**Table S1.** Microcystin congeners reported in the literature as identified from cyanobacterial cultures and field samples

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Entry** | **Microcystin** | **Molecular Formula** | **Exact****Massa** | **Characterization** | **Reference** |
| 1 | [D‐Asp³,DMAdda5]MC‐LA | C44H63N7O12 | 881.4535 | LC-MS/MS | [33] |
| 2 | [D‐Asp³]MC‐VA | C44H63N7O12 | 881.4535 | LC-MS/MS | [33] |
| 3 | [D-Asp3]MC-LA | C45H65N7O12 | 895.4691 | LC-HRMS/MS | [93] |
| 4 | [Dha7]MC‐LA | C45H65N7O12 | 895.4691 | LC-MS/MS | [33] |
| 5 | [DMAdda5]MC‐LA | C45H65N7O12 | 895.4691 | LC–MS/MS, thiol  | [127] |
| 6 | MC‐VA | C45H65N7O12 | 895.4691 | LC-MS/MS | [33] |
| 7 | MC-LA | C46H67N7O12 | 909.4848 | MS, NMR, AA, LC-HRMS/MS | [15,93] |
| 8 | MC-LAbu | C47H69N7O12 | 923.5004 | HRFABMS, AA, NMR | [128] |
| 9 | [D-Asp3,D-Glu(OMe)6]MC-LAbub | C47H69N7O12 | 923.5004 | LC-HRMS/MS | [38] |
| 10 | [D‐Asp³]MC‐LV | C47H69N7O12 | 923.5004 | LC-MS/MS | [33] |
| 11 | [D-Asp³]MC-FA | C48H63N7O12 | 929.4535 | LC-MS/MS, thiol | [12] |
| 12 | [D-Asp³,Dha7]MC‐YA | C47H61N7O13 | 931.4327 | MALDI-TOF MS | [88] |
| 13 | [D-Asp3]MC-LL | C48H71N7O12 | 937.5161 | LC-HRMS/MS | [93] |
| 14 | MC‐LV | C48H71N7O12 | 937.5161 | AA, LC-MS/MS | [33,129] |
| 15 | [D-Asp³]MC-RA | C45H66N10O12 | 938.4862 | LC-MS/MS, thiol | [12,33] |
| 16 | MC-FA | C49H65N7O12 | 943.4691 | NMR, LC-MS/MS, AA, thiol | [130] |
| 17 | MC-LL | C49H73N7O12 | 951.5317 | LC-HRMS/MS, AA | [93,129] |
| 18 | MC-AR | C46H68N10O12 | 952.5018 | AA, HRMS,NMR | [75] |
| 19 | MC-RA | C46H68N10O12 | 952.5018 | LC-MS/MS, NMR, thiol | [76,131] |
| 20 | [D-Asp³]MC-RAbu | C46H68N10O12 | 952.5018 | LC-MS/MS, thiol | [12] |
| 21 | MC-FAbu  | C50H67N7O12 | 957.4848 | LC-MS/MS, thiol | [12] |
| 22 | MC-YA | C49H65N7O13 | 959.4640 | AA, NMR,MS, LC-MS/MS, thiol | [16,76] |
| 23 | MC‐AHar | C47H70N10O12 | 966.5175 | LC-MS/MS | [132] |
| 24 | [Gly1,D-Asp3]MC-LR | C47H70N10O12 | 966.5175 | LC-MS/MS | [91] |
| 25 | [D-Asp3,Dha7]MC-LR | C47H70N10O12 | 966.5175 | AA, FABMS/MS | [83] |
| 26 | [D‐Asp³,DMAdda5]MC‐LR | C47H70N10O12 | 966.5175 | LC-MS/MS | [133] |
| 27 | [D-Asp³,DMAdda5,Dhb7]MC‐LR | C47H70N10O12 | 966.5175 | LC-MS/MS, thiol | [106] |
| 28 | [Gly¹,D-Asp3,Dhb7]MC-LR | C47H70N10O12 | 966.5175 | LC-MS/MS, HRMS, AA, thiol | [90] |
| 29 | MC‐RAbu | C47H70N10O12 | 966.5175 | LC-MS/MS, thiol | [76] |
| 30 | [D-Asp3]MC-HarAbu | C47H70N10O12 | 966.5175 | LC-MS/MS | [40] |
| 31 | [D-Asp³]MC-WA | C50H64N8O12 | 968.4644 | LC-MS/MS, thiol | [12] |
| 32 | [D-Asp3,Dha7]MC-EE(OMe)b | C46H63N7O16 | 969.4331 | HRMS, MS/MS | [134] |
| 33 | MC-LM | C48H71N7O12S | 969.4881 | AA, MS | [129] |
| 34 | [D-Asp3]MC-LF | C51H69N7O12 | 971.5004 | LC-MS, MS/MS, LC-MS/MS, thiol | [105,135] |
| 35 | MC-VF | C51H69N7O12 | 971.5004 | LC-MS/MS, 15N-enrichment | [136] |
| 36 | [D-Asp3,Dha7]MC‐LY | C50H67N7O13 | 973.4797 | LC-MS/MS, thiol | [105] |
| 37 | MC‐YAbu | C50H67N7O13 | 973.4797 | LC-MS/MS, thiol | [76] |
