

**Contrasting Dihydronaphthoquinone Patterns in Closely Related *Drosera* (Sundew) Species
Enable Taxonomic Distinction and Identification**

**Jan Schlauer¹, Siegfried R. H. Hartmeyer², Irmgard Hartmeyer², Tuulikki Seppänen-Laakso³,
Heiko Rischer³**

Affiliation

¹ University of Tuebingen, ZMBP, Auf der Morgenstelle 32, D-72076 Tuebingen, Germany

² Wittlinger Str. 5, D-79576 Weil am Rhein, Germany

³ VTT Technical Research Centre of Finland Ltd., Tietotie 2, FIN-02044 Espoo, Finland

Correspondence

Jan Schlauer

University of Tuebingen, ZMBP
Auf der Morgenstelle 32
D-72076 Tübingen
Germany
jan@carnivorousplants.org

Heiko Rischer

VTT Technical Research Centre of Finland Ltd.
Tietotie 2
FIN-02044 Espoo
Finland
heiko.rischer@vtt.fi

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Table 1S. MS Data of Identified Naphthoquinone Derivatives

Fig. 1S. MS of dihydroplumbagin (**5**).

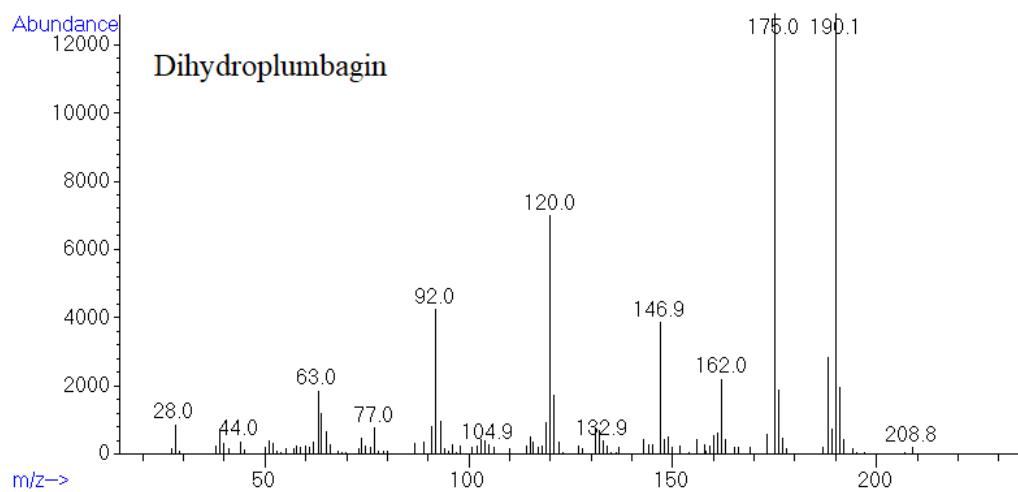


Fig. 2S. MS of dihydroramentaceone (**6**).

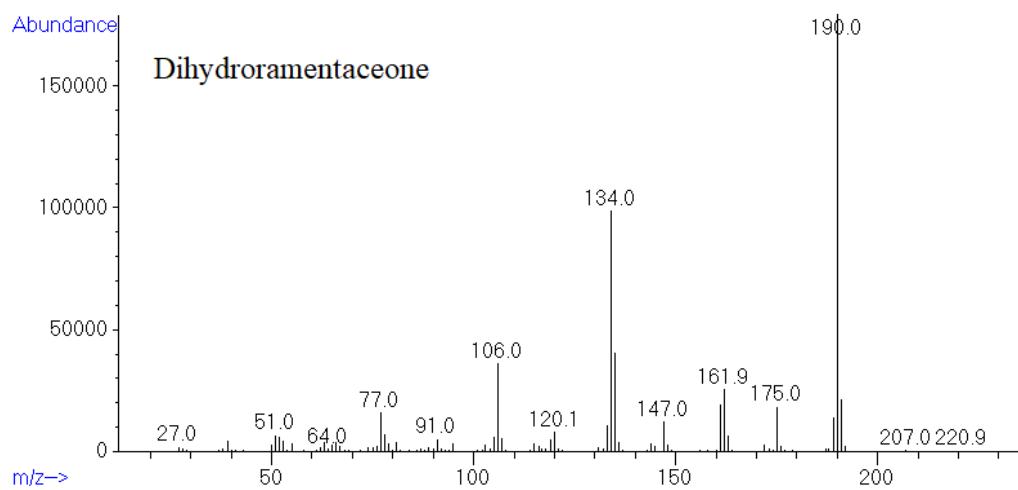


Fig. 3S. MS of TMS derivative compound **1a**.

