

Mass Spectra of Some 2-Substituted Derivatives of Quinoline-4-carboxylic Acids and their Amides

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Received 1 April 1999

Electron ionization mass spectra of ten various 2-substituted quinoline-4-carboxylic acids and their six amides are presented. Spectral fragmentations are discussed. New mass spectra were measured.

Quinoline-4-carboxylic acids are of general interest due to their wide medical applications [1–3]. The limited data available in literature on the mass spectra of these compounds with a variety of substituents prompted us to record some of their mass spectral patterns. On the other hand, the mass spectra of alkylquinolines [4] and arylquinolines [5] were presented in literature long ago.

The most important fragment ion at m/z 102 (20 %) of quinoline itself is formed by the expulsion of the molecule HCN from $M^{+\bullet}$ [6]. This fragment ion decomposes further by the expulsion of the molecule C_2H_2 to give the $[C_6H_4]^+$ ion at m/z 76 (10 %). The different substitutions on the quinoline ring may have a pronounced effect on the mass spectral pattern.

The structural formulae of the compounds studied in the present paper are shown in Table 1. These are the new compounds without *I–III* but their mass spectra were not published [7]. The relative abundances of the mass spectra of *I–XVI* are given in Table 2.

The corresponding molecular ions are observed in the electron ionization mass spectra of all studied compounds. In *I–VIII* the molecular ions represent the base peaks in the spectra and so reflect their stable nature under electron impact. The main fragmentation pathways include the elimination of 45 mass units from the molecular ions to produce fragment ions $[M - COOH]^+$, which further lose HCN. In addition to the ions $[M - COOH]^+$ the ions $[M - CO_2]^+$ are also significant. The presence of the furan ring *III* results in the expulsion of CO (m/z 211) and \cdot CHO (m/z 210)

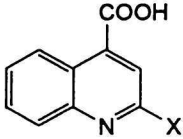
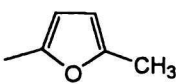
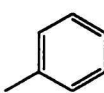
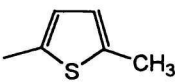
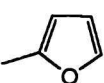
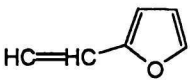
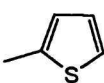
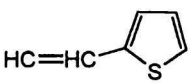
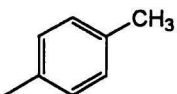
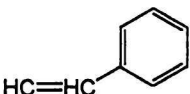
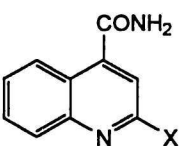
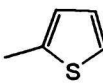
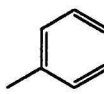
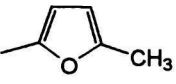
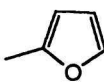
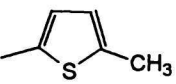
from molecular ion [6]. The fragment ion $[M - CO]^+$ further loses \cdot OH from carboxyl group to yield $[M - 45]^+$. All of the above described fragmentation pathways were confirmed by the metastable transitions. The similar fragmentation is proposed in *V*, which further loses the \cdot CH₃ radical from $[M - CO_2]^+$ to give the ion at m/z 204. The other fragmentation of the molecular ion is in *VI* with 2-methylfuroyl substituent, which after the loss of \cdot CH₃ radical from $M^{+\bullet}$ follows the CO expulsion to form the fragment ion at m/z 210. The usual loss of \cdot CHO from $M^{+\bullet}$ gives $[M - 29]^+$ at m/z 224. In case of *VII* with 2-methylthiophene substituent, the relative abundances of all fragment ions have mostly a lower intensity apart from $[M - \cdot H]^+$ at m/z 268 (30 %).

The loss of the hydrogen radical from the molecular ions is the leading process to the base peaks in cases of *IX* and *X*. The elimination of the radical \cdot COOH from $M^{+\bullet}$ shows a rise in the second most abundant fragment ions $[M - \cdot COOH]^+$ at m/z 236 and m/z 230, respectively. In case of *VIII*, the presence of the furan ring enables the CO and CO + \cdot H losses from $M^{+\bullet}$ to yield the fragment ions at m/z 237 and m/z 236. The subsequent decomposition of the ion $[M - CO - \cdot H]^+$ shows a rise in the ion at m/z 191 by the elimination of the \cdot COOH radical. The relative abundant ion at m/z 211 is originated by the loss of 54 mass units (probably as C_3H_2O) from $M^{+\bullet}$. In this case, the metastable transition has not been found.

The mass spectra of some amides of the quinoline-4-carboxylic acids *XI–XVI* are also given in Table 2. The molecular ions represent the base peaks in the

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Table 1. Compounds Studied

			
Compound	X	Compound	X
I	CH ₃	VI	
II		VII	
III		VIII	
IV		IX	
V		X	
			
Compound	X	Compound	X
XI	CH ₃	XIV	
XII		XV	
XIII		XVI	

electron impact mass spectra of all studied amides. The general fragmentation pathway includes the elimination of 44 mass units from the molecular ions to produce the fragment ions $[M - \cdot\text{NH}_2 - \text{CO}]^+$. From this species the subsequent loss of HCN is noticeable only in XI and the fragment ion $[M - \cdot\text{NH}_2]^+$ itself as well. The other principal fragment ions depend on the substituents X and are formed in a manner similar to that described above for the quinoline-4-carboxylic acids. All of the above fragmentation pathways described were confirmed by the metastable transitions.