| 38 | [D-Asp3]MC-LR | C48H72N10O12 | 980.5331 | MS/MS, HRMS, AA | [137] |
| 39 | [D-Asp3,(*E*)-Dhb7]MC-LR | C48H72N10O12 | 980.5331 | NMR, AA, HRMS | [138] |
| 40 | [D-Asp3,(*Z*)-Dhb7]MC-LR | C48H72N10O12 | 980.5331 | NMR, AA, HRMS | [138] |
| 41 | [Dha7]MC-LR | C48H72N10O12 | 980.5331 | AA, FABMS/MS | [83] |
| 42 | [DMAdda5]MC-LR | C48H72N10O12 | 980.5331 | AA, HRMS,NMR | [75] |
| 43 | [Gly1,D-Asp3,Dhb7]MC-LHar | C48H72N10O12 | 980.5331 | LC-MS/MS, HRMS, AA, thiol | [90] |
| 44 | MC‐RApa | C48H72N10O12 | 980.5331 | LC-MS/MS, thiol | [76] |
| 45 | MC‐VR | C48H72N10O12 | 980.5331 | LC-MS/MS | [139] |
| 46 | MC-WA | C51H66N8O12 | 982.4800 | NMR, LC-MS/MS, AA, thiol | [130] |
| 47 | [D-Ser1,D‐Asp³,Dha7]MC‐LR | C47H70N10O13 | 982.5124 | LC-MS/MS | [33] |
| 48 | [Dha7]MC-EE(OMe)b | C47H65N7O16 | 983.4488 | HRMS, MS/MS | [134] |
| 49 | [D-Asp3,Dha7]MC-E(OMe)E(OMe)b | C47H65N7O16 | 983.4488 | HRMS, MS/MS | [134] |
| 50 | MC-FL | C52H71N7O12 | 985.5161 | LC-MS/MS, thiol | [12] |
| 51 | MC-LF | C52H71N7O12 | 985.5161 | AA, MS | [129] |
| 52 | MC-KynAb | C50H66N8O13 | 986.4749 | LC-MS/MS, HRMS, thiol | [89] |
| 53 | [D-Asp³]MC‐LY | C51H69N7O13 | 987.4953 | LC-MS/MS, thiol | [105] |
| 54 | [D-Asp3,(*E*)-Dhb7]MC-LY | C51H69N7O13 | 987.4953 | NMR, LC-HRMS/MS, thiol | [106] |
| 55 | [D-Gly1,D-Asp3,ADMAdda5]MC-LR | C48H70N10O13 | 994.5124 | LC-MS/MS | [91] |
| 56 | [Gly1,D-Asp³,ADMAdda5,Dhb7]MC‐LR | C48H70N10O13 | 994.5124 | LC-MS/MS, HRMS, AA, thiol | [90] |
| 57 | [D‐Asp³,ADMAdda5]MC‐VR | C48H70N10O13 | 994.5124 | LC-MS/MS | [33] |
| 58 | [D‐Asp³,Dhb7]MC‐AhaR | C49H74N10O12 | 994.5488 | LC-MS/MS, thiol | [106] |
| 59 | [D‐Asp³]MC‐Hil/HleR | C49H74N10O12 | 994.5488 | LC-MS/MS | [33] |
| 60 | [D‐Asp³,(*E*)‐Dhb7]MC‐HilR  | C49H74N10O12 | 994.5488 | NMR, HRMS, AA | [140] |
| 61 | [Dha7]MC-HilR | C49H74N10O12 | 994.5488 | HRMS, NMR, AA | [141] |
| 62 | [DMAdda5]MC‐HilR | C49H74N10O12 | 994.5488 | LC-MS/MS | [33] |
| 63 | [DMAdda5]MC‐LHar | C49H74N10O12 | 994.5488 | LC-MS/MS | [33] |
| 64 | [D-Asp3,D-Glu(OMe)6]MC-LRb | C49H74N10O12 | 994.5488 | HRMS, MS/MS, AA | [84] |
| 65 | MC-LR | C49H74N10O12 | 994.5488 | AA, NMR, HRMS, LC-MS/MS | [16,137,142] |
| 66 | [(6*Z*)-Adda5]MC-LRb | C49H74N10O12 | 994.5488 | NMR, AA, MS | [111,143] |
| 67 | MC‐RL | C49H74N10O12 | 994.5488 | LC-MS/MS, thiol | [76] |
| 68 | MC-WAbu | C52H68N8O12 | 996.4957 | LC-MS/MS, thiol | [89] |
| 69 | [Dha7]MC-E(OMe)E(OMe) b | C48H67N7O16 | 997.4644 | HRMS, MS/MS | [134] |
| 70 | MC-OiaAb | C51H66N8O13 | 998.4749 | LC-MS/MS, HRMS, thiol | [89] |
| 71 | [D-Asp³]MC‐MR | C47H70N10O12S | 998.4895 | LC-MS/MS, thiol, *S*-oxidation | [92] |
| 72 | [seco‐4/5][D-Asp³]MC‐LRb | C48H74N10O13 | 998.5437 | LC-MS/MS, thiol | [92] |
| 73 | [D-Asp³,Mser7]MC‐LR | C48H74N10O13 | 998.5437 | LC-MS/MS, MS/MS, thiol | [87,92] |
| 74 | [Ser7]MC-LR | C48H74N10O13 | 999.5437 | AA, HRMS, MS/MS | [83] |
| 75 | MC‐LHph | C53H73N7O12 | 999.5317 | LC-MS/MS | [74] |
