MASS SPECTROMETRY FOR ANALYSIS OF MONOHYDRIC PHENOLS

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Mass spectrometry behaviour of monohydric phenols is discussed, and so far unpublished mass spectra of 32 monohydric phenols C_9 to C_{18} are given.

Phenols are widely used raw materials in modern petrochemical industry. Many compounds derived from phenols also are final products used as antioxidants, insecticides, disinfectants, fungicides *etc.* On the other hand, their significant amounts also are present in wastes of petrochemical and energetical complexes. Decontamination of phenolic wastes presents serious problems to many industrial processes. Of course, the first prerequisite of competent control of phenolic compounds in general consists in sufficiently sensitive and selective analytical method. Advantages and disadvantages of various separation and identification methods were discussed in ref.[1] in detail. Mass spectrometry belongs to the most effective methods (sensitivity and versatility) especially so if combined directly with gas chromatography (GC-MS). In our opinion there are relatively few published data about mass spectrometry of phenols, which prevents full use of GC-MS in everyday analytical practice.

The published mass spectra of monohydric phenols were arranged in tables[2,3] to make solution of individual analytical tasks easier and faster. The reports[2,3] are now extended by 32 not yet published spectra of monohydric phenols C_9 to C_{18} given in Table I.

EXPERIMENTAL

Set of the Used Standard Compounds

Most of the substances used are commercial samples. The following compounds were synthetized in our laboratory: 2-ethyl-6-methylphenol, 2-ethyl-4,5-dimethylphenol, 2-methyl-4-n-propylphenol, 2-methyl-6-n-propylphenol, 3-methyl-6-n-propylphenol, 2- and 4-isobutylphenol, 2- and 4-n-hexylphenol. These compounds were prepared by reduction of the respective aromatic hydroxy ketones with gaseous hydrogen under pressure at enhanced temperature with catalysis of MoS_2 (ref.[4]). The starting aromatic hydroxy ketones were obtained from the corresponding esters or alkyl esters by the Fries reaction.

TABLE I

So far Not Published Mass Spectra of Monohydric Phenols

2-Ethyl-5-methylphenol, $C_9H_{12}O$, 136

m/e	137	136	135	134	122	121	120	119
rel. int.	4	36	4	1	10	100	1	1
m/e	117	115	108	107	105	103	102	94
rel. int.	3	4	1	4	2	3	1	1
m/e	93	92	89	79	78	77	67	66
rel. int.	7	3	20	2	3	19	3	2
m/e	65	63	62	60	55	53	52	51
rel. int.	8	4	2	1	2	6	3	8
m/e	50	43	41	40	39	38		
rel. int.	3	2	5	2	11	2		

4-Ethyl-3-methylphenol, $C_9H_{12}O$, 136

m/e	136	135	133	125	122	121	120	119
rel. int.	28	2	1	4	10	100	2	1
m/e	117	115	108	107	105	103	102	94
rel. int.	1	2	1	3	2	3	1	1
m/e	93	92	91	89	81	79	78	77
rel. int.	2	2	15	1	1	3	3	15
m/e	76	75	74	65	64	63	62	55
rel. int.	1	1	1	5	1	3	1	3
m/e	53	52	51	50	45	43	41	40
rel. int.	5	3	7	3	1	2	4	2
m/e	39	38						
rel. int.	10	1						

2-Ethyl-6-methylphenol, $C_9H_{12}O$, 136

m/e	137	136	135	122	121	119	118	117
rel. int.	4	34	3	10	100	1	1	4
m/e	116	115	108	107	105	103	102	94
rel. int.	1	4	2	5	2	4	1	1
m/e	93	92	91	90	89	79	78	77
rel. int.	7	4	27	1	2	5	6	29
m/e	76	75	74	67	66	65	64	63
rel. int.	1	1	1	4	3	10	1	6
m/e	62	60·5	55	53	52	51	50	43
rel. int.	2	1	3	9	5	13	5	4
m/e	41	40	39	38				
rel. int.	8	3	20	3				

