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Mass Spectra of Aliphatic Dicarboxylic Acids and their Dimethyl Esters: Cyclic Structures for the $[M-H_2O]^{+\cdot}$ Ions from the Diacids and $[M-MeOH]^{+\cdot}$ Ions from the Dimethyl Esters

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Methyl 2-oxocycloalkane carboxylate structures are proposed for the $[M - MeOH]^{+\cdot}$ ions from dimethyl adipate, pimelate, suberate and azelate. This proposal is based on a comparison of the metastable ion mass spectra and the kinetic energy releases for the major fragmentation reaction of these species with the same data for the molecular ions of authentic cyclic β-keto esters. The mass spectra of α,α,α′,α′-d_4-pimelic acid and its dimethyl ester indicate that the α-hydrogens are involved only to a minor extent in the formation of $[M - ROH]^{+\cdot}$ and $[M - 2ROH]^{+\cdot}$ ions, while these α-hydrogens are involved almost exclusively in the loss of ROH from the $[M - RO^{\cdot}]^{+}$ ions (R = H or CH_3). The molecules $XCO(CH_2)_7COOMe$ (X = OH, Cl) form abundant ions in their mass spectra with the same structure as the $[M - 2MeOH]^{+\cdot}$ ions from dimethyl azelate.

INTRODUCTION

Aliphatic dicarboxylic acids are not reported to occur widely in nature, but they are frequently encountered as oxidation products from oils, fats and lipids.[1] Their presence in human fluids such as blood, serum and urine has been demonstrated by derivatization as their dimethyl esters followed by gas chromatography/mass spectrometry (GC/MS).[2–5] A compound of particular interest is nonanedioic acid (azelaic acid), which is isolated as the oxidative degradation product from a variety of natural materials containing oleyl chains.[6] This C_9-diacid, along with its esters, finds wide applicability as a plasticizer and resin.[1] Recently, its pharmacology in humans and animals has been reviewed.[7] In addition, this diacid and its derivatives are used extensively in the synthesis of complex organic products.[8]

The mass spectra of the homologous series of linear dicarboxylic acids, $HOOC(CH_2)_nCOOH$, were investigated by Holmes and St Jean.[9] An interesting feature in these spectra is the appearance of an abundant $[M - 2H_2O]^{+\cdot}$ ion from pimelic acid ($n = 5$), whose abundance increases for the homologues $n = 6$ and $n = 7$ and then decreases as the carbon number increases further. Adipic acid ($n = 4$) and lower members of the series do not exhibit this ion. The dimethyl esters of the linear dicarboxylic acids ($n = 0$ to 8) display a similar behaviour in their mass spectra.[10–13] Thus, dimethyl adipate ($n = 4$) exhibits an insignificant $[M - 2MeOH]^{+\cdot}$ ion in its mass spectrum, but this ion is a major fragment ion in the mass spectra of esters with $n = 5$, 6 and 7, with the abundance of the ion increasing in that order. Winnik[14] postulated a mechanism for formation of $[M - 2MeOH]^{+\cdot}$ which involved participation of the α-hydrogens exclusively. With the exception of this proposal, no other report deals with the structure of the $[M - 2MeOH]^{+\cdot}$ ions resulting from the dimethyl dicarboxylates.

We have investigated the mass spectra of pimelic acid (**1**), azelaic acid (**3**) and their dimethyl esters (**2** and **4**, respectively) using deuterium labelling and metastable ion studies, with emphasis on the mechanism(s) of formation and structure(s) of the $[M - 2H_2O]^{+\cdot}$ ions from the acids and the $[M - 2MeOH]^{+\cdot}$ ions from the corresponding dimethyl esters (see Scheme 1). The current study includes the dimethyl esters of adipic (**5**) and suberic (**6**) acids for comparison. The azelaic acid derivatives **7–10** also were included.