| 76 | MC-KynAbub | C50H68N10O12 | 1000.5018 | LC-MS/MS, thiol | [89] |
| 77 | [D‐Asp³,Dha7]MC‐FR | C50H68N10O12 | 1000.5018 | LC-MS/MS | [33] |
| 78 | [Ser7]MC-EE(OMe)b | C47H67N7O17 | 1001.4593 | HRMS, MS/MS | [134] |
| 79 | [D-Asp3,Ser7]MC-E(OMe)E(OMe)b | C47H67N7O17 | 1001.4593 | HRMS, MS/MS | [134] |
| 80 | [D-Asp³]MC‐HilY | C52H71N7O13 | 1001.5110 | LC-MS/MS, thiol | [105] |
| 81 | MC-LY | C52H71N7O13 | 1001.5110 | LC-MS/MS, NMR | [38,144] |
| 82 | MC-YL | C52H71N7O13 | 1001.5110 | LC-MS/MS | [38] |
| 83 | [D‐Asp³,Mser7]MC‐LY | C51H71N7O14 | 1005.5059 | LC-MS/MS, thiol | [105] |
| 84 | [D‐Asp³,ADMAdda5,Dha7]MC‐HilR | C49H72N10O13 | 1008.5280 | LC-MS/MS | [33] |
| 85 | [Gly1,D-Asp3,ADMAdda5,Dhb7]MC-LHar | C49H72N10O13 | 1008.5280 | LC-MS/MS, HRMS, AA, thiol | [90] |
| 86 | [Gly1,D-Asp3,ADMAdda5]MC-LHar | C49H72N10O13 | 1008.5280 | LC-MS/MS | [91] |
| 87 | [D-Asp3,ADMAdda5]MC-LR | C49H72N10O13 | 1008.5280 | HRMS, NMR, AA, MS/MS, LC-MS/MS | [77,78,145] |
| 88 | [ADMAdda5,Dha7]MC‐LR | C49H72N10O13 | 1008.5280 | LC-MS/MS | [33] |
| 89 | [D-Asp³,ADMAdda5,Dhb7]MC‐LR | C49H72N10O13 | 1008.5280 | NMR, HRMS, AA | [146] |
| 90 | MC-HilR | C50H76N10O12 | 1008.5644 | MS/MS, HRMS, NMR, AA | [79] |
| 91 | MC-LHar | C50H76N10O12 | 1008.5644 | AA, MS/MS, HRMS, NMR | [147] |
| 92 | [D-Glu(OMe)6]MC-LRb | C50H76N10O12 | 1008.5644 | HRMS, MS/MS, AA, HRMS/MS | [84,148] |
| 93 | [Mdhb7]MC-LR | C50H76N10O12 | 1008.5644 | AA, MS | [78] |
| 94 | [D-Leu1,D-Asp³,DMAdda5]MC‐LR | C50H76N10O12 | 1008.5644 | LC-MS/MS | [149] |
| 95 | [D-Asp3,Dha7]MC-RR | C47H71N13O12 | 1009.5345 | AA, NMR, HRMS | [75] |
| 96 | [D-Asp³,DMAdda5]MC‐RR | C47H71N13O12 | 1009.5345 | MS, MS/MS | [54] |
| 97 | [D-Gly1,D-Asp3]MC-RR | C47H71N13O12 | 1009.5345 | LC-MS/MS | [91] |
| 98 | [Gly1,D-Asp3,Dhb7]MC-RR | C47H71N13O12 | 1009.5345 | LC-MS/MS, HRMS, AA, thiol | [90] |
| 99 | [D-Asp3]MC-LW | C53H70N8O12 | 1010.5113 | LC-MS, MS/MS | [135] |
| 100 | [D-Asp3,(*E*)-Dhb7]MC-LW | C53H70N8O12 | 1010.5113 | NMR, LC-HRMS/MS | [94] |
| 101 | MC-OiaAbub | C52H68N8O13 | 1012.4906 | LC-MS/MS, thiol | [89] |
| 102 | MC‐MR | C48H72N10O12S | 1012.5052 | LC-MS/MS, thiol, *S*-oxidation | [92] |
| 103 | [Mser7]MC-LR | C49H76N10O13 | 1012.5593 | LC-HRMS | [79,93] |
| 104 | [seco‐4/5]MC‐LRb | C49H76N10O13 | 1012.5593 | LC-MS/MS, HRMS, thiol,NMR | [92,150] |
| 105 | [seco‐1/2]MC‐LRb | C49H76N10O13 | 1012.5593 | MS/MS, HRMS, NMR | [150] |
|
| 106 | MC-NfkAb | C51H66N8O14 | 1014.4698 | NMR, LC-MS/MS, HRMS, thiol | [89] |
| 107 | [D-Asp³]MC‐M(O)Rb | C47H70N10O13S | 1014.4845 | LC-MS/MS, thiol, *S*-oxidation | [92] |
| 108 | [D‐Asp³,Dha7]MC‐HphR | C51H70N10O12 | 1014.5175 | LC-MS/MS | [33] |
| 109 | [D-Asp3]MC-FR | C51H70N10O12 | 1014.5175 | AA, MS, NMR | [86] |
| 110 | [Dha7]MC-FR | C51H70N10O12 | 1014.5175 | AA, HRMS, MS/MS | [151] |
| 111 | [DMAdda5]MC‐FR | C51H70N10O12 | 1014.5175 | LC-MS/MS | [133] |
| 112 | [D-Asp³]MC‐RF | C51H70N10O12 | 1014.5175 | LC-MS/MS, thiol | [105] |