TABLE I
(*Continued*)

2-n-Propylphenol, $C_9H_{12}O$, 136

m/e	137	136	135	121	120	119	117	115
rel. int.	3	30	2	1	1	1	1	2
m/e	108	107	105	103	94	92	91	90
rel. int.	10	100	2	1	2	1	5	1
m/e	89	80	79	78	77	76	75	74
rel. int.	2	1	14	6	22	1	2	1
m/e	73	66	65	64	63	62	59	55
rel. int.	1	2	4	1	3	13	1	2
m/e	53	52	51	50	45	43	41	40
rel. int.	5	4	8	3	2	2	3	2
m/e	39	38	32	31				
rel. int.	11	2	1	1				

3-n-Propylphenol, $C_9H_{12}O$, 136

m/e	137	136	122	121	120	115	109	108
rel. int.	4	36	2	15	1	1	4	49
m/e	107	105	103	95	94	93	92	91
rel. int.	100	1	3	1	7	2	1	6
m/e	90	89	81	80	79	78	77	75
rel. int.	2	2	2	2	10	7	30	2
m/e	74	67	66	65	64	63	62	55
rel. int.	1	2	3	7	2	6	2	5
m/e	53	52	51	50	43	41	40	39
rel. int.	8	5	11	4	2	7	3	2
m/e	38	32						
rel. int.	4	2						

4-n-Propylphenol, $C_9H_{12}O$, 136

m/e	137	136	135	133	121	120	119	117
rel. int.	3	21	5	2	2	2	1	1
m/e	115	108	107	105	103	94	93	91
rel. int.	2	9	100	2	2	2	1	4
m/e	89	81	79	78	77	75	67	66
rel. int.	1	1	4	5	15	1	1	2
m/e	65	64	63	62	59	55	53	52
rel. int.	4	1	3	1	1	3	5	3
m/e	51	50	45	43	41	40	31	
rel. int.	6	3	2	2	3	1	1	

TABLE I
(*Continued*)

3-Isopropylphenol, $C_9H_{12}O$, 136

m/e	137	136	135	121	120	119	108	107
rel. int.	4	33	2	100	3	2	2	7
m/e	104	103	95	94	93	92	91	89
rel. int.	2	18	4	5	10	4	22	3
m/e	79	78	77	75	74	67	66	65
rel. int.	4	4	31	2	2	3	5	15
m/e	64	63	62	61	59	55	53	52
rel. int.	3	8	3	3	3	6	8	4
m/e	51	50	43	42	41	40	39	38
rel. int.	12	5	5	2	15	5	32	6
m/e	37							
rel. int.	2							

4,5-Dimethyl-2-ethylphenol, $C_{10}H_{14}O$, 150

m/e	151	150	149	136	135	133	131	121
rel. int.	5	38	4	11	100	2	2	7
m/e	119	117	116	115	107	106	105	103
rel. int.	1	3	2	4	7	2	7	3
m/e	93	92	91	89	80	79	78	77
rel. int.	2	3	23	1	1	11	3	11
m/e	75	74	68	67	66	65	64	63
rel. int.	1	1	2	2	3	8	2	4
m/e	62	58	55	53	52	51	50	43
rel. int.	1	1	3	7	3	8	3	3
m/e	41	40	39	38				
rel. int.	9	3	16	2				

2-Methyl-4-propylphenol, $C_{10}H_{14}O$, 150

m/e	151	150	149	135	134	133	122	121
rel. int.	2	19	1	1	1	1	10	100
m/e	120	115	107	106	105	103	102	93
rel. int.	2	1	1	3	1	2	1	1
m/e	92	91	89	73	72	71	67	66
rel. int.	2	9	1	2	3	12	1	1
m/e	65	64	63	62	55	53	51	50
rel. int.	4	1	2	1	2	3	5	2
m/e	43	41	40	39	38			
rel. int.	2	4	1	7	1			

