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Characterization of Novel 10-Substituted 1,8-Dihydroxy-9(10H)-Anthracenone Derivatives by Mass Spectrometry

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ABSTRACT

Anthralin and its derivatives containing a variety of simple or functionalized aliphatic and aromatic substituents are of special interest in research on psoriasis. In this connection, 10-arylthio-1,8-dihydroxy-9(10H)-anthracenones were synthesized and examined by means of mass spectrometry. In general, the molecules in question fragmented upon electron impact into ions at m/z 225 (C-S bond cleavage and charge retention at the anthralin component) and into ions of unknown structure at m/z 226, requiring H-migration from the S-bound substituent R into the anthralin moiety. Since mass spectrometry methods furnished us elegant, matchless means of tracing the amounts of material in the analysis, especially in the case of physiologically active compounds, we decided to use mass spectrometry procedures for unequivocal identification and purity determination of 10-arylthio-anthralins.

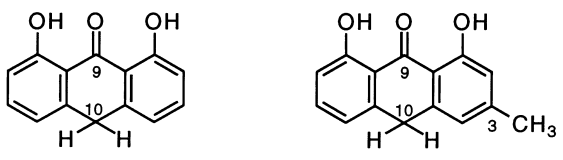
Key Words: psoriasis, H-migration, C-S bond cleavage, anthralin, chrysarobin, McLafferty rearrangement, *ipso*-cleavage

I. Introduction

Psoriasis is a widespread, scaling skin disease, mainly characterized by increased cell proliferation in the epidermis. However, it has been suggested that hyperproliferation alone is not sufficient to produce a psoriatic lesion, and that the inflammatory component is an important part of the disease process (Müller *et al*., 1993, 1994; d'Ischia *et al*., 1986; Khalafy and Bruce, 1990; Fry, 1988). Anthralin (dithranol, 1) (Fig. 1(a)) was first developed in 1916 as a substitute for chrysarobin (2) (Fig. 1(b)), which is among the most widely used drugs in the treatment of psoriasis (Müller and Huang, 1996; Müller *et al*., 1996, 1997). From the mass spectra, one can directly deduce the mass and abundance of molecular and fragment ions. Molecular ions of higher mass than the original compound are found very rarely and only under thermal decomposition. Hydrogen rearrangements (e.g., the McLafferty rearrangement) are most common, best understood, and generally most useful for deducing ion structures (McLafferty, 1993). In general, the molecules in question fragment upon electron impact into ions at m/z 225 (C-S bond cleavage and charge retention at the anthralin component) and ions of unknown structure at m/z 226, requiring H-migration from the S-bound substituent R into the anthralin moiety (Fig. 2).

II. Experimental Section

Melting points were determined on a Büchi 510 (Swiss) apparatus and were uncorrected. Mass spectra were recorded on a Varian MAT 311 A EI-MS (70 eV) (Regensburg, Germany) and a Finnigan MAT 95 El-MS (70 eV) (Regensburg, Germany). EIMS (70/12 eV), FDMS and MIMS were measured on a Finnigan



Anthralin (**1**)
(a)

Chrysarobin (**2**)
(b)

Fig. 1. Structures of anthralin and chrysarobin.

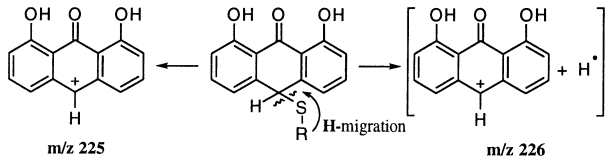


Fig. 2. Proposed mechanism for C-S bond cleavage (*ipso*-cleavage) of 10-thio-anthralin derivatives.

MAT 95 double-focusing instrument (Regensburg, Germany). The samples were introduced by means of direct insertion (quartz crucibles) at T = 100˚C, and an ion source temperature of 100-120˚C. High resolution measurements were performed with m/Δm = 15000. Relative intensities (r. i., %) are shown in parentheses.

1. General Procedure for the Preparation of 10-Alkylthio- and 10-Arylthio-1,8-Dihydroxy-9(10H)-Anthracenone

To a solution of 10-bromo-1,8-dihydroxy-9-anthrone (305 mg, 1.0 mmol) and 0.1 ml of trifluoroacetic acid in dry CH_2C1_2 (20 ml) was added the appropriate thiol (1.5 mmol) under N_2. The reaction mixture was stirred at room temperature for several hours. Removal of the solvent and recrystallization of the residue or purification by means of chromatography produced yellow crystals.

