Supplementary Material

Biosynthesis of natural and non-natural genistein glycosides

Prakash Parajuli,[a] Ramesh Prasad Pandey,[a,b] Trang Thi Huyen Nguyen, [a] Biplav Shrestha,[a] Tokutaro Yamaguchi, [a,b] Jae Kyung Sohng[a,b]

[a]*Department of Life Science and Biochemical Engineering, Sun Moon University, 70 Sunmoon-ro 221, Tangjeong-myeon Asan-Si, Chungnam 31460, Republic of Korea*

[b]*Department of BT-Convergent Pharmaceutical Engineering, Sun Moon University, 70 Sunmoon-ro 221, Tangjeong-myeon Asan-Si, Chungnam 31460, Republic of Korea*

Running Title: Natural product modification and biosynthesis

Address correspondence to Prof. Jae Kyung Sohng
Tel: +82(41)530-2246
Fax: +82(41)544-2919
Email: sohng@sunmoon.ac.kr

Figure Legends

Figure S1

Confirmation of gene cloning in agarosegel electrophoresis of two surgar *O*-methyltransferases. **A)** Gel picture of PCR amplication of SpnH and SpnK with exact gene size 753 bp and 1194 bp respectively. **B)** Confirmation of each SpnH and SpnK gene ligation into pGEM® -T easy vector by enzyme restriction digestion. **C)** Confirmation of each SpnH and SpnK gene ligation into expression vector pET32a by enzyme restriction digestion.

Figure S2

SDS-PAGE analyses of soluble fractions of sugar *O*-methyltransferases (SpnK and SpnH) proteins compared with the standard 100 kDa sized marker in the middle including BL21 (DE3)-pET32a as control.

Figure S3

HRQTOF ESI/MS analyses of the reaction mixtures catalyzed by GTs and along with SOMTs. Mass analyses of reaction mixtures catalyzed by AtUGT89C1 (A and B), Mass analyses of reaction mixture catalyzed by AtUGT89C1 co-expression with SpnK (C), Mass analyses of reaction mixture catalyzed by AtUGT89C1 co-expression with SpnH (D), Mass analyses of *in vivo* reaction mixture catalyzed by YjiC (E, F and G) and Mass analyses of *in vitro* reaction mixture catalyzed by YjiC (H, I, J and K)

Figure S4

A. Genistein 7-*O*-*α*-L-rhamnopyranoside (^{1}H NMR)
B. Genistein 7-*O*-*α*-L-rhamnopyranoside (^{13}C NMR)
C. Genistein 7-*O*-*α*-L-rhamnopyranoside (HMBC)

Figure S5

A. Genistein 7-*O*- *β*-D-glucopyranoside (^{1}H NMR)
B. Genistein 7-*O*- *β* -D-glucopyranoside (^{13}C NMR)
C. Genistein 7-*O*- *β* -D-glucopyranoside (HMBC)
D. Genistein 7-*O*- *β* -D-glucopyranoside (HMBC)

Figure S6

A. Genistein 7-*O*- 3''-*O*-methyl -*α*-L-rhamnopyranoside (^{1}H NMR)
B. Genistein 7-*O*- 3''-*O*-methyl -*α*-L-rhamnopyranoside (^{13}C NMR)
C. Genistein 7-*O*- 3''-*O*-methyl -*α*-L-rhamnopyranoside (HMBC)
D. Genistein 7-*O*- 3''-*O*-methyl -*α*-L-rhamnopyranoside (HMBC)

Figure S7

A. Genistein 7-*O*- 4''-*O*-methyl -*α*-L-rhamnopyranoside (^{1}H NMR)

B. Genistein 7-*O*- 4''-*O*-methyl -*α*-L-rhamnopyranoside (^{13}C NMR)

C. Genistein 7-*O*- 4''-*O*-methyl -*α*-L-rhamnopyranoside (HMBC)

D. Genistein 7-*O*- 4''-*O*-methyl -*α*-L-rhamnopyranoside (HMBC)

Figure S8

A. Genistein 4', 7-*O*-*β*-2-D-diglucopyranoside (^{1}H NMR)

B. Genistein 4', 7-*O*-*β*-2-D-diglucopyranoside (^{13}C NMR)

C. Genistein 4', 7-*O*-*β*-2-D-diglucopyranoside (HMBC)

Figure S9

A. Genistein 4'-*O*-*β*-2-D-glucopyranoside (^{1}H NMR)

B. Genistein 4'-*O*-*β*-2-D-glucopyranoside (^{13}C NMR)

C. Genistein 4'-*O*-*β*-2-D-glucopyranoside (HMBC)

Figure S10

A. Genistein 7-*O*-*β*-2-D-glucopyranoside (^{1}H NMR)

B. Genistein 7-*O*-*β*-2-D-glucopyranoside (^{13}C NMR)

C. Genistein 7-*O*-*β*-2-D-glucopyranoside (HMBC)

Figure S11

A. Genistein 4', 7-*O*- *β* -2-deoxy D-diglucopyranoside (^{1}H NMR)

B. Genistein 4', 7-*O*- *β* -2-deoxy D-diglucopyranoside (^{13}C NMR)

C. Genistein 4', 7-*O*- *β* -2-deoxy D-diglucopyranoside (HMBC)

D. Genistein 4', 7-*O*- *β* -2-deoxy D-diglucopyranoside (HMBC)

Figure S12

A. Genistein 4'-*O*- *β* -2-deoxy D-glucopyranoside (^{1}H NMR)

B. Genistein 4'-*O*- *β* -2-deoxy D-glucopyranoside (^{13}C NMR)

C. Genistein 4'-*O*- *β* -2-deoxy D-glucopyranoside (HMBC)

D. Genistein 4'-*O*- *β* -2-deoxy D-glucopyranoside (HMBC)

Figure S13

A. Genistein 7-*O*- *β* -2-deoxy D-glucopyranoside (^{1}H NMR)

B. Genistein 7-*O*- *β* -2-deoxy D-glucopyranoside (^{13}C NMR)

C. Genistein 7-*O*- *β* -2-deoxy D-glucopyranoside (HMBC)

D. Genistein 7-*O*- *β* -2-deoxy D-glucopyranoside (HMBC)

Figure S14

Anti-fungal activity test of each genistein derivatives (concentration was 500 µg/mL) comparing with 100 µg/mL concentration Nystatin A1 (Ny-A1) antifungal agent. DMSO (100%) was also used as control since each compounds were dissolved in DMSO. The number represents: 1. Genistien, 2. Genistein 7-*O*-*α*-L-rhamnopyranoside, 3. Genistein 7-*O*-3″-*O*-*α*-L-rhamnopyranoside, 4. Genistein 7-*O*-4″-*O*-*α*-L-rhamnopyranoside, 5. Genistein 7-*O*-*β*-D-glucopyranoside, 6. Genistein 4′, 7-*O*-*β*-D-diglucopyranoside, 7. Genistein 4′-*O*-*β*-D-glucopyranoside, 8. Genistein 7-*O*-*β*-D-2-deoxy glucopyranoside, 9. Genistein 4′-*O*-*β*-D-2-deoxy glucopyranoside, 11. Genistein 4′, 7-*O*-*β*-D-2-deoxy diglucopyranoside.

Cloning of SOMTs

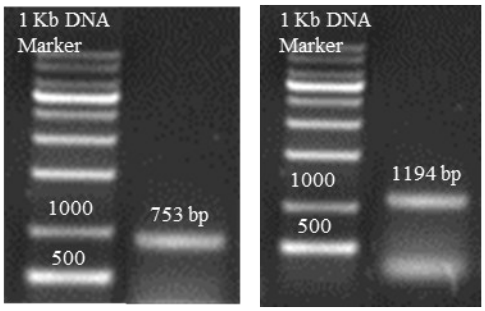
Two SOMTs from *S. spinosa* were PCR amplified to the size of *spnK* (1194 bp) and *spnH* (753 bp). These PCR products were ligated into the pGEM®-T easy vector. The sequence for each gene was confirmed and inserted into the expression vector pET32a+ in the respective restriction site as explained in the materials and methods. After cloning into vectors, enzyme restriction digestions were performed to confirm the ligation of the target genes (Fig. S1). These recombinant plasmids were transformed into *E. coli* BL21 (DE3) expression hosts for protein expression analyses and further biotransformation experiments.

SDS-PAGE analysis for sugar *O*-methyltransferase

Recombinant strains harboring SOMTs were cultured in LB medium and prepared for protein expression. The culture conditions were maintained and induced by IPTG as mentioned in the materials and methods. Properly grown cells were finally harvested for analysis of the soluble proteins. Soluble and insoluble lysates were separated. Only soluble fractions of both proteins were analyzed by SDS-PAGE gel electrophoresis to determine the functional expression for comparison with the 100 kDa sized marker. The recombinant strain with the expression vector pET32a+ without genes was used as the control. During the analysis, distinct protein bands for *spnK* and *spnH* were visible at ~ 56.7 kDa and ~ 41.8 kDa, respectively (Fig. S2).

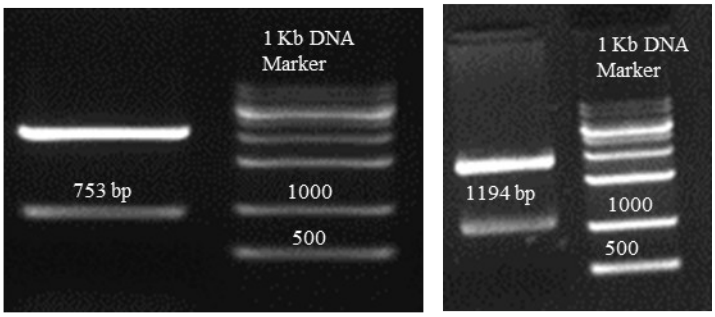
Figure S1

A



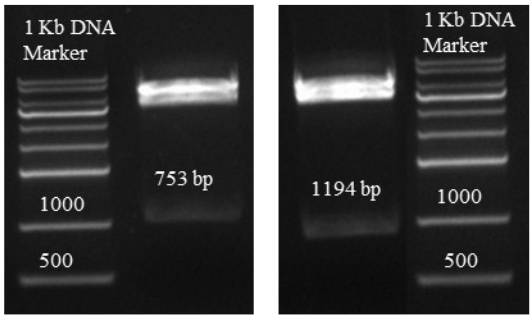
PCR amplification of SpnH and SpnK
Size (SpnH: 753 bp and SpnK: 1194 bp)

B



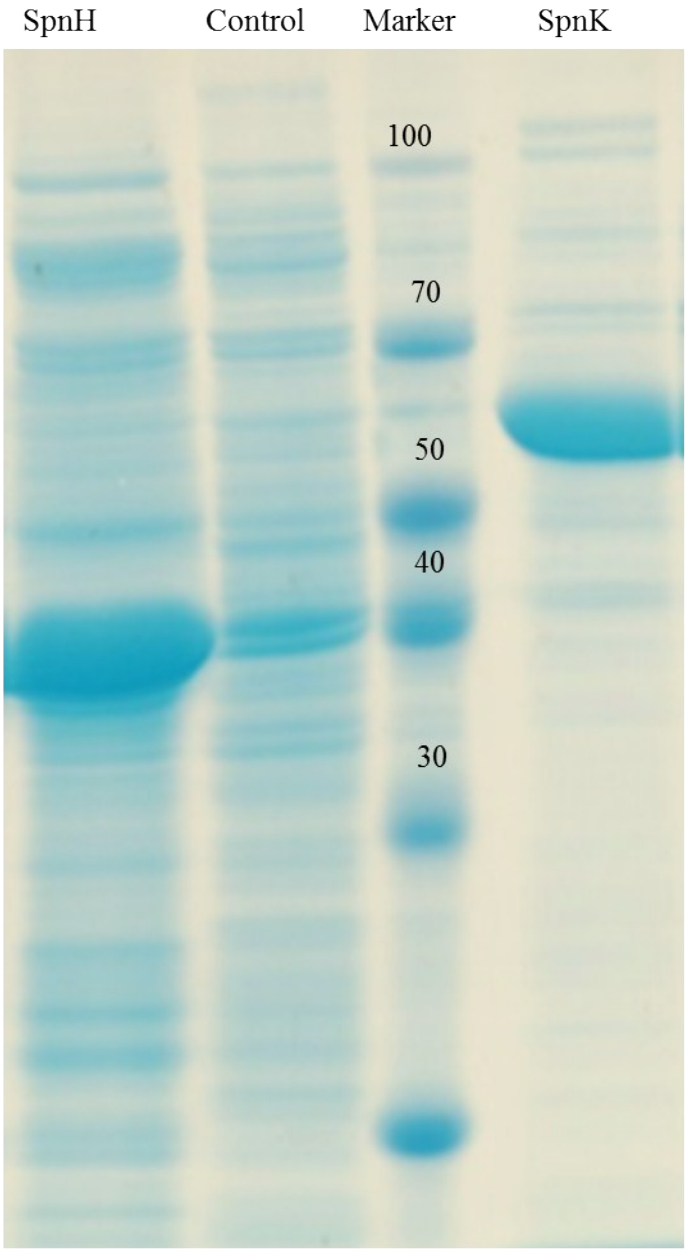
pGEM®-T easy vector ligation of SpnH and SpnK

C



pET32a+ vector ligation of SpnH and SpnK

Figure S2



SpnH: Soluble fraction of SpnH; SpnK: Soluble fraction of SpnK; Control: BL21 (DE3)-pET32a and Marker: Standard size marker (100 kDa).

