Mass Spectra of Chlorinated Aromatics Formed in Pulp Bleaching

2—Chlorinated Guaiacols

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The fragmentation of chlorinated guaiacols (2-methoxyphenols) on electron impact has been studied. The most common fragmentation processes are interpreted and in some cases the small differences between spectra of positional isomers are explained. In addition to the well-known alkyl-oxygen fission (loss of methyl radical), metastable ion studies and deuterium labelling have indicated several new fragmentation pathways. The most characteristic are the formation of $[M-CH_3-HCl]^+$ and $[M-CH_3-Cl]^{+\cdot}$ ions. In general, however, the spectra of positional isomers are shown to be very similar.

INTRODUCTION

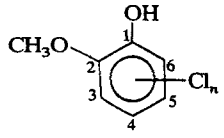
The positive ion mass spectrum of guaiacol has been reported previously, e.g. by Barnes and Occolowitz,[1] Thomas[2] and Kováčik *et al.*[3] The spectra of acetylated guaiacol and chlorinated guaiacols have been used for analysing individual guaiacols in spent bleach liquors from the pulp mills.[4,5] However, only partial mass spectral data of some non-derivatized chloroguaiacols have until now been reported.[6,7]

In Part 1 of our series[8] it was established that the influence of the position of the chloro substituents can be successfully used to distinguish the structural isomers of chlorinated catechols (1,2-dihydroxybenzenes). In this respect, one of the most characteristic fragment ions has been shown to be formed by loss of HCl molecule(s) from chlorocatechol[8] and chlorophenol[9] molecular ions. On the other hand, it has been reported that the most prominent primary fragmentation of guaiacol is the loss of the methyl radical. This ion, having a quinonoid structure, further fragmentates by subsequent losses of two CO molecules.[1,3] However, the remarkable loss of HCl molecule directly from the chloroguaiacol molecular ion has not been observed.[6,7]

The object of this study was, using a double focusing mass spectrometer and some deuterium-labelled compounds, to study new metastable transitions and to propose a more complete description of the competing fragmentation mechanisms of chloroguaiacols. So far as we know, any related study on these important chemicals has never been reported.

RESULTS AND DISCUSSION

The mass spectra of the following guaiacols were investigated: 3-chloroguaiacol (**1**), 4-chloroguaiacol (**2**), 5-chloroguaiacol (**3**), 6-chloroguaiacol (**4**), 3,4-dichloroguaiacol (**5**), 3,5-dichloroguaiacol (**6**), 3,6-dichloroguaiacol (**7**), 4,5-dichloroguaiacol (**8**), 4,6-dichloroguaiacol (**9**), 5,6-dichloroguaiacol (**10**), 3,4,5-trichloroguaiacol (**11**), 3,4,6-trichloroguaiacol (**12**), 3,5,6-trichloroguaiacol (**13**), 4,5,6-trichloroguaiacol (**14**) and tetrachloroguaiacol (**15**). The fragmentation of the monochlorinated trideuteriomethoxyphenols (**1'–4'**) was also studied.



[n = 1–4, **1–15**]

Figures 1 and 2 give the 70 eV mass spectra of **1**, **1'**, **2** and **2'**, and **7**, **8**, **13** and **15**. The most characteristic peaks in the spectra of **3–6**, **9–12** and **14** are given in Table 1. The fragmentation pathways of **7**, based on first FFR metastable ions, are presented in Scheme 1.

As can be seen in Fig. 1 and Table 1, the position of a chlorine substituent gives rise to negligible differences in the spectra of the positional isomers. Nearly similar spectra were detected for the compound pairs **1** and **4** and **2** and **3**. The peak at m/z 107 constitutes the greatest disparity between **1–4** (Fig. 1 and Table 1), the corresponding ion being formed by subsequent loss of $CH_3^{\cdot}$ ($CD_3^{\cdot}$) and HCl. On the other hand, the peak at m/z 108 $[M-CH_3-Cl]^{+\cdot}$, is clearly more abundant than the peak at m/z 107 in the spectra of **2** and **3**. With higher chlorinated guaiacols (**5–15**) the abundance ratios of these ions are not as characteristic for distinguishing the positional isomers (Fig. 2 and Table 1).