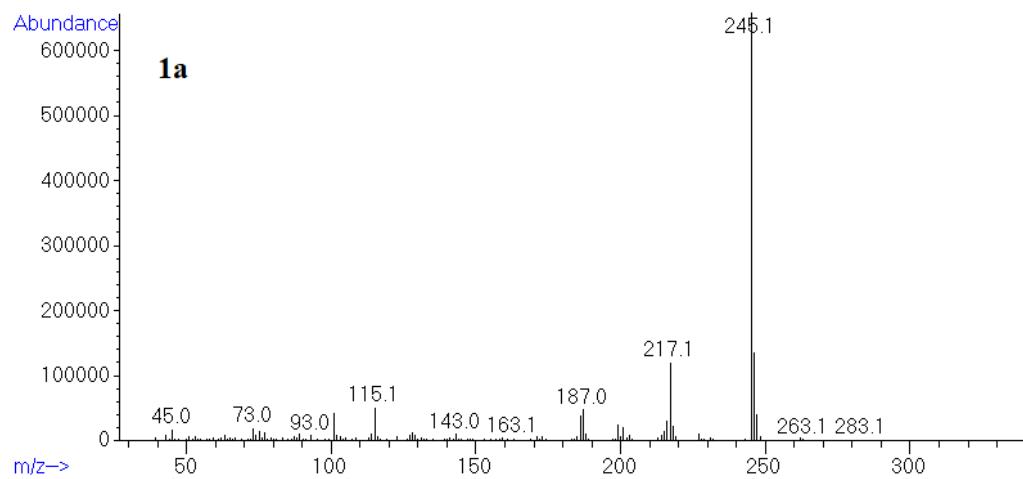


Fig. 4S. MS of TMS derivative compound **2a**.

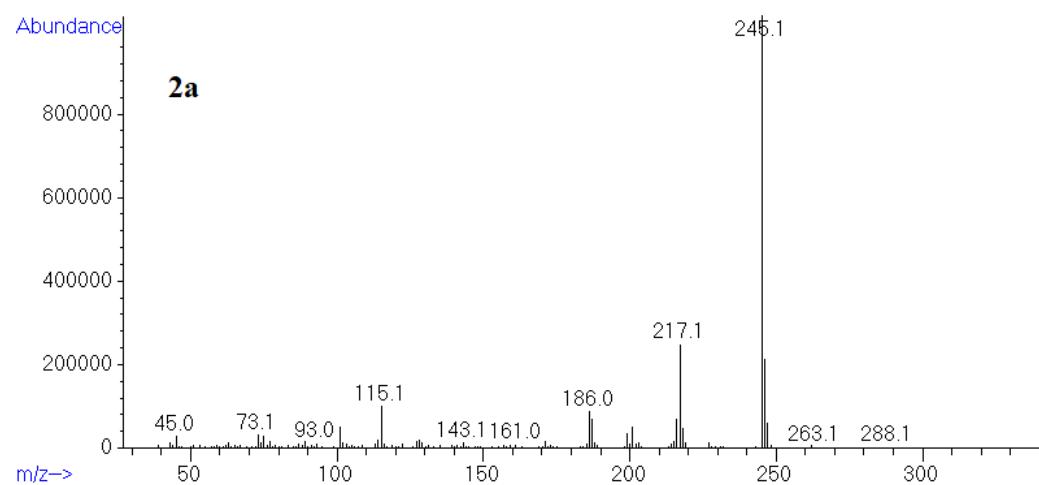


Fig. 5S. MS of TMS derivative compound **3a**.