Figure S3

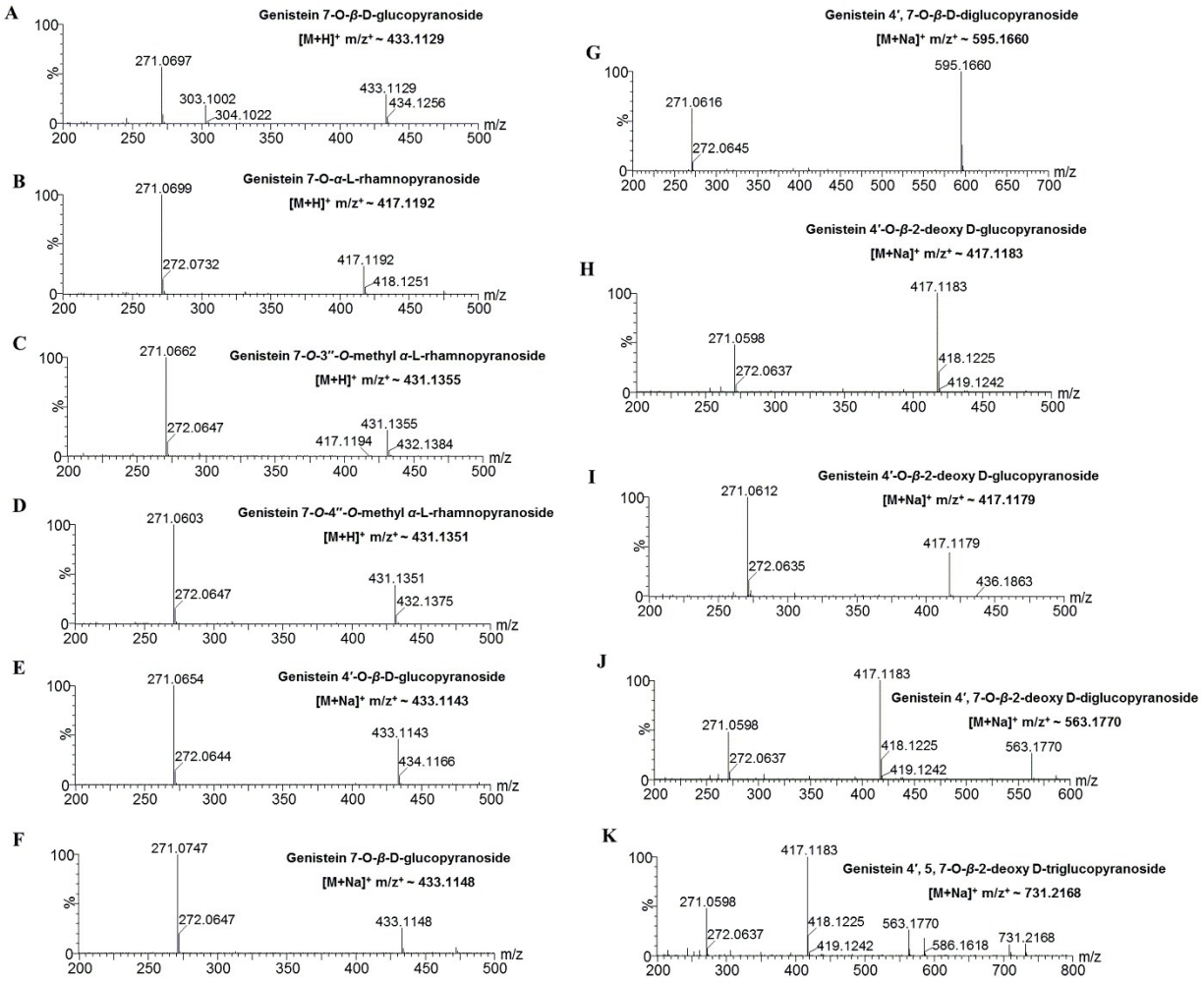
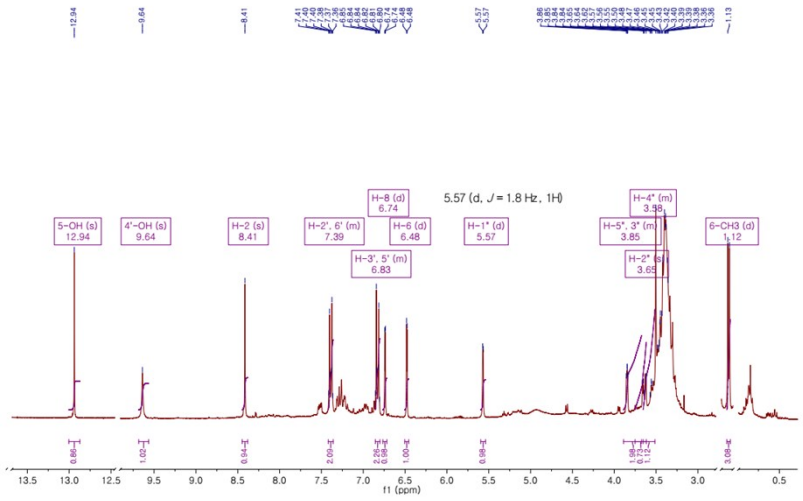

A
Genistein 7-O-β-D-glucopyranoside
[M+H]+ m/z+ ~ 433.1129
271.0697
303.1002
304.1022
433.1129
434.1256
B
Genistein 7-O-α-L-rhamnopyranoside
[M+H]+ m/z+ ~ 417.1192
271.0699
272.0732
417.1192
418.1251
C
Genistein 7-O-3''-O-methyl α-L-rhamnopyranoside
[M+H]+ m/z+ ~ 431.1355
271.0662
272.0647
417.1194
431.1355
432.1384
D
Genistein 7-O-4''-O-methyl α-L-rhamnopyranoside
[M+H]+ m/z+ ~ 431.1351
271.0603
272.0647
431.1351
432.1375
E
Genistein 4'-O-β-D-glucopyranoside
[M+Na]+ m/z+ ~ 433.1143
271.0654
272.0644
433.1143
434.1166
F
Genistein 7-O-β-D-glucopyranoside
[M+Na]+ m/z+ ~ 433.1148
271.0747
272.0647
433.1148
G
Genistein 4', 7-O-β-D-diglucopyranoside
[M+Na]+ m/z+ ~ 595.1660
271.0616
272.0645
595.1660
H
Genistein 4'-O-β-2-deoxy D-glucopyranoside
[M+Na]+ m/z+ ~ 417.1183
271.0598
272.0637
417.1183
418.1225
419.1242
I
Genistein 4'-O-β-2-deoxy D-glucopyranoside
[M+Na]+ m/z+ ~ 417.1179
271.0612
272.0635
417.1179
436.1863
J
Genistein 4', 7-O-β-2-deoxy D-diglucopyranoside
[M+Na]+ m/z+ ~ 563.1770
271.0598
272.0637
417.1183
418.1225
419.1242
563.1770
K
Genistein 4', 5, 7-O-β-2-deoxy D-triglucopyranoside
[M+Na]+ m/z+ ~ 731.2168
271.0598
272.0637
417.1183
418.1225
419.1242
563.1770
586.1618
731.2168

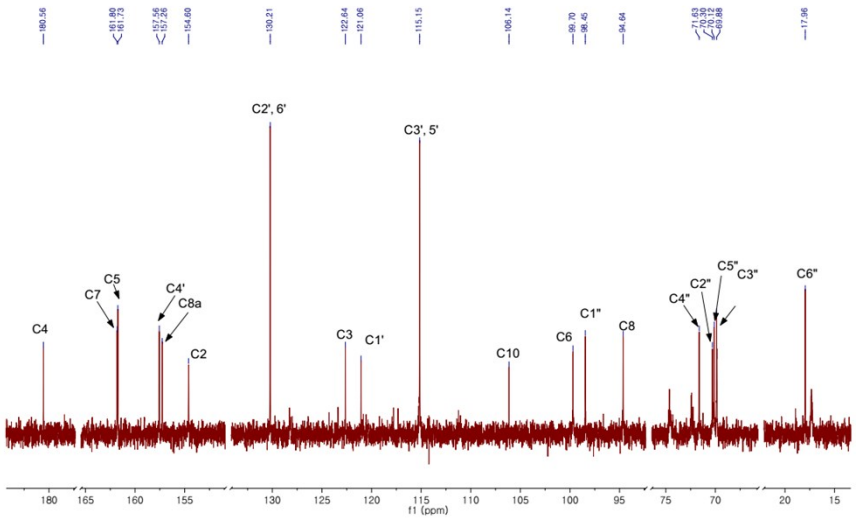
Figure S4

A. Genistein 7-*O*-*α*-L-rhamnpyranoside (^{1}H NMR)



(^{1}H NMR) δ_H (300 MHz, dmso) 1.12 (6-CH_3), 3.0 - 4.0 (Sugar protons), 5.57 (1"-H), 6.48 (6-H), 6.74 (8-H), 6.83 (3', 5'-H), 7.39 (2', 6'-H), 8.41 (2-H), 12.94 (5-OH).

B. Genistein 7-*O*-*α*-L-rhamnopyranoside (^{13}C NMR)



(^{13}C NMR) δ_C (75 MHz, dmso) 17.96 (C6"), 69.88 (C3"), 70.12 (C5"), 70.30 (C2"), 71.63 (C4"), 94.64 (C8), 98.45 (C1"), 99.70 (C6), 106.14 (C10), 115.15 (3', 5'-C), 121.06 (C1'), 122.64 (C3), 130.21 (2', 6'-C), 154.60 (C2), 157.26 (C8a), 157.56 (C4'), 161.73 (C5), 161.80 (C7), 180.56(C4).

C. Genistein 7-*O*-*α*-L-rhamnopyranoside (HMBC)

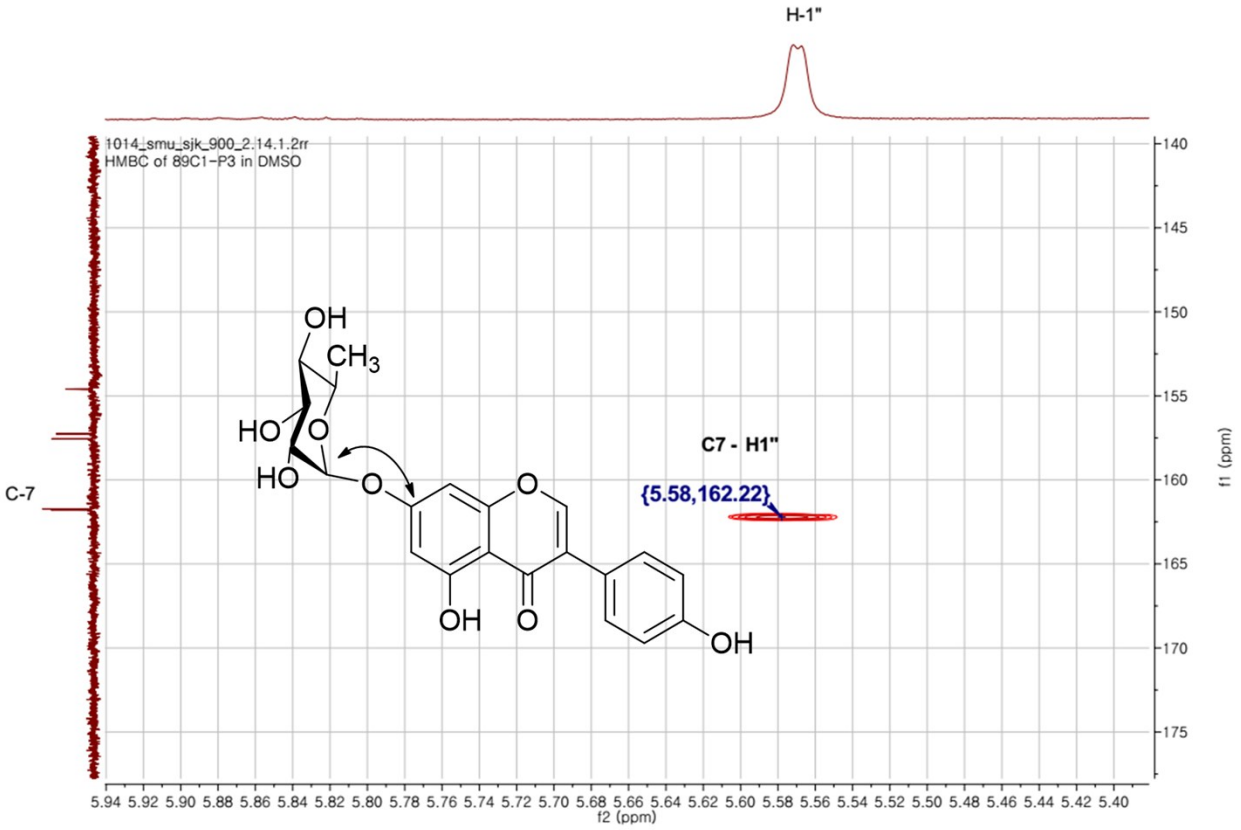
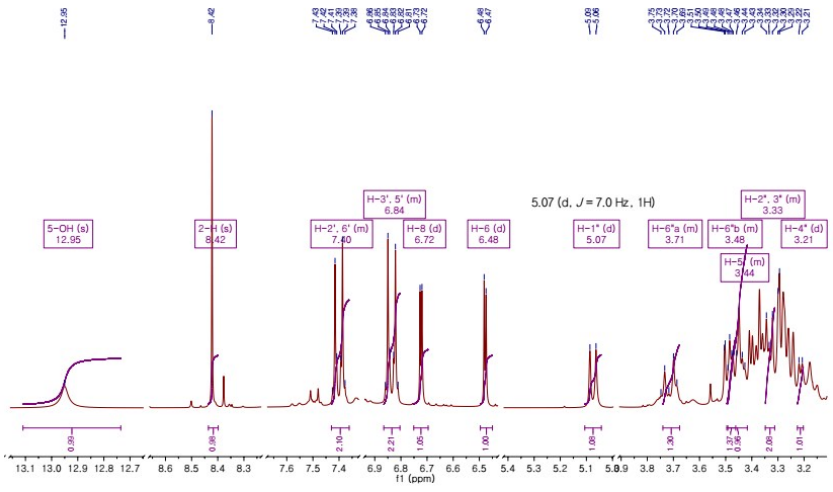


