

Supporting Information

Characterization and comparison of steroidal glycosides from *Polygonatum* species by High-Performance Liquid Chromatography–Electrospray Ionization Mass Spectrometry

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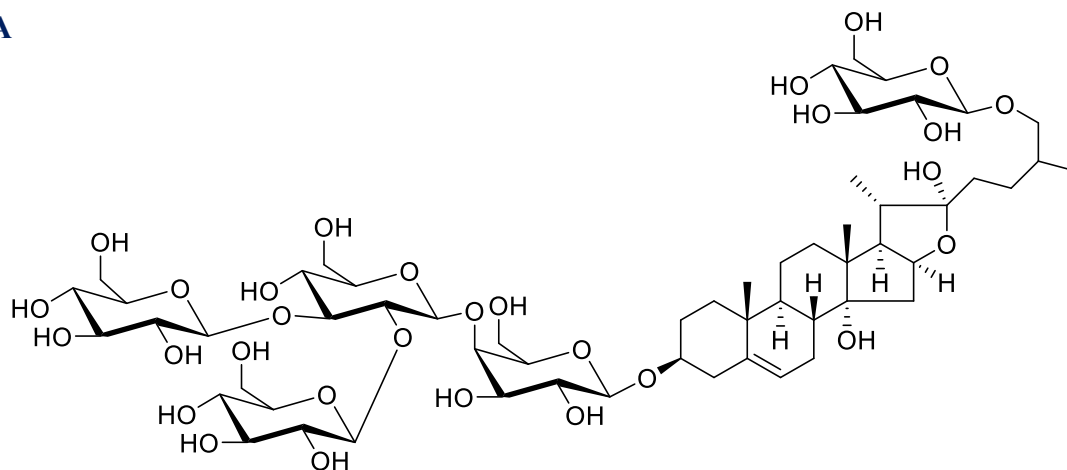
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takashi.kikuchi@phar.toho-u.ac.jp (T. Kikuchi)

Figure (S1-S32). Structure and (+) and (–) ESI-MS of 31 compounds and biogenetic pathway for the steroidal glycoside from *Polygonatum* species.

Table S1. NMR Spectroscopic Data (500 MHz for ^1H and 125 MHz for ^{13}C , in Pyridine-*d*5) of Compound **15**.

A



CAS Registry Number: Unregistered

Proposed Structure Name: 26-*O*-(β-D-glucopyranosyl)-furost-5-ene-3β,14α,22α,26-tetraol 3-*O*-β-D-glucopyranosyl-(1→2)-[β-D-glucopyranosyl-(1→3)]-β-D-glucopyranosyl-(1→4)-β-D-galactopyranoside

Chemical Formula: C₅₇H₉₄O₃₀

MW: 1258.6

Plant Material: *P. macranthum*, *P. odoratum* var. *maximowiczii*

Rt: 8.90 min

B

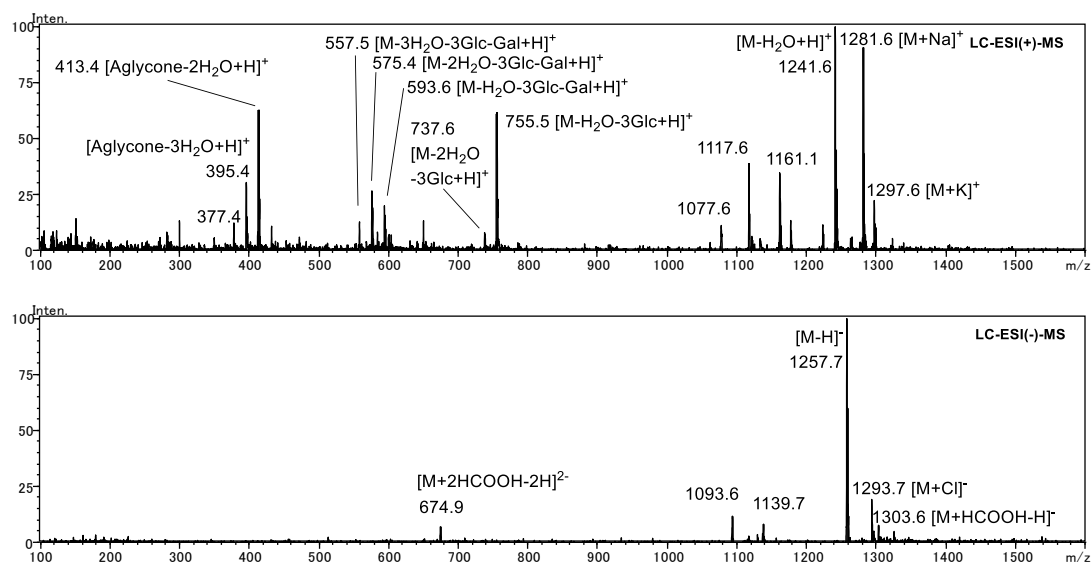
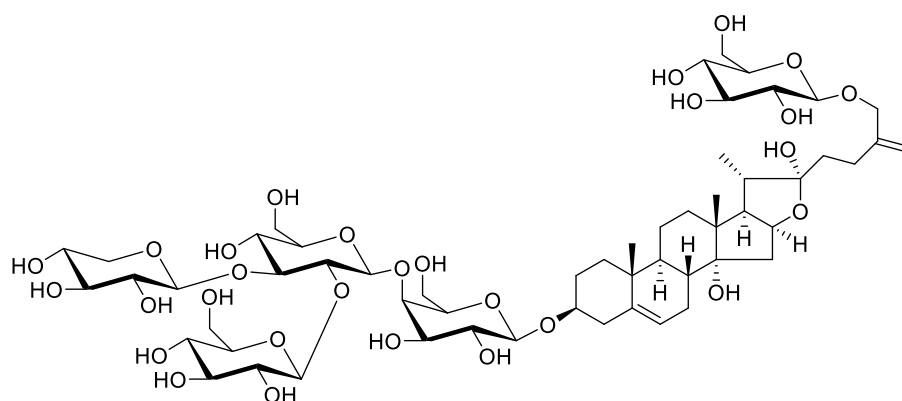


Figure S1. (A) Structure of Compound 1. (B) ESI-MS of Compound 1.

A



CAS Registry Number: Unregistered

Proposed Structure Name: 26-*O*-(β -D-glucopyranosyl)-furost-5,25(27)-diene-3 β ,14 α ,22 α ,26-tetraol 3-*O*- β -D-glucopyranosyl-(1 \rightarrow 2)-[β -D-xylopyranosyl-(1 \rightarrow 3)]- β -D-glucopyranosyl-(1 \rightarrow 4)- β -D-galactopyranoside

Chemical Formula: C₅₆H₉₀O₂₉

MW: 1226.6

Plant Material: *P. falcatum*, *P. macranthum*

Rt: 9.11 min

B

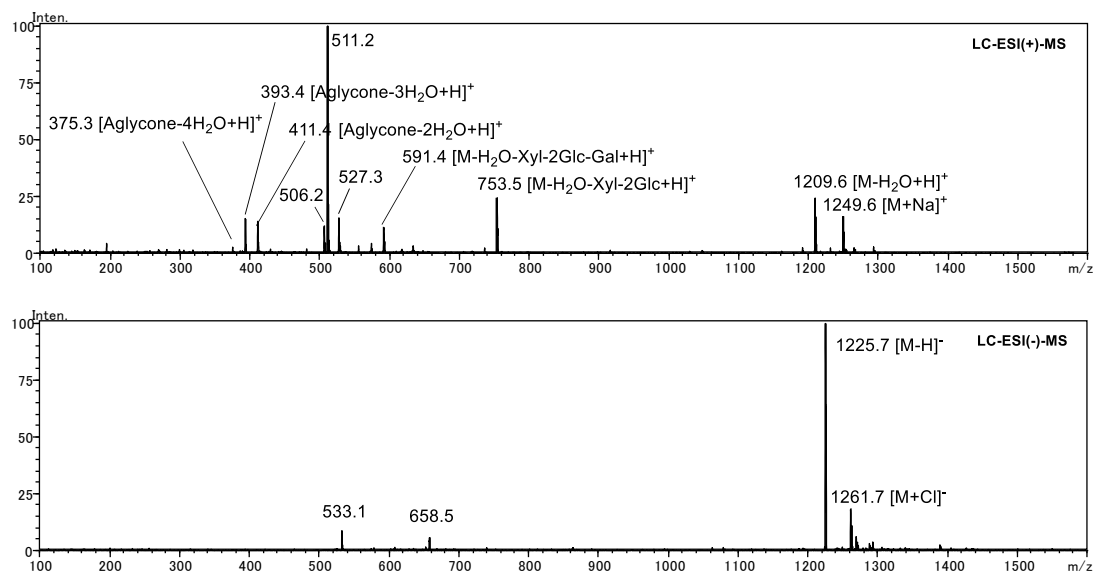
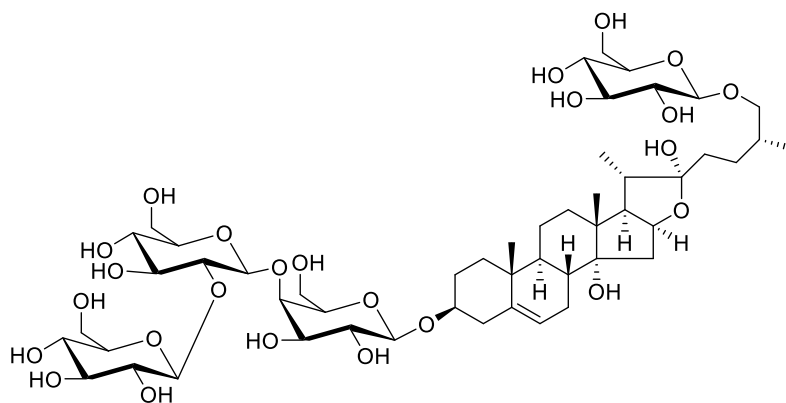


Figure S2. (A) Structure of Compound 2. (B) ESI-MS of Compound 2.

A



CAS Registry Number: 1351935-50-6

Name: (3 β ,22 α ,25 R)-26-(β -D-glucopyranosyloxy)-14,22-dihydroxyfurost-5-en-3-yl O- β -D-glucopyranosyl-(1 \rightarrow 2)-O- β -D-glucopyranosyl-(1 \rightarrow 4)- β -D-galactopyranoside

Chemical Formula: C₅₁H₈₄O₂₅

MW: 1096.5

Plant Material: *P. odoratum*, *P. falcatum*, *P. macranthum*

Rt: 9.18 min

B

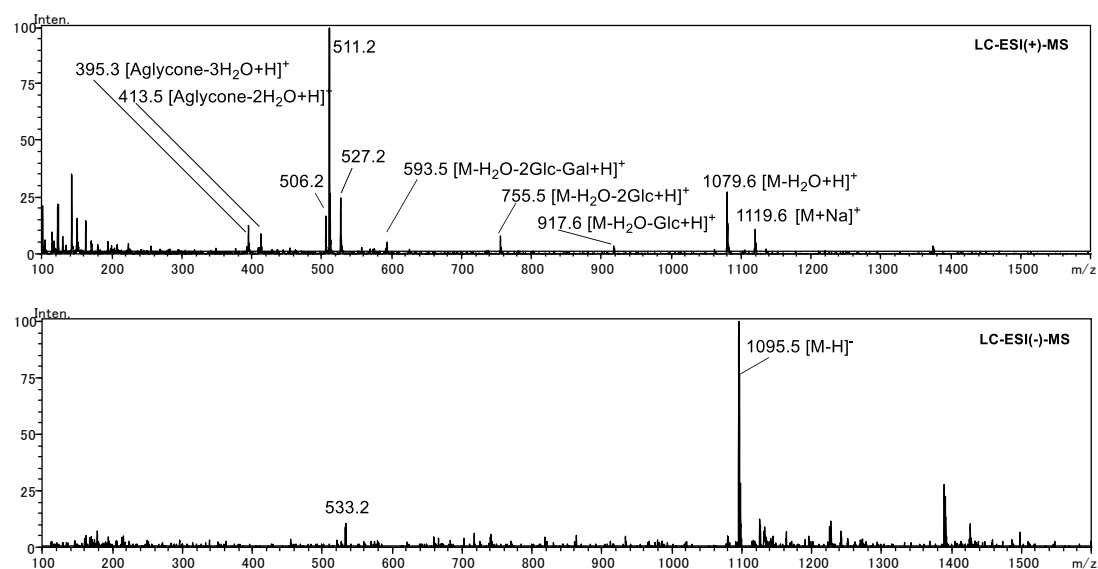
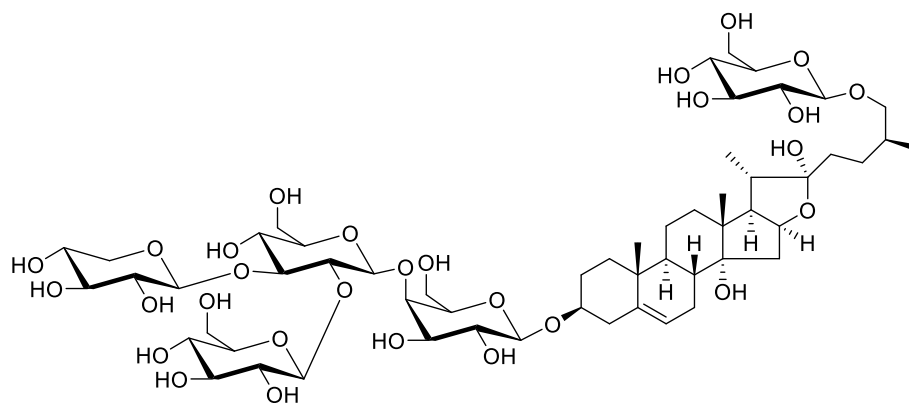


Figure S3. (A) Structure of Compound **3**. (B) ESI-MS of Compound **3**.

A



CAS Registry Number: 2210235-73-5

Name: polygonatumoside F

Chemical Formula: $C_{56}H_{92}O_{29}$

MW: 1228.6

Plant Material: *P. odoratum*, *P. falcatum*, *P. macranthum*, *P. odoratum* var. *maximowiczii*

Rt: 9.38 min

B

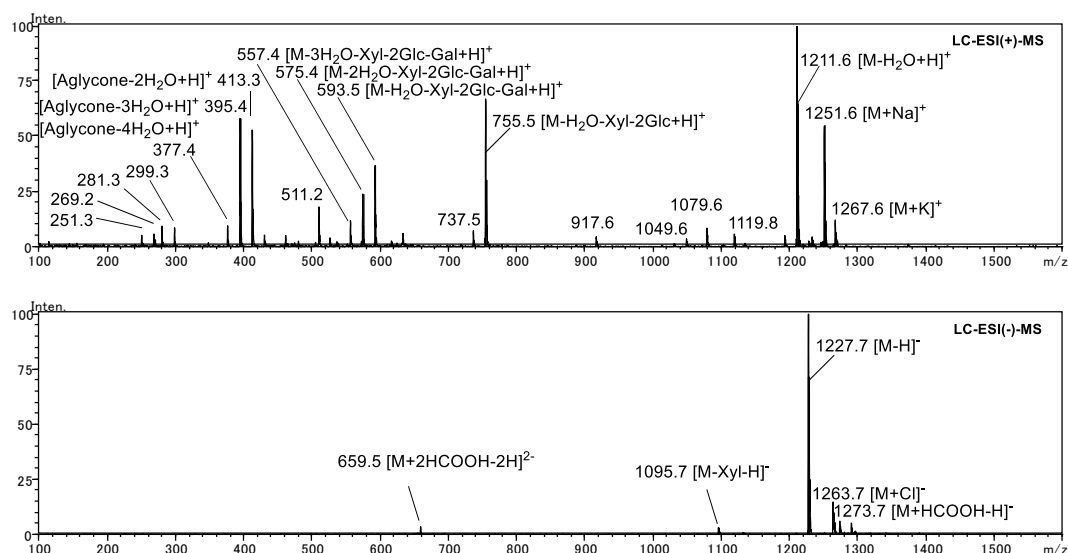
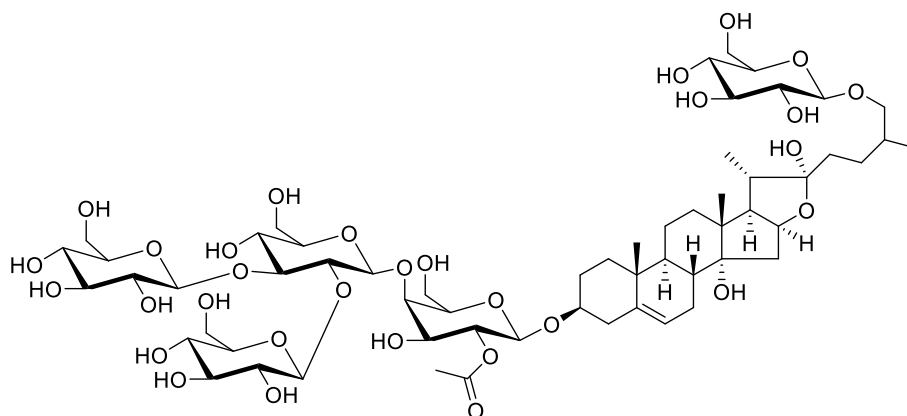


Figure S4. (A) Structure of Compound 4. (B) ESI-MS of Compound 4.