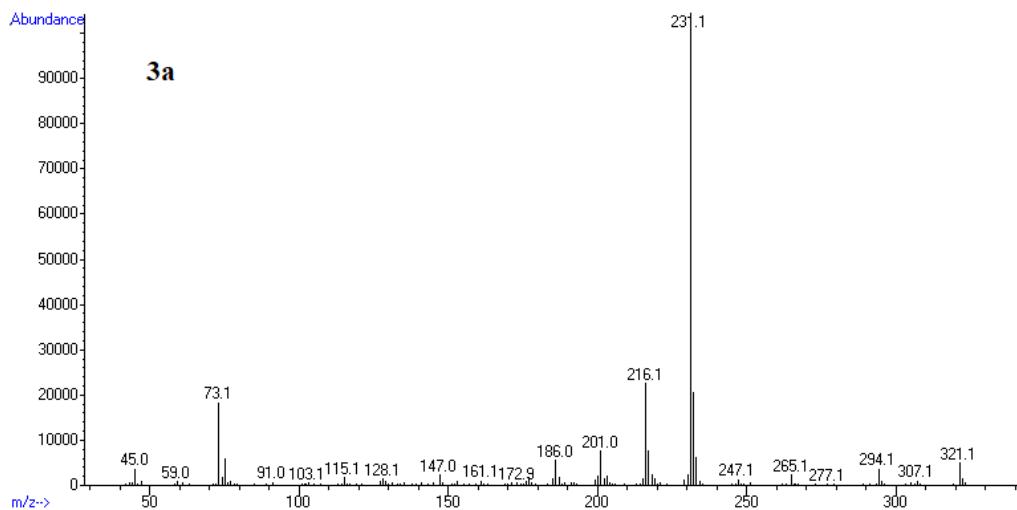


Fig. 6S. MS of TMS derivative compound **4a**.

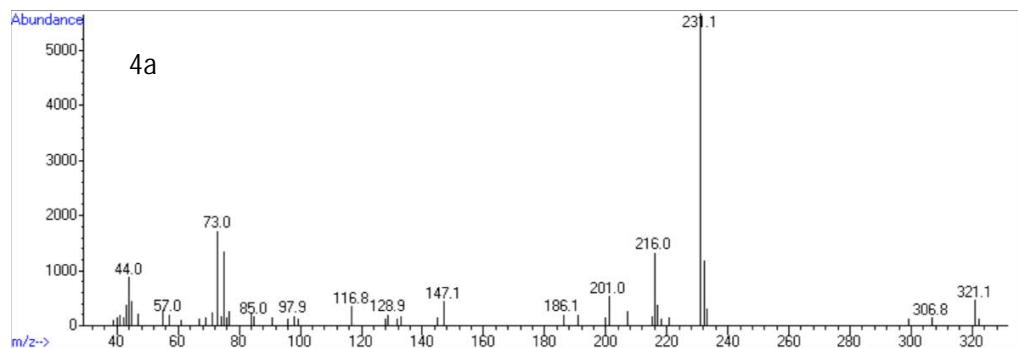


Fig. 7S. MS of TMS derivative compound **5a**.

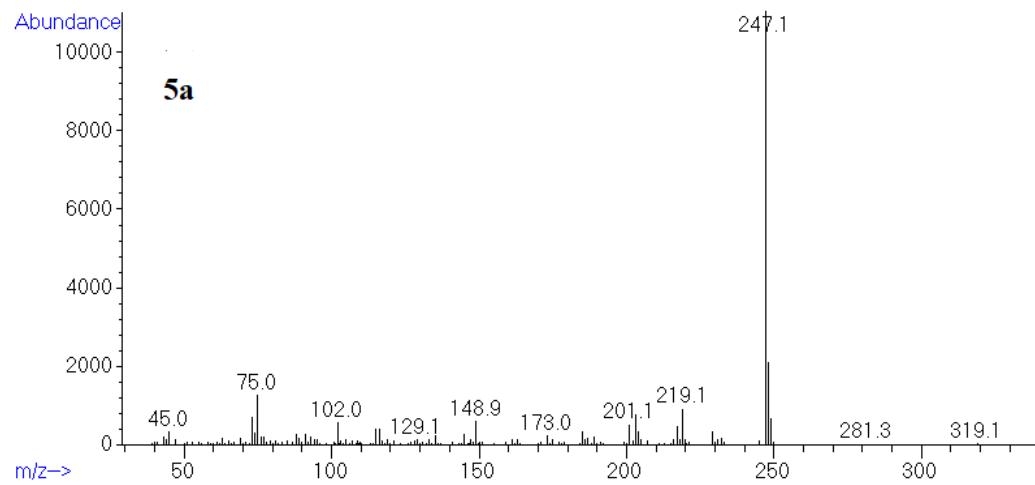


Fig. 8S. MS of TMS derivative compound **6a**.

