Electronic Supplementary Information for

New Rearranged Limonoids from *Walsura cochinchinensis*

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Table S1. X-ray crystallographic data for walsucochinoid C (1)
Table S2. X-ray crystallographic data for walsucochinoid L (10)

Figure S1. $^1$H NMR spectrum of walsucochinoid C (1) in CDCl$_3$
Figure S2. $^{13}$C NMR spectrum of walsucochinoid C (1) in CDCl$_3$
Figure S3. HSQC spectrum of walsucochinoid C (1) in CDCl$_3$
Figure S4. HMBC spectrum of walsucochinoid C (1) in CDCl$_3$
Figure S5. NOESY spectrum of walsucochinoid C (1) in CDCl$_3$
Figure S6. ESI(+)MS spectrum of walsucochinoid C (1)
Figure S7. ESI(−)MS spectrum of walsucochinoid C (1)
Figure S8. HRESI(−)MS spectrum of walsucochinoid C (1)
Figure S9. IR spectrum of walsucochinoid C (1)

Figure S10. $^1$H NMR spectrum of walsucochinoid D (2) in CDCl$_3$
Figure S11. $^{13}$C NMR spectrum of walsucochinoid D (2) in CDCl$_3$
Figure S12. HMBC spectrum of walsucochinoid D (2) in CDCl$_3$
Figure S13. ROESY spectrum of walsucochinoid D (2) in CDCl$_3$
Figure S14. ESI(+)MS spectrum of walsucochinoid D (2)
Figure S15. HRESI(+)MS spectrum of walsucochinoid D (2)
Figure S16. IR spectrum of walsucochinoid D (2)

Figure S17. $^1$H NMR spectrum of walsucochinoid E (3) in CDCl$_3$
Figure S18. $^{13}$C NMR spectrum of walsucochinoid E (3) in CDCl$_3$
Figure S19. HMBC spectrum of walsucochinoid E (3) in CDCl$_3$
Figure S20. ROESY spectrum of walsucochinoid E (3) in CDCl$_3$
Figure S21. ESI(+)MS spectrum of walsucochinoid E (3)
Figure S22. HRESI(+)MS spectrum of walsucochinoid E (3)
Figure S23. IR spectrum of walsucochinoid E (3)

Figure S24. $^1$H NMR spectrum of walsucochinoid F (4) in CDCl$_3$
Figure S25. $^{13}$C NMR spectrum of walsucochinoid F (4) in CDCl$_3$

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Figure S26. ROESY spectrum of walsucochinoid F (4) in CDCl₃
Figure S27. ESI(+)MS spectrum of walsucochinoid F (4)
Figure S28. ESI(−)MS spectrum of walsucochinoid F (4)
Figure S29. HRESI(−)MS spectrum of walsucochinoid F (4)
Figure S30. IR spectrum of walsucochinoid F (4)

Figure S31. ¹H NMR spectrum of walsucochinoid G (5) in CDCl₃
Figure S32. ¹³C NMR spectrum of walsucochinoid G (5) in CDCl₃
Figure S33. HSQC spectrum of walsucochinoid G (5) in CDCl₃
Figure S34. HMBC spectrum of walsucochinoid G (5) in CDCl₃
Figure S35. ROESY spectrum of walsucochinoid G (5) in CDCl₃
Figure S36. ESI(+)MS spectrum of walsucochinoid G (5) in CDCl₃
Figure S37. ESI(−)MS spectrum of walsucochinoid G (5) in CDCl₃
Figure S38. HRESI(−)MS spectrum of walsucochinoid G (5) in CDCl₃
Figure S39. IR spectrum of walsucochinoid G (5)

Figure S40. ¹H NMR spectrum of walsucochinoid H (6) in CDCl₃
Figure S41. ¹³C NMR spectrum of walsucochinoid H (6) in CDCl₃
Figure S42. HSQC spectrum of walsucochinoid H (6) in CDCl₃
Figure S43. HMBC spectrum of walsucochinoid H (6) in CDCl₃
Figure S44. NOESY spectrum of walsucochinoid H (6) in CDCl₃
Figure S45. ESI(+)MS spectrum of walsucochinoid H (6)
Figure S46. ESI(−)MS spectrum of walsucochinoid H (6)
Figure S47. HRESI(−)MS spectrum of walsucochinoid H (6)
Figure S48. IR spectrum of walsucochinoid H (6)