$HOOC(CH_2)_5COOH$	**1**	Heptanedioic acid (pimelic acid)
$MeOOC(CH_2)_5COOMe$	**2**	Dimethyl pimelate
$HOOC(CH_2)_7COOH$	**3**	Nonanedioic acid (azelaic acid)
$MeOOC(CH_2)_7COOMe$	**4**	Dimethyl azelate
$MeOOC(CH_2)_4COOMe$	**5**	Dimethyl adipate
$MeOOC(CH_2)_6COOMe$	**6**	Dimethyl suberate
$HOOC(CH_2)_7COOMe$	**7**	Monomethyl azelate
$MeOOC(CH_2)_7COCl$	**8**	Monomethyl azelate acid chloride
$HOOC(CH_2)_7CHO$	**9**	9-Oxononanoic acid
$HOOC(CH_2)_7CH_2OH$	**10**	9-Hydroxynonanoic acid
$HOOC(CH_2)_7COOCD_3$	**11**	Monomethyl-d_3-azelate
$D_3COOC(CH_2)_7COOCD_3$	**12**	Dimethyl-d_6-azelate
$HOOCD_2(CH_2)_3CD_2COOH$	**13**	α,α,α′,α′-d_4-Pimelic acid
$MeOOCD_2(CH_2)_3CD_2COOMe$	**14**	Dimethyl α,α,α′,α′-d_4-pimelate

Scheme 1

RESULTS AND DISCUSSION

The low-resolution mass spectra of **7–14**, hitherto unreported, are presented in Table 1; the mass spectra of **1–6** were in good agreement with spectra previously reported.[9–13] Table 2 presents the relative abundances of the $[M - RO^{\cdot} - ROH]^{+}$ and $[M - 2ROH]^{+\cdot}$

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Table 1. Low-resolution mass spectra of 7–14

Monomethyl azelate (**7**, RMM 202):

m/z	185	184	171	153		152	143	137	125	124	111	98	97	87	84	83	
%RA	15	5	15	6		54	10	4	6	13	24	19	14	23	26	31	
m/z	74	69	60	59	55	43	41										
%RA	100	26	13	24	65	44	50										

Monomethyl azelate monoacid chloride (**8**, RMM 220):

m/z	189	(191)		185	153	152	143	125	124	111	98	97	87	84	83	74	69
%RA	14	(5)		32	11	70	4	13	31	31	31	23	16	31	35	100	20
m/z	69	67	59	55	43	41											
%RA	11	11	53	97	43	67											

9-Oxononanoic acid (**9**, RMM 172):

m/z	155	154		144	136	129		111	101	98	97	95	94	87	84	83	81	73
%RA	5	10		21	6	28		56	17	21	8	16	10	14	14	52	12	100
m/z	69	68	67	60	57	55	45	43	41									
%RA	64	30	20	60	33	83	26	37	83									

9-Hydroxynonanoic acid (**10**, RMM 174):

m/z	144	138	112	110	101	97	96	84	83	82	73	69	69	60	55	45	43	41
%RA	21	13	12	17	16	30	17	32	18	12	53	39	35	55	100	18	26	60

Monomethyl-d_3-azelate (**11**, RMM 205):

m/z	188	187		171	153	152	146	125	124	111	104	98	97	90	84	83	77	
%RA	1.5	1		18	6	53	7	6	18	26	5	17	15	28	29	36	100	
m/z	73	69	55	45	43	41												
%RA	7	25	53	10	41	39												

Dimethyl-d_6-azelate (**12**, RMM 222):

m/z	188	187	153	152	146	125	124	111	98	97	90	84	83	77	76	69	
%RA	30	5	9	61	31	10	19	46	11	24	33	31	63	91	12	43	
m/z	55	43	41														
%RA	100	61	65														

α,α,α',α'-Tetradeuteropimelic acid (**13**, RMM 164):

m/z	147	146		145	129	128	127	126		118	117	116	103	88	85	84	75
%RA	3	1		0.5	1.5	14	6.5	2.5		39	7	15	44	13	58	7	15
m/z	74	73	72	71	63	62	60	59	58	57							
%RA	16	19	22	14	14	64	9	18	16	100							

Dimethyl α,α,α',α'-Tetradeuteropimelate (**14**, RMM 192):

m/z	161	160		159	132		131	128	127	117	113	102	101	100	89	85	76
%RA	46	6		3	23		10	57	5	100	15	14	23	13	18	40	72
m/z	73	72	71	59	58	57	56	45	43	42	41						
%RA	82	29	11	65	9	51	32	14	10	15	17						

RMM, relative molecular mass; RA, relative abundance.

