Supporting Information

***Rec. Nat. Prod*. X:X (202X) XX-XX**

Butanedioic Acid Benzyl Ester Glycosides from *Pleione bulbocodioides* (Franch.) Rolfe: Promising Fungicide against *Phoma herbarum*

Shilin Liu[1#], Jiarui Fu[1#], Yuping Fu[1], Yuanan Chen[1], Lijun Zheng[2], Huiyou Xu[1], and Lin Ni[1*]

[1] *College of Plant Protection, Fujian Agriculture and Forestry University, Fuzhou 350002, People's Republic of China*

[2]*Department of Pharmacy, Fujian Medical University Union Hospital, Fuzhou 350002, People's Republic of China*

© 2024 ACG Publications. All rights reserved.

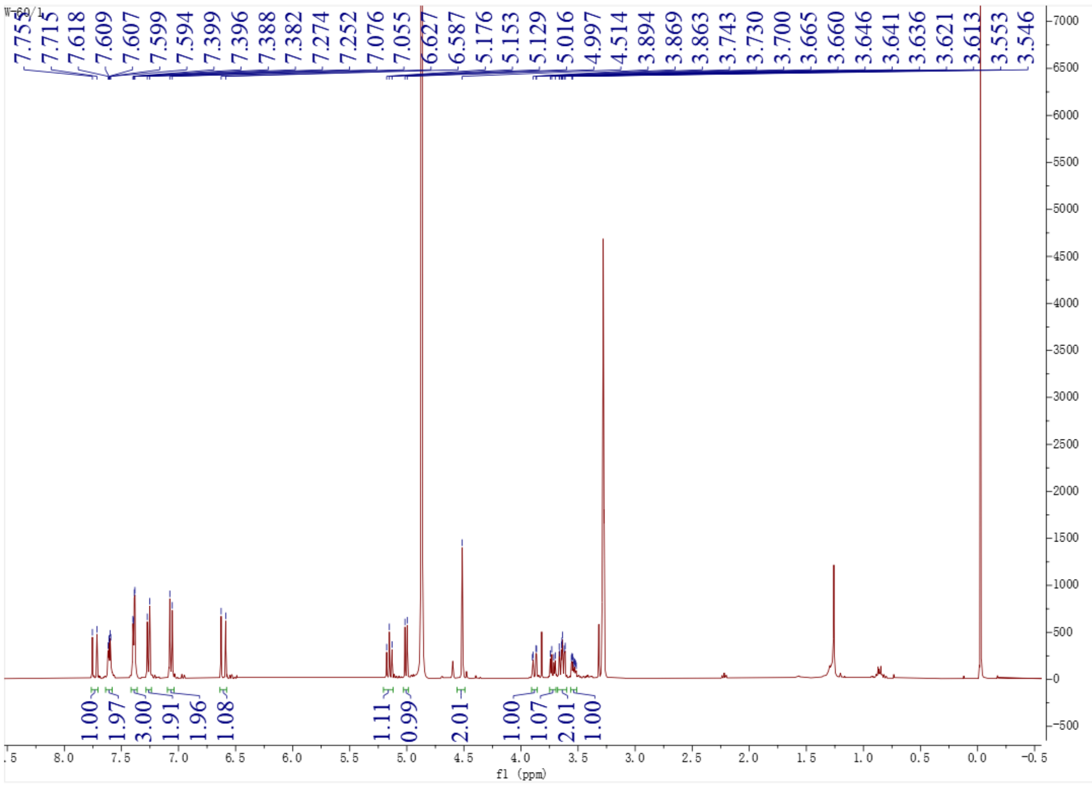

Figure S1: ^{1}H-NMR (400 MHz, Methanol-d_4) spectrum of **1**

1-*O*-(4-hydroxymethylphenoxy)-*3*-*O*-trans-cinnamoyl-*β*-D-glucoside)

^{1}H-NMR (400 MHz, Methanol-d_4): 7.73 (1H, d, *J* = 16.0 Hz, H-7"), 7.61 (2H, m, H-2", 6"), 7.40 (2H, m, H-3",5"), 7.38(1H, m, H-4"), 7.26 (2H, d, *J* = 8.8 Hz, H-3', 5'), 7.07 (2H, d, *J* = 8.4 Hz, H-2', 6'), 6.61 (1H, d, *J* = 16.0 Hz, H-8"), 5.15 (1H, t, *J* = 9.4 Hz, H-3), 5.01 (1H, d, *J* = 7.8 Hz, H-1), 4.51 (2H, s, H-7'), 3.64 (2H, m, H-2), 3.88 (1H, dd, *J* = 2.0 Hz, 12.0 Hz, H-6a), 3.54-3.72 (4H, m, H-2, 4, 5, 6b).

© 2024 ACG Publications. All rights reserved.

