

Supporting Information

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Flavonoid Derivatives from the Aerial Parts of *Trifolium trichocephalum* M. Bieb. and Their Antioxidant and Cytotoxic Activity

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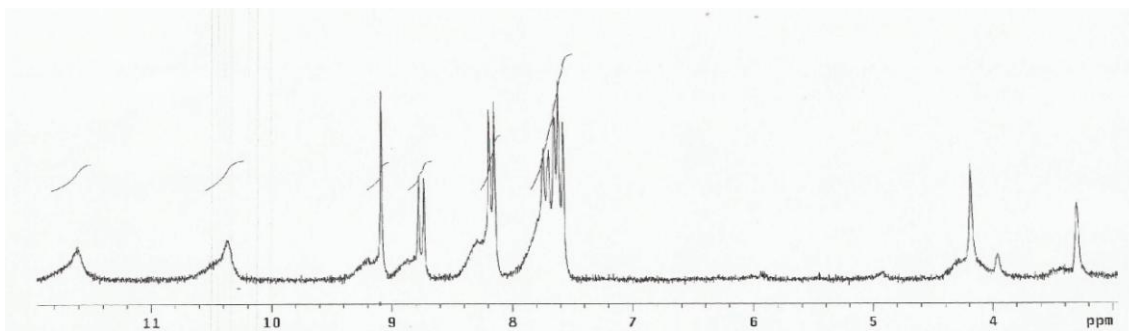
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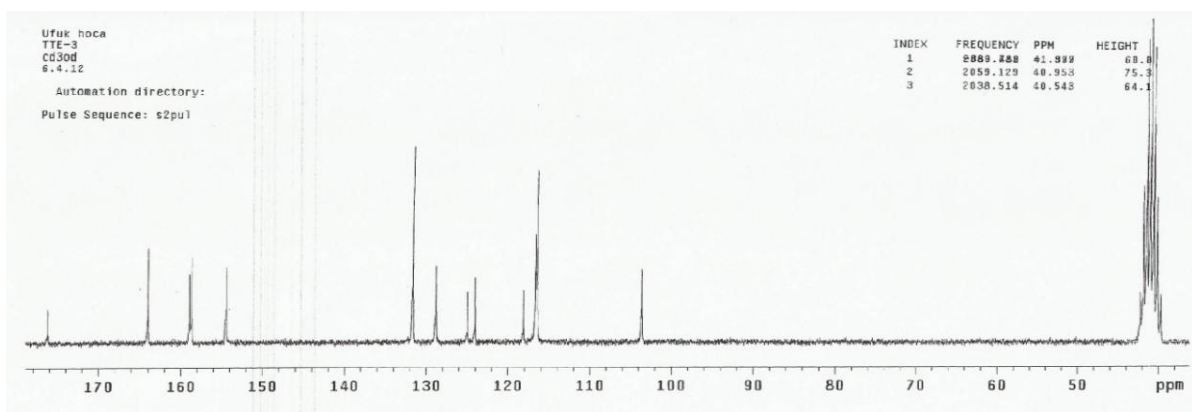
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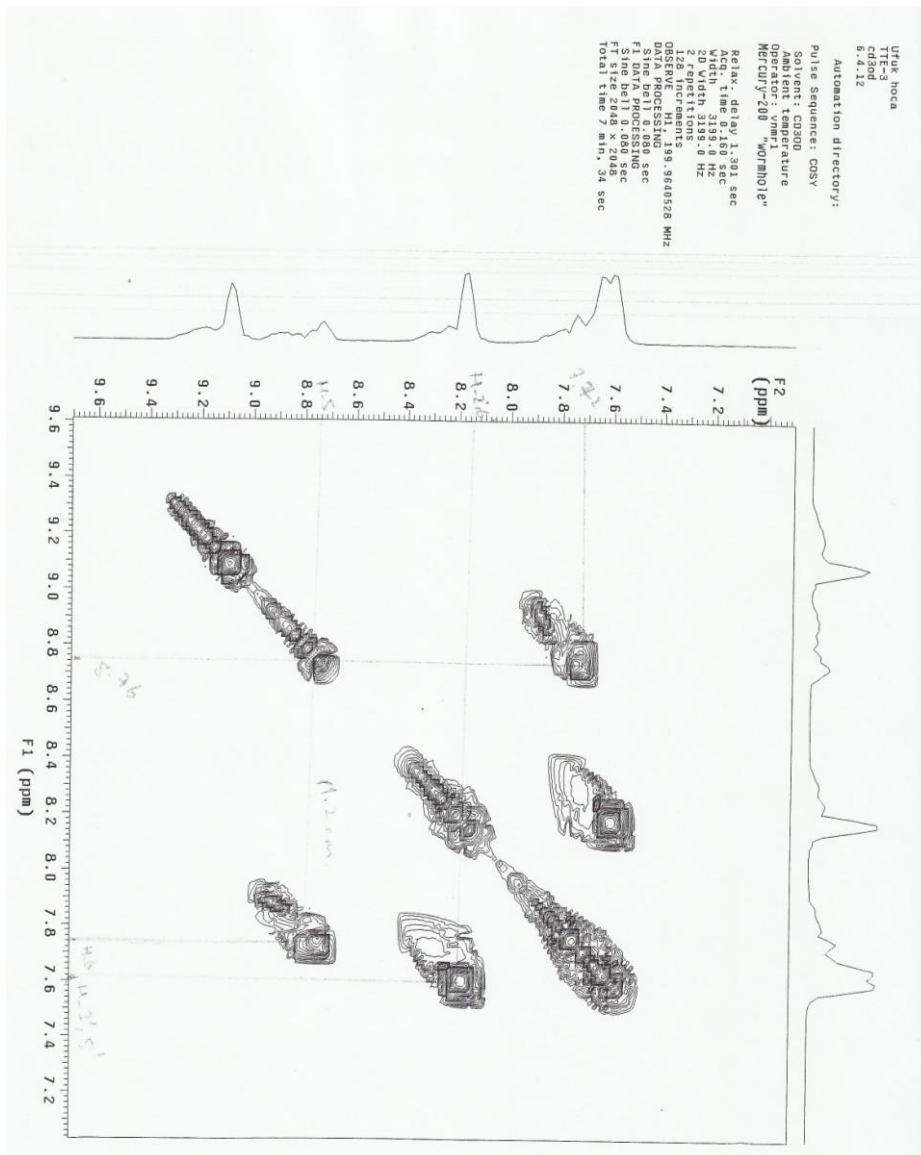


S1: ^1H -NMR (200 MHz, CDCl_3) Spectrum of Compound **1** (daidzein)

