

Fungal Depsides Naturally Inspiring Molecules: Biosynthesis, Structural Characterization, and Biological Activities

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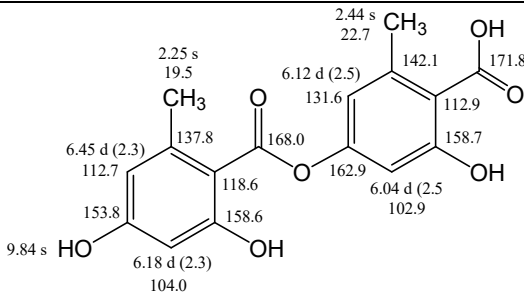
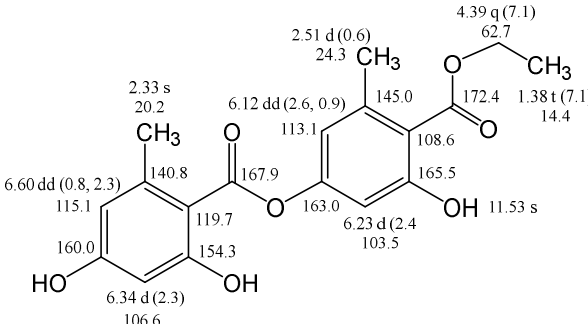
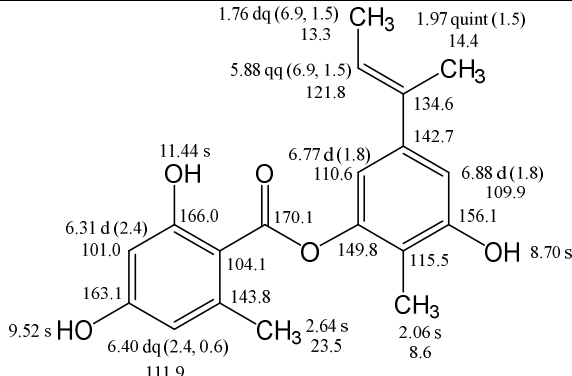
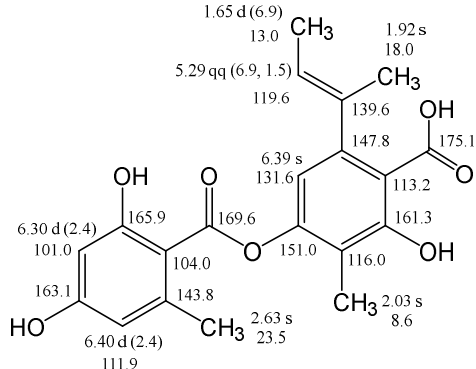
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Received: date; Accepted: date; Published: date

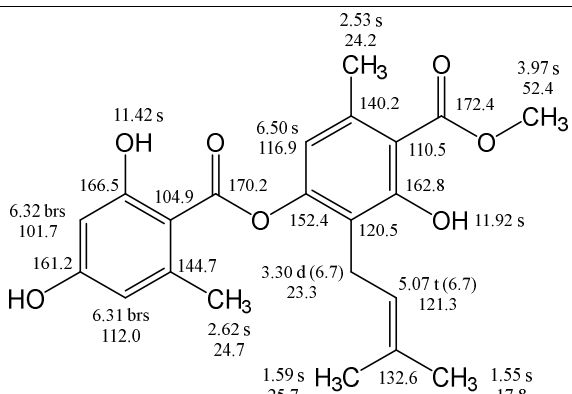
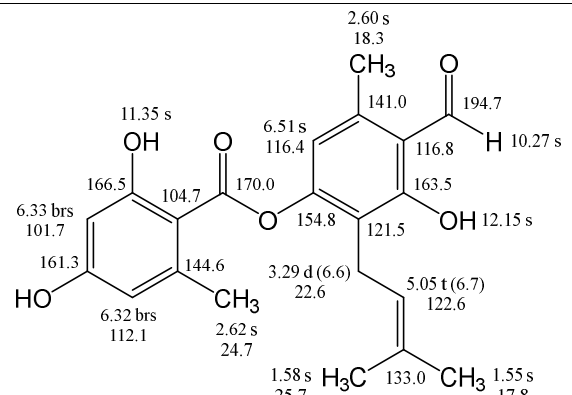
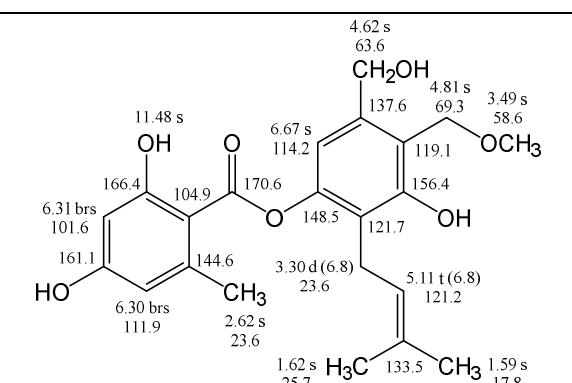
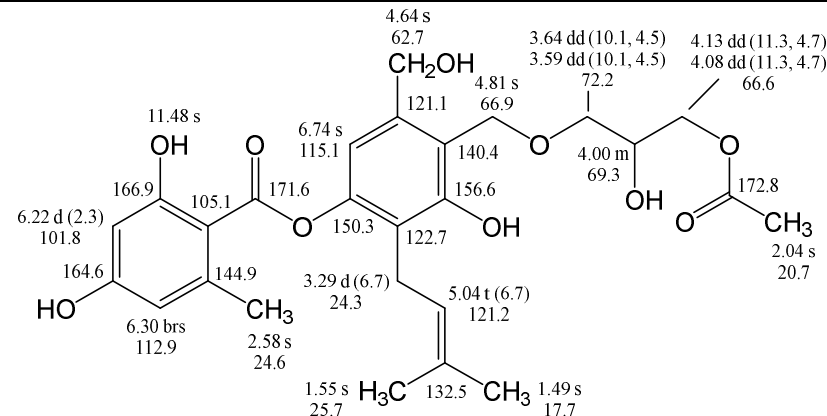
Table S1: Physical and spectral data of fungal depsides

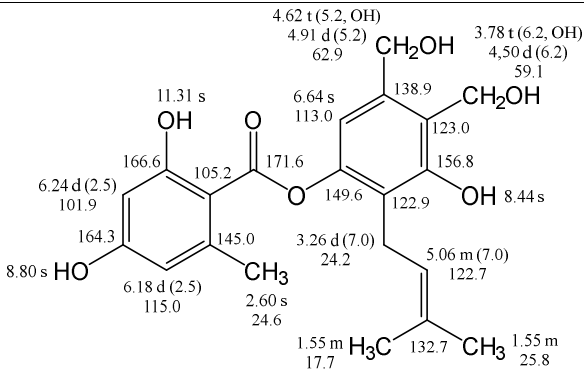
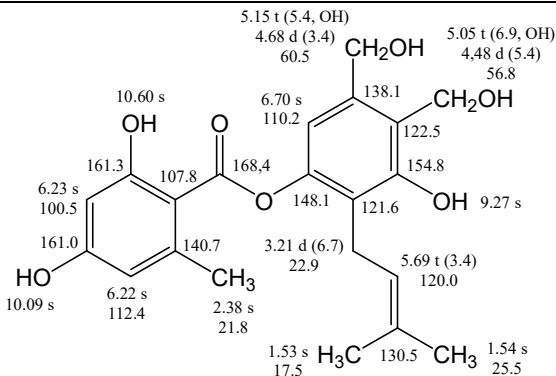
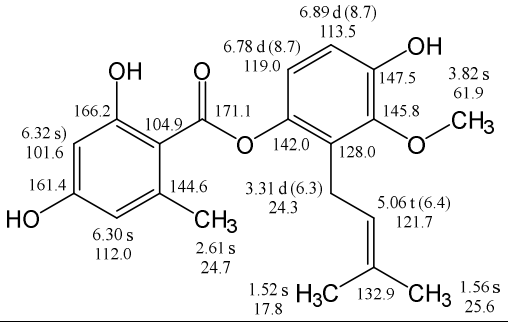
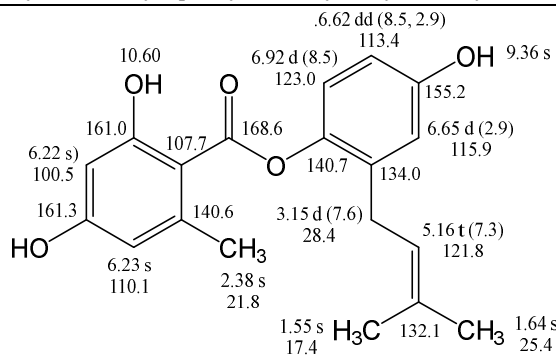
<p>Lecanoric acid (1)</p> 	<p>Colorless solid; UV (MeCN) λ_{max}: 236, 258, 290 nm; ESIHCDHRMS: m/z 317.0662, $[M-H]^-$ (calcd for $C_{16}H_{13}O_7$, m/z 317.0661; 1H NMR and ^{13}C NMR (600 and 150 MHz, DMSO-d_6) [37].</p>
<p>Ethyl lecanorate (2)</p> 	<p>Colorless solid; UV (MeCN) λ_{max}: 238, 257, 299 nm; ESIHCDHRMS: m/z 345.0978 $[M-H]^-$ (calcd for $C_{18}H_{17}O_7$, 345.0974); 1H and ^{13}C NMR (600 and 150 MHz, MeCN-d_3) [37].</p>
<p>Aspergicide A (3)</p> 	<p>Colorless solid; mp 187–188 °C; UV (MeOH) λ_{max} (log ϵ): 263 (3.57), 300 (3.30) nm; IR (neat) γ_{max} 3342, 1726 cm^{-1}; HRESIMS: m/z $[M+Na]^+$ 351.1208 (calcd for $C_{19}H_{20}O_5Na$, 351.1208); 1H and ^{13}C NMR (300 and 75 MHz, acetone-d_6) [38].</p>
<p>Aspergicide B (4)</p> 	<p>Colorless gum; UV (MeOH) λ_{max} (log ϵ): 262 (3.49), 308 (3.24) nm; IR (neat) γ_{max} 3406, 1723, 1710 cm^{-1}; HRESIMS: m/z 411.0843 $[M+K]^+$ (calcd for $C_{20}H_{20}O_7K$, 411.0846); 1H and ^{13}C NMR (500 and 125 MHz, acetone-d_6) [38].</p>
<p>Aspergicide C (5)</p>	

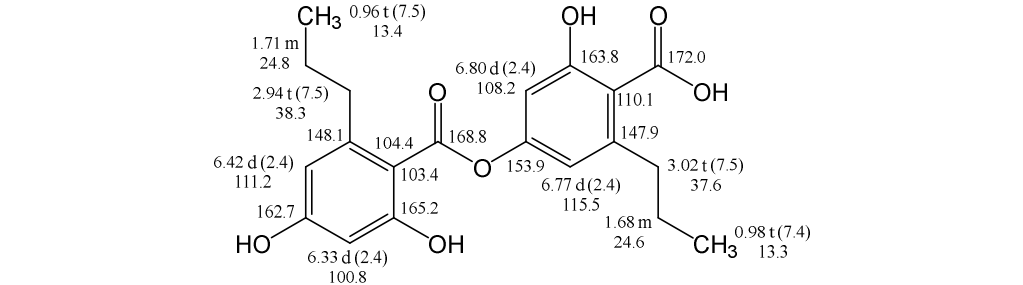
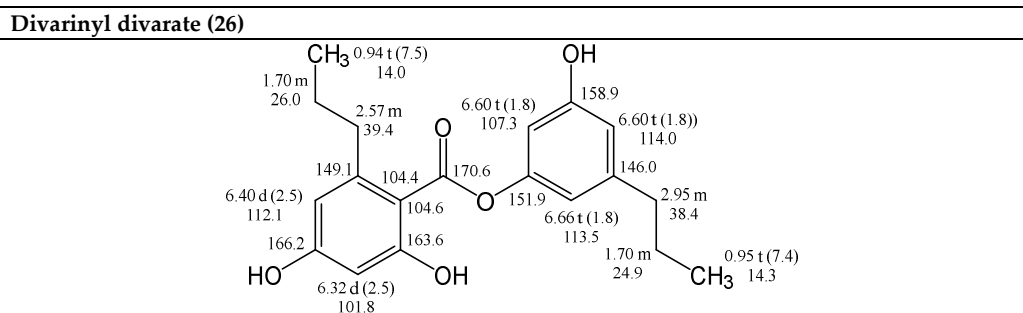
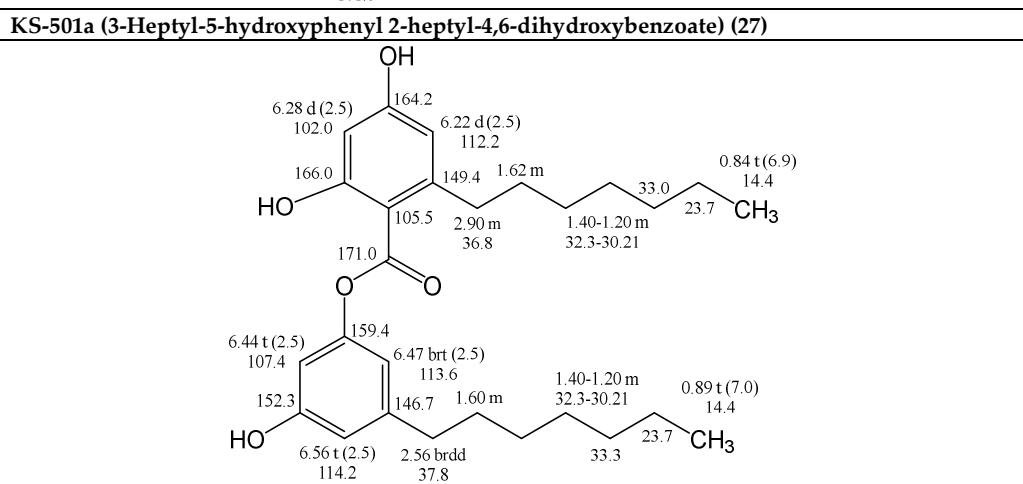
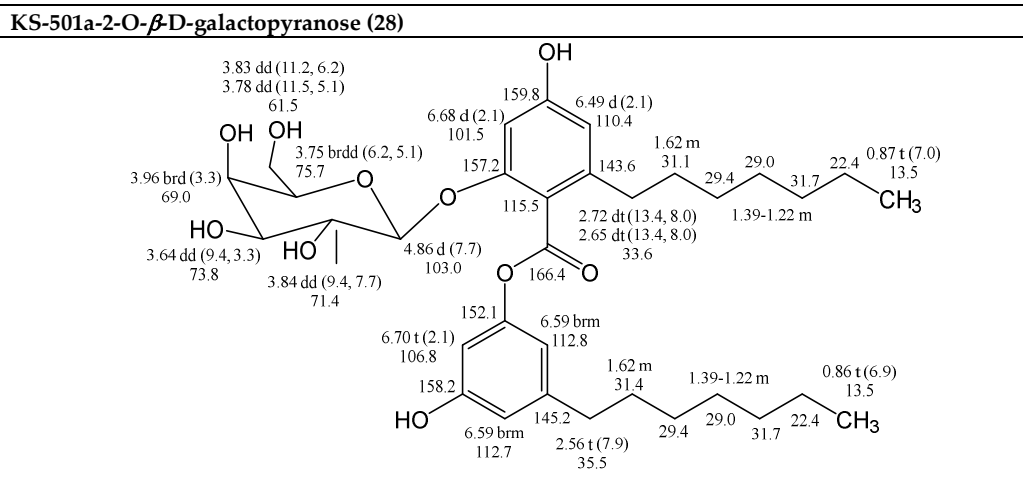

	<p>Colorless solid; mp 211–213 °C; $[\alpha]_D^{24}$ −57.0 (c 0.1, MeOH); UV (MeOH) λ_{max} (log ϵ): 261 (3.56), 300 (3.01) nm; IR (neat) γ_{max}: 3406, 1736, 1721 cm^{-1}; HRESIMS: m/z 449.1576 $[\text{M}+\text{Na}]^+$ (calcd for $\text{C}_{24}\text{H}_{26}\text{O}_7\text{Na}$, 449.1576); ^1H and ^{13}C NMR (300 and 75 MHz, CDCl_3) [38].</p>
<p>Lecanorin D (6)</p>	<p>White powder; UV (MeOH) λ_{max}: 217, 268, 305 nm; HRESIMS: m/z 301.1078 $[\text{M}-\text{H}]^-$ (calcd for $\text{C}_{17}\text{H}_{17}\text{O}_5$, 301.1076); ^1H NMR and ^{13}C NMR (800 and 200 MHz, CD_3OD) [19].</p>
<p>Lecanorin E (7)</p>	<p>White powder; UV (MeOH) λ_{max}: 222, 269, 305 nm; HRESIMS m/z: 287.0920 $[\text{M}-\text{H}]^-$ (calcd for $\text{C}_{16}\text{H}_{15}\text{O}_5$, 287.0920); ^1H NMR and ^{13}C NMR (500 and 125 MHz, CD_3OD) [19].</p>
<p>Lecanorin F (8)</p>	<p>White powder; UV (MeOH) λ_{max}: 218, 275, 312 nm; HRESIMS m/z: 287.0922 $[\text{M}-\text{H}]^-$ (calcd for $\text{C}_{16}\text{H}_{15}\text{O}_5$, 287.0920); ^1H NMR and ^{13}C NMR (800 and 200 MHz, CD_3OD) [19].</p>
<p>68- 3-Hydroxy-2,5-dimethylphenyl 2,4-dihydroxy-3,6-dimethylbenzoate (9)</p>	<p>White amorphous powder; UV (MeOH) λ_{max}: 222 (4.43), 276 (4.17), 306 (3.87) nm. IR (KBr) γ_{max}: 3421, 2925, 1652, 1643, 1635, 1271, 1155 cm^{-1}; ESIMS: m/z 301 (5, $[\text{M}-\text{H}]^-$), 163 (100). ESITOFMS: m/z 301.1067 ($[\text{M}-\text{H}]^-$, $\text{C}_{17}\text{H}_{17}\text{O}_5$; Calcd 301.1076); ^1H and ^{13}C NMR (400 and 100 MHz, CDCl_3 and CD_3OD) [49].</p>
<p>3-Hydroxy-2,4,5-trimethylphenyl 2,4-dihydroxy-3,6-dimethylbenzoate (10)</p>	

<p>Detailed description: Chemical structure of Colletotric acid C (11). It consists of two substituted benzene rings connected by an ester linkage. The left ring has a methyl group at position 2, a hydroxyl group at position 3, another methyl group at position 4, and a carboxylic acid group at position 5. The right ring has a methyl group at position 1, a hydroxyl group at position 2, a methyl group at position 3, and an ester group at position 4. Numerous NMR values are provided for both ¹H and ¹³C.</p>	<p>White amorphous powder; UV (MeOH) λ_{max}: 222 (4.43), 274 (4.19), 308 (3.85) nm; IR (KBr) γ_{max}: 3421, 2979, 1652, 1647, 1635, 1627, 1271, 1155 cm⁻¹; ESIMS: m/z 315 (2, [M-H]⁻), 163 (100); ESITOFMS: m/z 315.1227 [M-H]⁻ (calcd for C₁₈H₁₉O₅, 315.1232); ¹H and ¹³C NMR (400 and 100 MHz, CDCl₃ and CD₃OD) [49].</p>
<p>Detailed description: Chemical structure of Agonodepside A (12). It features two substituted benzene rings linked by an ester bond. The left ring is substituted with a methoxy group, two methyl groups, and a hydroxyl group. The right ring also has a methyl group, a hydroxyl group, and a methoxycarbonyl group. Extensive NMR data are listed for both isotopes.</p>	<p>White solid; IR (KBr) γ_{max}: 3346, 2866, 1783, 1672, 1638, 1445, 1311, 1237, 1150, 1065, 981 cm⁻¹; HRESIMS: m/z 389.1595 [M+H]⁺ (calcd for 389.1522, C₂₁H₂₆O₇); ¹H NMR and ¹³C NMR (500 and 125 MHz, CD₃OD) [46].</p>
<p>Detailed description: Chemical structure of Agonodepside B (13). This molecule contains two substituted benzene rings connected via an ester linkage. Both rings are heavily substituted with methyl groups and hydroxyl groups. Detailed NMR data are provided throughout the structure.</p>	<p>White powder; UV (MeOH) λ_{max} (log ε): 214 (4.57), 275 (4.16), 315 (2.82) nm; IR (KBr) γ_{max}: 3400, 2960, 1725, 1635 cm⁻¹; ESIMS: m/z 381 [M-H]⁻, 203; HRMS: m/z 381.1689 [M-H]⁻ (calcd for C₂₃H₂₅O₅, 381.1697); ¹H and ¹³C NMR (500 and 125 MHz, DMSO-<i>d</i>₆) [50].</p>
<p>Detailed description: Chemical structure of Guisinol (14). It shows two substituted benzene rings joined by an ester group. The left ring has a methyl group and a hydroxyl group. The right ring has a methyl group, a hydroxyl group, and a carboxylic acid group. NMR data are indicated on the structure.</p>	<p>White powder; UV (MeOH) λ_{max} (log ε): 214 (4.57), 275 (4.16), 315 (2.82) nm; IR (KBr) γ_{max}: 3400, 2960, 1725, 1635 cm⁻¹; ESIMS: m/z 381 [M-H]⁻, 203; HRMS: m/z 381.1689 (calcd for C₂₃H₂₅O₅, 381.1697); ¹H and ¹³C NMR (500 and 125 MHz, DMSO-<i>d</i>₆) [50].</p>