Scheme 1 shows the primary and secondary fragmentations found for 3,6-dichloroguaiacol (**7**). The most prominent route for all compounds studied is $[M-CH_3-CO-CO-HCl-Cl]$. As previously shown, the loss of HCl from the molecular ion is characteristic for chlorinated catechols[8] and phenols.[9] This loss would have been expected to occur at least with 6-chloroisomers (**4**, **7**, **9**, **10**, **12**, **13**, **14** and **15**),

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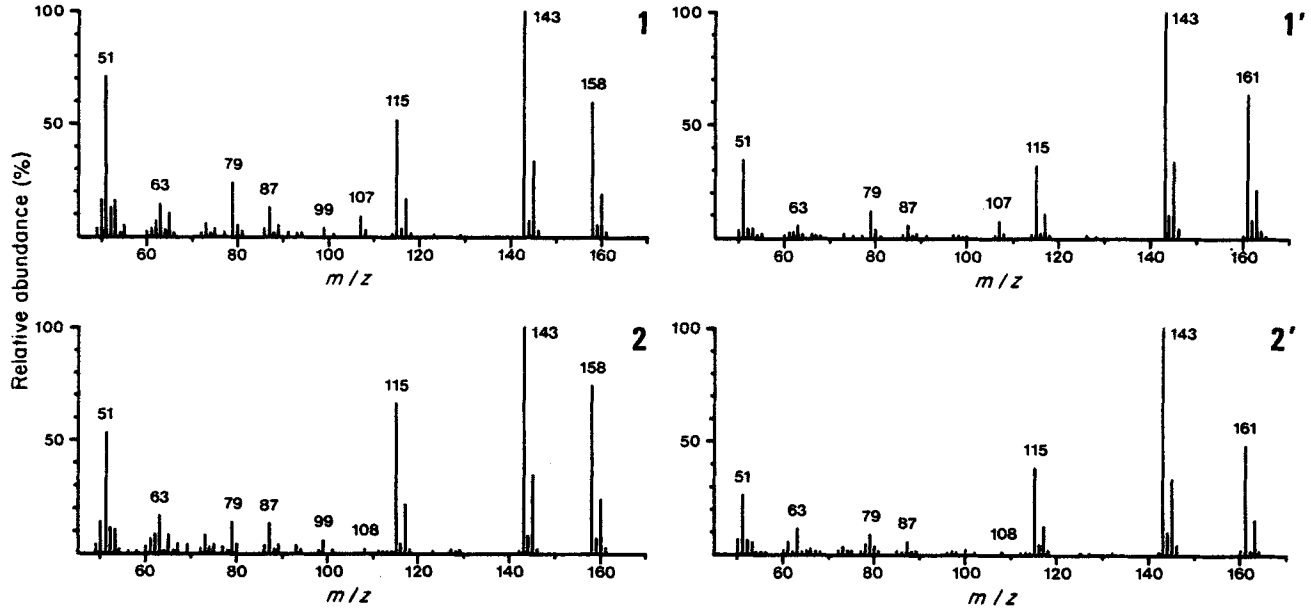


Figure 1. The 70 eV mass spectra of 3-chloroguaiacol (**1**), 2-trideuteriomethoxy-3-chlorophenol (**1'**), 4-chloroguaiacol (2) and 2-trideuteriomethoxy-4-chlorophenol (**2'**).