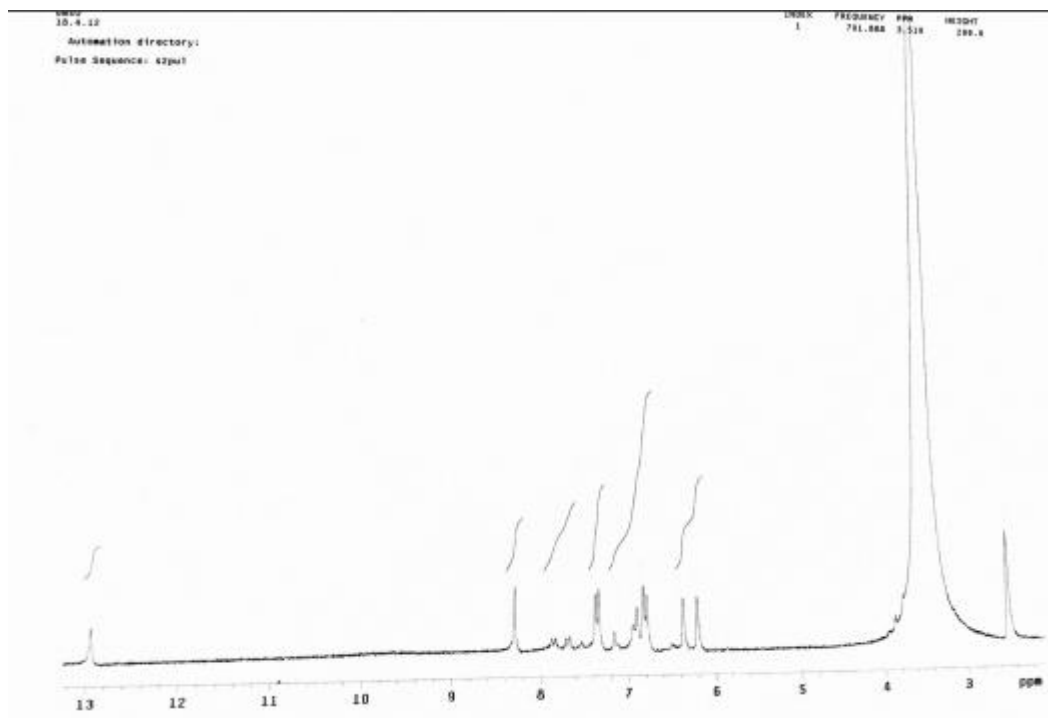
Daidzein (**1**): ^1H NMR (200 MHz, CD_3OD) δ : 8.28 (1H, H-2, s), 7.95 (1H, H-5, d, J = 9.0 Hz), 7.36 (2H, H-2',6', d, J = 8.2 Hz), 6.91 (1H, H-6, d, J = 8.6 Hz), 6.85 (1H, H-8, s), 6.79 (2H, H-3',5', d, J = 8.6 Hz); ^{13}C NMR (50 MHz, CD_3OD) δ : 176.2 (C-4), 164.0 (C-7), 158.9 (C-9), 158.7 (C-4'), 154.4 (C-2), 131.6 (x2C) (C-2',6'), 128.8 (C-5), 125.0 (C-1'), 124.0 (C-3), 118.1 (C-10), 116.6 (C-6), 116.4 (x2C) (C-3',5').



S2: ^{13}C -NMR (50 MHz, CDCl_3) Spectrum of Compound **1** (daidzein)

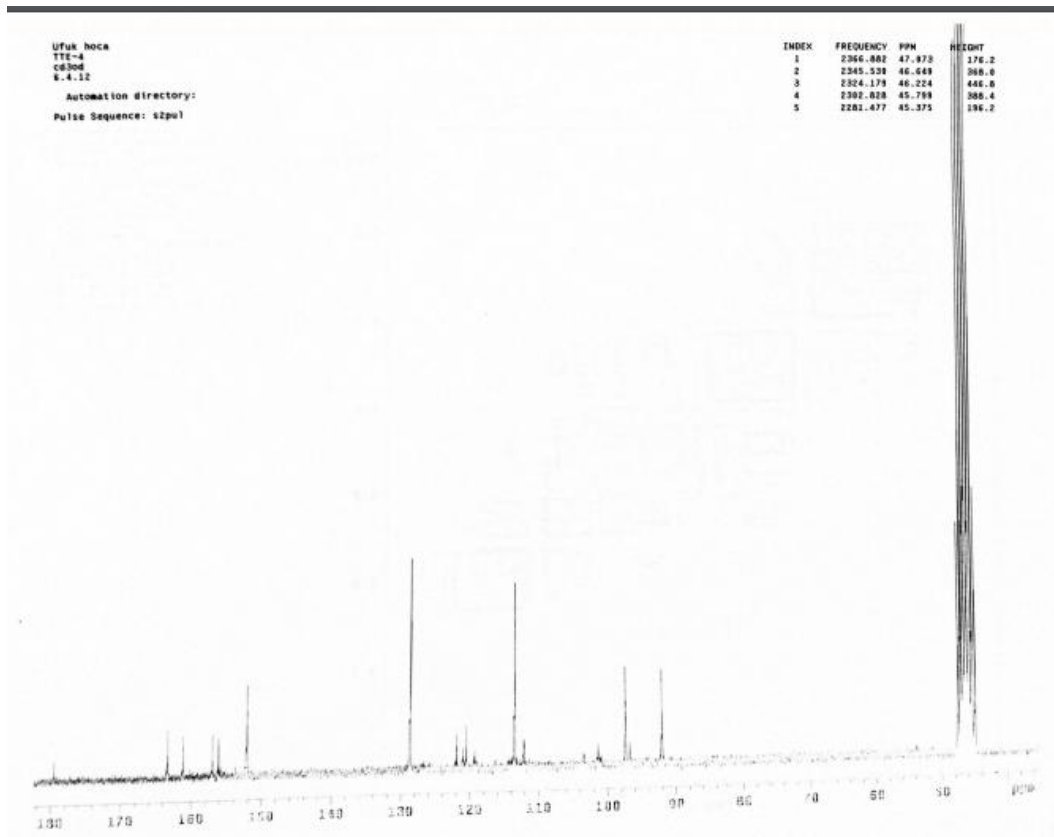


S3: COSY (200 MHz) Spectrum of Compound **1** (daidzein)