A



CAS Registry Number: Unregistered

Proposed Structure Name: 26-*O*-(β -D-glucopyranosyl)-furost-5-ene-3 β ,14 α ,22 α ,26-tetraol 3-*O*- β -D-glucopyranosyl-(1 \rightarrow 2)-[β -D-glucopyranosyl-(1 \rightarrow 3)]- β -D-glucopyranosyl-(1 \rightarrow 4)-2''-*O*-acetyl- β -D-galactopyranoside

Chemical Formula: C₅₉H₉₆O₃₁

MW: 1300.6

Plant Material: *P. macranthum*, *P. odoratum* var. *maximowiczii*

Rt: 10.28 min

B

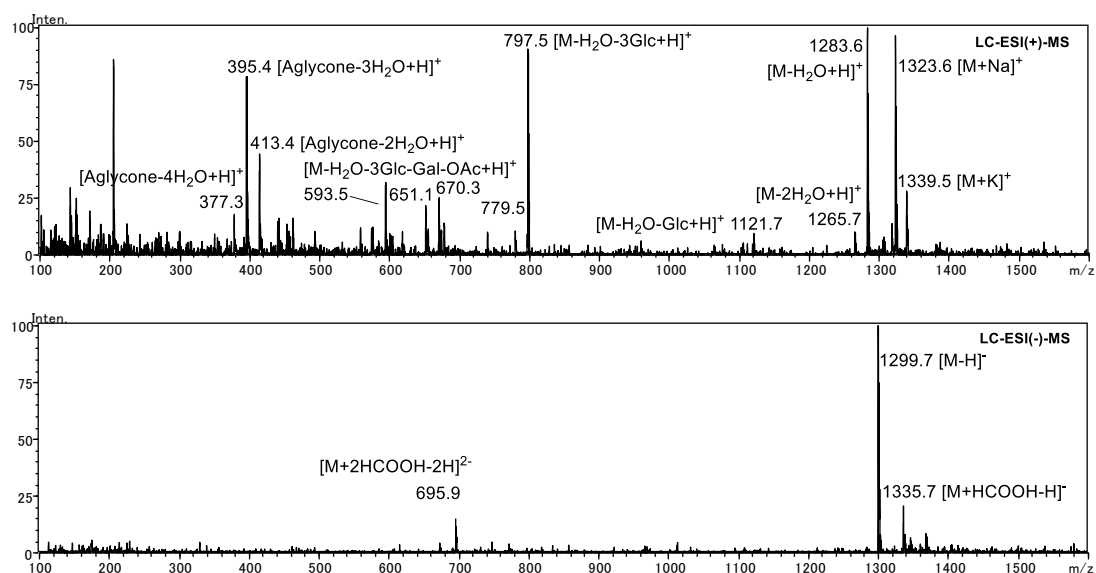
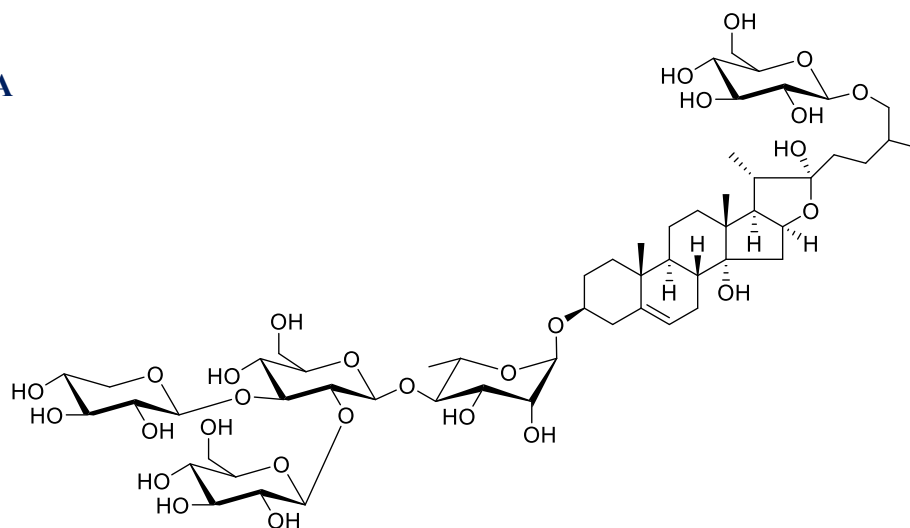


Figure S5. (A) Structure of Compound 5. (B) ESI-MS of Compound 5.

A



CAS Registry Number: Unregistered

Proposed Structure Name: 26-O-(β-D-glucopyranosyl)-furost-5-ene-3β,14α,22α,26-tetraol 3-O-β-D-glucopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→3)]-β-D-glucopyranosyl-(1→4)-α-L-rhamnopyranoside

Chemical Formula: C₅₆H₉₂O₂₈

MW: 1212.6

Plant Material: *P. odoratum*, *P. falcatum*

Rt: 10.31 min

B

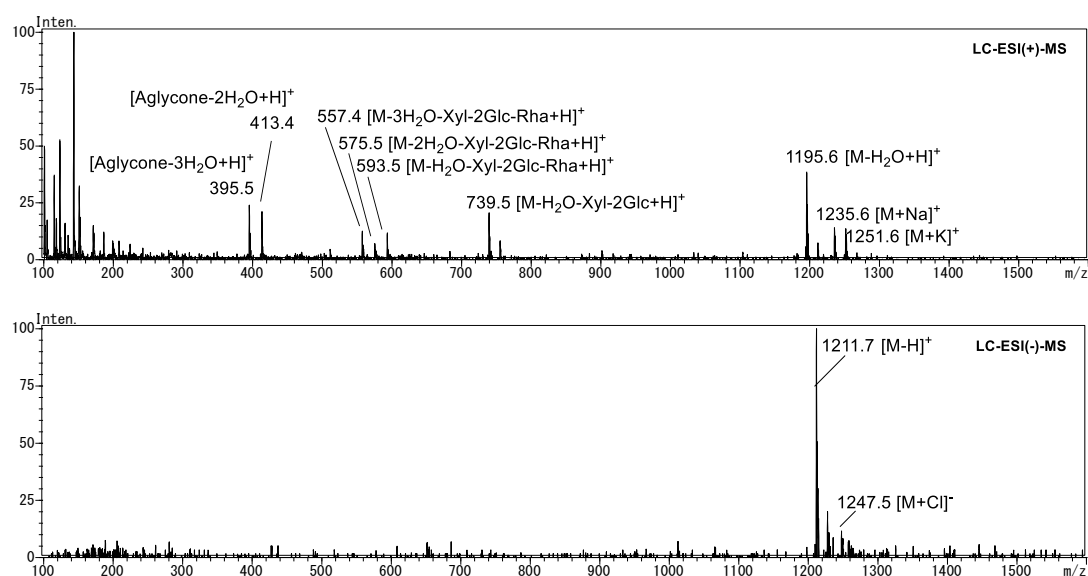
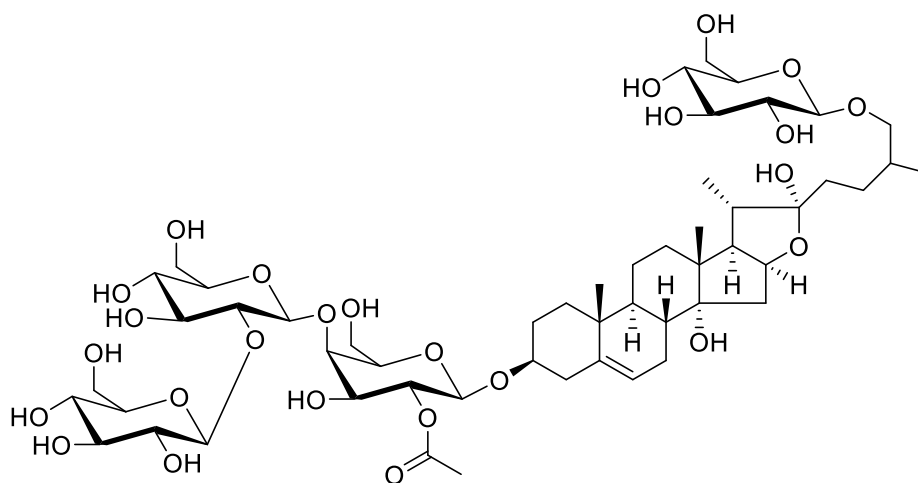


Figure S6. (A) Structure of Compound 6. (B) ESI-MS of Compound 6.

A



CAS Registry Number: Unregistered

Proposed Structure Name: 26-*O*-(β -D-glucopyranosyl)-furost-5-ene-3 β ,14 α ,22 α ,26-tetraol 3-*O*- β -D-glucopyranosyl-(1 \rightarrow 2)- β -D-glucopyranosyl-(1 \rightarrow 4)-2''-*O*-acetyl- β -D-galactopyranoside

Chemical Formula: C₅₃H₈₆O₂₆

MW: 1138.5

Plant Material: *P. macranthum*

Rt: 10.66 min

B

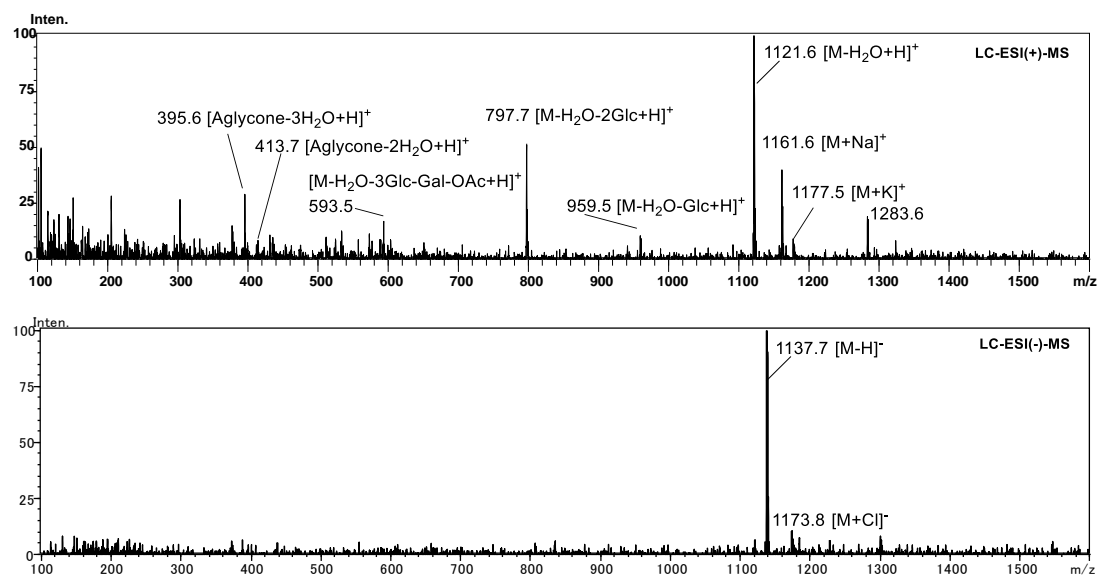
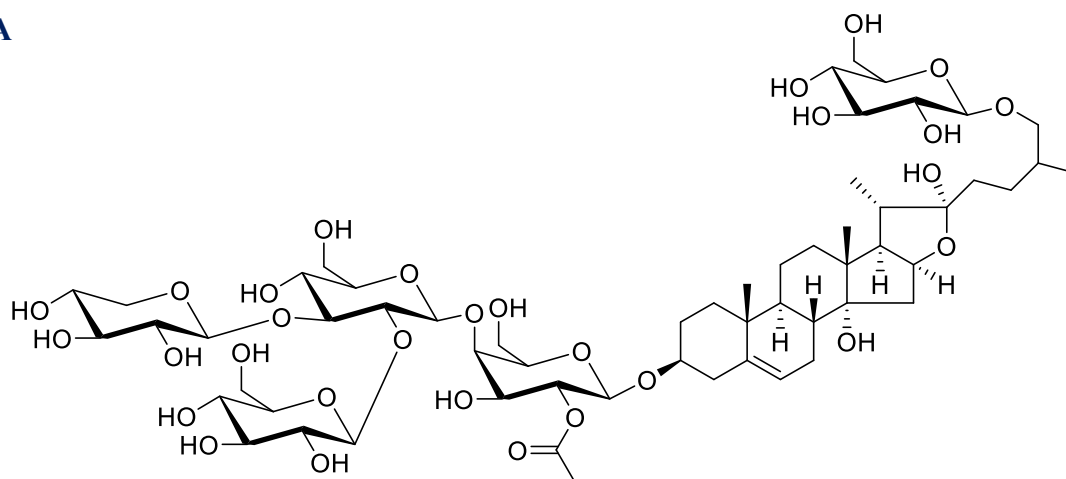


Figure S7. (A) Structure of Compound 7. (B) ESI-MS of Compound 7.