Figure S49. ¹H NMR spectrum of walsucochinoid I (7) in CDCl₃
Figure S50. ¹³C NMR spectrum of walsucochinoid I (7) in CDCl₃
Figure S51. HSQC spectrum of walsucochinoid I (7) in CDCl₃
Figure S52. HMBC spectrum of walsucochinoid I (7) in CDCl₃
Figure S53. ROESY spectrum of walsucochinoid I (7) in CDCl₃
Figure S54. ESI(+)MS spectrum of walsucochinoid I (7)
Figure S55. ESI(−)MS spectrum of walsucochinoid I (7)
Figure S56. HRESI(−)MS spectrum of walsucochinoid I (7)
Figure S57. IR spectrum of walsucochinoid I (7)

Figure S58. ¹H NMR spectrum of walsucochinoid J (8) in CDCl₃
Figure S59. ¹³C NMR spectrum of walsucochinoid J (8) in CDCl₃
Figure S60. HSQC spectrum of walsucochinoid J (8) in CDCl₃
Figure S61. HMBC spectrum of walsucochinoid J (8) in CDCl₃
Figure S62. ROESY spectrum of walsucochinoid J (8) in CDCl₃
Figure S63. ESI(+)MS spectrum of walsucochinoid J (8)
Figure S64. ESI(−)MS spectrum of walsucochinoid J (8)
Figure S65. HRESI(−)MS spectrum of walsucochinoid J (8)
Figure S66. IR spectrum of walsucochinoid J (8)

Figure S67. $^1$H NMR spectrum of walsucochinoid K (9) in CDCl$_3$
Figure S68. $^{13}$C NMR spectrum of walsucochinoid K (9) in CDCl$_3$
Figure S69. HSQC spectrum of walsucochinoid K (9) in CDCl$_3$
Figure S70. HMBC spectrum of walsucochinoid K (9) in CDCl$_3$
Figure S71. ROESY spectrum of walsucochinoid K (9)
Figure S72. ESI(+)MS spectrum of walsucochinoid K (9)
Figure S73. ESI(−)MS spectrum of walsucochinoid K (9)
Figure S74. HRESI(−)MS spectrum of walsucochinoid K (9)
Figure S75. IR spectrum of walsucochinoid K (9)

Figure S76. $^1$H NMR spectrum of walsucochinoid L (10) in CDCl$_3$
Figure S77. $^{13}$C NMR spectrum of walsucochinoid L (10) in CDCl$_3$
Figure S78. HSQC spectrum of walsucochinoid L (10) in CDCl$_3$
Figure S79. HMBC spectrum of walsucochinoid L (10) in CDCl$_3$
Figure S80. ROESY spectrum of walsucochinoid L (10) in CDCl$_3$
Figure S81. ESI(+)MS spectrum of walsucochinoid L (10)
Figure S82. ESI(−)MS spectrum of walsucochinoid L (10)
Figure S83. HRESI(−)MS spectrum of walsucochinoid L (10)
Figure S84. IR spectrum of walsucochinoid L (10)

Figure S85. $^1$H NMR spectrum of walsucochinoid M (11) in CDCl$_3$
Figure S86. $^{13}$C NMR spectrum of walsucochinoid M (11) in CDCl$_3$
Figure S87. HSQC spectrum of walsucochinoid M (11) in CDCl$_3$
Figure S88. HMBC spectrum of walsucochinoid M (11) in CDCl$_3$
Figure S89. ROESY spectrum of walsucochinoid M (11) in CDCl$_3$
Figure S90. ESI(+)MS spectrum of walsucochinoid M (11)
Figure S91. HRESI(+)MS spectrum of walsucochinoid M (11)
Figure S92. IR spectrum of walsucochinoid M (11)

Figure S93. $^1$H NMR spectrum of walsucochinoid N (12) in CDCl$_3$
Figure S94. $^{13}$C NMR spectrum of walsucochinoid N (12) in CDCl$_3$
Figure S95. HSQC spectrum of walsucochinoid N (12) in CDCl$_3$
Figure S96. HMBC spectrum of walsucochinoid N (12) in CDCl$_3$
Figure S97. ROESY spectrum of walsucochinoid N (12) in CDCl$_3$
Figure S98. ESI(+)MS spectrum of walsucochinoid N (12)
Figure S99. HRESI(+)MS spectrum of walsucochinoid N (12)
Figure S100. IR spectrum of walsucochinoid N (12)

