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Mass Spectra of 1-(2′-Hydroxy-5′-alkylphenyl)-1-alkanone (*E*)-Oximes

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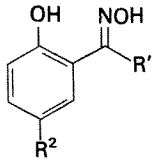
The mass spectra of 1-(2′-hydroxy-5′-alkylphenyl)-1-ethanone (*E*)-oximes 1–6 and 1-(2′-hydroxy-5′-methylphenyl)-1-alkanone (*E*)-oximes 7–12 are given and the major fragmentation pathways discussed. The simultaneous loss of water and alkyl moieties from the molecular ion indicates that a skeletal rearrangement take place and a cycloheptatrienyloheterocyclic system is formed. The McLafferty rearrangement, γ-fission in the side aliphatic chain and oxygen expulsion are discussed with evidence being drawn from accurate mass measurements, metastable ions and comparison with mass spectral data of related compounds.

INTRODUCTION

The reason for conducting this study was the growing interest in the hydrometallurgical utilization of hydroxyoximes, which indicates that mass spectrometry might be required in the identification of this extractant class.[1] The mass spectra of the 1-(2′-hydroxy-5′-alkylphenyl)-1-alkanone oximes **1–12** are discussed. It is convenient to discuss the result of fragmentation by electron impact in terms of the following two categories:

(i) 1-(2′-hydroxy-5′-alkylphenyl)-1-ethanone (*E*)-oximes (compounds **1–6**),

(ii) 1-(2′-hydroxy-5′-methylphenyl)-1-alkanone (*E*)-oximes (compounds **7–12**).



	R^1	R^2
1	CH_3	CH_3
2	CH_3	C_2H_5
3	CH_3	C_4H_9
4	CH_3	C_8H_{17}
5	CH_3	C_9H_{19}
6	CH_3	$C_{12}H_{25}$
7	C_2H_5	CH_3
8	C_3H_7	CH_3
9	C_5H_{11}	CH_3
10	C_7H_{15}	CH_3
11	C_9H_{19}	CH_3
12	$C_{11}H_{23}$	CH_3

RESULTS AND DISCUSSION

1-(2′-Hydroxy-5′-alkylphenyl)-1-ethanone (*E*)-oximes (1–6)

The oximes **1–6** give similar spectra, shown in Table 1. The fragmentation pathways of the molecular ion of 1-(2′-hydroxy-5′-butylphenyl)-1-ethanone (*E*)-oxime (**3**), given as an example (Fig. 1), are shown in Scheme 1. The elemental composition of all ions have been substantiated by high-resolution mass measurements. The pathways marked with an asterisk have been confirmed by the presence of metastable peaks.

The main fragmentation sequences can be described by simple β-cleavage of the alkyl substituent on the benzene ring, giving the ion *a* at *m/z* 164, and β-cleavage accompanied by water elimination and simultaneous rearrangement of a fragment formed to the ion *b* at *m/z* 146. In the case of the spectra of long-chain homologues the *m/z* 164 ions give base peaks.

Considering the subsequent fragmentation of the *m/z* 164 ion the nitrone-like structure *a* seems to be preferred. The mass spectra of compounds **2–6** show water expulsion giving *m/z* 146, but also exhibit the metastable loss of an oxygen atom. Isomerization of oxime molecular ions into nitrone molecular ions upon electron impact does not generally occur, but it has been established[2] that it is possible in the case of the proximity of hydrogen atom(s). For the suggested structure *a* the availability of the 2′-hydroxy group is sufficient for participation in oxime ⇆ nitrone isomerization, and additional stabilization through a hydrogen-like bond cannot be excluded. The loss of an oxygen atom from molecular ions of aliphatic and aromatic ketoximes is a very rare process,[3] and a temperature-dependent ion at $[M-16]^{+\cdot}$, interpreted previously as $[M-O]^{+\cdot}$, was considered as the $[M]^{+\cdot}$ of ketone imine, formed from the oxime losing oxygen prior to ionization.[4,5] In the investigated class of compounds, this process occurs to a very limited extent, and for a few oximes only it is confirmed by a high-resolution study of $[M-16]^{+\cdot}$ ions. On the other hand it is stated that the *N*-benzylidenemethylamine *N*-oxide gives an intense $[M-O]^{+\cdot}$ ion (24% of intensity of parent ion), while in none of the aldoxime ethers is a $[M-16]^{+\cdot}$ ion observed with more than 2% relative intensity.[6] By analogy with the last observations (*m/z* 148 ion *c* has 15% of intensity of *a*), we propose the nitrone structure for ion *a*, which implies the easy oxygen atom expulsion.