2. 1,8-Dihydroxy-10-Phenylthio-9(10H)-Anthracenone (3)

Compound **(3)** was synthesized using the general procedure as described above, as yellow needles (from CH_2C1_2). mp 149-150˚C; IR (KBr): 1629 cm^{-1} (CO···HO); ^{1}H-NMR (250 MHz, $CDC1_3$): δ (ppm) 5.40 (s, 1H, 10-H), 6.70 (dd, J = 8 Hz, 2H, 2-H, 7-H), 6.90 (dd, J = 8 Hz, 2H, H-4, H-5), 7.05 (d, J = 8 Hz, 2H, 2'-H, 6'-H), 7.15 (t, J = 8 Hz, 2H, 3'-H, 5'-H), 7.35 (t, J = 7.7 Hz, 1H, 4'-H), 7.49 (t, J = 7.7 Hz, 2H, 3-H, 6-H), 11.80 (s, 2H, 1-OH, 8-OH). Anal. Calcd: C, 71.4; H,4.22; Found: C,71.3; H, 4.19. a) EIMS (70/12 eV): 334(7/16), 226(35/40), 225(100/100), 197(43/1), 151(15/-), 110(13/11), 109(9/-). b) FDMS: m/z 334(100), 225(15). c) MIMS: $M^{+\bullet}$(m/z 334; B/E) 333(100), 302(3), 301(1), 256(2), 225(15) (quartz crucible). d) EIMS: m/z (70eV; Al/Au crucibles; % rel. int.): 334(2/3), 226(95/80), 225(100/100), 197(55/50), 151(25/25), 110(40/35), 109(25/20). e) B/E (m/z 334, $M^{+\bullet}$): 333 (100), 301 (1, -$^{\bullet}$SH), 300 (4, -H_2S), 256 (2, -C_6H_6), 225 (15, -$^{\bullet}$SPh), (without m/z 226). f) B^2/E (m/z 256): m/z 334 ($M^{+\bullet}$). g) HRMS m/z: $C_{34}H_{22}O_6S$ Calcd for 558.1137; Found 558.1133. Calcd for $C_{28}H_{18}O_6$ 450.1103; Found 450.1100. Calcd for $C_{26}H_{18}O_3S_2$ 442.0697; Found 442.0701. Calcd for $C_{20}H_{14}O_3S$ 334.0623; Found 334.0662. Calcd for $C_{14}H_{10}O_3$ 226.0623; Found 226.0624. Calcd for $C_{14}H_9O_3$ 225.0552; Found 225.0550. Calcd for $C_{12}H_{10}S_2$ 218.0224; Found 218.0219. Calcd for C_6H_6S 110.0190; Found 110.0192. Calcd for C_6H_5S 109.0112; Found 109.0109.

3. Thermolysis of Compound (3)

Pure compound **3** (1.0 mg) was placed in a silylated quartz tube (0.2 mm diameter) and kept for 1 to 30 min in a thermostated oil bath at 150˚C. After cooling, the lower part of the tube together with the dark solid was pulverized, and the org. substance was dissolved in absol. CH_2C1_2 (1 ml). The homogenous solution was used immediately for FDMS analysis.

4. 1,8-Dihydroxy-10-[2-Methoxyphenyl)thio]-9(10H)-Anthracenone (4)

Yellow needle; mp 135˚C; IR (KBr): 1626 cm^{-1} (CO···HO); ^{1}H-NMR (250 MHz, $CDCl_3$): δ (ppm) 3.63 (s; 3H, OCH_3), 5.51 (s; 1H, 10-H), 6.71-6.89 (m; 6H: 2-H, 7-H, 4-H, 5-H, 2H phenyl), 7.31-7.44 (m; 4H: 3-H, 6-H, 2H phenyl), 11.92 (s; 2H, 1-OH, 8-OH); EIMS (70 eV): m/z = 364 ($M^{+\bullet}$, 32), 278 [36, $C_6H_4(OCH_3)S$ - $SC_6H_4(OCH_3)$], 226(25), 225 (100), 197 (38), 151 (10), 140 [98,$C_6H_4(OCH_3)(SH)$], 139 [8, $C_6H_4(OCH_3)(S^+)$], 125 [56, $C_6H_4(O^+)(SH)$], 97 [45, $C_5H_4(SH)$]; (^{13}C-corrected); FDMS (12 eV; CH_2C1_2): m/z = 364 ($M^{+\bullet}$, 100), 139 (1); Anal. Calcd: C, 69.23; H, 4.39; Found: C, 69.40; H, 4.46.