(R = H or Me) ions in the mass spectra of **1–14** expressed as a percentage of total ionization. The ratio $[M - MeO^{\cdot} - MeOH]^+ : [M - 2MeOH]^{+\cdot}$ is 5:3 for **2** and 1:7 for **4**. The esters **2** and **4** both show abundant $[M - MeO^{\cdot}]^+$ ions in their mass spectra, while the abundances of the $[M - HO^{\cdot}]^+$ ions from the diacids **1** and **3** are insignificantly small. Further, the $[M - 2H_2O]^{+\cdot}$ ion abundances for the diacids **1** and **3** are nearly the same, while that for $[M - 2MeOH]^{+\cdot}$ from dimethyl azelate (**4**) is three times that of the corresponding ion from the pimelate (**2**). Within the azelaic series itself (**3**, **4**, **7**, **8**), the abundance of $[M - 2ROH]^{+\cdot}$ (*m/z* 152) from the parent acid **3** (R = H) is only a third of the abundances of the corresponding ions from **4**, **7** and **8** (see Table 2). In contrast, the abundance of the $[M - 2H_2O]^{+\cdot}$ ion from pimelic acid (**1**) is nearly the same as that of the $[M - 2MeOH]^{+\cdot}$ ion from the pimelate ester (**2**). Given these chain length dependences, it is possible that open chain structures may not promote methanol elimination. The differences discussed above can be interpreted as requiring an additional driving force for the pathway to $[M - 2ROH]^{+\cdot}$ (R = H or Me for **1–4**, **7**; $[M - HCl - MeOH]^{+\cdot}$ for **8**) beyond participation of γ-hydrogens, namely cyclization.

Since pimelic acid (**1**) and its dimethyl ester (**2**) are the first in the homologous series $ROOC(CH_2)_nCOOR$ (R = H or Me) to show abundant $[M - 2ROH]^{+\cdot}$ ions, the mass spectra of the deuterated analogues **13** and **14** were studied. The low-resolution mass spectra of **13** and **14** (Table 1) indicate that H_2O (for **13**) and MeOH (for **14**) loss from the corresponding molecular ions are

Table 2. Abundances of the $[M - 2ROH]^{+\cdot}$ and $[M - RO - ROH]^{+}$ ions in the spectra of 1–14

Compound	$[M-2ROH]^{+\cdot}$ m/z	(R = H or Me) $\%\Sigma_{40}$	$[M-RO-ROH]^{+}$ m/z	(R = H or Me) $\%\Sigma_{40}$
1	124	2.5	125	0.6
2	124	3.0	125	4.8
3	152	3.5	153	0.5
4	152	10.0	153	1.5
5	110	0.1	111	10.0
6	138	7.0	139	1.4
7	152	10.0	153	1.0
8	152	10.0[a]	153	1.5[b]
9	136	0.1	Not detected	
10	138	2.0	Not detected	
11	152	9.0	153	0.8
12	152	8.5	153	1.3
13	128	2.8	129	0.4
14	128	3.0	128	3.2

[a] Represents the $[M - MeOH - HCl]^{+\cdot}$ ion.
[b] Represents the $[M - Cl - MeOH]^{+}$ ion.

favoured by a 2:1 margin over the loss of HDO (**13**) or MeOD (**14**). The metastable ion mass spectra of the $[M - ROH]^{+\cdot}$ ions (Table 3) show predominant loss of H_2O (**13**) and MeOH (**14**). Thus, it appears that the α-deuteria are not involved significantly in either the first or second ROH loss from **13** (R = H) and **14** (R = Me), in contrast to Winnik's assumption.[14] Dimethyl α,α,α′,α′-tetradeuteroadipate has been reported to lose MeOD exclusively from its molecular ion,[12] while α,α,α′,α′-tetradeuteroadipic acid loses only H_2O from its molecular ion.[9]