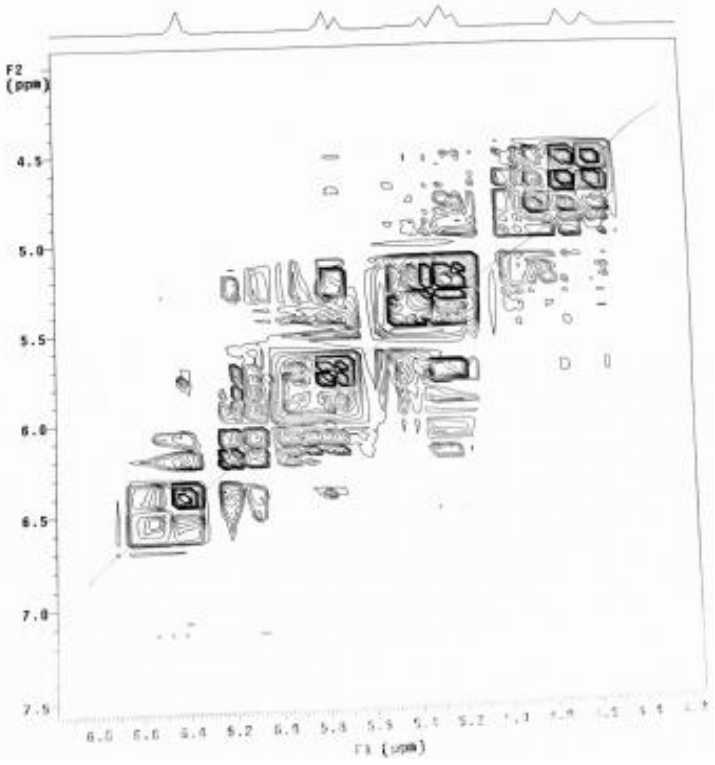
S4: ^1H -NMR (200 MHz, CDCl_3) Spectrum of Compound **2** (genistein)

Genistein: ^1H NMR (200 MHz, CD_3OD): d 8.10 (1H, H-2, s), 7.38 (2H, H-2',6', d, $J=8.2$ Hz), 6.86 (2H, H-3',5', d, $J=8.2$ Hz), 6.34 (1H, H-8, s), 6.22 (1H, H-6, s); ^{13}C NMR (50 MHz, CD_3OD): d 179.4 (C-4), 169.2 (C-7), 161.0 (C-5), 156.9 (C-9), 156.0 (C-4'), 152.0 (C-2), 128.6 (x2C) (C-2',6'), 121.9 (C-3), 120.5 (C-1'), 113.4 (x2C) (C-3', 5'), 101.3 (C-10), 97.3 (C-6), 92.0 (C-8).

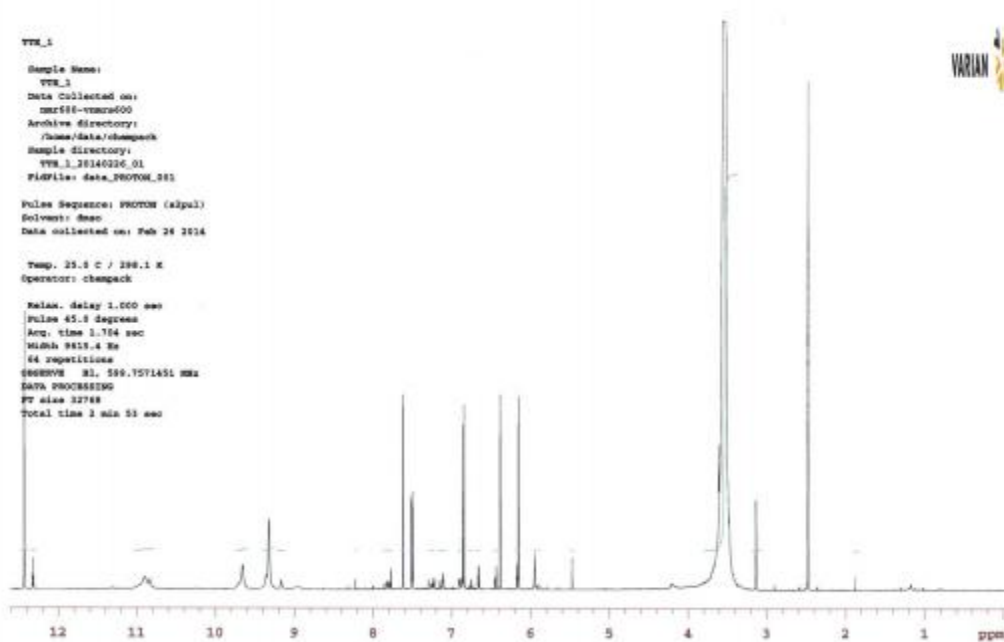


S5: ^{13}C -NMR (50 MHz, CDCl_3) Spectrum of Compound **2** (genistein)

UFS BOCA
TTE-4
C8000
6.4.12
Automation directory:
Pulse Sequence: COSY
Solvent: CD3OD
Ambient Temperature
Operator: vhr1
Mercury-200 "Verahole"
Relax. delay 1.000 sec
Acq. time 9.178 sec
Width 17000.7 Hz
SS width 17000.7 Hz
2 repetitions
120 increments
OBSERVE F1: 100.6248124 MHz
DATA PROCESSING
Sine bell 0.005 sec
F1 DATA PROCESSING
Sine bell 0.005 sec
FT size 65536 x 4096
Total time 7 min, 59 sec

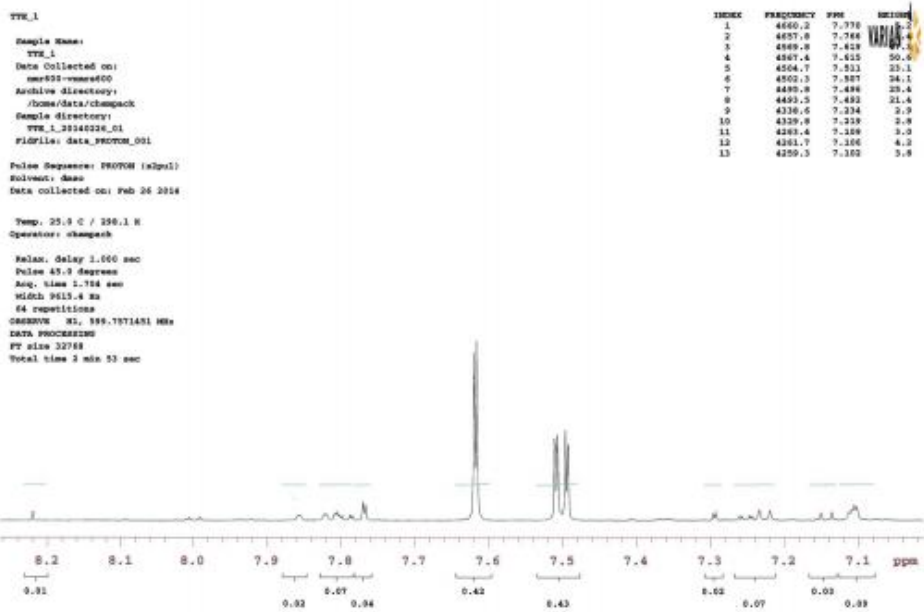


S6: COSY (200 MHz) Spectrum of Compound **2** (genistein)