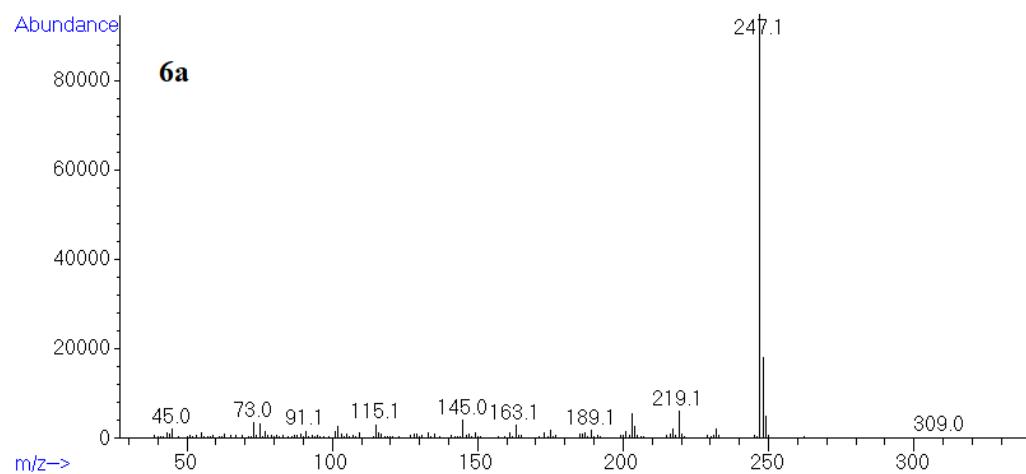


Fig. 9S. MS of TMS derivative compound **7a**.

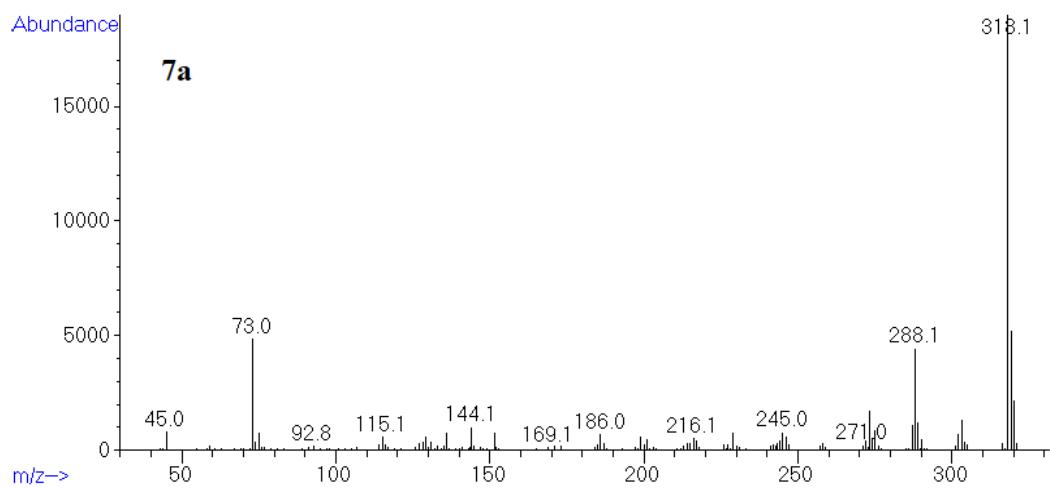


Fig. 10S. MS of TMS derivative compound **8a**.