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Table 1. Mass spectra of some 1-(2′-hydroxy-5′-alkyl)-1-alkanone (*E*)-oximes, 2′-OH-5′-R^2-C_6H_3-C(=NOH)R^1 [a]

1: $R^1 = CH_3$, $R^2 = CH_3$

m/z	166	165	149	148	147	146	134	133	132	131	121	120
I (%)	10	100	28	30	47	37	7.2	10	12	5.4	3.6	4.5
m/z	119	118	111	108	107	106	105	104	97	95	93	92
I (%)	22	55	4.5	3.6	9.1	9.1	16	12	6.3	5.4	3.6	5.9
m/z	91	83	81	79	78	77	71	70	69	68	67	64
I (%)	11	9.1	6.3	12	27	32	11	8.1	15	4.5	10	8.1
m/z	62	57	56	55	54	53	52	51				
I (%)	5.9	24	11	20	5.4	9.1	10	17				

2: $R^1 = CH_3$, $R^2 = C_2H_5$

m/z	180	179	164	162	161	147	146	133	132	119	118	105
I (%)	3.2	37	7.2	12	3.7	14	100	5.4	6.4	6.2	10	6.2
m/z	103	92	91	89	79	78	77	65	64	63	53	52
I (%)	5.2	4.4	31	5.9	4.7	6.4	28	13	4.4	10	4.2	7.7
m/z	51											
I (%)	16											

3: $R^1 = CH_3$, $R^2 = C_4H_9$ (see Fig. 1)

4: $R^1 = CH_3$, $R^2 = C_8H_{17}$

m/z	264	263	247	246	165	164	162	149	148	147	146	133
I (%)	12	69	3.8	9.2	10	100	3.8	8.4	16	13	77	7.7
m/z	132	131	106	105	104	91	77	57	55	51		
I (%)	4.6	4.8	4.6	3.8	4.6	12	10	8.5	8.8	4.6		

5: $R^1 = CH_3$, $R^2 = C_9H_{19}$

m/z	278	277	262	260	165	164	162	160	149	148	147	146
I (%)	10	55	3.0	9.6	12	100	3.0	3.2	6.1	20	14	74
m/z	133	132	131	119	107	106	105	91	78	77	65	
I (%)	7.1	4.2	4.4	3.0	3.2	3.9	4.2	9.6	3.2	8.4	3.2	

6: $R^1 = CH_3$, $R^2 = C_{12}H_{25}$

m/z	320	319	302	261	165	164	149	148	147	146	133	107
I (%)	19	85	20	15	15	100	15	32	18	65	10	50
m/z	106	105	91	77	58	51						
I (%)	5.2	7.8	15	15	40	4.9						

7: $R^1 = C_2H_5$, $R^2 = CH_3$

m/z	180	179	165	163	162	161	160	149	148	147	146	135
I (%)	7.0	58	4.8	6.4	9.7	6.5	13	18	8.0	8.0	26	4.8
m/z	134	133	132	119	118	117	115	107	106	105	104	91
I (%)	13	100	29	4.6	10	6.5	6.5	6.0	8.0	16	19	9.8
m/z	89	83	79	78	77	71	69	67	65	63	62	57
I (%)	4.2	4.5	6.5	15	24	6.1	6.4	6.9	4.8	4.8	4.3	11
m/z	56	55	54	53	562	51						
I (%)	8.2	9.7	3.9	7.8	8.0	16						

8: $R^1 = C_3H_7$, $R^2 = CH_3$

m/z	194	193	176	175	162	161	160	149	147	146	134	133
I (%)	5.2	44	5.2	4.7	6.9	3.4	19	6.1	12	6.5	18	100
m/z	132	107	106	105	104	91	79	78	77	65	57	52
I (%)	17	3.5	4.8	11	8.2	5.2	4.3	7.8	11	3.2	3.4	3.9
m/z	51											
I (%)	6.1											