Figure S101. $^1$H NMR spectrum of walsucochinoid O (13) in CDCl$_3$
Figure S102. $^{13}$C NMR spectrum of walsucochinoid O (13) in CDCl$_3$
Figure S103. HSQC spectrum of walsucochinoid O (13) in CDCl$_3$
Figure S104. HMBC spectrum of walsucochinoid O (13) in CDCl$_3$
Figure S105. ROESY spectrum of walsucochinoid O (13) in CDCl₃
Figure S106. ESI(+)MS spectrum of walsucochinoid O (13)
Figure S107. ESI(−)MS spectrum of walsucochinoid O (13)
Figure S108. HRESI(+)MS spectrum of walsucochinoid O (13)
Figure S109. IR spectrum of walsucochinoid O (13)

Figure S110. ¹H NMR spectrum of walsucochinoid P (14) in CDCl₃
Figure S111. ¹³C NMR spectrum of walsucochinoid P (14) in CDCl₃
Figure S112. HSQC spectrum of walsucochinoid P (14) in CDCl₃
Figure S113. ROESY spectrum of walsucochinoid P (14) in CDCl₃
Figure S114. ESI(+)MS spectrum of walsucochinoid P (14)
Figure S115. ESI(−)MS spectrum of walsucochinoid P (14)
Figure S116. HRESI(+)MS spectrum of walsucochinoid P (14)
Figure S117. IR spectrum of walsucochinoid P (14)

Figure S118. ¹H NMR spectrum of walsucochinoid Q (15) in CDCl₃
Figure S119. ¹³C NMR spectrum of walsucochinoid Q (15) in CDCl₃
Figure S120. HSQC spectrum of walsucochinoid Q (15) in CDCl₃
Figure S121. HMBC spectrum of walsucochinoid Q (15) in CDCl₃
Figure S122. ROESY spectrum of walsucochinoid Q (15) in CDCl₃
Figure S123. ESI(+)MS spectrum of walsucochinoid Q (15)
Figure S124. ESI(−)MS spectrum of walsucochinoid Q (15)
Figure S125. HRESI(+)MS spectrum of walsucochinoid Q (15)
Figure S126. IR spectrum of walsucochinoid Q (15)

Figure S127. ¹H NMR spectrum of walsucochinoid R (16) in CDCl₃
Figure S128. ¹³C NMR spectrum of walsucochinoid R (16) in CDCl₃
Figure S129. HSQC spectrum of walsucochinoid R (16) in CDCl₃
Figure S130. HMBC spectrum of walsucochinoid R (16) in CDCl₃
Figure S131. ROESY spectrum of walsucochinoid R (16) in CDCl₃
Figure S132. ESI(+)MS spectrum of walsucochinoid R (16)
Figure S133. HRESI(+)MS spectrum of walsucochinoid R (16)
Figure S134. IR spectrum of walsucochinoid R (16)
Table S1. X-ray crystallographic data for walsucochinoid C (1).a

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<th>Property</th>
<th>Value</th>
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<tr>
<td>Empirical formula</td>
<td>C_{27}H_{32}O_{4}</td>
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<td>Formula weight</td>
<td>420.53</td>
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<tr>
<td>Temperature</td>
<td>133(2) K</td>
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<tr>
<td>Wavelength</td>
<td>1.54178 Å</td>
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<td>Crystal system</td>
<td>Orthorhombic</td>
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<td>Space group</td>
<td>P2(1)2(1)2(1)</td>
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<tr>
<td>Unit cell dimensions</td>
<td>a = 5.96350 (10) Å, α = 90°</td>
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<tr>
<td></td>
<td>b = 13.7471 (3) Å, β = 90°</td>
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<tr>
<td></td>
<td>c = 28.1129 (6) Å, γ = 90°</td>
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<tr>
<td>Volume</td>
<td>2304.72(8) Å3</td>
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<td>Z</td>
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<td>Calculated density</td>
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<td>Crystal size</td>
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<tr>
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<tr>
<td>Index ranges</td>
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</tr>
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<tr>
<td>Independent collections</td>
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<td>Absorption correction</td>
<td>Semi-empirical</td>
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<td>Max. and min. transmission</td>
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<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
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<td>Data / restraints / parameters</td>
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<tr>
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<td>Largest diff. peak and hole</td>
<td>0.416 and -0.424 e. Å⁻³</td>
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*a I was crystallized from MeOH/H₂O (50:1)
Table S2. X-ray crystallographic data for walsucochinoid L (10).a