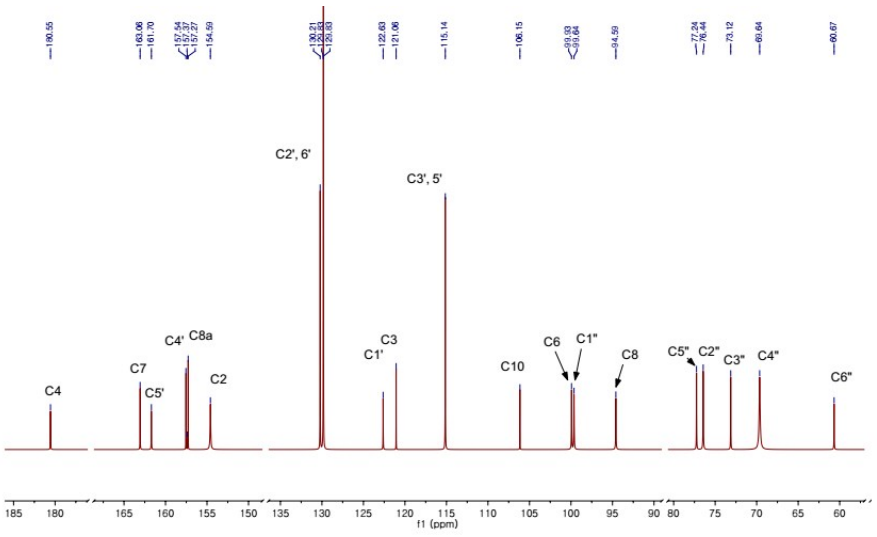
Figure S5

A. Genistein 7-*O*-*β*-D-glucopyranoside (^{1}H NMR)



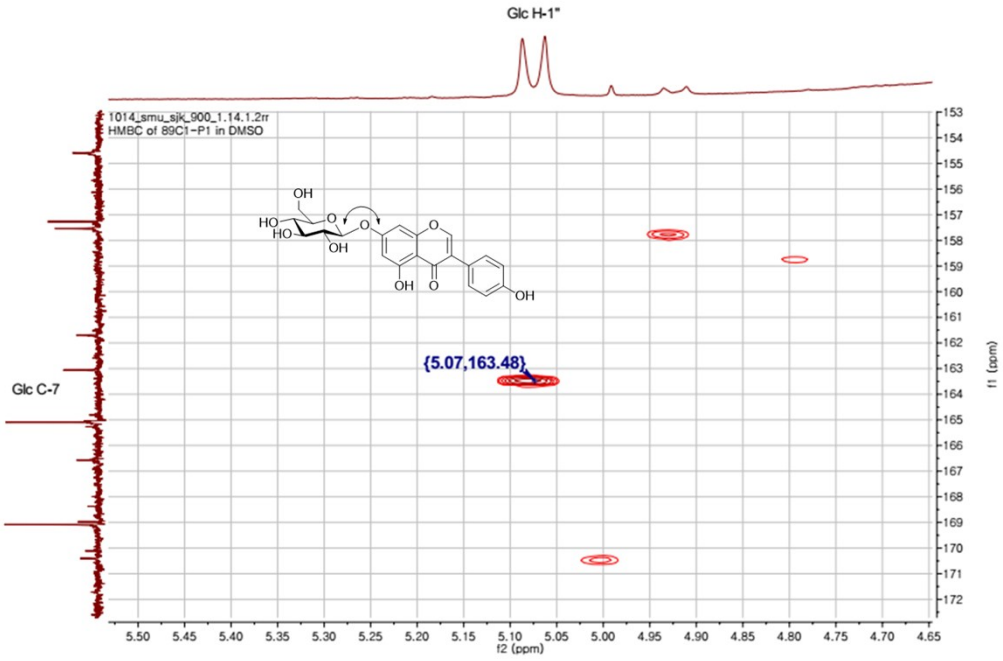
(^{1}H NMR) δ_H (300 MHz) 3.0 - 4.0 (Sugar protons), 5.07 (1"-H), 6.48 (H-6), 6.72 (H-8), 6.84 (3', 5'-H), 7.40 (2', 6'-H), 7.42 (2-H), 12.95 (5-OH).

B. Genistein 7-*O*-*β*-D-glucopyranoside (^{13}C NMR)



(^{13}C NMR) δ_C (75 MHz,) 60.67 (C6"), 69.64 (C4"), 73.12 (C3"), 76.44 (C2"), 77.24 (C5"), 94.59 (C8), 99.64 (C1"), 99.93 (C6), 106.15 (C10), 115.14 (3', 5'-C), 121.06 (C3), 122.63 (C1') , 129.827, 129.827, 130.214, 154.592, 157.270, 157.366, 157.539, 161.699, 163.057, 180.553.

C. Genistein 7-*O*-*β*-D-glucopyranoside (HMBC)



D. Genistein 7-*O*-*β*-D-glucopyranoside (HMBC)

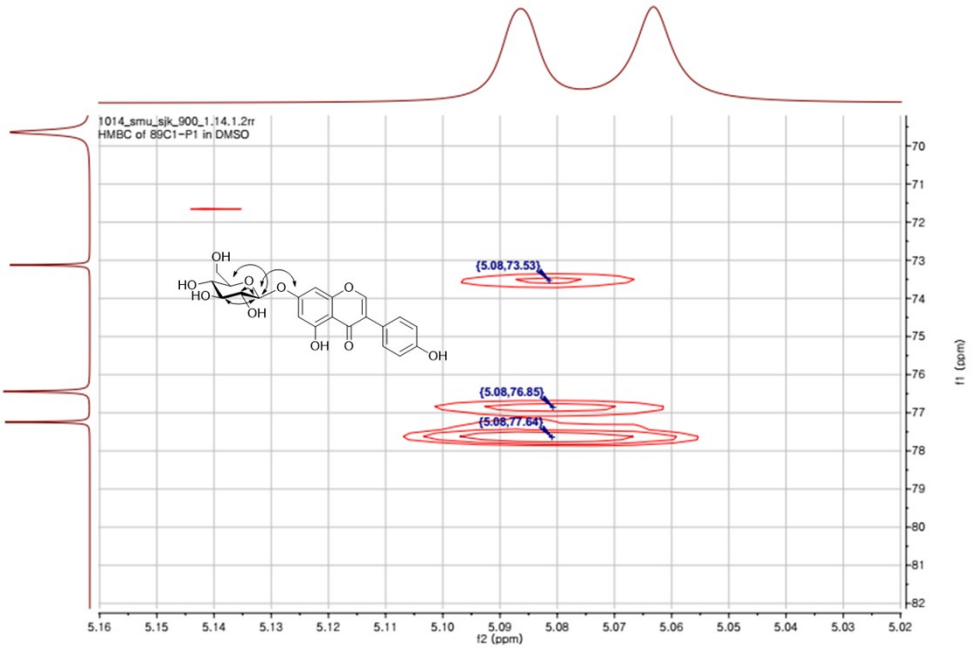
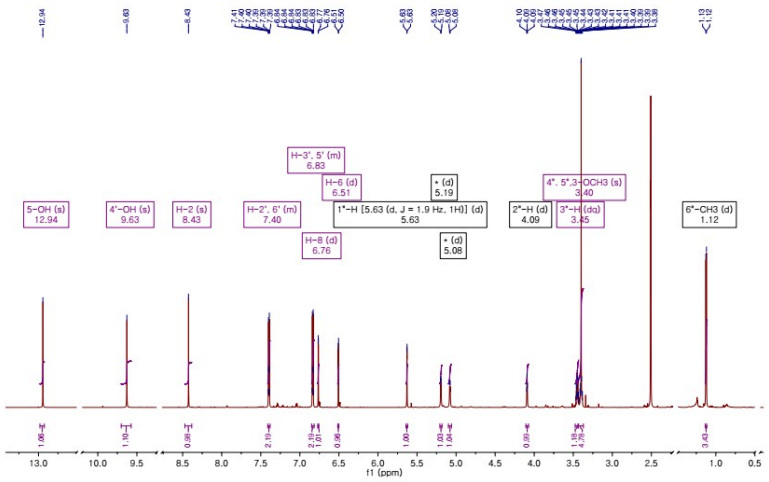


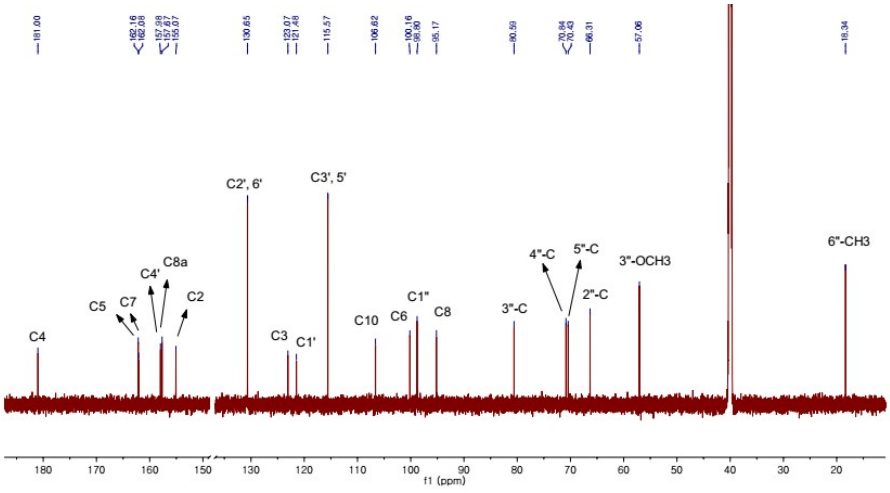
Figure S6

A. Genistein 7-*O*- 3''-*O*-methyl -*α*-L-rhamnopyranoside (^{1}H NMR)



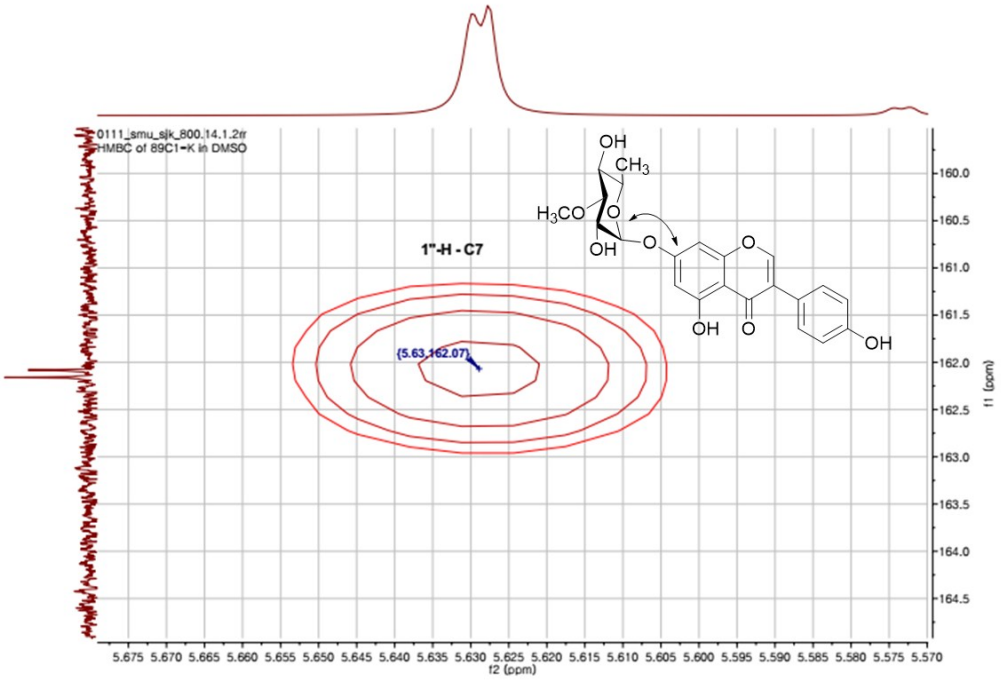
(^{1}H NMR) δ_H (800 MHz,) 1.12-1.13 (6"-CH_3), 3.0 - 4.0 (Sugar protons) 3.40 (3-OCH_3), 4.09 - 5.19 (Sugar Hydroxyls), 5.63 (1"-H), 6.51 (6-H), 6.76 (8-H), 6.83 (3', 5'-H), 7.40 (2', 6'-H), 8.43 (2-H), 9.63 (4'-OH), 12.94 (5-OH).