9: $R^1 = C_5H_{11}$, $R^2 = CH_3$

m/z	222	221	204	189	188	178	165	162	161	160	148	147
I (%)	3.8	32	6.2	5.6	6.2	16	13	4.4	5.3	28	7.1	22
m/z	146	134	133	132	121	119	118	115	107	106	105	104
I (%)	6.8	32	100	15	8.2	5.6	7.1	6.2	4.1	4.7	14	13
m/z	91	89	79	78	77	65	63	57	56	55	53	51
I (%)	9.7	5.0	7.3	17	24	5.6	5.3	36	27	11	6.2	10

Table 1. (continued)

10: $R^1 = C_7H_{15}$, $R^2 = CH_3$

m/z	250	249	233	232	216	189	179	175	166	165	164	162		
I (%)	8.1	50	3.7	11	5.0	5.5	26	4.8	3.7	50	3.5	12		
m/z	160	149	148	147	146	134	133	132	121	119	118	107		
I (%)	26	7.0	5.0	24	11	37	100	10	14	3.6	6.1	4.4		
m/z	106	105	104	91	79	78	77	60	59	57	56	55	53	51
I (%)	3.0	7.5	6.9	5.6	4.3	6.9	12	5.0	9.4	26	11	12	4.1	3.8

11: $R^1 = C_9H_{19}$, $R^2 = CH_3$

m/z	278	277	261	260	188	178	173	165	162	161	160	148
I (%)	12	65	5.5	21	7.5	35	6.0	55	20	7.5	31	18
m/z	147	146	135	134	133	132	121	107	105	91	85	84
I (%)	35	13	5.8	45	100	11	21	6.0	8.4	6.5	5.5	6.2
m/z	79	78	77	71	70	69	57	56	55	51		
I (%)	5.2	7.5	13	11	10	11	21	15	20	4.0		

12: $R^1 = C_{11}H_{23}$, $R^2 = CH_3$ (see Fig. 2)

[a] Peak heights expressed as percent of the base peak.

The loss of methyl radical from *c* gives an ion *d* at *m/z* 133. The metastable transition is observed for this fragmentation for **1** and **2** only. That the resulting ion *d* has the cyclic structure is supported by the high intensity of its signal in the spectra of 1-(2′-hydroxy-5′-methylphenyl)-1-alkanone oximes (see below). The anticipated ring fission takes place and may lead to an ion with the ring-expanded structure analogous to the tropylium ion at *m/z* 105, which then decomposes by ejection of carbon monoxide.

It is difficult to assign with certainty a structure to the ion at *m/z* 146 (Scheme 1). An isoxazole ring