A



CAS Registry Number: Unregistered

Proposed Structure Name: 26-*O*-(β -D-glucopyranosyl)-furost-5-ene-3 β ,14 α ,22 α ,26-tetraol 3-*O*- β -D-glucopyranosyl-(1 \rightarrow 2)-[β -D-xylopyranosyl-(1 \rightarrow 3)]- β -D-glucopyranosyl-(1 \rightarrow 4)-2''-*O*-acetyl- β -D-galactopyranoside

Chemical Formula: C₅₈H₉₄O₃₀

MW: 1270.6

Plant Material: *P. falcatum*

Rt: 10.78 min

B

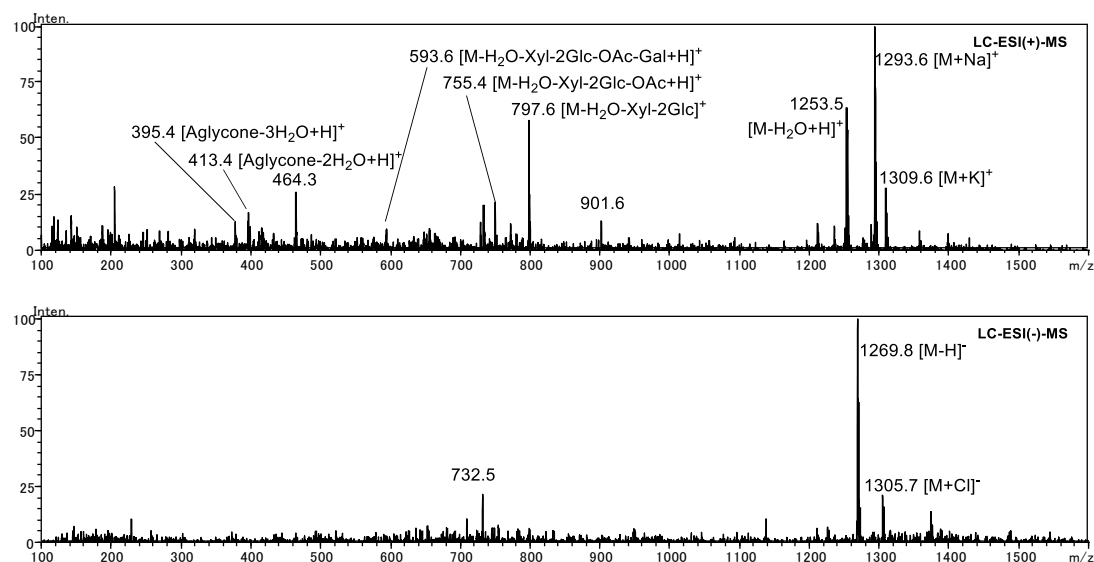
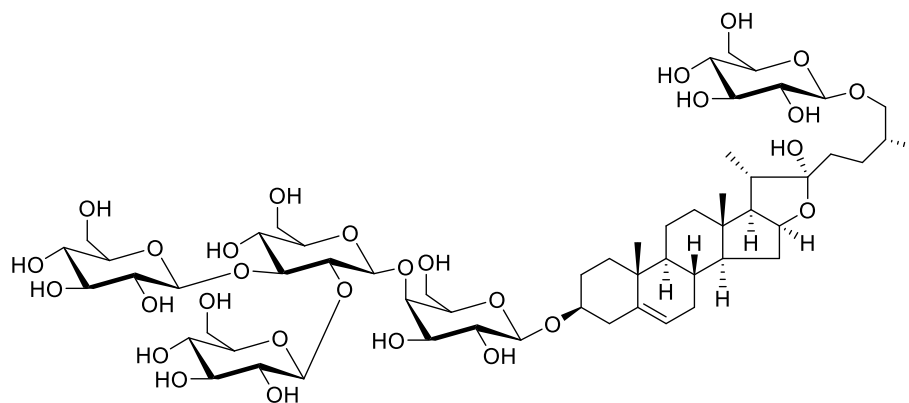


Figure S8. (A) Structure of Compound **8**. (B) ESI-MS of Compound **8**.

A



CAS Registry Number: 108886-03-9

Name: polyfuroside

Chemical Formula: $C_{57}H_{94}O_{29}$

MW: 1242.6

Plant Material: *P. macranthum*, *P. odoratum* var. *maximowiczii*

Rt: 11.87 min

B

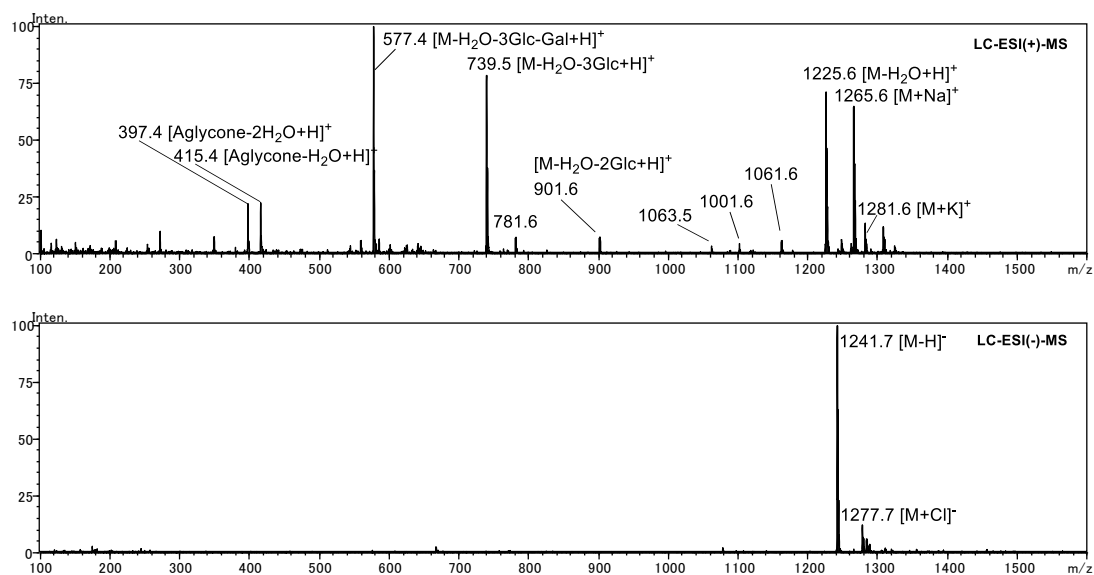
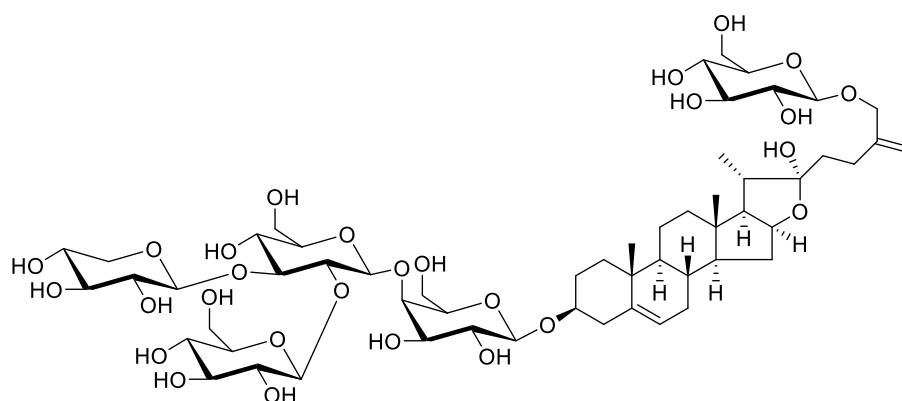


Figure S9. (A) Structure of Compound **9**. (B) ESI-MS of Compound **9**.

A



CAS Registry Number: Unregistered

Proposed Structure Name: 26-*O*-(β -D-glucopyranosyl)-furost-5,25(27)-diene-3 β ,22 α ,26-triol 3-*O*- β -D-glucopyranosyl-(1 \rightarrow 2)-[β -D-xylopyranosyl-(1 \rightarrow 3)]- β -D-glucopyranosyl-(1 \rightarrow 4)- β -D-galactopyranoside

Chemical Formula: C₅₆H₉₀O₂₈

MW: 1210.6

Plant Material: *P. falcatum*, *P. macranthum*

Rt: 12.01 min

B

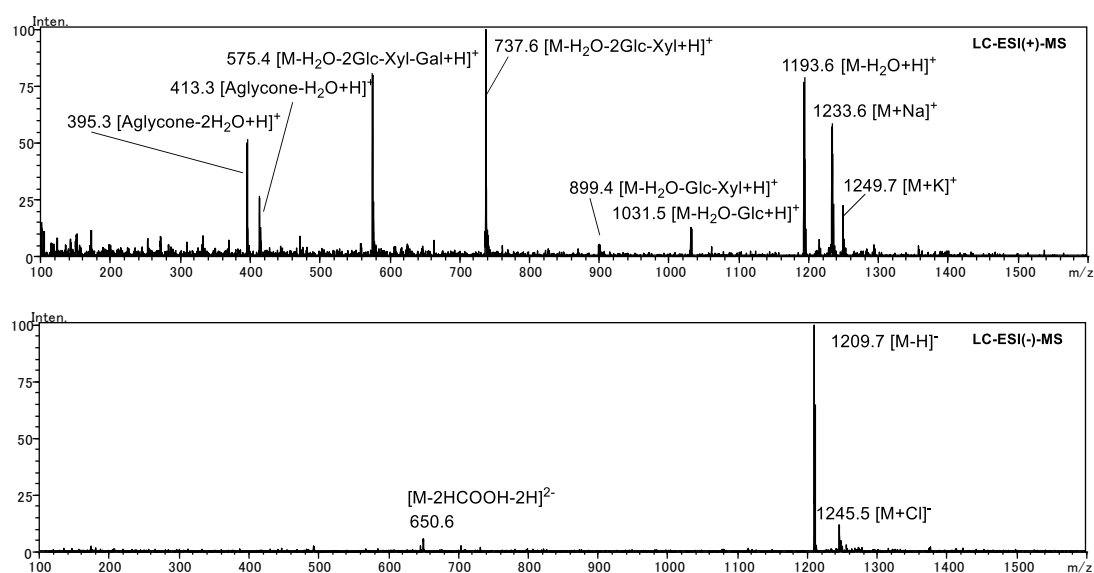
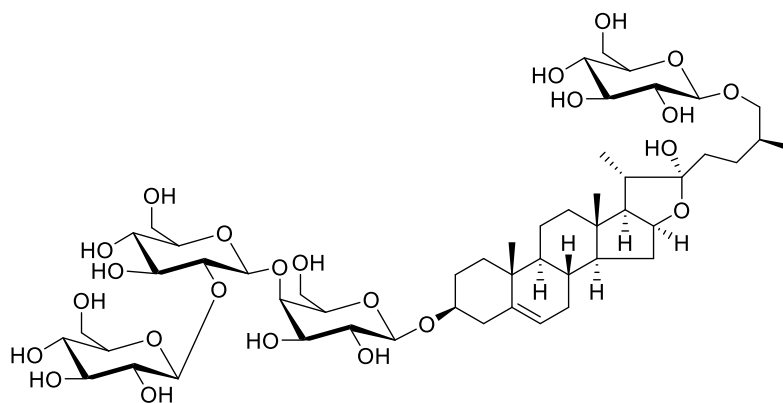


Figure S10. (A) Structure of Compound 10. (B) ESI-MS of Compound 10.

A



CAS Registry Number: 78101-14-1

Proposed Structure Name: (3 β ,22 α ,25 S)-26-(β -D-Glucopyranosyloxy)-22-hydroxyfurost-5-en-3-yl O- β -D-glucopyranosyl-(1 \rightarrow 2)-O- β -D-glucopyranosyl-(1 \rightarrow 4)- β -D-galactopyranoside

Chemical Formula: C₅₁H₈₄O₂₄

MW: 1080.5

Plant Material: *P. macranthum*, *P. odoratum* var. *maximowiczii*

Rt: 12.18 min

B

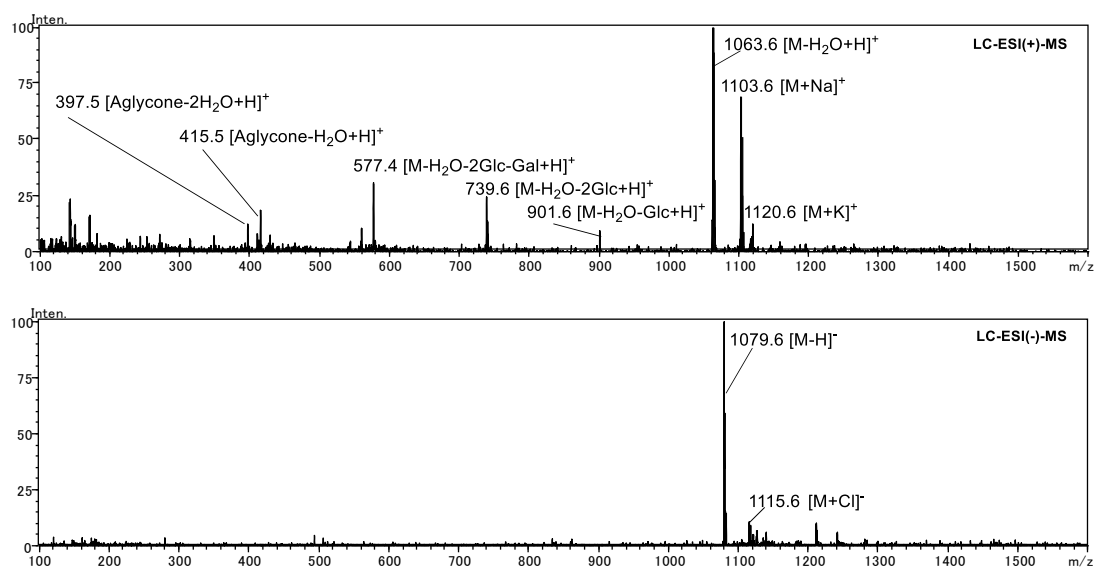
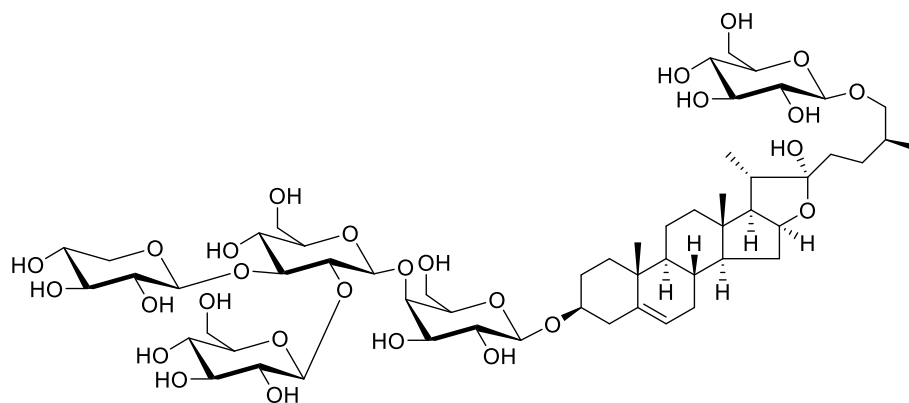


Figure S11. (A) Structure of Compound 11. (B) ESI-MS of Compound 11.