TABLE I
(*Continued*)

4-Methyl-2-propylphenol, $C_{10}H_{14}O$, 150

m/e	151	150	149	148	135	134	133	121
rel. int.	3	27	1	1	1	1	2	1
m/e	121	120	119	117	116	115	108	107
rel. int.	100	2	1	1	1	2	2	4
m/e	105	103	94	93	92	91	89	79
rel. int.	2	2	1	6	3	16	2	3
m/e	78	77	67	66	65	64	63	62
rel. int.	4	18	1	1	5	1	3	1
m/e	58	55	53	52	51	48	44	43
rel. int.	5	2	4	3	6	2	2	18
m/e	42	41	40	39	38			
rel. int.	2	5	1	8	1			

2-Methyl-6-propylphenol, $C_{10}H_{14}O$, 150

m/e	151	150	122	121	115	107	92	91
rel. int.	3	23	11	100	3	4	3	20
m/e	89	79	78	77	65	63	55	53
rel. int.	2	3	5	23	7	4	2	7
m/e	52	51	50	43	41	40	39	
rel. int.	3	7	3	3	6	2	14	

3-Methyl-6-propylphenol, $C_{10}H_{14}O$, 150

m/e	151	150	149	135	134	133	131	129
rel. int.	10	65	2	9	2	2	1	1
m/e	128	123	122	121	120	119	117	116
rel. int.	1	2	26	100	2	2	2	3
m/e	115	108	107	105	103	102	94	93
rel. int.	5	3	7	4	4	1	2	12
m/e	92	91	90	89	79	78	77	76
rel. int.	6	35	2	3	6	10	41	1
m/e	75	67	66	65	64	63	62	55
rel. int.	2	2	3	12	2	6	2	4
m/e	53	52	51	50	43	41	40	39
rel. int.	10	5	12	4	2	10	3	16
m/e	38							
rel. int.	2							

TABLE I
(*Continued*)

2,3,5,6-Tetramethylphenol, $C_{10}H_{14}O$, 150

m/e	151	150	149	136	135	133	131	122
rel. int.	9	75	15	11	100	3	3	3
m/e	121	117	116	115	109	103	107	146
rel. int.	4	10	3	5	3	12	3	12
m/e	104	93	92	91	79	78	77	75
rel. int.	3	5	3	25	14	5	15	3
m/e	74	67	66	65	64	63	55	53
rel. int.	2	6	4	10	3	6	6	11
m/e	52	51	50	43	41	40	39	
rel. int.	5	12	4	12	16	5	23	

2,5-Diethylphenol, $C_{10}H_{14}O$, 150

m/e	151	150	149	136	135	134	133	131
rel. int.	4	35	3	15	100	2	5	2
m/e	122	121	120	117	116	115	108	107
rel. int.	4	28	5	4	3	6	2	12
m/e	106	105	104	103	102	94	93	92
rel. int.	1	6	1	8	1	1	5	5
m/e	91	90	89	87	79	78	77	75
rel. int.	25	1	4	1	11	4	17	2
m/e	73	67	66	65	63	59	55	53
rel. int.	2	2	2	8	4	2	5	6
m/e	52	51	50	45	43	41	39	
rel. int.	3	9	3	7	5	7	12	

3,4-Diethylphenol, $C_{10}H_{14}O$, 150

m/e	151	150	149	136	135	134	133	131
rel. int.	5	37	2	11	100	2	5	2
m/e	122	121	120	119	117	116	115	108
rel. int.	3	20	5	2	9	2	8	2
m/e	107	105	104	94	93	92	91	89
rel. int.	13	7	6	2	4	4	24	2
m/e	80	78	77	65	64	63	55	53
rel. int.	8	4	15	8	1	4	5	6
m/e	52	51	50	45	43	41	40	39
rel. int.	3	8	2	3	3	6	2	11
m/e	38							
rel. int.	1							

TABLE I
(*Continued*)