5. 1,8-Dihydroxy-10-[(3-Methoxyphenyl)thio]-9(10H)-Anthracenone (5)

Yellow needle; mp 96-97˚C; IR (KBr): 1628 cm^{-1} (CO···HO); ^{1}H-NMR (250 MHz,$CDCl_3$): δ (ppm) 3.58 (s; 3H, OCH_3), 5.43 (s; 1H, 10-H), 6.23 (dd; J = 2.5 Hz, H, 2'-H), 6.356.38 (m; H, 6'-H), 6.86-6.89 (m; 3H: 2-H, 7-H, H phenyl), 6.99-7.06 (m; 3H: 4-H, 5-H, H phenyl), 7.49 (t; J = 8.0 Hz, 2H: 3-H, 6-H), 11.85 (s; 2H: 1-OH, 8-OH); EIMS (70 eV): m/z 364 ($M^{+\bullet}$, 12), 278 (6), 226 (20), 225 (100), 197 (35), 151 (9), 140 (45), 139 (10), 125 (17), 97 (13); FDMS (12 eV; CH_2C1_2): m/z 364 ($M^{+\bullet}$, 100), 225 (2); Anal. Calcd $C_{21}H_{16}O_4S$ (364.4): C, 69.23; H, 4.39; Found: C, 69.47; H, 4.38.

6. 1,8-Dihydroxy-10-[(4-Methoxyphenyl)thio]-9(10H)-Anthracenone (6)

Yellow needle; mp 143-144˚C; IR (KBr): 1628

cm^{-1} (CO···HO); ^{1}H-NMR (250 MHz, $CDCl_3$): δ (ppm) 3.77 (s; 3H, OCH_3), 5.34 (s; 1H, 10-H), 6.56-6.65 (m; 4H, C_6H_4), 6.87 (dd; J = 8.4 Hz, 2H, 2-H, 7-H), 6.99 (dd; J = 7.5 Hz, 2H, 4-H, 5-H), 7.48 (t; J = 8 Hz, 3-H, 6-H), 11.82 (s; 2H, 1-OH, 8-OH); EIMS (70/12 eV): m/z 364 ($M^{+\bullet}$, 8/43), 278 (4/9), 226 (25/16), 225 (100/100), 197 (26/-), 151 (8/-), 140 (16/15), 139 (14/1), 125 (11/-), 97 (4/-); FDMS (CH_2C1_2): m/z 364 (100), 225 (1), 139 (1); B/E (m/z 364, $M^{+\bullet}$): m/z 333 (3), 256 (2, M-$C_6H_5OCH_3$), 225 (100); Anal. Calcd $C_{21}H_{16}O_4S$ (364.4): C, 69.23; H, 4.39; Found: C, 69.35; H, 4.51.

7. 10-[(2-Aminophenyl)thio]-1,8-Dihydroxy-9(10H)-Anthracenone (7)

Yellow needle; mp 132-133˚C; IR (KBr): 1628 cm^{-1} (CO···HO); ^{1}H-NMR (250 MHz, $CDCl_3$): δ (ppm) 4.47 (br; 2H, NH_2), 5.86 (s; 1H, 10H), 6.18-6.31 (m; 2H: H phenyl), 6.61 (d; J = 7.7 Hz, H: 3'-H), 6.91 (dd; J = 8.3 Hz, 2H: 2-H, 7-H), 7.01-7.19 (m, 3H: 4-H, 5-H, H phenyl), 7.52(t; J = 8.0 Hz, 2H: 3-H, 6-H), 11.70 (s; 2H, 1-OH, 8-OH); EIMS (70 eV): m/z 349 ($M^{+\bullet}$, 2), 248 (13), 226 (100), 225 (8), 198 (13), 197 (15), 125 (55), 124 (41) (^{13}C-corrected); FDMS (CH_2C1_2): m/z 248, m/z 125, m/z 124; Anal. Calcd $C_{20}H_{15}NO_3S$ (349.3): C, 68.76; H, 4.33; N, 4.01; Found: C, 68.57; H, 4.58; N, 4.32.