A



CAS Registry Number: 288142-06-3

Name: timosaponin H1

Chemical Formula: $C_{56}H_{92}O_{28}$

MW: 1212.6

Plant Material: *P. odoratum*, *P. falcatum*, *P. macranthum*

Rt: 12.28 min

B

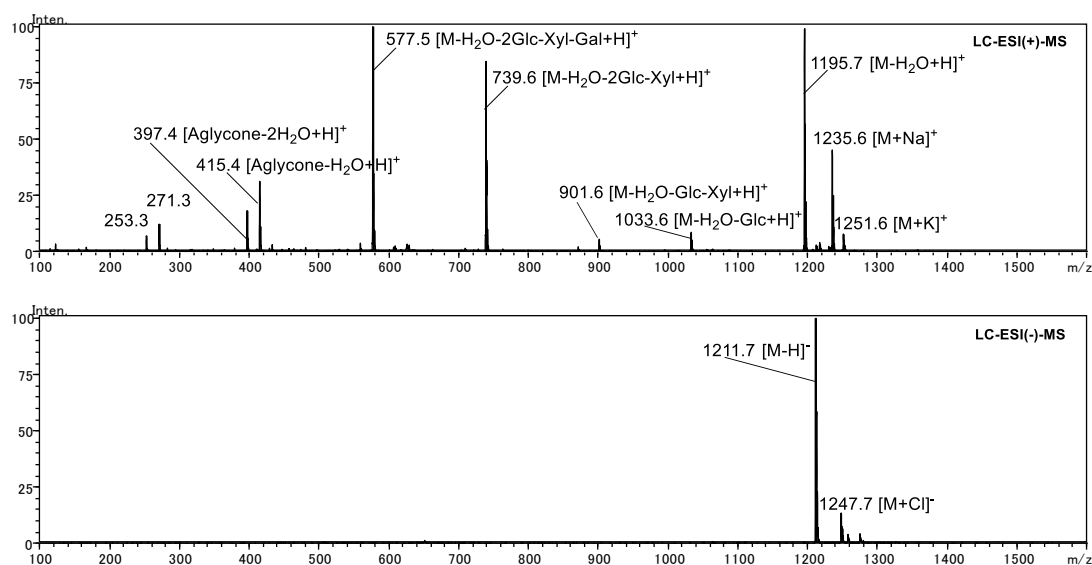
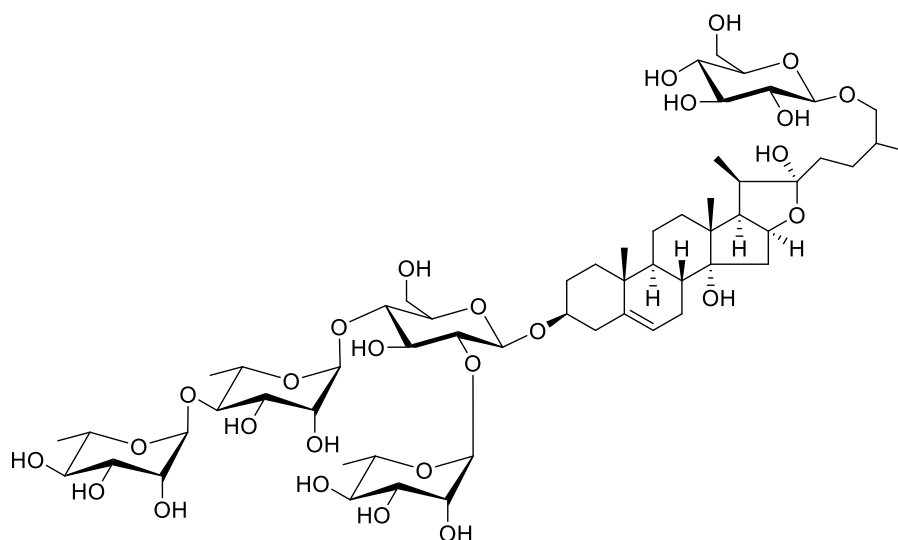


Figure S12. (A) Structure of Compound 12. (B) ESI-MS of Compound 12.

A



CAS Registry Number: Unregistered

Proposed Structure Name: 26-*O*-(β -D-glucopyranosyl)-furost-5-ene-3 β ,14 α ,22 α ,26-triol 3-*O*- α -L-rhamnopyranosyl-(1 \rightarrow 2)-[α -L-rhamnopyranosyl-(1 \rightarrow 4)]- α -L-rhamnopyranosyl-(1 \rightarrow 4)- β -D-glucopyranoside

Chemical Formula: C₅₇H₉₄O₂₇

MW: 1210.6

Plant Material: *P. odoratum*, *P. falcatum*

Rt: 13.08 min

B

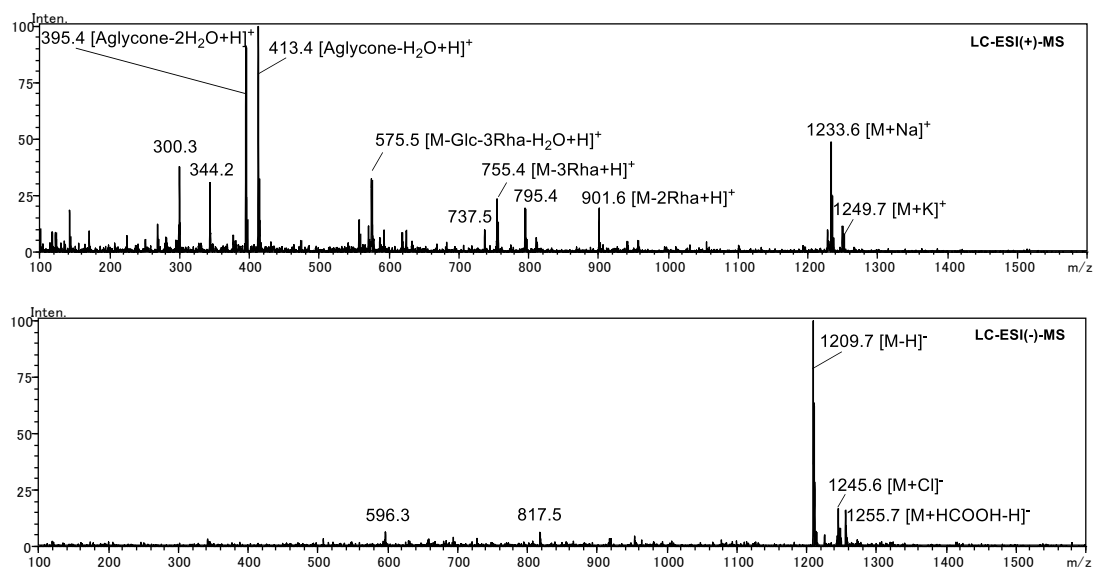
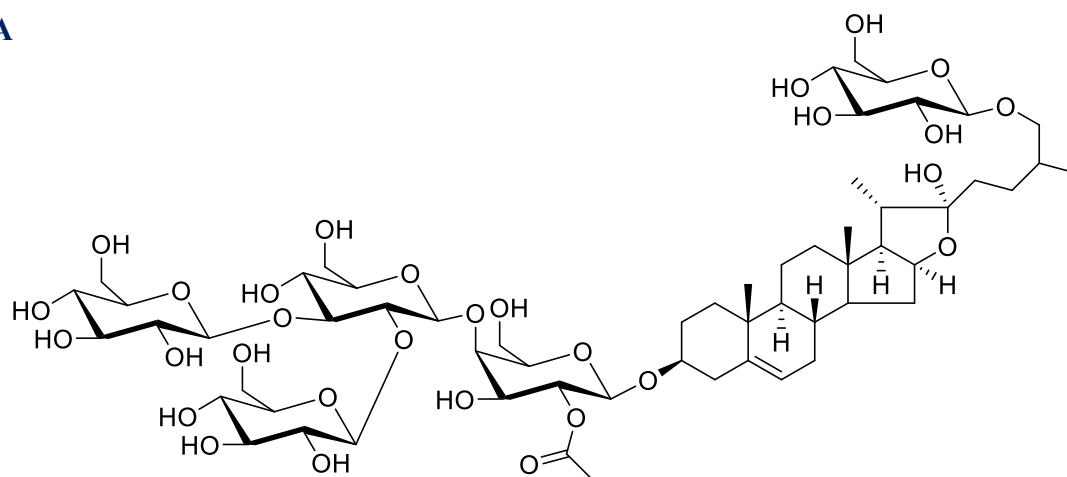


Figure S13. (A) Structure of Compound 13. (B) ESI-MS of Compound 13.

A



CAS Registry Number: Unregistered

Proposed Structure Name: 26-*O*-(β -D-glucopyranosyl)-furost-5-ene-3 β ,22 α ,26-triol 3-*O*- β -D-glucopyranosyl-(1 \rightarrow 2)-[β -D-glucopyranosyl-(1 \rightarrow 3)]- β -D-glucopyranosyl-(1 \rightarrow 4)-2''-*O*-acetyl- β -D-galactopyranoside

Chemical Formula: C₅₉H₉₆O₃₀

MW: 1284.6

Plant Material: *P. macranthum*, *P. odoratum* var. *maximowiczii*

Rt: 13.32 min

B

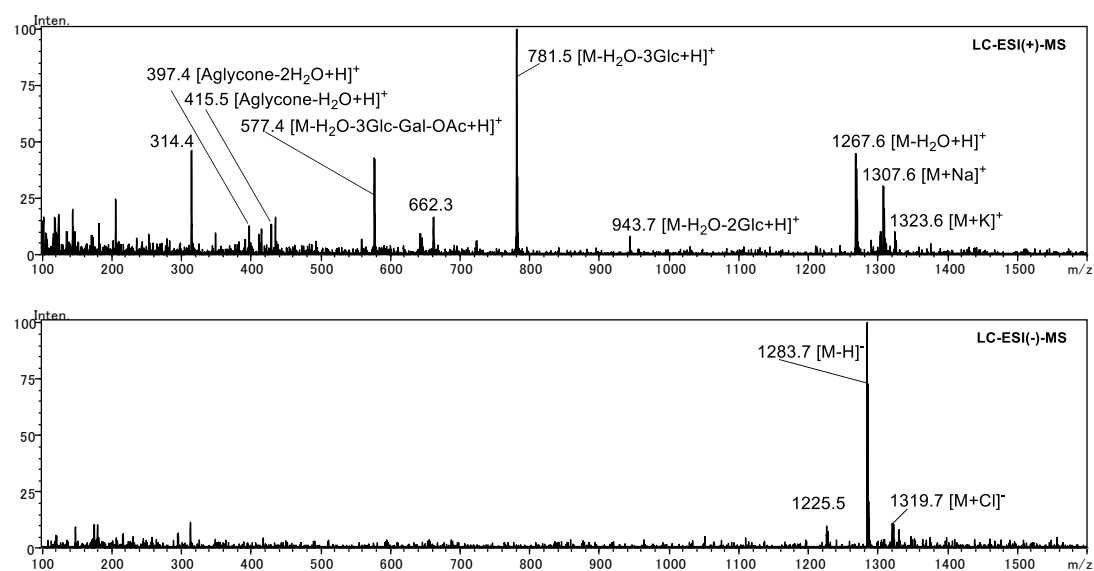
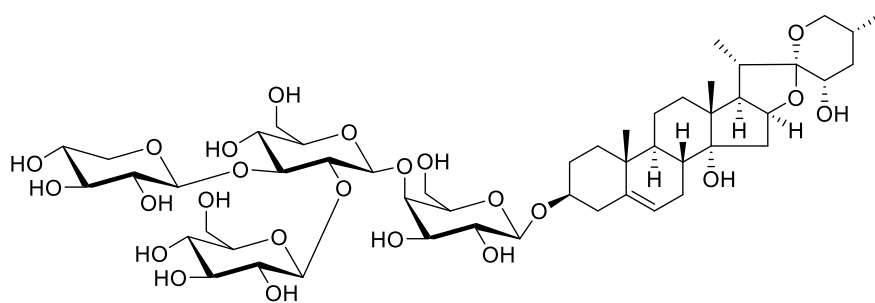


Figure S14. (A) Structure of Compound 14. (B) ESI-MS of Compound 14.

A



CAS Registry Number: 128741-17-3

Name: sibiricoside B

Chemical Formula: $C_{50}H_{80}O_{24}$

MW: 1064.5

Plant Material: *P. odoratum*, *P. falcatum*, *P. macranthum*

Rt: 15.14 min

B

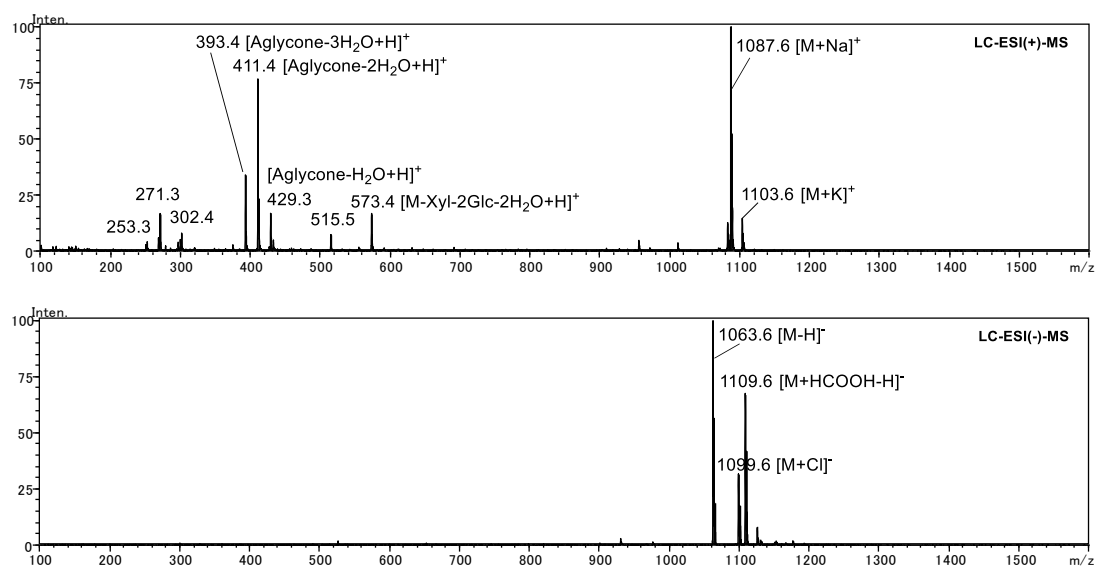
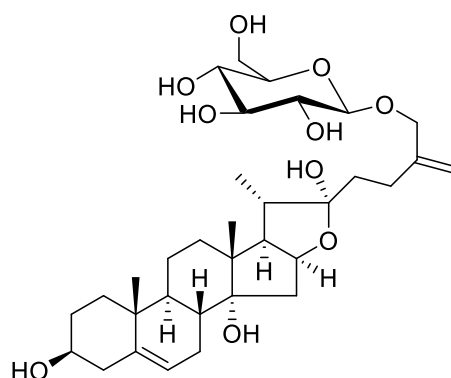


Figure S15. (A) Structure of Compound 15. (B) ESI-MS of Compound 15.

A



CAS Registry Number: Unregistered

Proposed Structure Name: furost-5,25(27)-diene-1 β ,14 α ,22 α ,26-tetraol 26-*O*- β -D-glucopyranoside

Chemical Formula: C₃₃H₅₂O₁₀

MW: 608.4

Plant Material: *P. falcatum*

Rt: 15.32 min

B

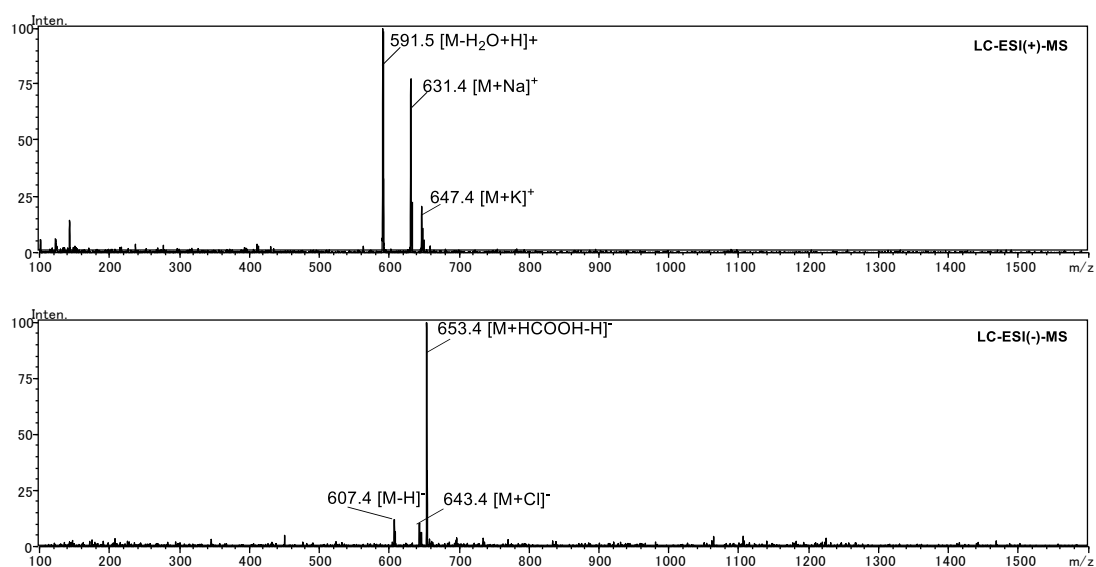
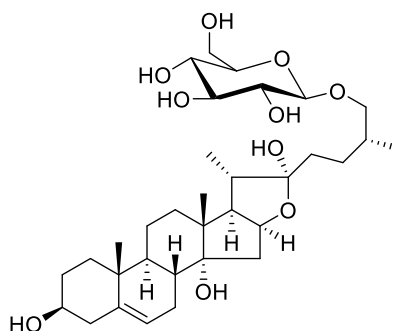


Figure S16. (A) Structure of Compound 16. (B) ESI-MS of Compound 16.