2-n-Butylphenol, $C_{10}H_{14}O$, 150

m/e	151	150	133	131	122	121	120	119
rel. int.	3	22	1	1	1	3	1	1
m/e	115	109	108	107	105	103	93	92
rel. int.	1	1	14	100	1	2	1	1
m/e	91	90	89	80	79	78	77	76
rel. int.	5	1	1	1	11	5	18	1
m/e	75	65	64	63	62	58	55	53
rel. int.	1	3	1	3	1	5	2	4
m/e	52	51	50	43	42	41	40	39
rel. int.	3	6	2	17	2	2	1	9
m/e	38							
rel. int.	2							

3-n-Butylphenol, $C_{10}H_{14}O$, 150

m/e	151	150	135	133	131	122	121	120
rel. int.	3	22	1	1	1	1	7	2
m/e	115	108	107	106	105	94	93	92
rel. int.	1	100	53	2	1	1	3	1
m/e	91	90	89	81	80	79	78	77
rel. int.	7	3	1	2	3	9	5	24
m/e	75	67	66	65	64	63	62	55
rel. int.	1	1	2	6	2	4	1	5
m/e	53	52	51	50	43	41	40	39
rel. int.	6	3	7	2	4	8	2	17
m/e	38							
rel. int.	2							

4-n-Butylphenol, $C_{10}H_{14}O$, 150

m/e	151	150	136	133	121	120	108	107
rel. int.	2	17	1	1	5	1	10	100
m/e	105	103	94	93	92	91	89	81
rel. int.	1	1	2	1	1	3	1	7
m/e	79	78	77	75	67	66	65	64
rel. int.	2	4	13	1	1	1	4	1
m/e	63	62	55	53	52	51	50	43
rel. int.	2	1	3	4	2	4	1	1
m/e	41	40	39	38				
rel. int.	3	1	7	1				

TABLE I
(*Continued*)

2-Isobutylphenol, $C_{10}H_{14}O$, 150

m/e	151	150	135	133	121	119	117	115
rel. int.	3	25	1	2	1	2	2	3
m/e	109	108	107	105	94	91	90	89
rel. int.	2	22	100	2	1	5	2	2
m/e	80	79	78	77	75	67	65	63
rel. int.	2	11	5	17	1	1	3	3
m/e	54	52	51	50	44	43	41	39
rel. int.	3	4	5	2	1	6	7	9

4-Isobutylphenol, $C_{10}H_{14}O$, 150

m/e	151	150	149	135	133	123	122	121
rel. int.	2	17	2	1	1	2	5	6
m/e	115	109	108	107	106	105	103	93
rel. int.	1	1	11	100	1	1	1	3
m/e	94	91	89	81	79	78	77	75
rel. int.	2	2	1	1	3	4	13	1
m/e	66	65	64	63	62	55	53	52
rel. int.	2	5	1	3	1	3	4	3
m/e	51	50	49	43	41	40	39	38
rel. int.	5	2	2	4	5	2	10	2

2-Ethyl-5-n-propylphenol, $C_{11}H_{16}O$, 164

m/e	165	164	163	150	149	147	136	135
rel. int.	9	62	2	13	94	2	22	100
m/e	134	133	131	128	122	121	120	119
rel. int.	3	7	2	2	6	34	11	2
m/e	117	116	115	108	107	105	103	93
rel. int.	7	4	13	4	33	7	7	10
m/e	92	91	90	89	79	78	77	69
rel. int.	10	33	2	3	15	6	21	2
m/e	67	65	63	55	53	52	51	50
rel. int.	3	11	6	9	7	4	11	3
m/e	43	41	40	39				
rel. int.	10	14	2	15				

TABLE I
(*Continued*)