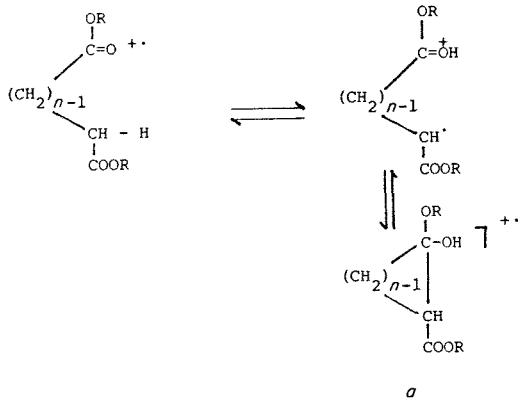
The metastable ion mass spectrum of the $[M - MeO]^{+}$ ions from **14** contains ion signals of equal intensities for the loss of MeOD and D_2O (see Table 3). Similarly, equal intensities were recorded for the ion signals corresponding to the elimination of HDO and D_2O in the metastable ion mass spectrum of the $[M - HO]^{+}$ ions from **13** (Table 3). These results indicate that only the α-hydrogens (along with the R group) contribute to the elimination of ROH (R = H or Me) from the $[M - RO]^{+}$ ions. It is difficult to visualize a mechanism for D_2O loss from the $[M - RO]^{+}$

Table 3. Metastable ion spectra of selected ions from pimelic acid (1), dimethyl pimelate (2) and their deuterated derivatives 13 and 14

Pimelic acid (1) — Unimolecular decomposition				Dimethyl pimelate (2) — Unimolecular decomposition			
Ion (m/z)	Product ion (m/z)	Neutral lost	%	Ion (m/z)	Product ion (m/z)	Neutral lost	%
$[M-OH]^{+}$ (143)	125	H_2O	100	$[M-MeO]^{+}$ (157)	139	H_2O	48
					125	MeOH	52
$[M-H_2O]^{+}$ (142)	124	H_2O	50	$[M-MeOH]^{+}$ (156)	124	MeOH	80
	114	CO	5		97	COOMe	10
	97	COOH	45	$[M-MeO-MeOH]^{+}$ (125)	97	CO	100
$[M-OH-H_2O]^{+}$	97	CO	100				
$[M-2H_2O]^{+}$	123	H	5	$[M-2MeOH]^{+}$ (124)	123	H	5
	96	CO	95		96	CO	95
α,α,α′,α′-d_4-Pimelic acid (13)				Dimethyl α,α,α′,α′-d_4-pimelate (14)			
$[M-OH]^{+}$ (147)	128	HDO	52	$[M-MeO]^{+}$ (161)	141	D_2O	45
	127	D_2O	45		128	MeOD	55
	119	CO	3	$[M-MeOH]^{+}$ (160)	128	MeOH	66
$[M-H_2O]^{+}$ (146)	128	H_2O	55		127	MeOD	13
	127	HDO	15		101	COOMe	7
	126	D_2O	3		132	CO	6
	118	CO	12	$[M-2MeOH]^{+}$ (128)	127	H	4
	101	COOH	8		100	CO	96
	100	$CO + H_2O$	7				
$[M-2H_2O]^{+}$ (128)	127	H	4				
	100	CO	96				

ions from **13** and **14** if these fragment ions are represented as open chain structures.

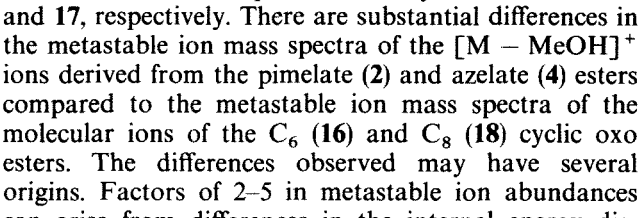
The results discussed above are consistent with the generation of cyclic structures (such as *a* in Scheme 2) obtained by the closure of distonic ions derived from the molecular ions of **1–8** prior to fragmentation. Such a closure requires prior hydrogen abstraction from one of the α-carbons by an ionized oxygen at the other end of the chain. It is known from solution chemistry[15,16] that free radical reagents can abstract an α-hydrogen from esters of the type $MeOOC(CH_2)_nCOOMe$ and that the rate of this reaction increases linearly with increasing value of *n*.