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<tr>
<th>Property</th>
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<td>424.56</td>
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<tr>
<td>Temperature</td>
<td>133(2) K</td>
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<tr>
<td>Wavelength</td>
<td>1.54178 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2(1)2(1)2(1)</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>(a = 8.2016 (5) ) Å, (\alpha = 90^\circ)</td>
<td></td>
</tr>
<tr>
<td>(b = 10.1084 (6) ) Å, (\beta = 90^\circ)</td>
<td></td>
</tr>
<tr>
<td>(c = 13.3847 (8) ) Å, (\gamma = 90^\circ)</td>
<td></td>
</tr>
<tr>
<td>Volume</td>
<td>1109.36(12) Å³</td>
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<tr>
<td>Z</td>
<td>2</td>
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<tr>
<td>Calculated density</td>
<td>1.271 Mg/m³</td>
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<td>Absorption coefficient</td>
<td>0.661 mm⁻¹</td>
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<tr>
<td>F(000)</td>
<td>460</td>
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<tr>
<td>Crystal size</td>
<td>0.15 × 0.12 × 0.10 mm³</td>
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<tr>
<td>Theta range for data collection</td>
<td>3.30 to 64.98°</td>
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<tr>
<td>Index ranges</td>
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<tr>
<td>Reflections collected</td>
<td>6271</td>
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<tr>
<td>Independent collections</td>
<td>3273 [R(int) = 0.0622]</td>
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<tr>
<td>Completeness to theta = 66.32°</td>
<td>94.4 %</td>
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<tr>
<td>Absorption correction</td>
<td>Semi-empirical</td>
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<td>Max. and min. transmission</td>
<td>0.9368 and 0.9073</td>
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<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
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<td>Data / restraints / parameters</td>
<td>3273 / 1 / 289</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.069</td>
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<td>Final R indices [I&gt;2σ(I)]</td>
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<td>R indices (all data)</td>
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<td>Absolute structure parameter</td>
<td>0.0(4)</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>0.395 and −0.319 e. Å⁻³</td>
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</tbody>
</table>

a 10 was crystallized from MeOH/H₂O (100:1)
Figure S1. $^1$H NMR spectrum of walsucochinoid C (1) in CDCl$_3$
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Figure S3. HSQC spectrum of walsucochinoid C (1) in CDCl₃
Figure S4. HMBC spectrum of walsucochinoid C (1) in CDCl₃
Figure S5. NOESY spectrum of walsucochinoid C (1) in CDCl$_3$
Figure S6. ESI(+)MS spectrum of walsucochinoid C (1)
Figure S7. ESI(−)MS spectrum of walsucochinoid C (1)
Figure S8. HRESI(−)MS spectrum of walsucochinoid C (1)
**Figure S9.** IR spectrum of walsucochinoid C (1)
Figure S10. $^1$H NMR spectrum of walsucochinoid D (2) in CDCl$_3$
Figure S11. $^{13}$C NMR spectrum of walsucochinoid D (2) in CDCl$_3$
Figure S12. HMBC spectrum of walsucochinoid D (2) in CDCl$_3$
Figure S13. ROESY spectrum of walsucochinoid D (2) in CDCl$_3$
**Figure S14.** ESI(+)MS spectrum of walsucochinoid D (2)
Figure S15. HRESI(+)MS spectrum of walsucochinoid D (2)
**Figure S16.** IR spectrum of walsucochinoid D (2)
Figure S17. $^1$H NMR spectrum of walsucochinoid E (3) in CDCl$_3$
Figure S18. $^{13}$C NMR spectrum of walsucochinoid E (3) in CDCl$_3$
Figure S19. HMBC spectrum of walsucochinoid E (3) in CDCl$_3$
Figure S20. ROESY spectrum of walsucochinoid E (3) in CDCl$_3$
Figure S21. ESI(+)MS spectrum of walsucochinoid E (3)
Figure S22. HRESI(+)MS spectrum of walsucochinoid E (3)