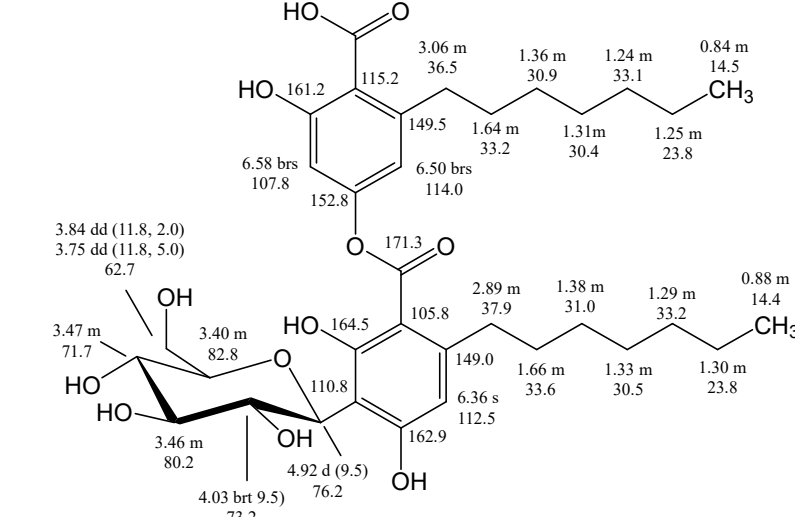
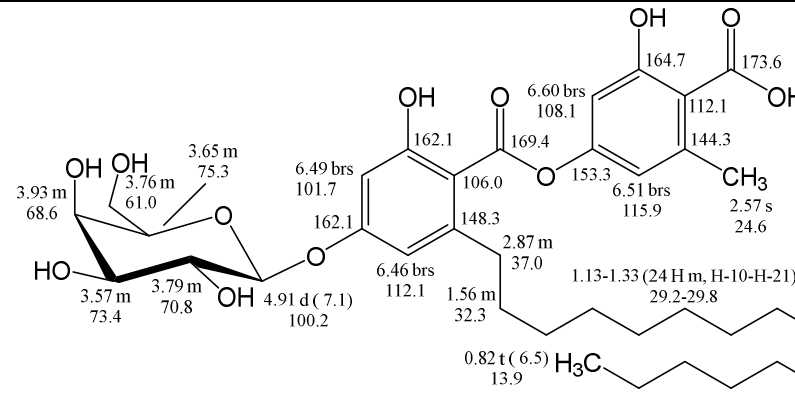
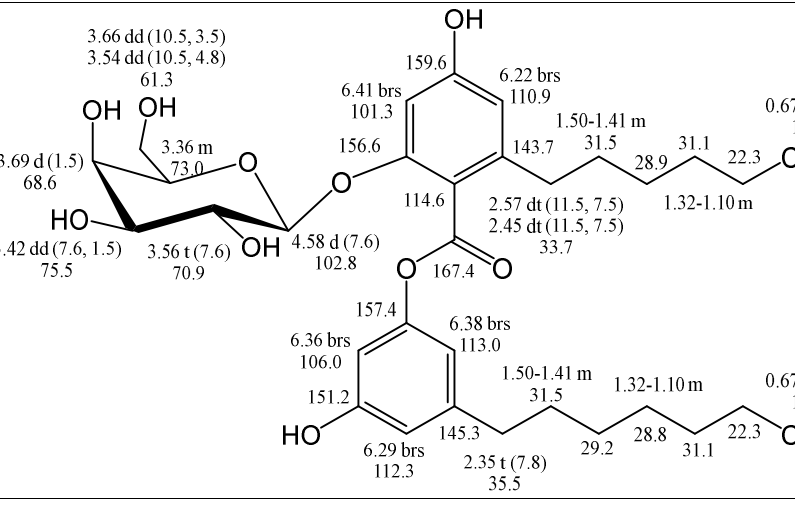
	<p>Yellowish oil; UV (MeOH) λ_{max} (log ϵ): 318 (3.81), 254 (4.09), 216 sh (4.53) nm; HREIMS: m/z 416.1396 (calcd for $C_{23}H_{25}O_5Cl$) (11)/418 (4), 239 (100)/241 (38), 211 (14)/213 (5), 178 (89), 163 (21); 1H and ^{13}C NMR (400 and 100 MHz, $CDCl_3$) [51].</p>
<p>Thielavin Z₇ (15)</p>	<p>White powder; UV (ACN) λ_{max}: 215.8, 276.1, 308.9 nm; HRESIMS: m/z 375.1464 $[M+H]^+$ (calcd. for $C_{20}H_{23}O_7$, 375.1438); 1H NMR and ^{13}C NMR (500 and 125 MHz, $DMSO-d_6$) [52].</p>
<p>Sterenin J (16)</p>	<p>Colorless oil (MeOH); UV (MeOH) λ_{max}: (log ϵ): 272 (4.15) nm; $[\alpha]^{20}_D$ -11.05 (c 0.5, MeOH); IR γ_{max}: 2985, 2925, 2667, 1718, 1654, 1618, 1583, 1449, 1305, 1252, 1202, 1169, 1094, 852, 795 cm^{-1}; HRTOFMS: m/z 403.1381 $[M+H]^+$ (calcd. for $C_{21}H_{22}O_8H$, 403.1387); 1H NMR and ^{13}C NMR (500 and 125 MHz, CD_3OD) [53].</p>
<p>Sterenin E (17)</p>	<p>Brown amorphous powder (MeOH); UV (MeOH) λ_{max} (log ϵ): 266 (4.21) nm; IR γ_{max}: 3360, 3071, 2979, 2938, 1700, 1685, 1641, 1617, 1585, 1441, 1310, 1284, 1157, 1096, 846 cm^{-1}; HRTOFMS: m/z 409.1258 $[M+Na]^+$ (calcd. for $C_{21}H_{22}O_7Na$, 409.1258); 1H NMR and ^{13}C NMR (500 and 125 MHz, CD_3OD) [53].</p>
<p>Sterenin F (18)</p>	

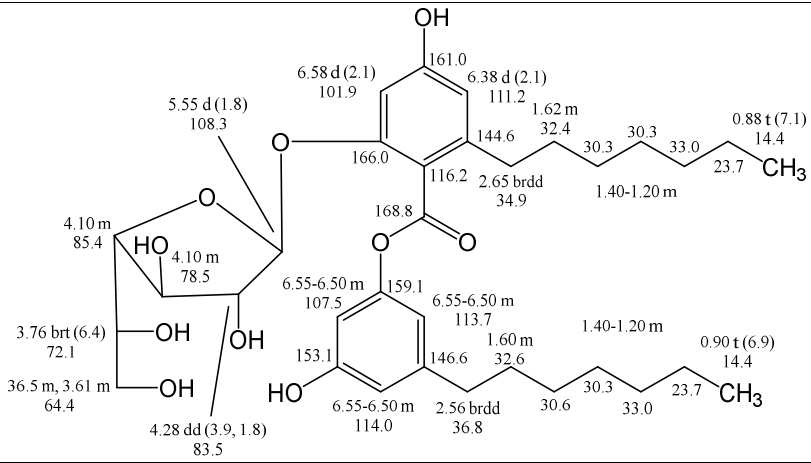
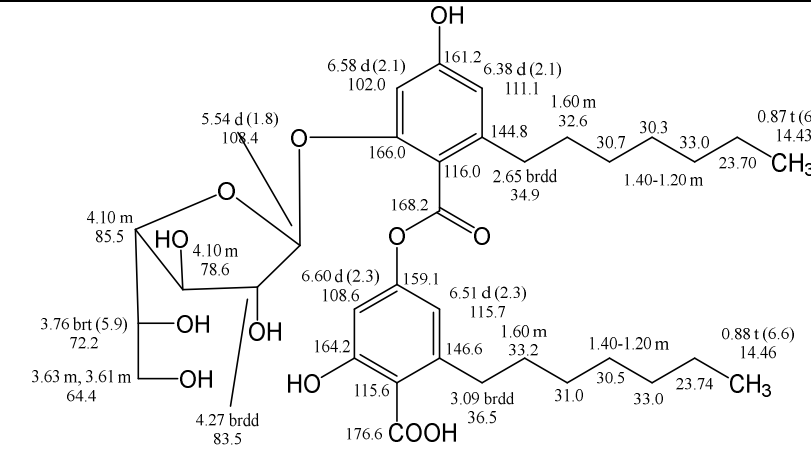
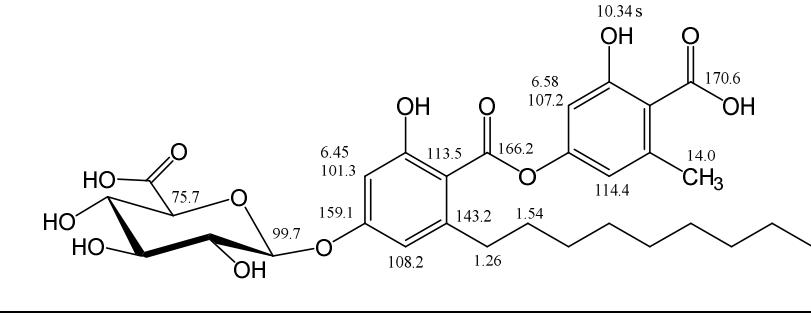
 <p>¹H NMR and ¹³C NMR (500 and 125 MHz, CDCl₃) [53].</p>	<p>Brown amorphous powder (MeOH); UV (MeOH) λ_{max} (log ϵ): 265 (4.51) nm; IR γ_{max}: 3370, 2928, 2855, 1663, 1617, 1443, 1403, 1377, 1310, 1250, 1195, 1149, 1095, 806 cm⁻¹; HRTOFMS: m/z 423.1419 [M+Na]⁺ (calcd. for C₂₂H₂₄O₇Na, 423.1414; ¹H NMR and ¹³C NMR (500 and 125 MHz, CDCl₃) [53].</p>
<p>Sterenin G (19)</p>  <p>¹H NMR and ¹³C NMR (500 and 125 MHz, CDCl₃) [53].</p>	<p>Brown amorphous powder (MeOH); UV (MeOH) λ_{max} (log ϵ): 260 (4.51) nm; IR γ_{max}: 3375, 2979, 2881, 1719, 1653, 1640, 1617, 1444, 1406, 1377, 1313, 1240, 1197, 1163, 1095, 846 cm⁻¹; HRTOFMS: m/z 371.1489 [M+H]⁺ (calcd. for C₂₁H₂₂O₆H, 371.1489); ¹H NMR and ¹³C NMR (500 and 125 MHz, CDCl₃) [53].</p>
<p>Sterenin H (20)</p>  <p>¹H NMR and ¹³C NMR (500 and 125 MHz, CDCl₃) [53].</p>	<p>Colorless oil (MeOH); UV (MeOH) λ_{max} (log ϵ): 270 (4.23) nm; IR γ_{max}: 3306, 2971, 2931, 1658, 1621, 1586, 1445, 1426, 1376, 1312, 1254, 1198, 1166, 1097, 1009, 845, 792, 697 cm⁻¹; HRTOFMS: m/z 425.1569 [M+Na]⁺ (calcd. for C₂₂H₂₆O₇Na, 425.1571); ¹H NMR and ¹³C NMR (500 and 125 MHz, CDCl₃) [53].</p>
<p>Sterenin I (21)</p>  <p>¹H NMR and ¹³C NMR (500 and 125 MHz, CD₃OD); HRTOFMS: m/z: 527.1891 [M+Na]⁺ (calcd. for C₂₆H₃₂O₁₀Na, 527.1888).</p>	<p>Colorless oil (MeOH); UV (MeOH) λ_{max} (log ϵ): 270 (1.73) nm; [α]_D²⁰ +14.29 (c 0.3, MeOH); IR γ_{max}: 3370, 2973, 2951, 1721, 1658, 1621, 1586, 1444, 1426, 1376, 1311, 1255, 1201, 1169, 1098, 1043, 846, 792, 697 cm⁻¹; ¹H NMR and ¹³C NMR (500 and 125 MHz, CD₃OD); HRTOFMS: m/z: 527.1891 [M+Na]⁺ (calcd. for C₂₆H₃₂O₁₀Na, 527.1888).</p>
<p>MS-3 (22)</p>	

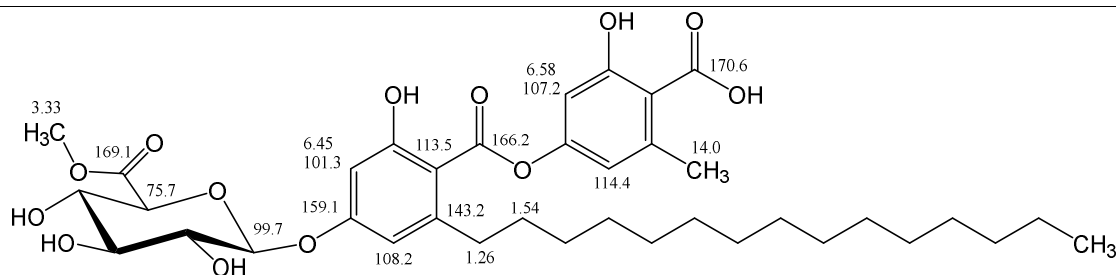
 <p>¹H NMR and ¹³C NMR (500 and 125 MHz, DMSO-<i>d</i>₆)</p>	<p>Colorless needle crystals; mp 92 °C; UV (MeOH) λ_{max} (ϵ): 270 (23280), 305 (86300 nm; IR (KBr) γ_{max}: 3400, 2950, 1655, 1615, 1580, 1495, 1440, 1430, 1375, 1320, 1255, 1190, 1165, 1095, 1060, 1035, 990, 885, 845, 790, 695 cm⁻¹; elemental analysis; 64.91 (C), 6.19 (H), 28.29 (O), C₂₁H₂₄O₇; ¹H NMR and ¹³C NMR (100 and 25 MHz, dioxane-<i>d</i>₈, CD₃OD) [39,55, 56].</p>
 <p>¹H NMR and ¹³C NMR (500 and 125 MHz, DMSO-<i>d</i>₆)</p>	<p>HRESIMS: m/z 777.3154 [M+H]⁺ (calcd for C₄₂H₄₈O₁₄, 777.3122); 799.2968 [M+Na]⁺; ¹H NMR and ¹³C NMR (500 and 125 MHz, DMSO-<i>d</i>₆) [57,58]</p>
<p>4'-Hydroxy-5'-methoxy-6'-(3''-methyl-2''-butenyl)-phenyl-2,4-dihydroxy-6-methyl-benzoate (23)</p>	 <p>¹H NMR and ¹³C NMR (500 and 125 MHz, CDCl₃) [40].</p>
<p>4'-Hydroxy-6'-(3''-methyl-2''-butenyl)-phenyl-2,4-dihydroxy-6-methyl-benzoate (24)</p>	 <p>¹H NMR and ¹³C NMR (500 and 125 MHz, DMSO-<i>d</i>₆)</p>
<p>Nordivarcic acid (25)</p>	<p>Brown oil; UV (meOH) λ_{max} (log ϵ): 213 (4.12), 268 (4.10), 302 (3.93) nm; IR (neat) γ_{max}: 3342, 2930, 1679, 1624, 1495, 1445 cm⁻¹; HRTOFMS: m/z 329.1384 [M+H]⁺ (calcd. for C₁₉H₂₁O₅, 329.1385) [40].</p>

 <p>Chemical structure of Divarinyll divarate (26) is shown with ¹H and ¹³C NMR data. The structure features two phenolic rings linked by an ester group. The left ring has a hydroxyl group and a methyl group. The right ring has a hydroxyl group and a methyl group. The ¹H NMR data (in parentheses) and ¹³C NMR data are provided for each proton and carbon.</p>	<p>White amorphous powder; ES-IMS: <i>m/z</i> 373 [M-H][−]; ¹H NMR and ¹³C NMR (500 and 125 MHz, acetone-<i>d</i>₆) [25].</p>
<p>Divarinyll divarate (26)</p>  <p>Chemical structure of Divarinyll divarate (26) is shown with ¹H and ¹³C NMR data. The structure features two phenolic rings linked by an ester group. The left ring has a hydroxyl group and a methyl group. The right ring has a hydroxyl group and a methyl group. The ¹H NMR data (in parentheses) and ¹³C NMR data are provided for each proton and carbon.</p>	<p>White amorphous powder; ES-IMS: <i>m/z</i> 329 [M-H][−]; ¹H NMR and ¹³C NMR (500 and 125 MHz, acetone-<i>d</i>₆) [25].</p>
<p>KS-501a (3-Heptyl-5-hydroxyphenyl 2-heptyl-4,6-dihydroxybenzoate) (27)</p>  <p>Chemical structure of KS-501a (27) is shown with ¹H and ¹³C NMR data. The structure features two phenolic rings linked by an ester group. The left ring has a hydroxyl group and a methyl group. The right ring has a hydroxyl group and a methyl group. The ¹H NMR data (in parentheses) and ¹³C NMR data are provided for each proton and carbon.</p>	<p>Colorless powder; EIMS: <i>m/z</i> 442 (M)⁺, 235, 208, 166, 137, 124; ¹H and ¹³C NMR (400 and 100 MHz, CD₃OD) [41,120].</p>
<p>KS-501a-2-O-β-D-galactopyranose (28)</p>  <p>Chemical structure of KS-501a-2-O-β-D-galactopyranose (28) is shown with ¹H and ¹³C NMR data. The structure features two phenolic rings linked by an ester group. The left ring has a hydroxyl group and a methyl group. The right ring has a hydroxyl group and a methyl group. The ¹H NMR data (in parentheses) and ¹³C NMR data are provided for each proton and carbon.</p>	<p>White solid; mp 174-176 °C; [α]_D²⁷ -3.3 (c 0.10, MeOH); UV (MeOH) λ_{max} (log ε): 203 (4.66), 255 (3.87) nm; IR (CHCl₃) γ_{max}: 3423, 926, 1728, 1613, 1592, 1465, 1260, 1073 cm^{−1}; HRESITOF: <i>m/z</i> 627.3152 [M+Na]⁺ (calcd for C₃₃H₄₈O₁₀Na, 627.3145); ¹H and ¹³C NMR (500 and 125 MHz, acetone-<i>d</i>₆) [41].</p>
<p>KS-501a-2-O-β-D-digalactopyranose (29)</p>  <p>Chemical structure of KS-501a-2-O-β-D-digalactopyranose (29) is shown with ¹H and ¹³C NMR data. The structure features two phenolic rings linked by an ester group. The left ring has a hydroxyl group and a methyl group. The right ring has a hydroxyl group and a methyl group. The ¹H NMR data (in parentheses) and ¹³C NMR data are provided for each proton and carbon.</p>	