EXPERIMENTAL

The EI mass spectra (low resolution) were recorded on MS 25 RFA (Kratos Analytical, Manchester) gas chromatograph/mass spectrometer/data system using a direct probe heated to the suitable temperature. The ionizing energy was maintained at 70 eV and the electron current was 100 μA . The temperature of the ion source was kept at 473 K.

The compounds studied in the present paper were synthesized using Pfitzinger reaction [7, 8].

Table 2. EI Mass Spectra of Compounds I—XVI

Compound	<i>m/z</i> (relative abundance/%) ^a
I	188 (13), 187 M ⁺ · (100), 143 (8), 142 (15), 141 (7), 116 (4), 115 (8), 101 (12), 75 (11), 63 (4), 51 (8), 39 (4).
II	250 (18), 249 M ⁺ · (100), 248 (8), 206 (4), 205 (30), 204 (53), 203 (16), 202 (4), 176 (5), 168.5 (5), 124.5 (6), 102 (9), 101.5 (6), 101 (12), 88 (6), 75 (14), 51 (10).
III	240 (16), 239 M ⁺ · (100), 238 (18), 211 (11), 210 (9), 195 (4), 194 (5), 166 (10), 140 (5), 139 (5), 119.5 (5), 101 (7), 75 (9), 63 (4), 51 (6), 39 (6).
IV	257 (7), 256 (17), 255 M ⁺ · (100), 211 (20), 210 (22), 209 (10), 127.5 (6), 105 (4), 101 (9), 75 (11), 51 (7).
V	264 (18), 263 M ⁺ · (100), 262 (9), 220 (4), 219 (25), 218 (27), 217 (16), 216 (8), 204 (12), 203 (5), 131.5 (4), 108.5 (9), 101 (7), 91 (6), 89 (4), 75 (11), 51 (8), 39 (4).
VI	254 (16), 253 M ⁺ · (100), 252 (9), 238 (22), 224 (15), 210 (8), 128 (4), 126.5 (5), 101 (5), 75 (6), 53 (8), 51 (6), 43 (10).
VII	271 (6), 270 (18), 269 M ⁺ · (100), 268 (30), 267 (4), 225 (5), 224 (10), 223 (5), 134.5 (6), 111.5 (5), 97 (7), 75 (7).
VIII	266 (15), 265 M ⁺ · (100), 248 (16), 237 (21), 236 (57), 235 (13), 224 (23), 211 (65), 191 (33), 190 (23).
IX	282 (14), 281 M ⁺ · (58), 280 (100), 249 (5), 248 (12), 236 (14), 237 (7), 236 (5), 224 (4), 204 (6), 191 (4), 131.5 (8), 128 (5), 117.5 (10), 117 (6), 101 (5), 95.5 (8), 75 (7), 51 (5).
X	276 (10), 275 M ⁺ · (56), 274 (100), 231 (25), 230 (83), 229 (24), 228 (13), 202 (6), 129 (5), 128.5 (6), 128 (10), 115 (10), 114.5 (12), 114 (19), 102 (11), 101 (11), 77 (9), 76 (5), 75 (10), 63 (4), 51 (12), 50 (4).
XI	187 (12), 186 M ⁺ · (100), 185 (19), 171 (4), 170 (30), 169 (6), 168 (7), 143 (12), 142 (56), 141 (8), 140 (7), 116 (7), 115 (12), 102 (4), 101 (22), 93 (7), 76 (4), 75 (19), 74 (6), 63 (6), 51 (13), 50 (5), 39 (6).
XII	249 (17), 248 M ⁺ · (100), 247 (10), 231 (5), 230 (12), 229 (8), 220 (12), 219 (5), 206 (10), 205 (71), 204 (63), 177 (8), 176 (11), 124 (6), 102 (8), 101.5 (4), 101 (10).
XIII	239 (15), 238 M ⁺ · (100), 237 (14), 222 (7), 220 (7), 210 (5), 209 (4), 194 (21), 166 (11), 164 (4), 140 (7), 139 (7), 119 (6), 110 (9), 101 (8), 95 (21), 83 (5), 75 (11), 51 (7), 39 (10).
XIV	256 (6), 255 (17), 254 M ⁺ · (100), 253 (8), 238 (7), 236 (5), 211 (10), 210 (32), 209 (13), 166 (4), 127 (8), 105 (6), 101 (11), 75 (13), 51 (7), 39 (4).
XV	253 (17), 252 M ⁺ · (100), 251 (8), 237 (23), 223 (11), 209 (8), 208 (9), 180 (5), 128 (5), 126 (6), 101 (8), 75 (9), 53 (8), 51 (7), 43 (13), 39 (4).
XVI	270 (6), 269 (18), 268 M ⁺ · (100), 267 (23), 250 (8), 225 (4), 224 (13), 223 (11), 222 (5), 134 (6), 111.5 (6), 101 (6), 97 (5), 75 (7), 51 (4).

^a) All peaks greater than 4 % of the base peak (100 %) are recorded.

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