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MASS SPECTROMETRY OF SOME N-TRYPTOPHYL-4-THIAZOLIDINONE AND N-TRYPTOPHYL-5-BENZYLIDENE-4-THIAZOLIDINONE DERIVATIVES

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**MASS SPECTROMETRY OF SOME
N-TRYPTOPHYL-4-THIAZOLIDINONE
AND N-TRYPTOPHYL-5-BENZYLIDENE-4-
THIAZOLIDINONE DERIVATIVES**

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ABSTRACT

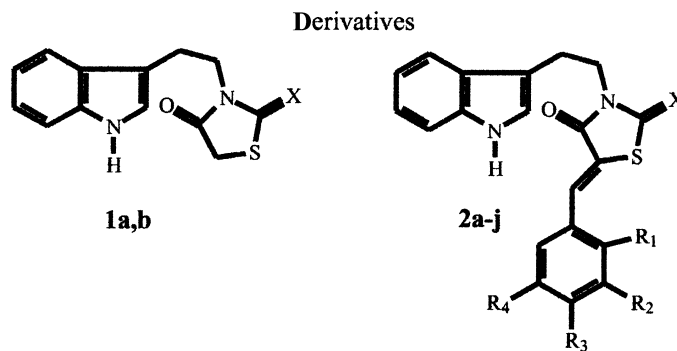
The electron impact mass spectrometry data are reported for 12 compounds of a series of N-tryptophyl-4-thiazolidinone and N-tryptophyl-5-benzylidene-4-thiazolidinone derivatives synthesized in our laboratory.

Key Words: Mass spectra; N-tryptophyl-5-benzylidene-4-thiazolidinone; N-tryptophyl-4-thiazolidinone

INTRODUCTION

Thiazolidinones are heterocyclic compounds having antimicrobial¹, hypoglycemic^{2,3} and anti-inflammatory⁴ activities. A search for new active compounds, using the method of molecular variation, led us to synthesize two new series of 4-thiazolidinones⁵, N-tryptophyl-4-thiazolidinones 1a,b and N-tryptophyl-5-benzylidene-4-thiazolidinones 2a-j (Table 1). This paper reports the possible fragmentation patterns of these compounds by electron-impact mass spectrometry.

Table 1. N-Tryptophyl-4-thiazolidinone and N-Tryptophyl-5-benzylidene-4-thiazolidinone Derivatives



Compounds	X	R ₁	R ₂	R ₃	R ₄	Formula	M
1a	O					C ₁₃ H ₁₂ N ₂ O ₂ S	260
1b	S					C ₁₃ H ₁₂ N ₂ OS ₂	276
2a	O	H	H	OCH ₃	H	C ₂₁ H ₁₈ N ₂ O ₃ S	378
2b	O	H	H	Cl	H	C ₂₀ H ₁₅ ClN ₂ O ₂ S	382
2c	O	OCH ₃	H	OCH ₃	H	C ₂₂ H ₂₀ N ₂ O ₄ S	408
2d	O	Cl	H	Cl	H	C ₂₀ H ₁₄ Cl ₂ N ₂ O ₂ S	416
2e	O	H	C(CH ₃) ₃	OH	C(CH ₃) ₃	C ₂₈ H ₃₂ N ₂ O ₃ S	476
2f	S	H	H	OCH ₃	H	C ₂₁ H ₁₈ N ₂ O ₂ S ₂	394
2g	S	H	H	Cl	H	C ₂₀ H ₁₅ ClN ₂ OS ₂	398
2h	S	OCH ₃	H	OCH ₃	H	C ₂₂ H ₂₀ N ₂ O ₃ S ₂	424
2i	S	Cl	H	Cl	H	C ₂₀ H ₁₄ Cl ₂ N ₂ OS ₂	432
2j	S	H	C(CH ₃) ₃	OH	C(CH ₃) ₃	C ₂₈ H ₃₂ N ₂ O ₂ S ₂	492



EXPERIMENTAL

Electron impact mass spectra were recorded using a ION-TRAP FINNIGAN MAT GCQ instrument operating at 70 eV ionizing energy. Samples were introduced by using a direct inlet system with a source temperature of 175°C.

RESULTS AND DISCUSSION

Plausible fragmentation pathways consistent with the spectral data and structures are suggested for fragment ions and are shown in Schemes 1 and 2.