B. Genistein 7-*O*-3''-*O*-methyl -*α*-L-rhamnopyranoside (^{13}C NMR)



(^{13}C NMR) δ_C (201 MHz, DMSO) 18.34 (C6"), 57.06 (3"-OCH_3), 66.31 (C2"), 70.43 (C5"), 70.84 (C4"), 80.59 (C3"), 95.17 (C8), 98.80 (C1"), 100.16 (C6), 106.62 (C10), 115.57 (3', 5'-C), 121.48 (C1'), 123.07 (C3), 130.65 (2', 6'-C), 155.07 (C2), 157.67 (C8a), 157.98 (C4'), 162.08 (C7), 162.16 (C5), 181.00 (C4).

C. Genistein 7-*O*- 3''-*O*-methyl -*α*-L-rhamnopyranoside (HMBC)



D. Genistein 7-*O*- 3''-*O*-methyl -*α*-L-rhamnopyranoside (HMBC)

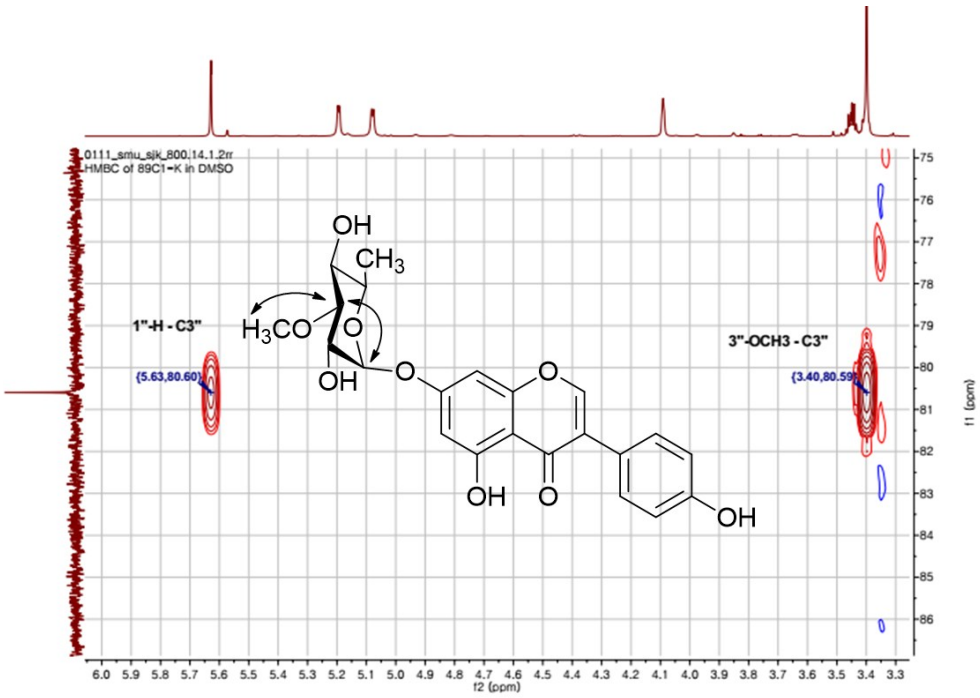
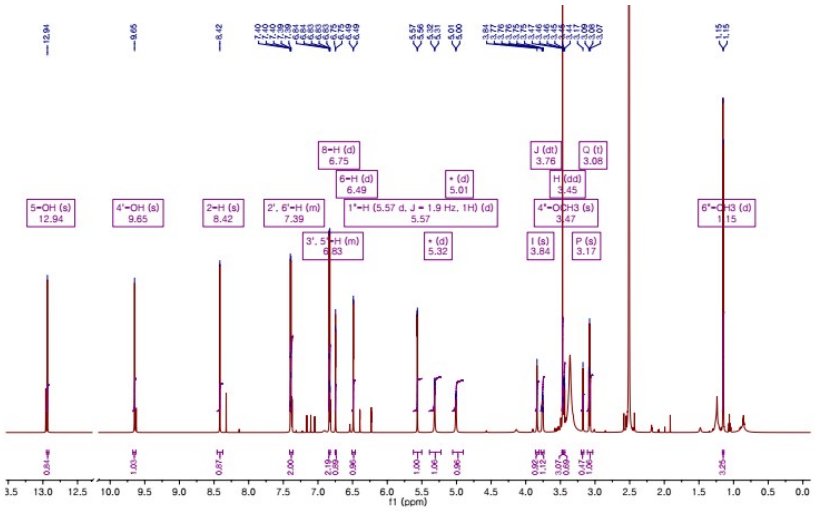


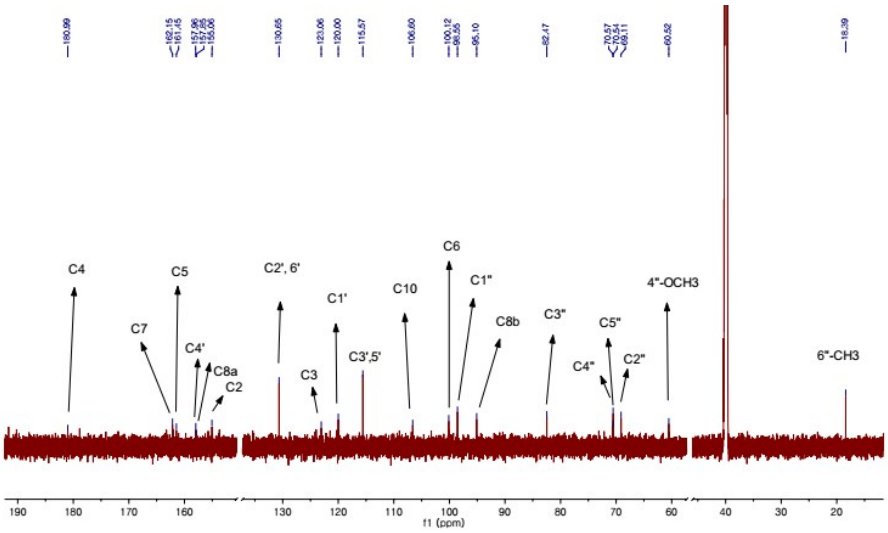
Figure S7

A. Genistein 7-*O*- 4''-*O*-methyl -*α*-L-rhamnopyranoside (^{1}H NMR)



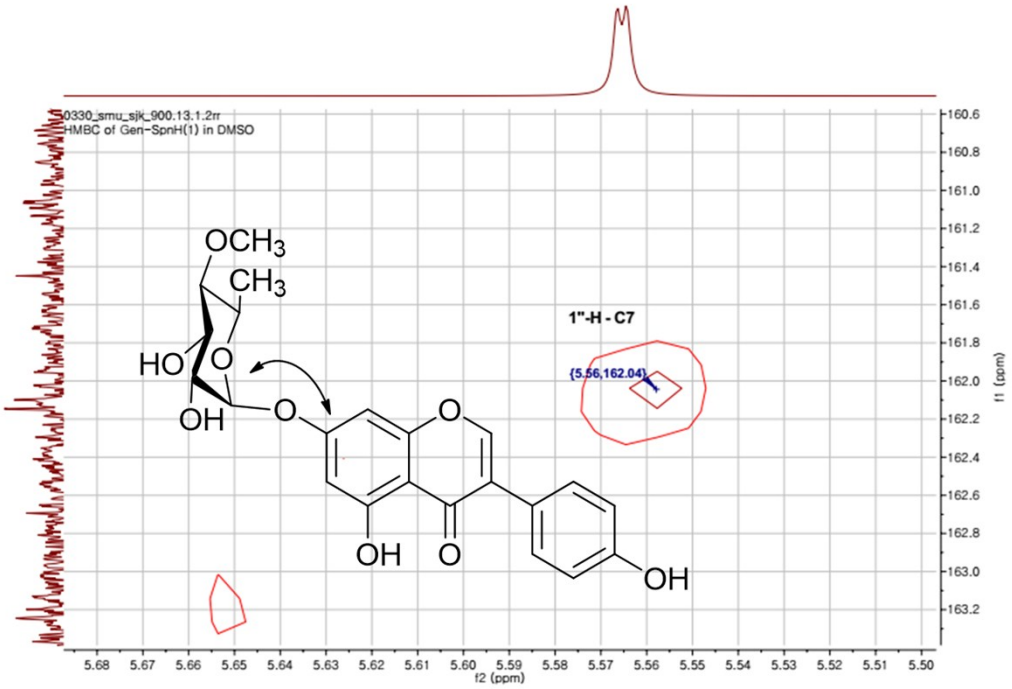
(^{1}H NMR) δ_H (900 MHz,) 1.15 (6''-CH_3), 3.0 - 4.0 (Sugar protons), 5.01 - 5.32 (Sugar Hydroxyls), 5.57 (1''-H), 6.49 (6-H), 6.75 (8-H), 6.83 (3', 5'-H), 7.39 (2', 6'-H), 8.42 (2-H), 9.65 (4'-OH), 12.94 (5-OH).

B. Genistein 7-*O*- 4''-*O*-methyl -*α*-L-rhamnopyranoside (^{13}C NMR)



(^{13}C NMR) δ_C (226 MHz, DMSO) 18.39 (6''-CH_3), 60.52 (4''-OCH_3), 69.11 (C2''), 70.54 (C5''), 82.47 (C3''), 95.10 (C8b), 98.55 (C1''), 100.12 (C6), 106.60 (C10), 115.57 (3', 5'-C), 120.00 (C1'), 123.06 (C3), 130.65 (2', 6'-C), 155.06 (C2), 157.85 (C8a), 157.96 (C4'), 161.45 (C7), 162.15 (C5), 180.99 (C4).

C. Genistein 7-*O*- 4''-*O*-methyl -α-L-rhamnopyranoside (HMBC)



D. Genistein 7-*O*- 4''-*O*-methyl -α-L-rhamnopyranoside (HMBC)

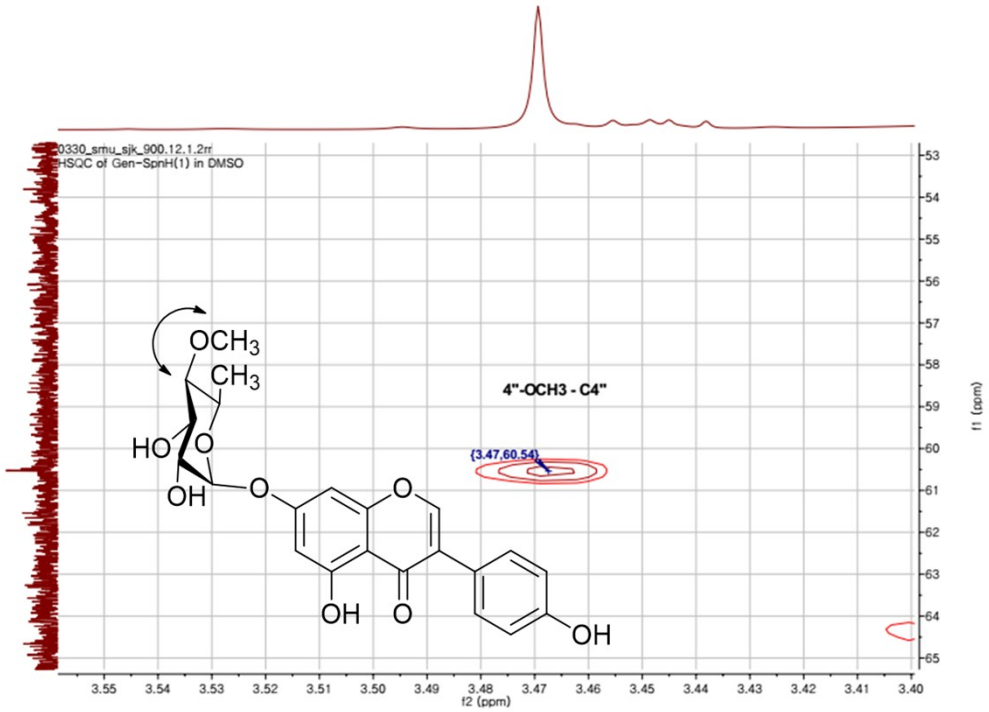
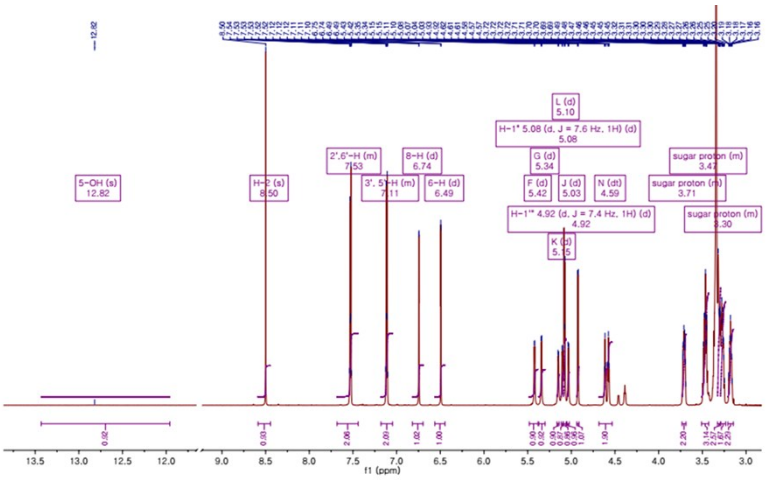