8. 10-[(4-Aminophenyl)thio]-1,8-Dihydroxy-9(10H)-Anthracenone (9)

Yellow needle; mp 160-161˚C; IR (KBr): 3382 (N-H), 1628 cm^{-1} (CO···HO); ^{1}H-NMR (250 MHz, $CDC1_3$): δ (ppm) 4.49 (br; 2H, NH_2), 5.77 (s; 1H, 10-H), 6.14-6.29 (m; 4H: H phenyl), 6.87 (dd; 2H: 2-H, 7-H), 7.12 (dd, 2H: 4-H, 5-H), 7.58 (t; 2H: 3-H, 6-H), 11.63 (s; 2H, 1-OH, 8-OH); EIMS (70 eV): m/z 349 ($M^{+\bullet}$, 10), 248 (6), 226 (10), 225 (35), 198 (26), 197 (39), 125 (75), 124 (65) (^{13}C-corrected); FDMS (CH_2C1_2): m/z 349 (100), 225 (10), 124 (2); Anal. Calcd $C_{20}H_{15}NO_3S$ (349.3): C, 68.76; H, 4.33; N, 4.01; Found: C, 68.52; H, 4.33; N, 4.14.

9. 1,8-Dihydroxy-10-[(2-Hydroxyphenyl)thio] -9(10H)-Anthracenone (10)

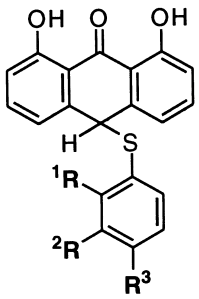
Yellow needle; mp 151-152˚C; IR (KBr): 3407 (OH), 1628 cm^{-1} (CO···HO); ^{1}H-NMR(250 MHz, $CDCl_3$): δ (ppm) 5.40 (s; 1H, 10-H), 5.83 (s; H, OH), 6.48 (dd; J = 7.8 Hz, H: aromatic H), 6.66 (t; J = 7.5 Hz, H: aromatic H), 6.79 (dd; J = 8.2 Hz, H: aromatic H), 6.95 (t; J = 7.4 Hz, 5H), 7.48 (t; J = 8.0 Hz, 2H: 3-H, 6-H), 11.79 (s; 2H, 1-OH, 8-OH); EIMS (70 eV): m/z = 350 ($M^{+\bullet}$, 4), 250 (7, Ar-S-S-Ar), 226 (12), 225 (100), 197 (29), 151 (6), 126 (12, Ar-SH), 125 (8, ArS), 97 (10, $C_5H_5S^+$) (^{13}C-corrected); Anal. Calcd $C_{20}H_{14}O_4S$ (350.3): C, 68.57; H, 4.03; Found: C, 68.40; H, 4.17.

10. 1,8-Dihydroxy-10-[(4-Hydroxypheny1) thio]-9(10H)-Anthracenone (11)

Yellow needle; mp 189-190˚C; IR (KBr): 3436 (OH), 1630 cm^{-1} (CO···HO); ^{1}H-NMR (250 MHz, $CDCl_3$): δ (ppm) 4.91 (s; H, OH), 5.35 (s; 1H, 10-H), 6.55 (s; 4H, C_6H_4), 6.87 (dd; J = 8.4 Hz, 2H, 2-H, 7-H), 7.01 (dd; J = 7.5 Hz, 2H, 4-H, 5-H), 7.49 (t; J = 8.0 Hz, 3-H, 6-H), 11.83 (s; 2H, 1-OH, 8-OH); EIMS (70 eV): m/z = 350 ($M^{+\bullet}$, 11), 250 (21), 226 (68), 225 (100), 197 (77), 151 (32), 126 (39), 125 (46), 97 (35) (^{13}C-corrected); Anal. Calcd $C_{20}H_{14}O_4S$ (350.3): C, 68.57 ; H, 4.03; Found: C, 68.35; H, 4.28.

III. Results and Discussions

The 70 and 12 eV electron impact mass spectrum (EIMS) of a series of 10-arylthio-anthralins agreed with data acquired for simple aromatic sulfides (Nibbering *et al*., 1993), showing $M^{+\bullet}$ ions at m/z 225 arising from *ipso*-cleavage and the loss of Ar-S$^\bullet$ radicals and ArS^+ ions (Fig. 3). Additionally, depending on the temperature of the insertion probe and inlet system, signals of varying intensity were encountered which corresponded to $C_{14}H_{10}O_3$ (m/z 226), Ph-S-S-



Compound no.	R^1	R^2	R^3
3	H	H	H
4	OCH_3	H	H
5	H	OCH_3	H
6	H	H	OCH_3
7	NH_2	H	H
8	H	NH_2	H
9	H	H	NH_2
10	OH	H	H
11	H	H	OH

Fig. 3. 10-Arylthio-anthralin derivatives.