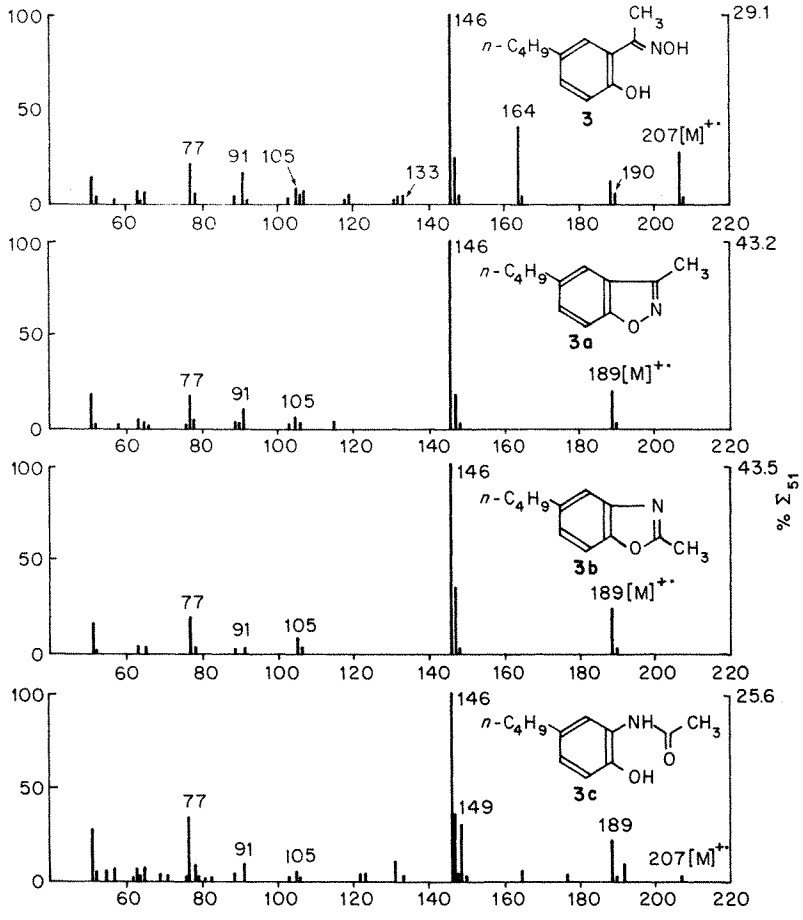
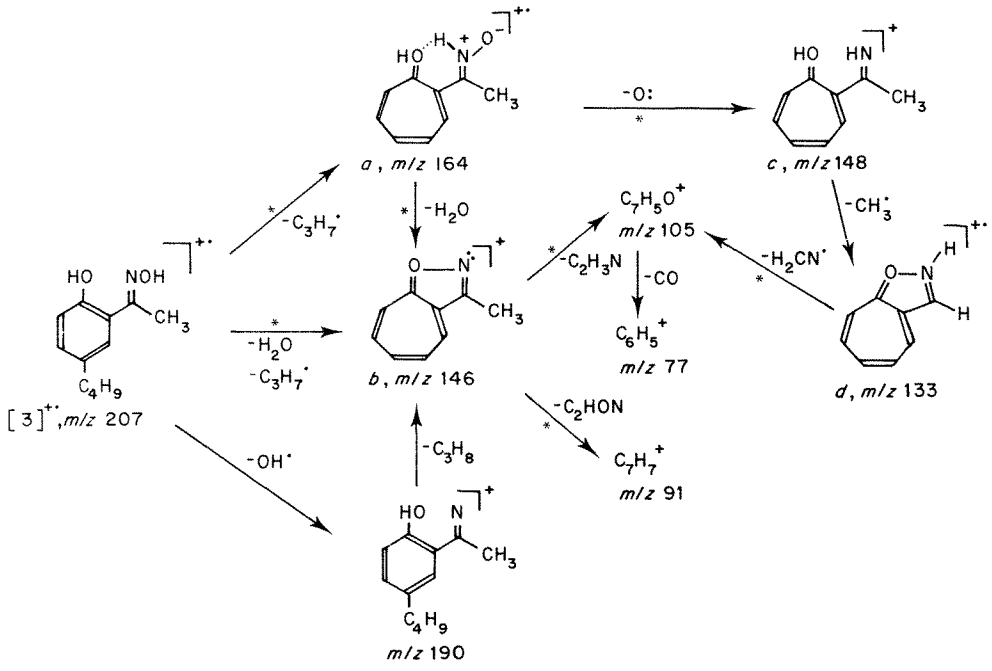


Figure 1. Mass spectra of 1-(2′-hydroxy-5′-butylphenyl)-1-ethanone (*E*)-oxime (**3**) and its related isoxazole (**3a**), oxazole (**3b**) and amide (**3c**).



Scheme 1. Fragmentation of 1-(2′-hydroxy-5′-butylphenyl)-1-ethanone (*E*)-oxime (**3**).

condensed with tropylium ion seems to be the most reasonable considering the fact of acetonitrile elimination (m/z 146 → m/z 105). In that formulation, however, the positive charge cannot be localized on the nitrogen atom, so it is inconsistent with the tendency to better charge stability with a nitrogen rather than an oxygen atom.

Therefore, contrary to the previous conclusion about the structure of ion *b*, we should take into consideration not only the cycloheptatrieneisoxazolium ion but also a possible cycloheptatrieneoxazolium stucture. The primary reason for the rearranged structure is the fact that the tropylium ion is formed from ion *b* by the ejection of C_2HNO, probably as hydrogen cyanide and carbon monoxide molecules (the concerted (CO + HCN) elimination can be expected).[7] Secondly, the isomerization facility of isoxazoles and oxazoles,[7] as well as their thio analogues[8] under electron impact is a well-recognized process. Thirdly, the oxazolium ion can be produced through the first-order Beckmann rearrangement of the $[M - OH]^+$ even-electron ion (Ref. 9; cf. Refs 10 and 11), because the alkylhydroxyphenyl substituent in the *E* configuration has a very high migratory facility.