| 113 | [Ser7]MC-E(OMe)E(OMe)b | C48H69N7O17 | 1015.4750 | HRMS, MS/MS | [134] |
| 114 | MC‐LHty | C53H73N7O13 | 1015.5266 | LC-MS/MS | [74] |
| 115 | [D-Asp³,Dha7]MC‐RY | C50H68N10O13 | 1016.4967 | LC-MS/MS, thiol | [105] |
| 116 | [D-Asp³,DMAdda5]MC‐RY | C50H68N10O13 | 1016.4967 | LC-MS/MS, thiol | [106] |
| 117 | MC-YM | C51H69N7O13S | 1019.4674 | AA, NMR, MS | [16] |
| 118 | [D-Asp3,ADMAdda5]MC-LHar | C50H74N10O13 | 1022.5437 | HRMS, MS/MS, AA | [85] |
| 119 | [ADMAdda5]MC‐LR | C50H74N10O13 | 1022.5437 | HRMS NMR, AA, MS/MS | [77,78] |
| 120 | [D-Leu1,DMAdda5]MC-LR | C51H78N10O12 | 1022.5801 | LC-HRMS/MS, thiol | [80] |
| 121 | [D-Leu1,dmAdda5]MC-LR (isomer 1)c | C51H78N10O12 | 1022.5801 | LC-HRMS/MS, thiol | [80] |
| 122 | [D-Leu1,dmAdda5]MC-LR (isomer 2)c | C51H78N10O12 | 1022.5801 | LC-HRMS/MS, thiol | [80] |
| 123 | [D-Leu1,D-Asp3]MC-LR | C51H78N10O12 | 1022.5801 | LC-MS/MS, HRMS/MS | [148,149] |
| 124 | [D-Leu1,Dha7]MC-LR | C51H78N10O12 | 1022.5801 | LC-MS/MS | [74] |
| 125 | [D-Val1]MC‐LR | C51H78N10O12 | 1022.5801 | LC-MS/MS | [74] |
| 126 | [Gly1,D-Asp³,Dhb7]MC‐RHar | C48H73N13O12 | 1023.5502 | LC-MS/MS, HRMS, AA, thiol | [90] |
| 127 | [D-Asp3]MC-RR | C48H73N13O12 | 1023.5502 | AA, HRMS,NMR | [75,152] |
| 128 | [Dha7]MC-RR | C48H73N13O12 | 1023.5502 | AA, HRMS, MS/MS, NMR | [153] |
| 129 | [D-Asp3,(*E*)-Dhb7]MC-RR | C48H73N13O12 | 1023.5502 | NMR, HRMS | [154] |
| 130 | [Gly1,D-Asp3]MC-RHar | C48H73N13O12 | 1023.5502 | LC-MS/MS | [91] |
| 131 | [DMAdda5]MC-RR | C48H73N13O12 | 1023.5502 | LC-HRMS/MS, thiol | [81] |
| 132 | MC-WL | C54H72N8O12 | 1023.5502 | LC-MS/MS, thiol | [89] |
| 133 | MC-LW | C54H72N8O12 | 1024.5270 | LC-MS/MS, 15N-enrichment | [136] |
| 134 | [Seco-1/2]MC-HilRb | C50H78N10O13 | 1024.5270 | MS/MS, HRMS | [79] |
| 135 | MC-NfkAbub | C52H68N8O14 | 1026.5750 | LC-MS/MS, thiol | [89] |
| 136 | MC-M(O)Rb | C48H72N10O13S | 1028.5001 | AA, HRMS,NMR | [75] |
| 137 | MC-FR | C52H72N10O12 | 1028.5331 | AA, HRMS,NMR | [75,155] |
| 138 | MC‐RF | C52H72N10O12 | 1028.5331 | LC-MS/MS, thiol | [76] |
| 139 | [D-Asp³]MC‐HphR | C52H72N10O12 | 1028.5331 | MS/MS | [87] |
| 140 | [Dha7]MC-HphR | C52H72N10O12 | 1028.5331 | AA, HRMS, MS/MS, 1H-NMR | [156] |
| 141 | [D-Asp³]MC‐M(O2)Rb | C47H70N10O14S | 1030.4794 | LC-MS/MS, thiol, *S*-oxidation | [92] |
| 142 | [D-Asp3,Dha7]MC-HtyR | C51H70N10O13 | 1030.5124 | AA, HRMS, MS/MS,NMR | [156] |
| 143 | [D-Asp³,DMAdda5]MC‐HtyR | C51H70N10O13 | 1030.5124 | MS/MS | [87] |
| 144 | [Dha7]MC-YR | C51H70N10O13 | 1030.5124 | HRMS, MS/MS, AA | [157] |
| 145 | [D-Asp3]MC-RY | C51H70N10O13 | 1030.5124 | HRMS,LC-MS/MS, thiol | [105,158,159] |
| 146 | [Dha7]MC‐RY | C51H70N10O13 | 1030.5124 | LC-MS/MS, thiol | [76] |
| 147 | [D-Asp³,Dhb7]MC‐RY | C51H70N10O13 | 1030.5124 | LC-MS/MS, thiol | [106] |
| 148 | [D-Asp3]MC-YR | C51H70N10O13 | 1030.5124 | AA, HRMS, MS/MS | [160] |
|
| 149 | [D-Asp3,(*E*)-Dhb7]MC-YR | C51H70N10O13 | 1030.5124 | NMR, LC-HRMS/MS | [94] |