<p># in DMSO-d_6</p>	
<p>Sugar part in ^1H NMR DMSO-d_6, 500 MHz</p>	<p>Pale yellow solid; mp 200–202 °C; $[\alpha]_D^{26}$ -10.6 (c 0.20, MeOH); UV (MeOH) λ_{max} (log ϵ): 203 (5.10), 253 (4.26) nm; IR (CHCl₃) γ_{max}: 3406, 2926, 1725, 1620, 1590, 1465, 1259, 1076 cm^{-1}; HRESITOF: m/z 789.3688 $[\text{M} + \text{Na}]^+$ (calcd for C₃₉H₅₈O₁₅Na, 789.3673); ^1H and ^{13}C NMR (500 and 125 MHz, acetone-d_6/D₂O, 95:5) [41].</p>
<p>Arenicolin A (30)</p>	<p>Off-white solid; $[\alpha]_D$ -29 (c 0.11, MeOH); UV (MeOH) λ_{max} (log ϵ): 221 (4.3), 272 (4.1), 308 (3.8) nm; ECD (MeOH 4.8 mM) λ_{max} ($\Delta\epsilon$): 225 (-15), 240 (-56), 262 (+20), 272 (+2.5), 275 (-3.5), 311 (+8.2) nm; HRESIMS m/z 803.3495 $[\text{M}-\text{H}]^-$ (calcd for C₄₁H₅₅O₁₆, 803.3490); ^1H NMR and ^{13}C NMR (500 and 125 MHz, CD₃OD) [42]</p>
<p>Arenicolin B (31)</p>	

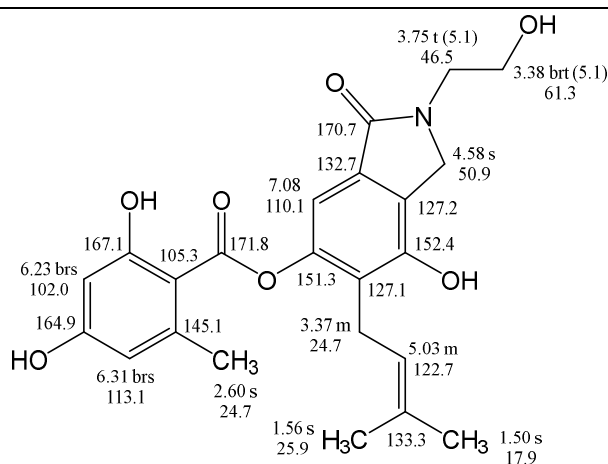
	<p>Off-white solid; $[\alpha]_D^{+16}$ (c 0.19, MeOH); UV (MeOH) λ_{max} (log ϵ): 220 (4.4), 273 (4.1), 307 (3.9) nm; ECD (MeOH, 7.4 mM) λ_{max} ($\Delta\epsilon$) 217 (-16), 227 (-4.6), 250 (-2.7), 311 (+4.3) nm; HRESIMS: m/z 647.3064 $[M-H]^-$ (calcd for $[C_{34}H_{48}O_{12}]$, 647.3068); 1H NMR and ^{13}C NMR (500 and 125 MHz, CD_3OD) [42].</p>
<p>72- Aquastatin A (32)</p> 	<p>White solid; UV (MeOH) λ_{max} (ϵ): 213 (52933), 265 (19033), 307 (10733) nm; IR ($CHCl_3$) γ_{max}: 2923, 2851, 1665, 1613, 1247, 1070 cm^{-1}; HRFABMS m/z: 677.3537 $[M+H]^+$ (calcd for $C_{36}H_{52}O_{12}$, 677.3537) [103]. 1H and ^{13}C NMR (400 and 100 MHz, $CDCl_3$); LRESIMS m/z: 675 $[M-H]^-$; HRESIMS m/z: 675.3350 $(M-H)^-$ (calcd for $C_{36}H_{51}O_{12}$, 675.3381) [60].</p>
<p>Depsitinuside (33)</p> 	<p>Colorless amorphous powder; IR (KBr) γ_{max}: 3475, 3120, 2920, 1720, 1610, 1560 nm; HRFABMS: m/z 589.3009 $[M-H]^-$ (calcd for $C_{32}H_{45}O_{10}$, 589.3012); 1H NMR and ^{13}C NMR (500 and 125 MHz, $CDCl_3$) [62].</p>
<p>KS-501 (2-(β-D-galactofuranosyloxy)-6-heptyl-4-hydroxybenzoic acid 3-heptyl-5-hydroxyphenyl ester) (34)</p>	

	<p>Colorless powder; $[\alpha]_D^{23}$ -53.0 (c 0.30, MeOH); UV (MeOH) λ_{max} (ϵ): 207 (35000), 254 (6600), 278 (5000) nm; IR (CHCl₃) γ_{max}: 3400, 1720, 1585, 1064 cm⁻¹; HRFABMS m/z: 603.3169 [M+H]⁺ (calcd for C₃₃H₄₇O₁₀, 603.3170); ¹H and ¹³C NMR (400 and 100 MHz, CD₃OD) [63, 120].</p>
<p>KS-502 (2-(β-D-galactofuranosyloxy)6-heptyl-4-hydroxybenzoic acid 4-carboxy-3-heptyl-5-hydroxyphenyl ester) (35)</p> 	<p>Colorless powder; $[\alpha]_D^{23}$ -45.0 (c 0.30, MeOH); UV (MeOH) λ_{max} (ϵ): 210 (56000), 245 (12000), 290 (6500) nm; IR (CHCl₃) γ_{max}: 3450, 1724, 1595, 1057 cm⁻¹; HRFABMS m/z: 647.3083 [M+H]⁺ (calcd for C₃₄H₄₇O₁₂, 647.3068); ¹H and ¹³C NMR (400 and 100 MHz, CD₃OD) [63,120].</p>
<p>CRM646-A (36)</p>	
	
<p>White solid; $[\alpha]_D^{20}$ -41.5 (c 0.31, MeOH); IR (KBr) γ_{max}: 3397, 2900, 1730, 1666, 1614 cm⁻¹; FABMS: m/z 689 [M-H]⁻ (C₃₆H₅₀O₁₃); ¹H and ¹³C NMR (300 and 75 MHz, DMSO-<i>d</i>₆); ¹H NMR (300 MHz, DMSO-<i>d</i>₆): δ_H 10.34 (brs, 1H), 6.57 (s, 1H), 6.49 (m, 3H), 5.70-5.20 (br, 2H), 5.05 (d, 1H, <i>J</i> = 7.5 Hz), 3.91 (d, 1H, <i>J</i> = 9.0 Hz), 3.46-3.30 (m, 3H), 2.65-2.60 (m, 2H), 2.45 (s, 3 H), 1.60-1.50 (m, 2H), 1.38-1.20 (m, 24H), 0.86 (m, 3H); ¹³C NMR (75 MHz, CDCl₃): δ_C 171.3, 170.2, 166.4, 160.8, 159.4, 157.5, 152.5, 143.4, 140.6, 116.5, 114.3, 113.8, 108.6, 107.4, 101.5, 100.0, 76.0, 75.8, 73.1, 71.6, 33.7, 31.5, 31.1, 29.2, 29.0, 28.9, 22.3, 21.8, 14.1 [43,44].</p>	
<p>CRM646-B (37)</p>	



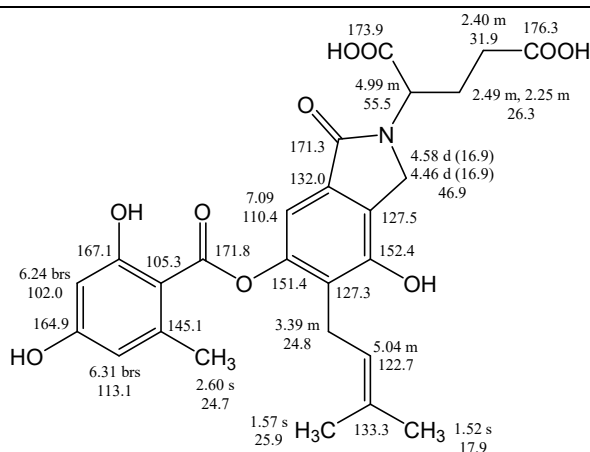
White solid; $[\alpha]_D^{20}$ -29.7 (c 0.31, CD₃COCD₃); ESIMS: m/z 703.3 [M-H]⁻; IR (KBr) γ_{max} : 3397, 2900, 1730, 1666, 1614 cm⁻¹; FABMS (-): m/z 703 [M-H]⁻, FABMS (-): m/z 705 [M+H]⁺; HRESIMS: m/z 727.3300 (calcd for C₃₇H₅₂O₁₃Na, 727.3306); ¹H NMR (300 MHz, CD₃COCD₃): δ_H 6.58-6.55 (m, 3H), 6.45 (d, 1H, J = 1.8 Hz), 5.28 (d, 1H, J = 7.5 Hz), 4.22 (d, 1H, J = 9.6 Hz), 3.76-3.73 (m, 4H), 3.74-3.60 (m, 3H), 2.93 (t, 2H, J = 7.8 Hz), 2.65 (s, 3H), 1.65-1.60 (m, 2H), 1.35-1.25 (m, 24H), 0.88 (t, 3H, J = 6.8 Hz); ¹³C NMR (75 MHz, CD₃COCD₃): δ_C 170.2, 165.2, 164.4, 162.6, 153.2, 148.5, 115.5, 112.3, 109.1, 108.4, 102.8, 101.1, 77.1, 76.7, 74.3, 72.7, 52.9, 37.2, 33.1, 32.9, 31.0, 30.7, 30.6, 30.5, 30.2, 29.9, 29.7, 29.4, 24.2, 23.6, 14.7 [43,44].

Sterenin A (38)



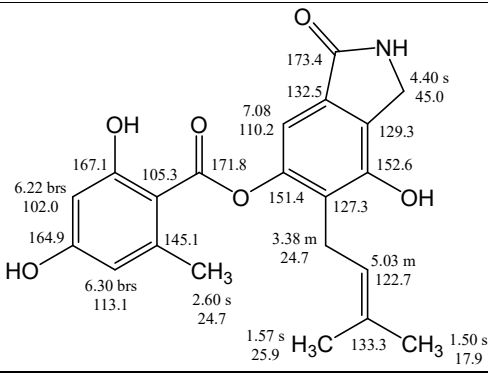
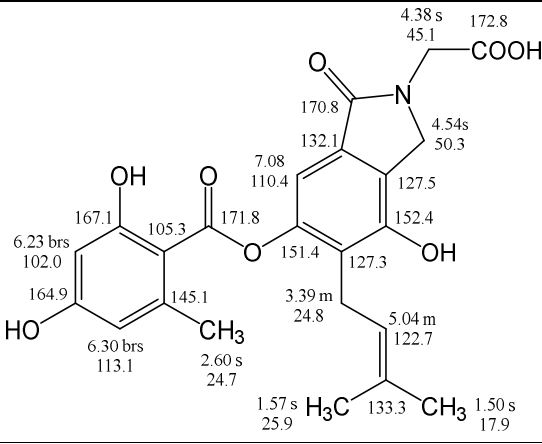
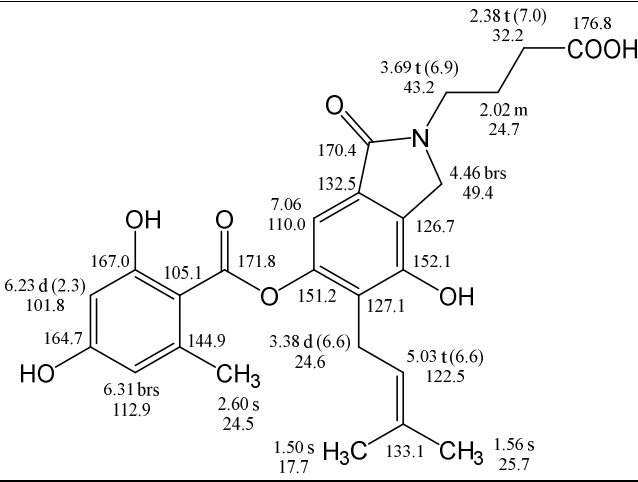
White powder; UV (MeOH) λ_{max} (ϵ): 212 (58600), 265 (24400), 297 (10900) nm; IR (KBr) γ_{max} : 3357, 3231, 2973, 2931, 1662, 1623, 1602, 1456, 1376, 1311, 1255, 1199, 1164, 1084, 1064, 1035, 990 cm⁻¹; FABMS: m/z 450 [M+Na]⁺; HRFABMS: m/z 450.1526 [M+Na]⁺ (calcd for C₂₃H₂₅NO₇Na, 450.1529); ¹H NMR and ¹³C NMR (500 and 125 MHz, CD₃OD) [64].

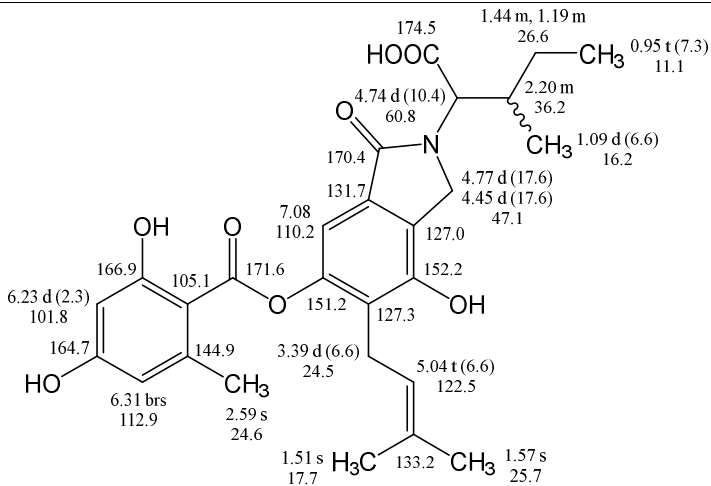
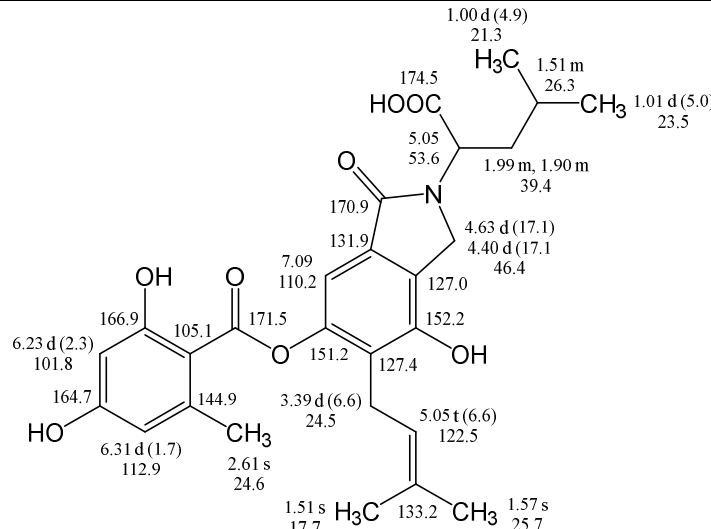
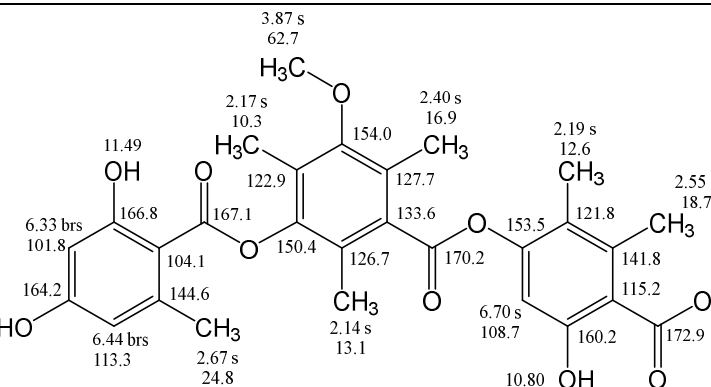
Sterenin B (39)

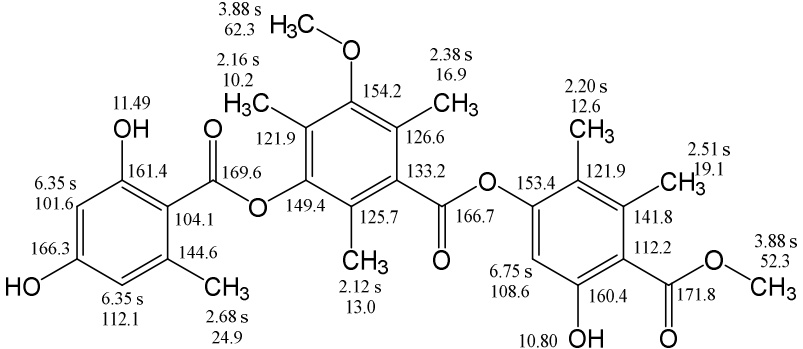
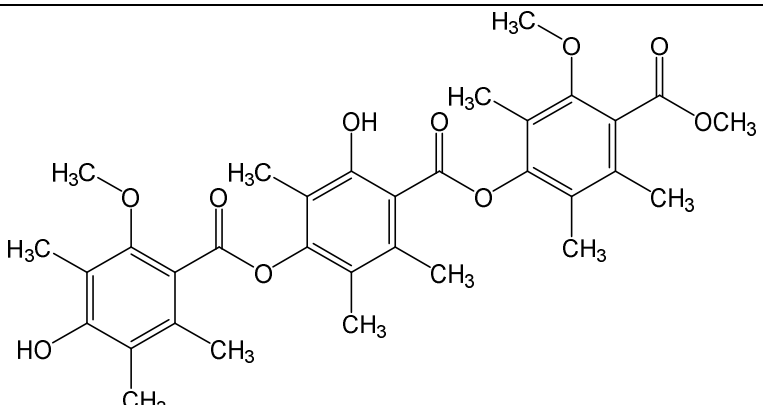
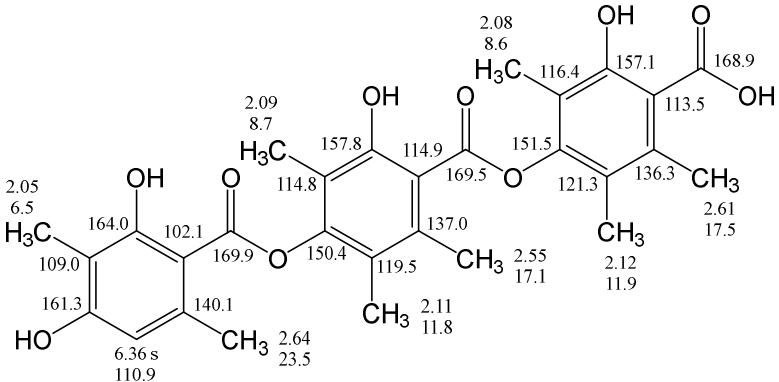
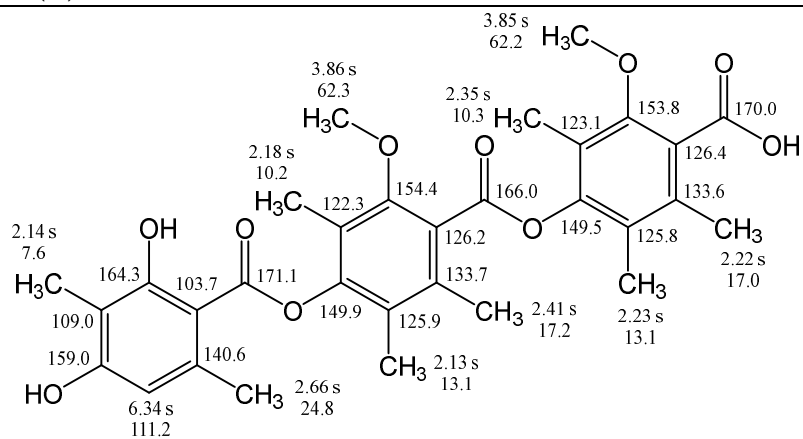