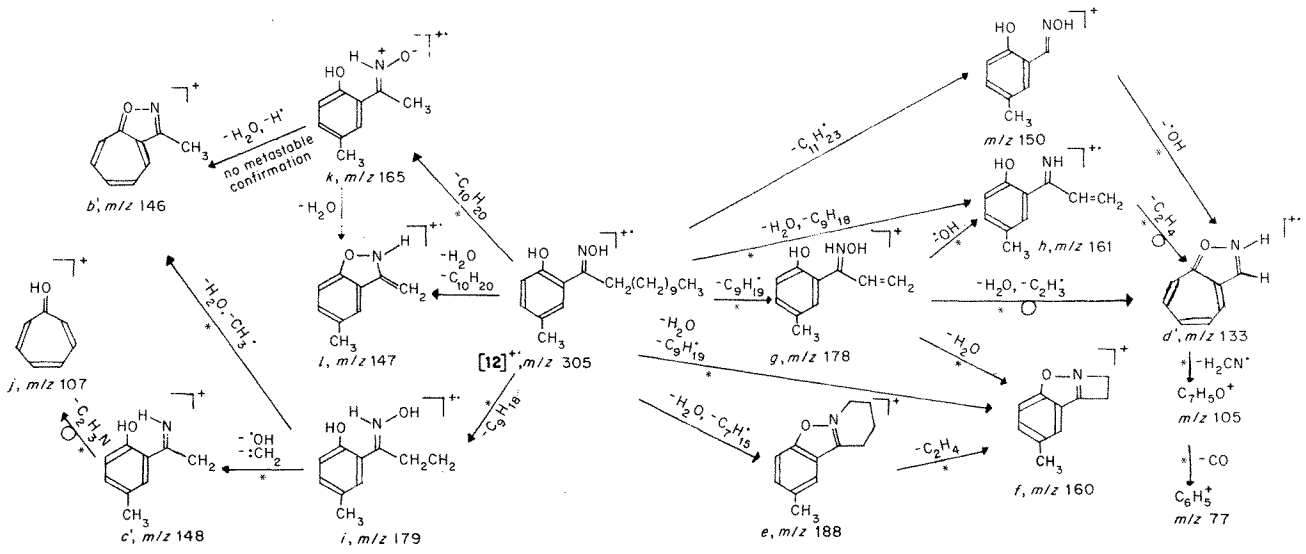
The discussion shows that the oxime **3** or its molecular ion would cyclize to an isoxazole ring, rearrange (at least partially) to an amide or rearrange and cyclize to an oxazole system before further fragmentation. These compounds were synthesized and their mass spectra at 75 eV (200 °C source temperature) are shown in Fig. 1.

The most significant feature of the oxime spectrum is the pronounced presence of the $[M - C_3H_7]^+$ ion at m/z 164, while in the amide spectrum it is quite absent. Moreover, the only indication of a possible Beckmann rearrangement of the neutral molecule **3** or $[3]^{+\cdot}$ is the small amount of the $[M - C_2H_4NO]^+$ ion at m/z 149 (0.6% in oxime spectrum and 30.5% in amide), but in view of some intensity of the m/z 148 ion in the oxime spectrum, it appears that **3** and $[3]^{+\cdot}$ are especially stable to thermal or catalytic rearrangement in the inlet system and in the ion source of the mass spectrometer. The rearrangement, if it takes place, is the rearrangement of postulated even-electron fragment ion *b*.

1-(2′-Hydroxy-5′-methylphenyl)-1-alkanone (*E*)-oximes 7–12

The fragmentation patterns of several 1-(2′-hydroxy-5′-methylphenyl)-1-alkanone (*E*)-oximes (whose mass spectral data are presented in Table 1) are exemplified in Scheme 2 for 1-(2′-hydroxy-5′-methylphenyl)-1-dodecanone (*E*)-oxime (**12**). The main features of the spectra can be assigned to fragments from olefin elimination (left side of Scheme 2) competing with the α, γ and ε carbon–carbon bond cleavages in the side hydrocarbon chain, followed by loss of a water molecule. The importance of the whole carbon–carbon cleavages can be seen by the amount of their contribution to the total ion current Σ_{51} (24.2% of Σ_{51} for the olefin elimination processes and 22.3% of Σ_{51} for the α, γ, ε cleavages is attained).