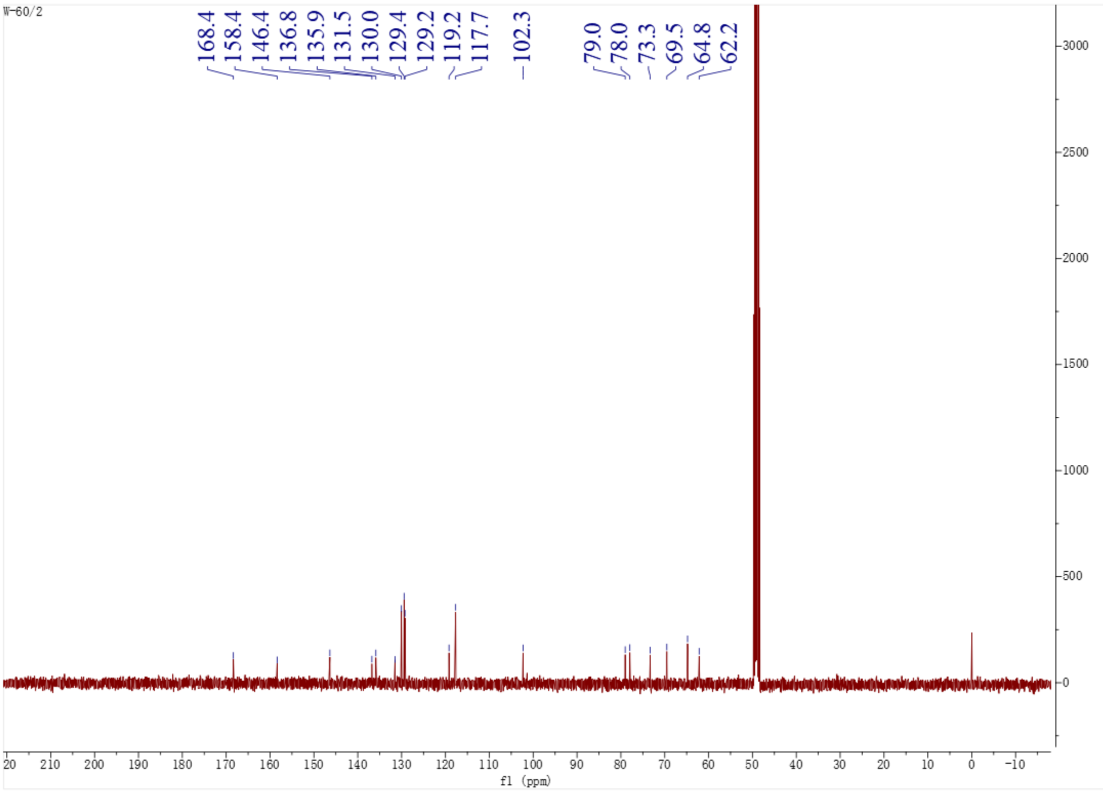

Figure S2: ^{13}C-NMR (100 MHz, Methanol-d_4) spectrum of **1**

(1-*O*-(4-hydroxymethylphenoxy)-3-*O*-*trans*-cinnamoyl-*β*-D-glucoside)

^{13}C-NMR(100 MHz, Methanol-d_4) δ: 102.3 (C-1), 73.3 (C-2), 78.0 (C-3), 69.5 (C-4), 79.0 (C-5), 62.2 (C-6), 158.4 (C-1'), 129.2 (C-3',C-5'), 136.8 (C-4'), 117.7 (C-6'), 64.8 (C-7'), 135.9 (C-1''), 129.4 (C-2'',C-6''), 130.0 (C-3'', C-5''), 131.5 (C-4''), 146.4 (C-7''), 119.2 (C-8''), 168.4 (C-9'').

© 2024 ACG Publications. All rights reserved.

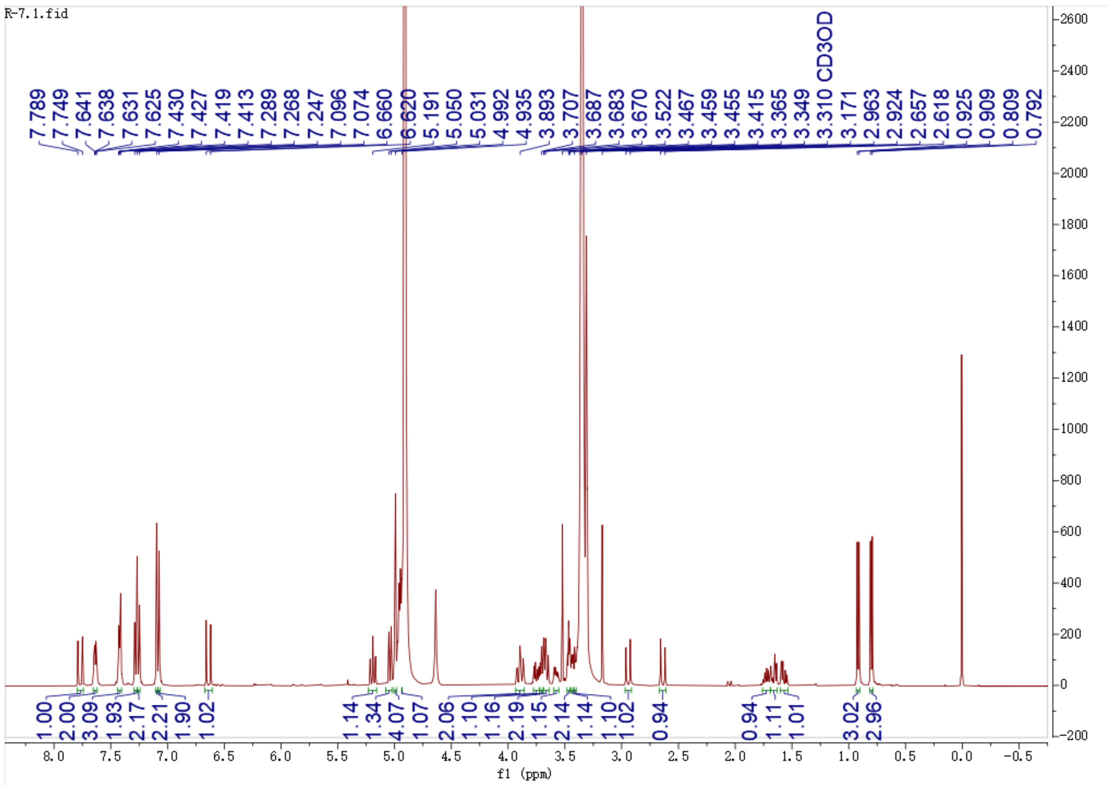

Figure S3: ^{1}H-NMR (400 MHz, Methanol-d_4) spectrum of **2** (Pleioneside C)