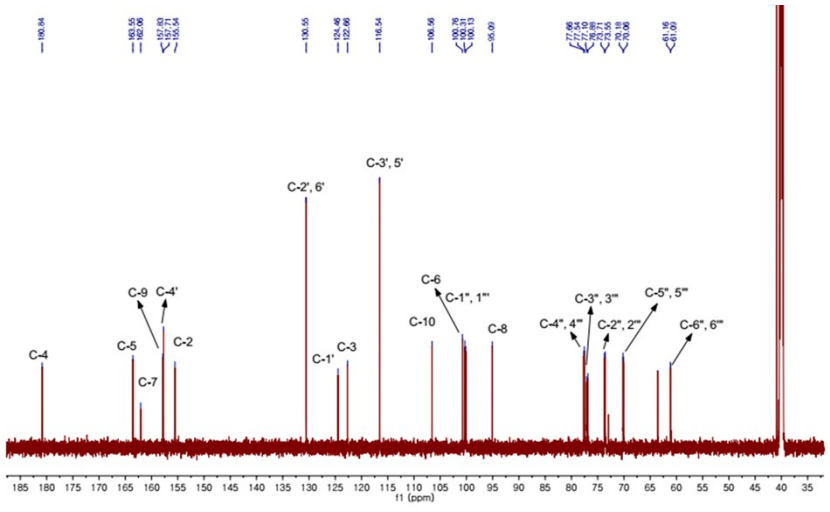
Figure S8

A. Genistein 4', 7-*O*-*β*- D-diglucopyranoside (^{1}H NMR)



(^{1}H NMR) δ_H (700 MHz, DMSO) 3.0 - 4.0 (Sugar protons), 4.50 - 5.42 (Sugar Hydroxyls), 4.92 (H-1'''), 5.08 (H-1''), 6.49 (H-6), 6.74(H-8), 7.11 (3', 5'-H), 7.53 (3', 6'-H), 8.50 (H-2), 12.82 (5-OH).

B. Genistein 4', 7-*O*-*β*- D-diglucopyranoside (^{13}C NMR)



(^{13}C NMR) δ_C (176 MHz, DMSO) 61.09 (C6'''), 61.16 (C6''), 70.06 (C5'''), 70.18 (C5''), 73.55 (C2'''), 73.71 (C2''), 76.88 (C3'''), 77.10 (C3''), 77.54 (C4'''), 77.66 (C4''), 95.09 (C8), 100.13 (C1'''), 100.31 (C1''), 100.77 (C6), 106.56 (C10), 116.54 (3', 5'-C), 122.66 (C3), 124.46 (C1'), 130.55 (2', 6'-C), 155.54 (C2), 157.71 (C4'), 157.83 (C9), 162.06 (C7), 163.55 (C5), 180.84 (C4).

C. Genistein 4', 7-*O*-*β*- D-diglucopyranoside (HMBC)

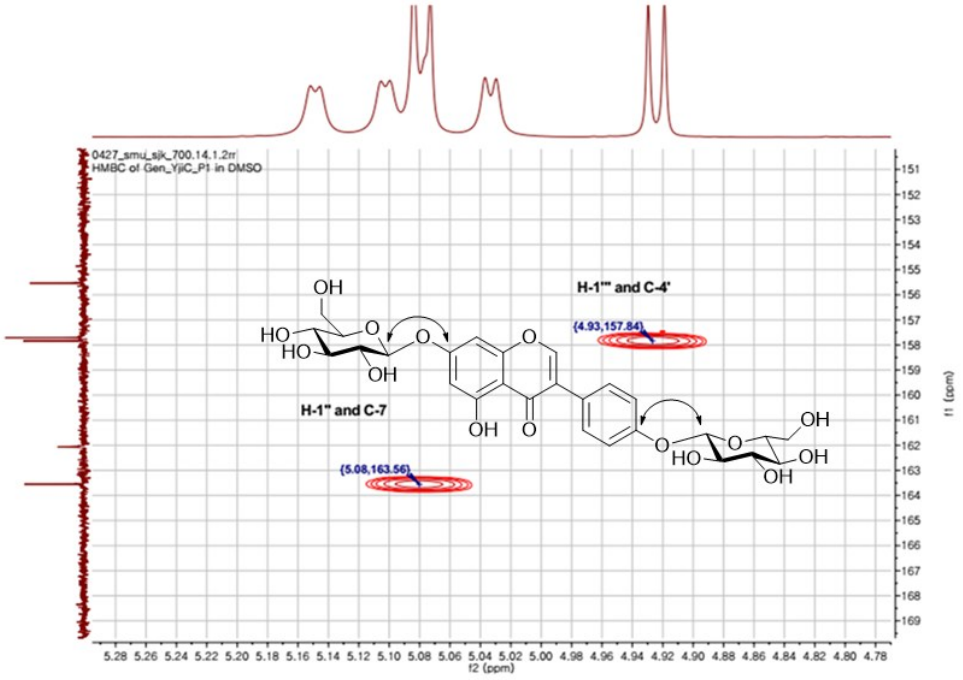
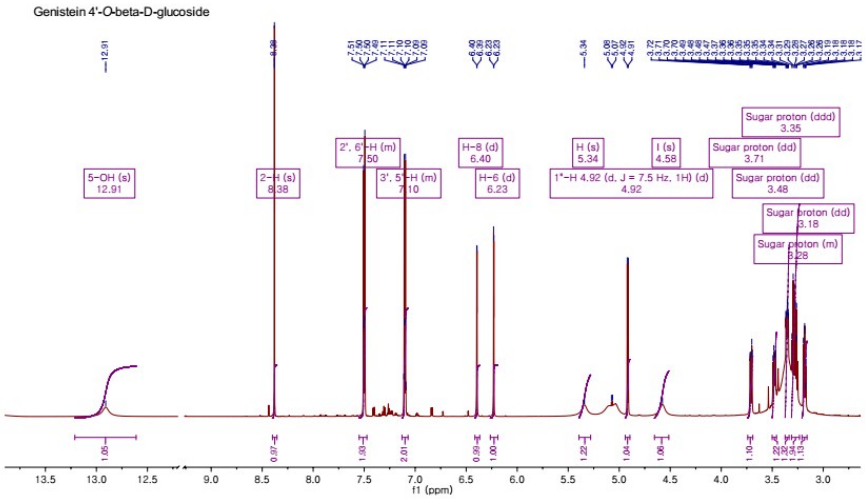


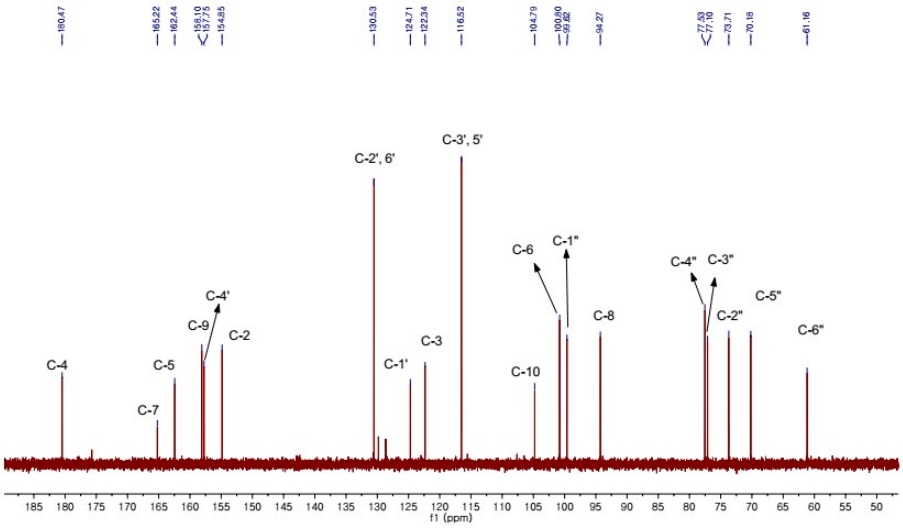
Figure S9

A. Genistein 4'-*O*-*β*-D-glucopyranoside (^{1}H NMR)



(^{1}H NMR) δ_H (700 MHz, DMSO) 3.0- 4.0 (Sugar protons), 4.58 (Sugar hydroxyl), 4.92 (H-1"), 5.34 (Sugar hydroxyl), 6.23 (6-H), 6.40 (8-H), 7.10 (3', 5'-H), 7.50 (2', 6'-H), 8.38 (2-H), 12.91 (5-OH).

B. Genistein 4'-*O*-*β*-D-glucopyranoside (^{13}C NMR)



(^{13}C NMR) δ_C (176 MHz, DMSO) 61.16 (C-6"), 70.18 (C5"), 73.71 (C2"), 77.10 (C3"), 77.53 (C4"), 94.27 (C8), 99.62 (C1"), 100.80 (C6), 104.79 (C10), 116.52 (3', 5'-C), 122.34 (C3), 124.71 (C1'), 130.53 (2', 5'-C), 154.85 (C2), 157.75 (C4'), 158.10 (C9), 162.44 (C5), 165.22 (C7), 180.47 (C4).

C. Genistein 4'-*O*-*β*-D-glucopyranoside (HMBC)

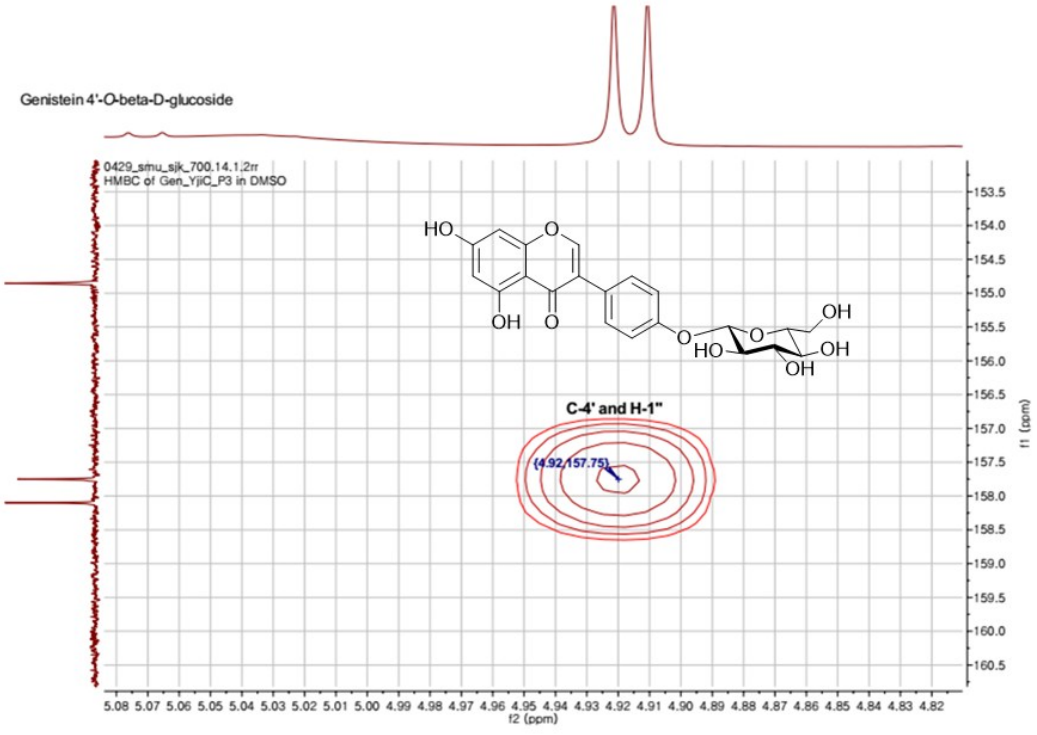
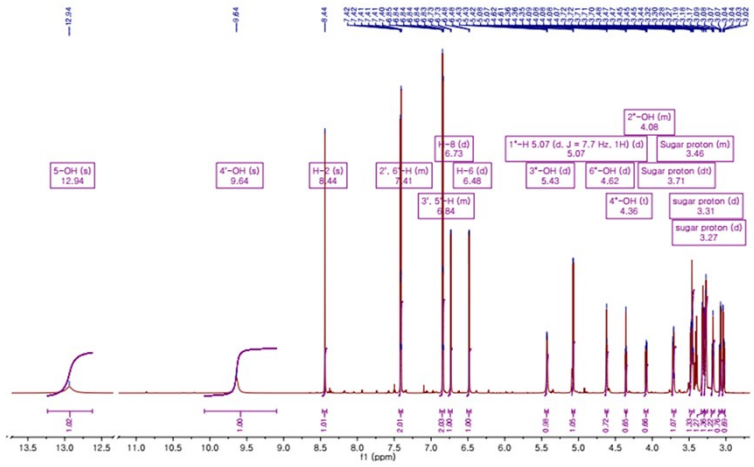