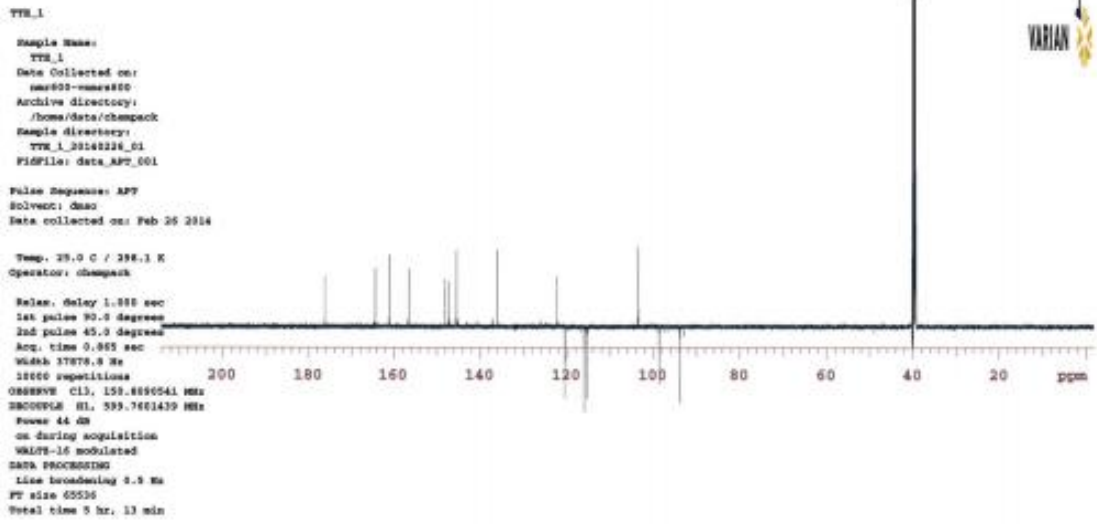


S7: $^1\text{H-NMR}$ (600 MHz, CDCl_3) Spectrum of Compound **3** (quercetin)

Quercetin: $^1\text{H NMR}$ (600 MHz, DMSO-d_6) d: 7.61 (1H, H-2', d, $J=2.4$ Hz), 7.50 (1H, H-6', dd, $J=2.4, 8.8$ Hz), 6.85 (1H, H-5', d, $J= 8.8$ Hz), 6.38 (1H, H-8, d, $J = 1.8$ Hz), 6.15(1H, H-6, d, $J = 2.3$ Hz); $^{13}\text{C NMR}$ (125 MHz, DMSO d_6): d 176.2 (C-4), 164.3 (C-7), 161.1 (C-5), 156.6 (C-9), 148.1 (C-4'), 147.2 (C-2), 145.5 (C-3'), 136.1 (C-3), 122.4 (C-1'), 120,5 (C-6'), 116.0 (C-5'), 115.4 (C-2'), 103.4 (C-10), 98.6 (C-6), 93.8 (C-8).

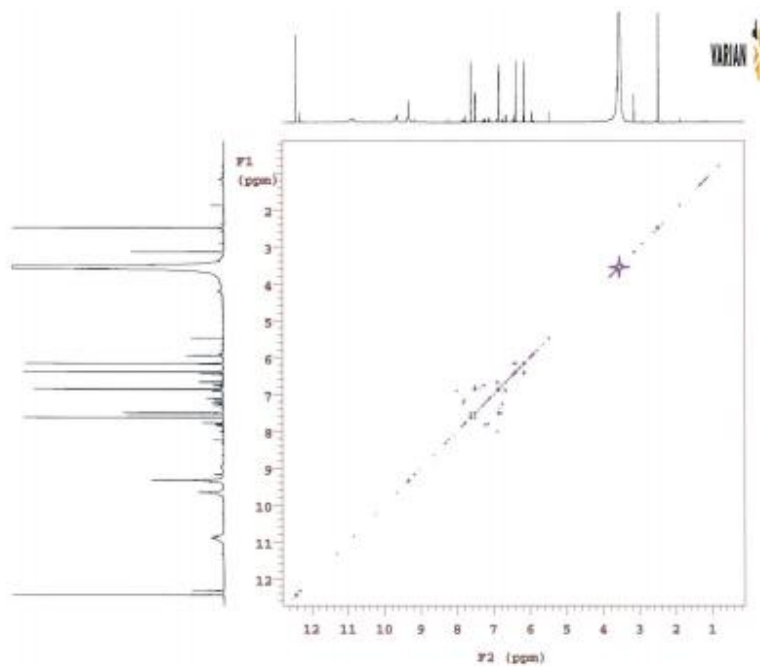


S8: Expansion of the $^1\text{H-NMR}$ Spectrum of Compound **3** (quercetin)



S9: ^{13}C -NMR + DEPT (125 MHz, CDCl_3) Spectrum of Compound **3** (quercetin)

VX1_1
Sample Name:
VX1_1
Data Collected on:
mar08-200400
Archive directory:
/home/data/champack
Sample directory:
VX1_1_20140226_01
FIDFile: data.gCOSY_001
Pulse Sequence: gCOSY
Solvent: dmsc
Date collected on: Feb 24 2014
Temp. 25.0 C / 298.1 K
Operator: champack
Relax. delay 1.000 sec
Acq. time 8.150 sec
Width 3198.0 Hz
2D Width 9188.0 Hz
8 repetitions
512 increments
CROSSPOW E1: 599.7971451 MHz
DATA PROCESSING
Sf. size 6e11 6.075 sec
F1 DATA PROCESSING
Sf. size 6e11 6.093 sec
SF size 4096 x 4096
Total time 1 hr, 22 min