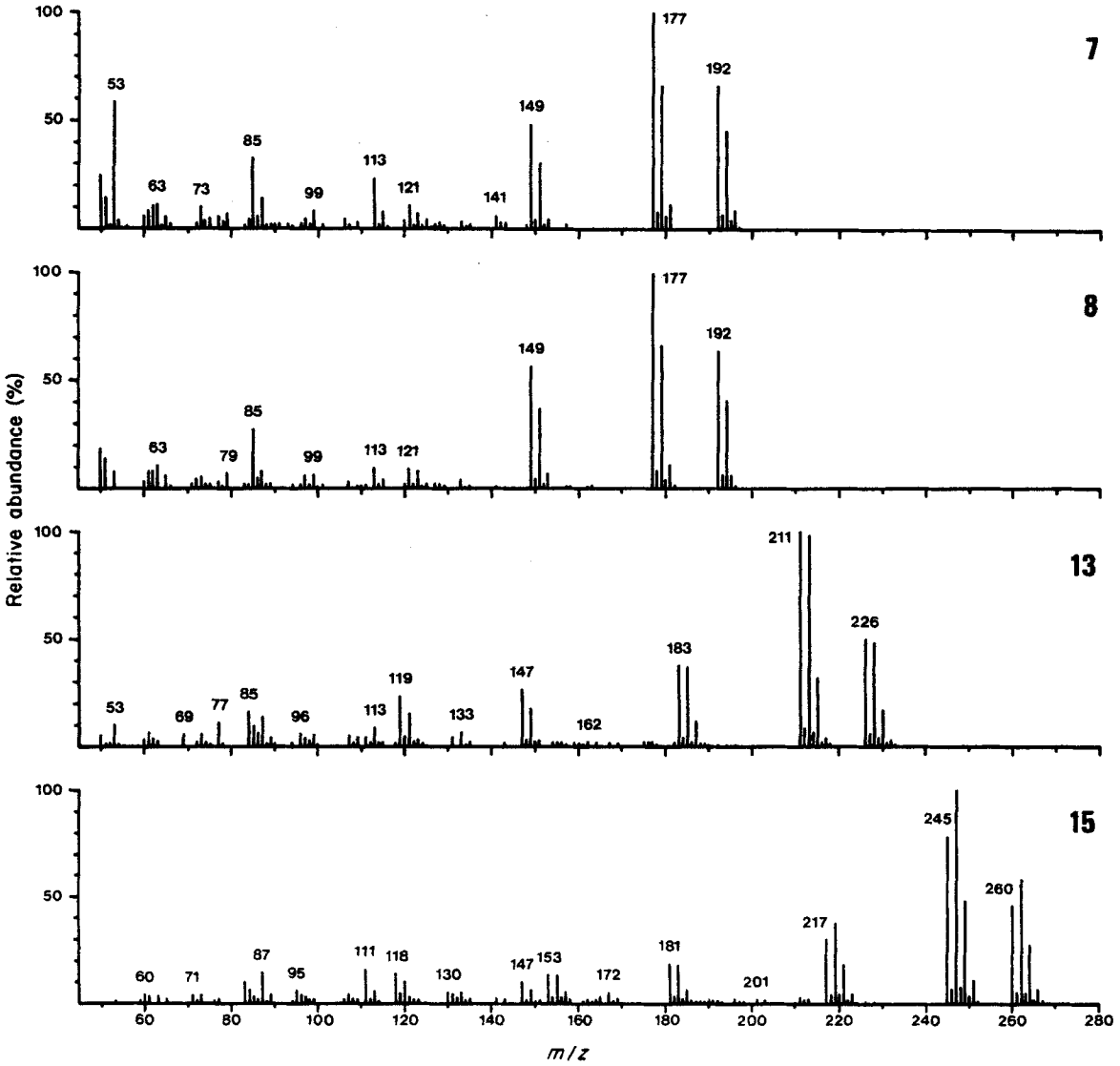


Figure 2. The 70 eV direct inlet spectra of 3,6-dichloroguaiacol (**7**), 4,5-dichloroguaiacol (**8**), 3,5,6-trichloroguaiacol (**13**) and tetrachloroguaiacol (**15**).

Table 1. The 70 eV direct inlet mass spectra of chlorinated guaiacols.[a] The spectra of 1, 2, 7, 8, 13 and 15 are shown in Figs. 1 and 2.