a

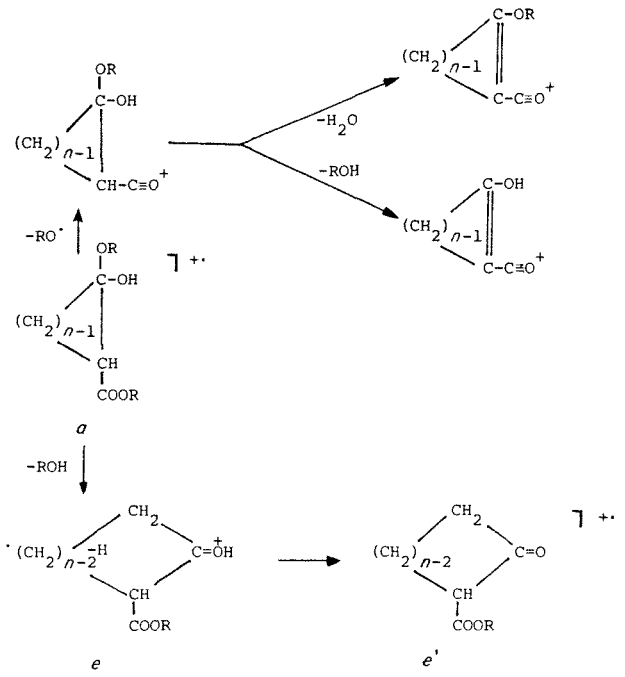
Scheme 2

Initially, we attempted to adduce unequivocal evidence for the formation of the rearranged structures *a* by comparing the metastable ion mass spectra of the primary fragment ions from the dimethyl esters **2**, **4**, **5** and **6** (they do not exhibit molecular ions) with similar ions from the hemiacetals of the cyclic 2-oxo esters **15–18** (Scheme 3). Unfortunately, none of these hemiacetals are stable. As an alternative we investigated the metastable ion mass spectra of the molecular ions from **15–18** in comparison with the metastable ion mass spectra of the $[M - MeOH]^+$ ions derived from the dimethyl esters **2**, **4**, **5** and **6**. The data, presented in Table 4, indicate good agreement between the metastable ion mass spectra of the $[M - MeOH]^+$ ions from the adipate (**5**) and suberate (**6**) esters and the metastable ion mass spectra of the cyclic keto esters **15** and **17**, respectively. There are substantial differences in the metastable ion mass spectra of the $[M - MeOH]^+$ ions derived from the pimelate (**2**) and azelate (**4**) esters compared to the metastable ion mass spectra of the molecular ions of the C_6 (**16**) and C_8 (**18**) cyclic oxo esters. The differences observed may have several origins. Factors of 2–5 in metastable ion abundances can arise from differences in the internal energy distribution of the fragmenting ions;[17,18] this may be particularly important in the present case where one set of ions involved in the comparison is formed in a dissociative ionization process and the other set of ions is formed in a simple vertical ionization process. In addition, as shown in Scheme 4, the distonic ion *e*, initially formed by loss of ROH, must undergo a further hydrogen migration to become isomeric with the cyclic keto ester molecular ion *e'* and some fragmentation from the distonic structure *e* may occur on the metastable ion time-scale. In addition, the keto esters, with the exception of **15**, exist, at least to a minor extent, in the enol form in the gas phase[19] and some of the observed fragmentation may occur from the ionized enol.



15 **16** **17** **18**

Scheme 3



a *e* *e'*

Scheme 4

Further support for the identity of the structures of the $[M - MeOH]^+$ ions derived from the esters and the molecular ions of the cyclic keto esters comes from a comparison of the kinetic energy releases associated with the major metastable ion fragmentation reaction of each species. For the $[M - MeOH]^+$ ions of **2**, **4** and **6** and the molecular ions of the corresponding keto esters **16**, **18** and **17** the major fragmentation reaction is loss of MeOH. As the results in Table 5 show, the kinetic energy releases are the same, within experimental error, for each pair. For the $[M - MeOH]^+$ ion derived from **5** and for the molecular ion of **15** the major metastable ion fragmentation reaction is elimination of CO and, as shown in Table 5, the kinetic energy releases are the same within experimental error.