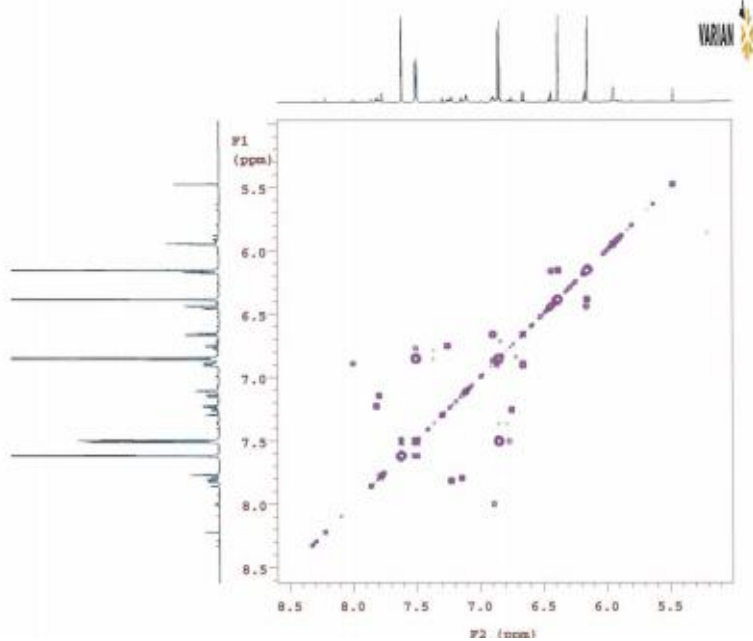
S10: COSY (600 MHz) Spectrum of Compound **3** (quercetin)

VTE_1
Sample Name:
VTE_1
Data Collected on:
msc60-vmsr455
Archive Directory:
/home/data/chempack
Sample Directory:
VTE_1_20140224_51
File(s): data_gCOSY_501

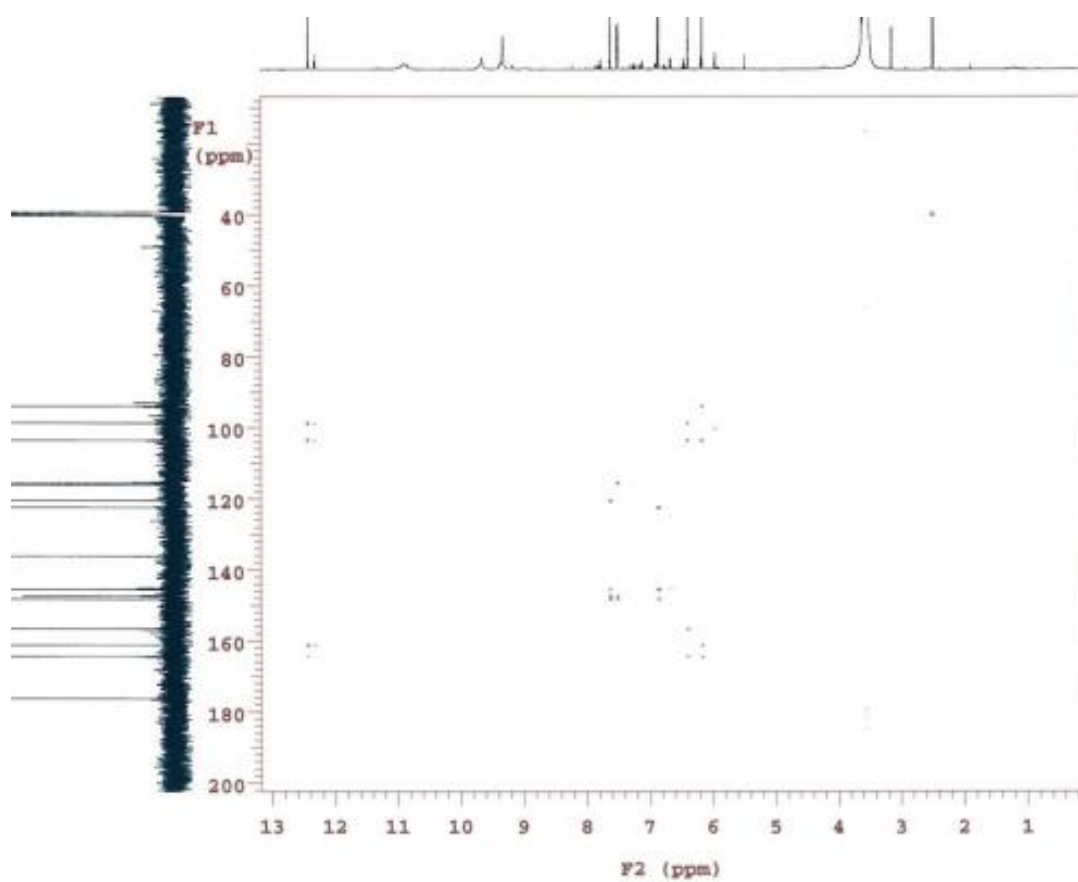
Pulse Sequence: gCOSY
Solvent: GMSO
Data collected on: Feb 24 2014

Temp: 25.0 C / 298.1 K
Operator: chempack

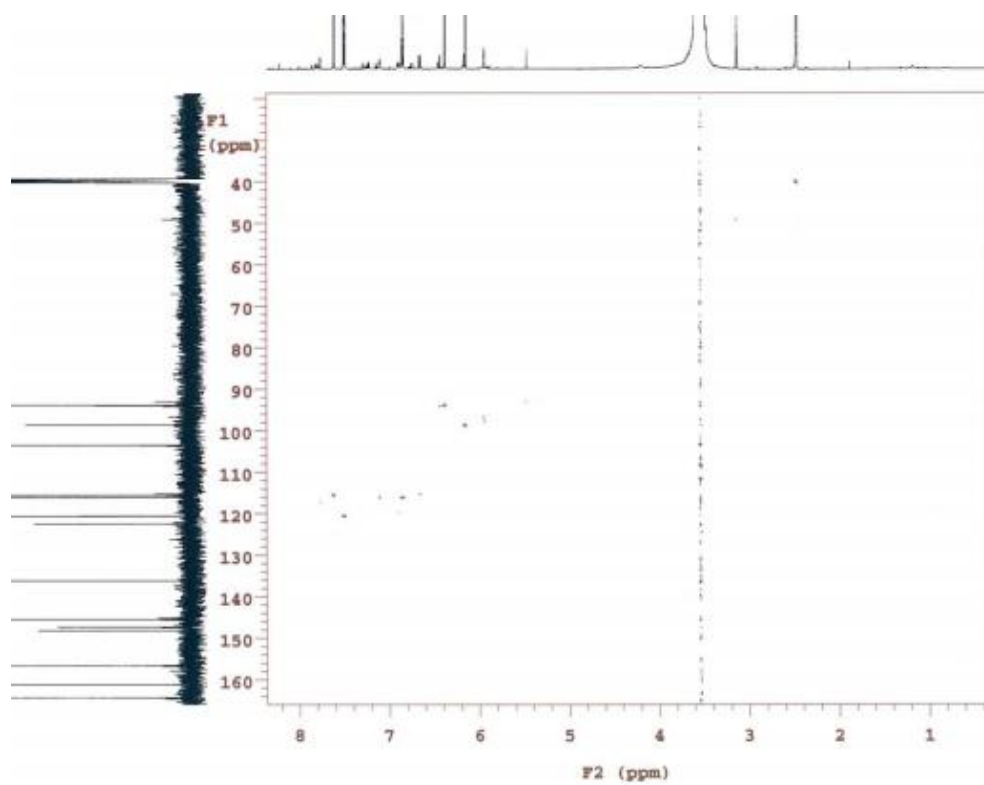
Solen. Delay 1.355 sec
Acq. time 2.152 sec
Width 9298.3 Hz
2D Width 9298.3 Hz
repetitions
312 scans/trace
CROSSPO - 91, 298.7571451 MHz
DATA PROCESSING
Sg. size half 8.875 sec
F1 DATA PROCESSING
Sg. size half 8.851 sec
FF size 4096 x 4096
Total time 1 hr, 22 min