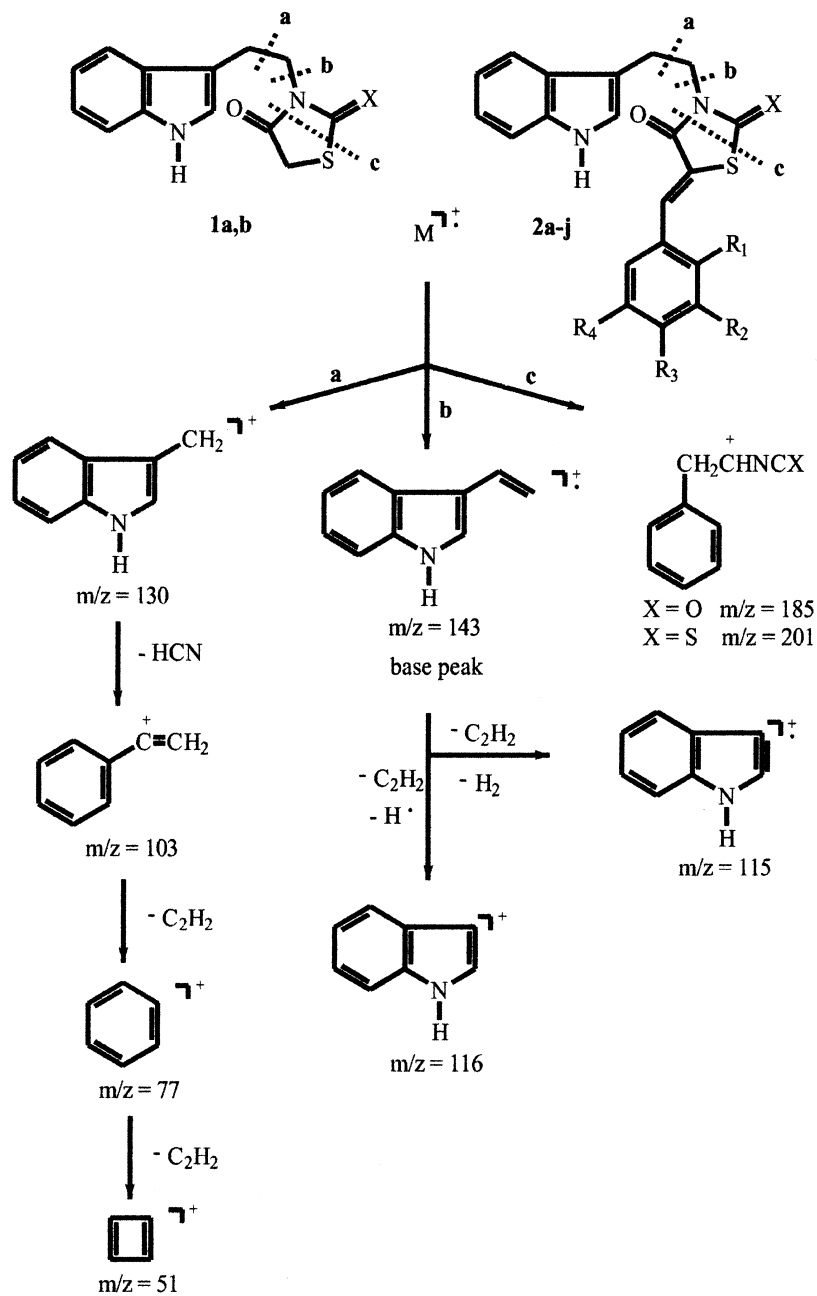
Significant peaks in the EI mass spectra of the compounds examined are shown in Tables 2 and 3. The molecular peak is generally weak or moderate in all compounds. The isotopic fragment $M + 2$ denotes the presence of sulfur and chlorine atoms. The observed fragmentation processes in the spectra of compounds N-tryptophyl-4-thiazolidinones 1a-b, are similar to those observed in N-tryptophyl-5-benzylidene-4-thiazolidinone derivatives 2a-J. The decomposition occurs according to four main pathways as shown below.

In path a, the ion at m/z 130 is the β -cleavage product of the indole ring. This ion leads to a fragment at m/z 103 by loss of HCN. Further, this ion presumably gives the peaks at m/z 77 and m/z 51 by two subsequent elimination of 26 units (C_2H_2).

According to path b the base peak m/z 143 appears to come from the scission of the indole ring γ -bond. This fragment can eliminate one molecule of ethene and hydrogen radical or molecular hydrogen leading to the ions m/z 116 and m/z 115, respectively.