A



CAS Registry Number: Unregistered

Name: (3 β ,22 α ,25 R)-3,14,22-Trihydroxyfurost-5-en-26-yl β -D-glucopyranoside

Chemical Formula: C₃₃H₅₄O₁₀

MW: 610.4

Plant Material: *P. odoratum*, *P. falcatum*, *P. macranthum*

Rt: 15.59 min

B

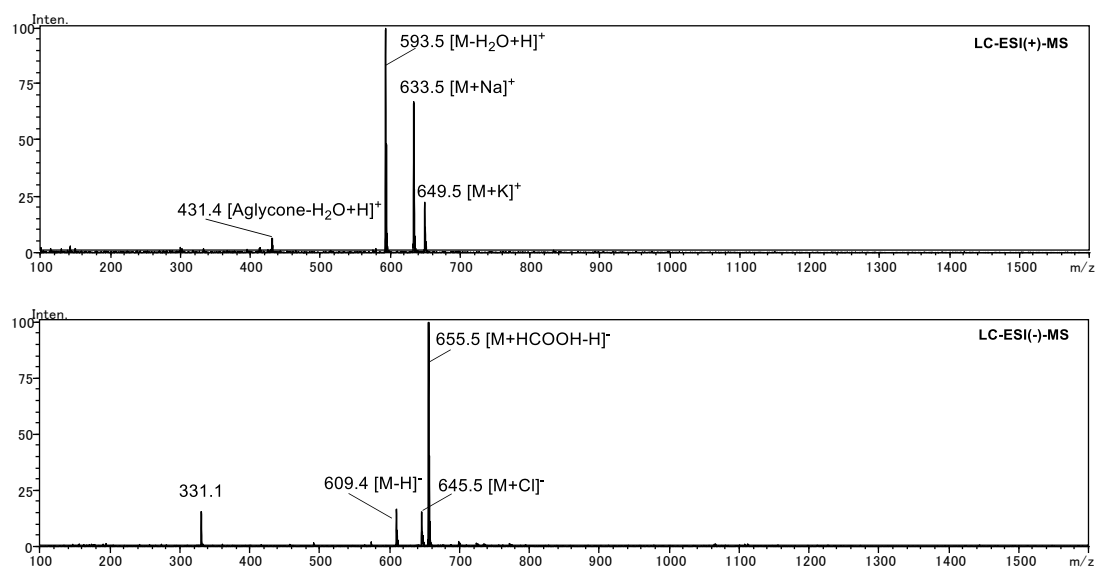
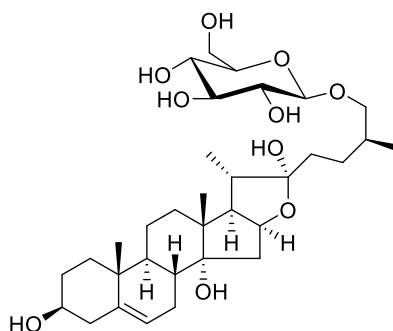


Figure S17. (A) Structure of Compound 17. (B) ESI-MS of Compound 17.

A



CAS Registry Number: 2210235-74-6

Name: poygonatumoside G

Chemical Formula: $C_{33}H_{54}O_{10}$

MW: 610.4

Plant Material: *P. odoratum*, *P. falcatum*, *P. macranthum*

Rt: 15.78 min

B

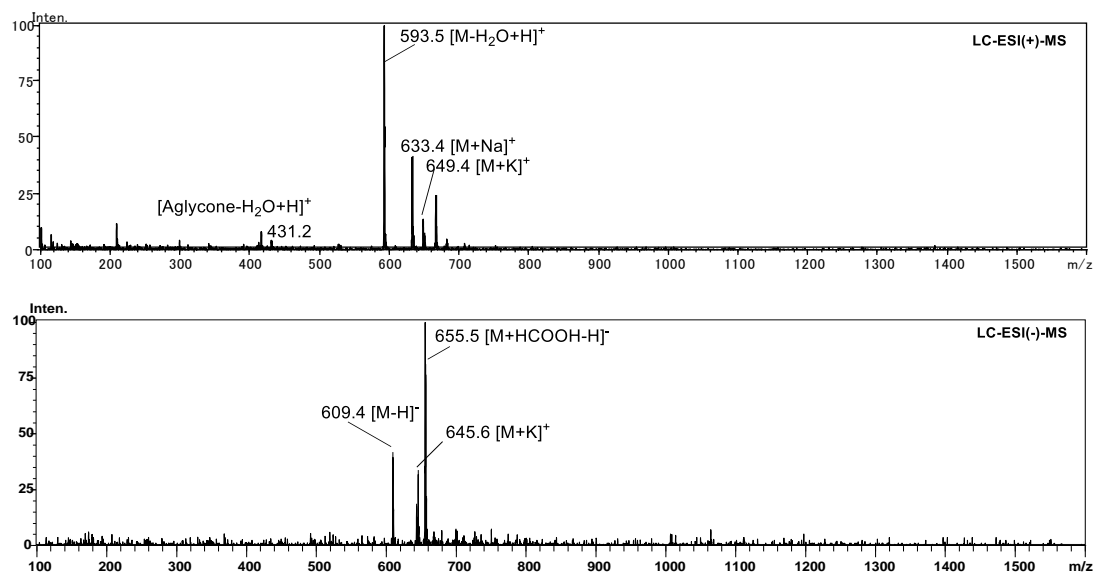
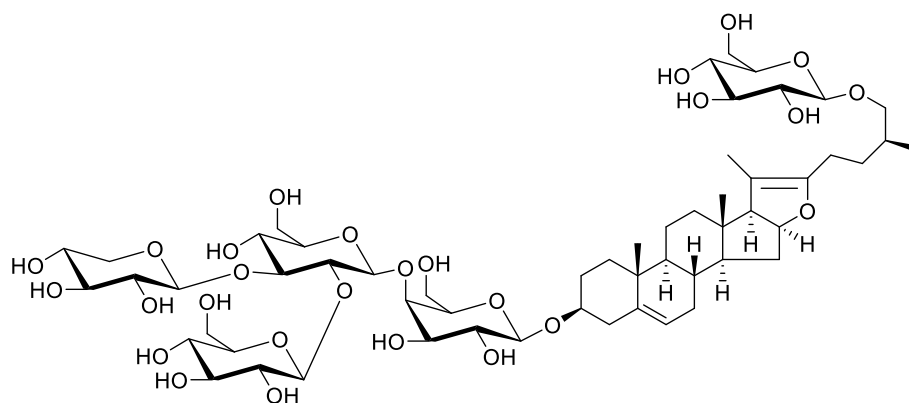


Figure S18. (A) Structure of Compound 18. (B) ESI-MS of Compound 18.

A



CAS Registry Number: 1622248-48-9

Name: polygodoside G

Chemical Formula: $C_{56}H_{90}O_{27}$

MW: 1194.6

Plant Material: *P. odoratum*, *P. falcatum*

Rt: 17.70 min

B

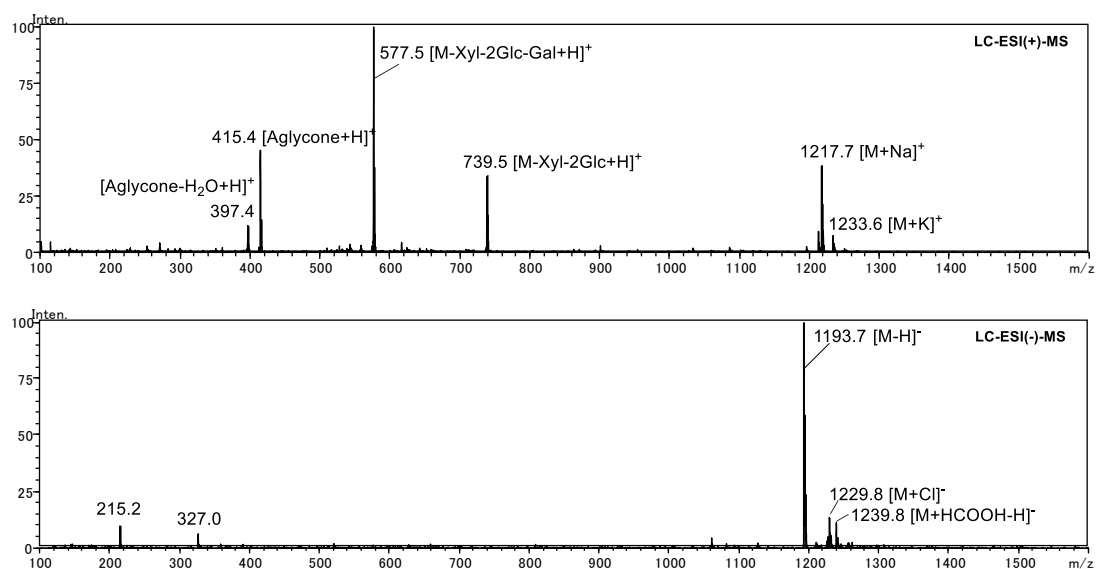
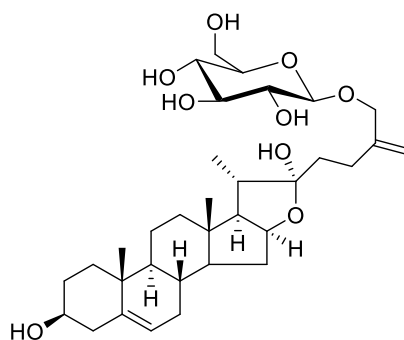


Figure S19. (A) Structure of Compound 19. (B) ESI-MS of Compound 19.

A



CAS Registry Number: Unregistered

Proposed Structure Name: furost-5,25(27)-diene-3 β ,22 α ,26-triol 26-O- β -D-glucopyranoside

Chemical Formula: C₃₃H₅₂O₉

MW: 592.4

Plant Material: *P. falcatum*

Rt: 20.74 min

B

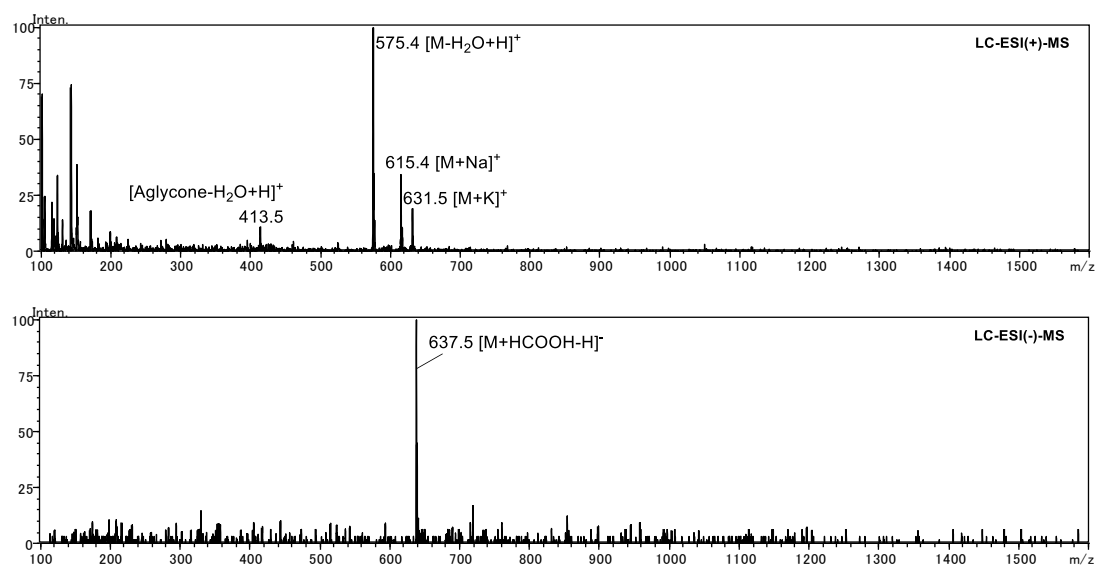
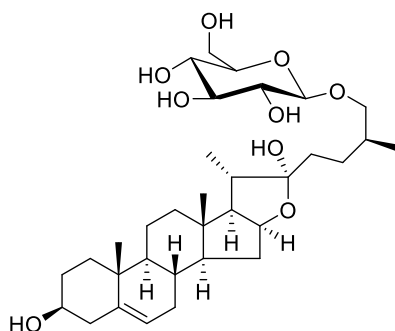


Figure S20. (A) Structure of Compound 20. (B) ESI-MS of Compound 20.

A



CAS Registry Number: 60433-65-0

Name: funkioside B

Chemical Formula: $C_{33}H_{54}O_9$

MW: 594.4

Plant Material: *P. odoratum*, *P. falcatum*, *P. macranthum*

Rt: 21.08 min

B

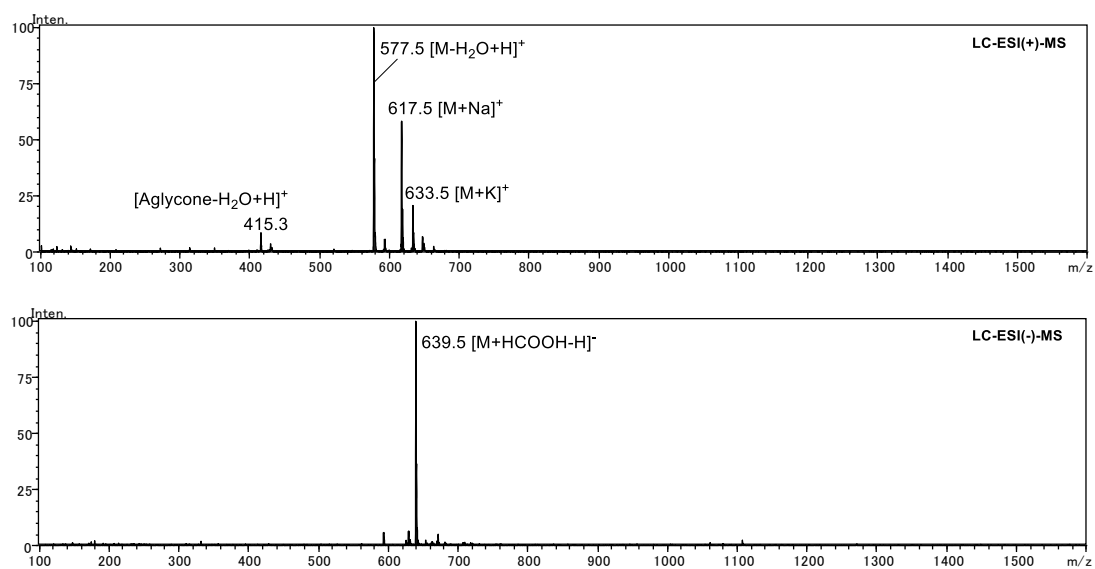
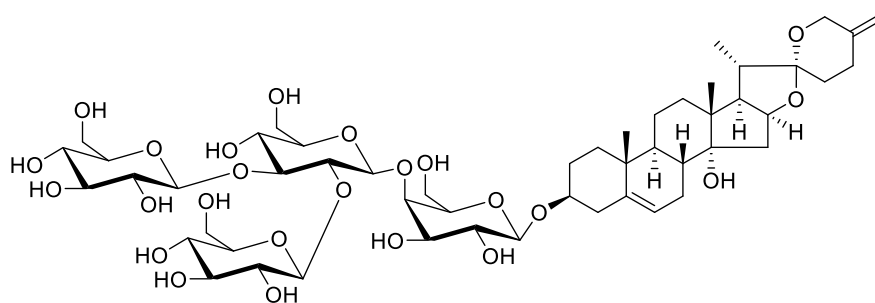


Figure S21. (A) Structure of Compound 21. (B) ESI-MS of Compound 21.