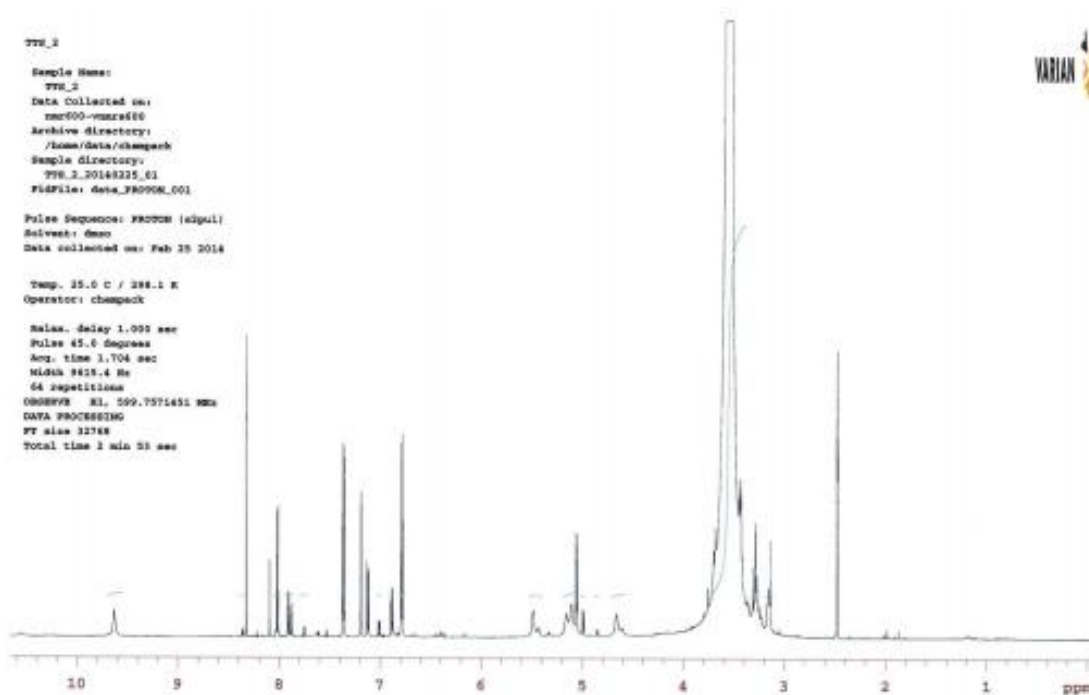
S11: Expansion of the COSY (600 MHz) Spectrum of Compound **3** (quercetin)



S12: HMBC (600 MHz) Spectrum of Compound **3** (quercetin)

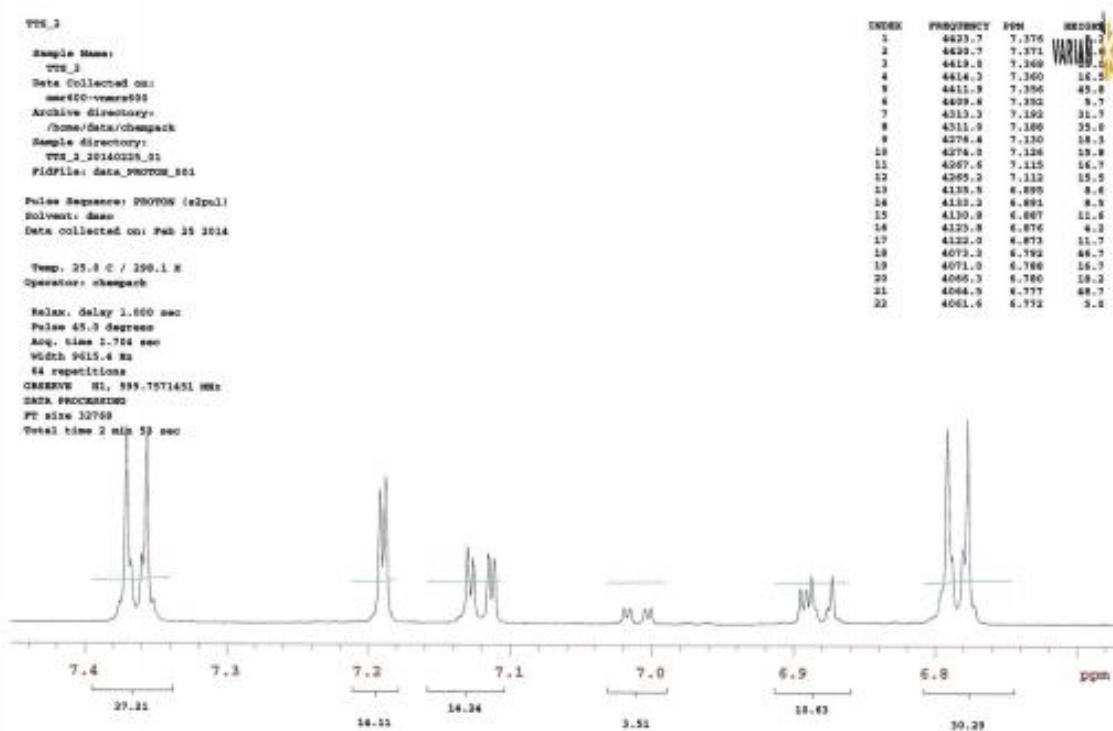


S13: HSQC (600 MHz) Spectrum of Compound **3** (quercetin)