The oxime **12** shows a small peak at m/z 188 for the loss of a heptyl radical and a water molecule. Further fragmentation of the ion *e* (m/z 188) is evidenced by a metastable peak for the formation of a more intense peak at m/z 160 (*f*). The same peak can be formed by simultaneous elimination of nonyl radical and water from the molecular ion. It is clear that these cleavages must be the result of the special stability of the species formed and that they are not the result of simple



Scheme 2. Fragmentation of 1-(2'-hydroxy-5'-methylphenyl)-1-dodecanone (*E*)-oxime (**12**).

losses of alkyl fragments. The observed γ-scission can be the result of an allylic cleavage in the tautomeric form of the molecular ion,[12] and/or its dehydration product. In addition, the preferential cleavage of C—C bonds in the γ-position to the functional group has been interpreted as a result of reciprocal hydrogen rearrangement.[13] The loss of the nonyl radical giving the ion *g* probably occurs via the same mechanism(s), and the presence in the first field-free region of metastable ions proves the fragmentation $[M]^{+\cdot} \xrightarrow{*} 178 \xrightarrow{*} 160$ and suggests that not only concerted but also two-step degradation of the molecular ion is involved. It is reasonable that the m/z 287 → 160 transition is due to the ion of the thermally dehydrated oxime molecule, although m/z 287 intensity in the spectrum of **12** is extremely low. It confirms that not only hydroxyoxime precursors, but also isoxazole ions, undergo the extensive γ-fission process.

It appears, that the scission α to the oximino group gives a low-intensity m/z 150 ion, and such a mechanism of formation of the m/z 133 ion is unimportant. One other aspect of the fragmentation patterns of **12** which should be noted is the formation of the m/z 133 ion, giving the base peak in the spectra of compounds **7–12**. The cycloheptatrieneisoxazolium structure *d'* is suggested, and it seems that any rearrangement in the heterocyclic ring cannot be considered as explaining the H_2CN radical elimination. Although hydrogen cyanide expulsion is a very common process in the fragmentation reaction of oxazoles and isoxazoles,[7] we have not met such a formulated suggestion for dehydroxotropylium ion formation.

Figure 2 shows the characteristic differences between the spectra of oxime **12** and its related isoxazole (**12a**), oxazole (**12b**) and amide (**12c**). A comparison of the fragmentation patterns of these compounds reveals that oxime and isoxazole molecular ions fragment (with a few exceptions) in a similar way and structure relationships between the m/z 133 ions for these two classes of compounds are highly possible.

The *ortho*-hydroxyoximes **8–12** would be expected to undergo McLafferty rearrangement analogously to other suitably substituted aldoximes and ketoximes.[12,14] The m/z 165 ion is formed and because of oxygen expulsion the nitrone form *k* is expected to be predominant (see above). Although the metastable evidence for such a process is lacking the following sequence

$$m/z\ 165 \xrightarrow{-O} m/z\ 149 \xrightarrow{-CH_3} m/z\ 134 \xrightarrow{-HCN} j$$

is proposed. The C_7H_7O ion has been earlier observed in the mass spectra of tropolone methyl ethers[15] and the extended ring structure has been proposed. Unfortunately there is no metastable confirmation for the transformation of the McLafferty product *k* into the proposed cycloheptatrieneisoxazolium ion *b'*, or $b' \rightarrow m/z\ 105 + CH_3CN$, so typical for oximes **1–6**. In the case of the m/z 179 ion (*i*, McLafferty ion's homologue) the stabilization after preceding degradation as cycloheptatriene species *b'* and *j* is confirmed and, therefore, suggested.

Although the McLafferty rearrangement $[M]^{+\cdot} \rightarrow k$ is for **12** the most important pathway for long-chain olefin elimination, the parallel process of simultaneous olefin and water molecule expulsion, $[M]^{+\cdot} \rightarrow l$, also occurs to a considerable extent (66% and 44%, respectively). The $[M]^{+\cdot} \rightarrow l$ process is less important for all long-chain derivatives **10–12** with a relative intensity ratio of 0.5–0.65. In the case of the related amide **12c**, however, the m/z 147 is the base peak (McLafferty rearrangement), as well as for isoxazole **12a** and oxazole **12b**, by reason of simple β-cleavage and hydrogen migration to the heterocyclic ring (Fig. 2).