^{1}H-NMR (400 MHz, Methanol-d_4): 7.77 (1H, d, *J* = 16.0 Hz, H-7'''''), 7.64 (2H, m, H-2''''', 6'''''), 7.42 (2H, m, H-3''''', 5'''''), 7.42 (1H, m, H-4'''''), 7.28 (2H, d, *J* =8.4 Hz, H-2'', 6''), 7.25 (2H, d, *J* =8.4 Hz, H-2', 6'), 7.10 (2H, d, *J* =8.4 Hz, H-3'', H-5''), 7.07 (2H, d, *J* =8.4 Hz, H-3', H-5'), 6.64 (1H, d, *J* = 16.0 Hz, H-8'''''), 5.19 (1H, t, *J* = 9.6 Hz, H-3'''), 5.04 (1H, d, *J* = 8.0 Hz, H-1'''), 4.99 (2H, overlapped, m, H-7', 7''), 4.93 (1H, d, *J* = 7.6 Hz, H-1''''), 3.89 (2H, dd, *J* = 12.0, 2.0 Hz, H-6′′′a, H-6′′′′a), 3.71 (1H, dd, *J* = 12.0, 5.2 Hz, H-6′′′b), 3.71 (1H, m, H-6′′′′b), 3.68 (1H, m, H-4′′′), 3.58 (1H, m, H-5′′′), 3.41~3.47 (4H, m, H-2'''', H-3'''', H-4'''', H-5''''), 2.94 (1H, d, *J* = 16.0 Hz, H-3a) , 2.64 (1H, d, *J* = 16.0 Hz, H-3b), 1.72 (1H, m, H-6), 1.57~1.66 (2H, H-5, m), 0.92 (3H, d, *J* = 8.0 Hz, H-7), 0.80 (3H, d, *J* =8.0 Hz, H-8).

© 2024 ACG Publications. All rights reserved.

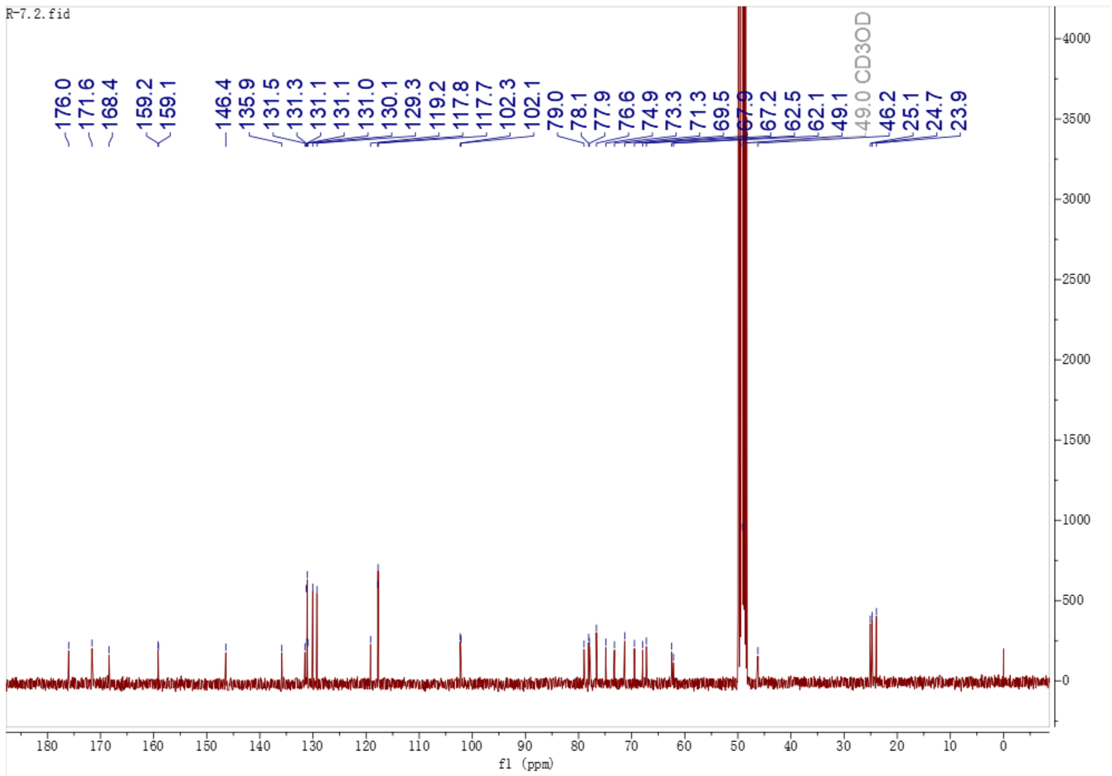

Figure S4: ^{13}C-NMR (100 MHz, Methanol-d_4) spectrum of **2** (Pleioneside C)

^{13}C-NMR (100 MHz, Methanol-d_4) δ: 176.0 (C-1), 76.6 (C-2), 46.2 (C-3), 171.6 (C-4), 49.1 (C-5), 25.1 (C-6), 24.7 (C-7), 23.9 (C-8), 131.1 (C-1', C-2'', C-6''), 131.3 (C-2', C-6'), 117.8 (C-3', C-5'), 159.2 (C-4'), 67.9 (C-7'), 131.0 (C-1''), 117.7 (C-3'', C-5''), 159.1 (C-4''), 67.2 (C-7''), 102.1 (C-1'''), 73.3 (C-2'''), 79.0(C-3'''), 69.5 (C-4'''), 78.0 (C-5'''), 62.1 (C-6'''), 102.3 (C-1''''), 74.9 (C-2''''), 77.9 (C-3''''), 71.3 (C-4''''), 78.1 (C-5''''), 62.5 (C-6''''), 135.9 (C-1'''''), 129.3 (C-2''''', C-6'''''), 130.1 (C-3''''', C-5'''''), 131.5 (C-4'''''), 146.4 (C-7'''''), 119.2 (C-8'''''), 168.4 (C-9''''').

© 2024 ACG Publications. All rights reserved.