| 150 | [DMAdda5]MC‐YR | C51H70N10O13 | 1030.5124 | LC–MS/MS, thiol | [127] |
| 151 | MC‐LY(OMe)  | C53H73N7O14 | 1031.5216 | LC-MS/MS, thiol | [105] |
| 152 | [D-Asp³]MC‐(H4)YR | C51H74N10O13 | 1034.5437 | LC–MS/MS, thiol | [127] |
| 153 | [Dha7]MC‐(H4)YR | C51H74N10O13 | 1034.5437 | HRMS, NMR, AA | [141] |
| 154 | [DMAdda5]MC‐(H4)YR | C51H74N10O13 | 1034.5437 | LC-MS/MS | [133] |
| 155 | MC-YM(O)b | C51H69N7O14S | 1035.4623 | AA, NMR, MS | [161] |
| 156 | [ADMAdda5]MC‐HilR | C51H76N10O13 | 1036.5593 | LC-MS/MS | [33] |
| 157 | [ADMAdda5]MC-LHar | C51H76N10O13 | 1036.5593 | HRMS, NMR, AA, MS/MS | [77,78] |
| 158 | MC‐AnaR | C52H80N10O12 | 1036.5957 | LC–MS/MS, thiol | [127] |
| 159 | [D-Leu1]MC-LR | C52H80N10O12 | 1036.5957 | NMR, HRMS, MS/MS, AA | [162,163] |
| 160 | [D-Asp³]MC‐YY | C54H67N7O14 | 1037.4746 | LC-MS/MS, thiol | [105] |
| 161 | [Gly1,D-Asp3,ADMAdda5,Dhb7]MC-RR | C48H71N13O13 | 1037.5294 | LC-MS/MS, HRMS, AA, thiol | [90] |
| 162 | MC-RR | C49H75N13O12 | 1037.5658 | NMR, AA, MS | [48] |
| 163 | [(6*Z*)-Adda5]MC-RRb | C49H75N13O12 | 1037.5658 | NMR, AA, MS | [111,143] |
| 164 | [D-Asp3,D-Glu(OMe)6]MC-RRb | C49H75N13O12 | 1037.5658 | NMR, AA, MS/MS | [164] |
| 165 | [Gly1,D-Asp3,ADMAdda5]MC-RR | C49H75N13O12 | 1037.5658 | LC-MS/MS | [91] |
| 166 | [D-Ser1,ADMAdda5]MC-LR | C50H74N10O14 | 1038.5386 | HRMS, MS/MS, AA | [85] |
| 167 | [D-Met1,D-Asp3]MC-LR | C50H76N10O12S | 1040.5365 | LC-MS/MS | [74] |
| 168 | [ADMAdda5,Mser7]MC-LR  | C50H76N10O14 | 1040.5542 | HRMS, MS/MS, AA | [85] |
| 169 | [Ser7]MC-RR | C48H75N13O13 | 1041.5607 | AA, HRMS, MS/MS | [83] |
| 170 | [D‐Asp³,Mser7]MC‐RR | C48H75N13O13 | 1041.5607 | AA, HRMS, MS/MS | [110] |
| 171 | [D-Asp³,Thr7]MC‐RR | C48H75N13O13 | 1041.5607 | MS/MS | [165] |
| 172 | [seco-1/6][D-Asp3]MC-RRb | C48H75N13O13 | 1041.5607 | NMR, AA, MS/MS | [164] |
| 173 | MC‐HphR | C53H74N10O12 | 1042.5488 | LC-MS/MS, thiol | [34,92] |
| 174 | [D-Glu(OMe)6]MC-FRb | C53H74N10O12 | 1042.5488 | LC-MS/MS | [40] |
| 175 | [D-Leu1]MC-LY | C55H77N7O13 | 1043.5579 | LC-HRMS/MS, LC-MS/MS | [96,166] |
| 176 | MC‐M(O2)Rb | C48H72N10O14S | 1044.4950 | LC-MS/MS, thiol, *S*-oxidation | [92] |
| 177 | [D-Asp3]MC-HtyR | C52H72N10O13 | 1044.5280 | AA**,** MS, NMR | [167] |
| 178 | [Dha7]MC-HtyR | C52H72N10O13 | 1044.5280 | AA, HRMS, MS/MS, 1H-NMR | [156] |
| 179 | [D-Asp3,(*E*)-Dhb7]MC-HtyR | C52H72N10O13 | 1044.5280 | NMR, AA, HRMS | [138] |
| 180 | [D-Asp3,(*Z*)-Dhb7]MC-HtyR | C52H72N10O13 | 1044.5280 | NMR, AA, HRMS | [138] |
| 181 | MC-RY | C52H72N10O13 | 1044.5280 | LC-MS/MS, NMR, thiol | [76,158] |
| 182 | MC-YR | C52H72N10O13 | 1044.5280 | AA, NMR, MS | [16] |
| 183 | [seco‐1/2]MC‐FRb | C52H74N10O13 | 1046.5437 | HRMS, MS/MS | [79,150] |
| 184 | MC-(H2)YR | C52H74N10O13 | 1046.5437 | LC-HRMS/MS, thiol | [81] |
| 185 | MC‐HphHph | C57H73N7O12 | 1047.5317 | LC-MS/MS | [74] |
| 186 | [D‐Asp³,Ser7]MC‐HtyR | C51H72N10O14 | 1048.5229 | LC-MS/MS | [33] |
| 187 | [D-Asp³,Mser7]MC‐RY | C51H72N10O14 | 1048.5229 | LC-MS/MS, thiol | [105] |