No.	Principal fragments (rel. int., %)
3	160(20), 159(6), 158(62), 145(32), 144(7), 143(100), 117(16), 115(52), 87(8), 79(7), 63(6), 51(15), 50(5).
4	160(24), 159(7), 158(78), 145(31), 144(6), 143(100), 117(15), 115(47), 107(11), 87(10), 79(23), 73(5), 65(7), 63(14), 62(6), 53(14), 52(11), 51(59), 50(14).
5	196(6), 194(35), 193(5), 192(55), 181(11), 180(5), 179(64), 178(7), 177(100), 151(28), 149(44), 115(16), 114(6), 113(49), 99(8), 97(7), 87(17), 86(7), 85(32), 84(5), 79(11), 77(5), 73(9), 65(5), 63(12), 62(11), 61(9), 53(13), 51(17), 50(28).
6	196(5), 194(31), 192(49), 181(10), 179(64), 178(7), 177(100), 153(5), 151(32), 149(51), 121(6), 113(12), 99(5), 87(8), 85(18), 73(5), 63(13), 62(6), 53(6), 51(6), 50(12).
9	169(9), 194(56), 193(7), 192(90), 181(10), 180(5), 179(67), 178(8), 177(100), 153(6), 151(38), 150(5), 149(63), 133(5), 121(8), 115(6), 113(17), 111(8), 99(8), 97(5), 96(5), 87(11), 86(6), 85(21), 79(7), 77(5), 73(8), 65(11), 63(27), 62(14), 61(10), 60(6), 53(19), 51(19), 50(32).
10	196(6), 194(38), 193(5), 192(58), 181(10), 180(5), 179(66), 178(7), 177(100), 151(23), 149(35), 115(12), 113(35), 99(5), 97(7), 87(11), 85(19), 79(9), 73(5), 63(5), 62(7), 61(5), 53(9), 51(9), 50(16).
11	230(15), 228(46), 226(47), 215(32), 214(7), 213(97), 212(7), 211(100), 187(15), 185(45), 183(50), 149(24), 148(5), 147(41), 135(6), 133(7), 131(7), 122(5), 121(14), 120(6), 119(16), 115(7), 113(9), 99(5), 98(5), 96(6), 89(5), 87(16), 86(11), 85(9), 84(21), 79(7), 77(10), 73(6), 67(15), 65(6), 63(16), 62(5), 61(11), 60(5), 53(10), 50(14).
12	230(21), 229(6), 228(65), 227(6), 226(70), 215(32), 214(7), 213(100), 212(9), 211(99), 187(15), 185(45), 184(5), 183(47), 177(5), 176(5), 149(26), 147(36), 135(5), 133(10), 131(7), 123(6), 121(21), 120(6), 119(35), 113(13), 107(7), 99(8), 98(5), 97(9), 96(10), 89(7), 87(21), 86(10), 85(17), 84(29), 77(17), 73(8), 63(7), 62(8), 61(15), 60(6), 53(23), 50(13).
14	230(21), 229(6), 228(66), 227(7), 226(66), 215(31), 214(6), 213(96), 212(8), 211(100), 187(15), 185(45), 183(47), 151(5), 149(27), 148(5), 147(42), 133(8), 131(8), 121(14), 120(6), 119(22), 115(7), 113(20), 111(5), 107(5), 99(8), 98(5), 97(8), 96(12), 89(5), 87(19), 86(12), 85(20), 84(32), 78(5), 77(26), 73(9), 72(5), 71(5), 65(8), 63(23), 62(9), 61(18), 60(8), 53(16), 50(16).

[a] All peaks greater than or equal to 5% of the base peak (100%) are recorded.

forming an epoxide ion but, in this study, this fragmentation was not observed. The latter phenomenon is due to the very easy formation of an $[M-CH_3]^+$ ion, *b* and *b'* (base peak in all spectra), found previously for guaiacol[1-3] and also for chlorinated anisoles[10] (Scheme 2). The other fragmentations are weak, however. For example, the ion *f* at *m/z* 99 in the spectra of the monochloroguaiacols (**1–4**) is probably formed via ions *d* and *e* by the losses of CHO˙ and OCH_2 from the molecular ion, *c* (Scheme 3). Route A is assumed to be the more prominent, since the metastable ions do not show the primary loss of OCH_2 (Scheme 1). The spectra of the deuteriated monochloroguaiacols **1'–4'** show the corresponding ion, *f'*, at *m/z* 100. Owing to the easy loss of CD_3˙, the fragments containing a deuterium atom in the spectra of **1'–4'** are few in number being still very weak. According to Granoth[10] the expulsion of CH_2O (Route B, Scheme 3) is a minor reaction in *o*- and *p*- but not *m*-chloroanisoles. In the spectra of **1–15** the intensity of the $[M-CH_2O]^{+\cdot}$ ion is weak (weaker than that of the $[M-CHO]^+$ ion) or the peak was not observed. The other fragmentations found for 3,6-dichloroguaiacol (**7**) are available in Scheme 1 and the fragmentations of the other compounds studied follow the pathways given.