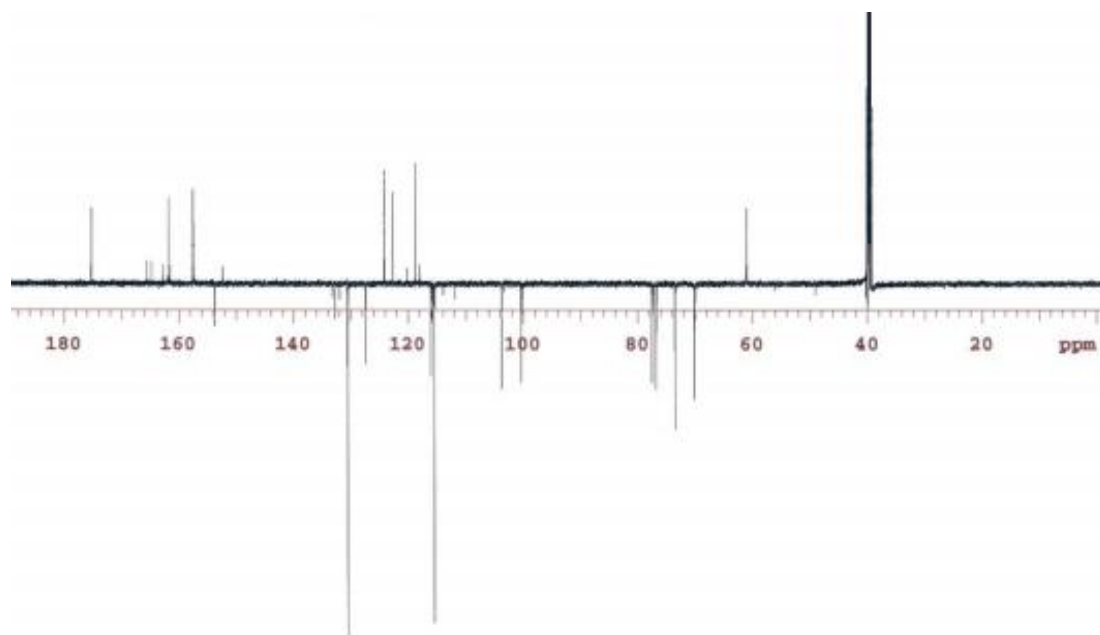


S14: $^1\text{H-NMR}$ (600 MHz, CDCl_3) Spectrum of Compound **4** (daidzein 4'- O - β -glucoside)

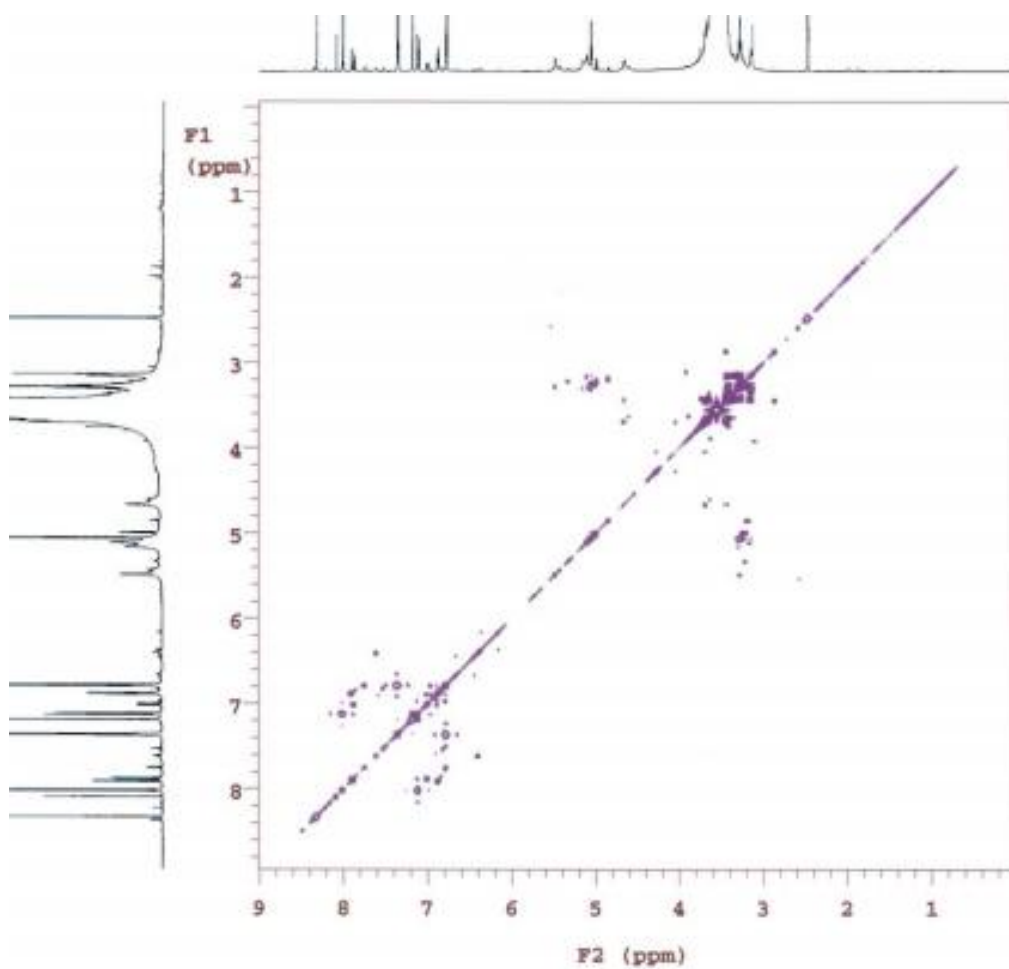
Daidzein 4'- O - β -glucoside: $^1\text{H NMR}$ (600 MHz, DMSO-d_6): δ 8.38 (1H, H-2, s), 8.04 (1H, H-5, d), 7.40 (2H, H-2',6', d), 7.22 (1H, H-8, s), 7.14 (1H, H-6, d), 6.81 (2H, H-3',5', d), 5.11 (1H, H-1'', d), 3.68-3.18 (6H, m, sugar protons); $^{13}\text{C NMR}$ (125 MHz, DMSO-d_6): δ 180.3 (C-4), 166.8 (C-7), 162.7 (C-9), 162.5 (C-4'), 158.3 (C-2), 135.6 (x2C) (C-2',6'), 132.4 (C-5), 129.1 (C-1'), 127.7 (C-3), 123.9 (C-10), 121.1 (C-6), 120.4 (x2C) (C-3', 5'), 108.8 (C-8), 105.3 (C-1''), 82.6 (C-5''), 81.8 (C-2''), 78.5 (C-3''), 75.0 (C-4''), 66.0 (C-6'').