$Ph^{+\bullet}$ (m/z 218) and $PhSH^{+\bullet}$ (m/z 110).

Even though the lowest possible inlet temperature (ca. 110˚C) was applied in order to vaporize a sufficient number of molecules of these compounds, no satisfactorily reproducible spectra could be obtained. As the differences of ion currents were particularly high when metal crucibles (Al, Au) were used, measurements were performed using quartz crucibles. The data listed in Table 1 are means of 20 scans at constant inlet temperature (150˚C). In order to exclude the possibility that the unexpected ions (m/z 226, 110, 218) were caused by the starting material or side-products, all the compounds were checked after careful purification by means of chromatography (high performance liguid chromatography, HPLC; thin layer chromatography, TLC) and FI/FDMS (Field ionization/ Field-desorption mass spectrum) (Table 2). All of them proved to be pure. In all cases, > 95% of the total ion current was carried by $M^{+\bullet}$. The only fragment ions were $(M\text{-}^{\bullet}S\text{-}Ar)^{+}$ and ArS^{+}; additional ions could not be detected.

Further evidence was obtained by analyzing the daughter ions of the molecular ions of **3**, **6** and **7** by means of MIMS (Metastable ion mass spectrum) (B/E = const. linked scan). This method made it feasible to register only those fragments which originated from $M^{+\bullet}$ directly and exclusively. The results (Table 3) unequivocally rule out the possibility that these irritating ions (m/z 226; $ArSH^{+\bullet}$; $Ar\text{-}S\text{-}S\text{-}Ar^{+\bullet}$) were daughter ions. Moreover, a search for parents of the m/z 226 ions in the MS of **3**, **6** and **7** using the B^2/E = const. mode was unsuccessful; *i.e.*, these ions had no precursor, so they represented separate molecular ions and were not generated by any electron impact induced dissociation.

From these results, it seems reasonable to infer that thermal decomposition of these 10-arylthio-anthralins (Table 1) occurred in the inlet-system (and possibly the ion-source) before ionization can take place. Thermally induced homolytic fission of sulphides (Colussi and Bebson, 1977; Failes *et al.*, 1993) results in the formation of reactive carbon and sulphide radicals which are set free in liquid media, to abstract $H^{\bullet}$ ($\rightarrow$ m/z 226), to dimerize ($\rightarrow$ Ar-S-S-Ar), and so on. In order to prove this, thoroughly purified samples of **3** (1.0 mg) were heated (150˚C) in silylated quartz tubes for 1-30 min, and the products were

Table 1. EIMS of Some 10-Arylthio-Anthralin Derivatives (T_{inlet} = 150˚C)

Compd. no.	m/z (70/12 eV; % rel. int.), ^{13}C corrected
3	334 ($M^{+\bullet}$; 7/17), 226 (21/26), 225 (100/100), 218 (5/7), 197 (43/-), 151(13/-), 110 (12/10), 109 (9/1).
4	364 ($M^{+\bullet}$; 32/35), 278 (36/35), 226 (25/23), 225 (100/100), 197 (38/-), 151(15/-), 140 (98/95), 139 (8/7), 125 (56/2), 97 (45/-).
5	364 ($M^{+\bullet}$; 12/18), 278 (6/10), 226 (20/21), 225 (100/100), 197 (35/-), 151(9/-), 140 (45/40), 139 (10/6), 125 (17/3), 97 (13/-).
6	364 ($M^{+\bullet}$; 8/43), 278 (4/9), 226 (25/16), 225 (100/100), 197 (26/-), 151(8/-), 140 (16/15), 139 (14/1), 125 (11/-), 97 (4/-).
7	349 ($M^{+\bullet}$; 2/5), 248 (13/15), 226 (100/100), 225 (8/9), 198 (13/-), 197 (15/-), 125 (55/37), 124 (41/20).
8	349 ($M^{+\bullet}$; 12/19), 248 (3/5), 226 (100/100), 225 (97/85), 198 (43/5), 197 (47/9), 125 (89/81), 124 (17/2).
9	349 ($M^{+\bullet}$; 10/16), 248 (6/6), 226 (100/100), 225 (35/31), 198 (26/7), 197 (39/2), 125 (75/74), 124 (65/39).
10	350 ($M^{+\bullet}$; 4/15), 250 (7/9), 226 (12/15), 225 (100/100), 197 (29/-), 151(6/-), 126 (12/11), 125 (8/1), 97 (10/-).
11	350 ($M^{+\bullet}$; 11/21), 250 (21/18), 226 (68/65), 225 (100/100), 197 (67/-), 151(32/-), 126 (39/35), 125 (46/28), 97 (35/-).