| 188 | [Ser7]MC-YR | C51H72N10O14 | 1048.5229 | LC–MS/MS | [100] |
| 189 | MC-(H4)YR | C52H76N10O13 | 1048.5593 | HRMS, MS/MS, NMR | [79] |
| 190 | [ADMAdda5]MC‐HilHar | C52H78N10O13 | 1050.5750 | LC-MS/MS | [33] |
| 191 | [D-Leu1, D-Asp³,ADMAdda5]MC‐LR | C52H78N10O13 | 1050.5750 | LC-MS/MS | [149] |
| 192 | [D-Leu1,Adda(O)5]MC-LRb | C52H78N10O13 | 1050.5750 | LC-MS/MS, thiol | [80] |
| 193 | [D-Leu1]MC‐HilR | C53H82N10O12 | 1050.6114 | LC-MS/MS | [74] |
| 194 | [D-Leu1]MC‐LHar | C53H82N10O12 | 1050.6114 | LC-MS/MS | [74] |
| 195 | [D-Leu1,Glu(OMe)6]MC-LRb | C53H82N10O12 | 1050.6114 | HRMS/MS | [148] |
| 196 | [Hil1]MC-LR | C53H82N10O12 | 1050.6114 | LC-MS/MS, thiol | [80] |
| 197 | [D‐Asp³,(*E*)‐Dhb7]MC‐HtyY | C55H69N7O14 | 1051.4902 | AA, NMR, HRMS | [168] |
| 198 | MC-YY | C55H69N7O14 | 1051.4902 | NMR, LC-HRMS/MS | [94] |
| 199 | [Gly1,D-Asp3,ADMAdda5]MC-RHar | C49H73N13O13 | 1051.5451 | LC-MS/MS | [91] |
| 200 | [Gly1,D-Asp3,ADMAdda5,Dhb7]MC-RHar | C49H73N13O13 | 1051.5451 | LC-MS/MS, HRMS, AA, thiol | [90] |
| 201 | [D-Asp³,ADMAdda5]MC‐RR | C49H73N13O13 | 1051.5451 | LC-MS/MS | [149] |
| 202 | [D-Asp3,ADMAdda5,Dhb7]MC-RR | C49H73N13O13 | 1051.5451 | NMR, HRMS, AA, LC-MS/MS | [146,169] |
| 203 | [D‐Glu(OC3H7O)6]MC‐LRb | C51H76N10O14 | 1052.5542 | AA, HRMS, NMR | [75] |
| 204 | [D‐Leu1,Adda(OH)5]MC‐LRb | C52H80N10O13 | 1052.5906 | LC-MS/MS, thiol | [80] |
| 205 | [D-Asp3]MC-WR | C53H71N11O12 | 1053.5284 | AA, NMR, MS | [86] |
| 206 | [Dha7]MC‐WR | C53H71N11O12 | 1053.5284 | LC–MS/MS, thiol | [127] |
| 207 | [DMAdda5]MC‐WR | C53H71N11O12 | 1053.5284 | LC–MS/MS, thiol | [127] |
| 208 | [D-Met1]MC-LR | C51H78N10O12S | 1054.5521 | LC-MS/MS | [74] |
| 209 | [D-Leu1]MC-MR | C51H78N10O12S | 1054.5521 | LC-HRMS/MS, thiol, *S*-oxidation | [80] |
| 210 | [D-Leu1,Mser7]MC-LR | C52H82N10O13 | 1054.6063 | HRMS/MS | [148] |
| 211 | [Mser7]MC-RR | C49H77N13O13 | 1055.5764 | LC-HRMS/MS, thiol | [81] |
| 212 | [ADMAdda5]MC‐FR | C53H72N10O13 | 1056.5280 | LC-MS/MS | [133] |
| 213 | [D-Asp³,ADMAdda5]MC‐HphR | C53H72N10O13 | 1056.5280 | LC-MS/MS | [149] |
| 214 | MC-HtyR | C53H74N10O13 | 1058.5437 | AA**,** MS, NMR | [167] |
| 215 | [D-Asp³,D-Glu(OMe)6]MC‐HtyRb | C53H74N10O13 | 1058.5437 | MS/MS | [87] |
| 216 | [D‐Glu(OMe)6]MC‐YRb | C53H74N10O13 | 1058.5437 | NMR, LC-HRMS/MS | [94] |
| 217 | [D-Ser1,D-Asp³]MC‐HtyR | C52H72N10O14 | 1060.5229 | LC-MS/MS, thiol | [92] |
| 218 | [D‐Asp³]MC‐Y(OMe)R | C52H72N10O14 | 1060.5229 | LC–MS/MS, thiol | [127] |
| 219 | [DMAdda5]MC‐Y(OMe)R | C52H72N10O14 | 1060.5229 | LC–MS/MS, thiol | [127] |
| 220 | [seco‐4/5][D-Asp³]MC‐HtyRb | C52H74N10O14 | 1062.5386 | LC-MS/MS, thiol | [92] |
| 221 | [Ser7]MC-HtyR | C52H74N10O14 | 1062.5386 | AA, HRMS, MS/MS,NMR | [156] |
| 222 | [D-Asp³,Mser7]MC‐HtyR | C52H74N10O14 | 1062.5386 | MALDI-TOF MS | [87] |
| 223 | [D‐Asp³,ADMAdda5]MC‐(H4)YR | C52H74N10O14 | 1062.5386 | LC-MS/MS | [149] |
| 224 | [Mser7]MC‐RY | C52H74N10O14 | 1062.5386 | LC-MS/MS, thiol | [76] |