Thus, both the metastable ion abundance data and the kinetic energy release data support the postulate that the initial step in the fragmentation of the molecular ions of the dicarboxylic acids and their methyl esters is a cyclization process, with subsequent elimination of MeOH leading to a cyclic 2-keto ester ion. As shown in Scheme 4, such a cyclization reaction also can rationalize the observation that the $[M - MeO]^+$ ions derived

Table 4. Metastable ion spectra of the molecular ions from the 2-oxo cycloalkane carboxylates 15–18 and the $[M - MeOH]^+$ ions from the dimethyl dicarboxylates 2, 4, 5 and 6

Product ion (*m/z*)	Unimolecular decomposition from M^+ of **15** (*m/z* 142)	Unimolecular decomposition from $[M - MeOH]^+$ from **5** (*m/z* 142)
127	10.9	1.0
114	77.8	80.7
110	8.3	9.2
83	3.0	8.0

Product ion (*m/z*)	Unimolecular decomposition from M^+ of **17** (*m/z* 170)	Unimolecular decomposition from $[M - MeOH]^+$ from **6** (*m/z* 170)
155	3.8	1.3
152	7.5	2.0
142	11.5	4.0
138	75.8	89.5
111	1.4	3.2

Product ion (*m/z*)	Unimolecular decomposition from M^+ of **16** (*m/z* 156)	Unimolecular decomposition from $[M - MeOH]^+$ from **2** (*m/z* 156)
141	7.0	5.7
138	3.2	0.6
128	8.1	1.3
124	66.8	90.3
97	15.0	1.8

Product ion (*m/z*)	Unimolecular decomposition from M^+ of **18** (*m/z* 184)	Unimolecular decomposition from $[M - MeOH]^+$ from **4** (*m/z* 184)
169	0.8	—
166	3.7	1.2
156	21.9	12.4
155	11.2	0.9
152	41.4	77.8
142	7.9	1.5
141	1.7	0.7
128	0.9	—
125	10.5	5.4

from **14** lose both D_2O and MeOD in metastable ion fragmentation reactions, while the $[M - OH]^+$ ions derived from **13** lose both HDO and D_2O in metastable ion fragmentation reactions.

EXPERIMENTAL

Compounds **1–7**, **15** and **17** were obtained from Aldrich Chemical Company and were purified by recrystallization or by distillation under vacuum. The monoester acid chloride (**8**) and 9-hydroxynonanoic acid (**10**) were made by known procedures.[20] Dimethyl $\alpha,\alpha,\alpha',\alpha'$-$d_4$-pimelate (**14**) was prepared by the esterification of $\alpha,\alpha,\alpha',\alpha'$-$d_4$-pimelic acid (**13**) (MSD Products, Montreal)

Table 5. Kinetic energy release comparison between the M^+ of methyl 2-oxocycloalkane carboxylates 15–18 and the $[M - MeOH]^+$ ions from dimethyl dicarboxylates 2, 4, 5 and 6 for the loss of methanol (loss of CO for 15 and 5)

M^+ or $[M - MeOH]^+$ from	$T_{1/2}$(±1 meV)
2	21.3
16	20.1
4	23.8
18	22.5
6	23.6
17	21.8
5	16.9
15	15.8

with methanol under standard conditions. Dimethyl-d_6-azelate (**12**) was synthesized from azelaic acid by esterification with CD_3OH. Monomethyl-d_3-azelate (**11**) was prepared by partial demethylation of the dimethyl-d_6-azelate following a procedure for making the unlabelled monoester.[21] The cyclic 2-oxo esters **16** and **18** were prepared by treating cyclohexanone and cyclooctanone, respectively, with dimethyl carbonate in the presence of sodium hydride following literature directions.[22] The 9-oxo compound (**9**) was made by the oxidation of 9,10-dihydroxystearic acid.[23]

Low-resolution mass spectra were obtained using either a DuPont 21-490 single-focusing mass spectrometer or a VG Analytical ZAB-2FQ double-focusing mass spectrometer operating at 70 eV ionizing electron energy and a source temperature of 200 °C. Liquid samples were introduced through a heated inlet system, while solid samples were introduced through a direct insertion probe. Spectra obtained on the two instruments were in good agreement.