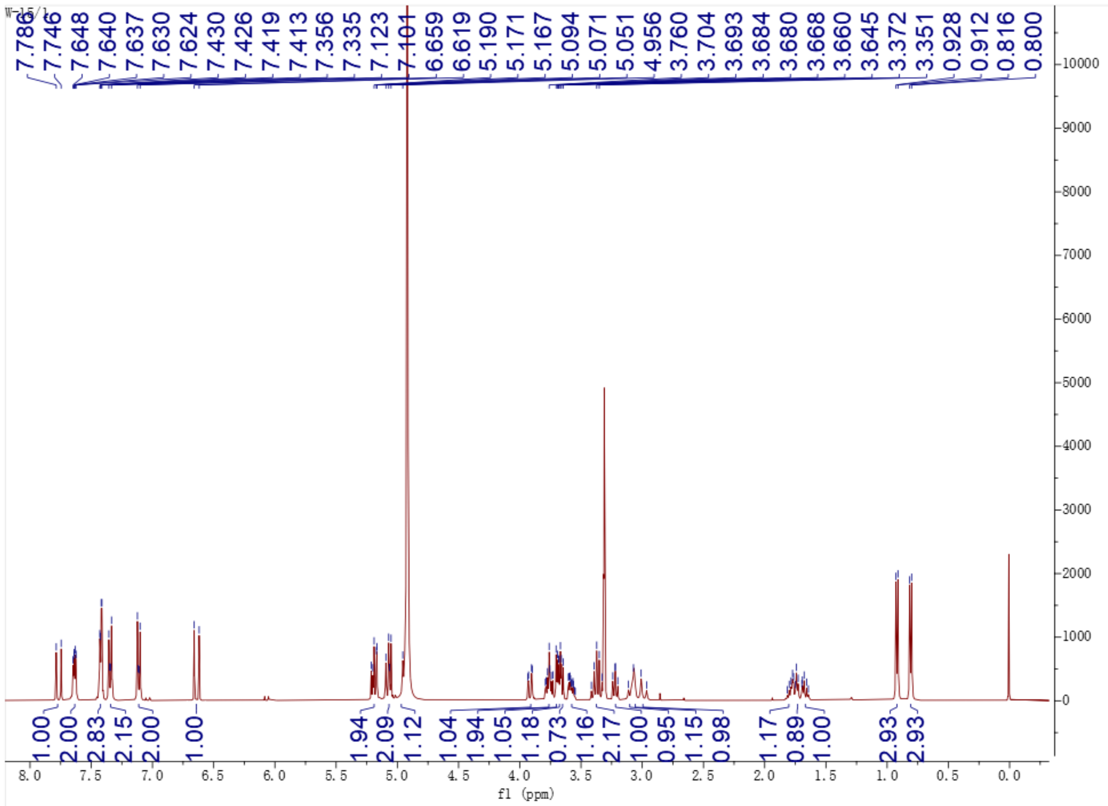

Figure S5: ^{1}H-NMR (400 MHz, Methanol-d_4) spectrum of **3** (Pleioneside B)

^{1}H-NMR (400 MHz, Methanol-d_4)：7.77 (1H, d, *J* = 16.0 Hz, H-7'''), 7.64 (2H, m, H-2''', 6'''), 7.42 (2H, m, H-3''', 5'''), 7.42 (1H, m, H-4'''), 7.35 (2H, d, *J* =6.4 Hz, H-2', 6'), 7.10 (2H, d, *J* =6.4 Hz, H-3', 5'), 6.64 (1H, d, *J* = 16.0 Hz, H-8'''), 5.20 (1H, m, H-3''), 5.17 (1H, d, *J* = 12.0 Hz, H-7'a), 5.08 (1H, d, *J* = 12.0 Hz, H-7'b), 5.05 (1H, d, *J* = 8.0 Hz, H-1''), 4.95 (1H, d, *J* = 8.0 Hz, H-1''''), 3.92 (1H, dd, *J* = 12.0, 2.0 Hz, H-6″a), 3.76 (1H, dd, *J* = 12.0, 5.2 Hz, H-6″b), 3.76 (1H, m, H-6″″a), 3.70 (1H, m, H-6″″b), 3.68 (1H, m, H-2″), 3.66 (1H, m, H-4″), 3.60 (1H, m, H-5″), 3.40 (1H, m, H-3″″), 3.36 (1H, m, H-5″″), 3.22 (1H, t, *J* = 8.0 Hz, H-2″″), 3.09 (2H, m, H-3), 1.78 (1H, m, H-6),1.73 (2H, m, H-5), 0.92 (3H, d, *J* =6.4 Hz, H-7), 0.80 (3H, d, *J* =6.4 Hz, H-8).

© 2024 ACG Publications. All rights reserved.

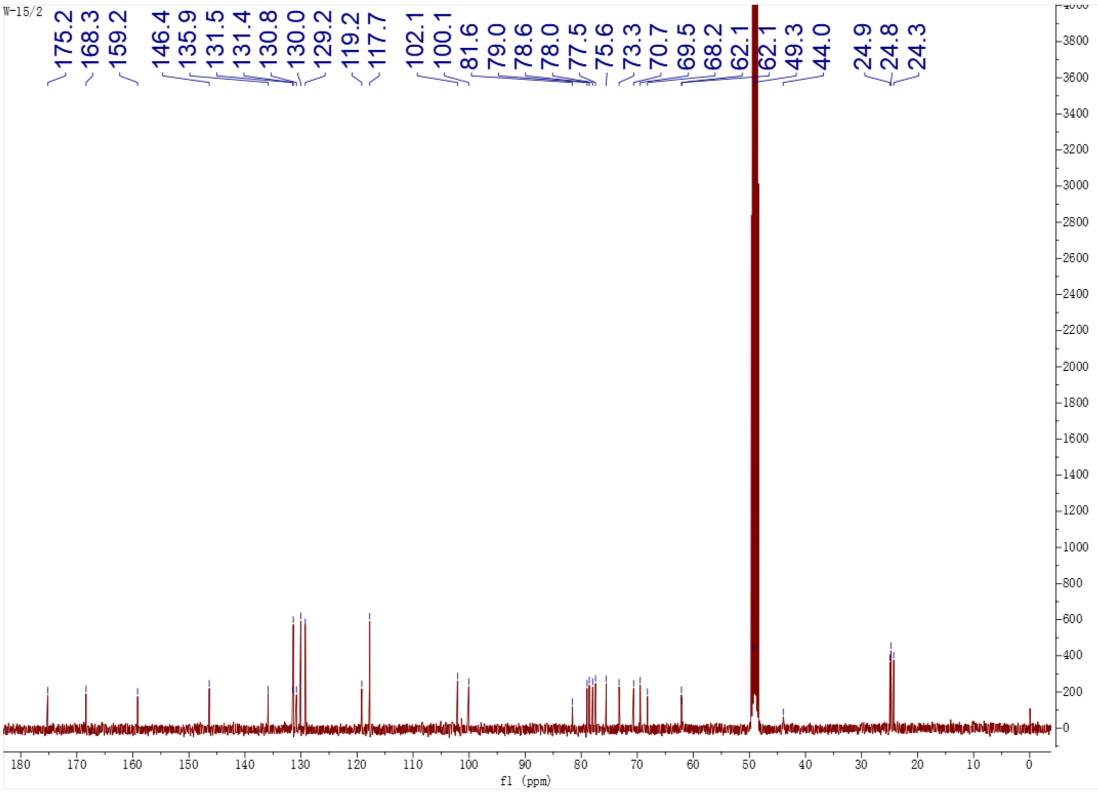

Figure S6: ^{13}C-NMR (100 MHz, Methanol-d_4) spectrum of **3** (Pleioneside B)