2-Ethyl-5-n-butylphenol, $C_{12}H_{18}O$, 178

m/e	179	178	177	164	163	162	150	149
rel. int.	7	52	3	8	47	3	3	9
m/e	147	137	136	135	134	133	131	122
rel. int.	3	12	100	74	5	10	3	6
m/e	121	120	119	117	116	115	108	107
rel. int.	42	11	16	9	4	13	14	64
m/e	105	103	93	92	91	89	79	78
rel. int.	10	11	10	9	41	7	16	7
m/e	77	73	65	63	59	58	57	55
rel. int.	26	7	11	5	7	10	5	10
m/e	53	51	45	42	39	31		
rel. int.	8	10	20	4	18	11		

2-n-Hexylphenol, $C_{12}H_{18}O$, 178

m/e	179	178	133	121	120	119	115	109
rel. int.	3	16	1	1	2	1	1	1
m/e	108	107	105	94	93	91	91	79
rel. int.	11	100	1	2	1	2	1	2
m/e	78	77	66	65	64	55	53	52
rel. int.	3	9	1	2	1	2	2	1
m/e	51	43	42	41	40	39		
rel. int.	2	2	1	4	1	4		

4-Methyl-2-benzylphenol, $C_{14}H_{14}O$, 198

m/e	199	198	197	195	184	183	182	181
rel. int.	16	100	10	3	5	34	7	12
m/e	179	178	166	165	155	154	153	152
rel. int.	7	5	7	24	6	7	8	9
m/e	141	139	135	127	121	120	119	115
rel. int.	4	2	3	4	16	81	5	8
m/e	107	105	99	98	97	93	92	91
rel. int.	8	12	5	4	3	3	31	36
m/e	89	78	77	76	65	63	55	53
rel. int.	12	6	20	7	12	6	6	4
m/e	52	51	50	41	39	32	31	
rel. int.	3	11	3	4	10	24	46	

TABLE I
(*Continued*)

2,5-Ditert-butylphenol, $C_{14}H_{22}O$, 206

m/e	207	206	193	192	191	177	176	175
rel. int.	3	19	2	16	100	2	5	3
m/e	173	163	161	158	149	147	143	141
rel. int.	1	7	4	1	2	3	2	1
m/e	135	133	131	129	128	127	121	119
rel. int.	4	3	2	2	3	1	3	2
m/e	117	116	115	107	105	103	91	88
rel. int.	2	2	5	4	2	1	5	4
m/e	79	77	74	73	72	71	69	67
rel. int.	2	4	5	5	2	2	1	1
m/e	66	65	64	58	57	55	53	51
rel. int.	2	2	1	2	26	3	2	2
m/e	41							
rel. int.	13							

3,5-Ditert-butylphenol, $C_{14}H_{22}O$, 206

m/e	207	206	192	191	177	175	163	161
rel. int.	7	40	21	100	3	2	6	2
m/e	149	147	145	135	133	131	128	120
rel. int.	2	5	1	4	4	1	2	4
m/e	119	117	116	115	105	103	95	91
rel. int.	3	3	2	4	8	2	2	8
m/e	89	88	78	76	74	73	72	67
rel. int.	3	7	4	7	9	7	2	2
m/e	66	65	64	63	57	55	51	43
rel. int.	4	4	2	5	25	6	2	3
m/e	41	39						
rel. int.	24	7						

4-Tert-octylphenol, $C_{14}H_{22}O$, 206

m/e	207	206	150	137	136	135	134	133
rel. int.	1	4	1	1	11	100	3	1
m/e	121	120	119	115	108	107	106	105
rel. int.	1	1	3	1	1	13	1	1
m/e	95	94	92	91	89	79	78	77
rel. int.	5	1	1	4	1	1	1	4

TABLE I
(*Continued*)

4-Tert-octylphenol, $C_{14}H_{20}O$, 206

m/e	65	63	58	57	56	55	53	52
rel. int.	3	1	1	14	1	3	1	1
m/e	51	43	42	41	40	39		
rel. int.	1	2	1	15	1	5		