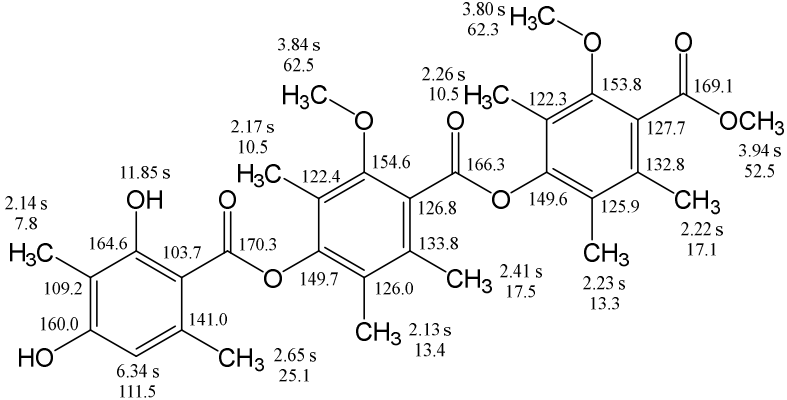
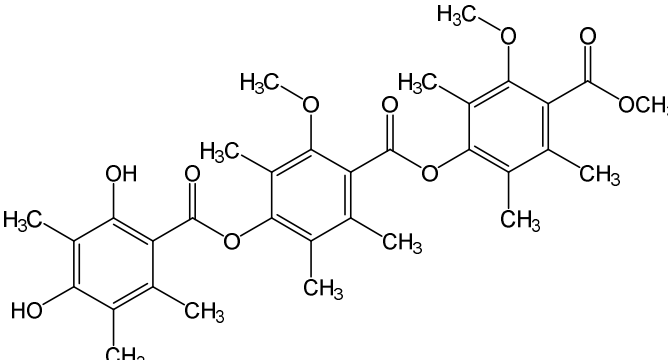
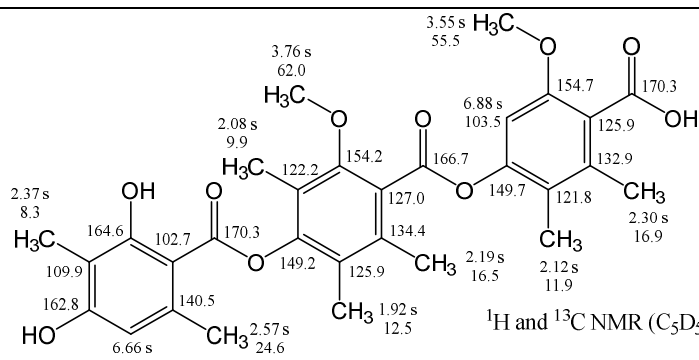
White powder; $[\alpha]_D$ -16.3 (c 0.05, MeOH); UV (MeOH) λ_{max} (ϵ): 214 (58100), 265 (26500), 296 (11100) nm; IR (KBr) γ_{max} : 3348, 3264, 2973, 2928, 2858, 1718, 1662, 1624, 1603, 1450, 1413, 1377, 1310, 1254, 1198, 1162, 1087, 1063, 1035, 991 cm⁻¹; FABMS m/z : 514 [M+H]⁺; HRFABMS: m/z 514.1697 [M+H]⁺ (calcd for C₂₆H₂₈NO₁₀, 514.1713); ¹H NMR and ¹³C NMR (500 and 125 MHz, CD₃OD) [64].

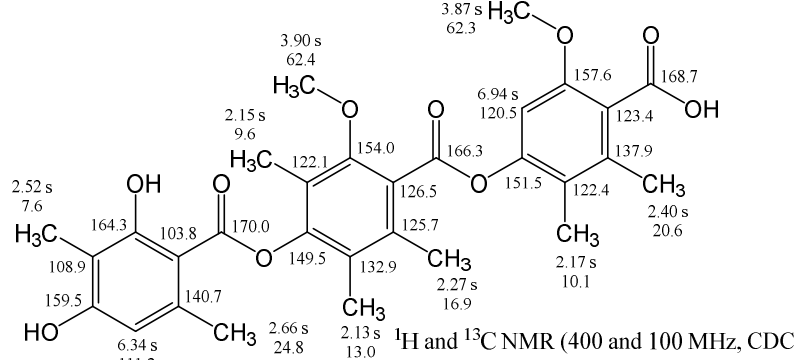
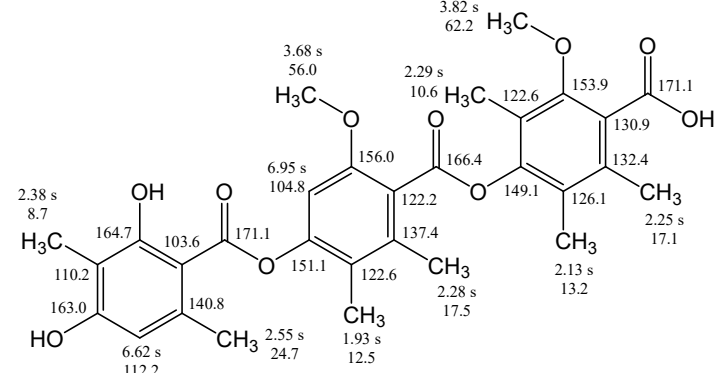
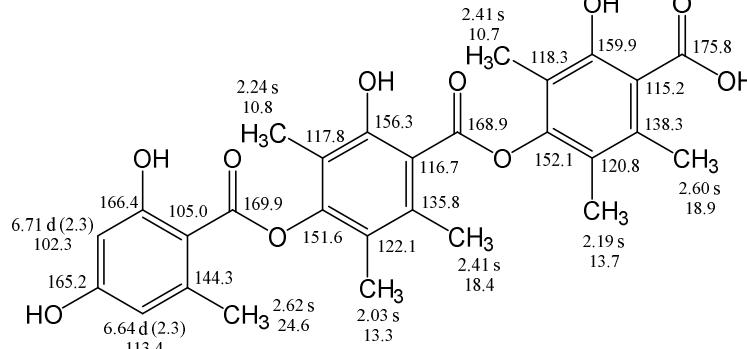
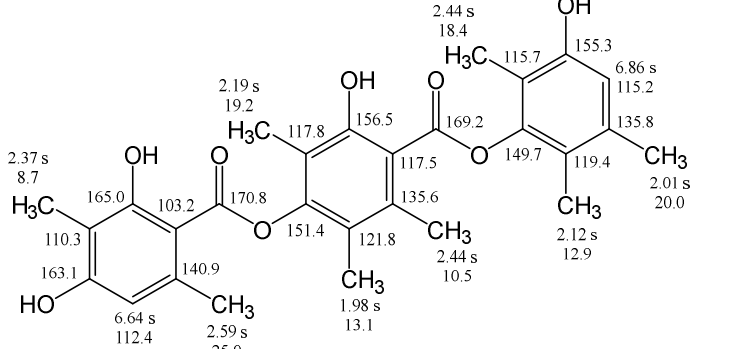
Sterenin C (40)

	<p>White powder; UV (MeOH) λ_{max} (ϵ): 213 (66700), 268 (23000), 297 (12000) nm; IR (KBr) γ_{max}: 3409, 3267, 2974, 2931, 1669, 1653, 1623, 1599, 1504, 1446, 1413, 1374, 1349, 1313, 1255, 1193, 1173, 1161, 1100, 1063, 1038, 998, 989 cm^{-1}; FABMS: m/z 406 $[\text{M}+\text{Na}]^+$; HRFABMS: m/z 406.1273 $[\text{M}+\text{Na}]^+$ (calcd for $\text{C}_{21}\text{H}_{21}\text{NO}_{10}\text{Na}$, 406.1267); ^1H NMR and ^{13}C NMR (500 and 125 MHz, CD_3OD) [64].</p>
<p>Sterenin D (41)</p> 	<p>White powder; UV (MeOH) λ_{max} (ϵ): 213 (96200), 265 (41300), 297 (17500) nm; IR (KBr) γ_{max}: 3366, 3245, 2973, 2929, 2733, 1662, 1624, 1601, 1458, 1448, 1401, 1377, 1349, 1311, 1254, 1201, 1165, 1103, 1081, 1035, 995, 946 cm^{-1}; FABMS: m/z 442 $(\text{M}+\text{H})^+$; HRFABMS m/z: 442.1495 $[\text{M}+\text{H}]^+$ (calcd for $\text{C}_{23}\text{H}_{24}\text{NO}_8$, 442.1502); ^1H NMR and ^{13}C NMR (500 and 125 MHz, CD_3OD) [64].</p>
<p>Sterenin K (42)</p> 	<p>White powder (MeOH); UV (MeOH) λ_{max} ($\log \epsilon$): 275 (3.41) nm; IR γ_{max}: 3202, 2972, 2930, 1709, 1661, 1601, 1447, 1311, 1254, 1200, 1162, 1104, 1058, 846, 792, 723 cm^{-1}; HRTOFMS: m/z 470.1809 $[\text{M}+\text{H}]^+$ (calcd. for $\text{C}_{25}\text{H}_{27}\text{NO}_8$, 470.1809); ^1H NMR and ^{13}C NMR (500 and 125 MHz, CD_3OD) [53].</p>
<p>Sterenin L (43)</p>	

 <p>Chemical structure of Sterenin M (44) with ¹H and ¹³C NMR data. The structure is a complex polycyclic molecule with a central benzene ring, a carboxylic acid group, and a side chain with a methyl group. NMR data includes ¹H NMR (400 MHz, CD₃OD) and ¹³C NMR (125 MHz, CD₃OD) peaks.</p>	<p>White powder (MeOH); UV (MeOH) λ_{max} (log ϵ): 263 (2.52) nm; [α]²⁰_D -12.05 (c 0.2, MeOH); IR γ_{max}: 3193, 2964, 2925, 2874, 1718, 1658, 1623, 1601, 1455, 1310, 1253, 1199, 1160, 1093, 1063, 846, 791 cm⁻¹; HRTOFMS: m/z 520.1940 [M+Na]⁺ (calcd for C₂₇H₃₁NO₈Na, 520.1942); ¹H NMR and ¹³C NMR (500 and 125 MHz, CD₃OD) [53].</p>
<p>Sterenin M (44)</p>  <p>Chemical structure of Sterenin M (44) with ¹H and ¹³C NMR data. The structure is a complex polycyclic molecule with a central benzene ring, a carboxylic acid group, and a side chain with a methyl group. NMR data includes ¹H NMR (400 MHz, CD₃OD) and ¹³C NMR (125 MHz, CD₃OD) peaks.</p>	<p>White powder (MeOH); UV (MeOH) λ_{max} (log ϵ): 264 (3.45) nm; [α]²⁰_D -11.33 (c 0.3, MeOH); IR γ_{max}: 3368, 2923, 2869, 1711, 1654, 1637, 1599, 1450, 1310, 1253, 1198, 1158, 1093, 1071, 844, 795, 725 cm⁻¹; HRTOFMS: m/z 498.2124 [M+H]⁺ (calcd for C₂₇H₃₁NO₈, 498.2122); ¹H NMR and ¹³C NMR (500 and 125 MHz, CD₃OD) [53].</p>
<p>5- Colletotric acid A (45)</p>  <p>Chemical structure of 5- Colletotric acid A (45) with ¹H and ¹³C NMR data. The structure is a complex polycyclic molecule with a central benzene ring, a carboxylic acid group, and a side chain with a methyl group. NMR data includes ¹H NMR (400 MHz, CD₃OD) and ¹³C NMR (125 MHz, CD₃OD) peaks.</p>	<p>White solid; mp 85–86 °C; EIMS: m/z 193 (63.1), 151 (9.1), 124 (66.6), 45 (100); FABMS: m/z 525 [M+H]⁺ (22), 375 (55), 343 (63); HRFABMS: m/z 525.1765 [M+H]⁺ (calcd for C₂₈H₂₈O₁₀, 525.1761); ¹H and ¹³C NMR (DMSO-<i>d</i>₆, 400, 125 MHz) [46].</p>
<p>Colletotric acid B (46)</p>	

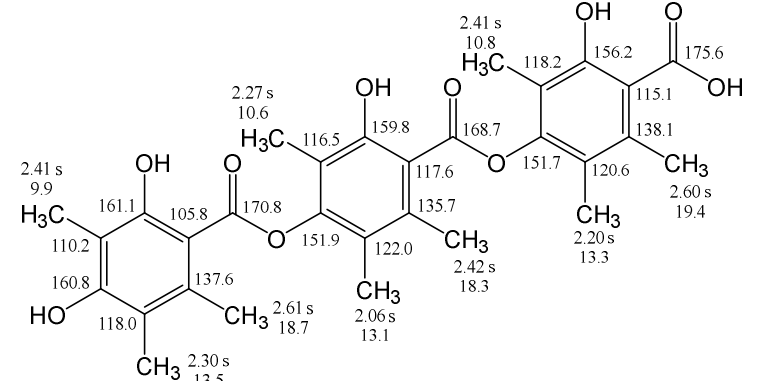
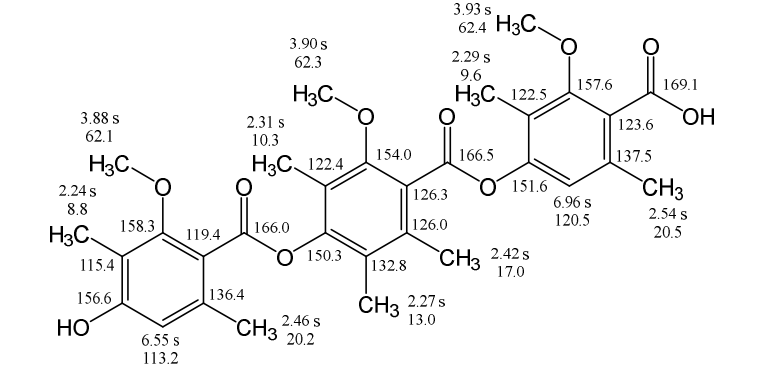
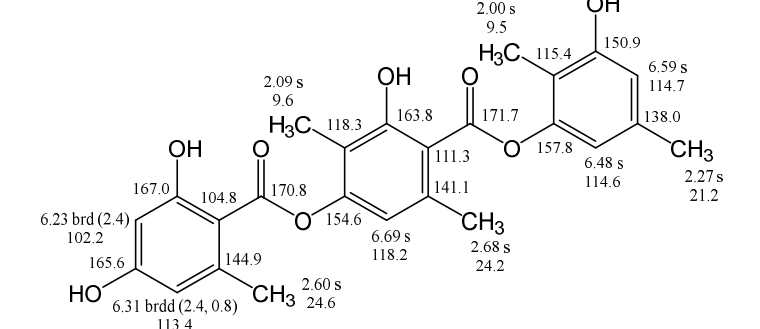
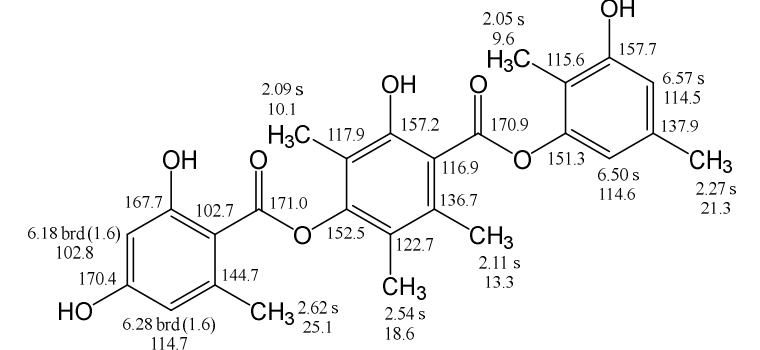
 <p>Chemical structure of PS-990 (47) is shown with ¹³C NMR (500 MHz, CDCl₃) and ¹H NMR (125 MHz, CDCl₃) data labels. The structure consists of three aromatic rings linked by ester groups. The left ring has a hydroxyl group and a methoxy group. The middle ring has a methoxy group and a methyl group. The right ring has a methoxy group and a methyl group. The ¹³C NMR data labels are: 166.3, 161.4, 101.6, 6.35 s, 112.1, 104.1, 144.6, 121.9, 126.6, 133.2, 154.2, 149.4, 125.7, 12.6, 121.9, 141.8, 112.2, 171.8, 160.4, 108.6, 6.75 s, 10.80, 2.51 s, 19.1, 3.88 s, 52.3, 2.38 s, 16.9, 2.16 s, 10.2, 3.88 s, 62.3, 11.49, 6.35 s, 101.6, 166.3, 112.1, 6.35 s, 104.1, 144.6, 121.9, 126.6, 133.2, 154.2, 149.4, 125.7, 12.6, 121.9, 141.8, 112.2, 171.8, 160.4, 108.6, 6.75 s, 10.80, 2.51 s, 19.1, 3.88 s, 52.3, 2.38 s, 16.9, 2.16 s, 10.2, 3.88 s, 62.3.</p>	<p>Amorphous powder; IR (KBr) γ_{\max}: 3440, 2925, 2860, 1728, 1661, 1450, 1314, 1255, 1173, 1098, 988 cm⁻¹; HRESIMS: m/z 537.1774 [M-H]⁻ (calcd for 37.1766, C₂₉H₃₀O₁₀); ¹H NMR and ¹³C NMR (500 and 125 MHz, CDCl₃) [46].</p>
<p>PS-990 (47)</p>  <p>Chemical structure of Thielavin A (48) is shown with ¹³C NMR (500 MHz, CDCl₃) and ¹H NMR (125 MHz, CDCl₃) data labels. The structure consists of three aromatic rings linked by ester groups. The left ring has a hydroxyl group and a methoxy group. The middle ring has a methoxy group and a methyl group. The right ring has a methoxy group and a methyl group. The ¹³C NMR data labels are: 166.3, 161.4, 101.6, 6.35 s, 112.1, 104.1, 144.6, 121.9, 126.6, 133.2, 154.2, 149.4, 125.7, 12.6, 121.9, 141.8, 112.2, 171.8, 160.4, 108.6, 6.75 s, 10.80, 2.51 s, 19.1, 3.88 s, 52.3, 2.38 s, 16.9, 2.16 s, 10.2, 3.88 s, 62.3.</p>	<p>Colorless crystalline; mp 183–185 °C; UV (MeOH) λ_{\max}: 215, 257, 323 nm; IR (neat) γ_{\max}: 3452, 2931, 1734, 1716, 1701, 1662, 1576, 1464, 1313, 1151, 1095, 1074 cm⁻¹; EIMS: m/z 179.2230 (calcd for C₃₂H₃₆O₁₀) [66].</p>
<p>Thielavin A (48)</p>  <p>Chemical structure of Thielavin B (49) is shown with ¹³C NMR (500 MHz, CDCl₃) and ¹H NMR (125 MHz, CDCl₃) data labels. The structure consists of three aromatic rings linked by ester groups. The left ring has a hydroxyl group and a methoxy group. The middle ring has a methoxy group and a methyl group. The right ring has a methoxy group and a methyl group. The ¹³C NMR data labels are: 166.3, 161.4, 101.6, 6.35 s, 112.1, 104.1, 144.6, 121.9, 126.6, 133.2, 154.2, 149.4, 125.7, 12.6, 121.9, 141.8, 112.2, 171.8, 160.4, 108.6, 6.75 s, 10.80, 2.51 s, 19.1, 3.88 s, 52.3, 2.38 s, 16.9, 2.16 s, 10.2, 3.88 s, 62.3.</p>	<p>White solid; UV (MeCN) λ_{\max}: 272, 315 nm; HRESIMS: m/z 537.1765 [M-H]⁻ (calcd. for C₂₉H₂₉O₁₀, 539.1772); ¹H and ¹³C NMR (500 and 125 MHz, CDCl₃/CD₃OD, 7:3) [67].</p>
<p>Thielavin B (49)</p>  <p>Chemical structure of Thielavin B Methyl Ester (50) is shown with ¹³C NMR (500 MHz, CDCl₃) and ¹H NMR (125 MHz, CDCl₃) data labels. The structure consists of three aromatic rings linked by ester groups. The left ring has a hydroxyl group and a methoxy group. The middle ring has a methoxy group and a methyl group. The right ring has a methoxy group and a methyl group. The ¹³C NMR data labels are: 166.3, 161.4, 101.6, 6.35 s, 112.1, 104.1, 144.6, 121.9, 126.6, 133.2, 154.2, 149.4, 125.7, 12.6, 121.9, 141.8, 112.2, 171.8, 160.4, 108.6, 6.75 s, 10.80, 2.51 s, 19.1, 3.88 s, 52.3, 2.38 s, 16.9, 2.16 s, 10.2, 3.88 s, 62.3.</p>	<p>Yellowish powder; ESIMS: m/z 589.7 [M+Na]⁺, 565.7 [M-H]⁻; ¹H and ¹³C NMR (400 and 100 MHz, CDCl₃) [68].</p>
<p>Thielavin B Methyl Ester (50)</p>	