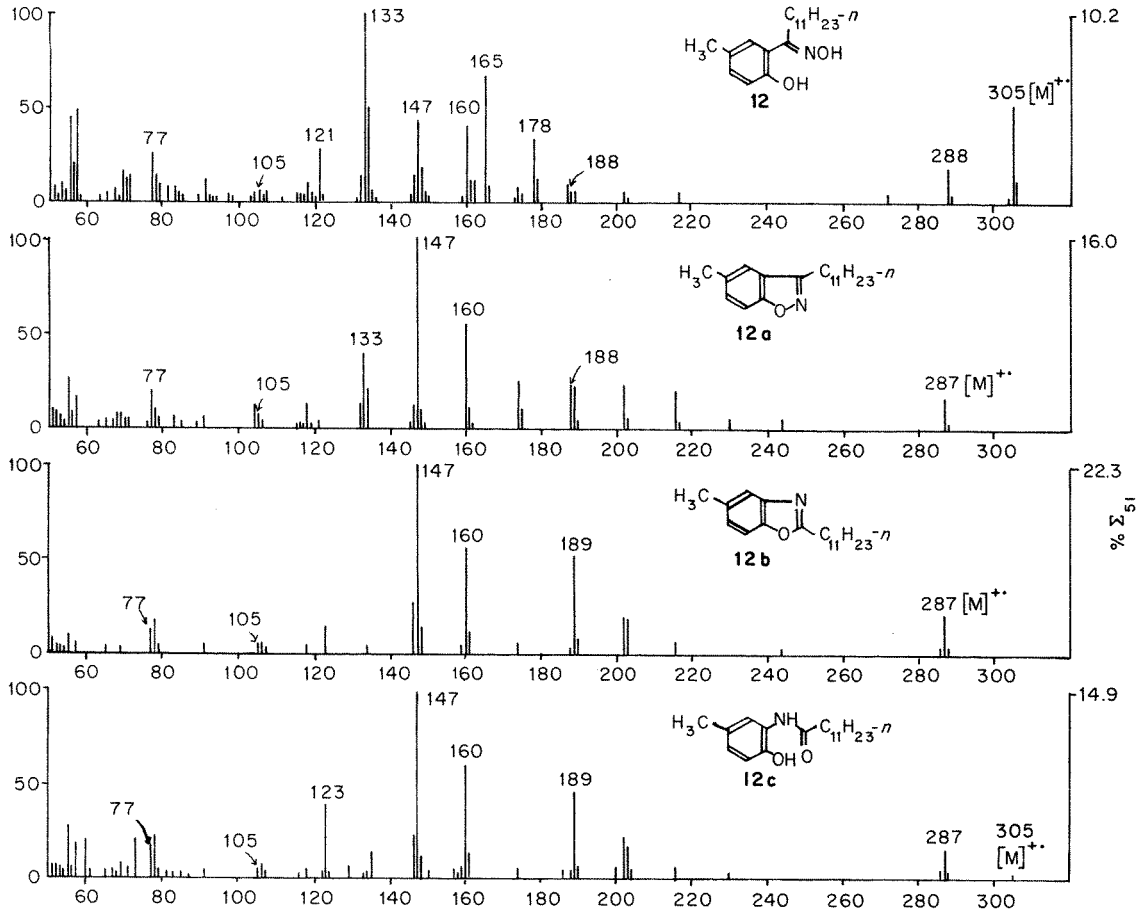


Figure 2. Mass spectra of 1-(2′-hydroxy-5′-methylphenyl)-1-dedecanone (*E*)-oxime (**12**) and its related isoxazole (**12a**), oxazole (**12b**) and amide (**12c**).

EXPERIMENTAL

The substituted *o*-hydroxyaryl ketones required as parent compounds were prepared by Fries reaction.[16] These were converted into their oximes by reacting freshly distilled or crystallized ketones with hydroxylamine hydrochloride and pyridine. The oximes were recrystallized from a hexane–ethanol mixture. Gas chromatograms of bisTMS oxime derivatives (on Se 30) showed single peaks.[17] The oximes obtained were identified by comparing their melting points with those reported in the literature and by spectral data. The stereochemical configuration was confirmed by Beckmann rearrangement of amides (PCl_5, absolute ether, 0 °C). The spectral data of reported oximes are similar and typical characteristics are as shown below.