A



CAS Registry Number: 1622248-43-4

Name: polygodoside B

Chemical Formula: $C_{51}H_{80}O_{24}$

MW: 1076.5

Plant Material: *P. macranthum*

Rt: 22.29 min

B

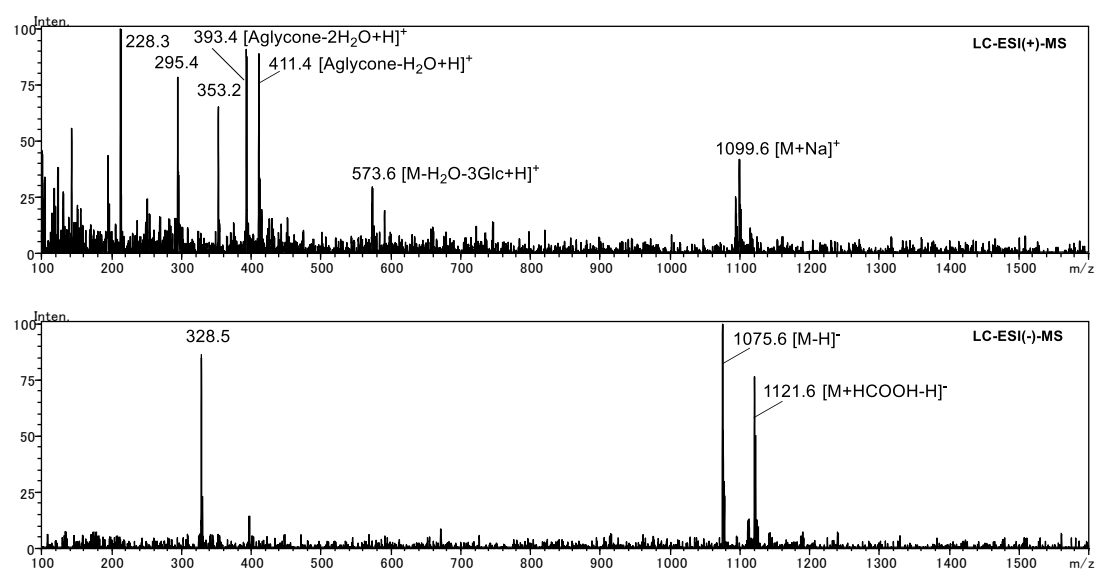
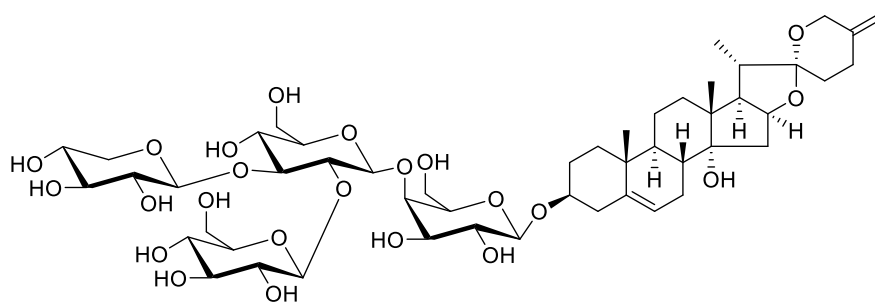


Figure S22. (A) Structure of Compound 22. (B) ESI-MS of Compound 22.

A



CAS Registry Number: 1622248-42-3

Name: polygodoside A

Chemical Formula: $C_{50}H_{78}O_{23}$

MW: 1046.5

Plant Material: *P. falcatum*, *P. macranthum*

Rt: 22.81 min

B

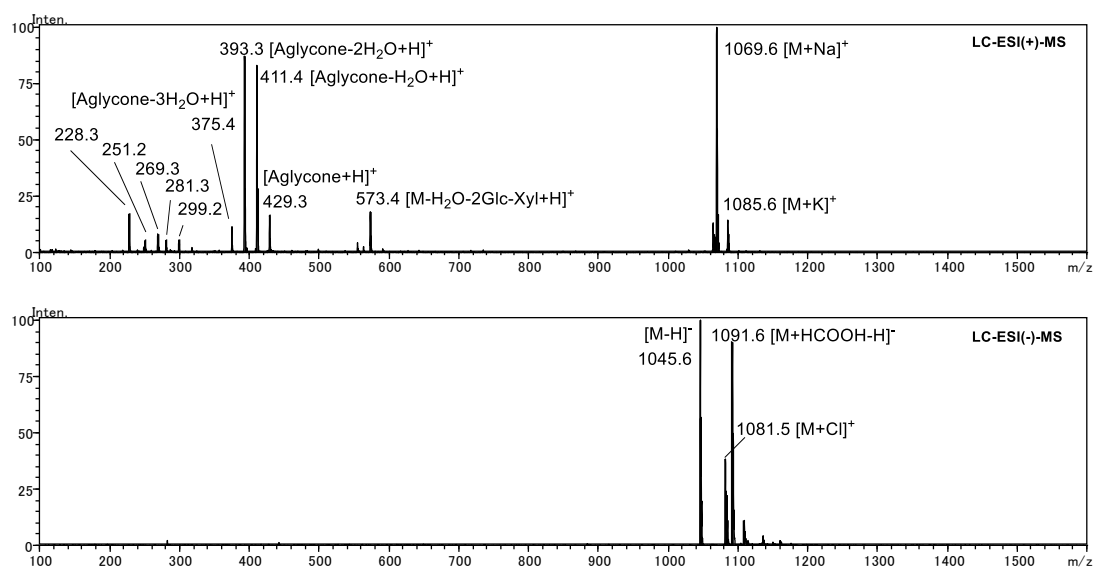
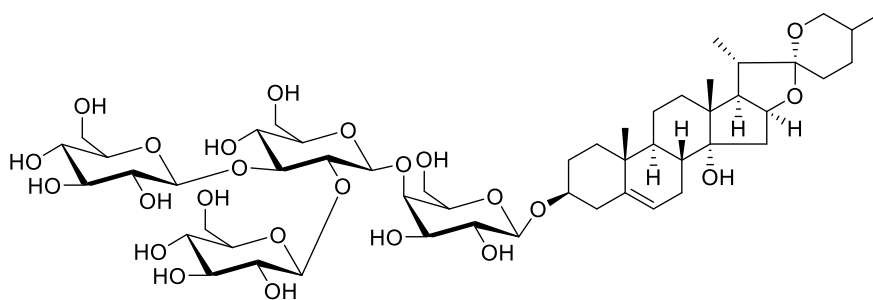


Figure S23. (A) Structure of Compound **23**. (B) ESI-MS of Compound **23**.

A



CAS Registry Number: 156886-91-8

Name: pod III

Chemical Formula: $C_{51}H_{82}O_{24}$

MW: 1078.5

Plant Material: *P. macranthum*, *P. odoratum* var. *maximowiczii*

Rt: 23.12 min

B

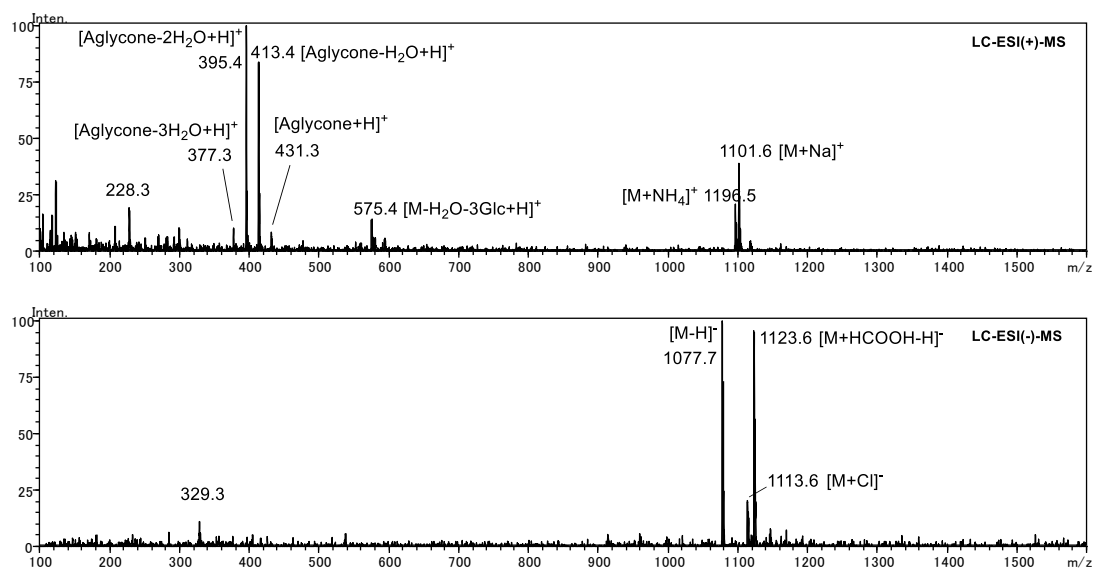
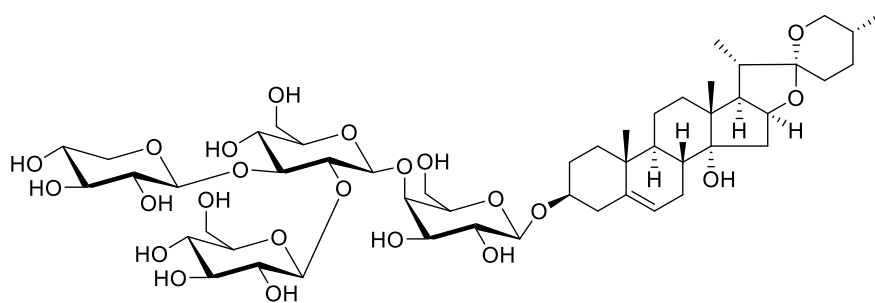


Figure S24. (A) Structure of Compound 24. (B) ESI-MS of Compound 24.

A



CAS Registry Number: Unregistered

Proposed Structure Name: (3 β ,25*R*)-14-Hydroxyspirost-5-en-3-yl *O*- β -D-glucopyranosyl-(1 \rightarrow 2)-*O*-[β -D-xylopyranosyl-(1 \rightarrow 3)]-*O*- β -D-glucopyranosyl-(1 \rightarrow 4)- β -D-galactopyranoside

Chemical Formula: C₅₀H₈₀O₂₃

MW: 1048.5

Plant Material: *P. odoratum*, *P. falcatum*, *P. macranthum*, *P. odoratum* var. *maximowiczii*

Rt: 23.69 min

B

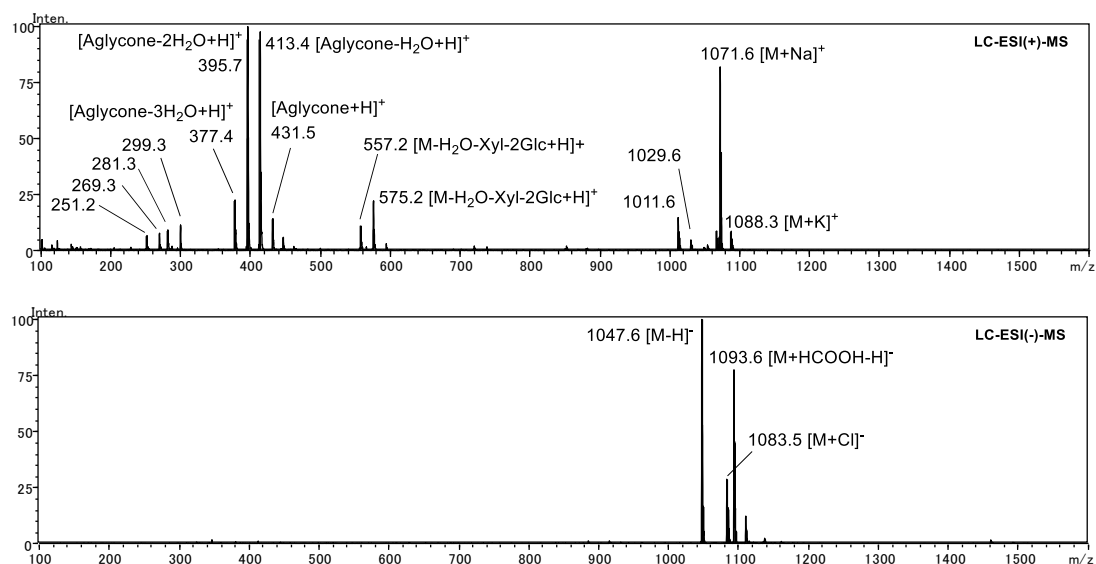
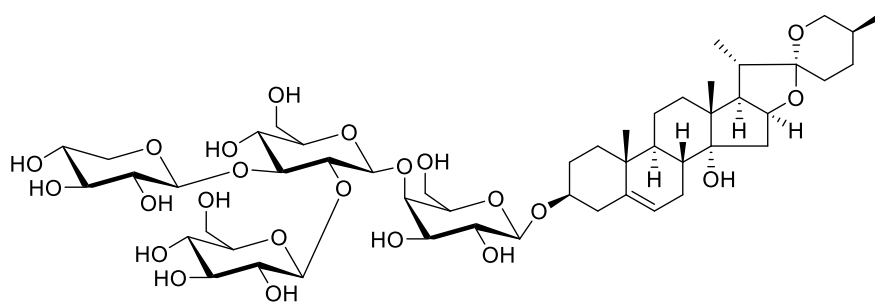


Figure S25. (A) Structure of Compound 25. (B) ESI-MS of Compound 25.