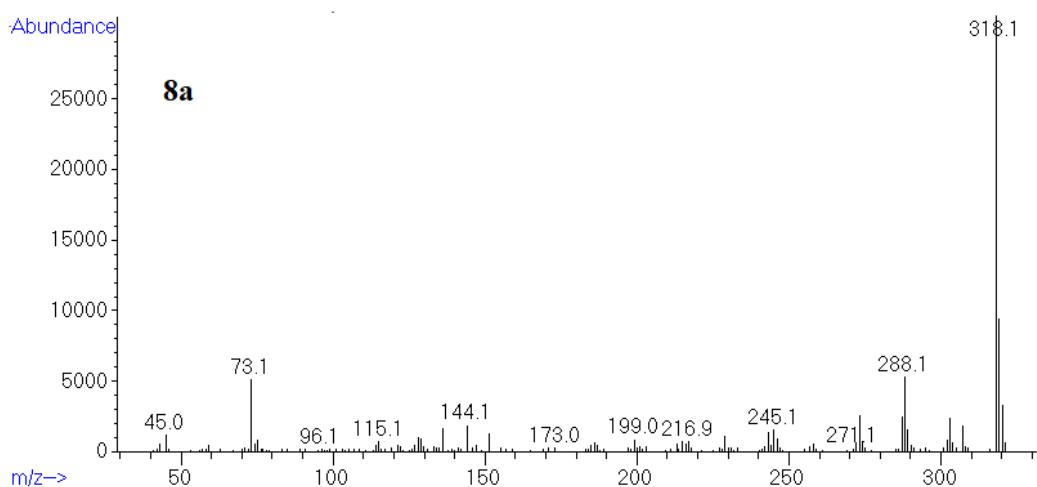


Fig. 11S. TLC of extracts from selected *Drosera* species

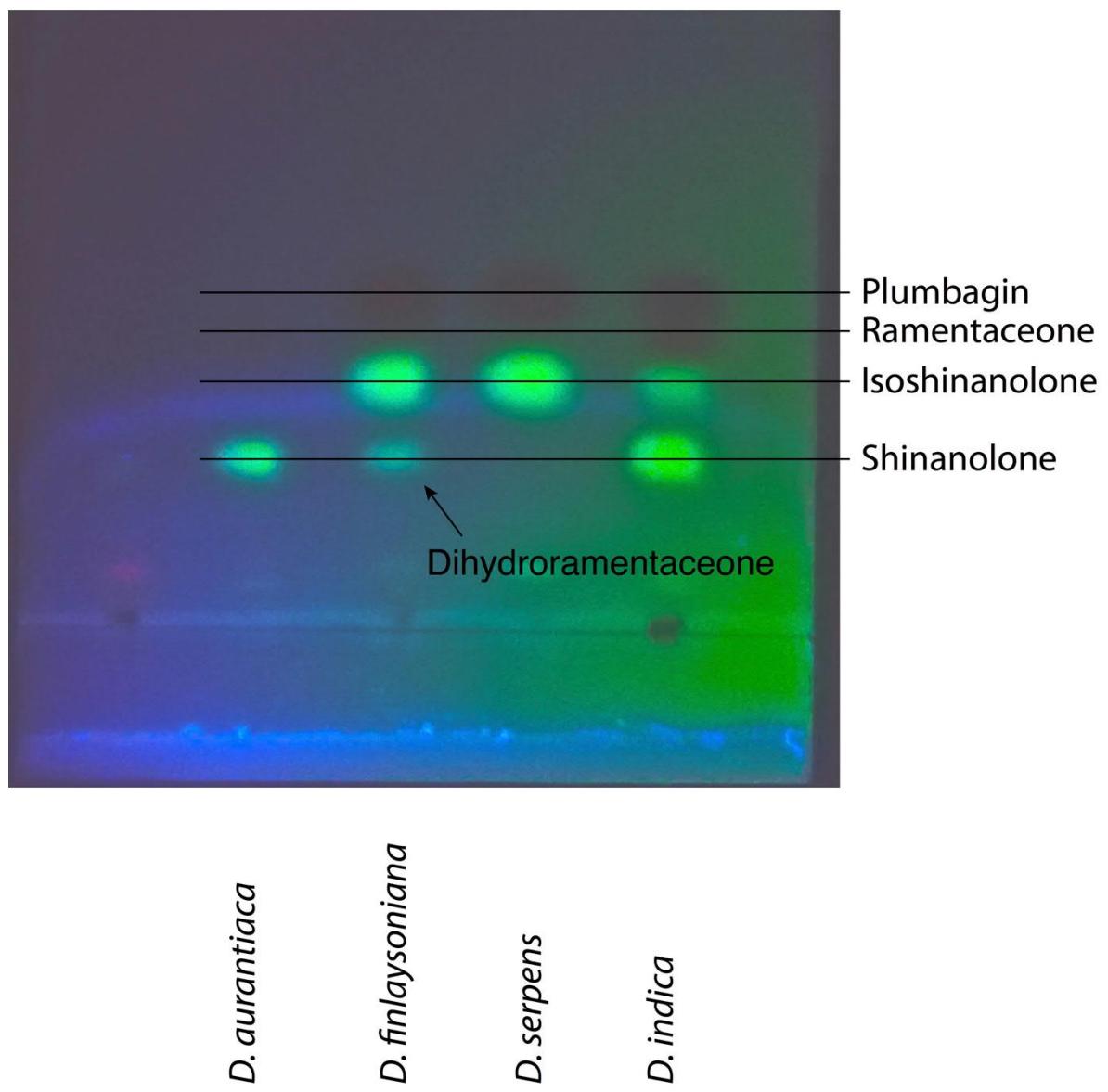


Table 1S. MS Data of Identified Naphthoquinone Derivatives

Name (no.)	Molecular formula	EIMS <i>m/z</i> (%) [interpretation]
<i>Plumbagin</i> (1)	C ₁₁ H ₈ O ₃	188 [M] ⁺ (100), 173 [M-CH ₃] ⁺ (30), 160 [M-CO] ⁺ (25), 132 (30), 131 [M-C ₃ H ₅ O] ⁺ (50), 121 [M-C ₄ H ₃ O] ⁺ (15), 120 [M-C ₄ H ₄ O] ⁺ (25), 103 [M-C ₄ H ₅ O ₂] ⁺ (10), 92 [M-C ₅ H ₄ O ₂] ⁺ (40), 77 (15), 63 (40)
<i>Ramentaceone</i> (2)	C ₁₁ H ₈ O ₃	188 [M] ⁺ (100), 187 [M-H] ⁺ (30), 173 [M-CH ₃] ⁺ (10), 160 [M-CO] ⁺ (15), 134 [M-C ₃ H ₂ O] ⁺ (20), 132 (30), 131 [M-C ₃ H ₅ O] ⁺ (30), 106 [M-C ₄ H ₂ O ₂] ⁺ (20), 104 (10), 103 [M-C ₄ H ₅ O ₂] ⁺ (10), 78 (15), 77 (25), 63 (15), 62 (10), 51 (25)
<i>Isoshinanolone</i> (3)	C ₁₁ H ₁₂ O ₃	192 [M] ⁺ (70), 177 [M-CH ₃] ⁺ (20), 174 [M-H ₂ O] ⁺ (10), 150 [M-C ₃ H ₆] ⁺ (40), 149 [M-C ₂ H ₃ O] ⁺ (25), 131 [M-C ₂ H ₅ O ₂] ⁺ (20), 122 [M-C ₃ H ₂ O ₂] ⁺ (45), 121 [M-C ₄ H ₇ O] ⁺ (100), 115 (10), 93 (25), 77 (20), 65 (30), 51 (20)