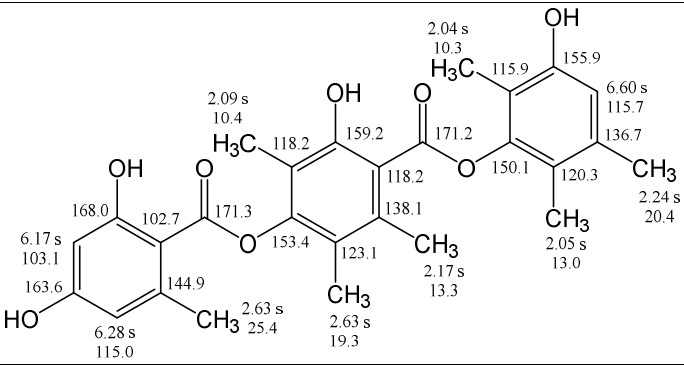
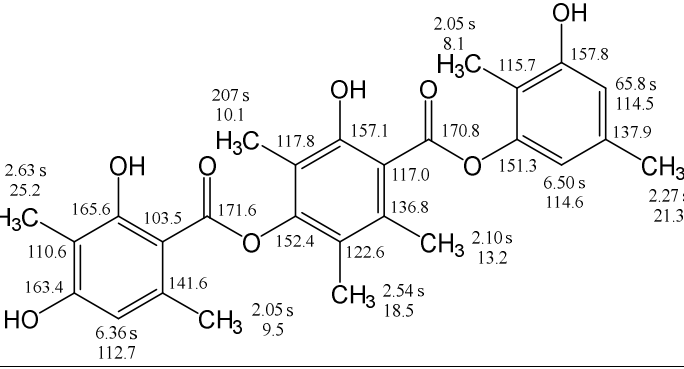
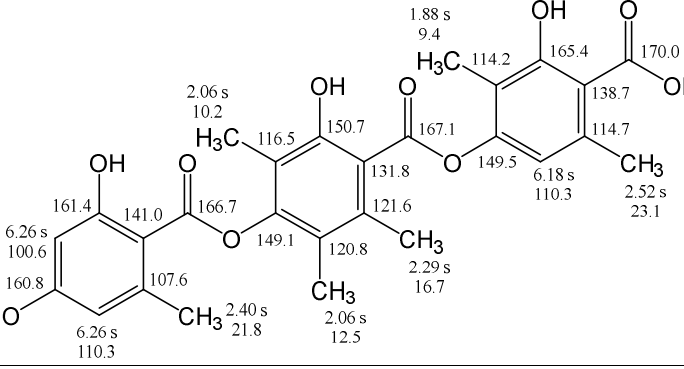
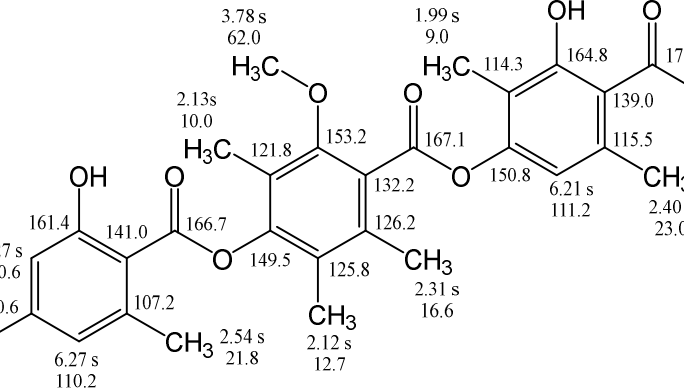
 <p>¹H and ¹³C NMR (500 and 125 MHz, CDCl₃) [48].</p>	<p>APPIHRMS: <i>m/z</i> 581.2378, [M+H]⁺, (calcd for 581.2387, C₃₂H₃₆O₁₀); ¹H and ¹³C NMR (500 and 125 MHz, CDCl₃) [48].</p>
<p>Thielavin C (51)</p> 	
<p>Thielavins D (52)* Colorless powder; mp 235–238°C; SI-MS: <i>m/z</i> 553 (C₃₀H₃₂O₁₀); UV (MeOH) λ_{max} (ε): 269.5 (23,110), 303.3 (7,590) nm; UV (dil HCl-MeOH) λ_{max} (ε): 270 (23,050), 302 (46,417) nm [70].</p>	
<p>Thielavins E (53)* Colorless powder; mp 217–220°C; SI-MS: <i>m/z</i> 553 (C₃₀H₃₂O₁₀); UV (MeOH) λ_{max} (ε): 275.9 (26,236), 305 (5,935) nm; UV (dil HCl-MeOH) λ_{max} (ε): 276.1 (24,679), 314.5 (43,205) nm [70].</p>	
<p>Thielavin F (54)</p>  <p>¹H and ¹³C NMR (C₅D₅N).</p>	<p>UV (MeOH) λ_{max}: 210, 276, 310 nm; IR (KBr) γ_{max}: 3400, 2937, 1743, 1652, 1604, 1461 cm⁻¹; HRF-ABMS: <i>m/z</i> 551.1928 [M-H]⁻ (calcd for C₃₀H₃₂O₁₀, 551.1917); LRFABMS: <i>m/z</i> 553, 535, 389, 357, 343, 193, 179, 165, 151; ¹H and ¹³C NMR (C₅D₅N) [121].</p>

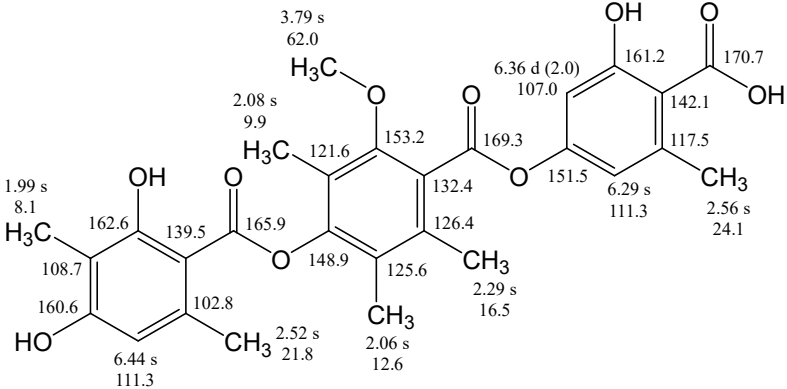
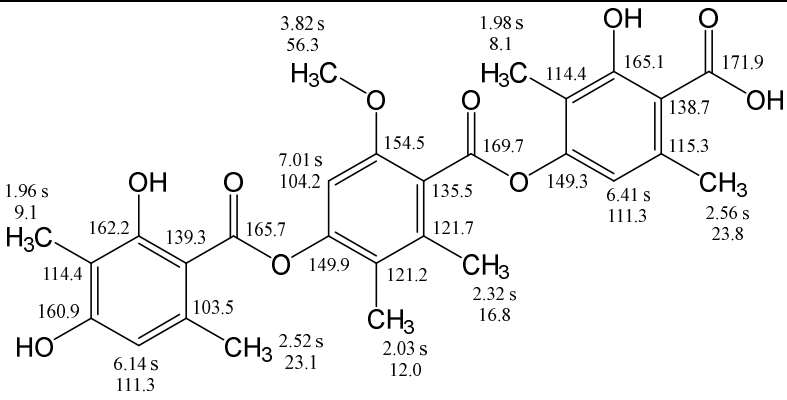
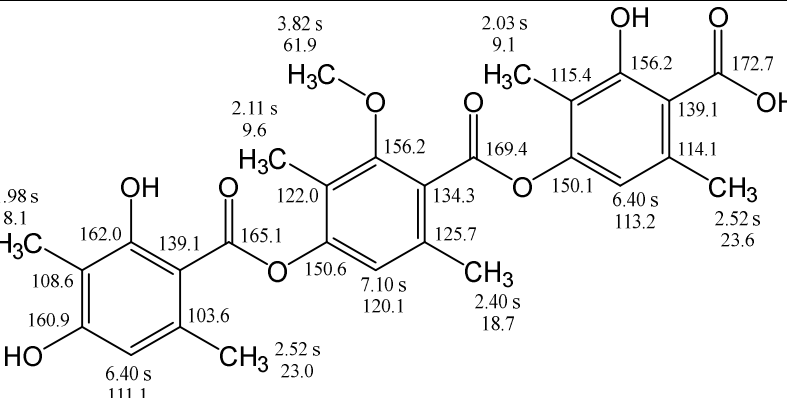
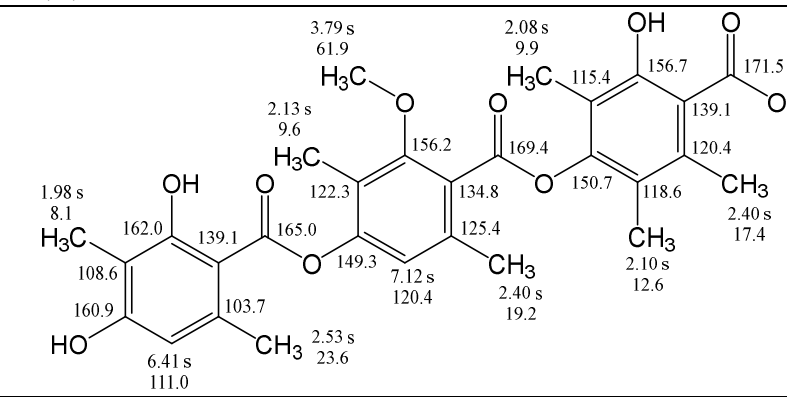
 <p>¹H and ¹³C NMR (400 and 100 MHz, CDCl₃)</p>	<p>Pale yellow amorphous powder; ESIMS: <i>m/z</i> 575.7 [M+Na]⁺, 551.7 [M-H]⁻; ¹H and ¹³C NMR (400 and 100 MHz, CDCl₃) [68].</p>
<p>Thielavin G (55)</p>	
	<p>UV (MeOH) λ_{max} 210, 276, 310 nm; IR (KBr) γ_{max}: 3400, 2941, 1743, 1651, 1419, 1269 cm⁻¹; HRFABMS: <i>m/z</i> 551.1912 [M-H]⁻ (calcd for C₃₀H₃₂O₁₀, 551.1918); LRFABMS: <i>m/z</i> 553, 535, 461, 389, 343, 329, 193, 179, 165; ¹H and ¹³C NMR (C₅D₅N) [121].</p>
<p>Thielavin H (56)</p>	
	<p>UV (MeOH) λ_{max}: 215, 267, 308 nm; IR (KBr) γ_{max}: 3400, 2929, 1660, 1446, 1315, 1255 cm⁻¹; HRFABMS: <i>m/z</i> 523.1601 [M-H]⁻ (calcd for C₂₈H₃₀O₁₀, 523.1604); LRFABMS: <i>m/z</i> 525, 375, 329, 179, 151; ¹H and ¹³C NMR (C₅D₅N) [121].</p>
<p>Thielavin I (57)</p>	
	<p>UV (MeOH) λ_{max}: 218, 275, 310 nm; IR (KBr) γ_{max}: 3398, 2931, 1660, 1622, 1417, 1307 cm⁻¹; HRFABMS: <i>m/z</i> 493.1862 [M-H]⁻ (calcd for C₂₈H₃₀O₈, 493.1862); LRFABMS: <i>m/z</i> 495, 343, 331, 231, 179, 165; ¹H and ¹³C NMR (C₅D₅N) [121].</p>
<p>Thielavin J (58)</p>	

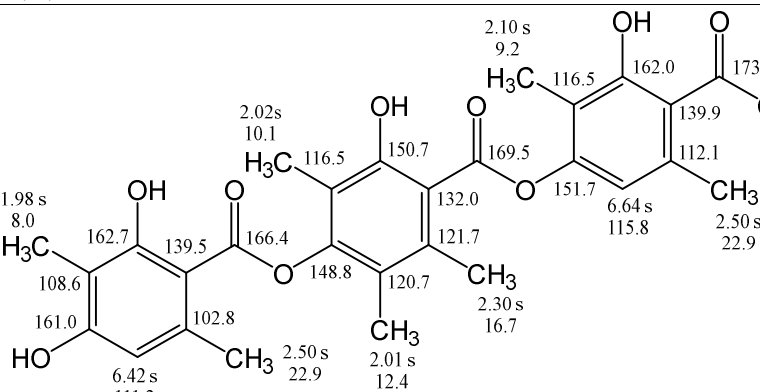
<p>¹H and ¹³C NMR (C₅D₅N)</p>	<p>UV (MeOH) λ_{max}: 214, 250, 275, 306 nm; IR (KBr) γ_{max}: 3400, 2933, 1654, 1622, 1456, 1265 cm⁻¹; HRFABMS: m/z 537.1750 [M-H]⁻ (calcd for C₂₉H₃₀O₁₀, 537.1760); LRFABMS: m/z 539, 375, 357, 343, 193, 165; ¹H and ¹³C NMR (C₅D₅N) [121].</p>
<p>¹H and ¹³C NMR (500 and 125 MHz, CDCl₃/CD₃OD, 7:3)</p>	<p>White solid; UV (MeOH) λ_{max}: 272, 308; IR γ_{max}: 3408, 2942, 1725, 1653, 1605 cm⁻¹; HRESIMS: m/z 539.19026 [M+H]⁺ (calcd. for C₂₉H₃₁O₁₀, 539.1911); ¹H and ¹³C NMR (500 and 125 MHz, CDCl₃/CD₃OD, 7:3) [67].</p>
Thielavin K (59)	
<p>¹H and ¹³C NMR (C₅D₅N)</p>	<p>UV (MeOH) λ_{max}: 215, 250, 274, 307 nm; IR (KBr) γ_{max}: 3400, 2935, 1726, 1620, 1417, 1265 cm⁻¹; HRFABM: m/z 551.1901 [M-H]⁻ (calcd for C₂₉H₃₀O₁₀, 551.1918); LRFABMS: m/z 553, 509, 389, 357, 193, 165; ¹H and ¹³C NMR (C₅D₅N) [121].</p>
<p>¹H and ¹³C NMR (500 and 125 MHz, CDCl₃/CD₃OD, 7:3)</p>	<p>White solid; UV (MeOH) λ_{max}: 271, 310 nm; IR (Reflectance) γ_{max}: 3405, 2932, 1728, 1653, 1618 cm⁻¹; HRESIMS: m/z 553.2060 [M+H]⁺ (calcd. for C₂₉H₃₁O₁₀, 553.2068); ¹H and ¹³C NMR (500 and 125 MHz, CDCl₃/CD₃OD, 7:3) [67].</p>
Thielavin L (60)	

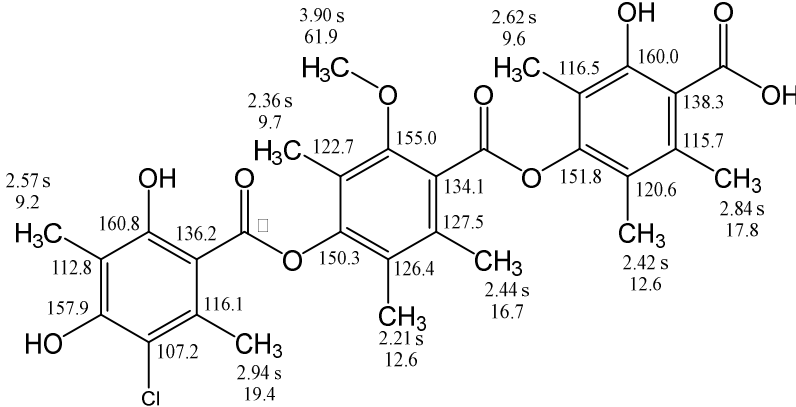
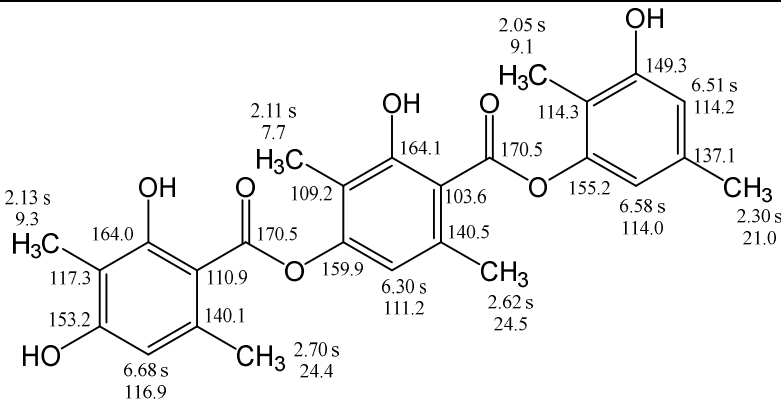
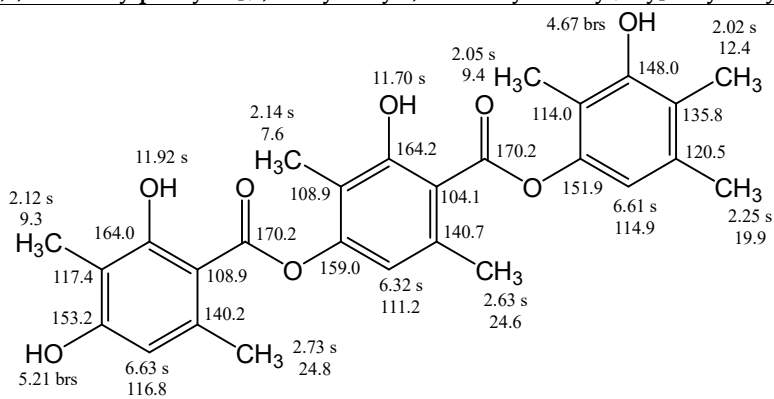
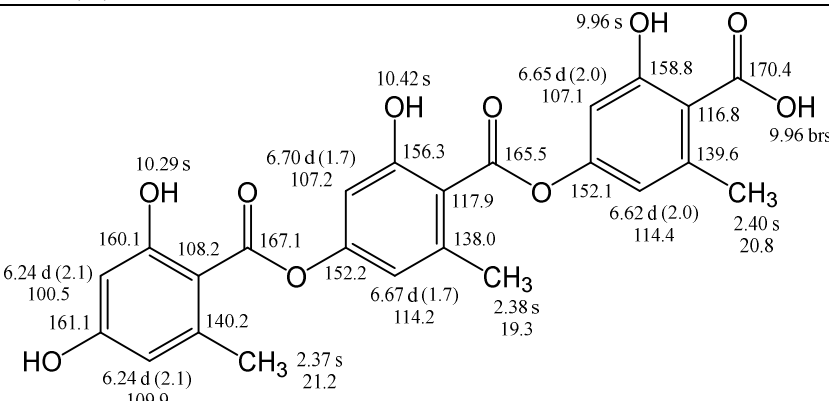
<p>Chemical structure of Thielavin M (61) is shown with ¹³C NMR chemical shifts and peak assignments. The structure is a complex polycyclic molecule with multiple methoxy and methyl groups. The shifts are: 2.38 s, 8.7, 110.3, 165.0, 163.2, 6.64 s, 112.4, 103.1, 170.1, 2.09 s, 10.3, 122.7, 154.8, 127.1, 133.9, 126.4, 1.94 s, 13.1, 2.23 s, 17.3, 2.39 s, 10.7, 117.5, 155.1, 166.5, 151.2, 121.5, 118.7, 135.3, 170.3, 4.83 dd (11.1, 4.3), 4.72 dd (11.1, 5.9), 4.40, m, 4.03 d (5.9), 2.26 s, 17.9, 2.12 s, 13.1.</p>	<p>UV (MeOH) λ_{max}: 214, 275, 310 nm; IR (KBr) γ_{max}: 3398, 2933, 1733, 1654, 1606, 1458 cm⁻¹; HRFABMS: <i>m</i>: 625.2280 [M-H]⁻ (calcd for C₃₃H₃₈O₁₂, 625.2285); LRFABMS: <i>m/z</i> 627, 535, 463, 357, 193, 165; ¹H and ¹³C NMR (C₅D₅N) [121].</p>
<p>Thielavin M (61)</p> <p>Chemical structure of Thielavin N (62) is shown with ¹³C NMR chemical shifts and peak assignments. The structure is a complex polycyclic molecule with multiple methoxy and methyl groups. The shifts are: 3.71 s, 62.3, 2.14 s, 10.4, 122.7, 154.9, 127.2, 133.9, 126.4, 2.00 s, 13.1, 2.25 s, 17.3, 2.44 s, 10.4, 116.6, 159.7, 175.6, 115.1, 138.1, 120.7, 2.62 s, 18.7, 2.23 s, 13.4, 166.5, 151.9, 149.4, 169.6, 104.9, 166.1, 6.71 d (2.3), 8102.2, 165.0, 6.64 d (2.3), 113.2, 144.0, 2.55 s, 24.4.</p>	<p>UV (MeOH) λ_{max}: 214, 275, 310 nm; IR (KBr) γ_{max}: 3400, 2929, 1733, 1652, 1624, 1458 cm⁻¹; HRFABMS: <i>m/z</i> 537.1766 [M-H]⁺ (calcd for C₂₉H₃₀O₁₀, 537.1760); LRFAB-MS: <i>m/z</i> 539, 389, 343, 193, 151; ¹H and ¹³C NMR (C₅D₅N) [121].</p>
<p>Thielavin N (62)</p> <p>Chemical structure of Thielavin O (63) is shown with ¹³C NMR chemical shifts and peak assignments. The structure is a complex polycyclic molecule with multiple methoxy and methyl groups. The shifts are: 3.67 s, 56.1, 2.45 s, 10.7, 116.7, 160.1, 166.5, 151.2, 120.8, 138.3, 2.65 s, 18.9, 2.22 s, 13.6, 6.94 s, 104.9, 156.2, 171.2, 112.9, 137.6, 122.5, 2.29 s, 17.7, 2.93 s, 12.6, 2.37 s, 8.9, 110.3, 164.9, 103.8, 171.2, 140.9, 163.1, 6.62 s, 112.4, 2.55 s, 24.9.</p>	<p>UV (MeOH) λ_{max}: 214, 253, 275, 318 nm; IR (KBr) γ_{max}: 3421, 2933, 1743, 1654, 1604, 1419 cm⁻¹; HRFABMS: <i>m/z</i> 537.1773 [M-H]⁺ (calcd for C₂₉H₃₀O₁₀, 537.1761); LRFAB-MS: <i>m/z</i> 539, 461, 318, 179, 165; ¹H and ¹³C NMR (C₅D₅N) [121].</p>
<p>Thielavin O (63)</p> <p>Chemical structure of Thielavin P (64) is shown with ¹³C NMR chemical shifts and peak assignments. The structure is a complex polycyclic molecule with multiple methoxy and methyl groups. The shifts are: 3.72 s, 62.5, 2.17 s, 10.6, 122.9, 155.1, 127.4, 134.1, 126.7, 2.26 s, 17.5, 2.02 s, 13.4, 2.61 s, 19.6, 2.42 s, 10.1, 110.4, 161.2, 106.0, 170.9, 150.7, 160.8, 118.2, 137.7, 118.2, 2.30 s, 13.2, 2.24 s, 13.6, 152.1, 120.9, 138.3, 115.3, 159.9, 175.8, 2.63 s, 18.9, 2.24 s, 13.6, 116.9, 159.9, 175.8, 115.3, 138.3, 120.9, 152.1, 166.7, 10.7, 2.45 s, 10.7.</p>	<p>UV (MeOH) λ_{max}: 214, 252, 275, 318 nm; IR (KBr) γ_{max}: 3421, 2929, 1733, 1652, 1651, 1610, 1458 cm⁻¹; HRFABMS: <i>m/z</i> 565.2078 [M-H]⁺ (calcd for C₃₁H₃₄O₁₀, 565.2073); LRFABMS: <i>m/z</i> 539, 389, 343, 193, 151; ¹H and ¹³C NMR (C₅D₅N) [121].</p>