Table 2. FI/FDMS (CH_2Cl_2) of Some 10-Arylthio-Anthralin Derivatives

Compound no.	m/z (% rel. int.)
3	334 (100), 225 (3).
4	364 (100), 225 (1), 139(1)
5	364 (100), 225 (2).
6	364 (100), 225 (1), 139(1).
7	349 (100), 225 (1), 124(1).
8	349 (100), 225 (1).
9	349 (100), 225 (1), 124 (2).
10	350 (100), 225 (4).

a) average of 5 runs.

Table 3. MIMS (70 eV; B/E-linked scan) of $M^{+\bullet}$ of Some 10-Arylthio-Anthralin Derivatives

Compound no.	m/z	(% rel. int.)
3	[334]	333 (100), 301 (1; -$^{\bullet}$SH), 300 (2; -H_2S), 257(1; -$^{\bullet}C_6H_5$), 256 (2; -C_6H_6), 225 (15; -$^{\bullet}SC_6H_5$).
6	[364]	363 (100), 257 (1), 256 (3), 225 (35).
7	[349]	348 (100), 257 (1), 256 (3), 225 (20).

Table 4. Thermolysis (150˚C) of compound **3** (EI-MS; 70 eV, % rel. int.)

t (min)	m/z 334 $C_{20}H_{14}O_3S$	m/z 226 $C_{14}H_{10}O_3$	m/z 225 $C_{14}H_9O_3$	m/z 218 $C_{12}H_{10}S_2$	m/z 110 C_6H_6S	m/z 109 C_6H_5S
0	20	10	100	1	18	5
1	15	25	100	1	20	35
5	2	35	20	100	10	85
15	<0.5	40	1	100	5	70
30	<0.5	50	2	100	10	80

a) Data ^{13}C-corrected; ion-source temp. 100˚C; average of 5 runs.

Table 5. Thermolysis (150°C) of Compound **3** (FD-MS; % rel. int.)

t (min)	m/z 558 $C_{34}H_{22}O_6S$	m/z 450 $C_{28}H_{18}O_6$	m/z 442 $C_{26}H_{18}O_3S_2$	m/z 334 $C_{20}H_{14}O_3S$	m/z 226 $C_{14}H_{10}O_3$	m/z 225 $C_{14}H_9O_3$	m/z 218 $C_{12}H_{10}S_2$
0	<0.5	<0.5	<0.5	100	-	10	-
1	1	1	2	100	12	15	2
5	15	20	10	100	15	40	2
10	20	55	15	100	35	75	15

a) Data ^{13}C-corrected; average of 5 runs.

identified by means of EIMS and FDMS. The results are summarized in Tables 4 and 5. A dramatic decrease of the intensity of $M^{+\bullet}$ (m/z 334) and m/z 225 ions with extended heating periods (1 to 30 min) is evident. In contrast, much stronger signals at m/z 109 ($C_6H_5S^+$), m/z 218 ($C_{12}H_{10}S_2$) and m/z 226 ($C_{14}H_{10}O_3$, anthralin?) are observed. Correspondingly, the FDMS results reveal an increase in radical recombination products of higher molecular mass at m/z 442 ($C_{26}H_{18}O_3S_2$), m/z 450 ($C_{28}H_{18}O_6$) and m/z 558 ($C_{34}H_{22}O_6S$).

Even though thermo-chemical decompositions on 10-arylanthralin derivatives could not be found in literature, it can be concluded from the available data on simple sulphides that in the case of 10-phenylthio-anthralin, the C(10)-S-bond requires the lowest amount of energy for homolytic cleavage (Fig. 4) (Chatgilialoglu and Gnerra, 1993). The resulting C(10)-radical is stabilized by mesomeric delocalization. The phenylthiyl radical is a well-known reactive intermediate in phenylsulphide pyrolysis (Fig. 5) (Martin, 1993).