Elemental Composition Report

Single Mass Analysis
Tolerance = 3.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
381 formula(s) evaluated with 3 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:
C: 10-70  H: 0-80  O: 0-30  Na: 0-1

WAL-48  LCT PKE KE324
WAL-48_1109 56 (1.216) AM2 (Ar,10000.00,0.00); ABS; Cm (46.05)

09-Nov-2011  16:03:09
1: TOF MS ES+  2.028+004
947.4720

Minimum:  -1.5  Mass  Calc. Mass  mDa  PPM  DBE  i-FIT  i-FIT (Norm)  Formula
Maximum:  -50.0
947.4720  947.4710  1.0  1.1  24.5  42.9  0.0  C58 H68 O10 Na
947.4724  -1.4  -1.5  27.3  46.1  3.2  C60 H67 O10
947.4699  -2.1  -2.2  5.5  53.9  11.1  C42 H75 O23
Figure S23. IR spectrum of walsucochinoid E (3)
Figure S24. $^1$H NMR spectrum of walsucochinoid F (4) in CDCl$_3$
Figure S25. $^{13}$C NMR spectrum of walsucochinoid F (4) in CDCl$_3$
Figure S26. ROESY spectrum of walsucochinoid F (4) in CDCl₃
Figure S27. ESI(+)MS spectrum of walsucochinoid F (4)
Figure S28. ESI(−)MS spectrum of walsucochinoid F (4)
Figure S29. HRESI(−)MS spectrum of walsucochinoid F (4)

Elemental Composition Report

Single Mass Analysis
Tolerance = 3.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
116 formula(s) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 10-70 H: 0-80 O: 0-30

WAL-52
LCT PXE KE324

WAL-52_1193_38 (0.742) AM2 (Au:10000.0,0.001,1.00), ABS, Cm (26:46)

09-Nov-2011
15:54:40
1: TOF MS ES-
8.93e+004

Maximum: 1.5
Minimum: 5.0 3.0 50.0

Mass  Calc. Mass  mDa  PPM  DBE  i-FIT  i-FIT (Norm)  Formula
493.2229 493.2226 0.3  0.6  13.5  156.3  0.0  C29 H33 O7
Figure S30. IR spectrum of walsucochinoid F (4)
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Figure S58. $^1$H NMR spectrum of walsucochinoid J (8) in CDCl$_3$
Figure S59. $^{13}$C NMR spectrum of walsucochinoid J (8) in CDCl$_3$. 
Figure S60. HSQC spectrum of walsucochinoid J (8) in CDCl₃
Figure S61. HMBC spectrum of walsucochinoid J (8) in CDCl₃
Figure S62. ROESY spectrum of walsucochinoid J (8) in CDCl₃
Figure S63. ESI(+)MS spectrum of walsuchochinoid J (8)
Figure S64. ESI(−)MS spectrum of walsucochinoid J (8)
Figure S65. HRESI(−)MS spectrum of walsucochinoid J (8)
Figure S66. IR spectrum of walsucochinoid J (8)
Figure S67. $^1$H NMR spectrum of walsucochinoid K (9) in CDCl$_3$
Figure S68. $^{13}$C NMR spectrum of walsucochinoid K (9) in CDCl$_3$
Figure S69. HSQC spectrum of walsucochinoid K (9) in CDCl₃
Figure S70. HMBC spectrum of walsucochinoid K (9) in CDCl₃
Figure S71. ROESY spectrum of walsucochinoid K (9) in CDCl₃
Figure S72. ESI(+)MS spectrum of walsucochinoid K (9)
Figure S73. ESI(−)MS spectrum of walsucochinoid K (9)
Figure S74. HRESI(-)MS spectrum of walsucochinoid K (9)
Figure S75. IR spectrum of walsucochinoid K (9)
Figure S76. $^1$H NMR spectrum of walsucochinoid L (10) in CDCl$_3$
Figure S77. $^{13}$C NMR spectrum of walsucochinoid L (10) in CDCl$_3$
Figure S78. HSQC spectrum of walsucochinoid L (10) in CDCl₃
Figure S79. HMBC spectrum of walsucochinoid L (10) in CDCl$_3$
Figure S80. ROESY spectrum of walsucochinoid L (10) in CDCl₃
Figure S81. ESI(+)MS spectrum of walsucochinoid L (10)
Figure S82. ESI(−)MS spectrum of walsucochinoid L (10)
**Figure S83.** HRESI(−)MS spectrum of walsucochinoid L (10)

