irradiated in benzene, no observable reaction occurred and starting material was recovered. But when *p*-methoxyphenacyl benzoate was irradiated in dioxane with a Pyrex filter, the ester cleavage reaction occurred to give benzoic acid in good yield. Encouraged by this observation the photolysis of phenacyl esters was investigated in considerable detail.

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