^{13}C-NMR (100 MHz, Methanol-d_4) δ: 175.2 (C-1), 81.6 (C-2), 44.0 (C-3), 174.7 (C-4), 49.3 (C-5), 24.9 (C-6), 24.8 (C-7), 24.3 (C-8), 130.8 (C-1'), 131.4 (C-2', 6'), 117.7 (C-3', 5'), 159.2 (C-4'), 68.2 (C-7'), 102.1 (C-1''), 73.3 (C-2''), 79.0 (C-3''), 69.5 (C-4''), 78.0 (C-5''), 62.1 (C-6'', 6''''), 135.9 (C-1'''), 129.2 (C-2''', 6'''), 130.1 (C-3''', 5'''), 131.5 (C-4'''), 146.3 (C-7'''), 119.2 (C-8'''), 168.5 (C-9'''), 100.1 (C-1''''), 75.6 (C-2''''), 77.4 (C-3''''), 70.7 (C-4''''), 78.6 (C-5'''').

© 2024 ACG Publications. All rights reserved.

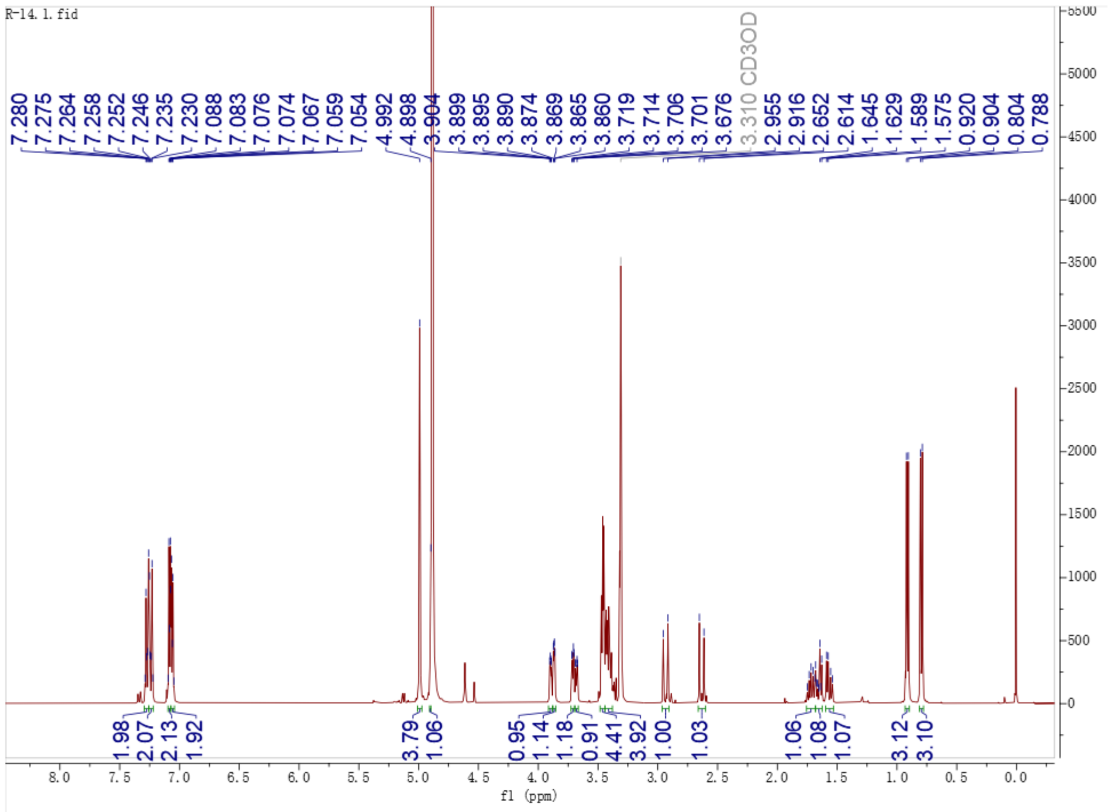

Figure S7: ^{1}H-NMR (400 MHz, Methanol-*d₄*) spectrum of **4** (militarine)

^{1}H-NMR (400 MHz, Methanol-d_4): 7.25 (4H, d, *J* = 8.8 Hz, H-2', 6',H-2''', 6'''), 7.08 (2H, d, *J* = 8.4 Hz, H-3', 5'), 7.06 (2H, d, *J* = 8.4 Hz, H-3''', 5'''), 4.99 (4H, s, H-7', 7''), 4.90 (1H, s, H-1''), 3.90 (2H, m, J = H-6″b, 6″″b) , 3.71 (2H, m, H-6″a, H-6″″a), 3.47 (2H, m, H-3″, 3″″) , 3.45 (2H, m, H-5″, 5″″) , 3.43 (2H, m, H-2″, 2″″) , 3. 40 (2H, m, H-4″, 4″″) , 2.94 (1H, d, *J* = 15.6 Hz, H-3a), 2.63 (1H, d, *J* = 15.6 Hz, H-3b) , 1.72 (1H, m, H-5a) ,1.65 (1H, m, H-6) , 1.56 (1H, m, H-5b), 0.91 (3H, d, *J* = 6.4 Hz, H-7), 0.80 (3H, d, *J* = 6.4 Hz, H-8).

© 2024 ACG Publications. All rights reserved.