4-Methyl-2-tert-octylphenol, $C_{15}H_{24}O$, 220

m/c	221	220	165	163	161	159	150	149
rel. int.	1	7	1	1	1	1	12	100
m/e	148	147	135	133	131	129	128	127
rel. int.	4	3	3	4	2	2	2	1
m/e	122	121	119	117	116	115	109	108
rel. int.	3	36	2	2	5	6	3	1
m/e	107	106	104	103	93	92	91	79
rel. int.	3	1	1	2	1	1	11	4
m/e	78	77	65	63	57	56	55	53
rel. int.	2	8	5	2	18	3	5	4
m/e	51	43	41	39				
rel. int.	3	6	21	7				

2-Methyl-4-tert-octylphenol, $C_{15}H_{24}O$, 220

m/e	221	220	205	151	150	149	148	147
rel. int.	1	8	1	1	12	100	5	1
m/e	135	134	133	132	131	122	121	120
rel. int.	1	1	4	1	1	1	10	1
m/e	119	117	116	115	109	108	107	105
rel. int.	1	1	1	1	5	1	2	3
m/e	103	94	93	92	91	89	81	79
rel. int.	1	1	1	1	5	1	1	2
m/e	78	77	67	65	63	58	57	56
rel. int.	1	5	1	2	1	1	11	1
m/e	55	53	52	51	43	41	39	
rel. int.	3	2	1	1	3	13	4	

2-Methyl-6-tert-octylphenol, $C_{15}H_{24}O$, 220

m/e	221	220	151	150	149	148	147	135
rel. int.	2	13	1	14	100	2	1	3

TABLE I
(*Continued*)

2-Methyl-6-tert-octylphenol, $C_{15}H_{24}O$, 220

m/e	134	133	131	129	128	124	123	122
rel. int.	1	3	2	2	1	5	4	3
m/e	121	119	116	117	115	109	108	107
rel. int.	23	1	1	4	4	2	1	2
m/e	106	105	103	95	93	92	91	79
rel. int.	1	5	1	1	1	1	8	3
m/e	78	77	69	67	65	57	56	55
rel. int.	2	5	1	1	2	13	1	3
m/e	53	52	51	43	41	40	39	
rel. int.	3	1	2	4	12	1	5	

4-(2-Phenylisopropyl)phenol, $C_{15}H_{16}O$, 212

m/e	213	212	211	198	197	182	181	179
rel. int.	7	39	2	17	100	5	5	5
m/e	178	167	165	153	152	143	141	135
rel. int.	4	3	5	4	5	4	2	8
m/e	128	120	119	115	107	105	103	91
rel. int.	3	3	21	6	5	5	22	28
m/e	82	79	78	77	76	74	70	68
rel. int.	3	3	4	16	4	4	7	3
m/e	59	55	53	52	51	50	44	43
rel. int.	6	3	2	2	7	2	5	4
m/e	41	39						
rel. int.	9	8						

2,4,6-Tritert-butylphenol, $C_{18}H_{30}O$, 262

m/e	263	262	248	247	231	222	219	217
rel. int.	4	21	22	100	4	2	1	1
m/e	207	205	191	187	175	173	149	147
rel. int.	1	2	1	1	1	1	1	1
m/e	145	143	142	141	135	133	131	129
rel. int.	1	1	1	1	1	1	2	1
m/e	128	121	119	117	116	115	108	107
rel. int.	1	1	1	1	4	2	3	1
m/e	105	102	94	91	80	79	77	69
rel. int.	2	4	6	3	7	2	2	1

TABLE I
(*Continued*)

2,4,6-Tritertbutylphenol, $C_{18}H_{30}O$, 262

m/e	67	65	58	57	55	53	43	41
rel. int.	1	2	2	39	4	1	3	16
m/e	39							
rel. int.	2							

Measurement of Mass Spectra

All the mass spectra were recorded with a LKB 9000 Gas Chromatograph — Mass Spectrometer. Most standards were pure enough (over 98%), and their spectra were measured with the use of reservoir inlet of the mass spectrometer. Temperature of the reservoir was 150°C, pressure 10^{-2} Pa. Temperature of ionic source 250°C, pressure in the source 10^{-4} Pa. In several cases the standard was not pure enough, and the phenol had to be separated by has chromatography before mass spectrometry. In these cases a glass column (13·5 m × 3 mm) packed with 5% Silikon Gummi Merck was used with programmed temperature. The obtained spectra are summarized in Table I.