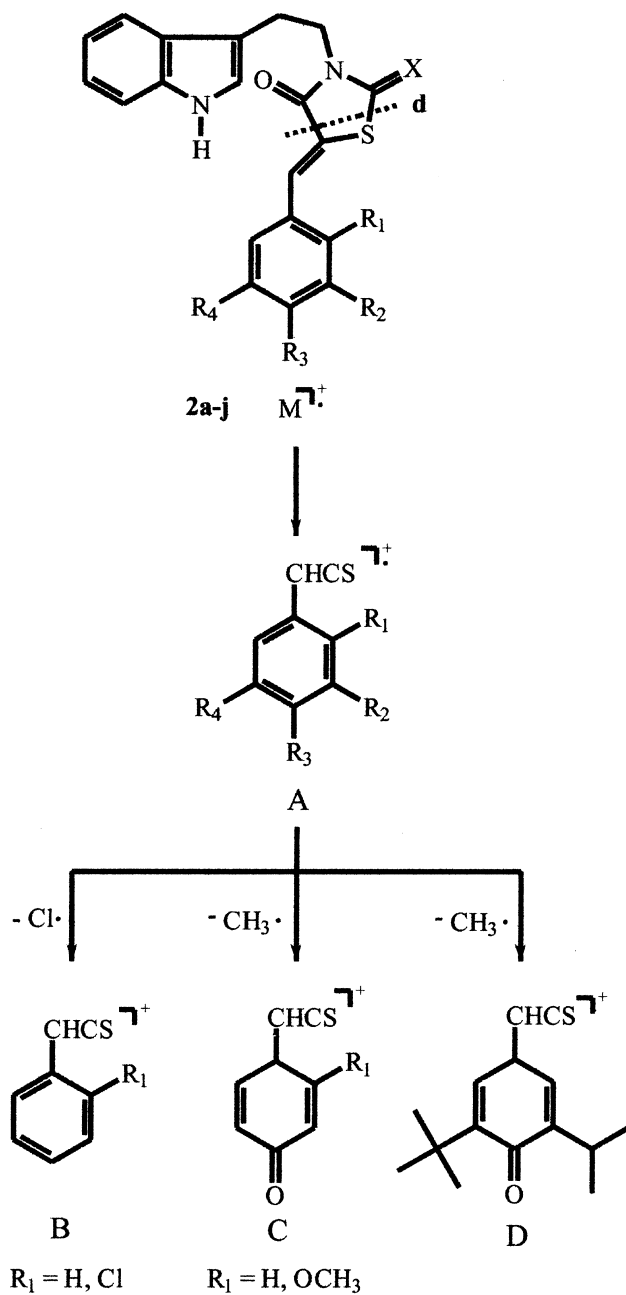
There are two fragmentation patterns of the 4-thiazolidinone ring. In path c, a cleavage of the α sulfur-carbon single bond in this heterocyclic ring and cleavage of γ nitrogen-carbon single bond leading to the formation of the ions at m/z 185 ($X=O$) and at m/z 201 ($X=S$) occurs for all compounds. For the 5-benzylidene derivatives the most fragmented route of the 4-thiazolidinone ring is shown in path d. This fragmentation is based on the α sulfur-carbon and γ carbon-carbon double cleavage to give ion A. This degradation pattern seems to be similar for various imidazolidinedione and thiazolidinedione congeners⁶⁻⁹. The compounds that contain a chlorine atom or a methoxy group at para-position (R_3) may give ions at m/z 133 (B) and at m/z 149 (C), by the loss of a chlorine atom or a methyl radical, respectively. In the same way,





Scheme 1.





Scheme 2.



Table 2. Main Fragments (m/z) and Their Relative Abundances for Paths a, b, and c

Compound	m/z (%)									
	M^+	201	185	143	130	116	115	103	77	51
1a	260(28)		1.00	100	86.57	5.04	7.70	7.67	7.77	2.96
1b	276(6.5)	3.00		100	8.44	4.40	8.23	5.30	2.39	1.06
2a	378(11)		2.26	100	16.56	5.56	5.85	2.03	3.84	1.52
2b	382(18)		0.80	100	2.30	6.68	7.00	4.05	4.05	2.26
2c	408(19)		1.57	100	12.48	4.33	3.94	2.08	2.38	0.50
2d	416(9.5)		1.70	100	43.48	7.87	11.27	6.04	7.05	3.70
2e	476(8.8)		2.48	100	14.39	2.24	2.49	1.14	1.05	
2f	394(7.5)	0.50		100	3.00	7.19	3.37	1.44	2.00	1.00
2g	398(4.0)	1.00		100	12.56	10.30	14.13	2.00	3.66	1.45
2h	424(7.0)	0.50		100	3.76	4.82	5.03	1.04	1.59	0.50
2i	432(7.4)	1.00		100	33.04	11.25	10.91	5.65	6.22	1.45
2j	492(1.5)	1.52		100	4.69	3.03	3.72	0.50	1.00	

Table 3. Main Fragments (m/z) and Their Relative Abundances for Path d

Compounds	m/z (%)			
	A	B	C	D
2a	164 (3.44)		149 (4.33)	
2b	168 (3.60)	133 (2.00)		
2c	194 (14.24)		179 (5.08)	
2d	202 (0.50)	167 (1.50)		
2e	262 (11.30)			247 (2.91)
2f	164 (5.50)		149 (3.97)	
2g	168 (3.48)	133 (1.45)		
2h	194 (19.40)		179 (5.11)	
2i	202 (4.68)	167 (3.55)		
2j	262 (21.41)			247 (5.04)

bis-substituted compounds give m/z 167 (B) when $R_1=R_2=Cl$ and m/z 179 (C) when $R_1=R_2=OCH_3$. The ion D (m/z 247) is formed by the loss of a methyl radical from tert-butyl group at the meta-position followed by hydrogen radical migration.



CONCLUSION

The compounds, in this study, showed spectra with similar peak profiles. The fragmentation occurs according to four important cleavage processes. All compounds show the same base peak at m/z 143.

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