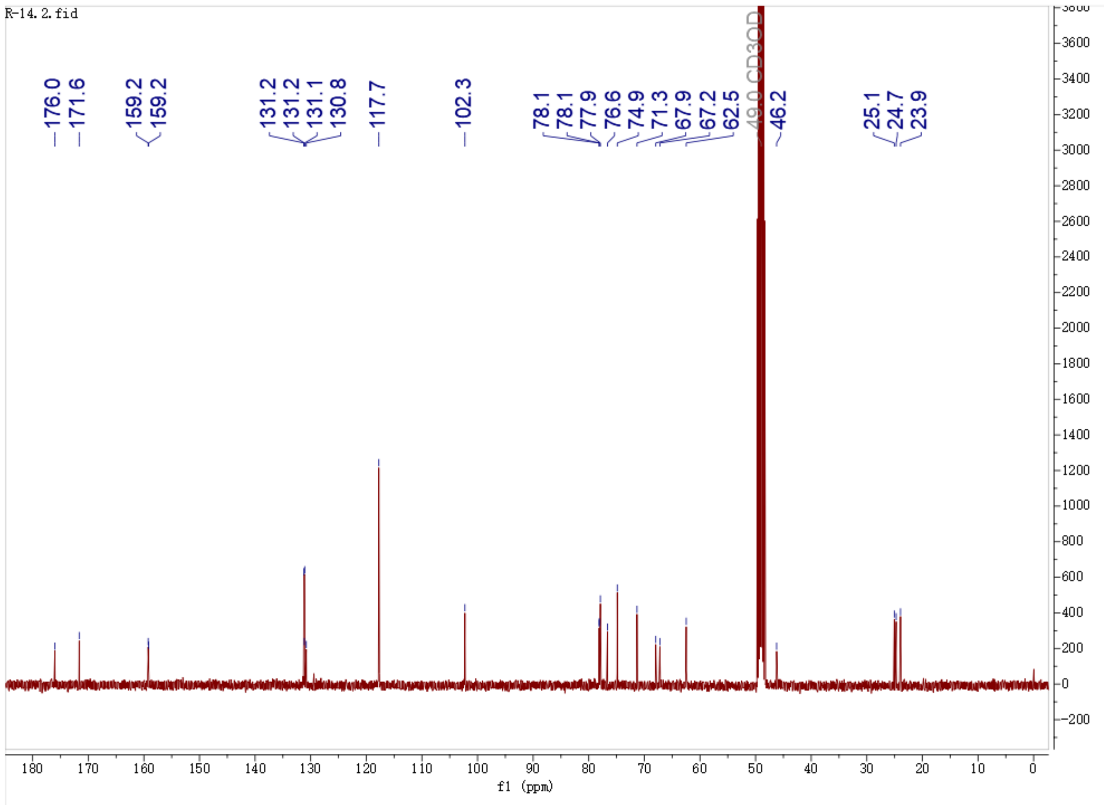

Figure S8: ^{13}C-NMR (100 MHz, Methanol-d_4) spectrum of **4** (militarine)

^{13}C-NMR (100 MHz, Methanol-d_4) δ: 176.0 (C-1), 76.6 (C-2), 46.2 (C-3), 171.6 (C-4), 49.3 (C-5), 25.1 (C-6), 24.7 (C-7), 23.9 (C-8), 131.2 (C-1', 2', 6'), 117.7 (C-3', 5', 3''', 5''), 159.2 (C-4', 4'''), 130.8 (C-1'''), 131.1 (C-2''', 6'''), 102.3 (C-1'', 1''''), 74.9 (C-2'', 2''''), 77.9 (C-3'', 3''''), 71.3 (C-4'', 4''''), 78.1 (C-5'', 5''''), 62.5 (C-6'', 6''''), 67.9 (C-7'), 67.2 (C-7''').

© 2024 ACG Publications. All rights reserved.

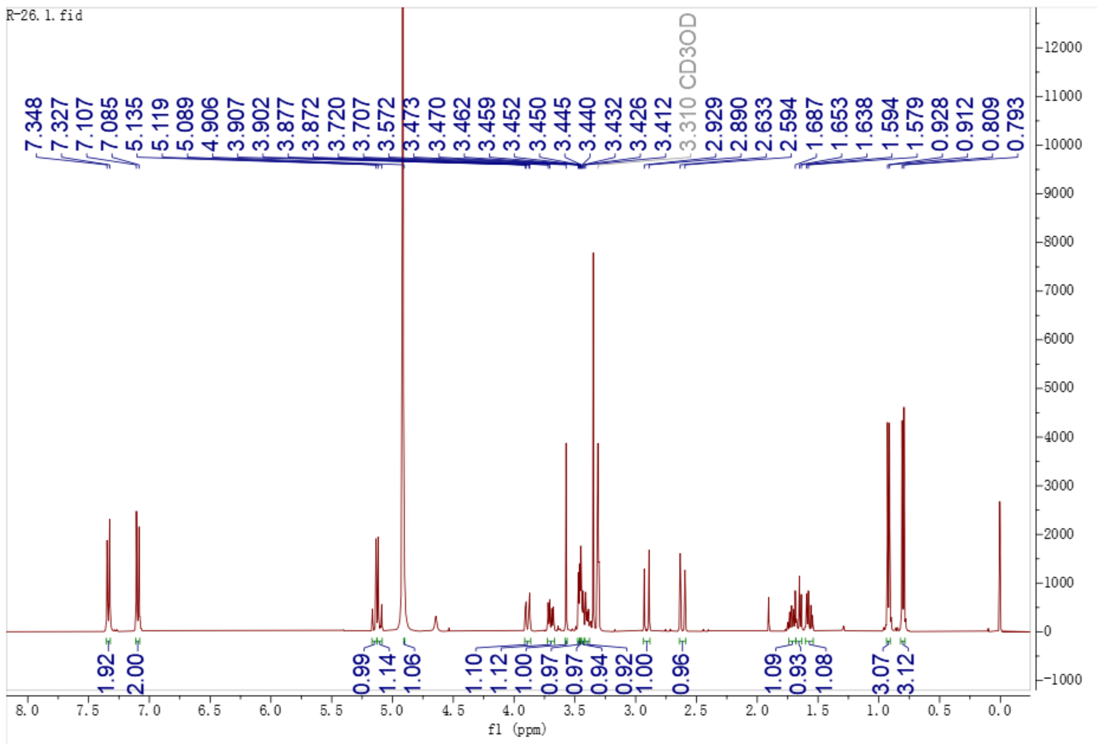

Figure S9: ^{1}H-NMR (400 MHz, CD_3OD-d_4) spectrum of **5** (1-(4-*β*-D-glucopyranosyloxyb-enzyl) 4-methyl (2R)-2-isobutylmalate)