<i>Shinanolone</i> (4)	C ₁₁ H ₁₂ O ₃	192 [M] ⁺ (70), 177 [M-CH ₃] ⁺ (10), 174 [M-H ₂ O] ⁺ (10), 164 [M-C ₂ H ₄] ⁺ (20), 149 [M-C ₂ H ₃ O] ⁺ (15), 135 [M-C ₃ H ₅ O] ⁺ (100), 107 [M-C ₄ H ₅ O ₂] ⁺ (20)
<i>Dihydroplumbagin</i> (5)	C ₁₁ H ₁₀ O ₃	190 [M] ⁺ (85), 175 [M-CH ₃] ⁺ (100), 162 [M-CO] ⁺ (20), 147 [M-C ₂ H ₃ O] ⁺ (20), 120 [M-C ₄ H ₆ O] ⁺ (60), 92 [M-C ₅ H ₄ O ₂] ⁺ (40), 63 (15)
<i>Dihydroramentaceone</i> (6)	C ₁₁ H ₁₀ O ₃	190 [M] ⁺ (100), 175 [M-CH ₃] ⁺ (10), 162 [M-CO] ⁺ (15), 134 [M-C ₃ H ₄ O] ⁺ (55), 106 [M-C ₄ H ₄ O ₂] ⁺ (20)
5- <i>O</i> -Trimethylsilyl- <i>plumbagin</i> (1a)	C ₁₄ H ₁₆ O ₃ Si	245 [M-CH ₃] ⁺ (100), 217 [M-CH ₃ -CO] ⁺ (30), 186 (10), 115 (10)
5- <i>O</i> -Trimethylsilyl- <i>ramentaceone</i> (2a)	C ₁₄ H ₁₆ O ₃ Si	245 [M-CH ₃] ⁺ (100), 217 [M-CH ₃ -CO] ⁺ (20), 187 (10), 115 (10)
4,8-Di-(<i>O</i> -trimethylsilyl)- <i>isoshinanolone</i> (3a)	C ₁₇ H ₂₈ O ₃ Si ₂	321 [M-CH ₃] ⁺ (5), 231 [M-CH ₃ -C ₃ H ₁₀ OSi] ⁺ (100), 216 [M-2CH ₃ -C ₃ H ₁₀ OSi] ⁺ (20), 201 [M-3CH ₃ -C ₃ H ₁₀ OSi] ⁺ (10), 186 [M-4CH ₃ -C ₃ H ₁₀ OSi] ⁺ (5)
4,8-Di-(<i>O</i> -trimethylsilyl)- <i>shinanolone</i> (4a)	C ₁₇ H ₂₈ O ₃ Si ₂	321 [M-CH ₃] ⁺ (5), 231 [M-CH ₃ -C ₃ H ₁₀ OSi] ⁺ (100), 216 [M-2CH ₃ -C ₃ H ₁₀ OSi] ⁺ (20), 201 [M-3CH ₃ -C ₃ H ₁₀ OSi] ⁺ (10), 186 [M-4CH ₃ -C ₃ H ₁₀ OSi] ⁺ (5)