**Elemental Composition Report**

**Single Mass Analysis**

Tolerance = 2.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monolabeled Mass, Even Electron loss

106 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

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**WAL-35n**

LCT PXE KE324

WAL-35n_1104 27 (0.563) AM2 (Ar:10000/0.001.00); ABS; Cm (9.34)

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| Maximum: | 50.0 | 50.0 | 50.0 |

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Figure S84. IR spectrum of walsucochinoid L (10)
Figure S85. $^1$H NMR spectrum of walsucochinoid M (11) in CDCl$_3$
Figure S86. $^{13}$C NMR spectrum of walsucochinoid M (11) in CDCl$_3$
Figure S87. HSQC spectrum of walsucochinoid M (11) in CDCl₃
Figure S88. HMBC spectrum of walsucochinoid M (11) in CDCl₃
Figure S89. ROESY spectrum of walsucochinoid M (11) in CDCl₃
Figure S90. ESI(+)MS spectrum of walsucochinoid M (11)
**Figure S91.** HRESI(+)MS spectrum of walsucochinoid M (11)

### Elemental Composition Report

**Single Mass Analysis**
- Tolerance = 2.0 mDa
- DBE: min = -1.5, max = 50.0
- Element prediction: Off
- Number of isotope peaks used for i-FIT = 3

**Monoisotopic Mass, Even Electron Ions**
- 418 formula(s) evaluated with 3 results within limits (up to 50 best isotopic matches for each mass)

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- 04-Nov-2011 15:34:28
- 1 TOF MS ES+
- 2.57e+064

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**Maximum:** 2.0 2.0 50.0

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Figure S92. IR spectrum of walsuchochoid M (11)
Figure S93. $^1$H NMR spectrum of walsucochinoid N (12) in CDCl$_3$
Figure S94. $^{13}$C NMR spectrum of walsucochinoid N (12) in CDCl$_3$
Figure S95. HSQC spectrum of walsucochinoid N (12) in CDCl₃
Figure S96. HMBC spectrum of walsucochinoid N (12) in CDCl₃
Figure S97. ROESY spectrum of walsucochinoid N (12) in CDCl₃
**Figure S98.** ESI(+)MS spectrum of walsucochinoid N (12)

**Display Report**

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**Intensity vs. time (min)**

- **007-1001 D** TIC + AIF MS
- **007-1001 D** TIC + AIF MS
- **007-1001 D** UV Chromatogram: 201 nm

**Intensity vs. m/z**

- **ESI, 0.2 min (#489)**
- **ESI, 0.2 min (#489)**
- **ESI, 0.2 min (#489)**

**Bruker Daltonics DataAnalysis 3.1** printed: 03/15/11 09:21:11 Page 1 of 1

104
Figure S99. HRESI(+)MS spectrum of walsucochinoid N (12)
Figure S100. IR spectrum of walsucochinoid N (12)
Figure S101. $^1$H NMR spectrum of walsucochinoid O (13) in CDCl$_3$
Figure S102. $^{13}$C NMR spectrum of walsucochinoid O (13) in CDCl$_3$
Figure S103. HSQC spectrum of walsucochinoid O (13) in CDCl$_3$
Figure S104. HMBC spectrum of walsuochinoid O (13) in CDCl₃
**Figure S105.** ROESY spectrum of walsucochinoid O (13) in CDCl$_3$
Figure S106. ESI(+)MS spectrum of walsucochinoid O (13)
Figure S107. ESI(−)MS spectrum of walsucochinoid O (13)
**Figure S108. HRESI(+)MS spectrum of walsucochinoid O (13)**