^{1}H NMR (400 MHz, CD_3OD-d_4): 7.34 (2H, d, *J* = 8.4 Hz, H-2', 6'), 7.10 (2H, d, *J* = 8.8 Hz, H-3', 5'), 5.14 (1H, d, *J* =12.0 Hz, H-7'a), 5.10 (1H, d, *J* =12.0 Hz, H-7'b), 4.91 (1H, s, H-1''), 3.89 (1H, dd, *J* = 12.0, 2.0 Hz, H-6''a), 3.70 (1H, dd, *J* = 12.0, 5.0 Hz, H-6''b), 3.40~3.47 (4H, m, H-2'', 3'', 4'', 5''), 2.91 (1H, d, *J* = 15.6 Hz, H-3a), 2.61 (1H, d, *J* = 15.6 Hz, H-3b), 1.71 (1H, m, H-6), 1.65 (1H, m, H-5a), 1.57 (1H, m, H-5b), 0.92 (3H, d, *J* = 6.4 Hz, H-7), 0.80 (3H, d, *J* = 6.4 Hz, H-8).

© 2024 ACG Publications. All rights reserved.

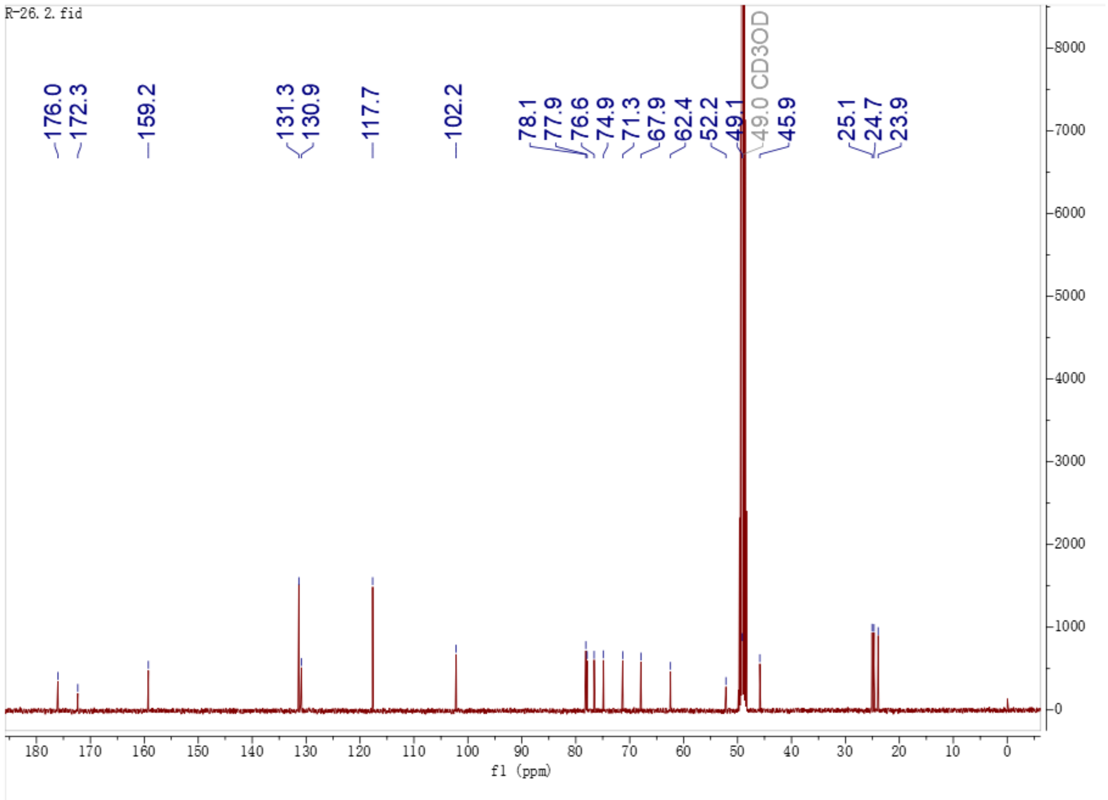

Figure S10: ^{13}C-NMR (100 MHz, CD_3OD-d_4) spectrum of **5** (1-(4-*β*-D-glucopyranosyloxyb-enzyl)4-methyl (2R)-2-isobutylmalate)

^{13}C-NMR (100 MHz, CD_3OD-d_4) δ:176.0 (C-1), 76.6 (C-2), 45.9 (C-3), 172.3 (C-4), 49.1 (C-5), 25.1 (C-6), 24.7 (C-7), 23.9 (C-8), 130.9 (C-1'), 131.3 (C-2', 6'), 117.7 (C-3', 5'), 159.2 (C-4'), 67.9 (C-7'), 102.2 (C-1''), 74.9 (C-2''), 77.9 (C-3''), 71.3 (C-4''), 78.1 (C-5''), 62.4 (C-6'').

© 2024 ACG Publications. All rights reserved.