RESULTS AND DISCUSSION

The reports by Beynon and coworkers[5], Aczel and Lumpkin[6] and Budzikiewitz and coworkers[7] can be considered fundamental works dealing with study of fragmentation mechanisms of phenol and its derivatives. High relative intensity of molecular ions of monohydroxybenzenes is due to resonance structure of the excited molecules involving unpaired electrons at oxygen atom. For structure identification of alkylphenols the most important are the ions $(M-1)^+$, $(M-15)^+$ or further $(M-R)^+$. On the contrary, ions *m/e* 77 and its higher homologues are less important for structure determination. The ions $(M-H_2O)^+$ formed by α-splitting and proton transfer from the alkyl substituent have a certain diagnostic value for location of substituents. Intensity of these ions increases with decreasing distance between substituent and hydroxyl. Importance of the ions $(M—CO)^+$ and $(M—CHO)^+$ for structural characterization of alkyl phenols is questionable, besides that they are little intensive.

Molecular ions of phenols with long alkyl chains are decomposed at β-bond with respect to benzene ring. If the chain is long enough, the process is accompanied by hydrogen migration to the charged fragment. With isomeric alkylphenols differing in position of benzene ring on the alkyl chain ions of various mass are formed by β-splitting[8] (Table II). If the hydroxyphenyl group is attached to primary carbon

atom of the alkyl chain, then the most intensive peak in mass spectra of the *ortho* and *para* isomers has the mass 107. This finding was verified for alkylphenols containing 2 to 11 carbon atoms in the alkyl chain. In mass spectra of the corresponding *meta*-isomers the most intensive peak has *m/e* 108. According to the distance of the hydroxyphenyl group from the alkyl group, the maximum peaks remain for the ions produced by simple splitting of β-bond with respect to benzene ring (in case of *ortho* and *para* isomers). In case of *meta* isomers, the maximum or at least very important peaks are always those of the ions produced with the proton transfer.

Probability of C–C bond splitting at α-position to ring increases in the series *ortho*, *meta*, *para* isomer.

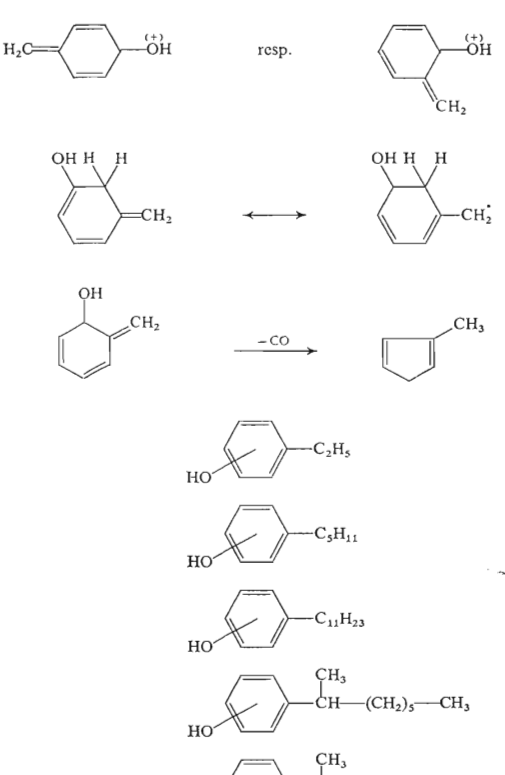
The mentioned published conclusions are based on evaluation of spectrometric data of a relatively small set of compounds. Although mass spectra of further alkylphenols were published later[9,10], they have not yet been evaluated in general structure-fragmentation correlations as far as we know. In this report a summary of mass-spectrometry behaviour of phenols is given.