### Elemental Composition Report

**Sample:** WAL-9

**LCT PXE KE324**

**WAL-9_1104 39 (0.847) AM2 (Ar:10000.0:0.001.00); ABS; Cm (9.41)**

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**Single Mass Analysis**

- **Tolerance:** 2.0 mDa / DBE: min = -1.5, max = 50.0
- **Element prediction:** Off
- **Number of isotope peaks used for i-FIT:** 3

**Monoisotopic Mass, Even Electron ions**

- 208 formula(s) evaluated with 1 result within limits (up to 50 best isotopic matches for each mass)

**Elements Used:**

| C: 10-70 | H: 0-80 | O: 0-30 | Na: 0-1 |

**04-Nov-2011 14:51:22**

1. TOF MS ES+
2. 2.97e+004
Figure S109. IR spectrum of walsucochinoid O (13)
Figure S110. $^1$H NMR spectrum of walsucochinoid P (14) in CDCl$_3$
Figure S111. $^{13}$C NMR spectrum of walsucochinoid P (14) in CDCl$_3$
Figure S112. HSQC spectrum of walsucochinoid P (14) in CDCl₃
Figure S113. ROESY spectrum of walsucochinoid P (14) in CDCl₃
Figure S114. ESI(+)MS spectrum of walsucochinoid P (14)
Figure S115. ESI(−)MS spectrum of walsucochinoid P (14)
Figure S116. HRESI(+)MS spectrum of walsucochinoid P (14)
Figure S117. IR spectrum of walsuochinoid P (14)
Figure S118. $^1$H NMR spectrum of walsucochinoid Q (15) in CDCl$_3$
Figure S119. $^{13}$C NMR spectrum of walsucochinoid Q (15) in CDCl₃
Figure S120. HSQC spectrum of walsucochinoid Q (15) in CDCl$_3$
Figure S121. HMBC spectrum of walsucochinoid Q (15) in CDCl₃
Figure S122. ROESY spectrum of walsucochinoid Q (15) in CDCl$_3$
Figure S123. ESI(+)MS spectrum of walsucochinoid Q (15)
Figure S124. ESI(−)MS spectrum of walsucochinoid Q (15)
**Figure S125. HRESI(+)MS spectrum of walsucochinoid Q (15)**

**Elemental Composition Report**

**Single Mass Analysis**
- Tolerance = 2.0 mDa / DBE: min = -1.5, max = 50.0
- Element prediction: Off
- Number of isotope peaks used for i-FIT = 3

**Monoisotopic Mass, Even Electron ions**
277 formula(e) evaluated with 2 results within limits (up to 50 best isotopic matches for each mass)

**Elements Used**
- C: 10-70
- H: 0-80
- O: 0-30
- Na: 0-1

**WAL-8**

**WAL-8_1104 19 (0.405) AM2 (Av:10000.0.00.00.100); ABS: Cm (5.28)**

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Figure S126. IR spectrum of walsucochinoid Q (15)
Figure S127. $^1$H NMR spectrum of walsucochinoid R (16) in CDCl$_3$
Figure S128. $^{13}$C NMR spectrum of walsucochinoid R (16) in CDCl$_3$
Figure S129. HSQC spectrum of walsucochinoid R (16) in CDCl₃
Figure S130. HMBC spectrum of walsuochinoid R (16) in CDCl$_3$
Figure S131. ROESY spectrum of walsucochinoid R (16) in CDCl₃
Figure S132. ESI(+)MS spectrum of walsucochinoid R (16)
**Figure S133. HRESI(+)MS spectrum of walsucochinoid R (16)**

**Elemental Composition Report**

**Single Mass Analysis**
- Tolerance = 2.0 PPM / DBE: min = -1.5, max = 50.0
- Element prediciton: Off
- Number of isotope peaks used for i-FIT = 3

**Monoisotopic Mass, Even Electron ions**
313 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

**Elements Used:**
- C: 10-70
- H: 0-80
- O: 0-30
- Na: 0-1

**WAL-22**

**LCT PXE KE324**

**WAL-22_D1226_11 (6.22%) AME (Ar,10000.0,0.00,1.00); ABS; Cm (11:30)**

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**Maximum:**
- 5.0
- 2.0
- 50.0

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Figure S134. IR spectrum of walsucochinoid R (16)