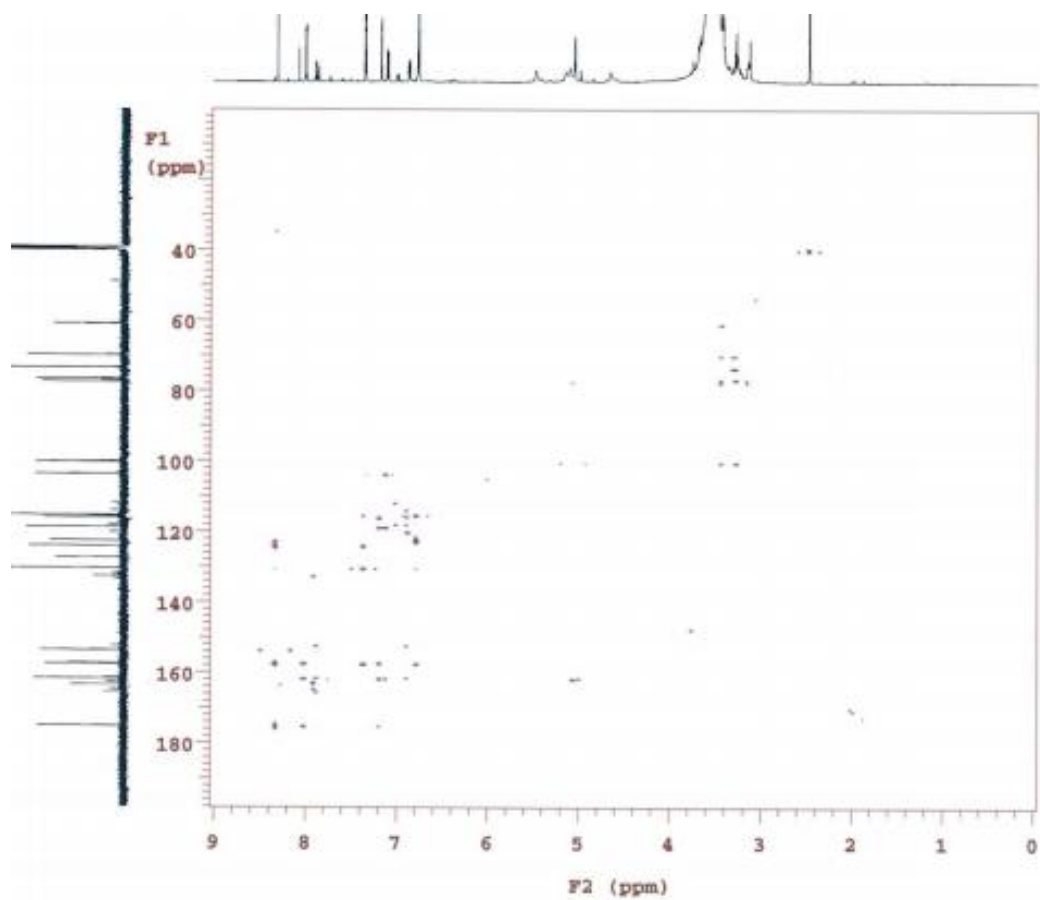
S15: Expansion of the ¹H-NMR Spectrum of Compound **4** (daidzein 4'-O-β-glucoside)



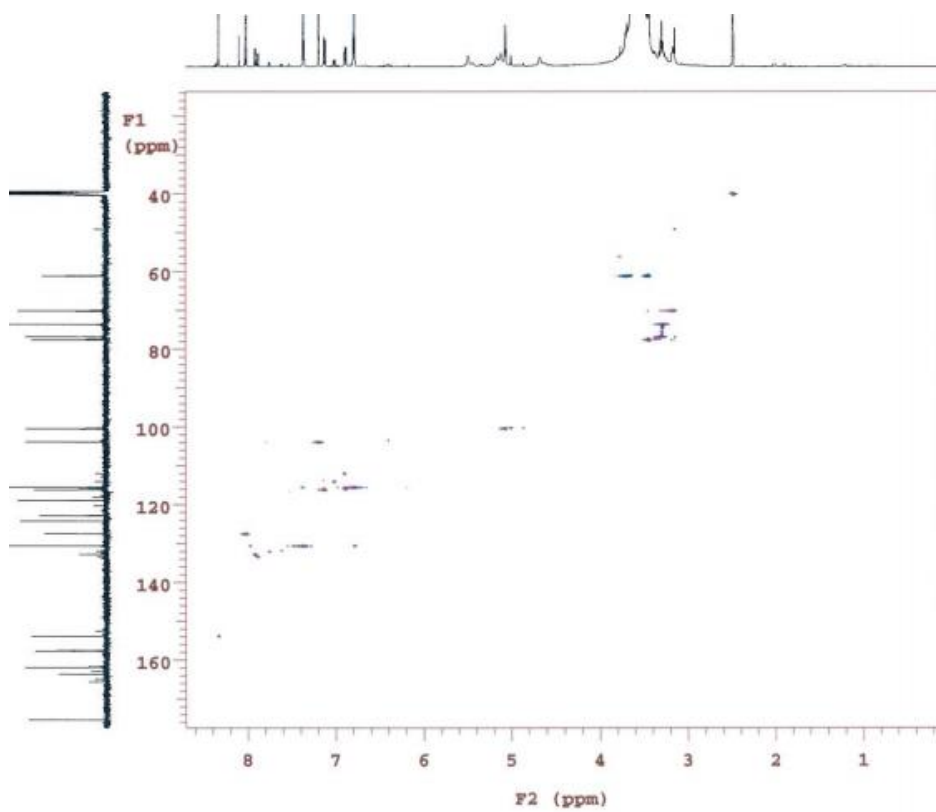
S16: ^{13}C -NMR + DEPT (125 MHz, CDCl_3) Spectrum of Compound **4** (daidzein 4'- O - β -glucoside)



S17: COSY (600 MHz) Spectrum of Compound **4** (daidzein 4'-*O*- β -glucoside)



S18: HMBC (600 MHz) Spectrum of Compound **4** (daidzein 4'-O-β-glucoside)



S19: HSQC (600 MHz) Spectrum of Compound **4** (daidzein 4'-*O*- β -glucoside)