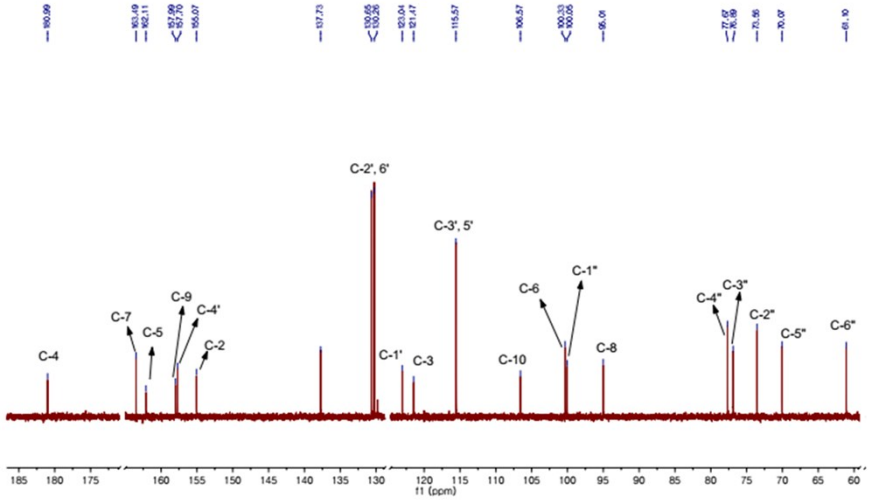
Figure S10

A. Genistein 7-*O*-*β*-D-glucopyranoside (^{1}H NMR)



(^{1}H NMR) δ_H (900 MHz) 3.0 - 4.0 (Sugar protons), 4.36, 4.62, 5.43 (Sugar hydroxyls), 5.07 (1''-H), 6.48 (6-H), 6.73 (8-H), 6.84 (3', 5'-H), 7.41 (2', 6'-H), 8.44 (2-H), 9.64 (4'-OH), 12.94 (5-OH).

B. Genistein 7-*O*-*β*-D-glucopyranoside (^{1}H NMR)



(^{13}C NMR) δ_C (226 MHz, DMSO) 61.10 (C6''), 70.07 (C5''), 73.56 (C2''), 76.89 (C3''), 77.67 (C4''), 95.01 (C8), 100.05 (C1''), 100.33 (C6), 106.57 (C10), 115.57 (3', 5'-C), 121.47 (C3), 123.04 (C1'), 130.26 (C6'), 130.65 (C2'), 155.07 (C2), 157.70 (C4'), 157.99 (C9), 162.11 (C5), 163.49 (C7), 180.99 (C4).

C. Genistein 7-*O*-*β*-D-glucopyranoside (HMBC)

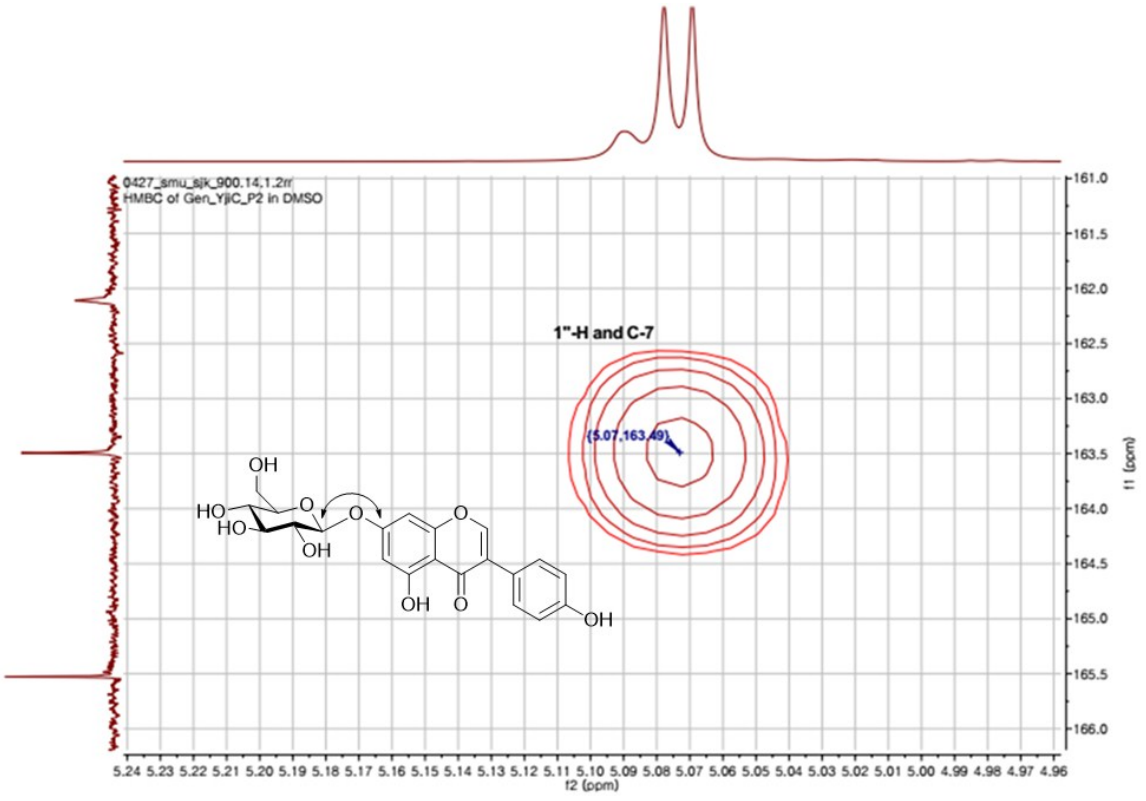
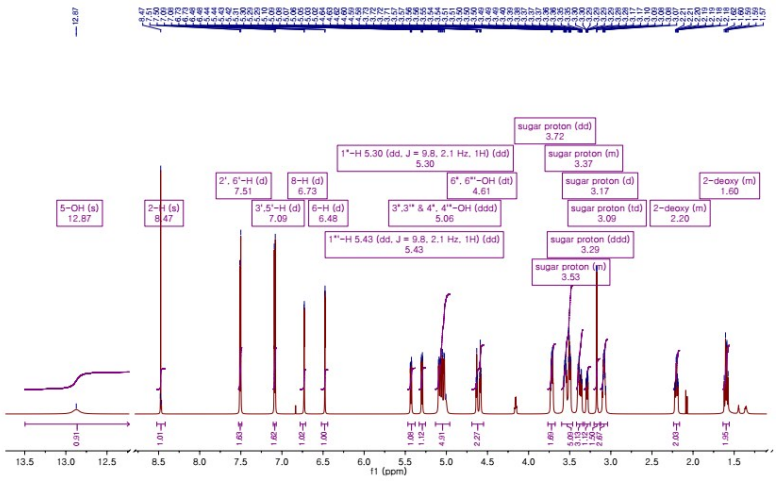


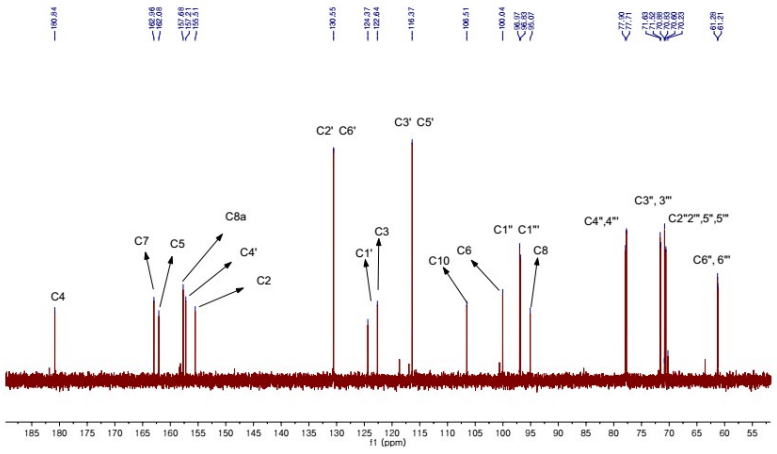
Figure S11

A. Genistein 4', 7-*O*-*β*-2-deoxy D-diglucopyranoside (^{1}H NMR)



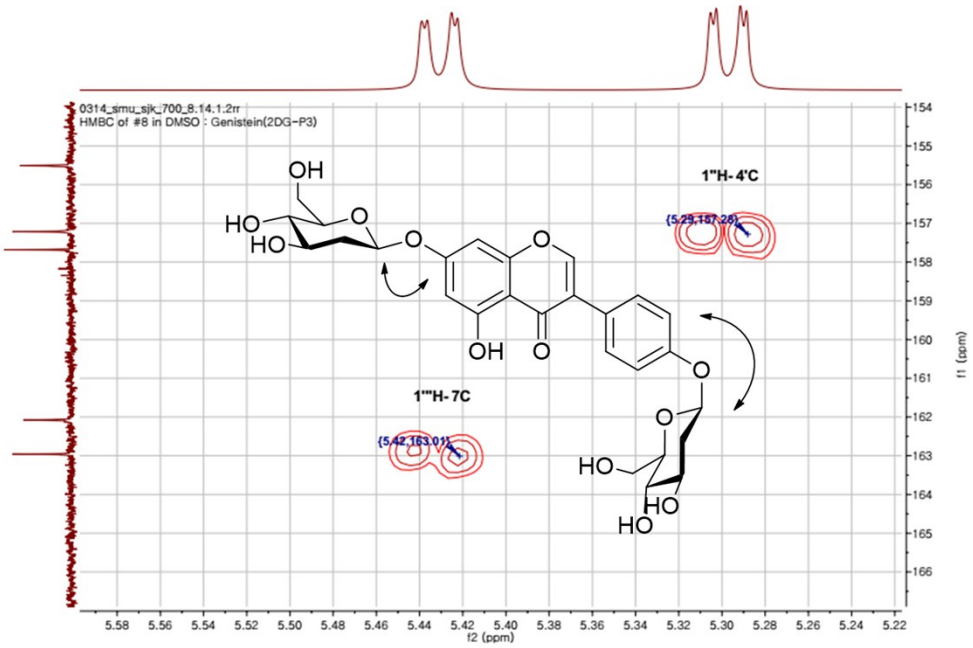
(^{1}H NMR) δ_H (700 MHz,) 1.57 - 1.62 (2-deoxy), 2.18 - 2.21 (2-deoxy), 3.06 - 4.0 (Sugar protons), 4.58 - 5.06 (Sugar hydroxyls), 5.30 (1"-H), 5.43 (1'"-H) , 6.48 (6-H), 6.73 (8-H), 7.09 (3', 5'-H), 7.51 (2', 6'-H), 8.47 (2-H), 12.87 (5-OH).

B. Genistein 4', 7-*O*-*β*-2-deoxy D-diglucopyranoside (^{13}C NMR)



(^{13}C NMR) δ_C (176 MHz, DMSO) 61.21 (6'"), 61.28 (6"), 70.23 (C5'"), 70.60 (C5"), 70.83 (C2'"), 70.88 (C2"), 71.52 (C3'"), 71.63 (C3"), 77.71 (C4'"), 77.90 (C4"), 95.07 (C8), 96.83 (C1'"), 96.97 (C1"), 100.034 (C6), 106.51 (C10), 116.37 (3', 5'-C), 122.64 (C3), 124.37 (C1'), 130.55 (2', 6'-C), 155.51 (C2), 157.21 (C4'), 157.68 (C8a), 162.08 (C5), 162.96 (C7), 180.84 (C4).