| 225 | [D-Asp³,Mser7]MC‐YHar | C52H74N10O14 | 1062.5386 | NMR, LC-HRMS/MS | [94] |
| 226 | [Mser7]MC‐YR | C52H74N10O14 | 1062.5386 | LC–MS/MS, NMR, thiol, HRMS | [127] |
| 227 | MC‐HphHty | C57H73N7O13 | 1063.5266 | LC-MS/MS | [74] |
| 228 | [D-Leu1,ADMAdda5]MC‐LR  | C53H80N10O13 | 1064.5906 | LC –MS/MS | [149] |
| 229 | [D-Leu1,Glu(OMe)6]MC-HilRb | C54H84N10O12 | 1064.6270 | HRMS/MS | [148] |
| 230 | [D‐Asp³,(*E*)‐Dhb7]MC‐HtyHty | C56H71N7O14 | 1065.5059 | AA, NMR, HRMS | [168] |
| 231 | [ADMAdda5]MC‐RR | C50H75N13O13 | 1065.5607 | LC-MS/MS,LC-HRMS/MS | [102,149] |
| 232 | MC‐HarHar | C51H79N13O12 | 1065.5971 | LC–MS/MS | [170] |
| 233 | [D-Leu1,D-Asp3]MC-RR | C51H79N13O12 | 1065.5971 | LC-MS/MS | [74] |
| 234 | MC-WR | C54H73N11O12 | 1067.5440 | AA, HRMS,NMR | [75] |
| 235 | [D-Leu1,D-Glu(OMe)6,Mser7]MC-LRb | C53H84N10O13 | 1068.6219 | HRMS/MS | [148] |
| 236 | [D-Met(O)1]MC-LRb  | C51H78N10O13S | 1070.5471 | HRMS/MS | [148] |
| 237 | [D-Leu1]MC‐M(O)Rb | C51H78N10O13S | 1070.5471 | LC-HRMS/MS, thiol, *S*-oxidation | [80,96] |
| 238 | [D-Leu1,D-Asp³]MC‐HphR | C55H78N10O12 | 1070.5801 | LC-MS/MS | [149] |
| 239 | [D-Phe1]MC‐LR | C55H78N10O12 | 1070.5801 | LC-MS/MS | [74] |
| 240 | [D-Leu1]MC‐FR | C55H78N10O12 | 1070.5801 | LC-MS/MS, thiol | [80] |
| 241 | MC-KynRb | C53H73N11O13 | 1071.5389 | LC-MS/MS, thiol | [89] |
| 242 | [D-Asp3,ADMAdda5]MC-HtyR | C53H72N10O14 | 1072.5229 | AA, HRMS, MS/MS | [171] |
| 243 | [D-Asp3,ADMAdda5,Dhb7]MC-HtyR | C53H72N10O14 | 1072.5229 | NMR, HRMS, AA | [146] |
| 244 | [ADMAdda5]MC‐YR | C53H72N10O14 | 1072.5229 | LC-MS/MS | [33] |
| 245 | MC‐MhtyR | C54H76N10O13 | 1072.5229 | LC-HRMS/MS | [95] |
| 246 | [D-Asp3,(*E*)-Dhb7]MC-HtyW | C57H70N8O13 | 1072.5593 | NMR, LC-HRMS/MS | [94] |
| 247 | MC‐RY(OMe) | C53H74N10O14 | 1074.5062 | LC-MS/MS, thiol | [76] |
| 248 | [D-Asp³]MC‐Hty(OMe)R | C53H74N10O14 | 1074.5386 | LC-MS/MS, thiol | [92] |
| 249 | MC‐Y(OMe)R | C53H74N10O14 | 1074.5386 | LC–MS/MS, thiol | [127] |
| 250 | [seco‐4/5]MC‐HtyRb | C53H76N10O14 | 1076.5542 | LC-MS/MS, thiol | [92] |
| 251 | [ADMAdda5]MC‐(H4)YR | C53H76N10O14 | 1076.5542 | LC-MS/MS | [133] |
| 252 | [Mser7]MC‐HtyR | C53H76N10O14 | 1076.5542 | LC-MS/MS, thiol | [92] |
| 253 | [D-Leu1,ADMAdda5]MC‐LHar | C54H82N10O13 | 1078.6063 | LC-MS/MS | [149] |
| 254 | [ADMAdda5]MC‐RHar | C51H77N13O13 | 1079.5764 | LC-MS/MS | [149] |
| 255 | [D-Leu1]MC-RR | C52H81N13O12 | 1079.6128 | LC-MS/MS | [74] |
| 256 | MC-OiaRb | C54H73N11O13 | 1083.5389 | LC-MS/MS, thiol | [89] |
| 257 | [D-Met(O)1,Glu(OMe)6]MC‐LRb | C52H80N10O13S | 1084.5627 | HRMS/MS | [148] |
| 258 | [D-Leu1]MC-HphR | C56H80N10O12 | 1084.5957 | LC-MS/MS | [74] |
| 259 | [D-Leu1]MC-M(O2)Rb | C51H78N10O14S | 1086.5420 | LC-HRMS/MS, thiol, *S*-oxidation | [80] |
| 260 | [ADMAdda5]MC‐(H4)YHar | C54H78N10O14 | 1090.5699 | LC-MS/MS | [133] |
| 261 | MC-NfkRb | C54H73N11O14 | 1099.5338 | LC-MS/MS, thiol | [89] |
| 262 | [D-Leu1]MC‐HtyR | C56H80N10O13 | 1100.5906 | LC-MS/MS | [149] |