Monoalkylphenols. Relative intensity of the molecular ions of alkylphenols decreases with increasing length of alkyl chain. Similar dependence on the chain length can be found with the alkyl ions (*m/e* 43, 57, 71 *etc.*), because these ions are generally very little populated. Fragmentation of alkylphenols does not much depend on length of the substituent. With all *ortho* and *para* ethyl-, propyl-, butyl- and hexylphenols the main ion of spectrum is *m/e* 107. n-Propyl- and higher *meta* alkylphenols form intensive ions *m/e* 108, their relative intensity being increased with increasing alkyl chain length (see spectra of 2-ethyl-5-n-propylphenol and 2-ethyl-5-n-butylphenol).

TABLE II

Mass Numbers of Ions Corresponding to Base Peak in Mass Spectra of Various Monoalkylphenols

Alkylphenol	Isomer		
	ortho	*meta*	*para*
$C_2H_5—C_6H_4—OH$	107	108	107
$C_5H_{11}—C_6H_4—OH$	107	108	107
$C_{11}H_{23}—C_6H_4—OH$	107	108	107
$CH_3(CH_2)_5CH(CH_3)—C_6H_4—OH$	121	—	121
$CH_3(CH_2)_4C(CH_3)_2—C_6H_4—OH$	135	—	135
$CH_3(CH_2)_4CH(C_2H_5)—C_6H_4—OH$	135	—	135



Their preferential formation from 3-alkylphenols is explained by the resonance structures[10]: Thus the ions *m/e* 108 have high diagnostic value for assignement of 3-alkyl substitution. Differentiation between 2- and 4-alkylphenols presents a rather

complicated problem. Although their mass spectra are very similar, we succeeded in finding a regularity differentiating between 2- and 4-monoalkylphenols. The ions *m/e* 79 are approximately five times less intensive with 4-alkylphenols than with 2-alkylphenols. Intensities of these ions *m/e* 79 of 3-alkylphenols are always between the respective values for the respective 2- and 4-isomers. In contrast to the rearrangement ions (*m/e* 108), the relative intensity of the ions *m/e* 79 does not depend on size of the alkyl. The above rule applies for methyl- and ethylphenols, too. Formation of the ions *m/e* 79 can be interpreted as elimination of CO group from the ion *m/e* 107 similar to splitting off of carbonyl from molecular ions of phenols[7]. The preferential interaction of hydroxyl with methyl group at 2-position represents then a reason of higher intensity of ions *m/e* 79 in the case of 2-alkylphenols.

Fragmentation of monoalkylphenols is markedly affected by branching of the alkyl chain, but only at α-position to the benzene ring. The main ion of the spectrum is always that one containing the larger alkyl, as it can be seen from spectra of tert-octylphenols. Chain branching at β and farther positions does not cause any characteristic splitting in mass spectra of the alkylphenols (compare the spectra of n-butyl- and isobutylphenols).

Polyalkylphenols. Predominant fragmentation of polyalkylphenols involves α-splitting in the alkyl substituent. Position of the substituent has no effect on fragmentation of methylalkylphenols, hence the mass spectra cannot be used for characterization of the position isomers. Another situation is encountered in determination of the substituent type. In this respect mass spectra can be interpreted unambiguously in most cases. Differentiation between polymethylphenols and methylethylphenols can present some difficulties, as the main ion of the spectra is always $(M-CH_3)^+$. In these cases the fact can be important that relative intensity of molecular ions increases with increasing number of methyl groups. The more highly substituted ethylphenols differ from the more highly substituted methylphenols by more intensive ions $(M-29)^+$. With more highly substituted alkylphenols the α-splitting is easier in the substituent having greater number of carbon atoms. For substituents above C_3 the spectra are complicated by the ions formed with simultaneous proton transfer, especially in the case of 3-substitution.

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