C. Genistein 4′, 7-*O*-*β*-2-deoxy D-diglucopyranoside (HMBC)



D. Genistein 4′, 7-*O*-*β*-2-deoxy D-diglucopyranoside (HMBC)

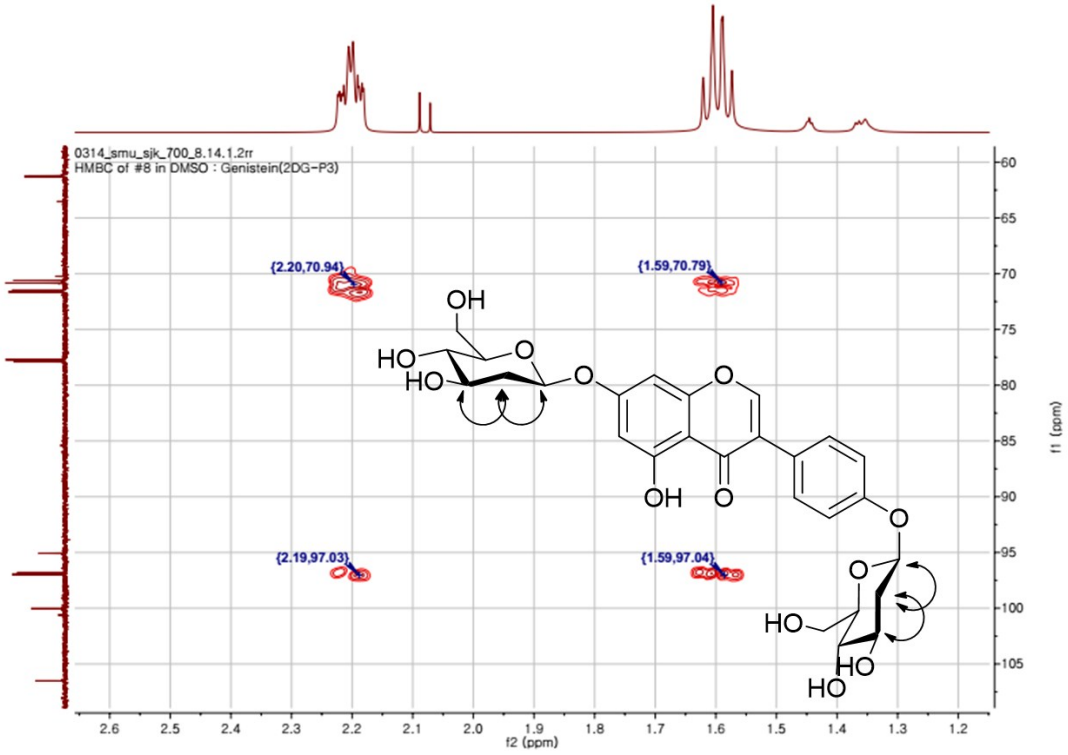
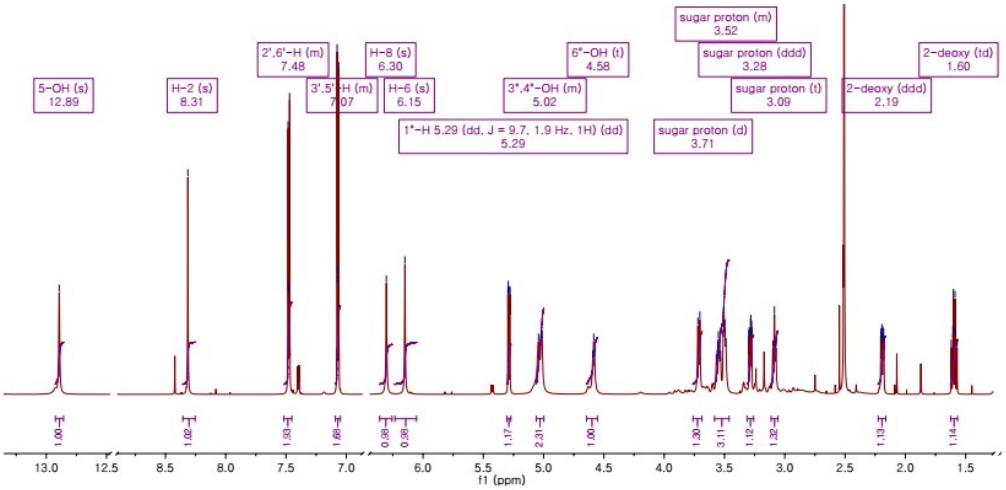


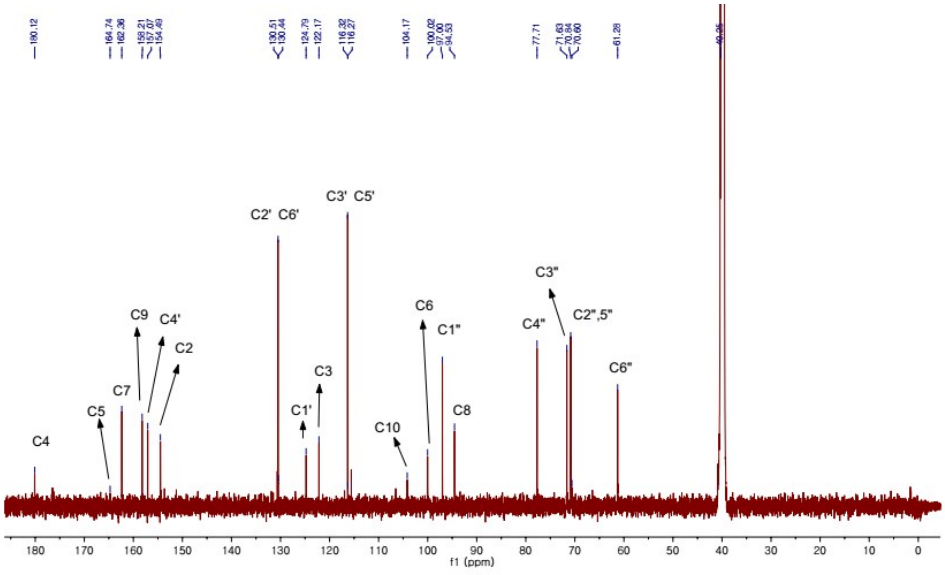
Figure S12

A. Genistein 4'-*O*- *β* -2-deoxy D-glucopyranoside (^{1}H NMR)



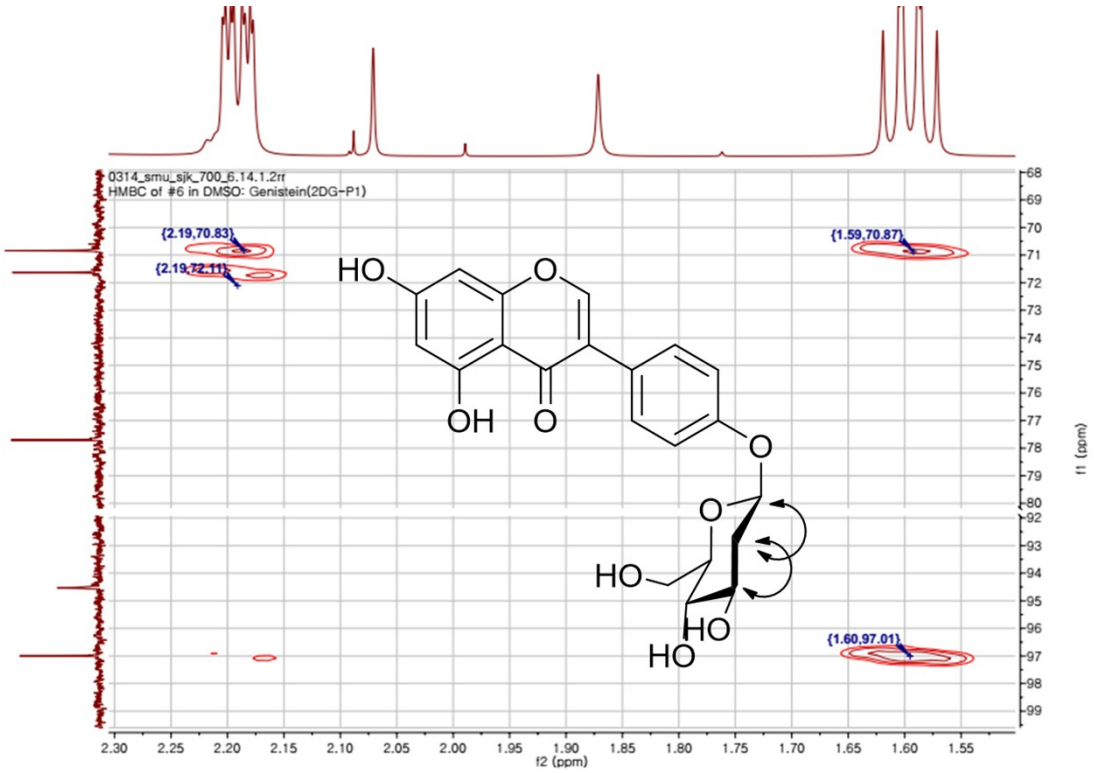
(^{1}H NMR) δ_H (700 MHz,) 1.51-1.62 (2-deoxy), 2.18- 2.20 (2-deoxy), 3.0-4.0 (Sugar protons), 4.0-5.0 (sugar hydroxyls) 5.29 (1"-H), 6.15 (6-H), 6.30 (H-8), 7.07 (3', 5'-H), 7.48 (2', 6'-H), 7.483, 8.31 (2-H), 12.89 (5-OH)

B. Genistein 4'-*O*- *β* -2-deoxy D-glucopyranoside (^{13}C NMR)



(^{13}C NMR) δ_C (176 MHz, DMSO) 61.28 (C6"), 70.60 (C5"), 70.84 (2C"), 71.63 (C3"), 77.71 (C4"), 94.53 (C8), 97.00 (C1"), 100.02 (C6), 104.17 (C10), 116.26 (C3'), 116.32 (C5'), 122.16 (C3), 124.78 (C1'), 130.43 (C2'), 130.51 (C6'), 154.48 (C2), 157.07 (C4'), 158.20 (C9), 162.35 (C7), 164.74 (C5), 180.12 (C4).

C. Genistein 4'-*O*- *β* -2-deoxy D-glucopyranoside (HMBC)



D. Genistein 4'-*O*- *β* -D-deoxy D-glucopyranoside (HMBC)

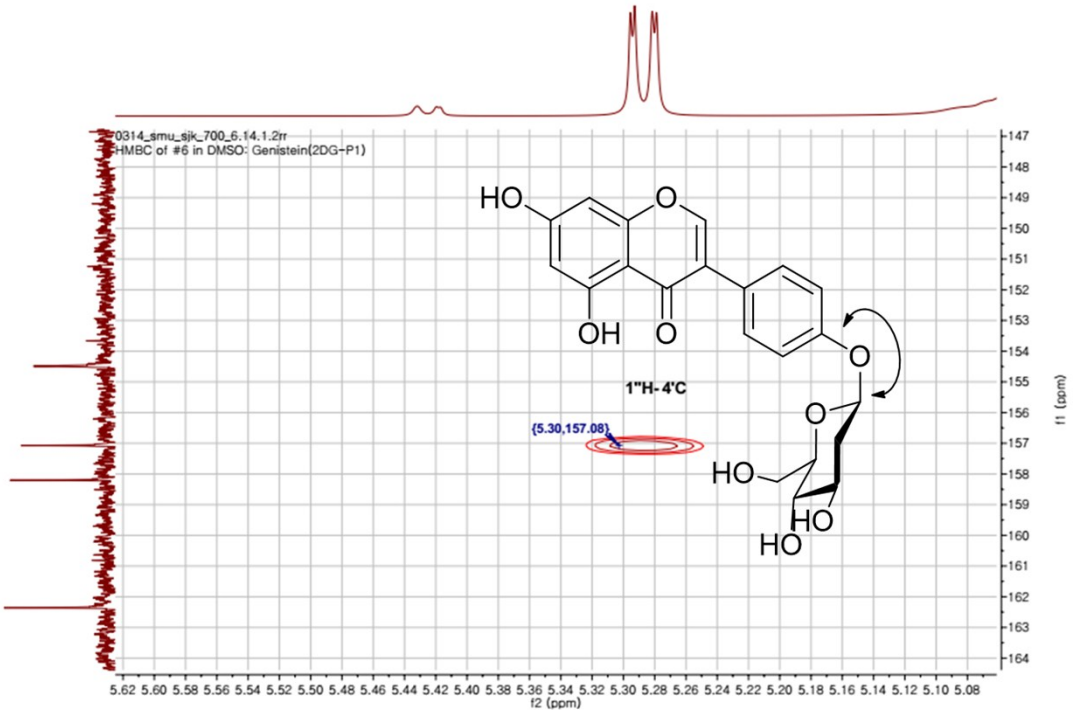
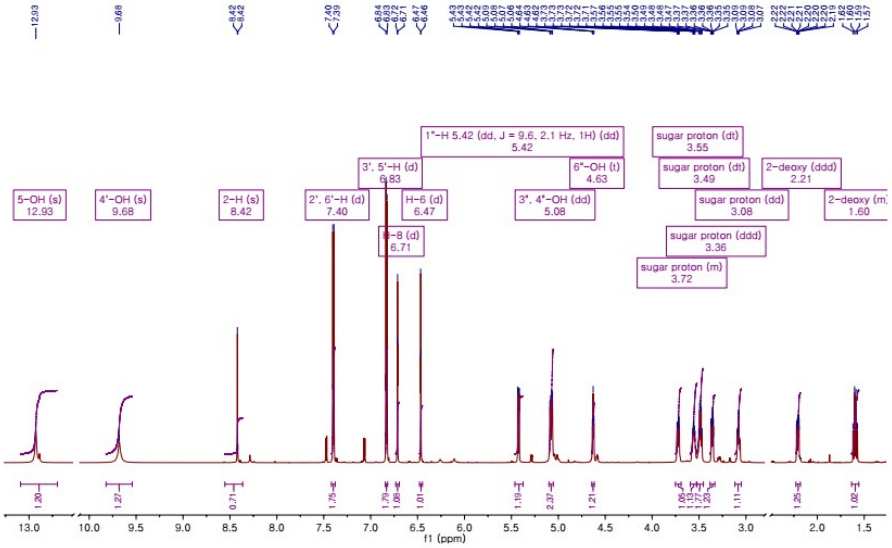