1-(2′-Hydroxy-5′-butylphenyl)-1-ethanone (*E*)-oxime (3): UV(CH_3OH), λ_{max}(nm), ($\log \varepsilon_{max}$): 254 (3.94), 310 (3.57); IR(CCl_4, CS_2), ν(cm^{-1}): 3550, 3360, 3020, 2920, 2845, 1625, 1485, 1410, 1375, 1285, 975, 825, 790, 715; PMR($(CD_3)_2SO$), δ(ppm): 0.93(t, 3H, CH_3), 1.38(m, 4H, CH_2), 2.66(m, 5H, CH_2, CH_3), 6.81–7.60(m, 3H, arom.), 11.66(s, 1H, OH), 11.80(s, 1H, OH).

1-(2′-Hydroxy-5′-methylphenyl)-1-dodecanone (*E*)-oxime (12): UV(CH_3OH), λ_{max}(nm), ($\log \varepsilon_{max}$): 254(3.13), 310(3.59); IR(CCl_4, CS_2), ν(cm^{-1}): 3550, 3360, 3010, 2910, 2840, 1620, 1490, 1400, 1285, 1200, 880, 825, 775, 710; PMR($(CD_3)_2SO$), δ(ppm): 0.93(t, 3H, CH_3), 1.30(m, 18H, CH_2), 2.35(s, 3H, CH_3), 2.71(t, 2H, CH_2), 6.67–7.53(m, 3H, arom.), 11.73(s, 2H, OH).

Characteristics of the amides are as follows: ***N*-(2′-hydroxy-5′-butylphenyl)acetamide (3c):** m.p. 89–91 °C; ***N*-(2′-hydroxy-5′-methylphenyl)dodecanoamide (12c):** m.p. 62–64 °C.

Benzoxazoles were obtained as described by Fujita.[18] Both benzoxazoles when heated with hydrochloric acid gave the appropriate amides (**12b → 12c**, **3b → 3c**). **2-Methyl-5-butylphenylbenzoxazole (3b):** b.p. 152–154 °C/5 Torr (colourless oil); IR (film), ν(cm^{-1}): 1605, 1580, 1260, 1175, 915, 800, **2-Undecyl-5-methylbenzoxazole (12b):** m.p. 15 °C (from acetonitrile); IR(film), ν(cm^{-1}): 1605, 1570, 1260, 1165, 920, 865, 800.

Benzisoxazoles were prepared as described by Lindemann.[19] **3-Methyl-5-butyl-1,2-benzisoxazole (3a):** b.p. 164 °C/5 Torr; IR(film), ν(cm^{-1}): 1610, 1455, 1235, 885, 805, 755. **3-Undecyl-5-methyl-1,2-benzisoxazole (12a):** b.p. 185–187 °C/1 Torr; IR(film), ν(cm^{-1}): 1620, 1455, 1235, 875, 820, 750.

The purification of amides, benzoxazoles and benzisoxazoles was performed on a micropreparative scale using thin-layer chromatography (10 × 20 cm

plates, silica gel 60 F_{254} Merck; solvent system: toluene–cyclohexane–ethyl acetate 80:80:10 v/v).

R_F of **1-(2′-hydroxy-5′-butylphenyl)-1-ethanone (*E*)-oxime** and its derivatives: 0.16(**3c**), 0.25(**3**), 0.32(**3b**), 0.50 (**3a**). R_F of **1-(2′-hydroxy-5′-methylphenyl)-1-dodecanone (*E*)-oxime** and its derivatives: 0.18(**12c**), 0.32(**12**), 0.43(**12b**), 0.58(**12a**).

Mass spectral, metastable ion and exact mass measurements were carried out on Jeol JMS-D-100 double focusing mass spectrometer, source temperature 130–200 °C, electron energy 75 eV, ionizing current 300 μA. The elemental compositions of ions were determined by computer with high-resolution mass measurements relative to PFK and PCR. Metastable peaks in the first field-free region were obtained using an MS-MT-01 metastable ion detector by scanning the accelerating voltage.

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