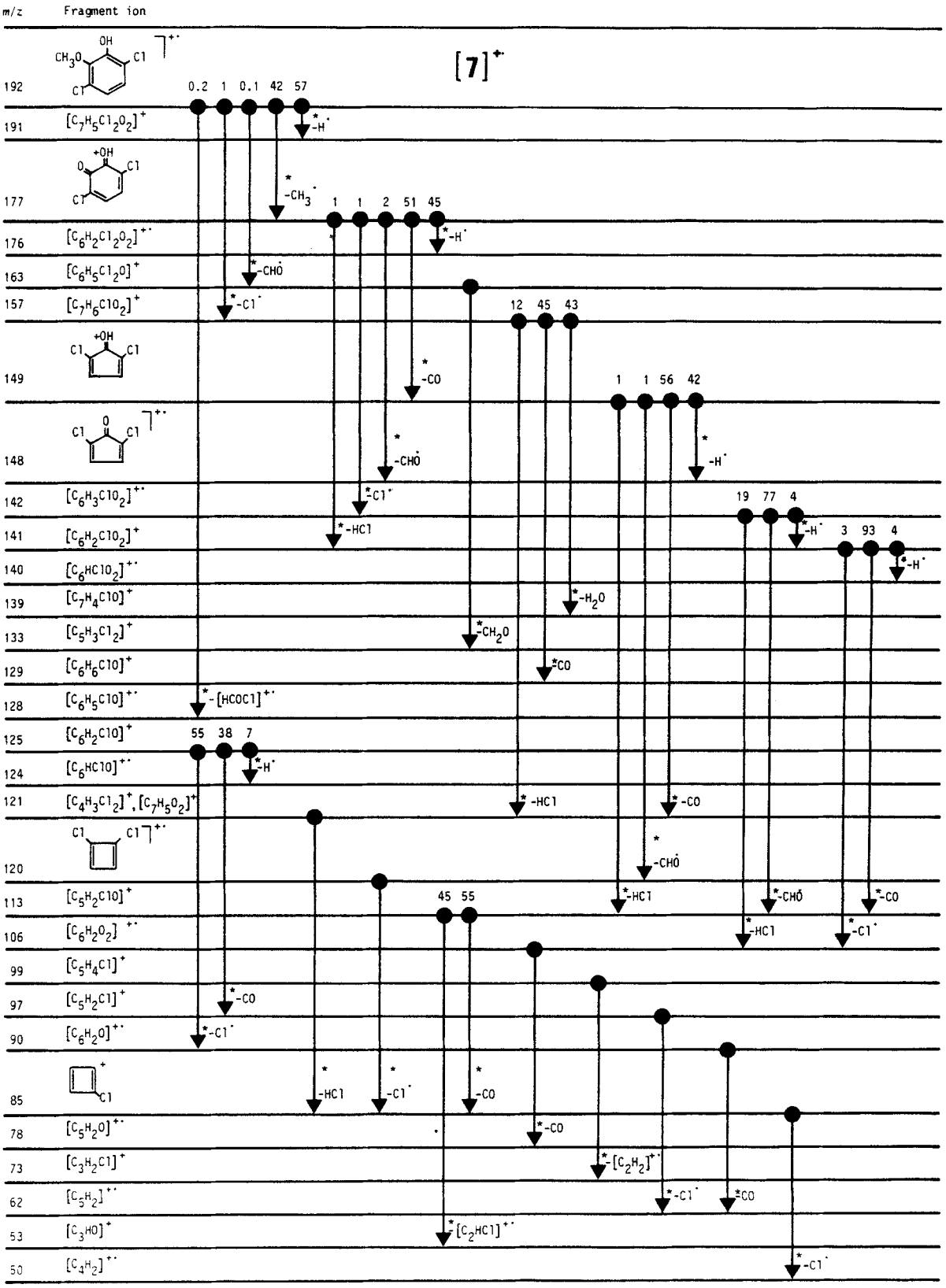
EXPERIMENTAL

Chlorinated guaiacols (**1–15**) were synthesized as reported earlier.[7,11] Pure 3,4,6-trichloroguaiacol (**12**) was prepared by chlorination of 3,6-dichloroguaiacol (**7**) in $CHCl_3$ with SO_2Cl_2. The spectrum of 3,5,6-trichloroguaiacol (**13**) was obtained from the mixture (*c.* 1 : 1) of **12** and **13**. The deuteriated guaiacols **1'** and **2'** (see Fig. 1) and the corresponding 5- and 6-chloro isomers were synthesized from monochlorocatechols applying the methylation method presented by Gillis.[12] In this procedure, monochlorocatechol (14.4 mg), 16 mg of finely powdered sodium hydroxide and CH_3SOCH_3 (2 ml) were stirred at room temperature for 5 min. 6 μl methyl-d_3 iodide was added and the mixture stirred at room temperature for 0.5 hour. Then the reaction mixture was acidified with D_2SO_4 and extracted with diethyl ether (5 ml) giving the sample suitable for GC/MS work.