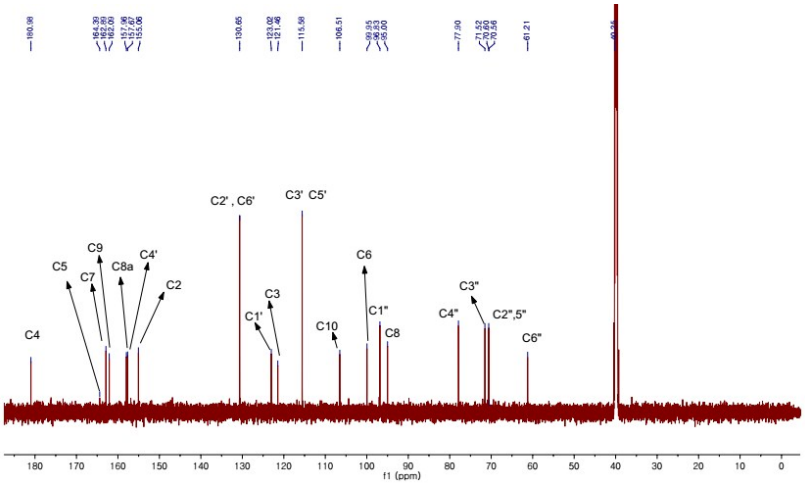
Figure S13

A. Genistein 7-*O*- *β* -2-deoxy D-glucopyranoside (^{1}H NMR)



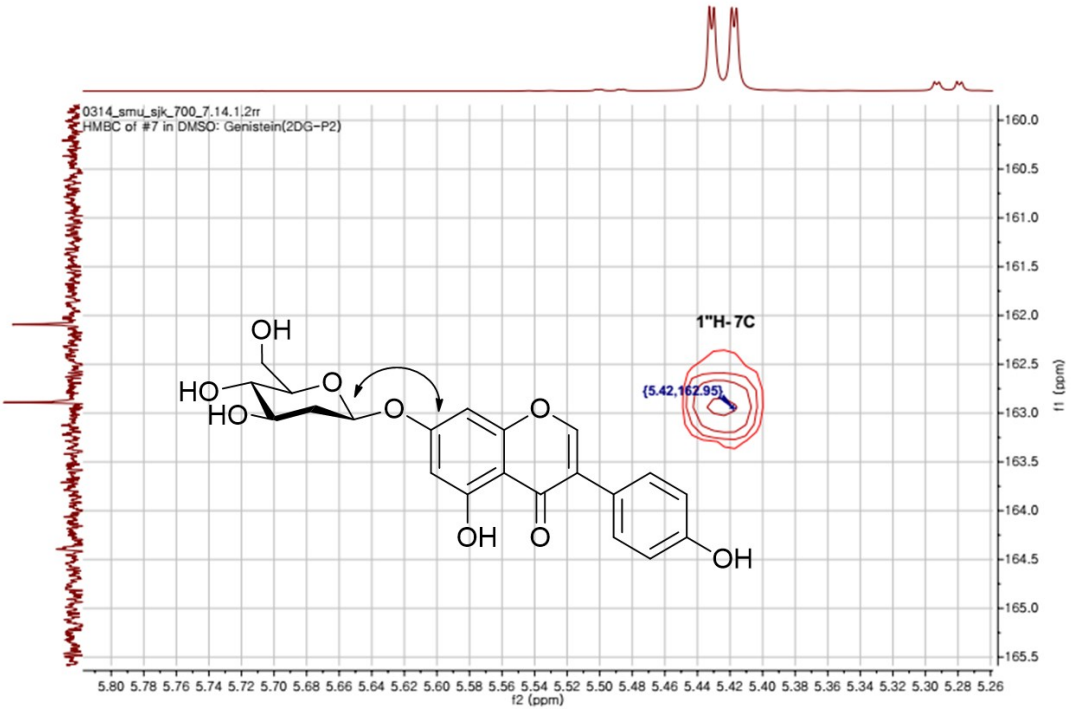
(^{1}H NMR) δ_H (700 MHz,) 1.57 - 1.61 (2-deoxy), 2.18- 2.22 (2-deoxy), 3.07- 4.0 (Sugar protons), 4.62 - 5.08 (sugar hydroxyls), 5.42 (1"-H), 6.47 (6-H), 6.71 (8-H), 6.83 (3', 5'-H), 7.40 (2', 6'-H), 8.42 (2-H), 9.68 (4'-OH), 12.93 (5-OH).

B. Genistein 7-*O*- *β* -2-deoxy D-glucopyranoside (^{13}C NMR)

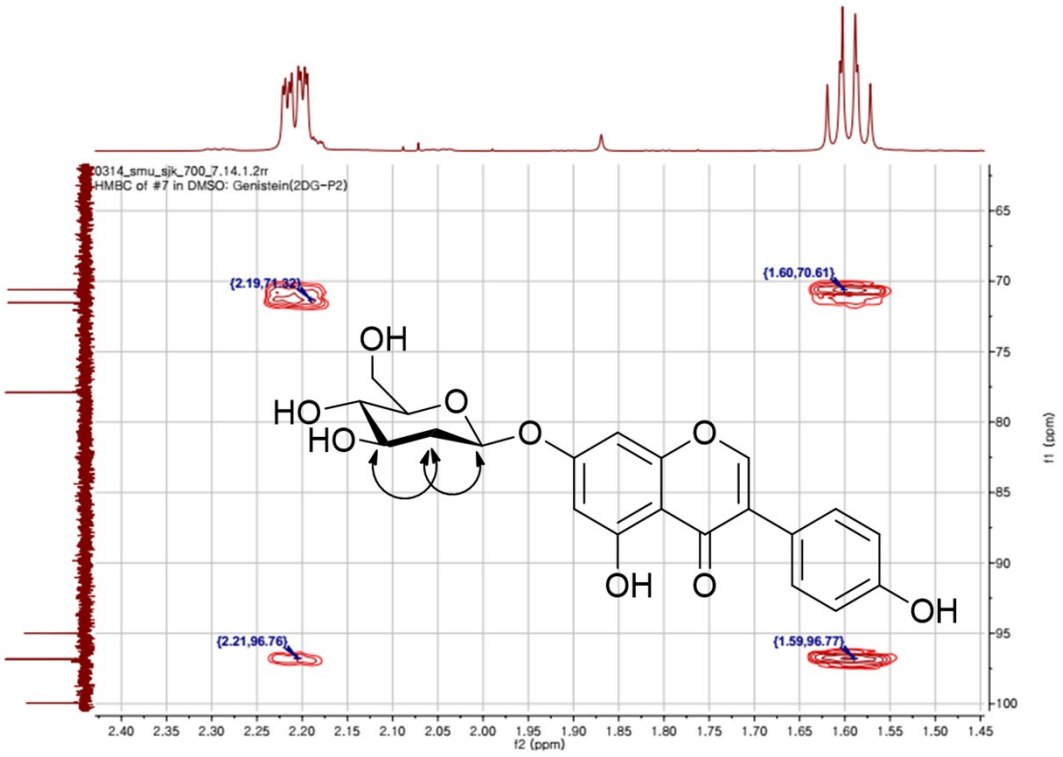


(^{13}C NMR) δ_C (176 MHz, DMSO) 40.254, 61.21 (C6"), 70.56 (C5"), 70.60 (C2"), 71.52 (C3"), 77.90 (C3"), 94.95 (C8), 96.83 (C1"), 99.95 (C6), 106.51 (C10), 115.58 (3', 5'-C), 121.46 (C3), 123.02 (C1'), 130.65 (2', 6'-C), 155.06 (C2), 157.67 (C4'), 157.96 (C8a), 162.09 (C9), 162.89 (C7), 164.39 (C5), 180.98 (C4).

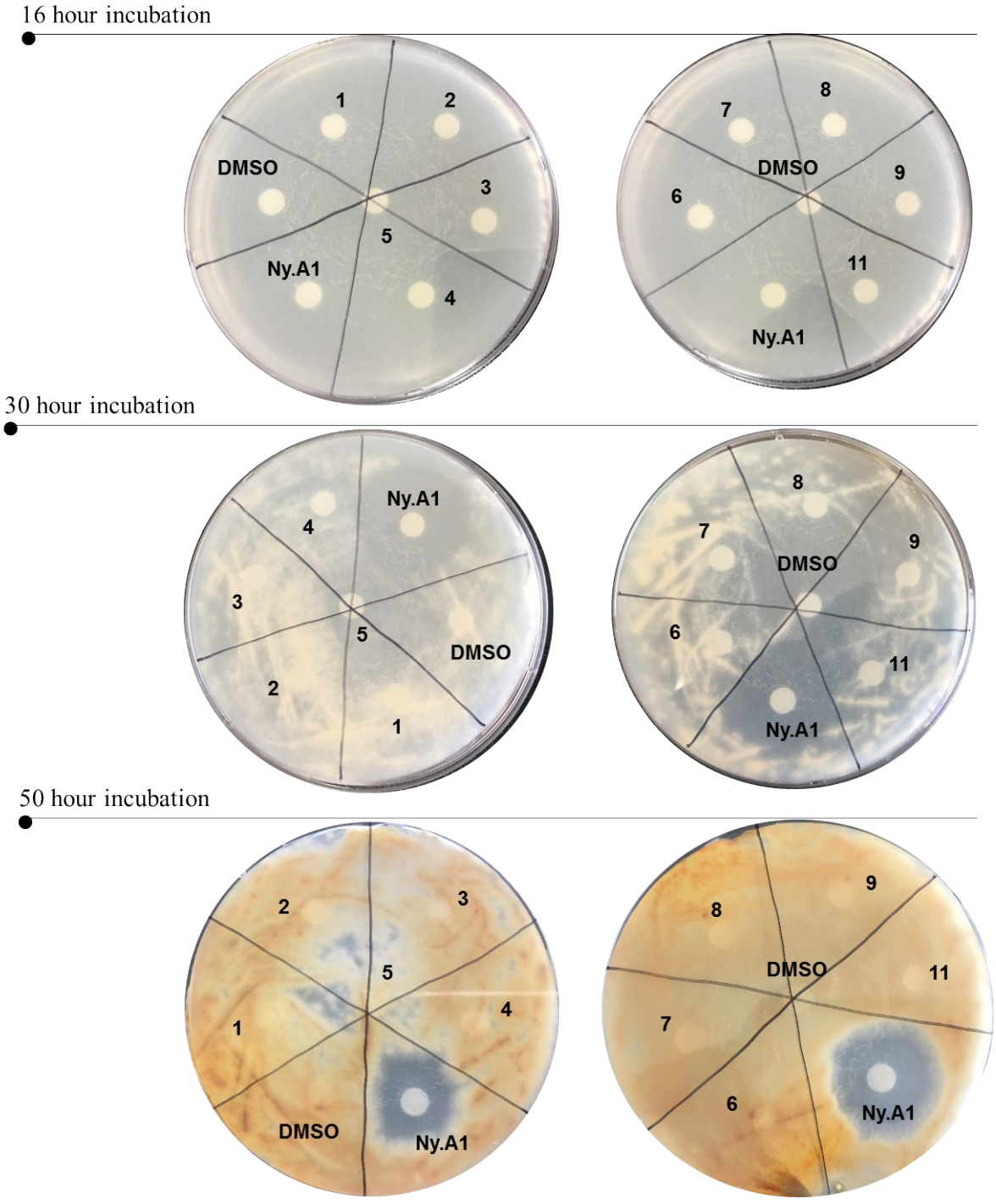
C. Genistein 7-*O*- *β* -2-deoxy D-glucopyranoside (HMBC)



D. Genistein 7-*O*- *β* -2-deoxy D-glucopyranoside (HMBC)



308 **Figure S14**



309