A



CAS Registry Number: 128820-36-0

Proposed Structure Name: (3 β ,25*S*)-14-hydroxyspirost-5-en-3-yl *O*- β -D-glucopyranosyl-(1 \rightarrow 2)-*O*-[β -D-xylopyranosyl-(1 \rightarrow 3)]-*O*- β -D-glucopyranosyl-(1 \rightarrow 4)- β -D-galactopyranoside

Chemical Formula: C₅₀H₈₀O₂₃

MW: 1048.5

Plant Material: *P. odoratum*, *P. falcatum*, *P. macranthum*, *P. odoratum* var. *maximowiczii*

Rt: 23.89 min

B

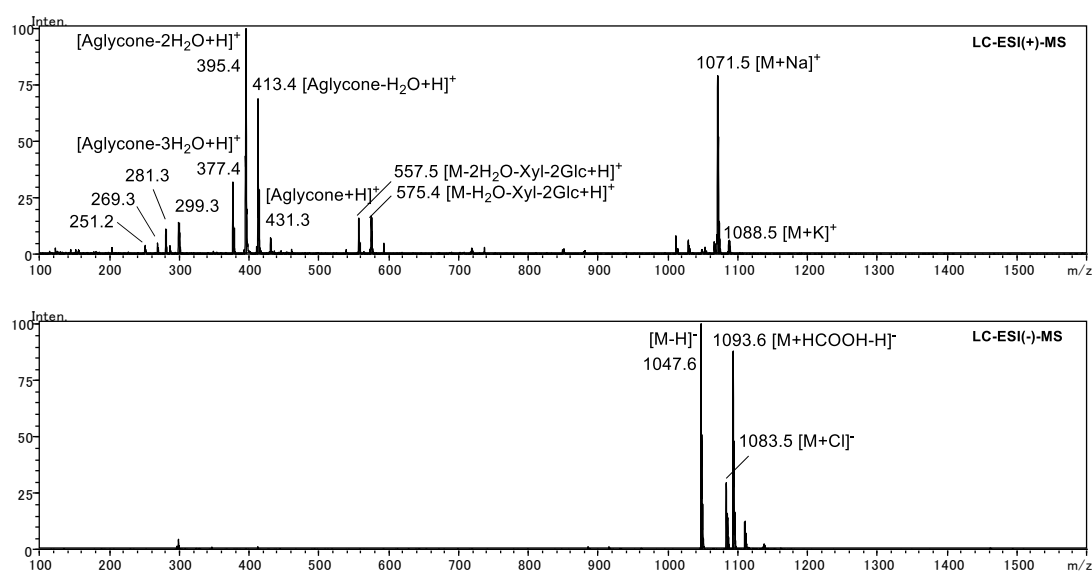
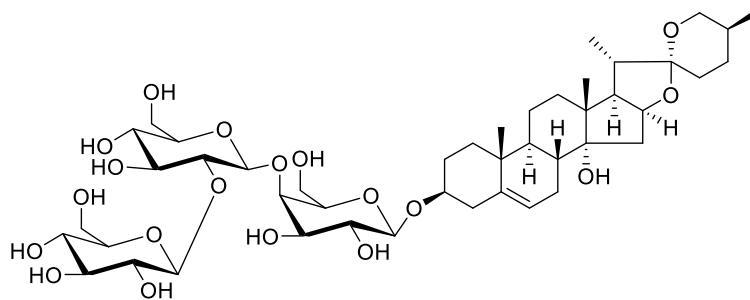


Figure S26. (A) Structure of Compound 26. (B) ESI-MS of Compound 26.

A



CAS Registry Number: 1558002-19-9

Name: polygonatumoside D

Chemical Formula: $C_{45}H_{72}O_{19}$

MW: 916.5

Plant Material: *P. odoratum*, *P. falcatum*, *P. macranthum*, *P. odoratum* var. *maximowiczii*

Rt: 24.26 min

B

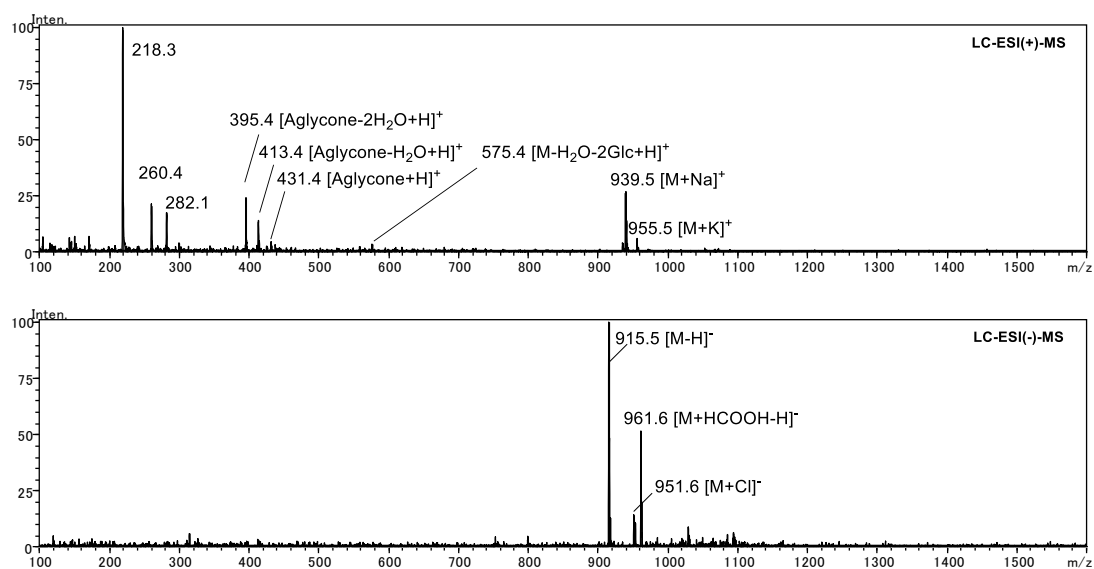
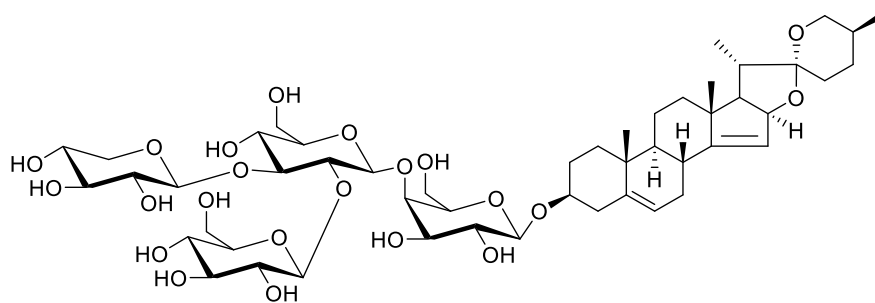


Figure S27. (A) Structure of Compound 27. (B) ESI-MS of Compound 27.

A



CAS Registry Number: 1203607-59-3

Name: (3 β ,25 S)-spirosta-5,14-dien-3-yl *O*- β -D-glucopyranosyl-(1 \rightarrow 2)-*O*-[β -D-xylopyranosyl-(1 \rightarrow 3)]-*O*- β -D-glucopyranosyl-(1 \rightarrow 4)- β -D-galactopyranoside,

Chemical Formula: C₅₀H₇₈O₂₂

MW: 1030.5

Plant Material: *P. falcatum*

Rt: 29.21 min

B

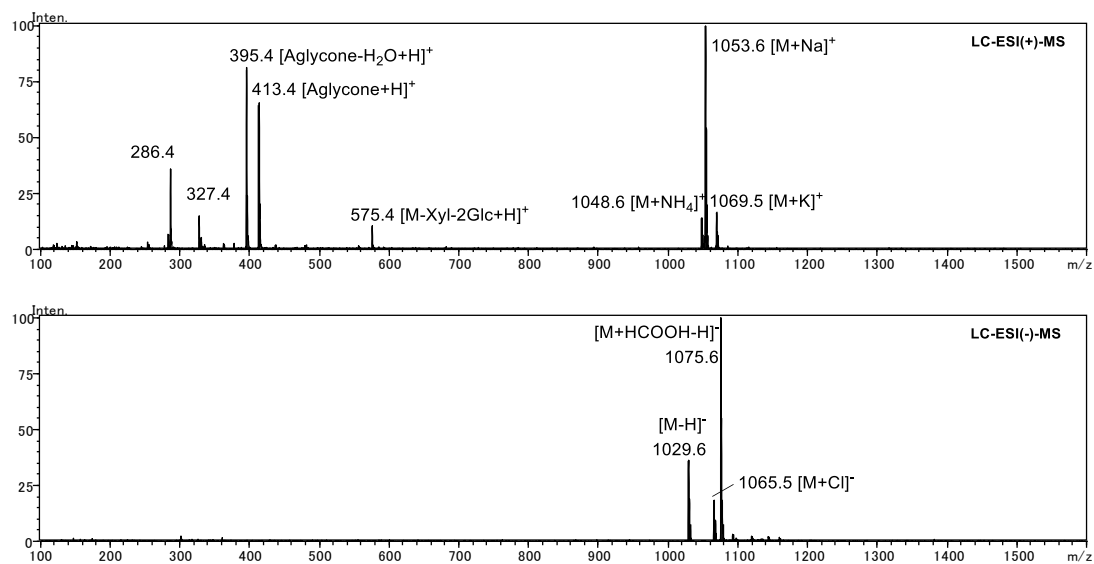
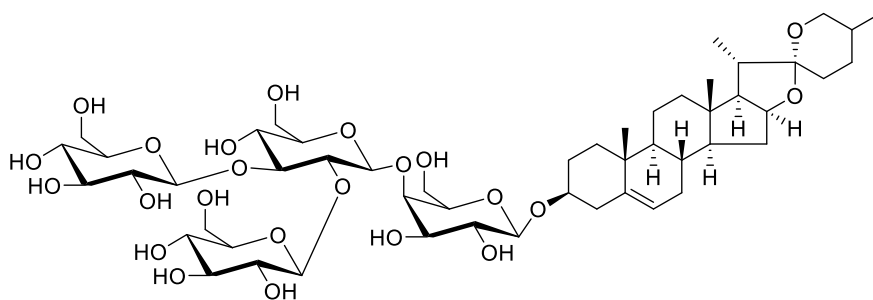


Figure S28. (A) Structure of Compound 28. (B) ESI-MS of Compound 28.

A



CAS Registry Number: 108886-02-8

Name: odospiroside, pod IV

Chemical Formula: $C_{51}H_{82}O_{23}$

MW: 1062.5

Plant Material: *P. macranthum*, *P. odoratum* var. *maximowiczii*

Rt: 29.71 min

B

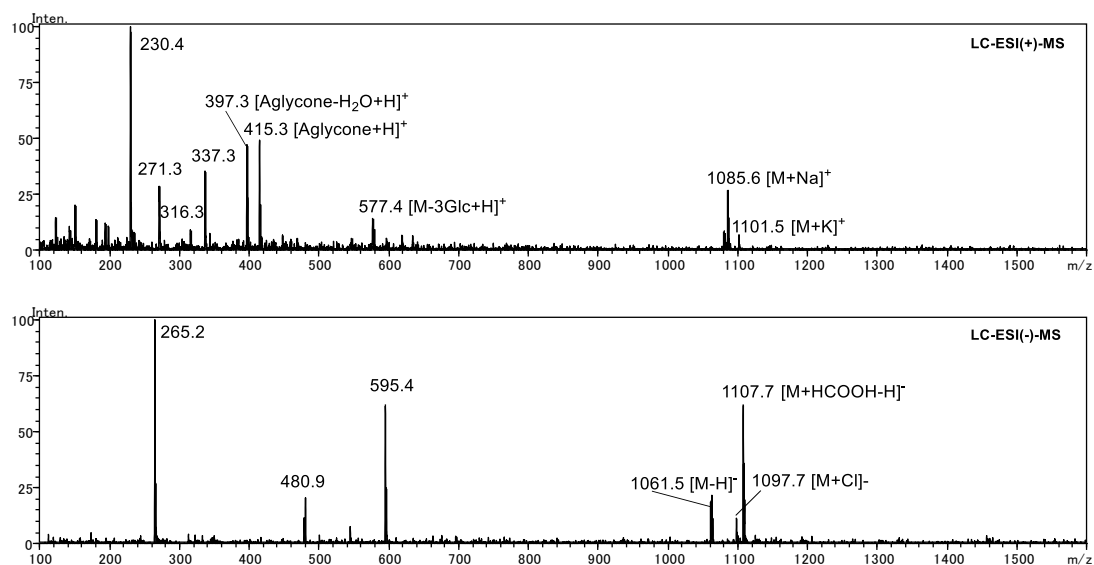
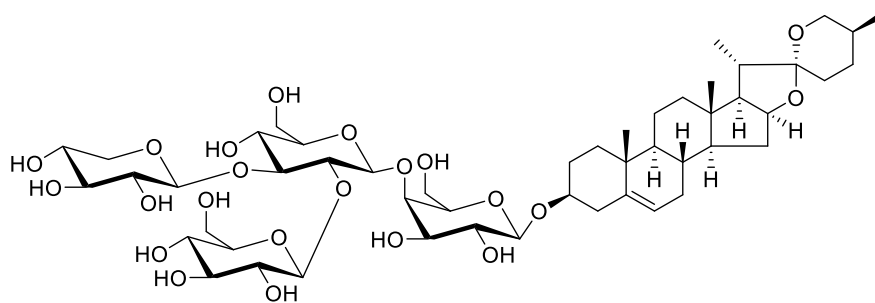


Figure S29. (A) Structure of Compound **29**. (B) ESI-MS of Compound **29**.

A



CAS Registry Number: 91327-42-3

Name: aspidistrin

Formula: $C_{50}H_{80}O_{22}$

MW: 1032.5

Plant Material: *P. odoratum*, *P. falcatum*, *P. macranthum*

Rt: 30.52 min

B

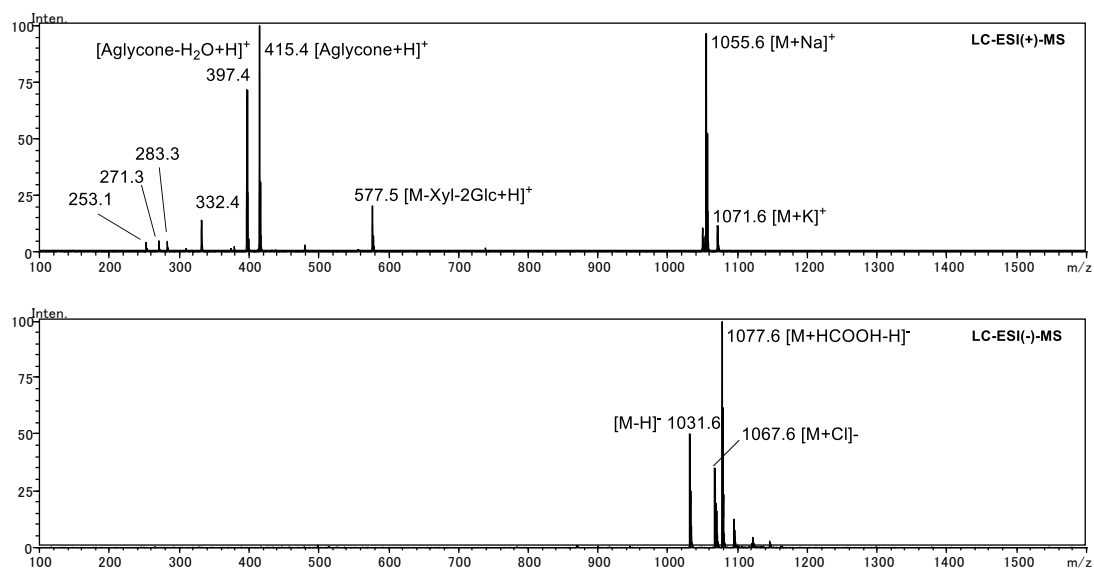
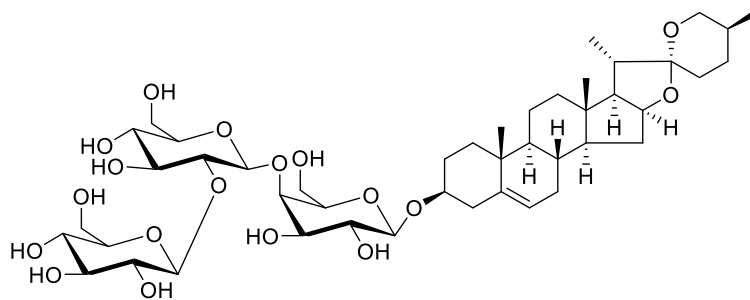


Figure S30. (A) Structure of Compound 30. (B) ESI-MS of Compound 30.