Under hot melt reaction conditions, these phenylthiyl radicals (PhS^{*}) either dimerized to produce Ph-S-S-Ph **(A)** and An-An **(B)** or abstracted $H^{\bullet}$ from neighbouring molecules to produce the products **C** and **D** (Fig. 6). The formation of the more complex compounds E and F (Fig. 7), identified by means of FDMS, can be understood based on analogous processes, $H^{\bullet}$-abstraction and radical recombination.

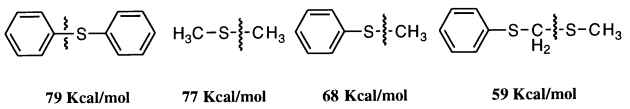


Fig. 4. Some examples of BDE (bond dissociation energy).

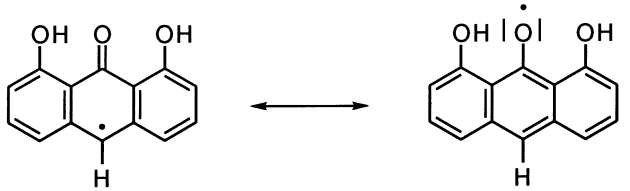


Fig. 5. Resonance-stabilized anthralin free radical.

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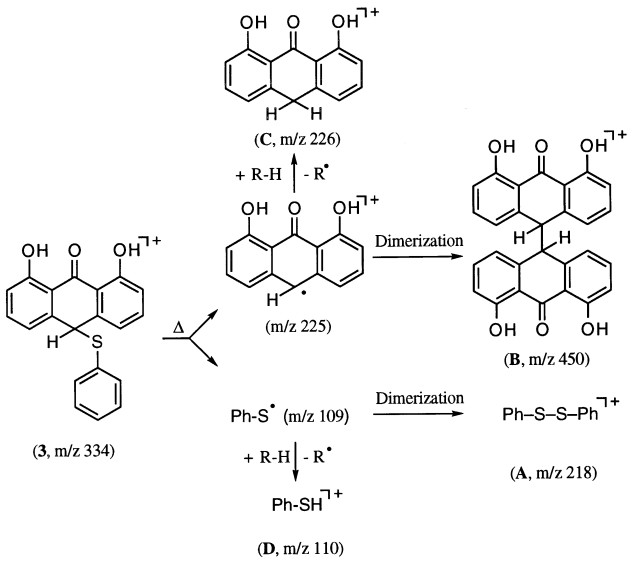

Fig. 6. Thermolysis of 10-phenylthio-anthralin.

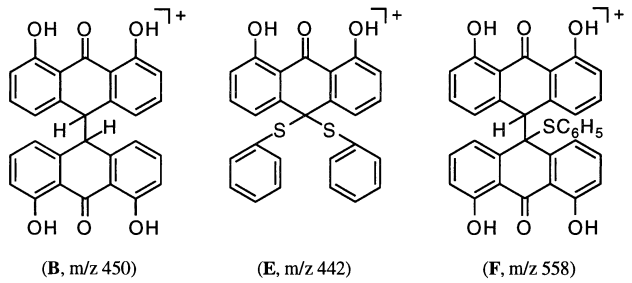

Fig. 7. Structures of high mass thermolytic products.

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新型 10-取代基-1,8-二羥基-9(10 氫)-蒽酮衍生物在質譜之化學特性

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摘　要

1,8-二羥基-9(10 氫)-蒽酮及其分子結構上含不同之簡單或脂肪鏈和芳香環取代基之衍生物是研究乾癬藥物的重點方向，而此研究的重點即是將所合成的10-取代基-1,8-二羥基-9(10氫)-蒽酮類衍生物用質譜分析的方式來探討其化學分子的特性。整體而言，吾們的研究發現此類分子由於碳-硫鍵的斷裂，在m/z 225有電子斷鍵和m/z 226此未知結構出現，因此推論m/z 226的未知結構必須依靠硫鍵取代基的一個電子轉移方可解釋此結構在質譜之出現，因此本研究即是應用質譜來分析此類衍生物來驗證此一電子轉移現象，藉以解釋此類化合物不安定的特性，並提供化合物鑑定純化之參考。