The metastable ion fragmentation reactions of selected ions in the electron impact (EI) mass spectra were examined by the mass analysed ion kinetic energy (MIKE) spectrometric technique[24,25] using the reversed-geometry ZAB-2FQ mass spectrometer[26] at 8 kV accelerating potential. The kinetic energy releases ($T_{1/2}$) associated with the unimolecular ion fragmentation reactions were evaluated from the peak widths at half-height after correction for the main beam width according to the relation[27]

$$W_{corr} = (W^2_{met} - W^2_{mb})^{1/2}$$

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REFERENCES

1. K. S. Markley, in *Fatty Acids: Their Chemistry, Properties, Production and Uses*, ed. by K. S. Markley, Part 1, pp. 93–108. Interscience, New York (1960).
2. G. Spiteller, *Pure Appl. Chem.* **50**, 205 (1978).
3. M. Spiteller and G. Spiteller, *J. Chromatogr.* **164**, 253 (1979).
4. D. G. Hine and K. Tanaka, *Biomed. Mass Spectrom.* **11**, 332 (1984).
5. H. M. Liebich, A. Pickert, V. Stierle and J. Woell, *J. Chromatogr.* **199**, 181 (1980).
6. D. A. Withycombe, L. M. Libbey and R. C. Lindsay, *Lipids* **6**, 758 (1971).
7. A. S. Breathnash, M. Nazzaro-Porro and S. Passi, *Brit. J. Dermatol.* **111**, 115 (1984).
8. (a) S. Mohanraj and W. T. Ford, *J. Org. Chem.* **50**, 1616 (1985); (b) B. M. Trost, T. N. Salzmann and K. Hiroi, *J. Am. Chem. Soc.* **98**, 4887 (1976); (c) T. Lin, G. T. Shiau, W. H. Prusoff and J. P. Neenan, *J. Carbohydr. Nucleosides, Nucleotides* **7**, 389 (1980); (d) N. N. Joshi, V. R. Mamdapur and M. S. Chada, *Tetrahedron* **40**, 3285 (1984); (e) R. K. M. R. Kallury, U. J. Krull and M. Thompson, *J. Org. Chem.* **52**, 5478 (1987).
9. J. L. Holmes and T. St Jean, *Org. Mass Spectrom.* **3**, 1505 (1970).
10. I. Howe and D. H. Williams, *J. Chem. Soc.* (*C*) 202 (1968).
11. H. Schwarz, *Org. Mass Spectrom.* **10**, 384 (1975).
12. I. Howe and D. H. Williams, *Chem. Commun.* 733 (1967).
13. N. Nguyen and A. Raal, in *New Concepts in Lipid Research*, ed. by R. T. Holman, pp. 195–206. Pergamon, Oxford (1978).
14. M. A. Winnik, *Org. Mass Spectrom.* **9**, 920 (1974).
15. N. L. Budeiko, V. E. Agabekov and N. I. Mitskevich, *Dokl. Akad. Nauk BSSR* **23**, 720 (1979).
16. V. E. Agabekov, E. T. Denisov, N. I. Mitskevich, T. G. Kosmacheva and G. B. Butovskaya, *Kinet. Katal.* **15**, 883 (1974).
17. A. N. Yeo and D. H. Williams, *J. Am. Chem. Soc.* **93**, 395 (1971).
18. C. W. Tsang and A. G. Harrison, *Org. Mass Spectrom.* **7**, 1377 (1973).
19. R. K. M. R. Kallury, U. J. Krull and M. Thompson, *J. Org. Chem.*, **53**, 1320 (1988).
20. J. Dale, *J. Chem. Soc.* 72 (1965).
21. J. Muggee and O. Vogl, *J. Polym. Sci., Polym. Chem. Ed.* **22**, 2501 (1984).
22. A. J. Frew and G. R. Proctor, *J. Chem. Soc., Perkin Trans. 1* 1245 (1980).
23. G. King, *J. Chem. Soc.* 1826 (1938).
24. R. G. Cooks, J. H. Beynon, R. M. Caprioli and G. R. Lester, *Metastable Ions*, Elsevier, New York (1973).
25. K. R. Jennings, in *Ionic Processes in the Gas Phase*, ed. by M. A. Almoster Ferreira, Reidel, Dordrecht (1984).
26. A. G. Harrison, R. S. Mercer, E. J. Reiner, A. B. Young, R. K. Boyd, R. E. March and C. J. Porter, *Int. J. Mass Spectrom. Ion Proc.* **74**, 13 (1986).
27. J. L. Holmes and J. K. Terlouw, *Org. Mass Spectrom.* **15**, 383 (1980).