| 263 | MC-LR Cys conjugateb | C52H81N11O14S | 1115.5685 | HRMS, MS/MS, semisynthesis | [79] |
| 264 | [D-Leu1]MC-LR Cys conjugateb | C55H87N11O14S | 1157.6155 | LC-HRMS/MS,semisynthesis | [80] |
| 265 | [D-Leu1]MC-LR Cys sulfoxide conjugateb | C55H87N11O15S | 1173.6104 | LC-HRMS/MS,semisynthesis, *S*-oxidation | [80] |
| 266 | [D-Leu1]MC-LR γ-GluCys conjugateb | C60H94N12O17S | 1286.6581 | LC-HRMS/MS,semisynthesis | [80] |
| 267 | [D-Leu1]MC-LR γ-GluCys sulfoxide conjugateb | C60H94N12O18S | 1302.6530 | LC-HRMS/MS,semisynthesis, *S*-oxidation | [80] |
| 268 | [D-Leu1]MC-LR GSH conjugateb | C62H97N13O18S | 1343.6795 | LC-HRMS/MS,semisynthesis | [80] |
| 269 | [D-Leu1]MC-LR GSH sulfoxide conjugateb | C62H97N13O19S | 1359.6744 | LC-HRMS/MS,semisynthesis, *S*-oxidation | [80] |

a Exact monoisotopic neutral mass. For protonated/deprotonated ions, *m*/*z* = (monoisotopic neutral mass +/− (*z* × 1.0073))/*z*.

b Congeners expected to form through chemical or biochemical transformations of other MCs rather than through biosynthesis by cyanobacteria, see section 5.7 for additional details.

c Entries 122 and 123 are a pair of congeners demethylated at different positions somewhere between C-2 and C-8 of their Adda moieties.

**Abbreviations**

*Amino acids.* Aha, aminoheptanoic acid; Abu (Aba), L-2-aminobutyric acid (L-2-aminobutanoic acid); Apa, aminopropionic acid; Aib, aminoisobutyric acid (aminoisobutyrate); Bu, 2-amino-butyric acid (L-butyrine); ADMAdda, *O*-acetyl-9-*O*-desmethylAdda; Dha, dehydroalanine; Dhb, dehydrobutyrine; DMAdda, 9-*O*-desmethylAdda; dmAdda, Adda demethylated at C-2, C-6 or C-8; E(OMe), glutamic acid methyl ester; H(2)Y, dihydrotyrosine; (H4)Y, 4,5,6,7-tetrahydrotyrosine; Har, homoarginine; Hil, homoisoleucine; Hph, homophenylalanine; Hty, homotyrosine; Kyn, Kynurenine; Me, CH3; Mdhb, *N*-methyldehydrobutyrine; M(O), methionine-*S*-oxide; M(O2), methionine *S*-sulfone; Mser, *N*-methylserine; Nfk, *N*-formylkynurenine; Oia, oxindolyalanine; Y(OMe), methoxytyrosine.

*Characterization Techniques*. AA, amino acid analysis; MS, mass spectrometry (low resolution MS analysis of isolated MCs implied); NMR, nuclear magnetic resonance (including 1H, 13C or 2-dimensional experiments); MS/MS, tandem mass spectrometry (direct analysis of isolated fractions using either ESI or MALDI ionization); HRMS, high resolution mass spectrometry (direct analysis of isolated fractions); LC-MS/MS, liquid chromatography-tandem mass spectrometry (without isolation); LC-HRMS/MS, liquid chromatography-high resolution tandem mass spectrometry (without isolation) thiol: reactivity with a thiol containing reagent (e.g. mercaptoethanol) used to confirm presence of an α,β-unsaturated amide such as in Mdha7; S-oxidation, selective oxidation with mild oxidant (e.g. periodate) to confirm the presence of methionine residues and thiol conjugates as well as their corresponding sulfones and sulfoxides.