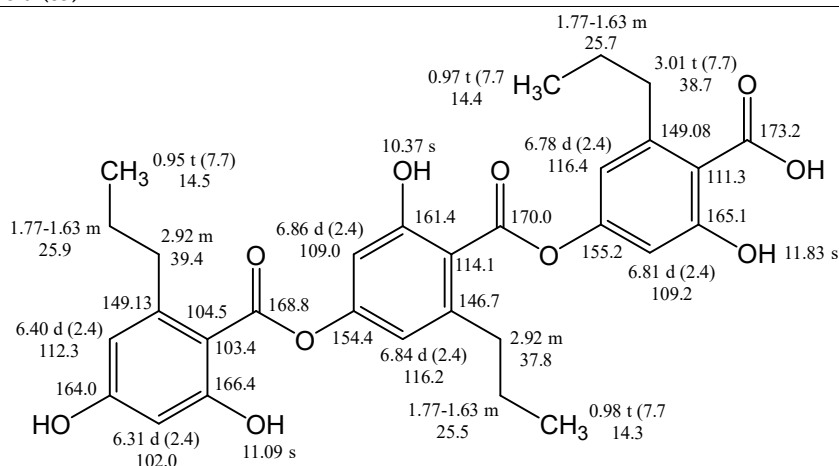
<p>Thielavin P (64)</p> 	<p>UV (MeOH) λ_{\max}: 216, 258, 273, 318 nm; IR (KBr) γ_{\max}: 3400, 2927, 1652, 1612, 1456, 1419 cm^{-1}; HRFABMS: m/z 551.1929 $[\text{M-H}]^-$ (calcd for $\text{C}_{30}\text{H}_{32}\text{O}_{10}$, 551.1918); LRFABMS: m/z 553, 344, 193, 179; ^1H and ^{13}C NMR ($\text{C}_5\text{D}_5\text{N}$) [121].</p>
<p>Thielavin Q (65)</p> 	<p>White amorphous powder; $[\alpha]_D^{25} +6.3$ (c 0.1, MeOH); UV (MeOH) λ_{\max} (log ϵ): 288 (3.31) nm; IR (KBr) γ_{\max}: 3426, 1734, 1666, 1402, 1376, 1172, 1075 cm^{-1}; HRESIMS: m/z 565.2075 $[\text{M-H}]^-$ (calcd for $\text{C}_{31}\text{H}_{34}\text{O}_{10}$, 565.2074); ^1H and ^{13}C NMR (900 and 225 CDCl_3) [68].</p>
<p>Thielavin S (66)</p> 	<p>White powder; UV (MeOH) λ_{\max}: 222, 272, 313 nm; HRESIMS: m/z 451.1394 $[\text{M-H}]^-$ (calcd for $\text{C}_{25}\text{H}_{23}\text{O}_8$, 451.1393); ^1H NMR and ^{13}C NMR (500 and 125 MHz, CD_3OD) [19].</p>
<p>Thielavin T (67)</p> 	<p>White powder; UV (MeOH) λ_{\max}: 225, 272, 308 nm; HRESIMS: m/z 465.1544 $[\text{M-H}]^-$ (calcd for $\text{C}_{26}\text{H}_{25}\text{O}_8$, 465.1549); ^1H NMR and ^{13}C NMR (400 and 100 MHz, CD_3OD) [19].</p>
<p>Thielavin U (68)</p>	

 <p>¹³C NMR (200 MHz, CD₃OD): 168.0, 163.6, 103.1, 102.7, 144.9, 171.3, 153.4, 118.2, 159.2, 118.2, 138.1, 123.1, 123.1, 2.63 s, 25.4, 2.63 s, 19.3, 2.17 s, 13.3, 2.04 s, 10.3, 115.9, 155.9, 150.1, 120.3, 136.7, 6.60 s, 115.7, 2.24 s, 20.4, 2.05 s, 13.0.</p> <p>¹H NMR (400 MHz, CD₃OD): 6.17 s, 6.28 s, 115.0.</p>	<p>White powder; UV (MeOH) λ_{max}: 218, 272, 310 nm; RESIMS: m/z 479.1707 [M-H]⁻ (calcd for C₂₇H₂₇O₈, 479.1706); ¹H NMR and ¹³C NMR (800 and 200 MHz, CD₃OD) [19].</p>
<p>Thielavin V (69)</p>  <p>¹³C NMR (200 MHz, CD₃OD): 2.63 s, 25.2, 110.6, 163.4, 165.6, 103.5, 171.6, 152.4, 117.8, 157.1, 117.0, 136.8, 122.6, 2.54 s, 18.5, 2.05 s, 9.5, 2.10 s, 13.2, 2.05 s, 8.1, 115.7, 157.8, 170.8, 151.3, 137.9, 6.50 s, 114.6, 6.58 s, 114.5, 2.27 s, 21.3.</p> <p>¹H NMR (400 MHz, CD₃OD): 2.63 s, 25.2, 6.36 s, 112.7, 2.05 s, 9.5.</p>	<p>White powder; UV (MeOH) λ_{max}: 224, 276, 313 nm; HRESIMS: m/z 479.1708 [M-H]⁻ (calcd for C₂₇H₂₇O₈, 479.1706); ¹H NMR and ¹³C NMR (400 and 100 MHz, CD₃OD) [19].</p>
<p>Thielavin W (70)</p>  <p>¹³C NMR (500 MHz, DMSO-<i>d</i>₆): 161.4, 160.8, 100.6, 141.0, 107.6, 166.7, 149.1, 116.5, 150.7, 131.8, 121.6, 120.8, 2.40 s, 21.8, 2.06 s, 12.5, 2.29 s, 16.7, 1.88 s, 9.4, 114.2, 165.4, 170.0, 138.7, 114.7, 6.18 s, 110.3, 2.52 s, 23.1.</p> <p>¹H NMR (500 MHz, DMSO-<i>d</i>₆): 6.26 s, 110.3, 2.06 s, 10.2, 2.06 s, 10.2.</p>	<p>White powder, UV (CAN) λ_{max}: 218.1, 267.8, 304.2 nm; HRESIMS: m/z 511.1604 [M+H]⁺ (calcd. for C₂₇H₂₇O₁₀, 511.1599); ¹H NMR and ¹³C NMR (500 and 125 MHz, DMSO-<i>d</i>₆) [52].</p>
<p>Thielavin X (71)</p>  <p>¹³C NMR (500 MHz, DMSO-<i>d</i>₆): 161.4, 160.6, 100.6, 141.0, 107.2, 166.7, 149.5, 121.8, 153.2, 132.2, 126.2, 125.8, 2.54 s, 21.8, 2.12 s, 12.7, 2.31 s, 16.6, 3.78 s, 62.0, 2.13 s, 10.0, 1.99 s, 9.0, 114.3, 164.8, 170.7, 139.0, 115.5, 6.21 s, 111.2, 2.40 s, 23.0.</p> <p>¹H NMR (500 MHz, DMSO-<i>d</i>₆): 6.27 s, 110.2, 2.27 s, 100.6, 6.27 s, 110.2.</p>	<p>White powder, UV (CAN) λ_{max}: 218.1, 267.8, 306.5 nm; HRESIMS: m/z 525.1727 [M+H]⁺ (calcd for C₂₈H₂₉O₁₀, 525.1755); ¹H NMR and ¹³C NMR (500 and 125 MHz, DMSO-<i>d</i>₆) [52].</p>
<p>Thielavin Y (72)</p>	

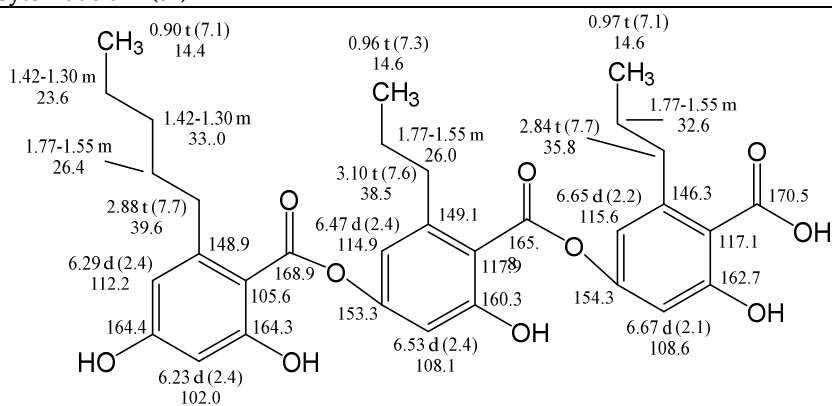
 <p>¹³C NMR (500 MHz, DMSO-<i>d</i>₆): 162.6, 139.5, 165.9, 121.6, 153.2, 132.4, 126.4, 125.6, 148.9, 102.8, 108.7, 160.6, 111.3, 6.44 s, 2.52 s, 2.06 s, 2.29 s, 16.5, 12.6, 2.08 s, 9.9, 3.79 s, 62.0, 107.0, 151.5, 111.3, 6.29 s, 117.5, 142.1, 161.2, 170.7, 2.56 s, 24.1.</p>	<p>White powder; UV (CAN) λ_{max}: 218.1, 276.1, 304.7 nm; HRESIMS: m/z 525.1765 [M+H]⁺ (calcd. for C₂₈H₂₉O₁₀, 525.1755); ¹H NMR and ¹³C NMR (500 and 125 MHz, DMSO-<i>d</i>₆) [52].</p>
<p>Thielavin Z (73)</p>  <p>¹³C NMR (500 MHz, DMSO-<i>d</i>₆): 162.2, 139.3, 165.7, 154.5, 135.5, 121.7, 121.2, 103.5, 160.9, 114.4, 111.3, 6.14 s, 2.52 s, 2.03 s, 2.32 s, 16.8, 7.01 s, 104.2, 149.9, 121.7, 154.5, 169.7, 114.4, 165.1, 138.7, 115.3, 6.41 s, 111.3, 2.56 s, 23.8, 1.98 s, 8.1, 3.82 s, 56.3, 1.96 s, 9.1, 114.4, 160.9, 103.5, 139.3, 165.7, 154.5, 135.5, 121.7, 121.2, 103.5, 160.9, 114.4, 111.3, 6.14 s, 2.52 s, 2.03 s, 2.32 s, 16.8, 7.01 s, 104.2, 149.9, 121.7, 154.5, 169.7, 114.4, 165.1, 138.7, 115.3, 6.41 s, 111.3, 2.56 s, 23.8, 1.98 s, 8.1, 3.82 s, 56.3.</p>	<p>White powder; UV (CAN) λ_{max}: 218.1, 276.1, 306.5 nm; HRESIMS: m/z 525.1757 [M+H]⁺ (calcd for C₂₈H₂₉O₁₀, 525.1755); ¹H NMR and ¹³C NMR (500 and 125 MHz, DMSO-<i>d</i>₆) [52].</p>
<p>Thielavin Z1 (74)</p>  <p>¹³C NMR (500 MHz, DMSO-<i>d</i>₆): 162.0, 139.1, 165.1, 156.2, 134.3, 125.7, 120.1, 103.6, 160.9, 108.6, 111.1, 6.40 s, 2.52 s, 2.40 s, 18.7, 7.10 s, 120.1, 150.6, 122.0, 156.2, 169.4, 115.4, 156.2, 139.1, 114.1, 6.40 s, 113.2, 2.52 s, 23.6, 2.03 s, 9.1, 3.82 s, 61.9, 2.11 s, 9.6, 1.98 s, 8.1, 162.0, 139.1, 165.1, 156.2, 134.3, 125.7, 120.1, 103.6, 160.9, 108.6, 111.1, 6.40 s, 2.52 s, 2.40 s, 18.7, 7.10 s, 120.1, 150.6, 122.0, 156.2, 169.4, 115.4, 156.2, 139.1, 114.1, 6.40 s, 113.2, 2.52 s, 23.6, 2.03 s, 9.1, 3.82 s, 61.9, 2.11 s, 9.6.</p>	<p>White powder; UV (CAN) λ_{max}: 218.1, 276.1, 306.9 nm; ¹H NMR and ¹³C NMR (500 and 125 MHz, DMSO-<i>d</i>₆); HRESIMS: m/z 525.1747 [M+H]⁺ (calcd for C₂₈H₂₉O₁₀, 525.1755) [52].</p>
<p>Thielavin Z2 (75)</p>  <p>¹³C NMR (500 MHz, DMSO-<i>d</i>₆): 162.0, 139.1, 165.0, 156.2, 134.8, 125.4, 120.4, 103.7, 160.9, 108.6, 111.0, 6.41 s, 2.53 s, 2.40 s, 19.2, 7.12 s, 120.4, 149.3, 122.3, 156.2, 169.4, 115.4, 156.7, 139.1, 120.4, 118.6, 2.10 s, 12.6, 2.08 s, 9.9, 3.79 s, 61.9, 2.13 s, 9.6, 1.98 s, 8.1, 162.0, 139.1, 165.0, 156.2, 134.8, 125.4, 120.4, 103.7, 160.9, 108.6, 111.0, 6.41 s, 2.53 s, 2.40 s, 19.2, 7.12 s, 120.4, 149.3, 122.3, 156.2, 169.4, 115.4, 156.7, 139.1, 120.4, 118.6, 2.10 s, 12.6, 2.08 s, 9.9, 3.79 s, 61.9, 2.13 s, 9.6.</p>	<p>White powder, UV ACN λ_{max}: 218.1, 267.8, 305.2 nm; ¹H NMR and ¹³C NMR (500 and 125 MHz, DMSO-<i>d</i>₆); HRESIMS m/z: 539.1916 [M+H]⁺ (calcd. for C₂₉H₃₁O₁₀, 539.1912); ISCID: 507.1, 375.2, 343.1, 179.1, 165.1 [52].</p>