A



CAS Registry Number: 78101-16-3

Name: 25S-neosibiricoside D

Chemical Formula: $C_{45}H_{72}O_{18}$

MW: 900.5

Plant Material: *P. odoratum*, *P. falcatum*, *P. macranthum*

Rt: 31.16 min

B

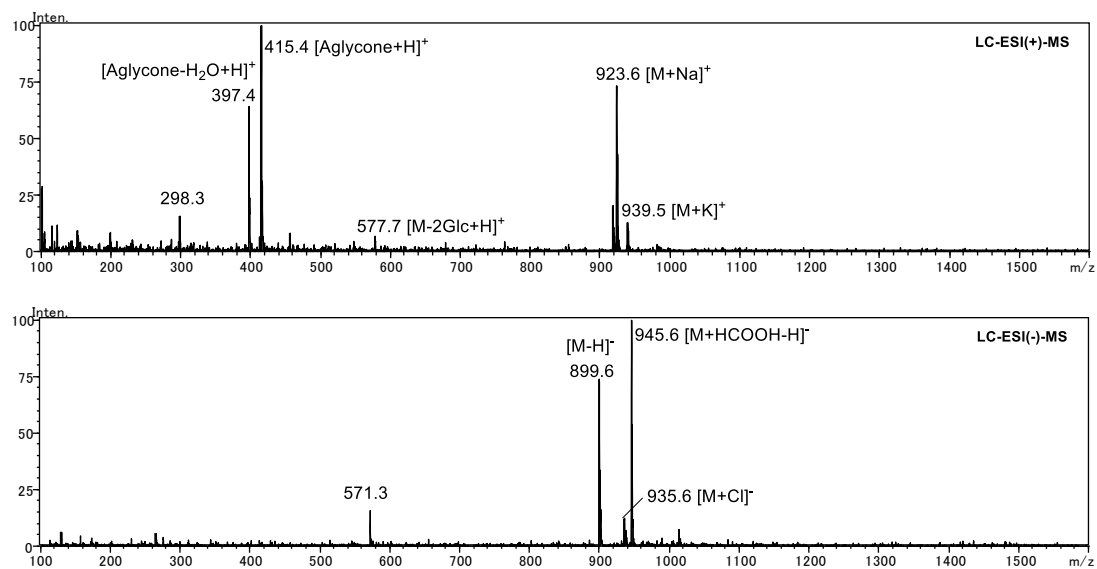
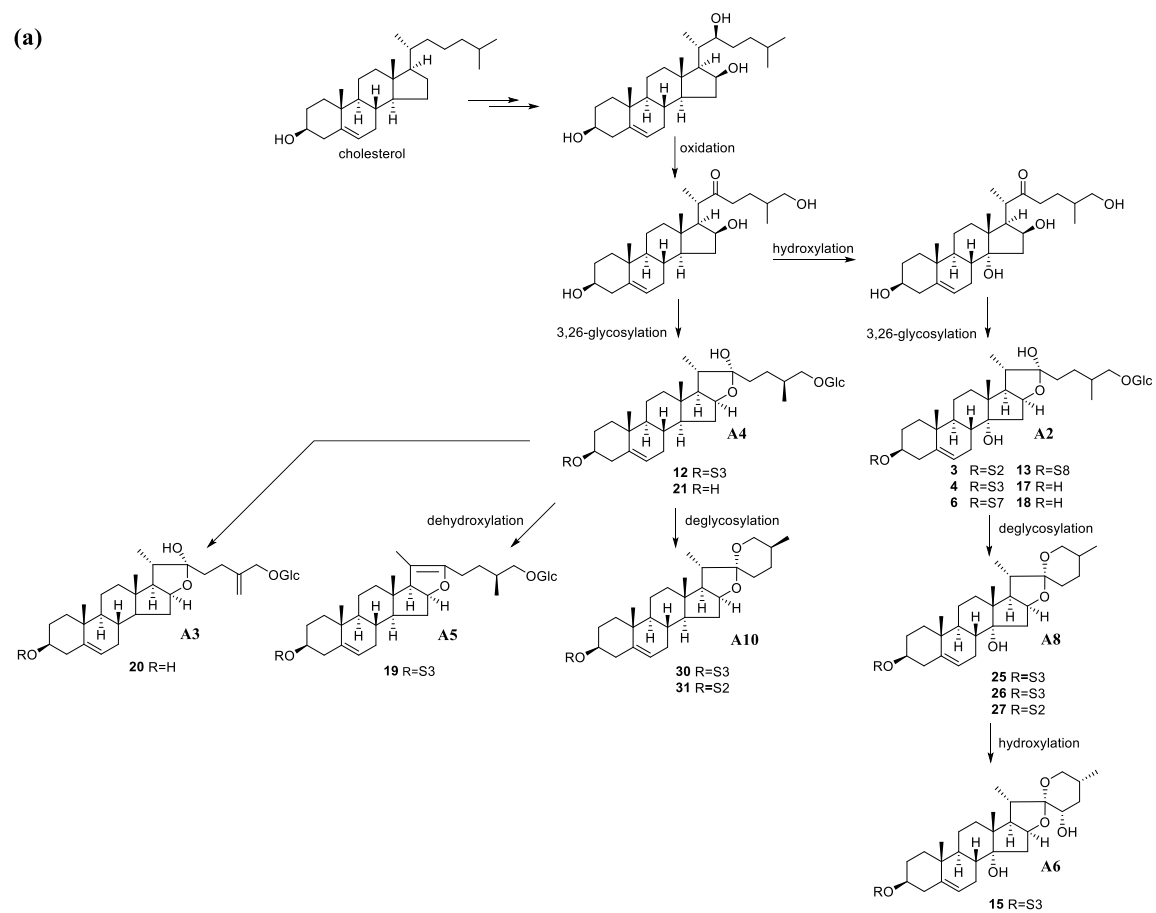
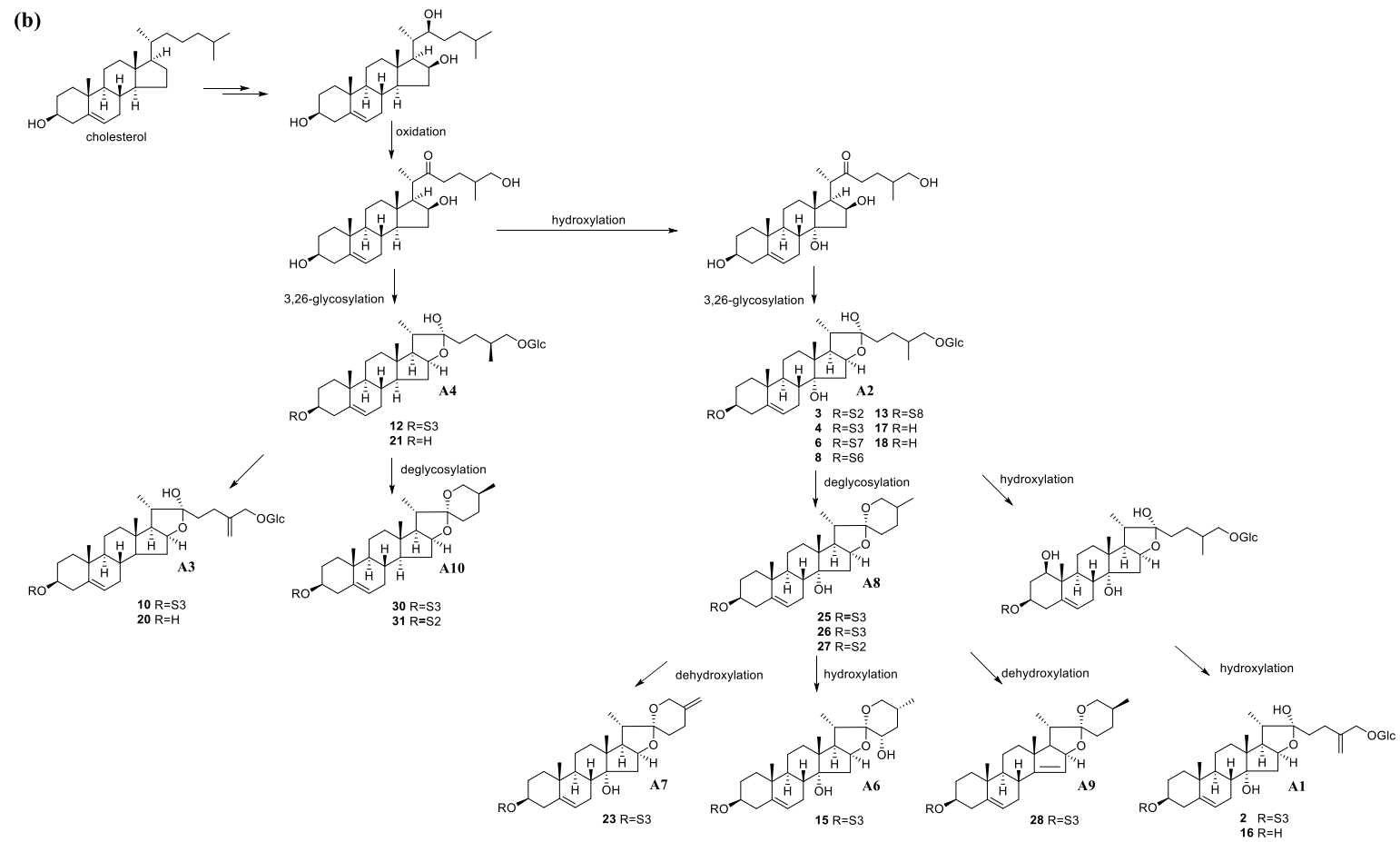


Figure S31. (A) Structure of Compound 31. (B) ESI-MS of Compound 31.

(a)





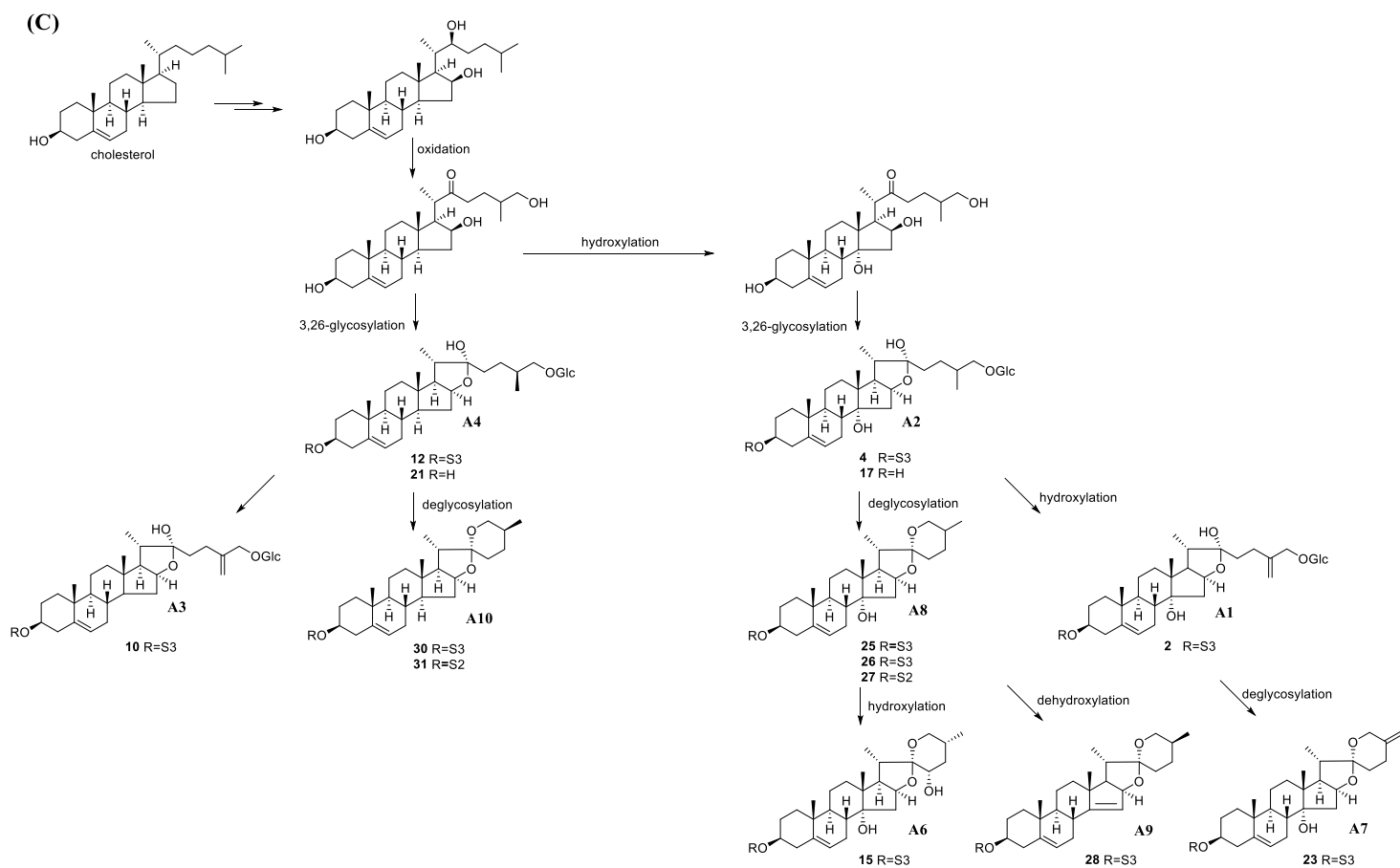


Figure S32. Biogenetic pathway for the steroidal glycoside from *Polygonatum* species collected in July: (a) *P. odoratum*; (b) *P. falcutum*; (c) *P. macranthum*.

Table S1. NMR Spectroscopic Data (500 MHz for ^1H and 125 MHz for ^{13}C , in Pyridine-*d*5) of Compound **15**.

number aglycone	δ_{C}	δ_{H}	number sugar	δ_{C}	δ_{H}
1	37.7	0.96, td (10.2, 3.0) 1.66, m	3- <i>O</i> -sugar β -D-Gal		
2	30.2	1.62 ^a , m 2.01 ^a , m	1	102.7	4.77, d (7.7)
3	78.3	3.77, m	2	73.2	4.32, dd (9.4, 7.7)
4	39.3	2.36, m 2.57, ddd (13.5, 4.6, 2.3)	3	75.6	4.00, dd (9.4, 3.3)
5	140.6		4	79.8	4.49, brd (3.3)
6	122.2	5.29, t (2.9, 2.0)	5	75.3	3.87 ^a , m
7	26.7	1.78, m 2.42, m	6	60.6	4.06 ^a 4.55, t (9.3)
8	35.5	1.96, td (11.2, 5.8)	β -D-Glc1		
9	43.6	1.72, m	1	105.1	5.08, d (7.7)
10	37.4		2	81.3	4.30, dd (8.6, 7.7)
11	20.4	1.45, 2H, m	3	87.0	4.06, t (8.6)
12	32.2	1.43, m 2.21, m	4	70.5	3.73, t (9.5)
13	45.7		5	77.6	3.77, m
14	86.6		6	63.0	3.97 ^a 4.42, dd (11.8, 1.8)
15	39.8	1.86, dd (12.3, 7.5) 2.27, dd (12.3, 7.5)	β -D-Glc2		
16	82.4	5.11, m	1	104.8	5.48, d (7.7)
17	59.6	2.76, t (7.5)	2	76.2	3.97, dd, (8.9, 7.7)
18	20.3	1.19, s	3	77.8	4.03, t (8.9)
19	19.3	0.86, s	4	71.2	4.10, t (8.9)
20	35.8	3.09, qui (6.9)	5	78.7	3.82, m
21	15.0	1.17, d (6.9)	6	62.6	4.29, dd (12.2, 4.6) 4.46, dd (12.2, 1.9)
22	111.9		β -D-Xyl		
23	67.6	3.82 ^a	1	105.0	5.14, d (7.8)
24	38.9	1.73, m 2.04, m	2	75.1	3.88, t (8.0)
25	31.7	1.74 ^a	3	78.7	3.99, t (8.9)
26	66.0	3.40, t (10.9) 3.44, ddd (10.9, 4.6, 1.4)	4	70.8	4.03, t (8.9)
			5	67.3	3.59, dd (11.0, 10.3) 4.15, dd (11.0, 4.9)

27 16.9 0.65, brd (6.1)

^aOverlapped with other signals.