5- <i>O</i> -Trimethylsilyl- <i>dihydroplumbagin</i> (5a)	C ₁₄ H ₁₈ O ₃ Si	247 [M-CH ₃] ⁺ (100), 219 [M-CH ₃ -CO] ⁺ (10)
5- <i>O</i> -Trimethylsilyl- <i>dihydroramentaceone</i> (6a)	C ₁₄ H ₁₈ O ₃ Si	247 [M-CH ₃] ⁺ (100), 219 [M-CH ₃ -CO] ⁺ (10)
1,5-Di-(<i>O</i> -trimethylsilyl)-2-methyl-naphtho-1,4,5-triol (7a)	C ₁₇ H ₂₆ O ₃ Si ₂	318 [M-CH ₄] ⁺ (100), 288 [M-CH ₄ -2CH ₃] ⁺ (20), 273 [M-CH ₄ -3CH ₃] ⁺ (10)
4,5-Di-(<i>O</i> -trimethylsilyl)-2-methyl-naphtho-1,4,5-triol (7b)	C ₁₇ H ₂₆ O ₃ Si ₂	319 [M-CH ₃] ⁺ (100), 245 (15), 217 (10)
2-Methyl-1,4,5-tri-(<i>O</i> -trimethylsilyl)-naphtho-1,4,5-triol (7c)	C ₂₀ H ₃₄ O ₃ Si ₃	406 [M] ⁺ (100)
1,5-Di-(<i>O</i> -trimethylsilyl)-7-methyl-naphtho-1,4,5-triol (8a)	C ₁₇ H ₂₆ O ₃ Si ₂	318 [M-CH ₄] ⁺ (100), 288 [M-CH ₄ -2CH ₃] ⁺ (20), 273 [M-CH ₄ -3CH ₃] ⁺ (10)
4,5-Di-(<i>O</i> -trimethylsilyl)-7-methyl-naphtho-1,4,5-triol (8b)	C ₁₇ H ₂₆ O ₃ Si ₂	319 [M-CH ₃] ⁺ (100), 245 (15), 217 (10)
7-Methyl-1,4,5-tri-(<i>O</i> -trimethylsilyl)-naphtho-1,4,5-triol (8c)	C ₂₀ H ₃₄ O ₃ Si ₃	406 [M] ⁺ (100)