<p>Thielavin Z₃ (76)</p>  <p>Chemical structure of Thielavin Z₃ (76) is shown with ¹³C NMR and ¹H NMR data. The structure is a dimeric flavonoid with two central carbonyl groups. The left ring has a methyl group at C-2, a hydroxyl group at C-3, and a methoxy group at C-4. The right ring has a methyl group at C-2, a hydroxyl group at C-3, and a methoxy group at C-4. The central carbonyl groups are at C-5 and C-5'. The ¹³C NMR data (ppm) are: 162.7, 139.5, 166.4, 148.8, 150.7, 132.0, 121.7, 120.7, 116.5, 115.8, 112.1, 139.9, 162.0, 173.0, 161.0, 108.6, 102.8, 111.2, 101.0, 100.7, 100.5, 100.3, 100.1, 100.0, 99.9, 99.8, 99.7, 99.6, 99.5, 99.4, 99.3, 99.2, 99.1, 99.0, 98.9, 98.8, 98.7, 98.6, 98.5, 98.4, 98.3, 98.2, 98.1, 98.0, 97.9, 97.8, 97.7, 97.6, 97.5, 97.4, 97.3, 97.2, 97.1, 97.0, 96.9, 96.8, 96.7, 96.6, 96.5, 96.4, 96.3, 96.2, 96.1, 96.0, 95.9, 95.8, 95.7, 95.6, 95.5, 95.4, 95.3, 95.2, 95.1, 95.0, 94.9, 94.8, 94.7, 94.6, 94.5, 94.4, 94.3, 94.2, 94.1, 94.0, 93.9, 93.8, 93.7, 93.6, 93.5, 93.4, 93.3, 93.2, 93.1, 93.0, 92.9, 92.8, 92.7, 92.6, 92.5, 92.4, 92.3, 92.2, 92.1, 92.0, 91.9, 91.8, 91.7, 91.6, 91.5, 91.4, 91.3, 91.2, 91.1, 91.0, 90.9, 90.8, 90.7, 90.6, 90.5, 90.4, 90.3, 90.2, 90.1, 90.0, 89.9, 89.8, 89.7, 89.6, 89.5, 89.4, 89.3, 89.2, 89.1, 89.0, 88.9, 88.8, 88.7, 88.6, 88.5, 88.4, 88.3, 88.2, 88.1, 88.0, 87.9, 87.8, 87.7, 87.6, 87.5, 87.4, 87.3, 87.2, 87.1, 87.0, 86.9, 86.8, 86.7, 86.6, 86.5, 86.4, 86.3, 86.2, 86.1, 86.0, 85.9, 85.8, 85.7, 85.6, 85.5, 85.4, 85.3, 85.2, 85.1, 85.0, 84.9, 84.8, 84.7, 84.6, 84.5, 84.4, 84.3, 84.2, 84.1, 84.0, 83.9, 83.8, 83.7, 83.6, 83.5, 83.4, 83.3, 83.2, 83.1, 83.0, 82.9, 82.8, 82.7, 82.6, 82.5, 82.4, 82.3, 82.2, 82.1, 82.0, 81.9, 81.8, 81.7, 81.6, 81.5, 81.4, 81.3, 81.2, 81.1, 81.0, 80.9, 80.8, 80.7, 80.6, 80.5, 80.4, 80.3, 80.2, 80.1, 80.0, 79.9, 79.8, 79.7, 79.6, 79.5, 79.4, 79.3, 79.2, 79.1, 79.0, 78.9, 78.8, 78.7, 78.6, 78.5, 78.4, 78.3, 78.2, 78.1, 78.0, 77.9, 77.8, 77.7, 77.6, 77.5, 77.4, 77.3, 77.2, 77.1, 77.0, 76.9, 76.8, 76.7, 76.6, 76.5, 76.4, 76.3, 76.2, 76.1, 76.0, 75.9, 75.8, 75.7, 75.6, 75.5, 75.4, 75.3, 75.2, 75.1, 75.0, 74.9, 74.8, 74.7, 74.6, 74.5, 74.4, 74.3, 74.2, 74.1, 74.0, 73.9, 73.8, 73.7, 73.6, 73.5, 73.4, 73.3, 73.2, 73.1, 73.0, 72.9, 72.8, 72.7, 72.6, 72.5, 72.4, 72.3, 72.2, 72.1, 72.0, 71.9, 71.8, 71.7, 71.6, 71.5, 71.4, 71.3, 71.2, 71.1, 71.0, 70.9, 70.8, 70.7, 70.6, 70.5, 70.4, 70.3, 70.2, 70.1, 70.0, 69.9, 69.8, 69.7, 69.6, 69.5, 69.4, 69.3, 69.2, 69.1, 69.0, 68.9, 68.8, 68.7, 68.6, 68.5, 68.4, 68.3, 68.2, 68.1, 68.0, 67.9, 67.8, 67.7, 67.6, 67.5, 67.4, 67.3, 67.2, 67.1, 67.0, 66.9, 66.8, 66.7, 66.6, 66.5, 66.4, 66.3, 66.2, 66.1, 66.0, 65.9, 65.8, 65.7, 65.6, 65.5, 65.4, 65.3, 65.2, 65.1, 65.0, 64.9, 64.8, 64.7, 64.6, 64.5, 64.4, 64.3, 64.2, 64.1, 64.0, 63.9, 63.8, 63.7, 63.6, 63.5, 63.4, 63.3, 63.2, 63.1, 63.0, 62.9, 62.8, 62.7, 62.6, 62.5, 62.4, 62.3, 62.2, 62.1, 62.0, 61.9, 61.8, 61.7, 61.6, 61.5, 61.4, 61.3, 61.2, 61.1, 61.0, 60.9, 60.8, 60.7, 60.6, 60.5, 60.4, 60.3, 60.2, 60.1, 60.0, 59.9, 59.8, 59.7, 59.6, 59.5, 59.4, 59.3, 59.2, 59.1, 59.0, 58.9, 58.8, 58.7, 58.6, 58.5, 58.4, 58.3, 58.2, 58.1, 58.0, 57.9, 57.8, 57.7, 57.6, 57.5, 57.4, 57.3, 57.2, 57.1, 57.0, 56.9, 56.8, 56.7, 56.6, 56.5, 56.4, 56.3, 56.2, 56.1, 56.0, 55.9, 55.8, 55.7, 55.6, 55.5, 55.4, 55.3, 55.2, 55.1, 55.0, 54.9, 54.8, 54.7, 54.6, 54.5, 54.4, 54.3, 54.2, 54.1, 54.0, 53.9, 53.8, 53.7, 53.6, 53.5, 53.4, 53.3, 53.2, 53.1, 53.0, 52.9, 52.8, 52.7, 52.6, 52.5, 52.4, 52.3, 52.2, 52.1, 52.0, 51.9, 51.8, 51.7, 51.6, 51.5, 51.4, 51.3, 51.2, 51.1, 51.0, 50.9, 50.8, 50.7, 50.6, 50.5, 50.4, 50.3, 50.2, 50.1, 50.0, 49.9, 49.8, 49.7, 49.6, 49.5, 49.4, 49.3, 49.2, 49.1, 49.0, 48.9, 48.8, 48.7, 48.6, 48.5, 48.4, 48.3, 48.2, 48.1, 48.0, 47.9, 47.8, 47.7, 47.6, 47.5, 47.4, 47.3, 47.2, 47.1, 47.0, 46.9, 46.8, 46.7, 46.6, 46.5, 46.4, 46.3, 46.2, 46.1, 46.0, 45.9, 45.8, 45.7, 45.6, 45.5, 45.4, 45.3, 45.2, 45.1, 45.0, 44.9, 44.8, 44.7, 44.6, 44.5, 44.4, 44.3, 44.2, 44.1, 44.0, 43.9, 43.8, 43.7, 43.6, 43.5, 43.4, 43.3, 43.2, 43.1, 43.0, 42.9, 42.8, 42.7, 42.6, 42.5, 42.4, 42.3, 42.2, 42.1, 42.0, 41.9, 41.8, 41.7, 41.6, 41.5, 41.4, 41.3, 41.2, 41.1, 41.0, 40.9, 40.8, 40.7, 40.6, 40.5, 40.4, 40.3, 40.2, 40.1, 40.0, 39.9, 39.8, 39.7, 39.6, 39.5, 39.4, 39.3, 39.2, 39.1, 39.0, 3</p>
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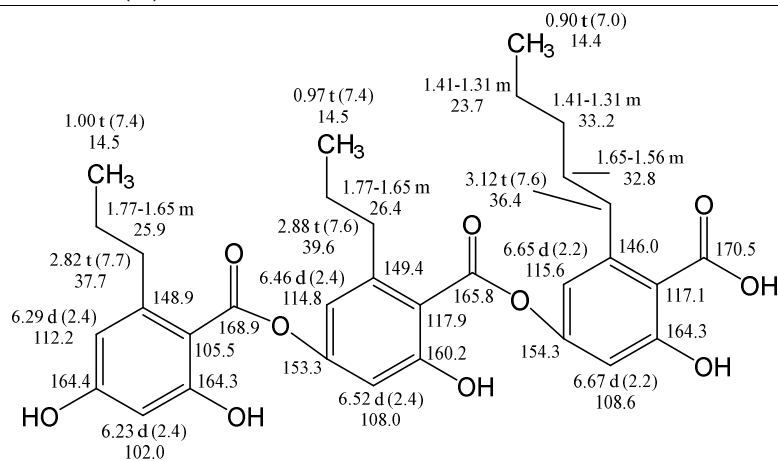
	White powder; UV (CAN) λ_{max} : 215.8, 276.1, 307.0 nm; HRESIMS: m/z 587.1719/589.1646 $[M+H]^+$ 3:1 (calcd for $C_{30}H_{32}ClO_{10}$, 587.1679); 1H NMR and ^{13}C NMR (500 and 125 MHz, $DMSO-d_6$) [52].
3-Hydroxy-2,5-dimethylphenyl 4-[(2,4-dihydroxy-3,6-dimethylbenzoyl)oxy]-2-hydroxy-3,6-dimethylbenzoate (80)	
	UV (MeOH) λ_{max} : 226 (4.39), 278 (4.13), 310 (3.81); IR (KBr) γ_{max} : 3419, 2925, 1664, 1623, 1583, 1147, 1257 cm^{-1} ; ESIMS: m/z 465 $[M-H]^-$, 301 (25), 163 (100); ESITOFMS: m/z 465.1522 $[M-H]^-$ (calcd for $C_{26}H_{25}O_8$, 465.1548); 1H and ^{13}C NMR (400 and 100 MHz, $CDCl_3$ and CD_3OD) [49].
3-Hydroxy-2,4,5-trimethylphenyl 4-[(2,4-dihydroxy-3,6-dimethylbenzoyl)oxy]-2-hydroxy-3,6-dimethylbenzoate (81)	
	White amorphous powder; UV λ_{max} : 226 (4.37), 278 (4.12), 310 (3.82) nm; IR (KBr) γ_{max} : 3421, 2931, 1706, 1654, 1623, 1585, 1143, 1257 cm^{-1} ; ESIMS: m/z 479 $[M-H]^-$, 315 (20), 163 (100); ESI-TOFMS: m/z 479.1674 $[M-H]^-$ (calcd for $C_{27}H_{27}O_8$, 479.1705); 1H and ^{13}C NMR (400 and 100 MHz, $CDCl_3$ and CD_3O) [49].
Gyrophoric acid (82)	
	Colorless materials; 1H and ^{13}C NMR (500 and 125 MHz, $DMSO-d_6$) [71,72].

Trivarc acid (83)

White amorphous powder; ESIMS: *m/z* 551 [M-H]⁻; ¹H NMR and ¹³C NMR (500 and 125 MHz, acetone-*d*₆) [25].

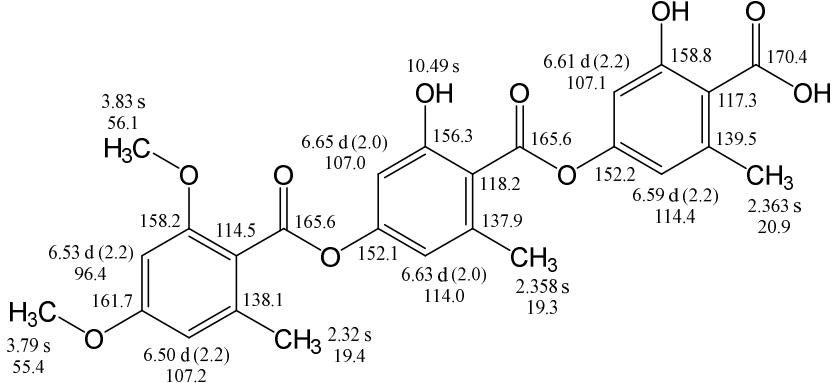
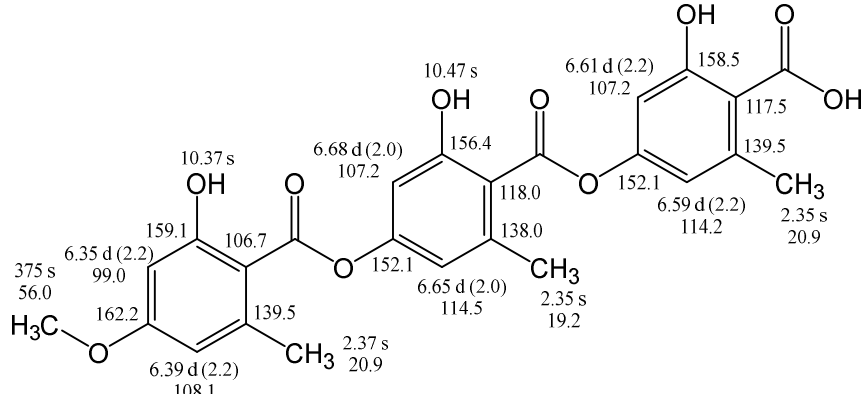
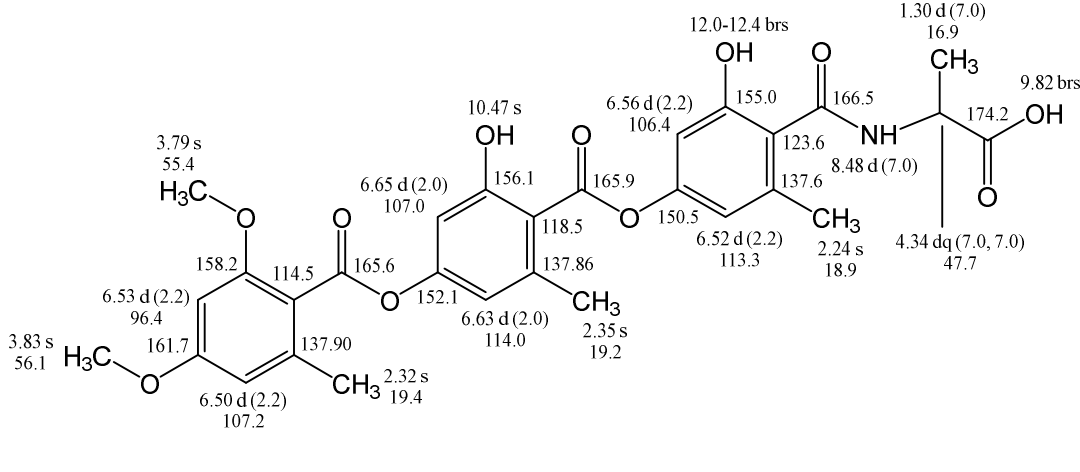
Cytionic acid A (84)

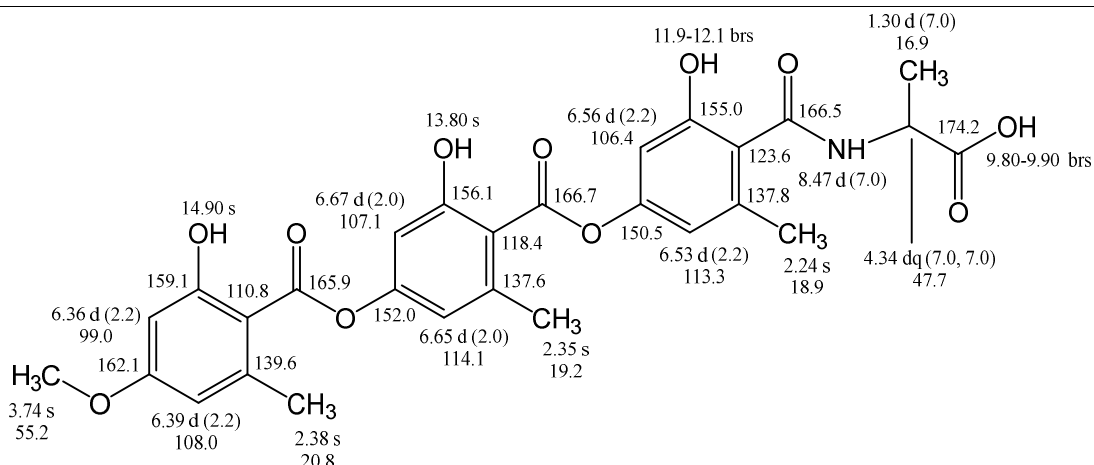
White powder; UV (MeOH) λ_{\max} (log ϵ): 211 (4.7), 253 (4.1), 284 (3.9) nm; IR (KBr) γ_{\max} : 3450, 1766, 1762, 1651, 1575, 1557, 1538, 1135, 1035, 824 cm⁻¹; (-) ESIMS: *m/z* 579 [M-H]⁻ (2.2%), 195 (100%), 177 (54.1%), 401 (42.2%), 151 (32.4%), 205 (26.8%), 133 (14.6%), 223 (15.5%), 373 (9.2%); (-) ESIMS: *m/z* 579: 579, 401, 373, 223, 195; (-) ESIMS: *m/z* 401: 195, 223, 401; ESIMS-MS: *m/z* 373, 195, 373; (-) ESIMS: *m/z* 223, 223, 179; (-) ESIMS: *m/zr* 195, 151, 195; (-) APCIMS: *m/z* 151 (100%), 195 (91.5%), 179 (48.3%), 137 (31.3%), 177 (22.5%), 223 (16.2%), 205 (18.6%); (-) HRMS: *m/z* 579.2214 [M-H]⁻ (calcd for C₃₂H₃₅O₁₀, 579.2227) (¹H and ¹³C NMR (400 and 100 MHz, CD₃OD) [73].

Cytionic acid B (85)

White powder; UV (MeOH) λ_{\max} (log ϵ): 212 (4.7), 250 (4.1), 286 (3.9) nm; IR (KBr) γ_{\max} : 3450, 1765, 1760, 1651, 1574, 1557, 1538, 1137, 1034, 828 cm⁻¹; (-) ESIMS: *m/z* 579 [M-H]⁻ (2.0%), 223 (100%), 401 (70.3%), 177 (52.7%), 133 (8.1%); (-) ESIMS: *m/z* 579: 579, 401, 223, 195, 373, 151; (-) ESIMS: *m/z* 401, 401, 223, 195, 177; (-) ESIMS: *m/z* 373, 195, 177, 151; (-) ESIMS: *m/z* 223, 179; (-) APCIMS: *m/z* 223 (100%), 177 (100%), 179 (75.5%), 133 (70.6%), 401 (2.7%); ¹H and ¹³C NMR (400 and 100 MHz, CD₃OD) [73].

Amidepsine D (86)

	<p>White powder; $[\alpha]_D^{25}$ 0.0 (c 0.1, MeOH); UV (MeOH) λ_{max} (ϵ): 217 (30700), 250 (17700), 294 (8900) nm; IR (KBr) γ_{max}: 1668, 1608, 1419, 1246, 1200, 1140 cm^{-1}; FAMMS: m/z 497 $[\text{M}+\text{H}]^+$, 519 $[\text{M}+\text{Na}]^+$, 495 $[\text{M}-\text{H}]^-$; HRFABMS 495.1294 $[\text{M}-\text{H}]^-$ (cald for $\text{C}_{26}\text{H}_{23}\text{O}_{10}$, 495.1291) ^1H and ^{13}C NMR (400 and 100 MHz, $\text{DMSO}-d_6$) [7475].</p>
<p>Amidepsine K (87)</p> 	<p>White powder; $[\alpha]_D^{25}$ 0.0 (c 0.1, MeOH); UV (MeOH) λ_{max} (ϵ): 213 (38500), 270 (7900) nm; IR (KBr) γ_{max}: 2979, 2935, 2852, 1662, 1610, 1581, 1421, 1248, 1201, 1148 cm^{-1}; FABMS: m/z 483 $[\text{M}+\text{H}]^+$, 505 $[\text{M}+\text{Na}]^+$, 481 $[\text{M}-\text{H}]^-$; HRFABMS: m/z 483.1274 $[\text{M}-\text{H}]^-$ (cald for $\text{C}_{25}\text{H}_{32}\text{O}_{10}$, 483.1291); ^1H and ^{13}C NMR (600 and 125 MHz, $\text{DMSO}-d_6$) [71].</p>
<p>Amidepsine A (88)</p> 	<p>Pale yellow powder; $[\alpha]_D^{25}$ - 10.0 (c 0.1, MeOH); UV (MeOH) λ_{max} (ϵ): 218 (35000), 254 (18000), 282 (10600) nm; IR (KBr) γ_{max}: 1660, 1583, 1506, 1410, 1246, 1136 cm^{-1}; FAMMS m/z: 568 $[\text{M}+\text{H}]^+$, 590 $[\text{M}+\text{Na}]^+$, 566 $[\text{M}-\text{H}]^-$; HRFABMS 566.1662 $[\text{M}-\text{H}]^-$ (cald for $\text{C}_{29}\text{H}_{28}\text{O}_{11}\text{N}$, 566.1674) ^1H and ^{13}C NMR (400 and 100 MHz, $\text{DMSO}-d_6$) [74,75].</p>
<p>86- Amidepsine B (89)</p>	

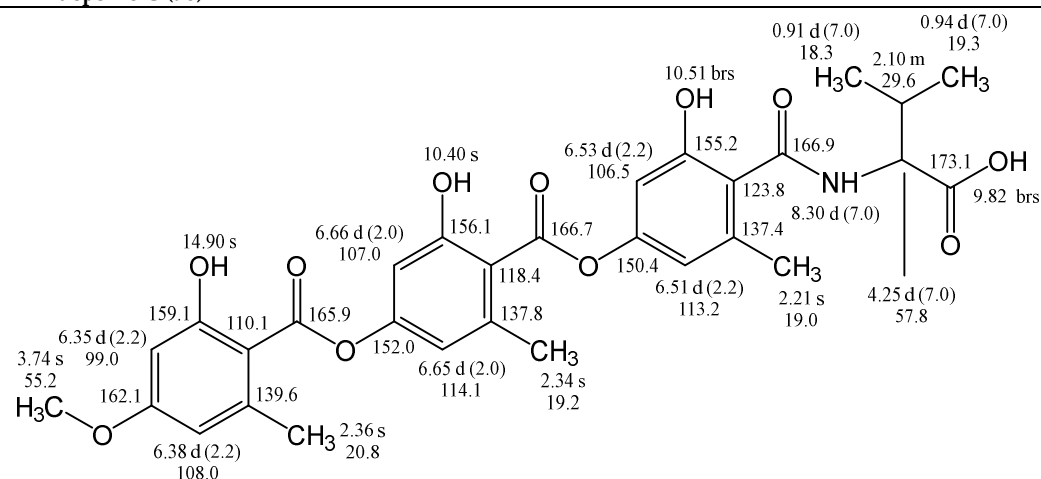


Pale yellow powder; $[\alpha]_D^{25}$ -16.0 (c 0.1, MeOH); UV (MeOH) λ_{max} (ϵ): 216 (34000), 266 (22160), 305 (11100) nm; IR (KBr) γ_{max} : 1656, 1583, 1400, 1248, 1163, 1144 cm⁻¹; FAMMS *m/z*: 554 [M+H]⁺, 576 [M+Na]⁺, 552 [M-H]⁻; HRFABMS: *m/z* 552.1506 [M-H]⁻ (calcd for C₂₈H₂₆O₁₁N, 552.1529); ¹H and ¹³C NMR (400 and 100 MHz, DMSO-*d*₆) [74,75].