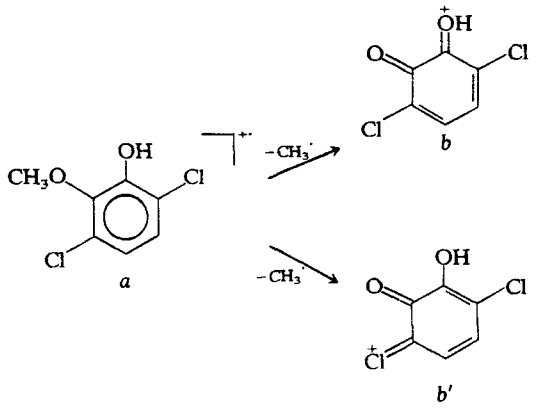
The spectra were recorded on a Varian MAT-212 mass spectrometer using the following operating conditions: ion accelerating voltage, 3 kV; trap current, 100 μA; ionizing energy, 70 eV and ion source temperature, *c.* 220 °C. The spectra (except for compound **13**) were obtained from solid samples using the direct insertion technique. The spectrum of **13** and the spectra of other compounds were also recorded by the GC/MS technique with a SE-30 quartz capillary column (25 m × 0.22 mm I.D.). The 1st FFR metastable ions were obtained by linked scans using a Varian Metascan unit. All mass spectral data were acquired and processed on a Spectro System MAT-188.

CONCLUSIONS

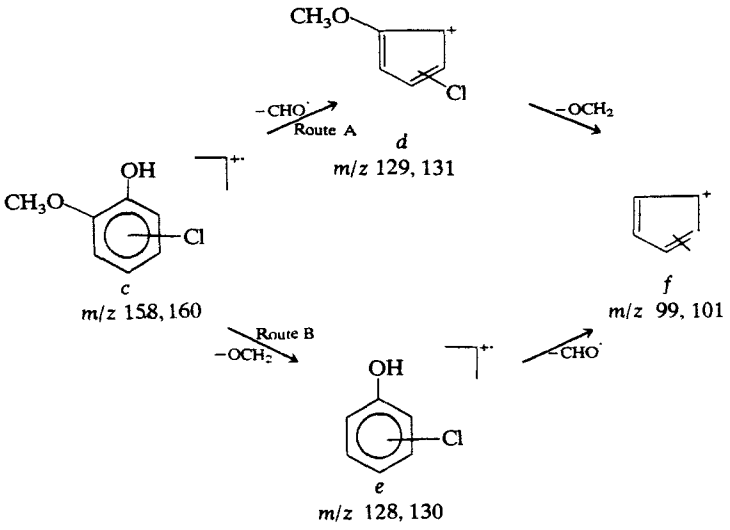
The present results show that the isomeric chloroguaiacols can hardly be distinguished by means of their electron impact mass spectra. In addition, the abundance of the characteristic peaks are weak, being less than *c.* 10% from the abundance of the base peak $[M-CH_3]^+$. The primary elimination of HCl was not observed, this elimination being very characteristic, e.g. for chlorinated phenols and catechols.[8,9] It should also be noted that the secondary fragmentations of acetylated guaiacol[2] and chloroguaiacols[4,5] and ethylated chloroguaiacols[13] generally follow the fragmentation mechanisms presented in this work. Thus, it is concluded that authentic reference substances must be used for unambiguous structure determinations of **1–14** by the GC/MS technique.



Scheme 1. The fragmentation pathways of 3,6-dichloroguaiacol (**7**) based on the first FFR metastable ions. The numbers indicate the abundances of the first FFR peaks (% of the sum).



Scheme 2



Scheme 3

Acknowledgements

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