Amidepsine B (-): White powder; mp 153–156 °C; $[\alpha]_D^{25}$ -17.3 (c 0.1, CH₃OH); IR (KBr) γ_{max} : 3087, 2937, 2858, 1668, 1610, 1454 cm⁻¹; ¹H NMR (270 MHz, CDCl₃): δ_H 10.4 (brs, 1H), 8.44 (d, *J* = 6.8 Hz, 1H), 6.68 (brs, 1H), 6.66 (brs, 1H), 6.56 (brs, 1H), 6.53 (brs, 1H), 6.39 (brs, 1H), 6.36 (brs, 1H), 4.35 (m, 1H), 3.74 (s, 3H), 2.45 (s, 3H), 2.38 (s, 3H), 2.35 (s, 3H), 1.31 (d, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ_c 174.1, 166.7, 166.4, 165.8, 162.1, 159.1, 156.1, 155.0, 152.0, 150.5, 139.6, 137.8, 137.6, 123.5, 118.4, 114.1, 113.3, 110.7, 108.1, 107.1, 106.4, 99.0, 55.2, 47.6, 20.8, 19.2, 18.8 and 16.9; HRFABMS: *m/z* 552.1510 [M-H]⁻ (calcd for C₂₈H₂₆NO₁₁, 552.1506) [79].

Amidepsine B (+): White powder; mp 156–159 °C; $[\alpha]_D^{25}$ +10.4 (c 0.1, CH₃OH); IR (KBr) γ_{max} : 3087, 2937, 2858, 1668, 1610, 1454 cm⁻¹; ¹H NMR (270 MHz, CDCl₃): δ_H 10.4 (brs, 1H), 8.44 (d, *J* = 6.8 Hz, 1H), 6.68 (brs, 1H), 6.66 (brs, 1H), 6.56 (brs, 1H), 6.53 (brs, 1H), 6.39 (brs, 1H), 6.36 (brs, 1H), 4.35 (m, 1H), 3.74 (s, 3H), 2.45 (s, 3H), 2.38 (s, 3H), 2.35 (s, 3H), 1.31 (d, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ_c 174.1, 166.7, 166.4, 165.8, 162.1, 159.1, 156.1, 155.0, 152.0, 150.5, 139.6, 137.8, 137.6, 123.5, 118.4, 114.1, 113.3, 110.7, 108.1, 107.1, 106.4, 99.0, 55.2, 47.6, 20.8, 19.2, 18.8 and 16.9; HRFABMS: *m/z* 554.1663 [M+H]⁺ (calcd for C₂₈H₂₈NO₁₁, 554.1662) [79].

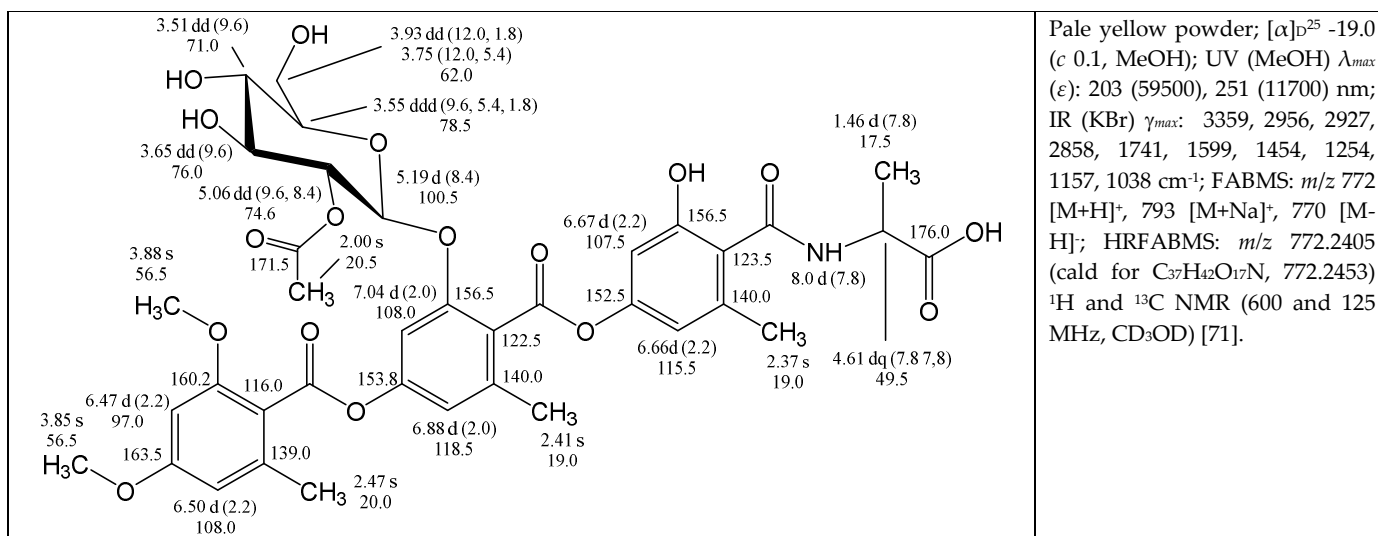
Amidepsine C (90)



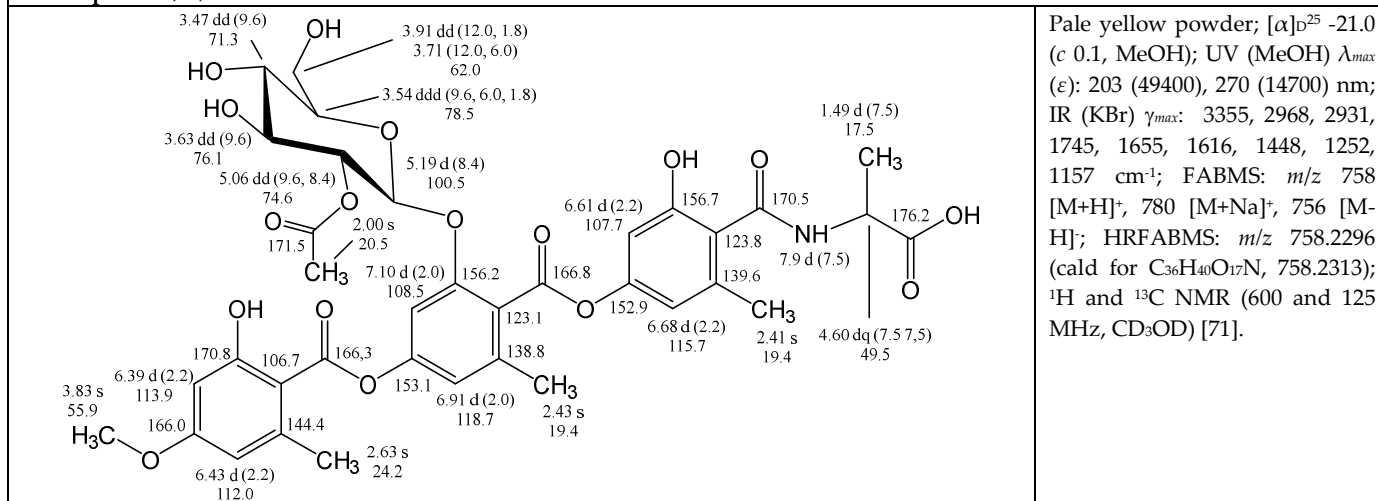
Pale yellow powder; $[\alpha]_D^{25}$ -94.0 (c 0.1, MeOH); UV (MeOH) λ_{max} (ϵ): 209 (37400), 269 (24200), 306 (12300) nm; IR (KBr) γ_{max} : 1670, 1612, 1583, 1313, 1248, 1140 cm⁻¹; FAMMS: *m/z* 582 [M+H]⁺, 604 [M+Na]⁺, 580 [M-H]⁻; HRFABMS: *m/z* 580.1822 (calcd for C₃₀H₃₀O₁₁N, 580.1819) ¹H and ¹³C NMR (400 and 100 MHz, DMSO-*d*₆) [74,75].

Amidepsine E (91)

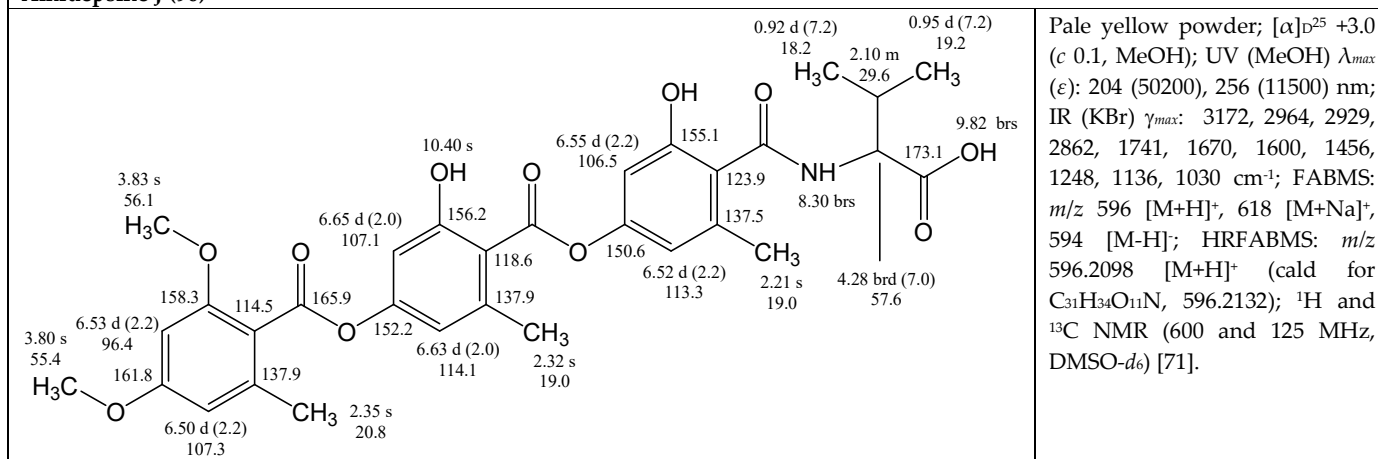
	<p>Pale yellow powder; mp 215 °C; $[\alpha]_D^{25}$ -7.0 (c 0.1, MeOH); λ_{max} (ϵ): 206 (75500), 246 (14000), 281 (10400) nm; IR (KBr) γ_{max}: 3410, 2927, 1732, 1597, 1462, 1327, 1250, 1139 cm^{-1}; FABMS m/z: 582 (M+H)⁺, 604 (M+Na)⁺, 580 (M-H)⁻; HRFABMS: m/z 582.1977 (calcd for C₃₀H₃₂O₁₁N, 582.1975); ¹H and ¹³C NMR (400 and 100 MHz, DMSO-<i>d</i>₆) [76].</p>
<p>Amidepsine F (92)</p>	<p>Pale yellow powder; $[\alpha]_D^{25}$ -10.0 (c 0.1, MeOH); UV (MeOH) λ_{max} (ϵ): 204 (48000), 281 (5600) nm; IR (KBr) γ_{max}: 3379, 2968, 2956, 2927, 2858, 1739, 1599, 1456, 1257, 1038 cm^{-1}; FABMS: m/z 730 [M+H]⁺, 752 [M+Na]⁺, 728 [M-H]⁻; HRFABMS: m/z 730.2307 (calcd for C₃₅H₄₀O₁₆N, 730.2347); ¹H and ¹³C NMR (600 and 125 MHz, CD₃OD) [71].</p>
<p>Amidepsine G (93)</p>	<p>Pale yellow powder; $[\alpha]_D^{25}$ -13.0 (c 0.1, MeOH); UV (MeOH) λ_{max} (ϵ): 203 (50500), 270 (15500) nm; IR (KBr) γ_{max}: 3311, 2929, 2860, 1738, 1657, 1603, 1450, 1657, 1603, 1450, 1254, 1157, 1063 cm^{-1}; FABMS: m/z 716 [M+H]⁺, 738 [M+Na]⁺, 714 [M-H]⁻; HRFABMS: m/z 716.2146 (calcd for C₃₄H₃₈O₁₆N, 716.2191); ¹H and ¹³C NMR (600 and 125 MHz, CD₃OD) [71].</p>
<p>Amidepsine H (94)</p>	



Amidepsine I (95)



Amidepsine J (96)



CJ-21,164 (97)

<p>NMR in acetone-d_6</p>	<p>White powder; UV (MeOH) λ_{max} (ϵ): 215 (78800), 252 (29900), 284 (12700), 315 (sh) nm; $[\alpha]^{25}_D$ +63.8 (c 1.00, MeOH); IR (KBr) γ_{max}: 3700-2500, 3408, 3250 (sh), 2937, 2937, 1760, 1725 (sh), 1676, 1618, 1583, 1445, 1385, 1348, 1296, 1258, 1190, 1140, 1084, 959, 881, 723 cm^{-1}; HRFABMS: m/z 751.1782 [M-H]$^-$ (calcd for $C_{38}H_{36}ClO_{14}$, 551.1794); LRFABMS: m/z 753/755 (5:2), 557/559, 393/395, 363/365, 359/361, 199/201, 195, 179, 168, 165; 1H and ^{13}C NMR (270 and 68 MHz, acetone-d_6 and CD_3OD) [77].</p>
<p>NMR in CD_3OD</p>	
Thielocin A1α (98)*	
Colorless powder; mp 203-206°C; HR-MS: m/z 997.3861 (calcd 997.3854, $C_{54}H_{60}O_{18}$); IR (KBr) γ_{max} : 3490, 1740, 1675, 1577, 1155, 1095 cm^{-1} [90]; 1H NMR (400 MHz, $CDCl_3$ - CD_3OD (20:1): δ_H 2.74 (1H, d, J = 16 Hz), 3.3 (1H, d, J = 16 Hz), 3.83 (9H, s, 3 \times OCH $_3$), 3.35 (3H, s, OCH $_3$), 1.33 (3H, s), 1.89 (3H, s), 2.23 (3H, s), 2.24 (3H, s), 2.26 (3H, s), 2.27 (3H, s), 2.40 (3H, s), 2.41 (3H, s), 2.27 (6H, s), 2.30 (3H, s), 2.32 (6H each, s) [78].	
Thielocin A1β (99)*	
Colorless powder; mp 203-206°C; HR-MS: m/z 997.3865 (calcd 997.3854, $C_{54}H_{60}O_{18}$); IR (KBr) γ_{max} : 3440, 1744, 1675, 1575, 1155, 1095 cm^{-1} [90]. 1H NMR (400 MHz, $CDCl_3$ - CD_3OD (20:1): δ_H 2.72 (1H, d, J = 16 Hz), 3.38 (1H, d, J = 16 Hz), 3.78 (3H, s, OCH $_3$), 3.81 (3H, s, OCH $_3$), 3.82 (9H, s, 3 \times OCH $_3$), 1.52 (3H, s), 1.75 (3H, s), 2.13 (3H, s), 2.20 (3H, s), 2.21 (3H, s), 2.22 (3H, s), 2.25 (3H, s), 2.34 (3H, s), 2.37 (3H, s), 2.40 (3H, s), 2.24 (6H, s), 2.28 (6H each, s) [78].	
Thielocin A2α (100)*	
Colorless powder; mp 203-206°C; HR-MS: m/z 1175.4479 (calcd 1175.4483, $C_{64}H_{70}O_{21}$); UV (MeOH+ dil HCl-MeOH) λ_{max} (ϵ): 274.6 (25,100), 316.7 (5,380) nm; UV (dil NaOH-MeOH) λ_{max} (ϵ): 260 (sh), 323.3 (52,800) nm; IR (KBr) γ_{max} : 3440, 1740, 1605, 1574, 1150, 1090 cm^{-1} [75].	
Thielocin A2β (101)*	
Colorless powder; mp 204-206°C; HR-MS: m/z 1175.4488 (calcd 1175.4483, $C_{64}H_{70}O_{21}$); UV (MeOH+ dil HCl-MeOH) λ_{max} (ϵ): 274.5 (22,900, sh), 321 (4,520) nm; UV (dil NaOH-MeOH) λ_{max} (ϵ): 260 (sh), 323 (51,300) nm; IR (KBr) γ_{max} : 3420, 1745, 1605, 1572, 1147, 1090 cm^{-1} [75].	
Thielocin A3 (104)*	
Colorless powder; mp 202-205°C; HR-MS: m/z 1175.4488 (calcd 1175.4470, $C_{64}H_{70}O_{21}$); UV (MeOH+ dil HCl-MeOH) λ_{max} (ϵ): 274.5 (22,512), 318.6 (5,232) nm; UV (dil NaOH-MeOH) λ_{max} (ϵ): 255 (sh), 323 (29,825) nm; IR (KBr) γ_{max} : 3440, 1743, 1657, 1608, 1576, 1097 cm^{-1} [75].	
Thielocin B1 (105)*	
Colorless powder; mp 175-182°C; HR-MS: m/z 967.3754 (calcd 967.3749, $C_{53}H_{58}O_{17}$); UV (MeOH+dil HCl-MeOH) λ_{max} (ϵ): 275 (24,150), 323 (5,120) nm; UV (dil NaOH-MeOH) λ_{max} (ϵ): 248 (21,250, sh), 331 (32,650); IR (KBr) γ_{max} : 3424, 1742, 1659, 1610, 1152, 1096 cm^{-1} [75].	

Thielocin B2 (106)*
Colorless powder; mp 180–186°C; HR-MS: m/z 967.3751 (calcd 967.3749, C ₅₃ H ₅₈ O ₁₇); UV (MeOH+dil HCl-MeOH) λ_{max} (ϵ): 245 (24,830 sh), 325 (3,579) nm; IR (KBr) γ_{max} : 3440, 1775, 1734, 1665, 1610, 1150 cm ⁻¹ [75 121].
Thielocin B3 (107)*
Colorless powder; mp 194–197°C; HR-MS: m/z 1131.4226 (calcd 1131.4226, C ₆₂ H ₆₆ O ₂₀); UV (MeOH+ dil HCl-MeOH) λ_{max} (ϵ): 276 (39,760), 306 (11,690 sh) nm; IR (KBr) γ_{max} : 3410, 1740, 1650, 1610, 1143, 1094 cm ⁻¹ [75].

* The spectral data were published in Japanese language [75].

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