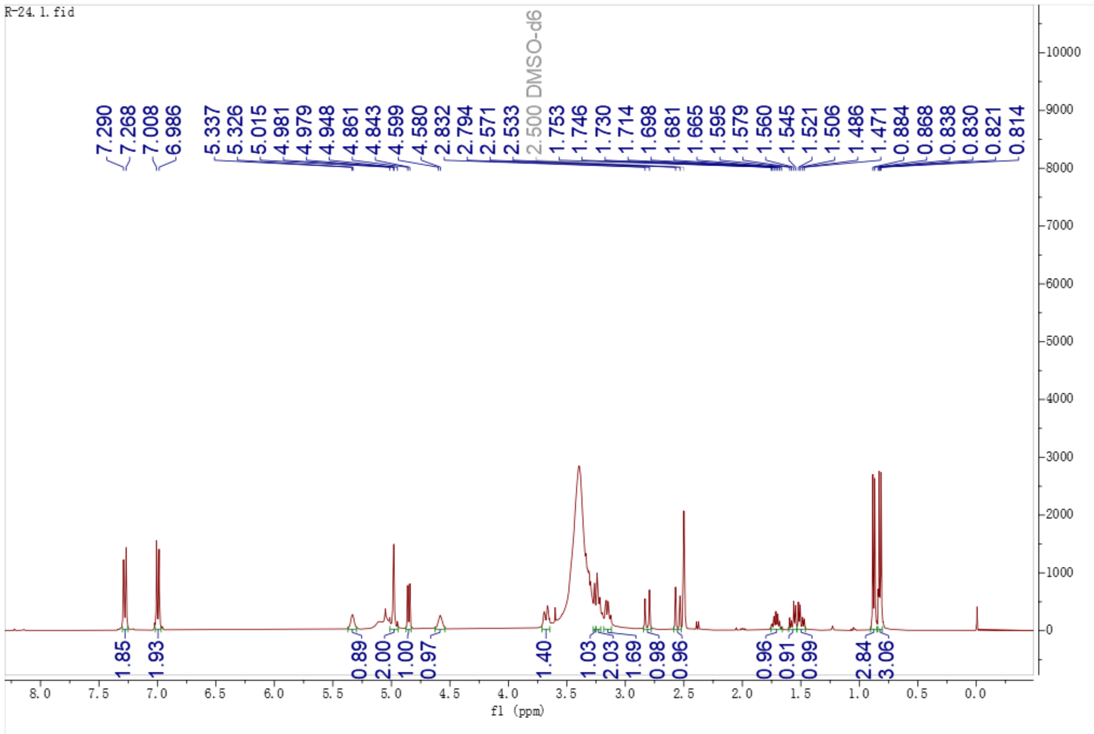

Figure S11: ^{1}H-NMR (400 MHz, DMSO-d_6) spectrum of **6** (gymnoside I)

^{1}H-NMR (400 MHz, DMSO-d_6): 7.28 (2H, d, *J* = 8.8 Hz, H-2', 6'), 7.00 (2H, d, *J* = 8.8 Hz, H-3', 5'), 4.98 (2H, d, *J* = 2.0 Hz, H-7'), 4.85 (1H, d, *J* = 7.2 Hz, H-1''), 3.68 (1H, d, *J* = 11.6 Hz, H-6a), 3.15~3.23 (4H, m, H-2'',3'',4'',5''), 2.81 (1H, d, *J* = 15.2 Hz, H-3a), 2.55 (1H, d, *J* = 15.2 Hz, H-3b), 1.71 (1H, m, H-6), 1.57 (1H, dd, *J* = 14.0, 6.4 Hz, H-5a), 1.50 (1H, dd, *J* = 14.0, 6.4 Hz, H-5b), 0.88 (3H, d, *J* = 6.4 Hz, H-7), 0.82 (3H, d, *J* = 6.4 Hz, H-8).

© 2024 ACG Publications. All rights reserved.

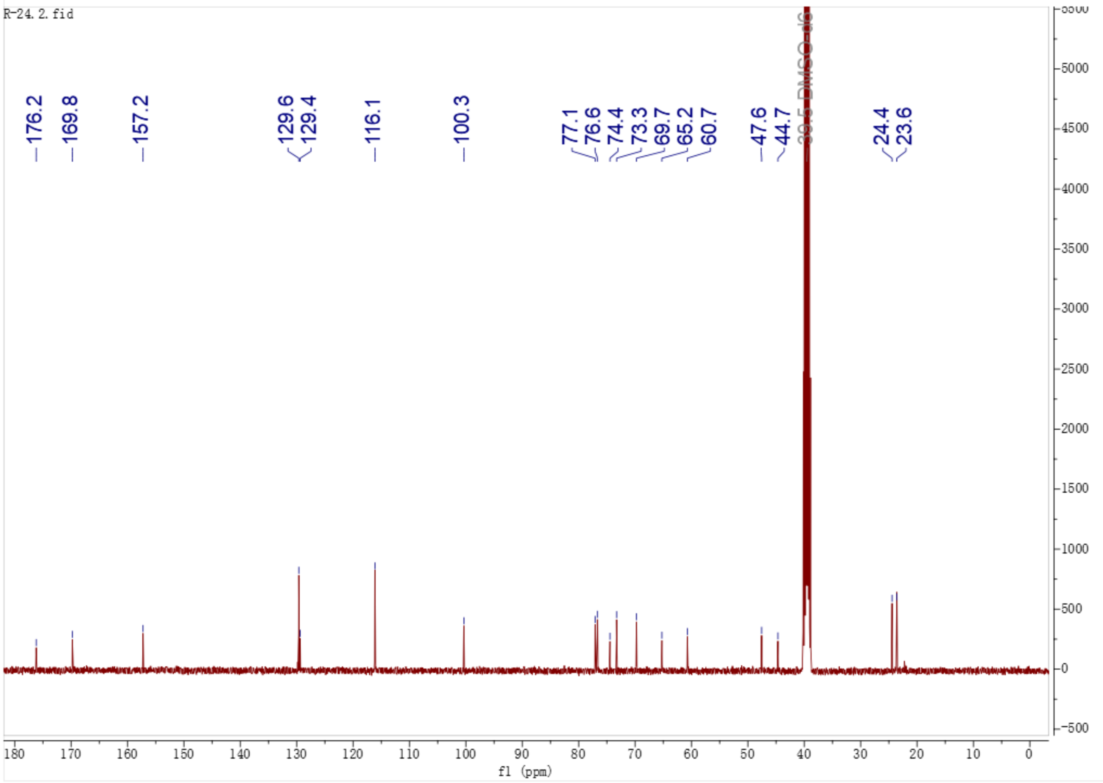

Figure S12: ^{13}C-NMR (100 MHz, DMSO-d_6) spectrum of **6** (gymnoside I)

^{13}C-NMR (100 MHz, DMSO-d_6) δ:176.2 (C-1), 74.4 (C-2), 44.7 (C-3), 169.8 (C-4), 47.6 (C-5), 24.4 (C-6), 23.6 (C-7), 23.6 (C-8), 129.4 (C-1'), 129.6 (C-2', 6'), 116.1 (C-3', 5'), 157.2 (C-4'), 65.2 (C-7'), 100.3 (C-1''), 73.3 (C-2''), 76.6 (C-3''), 69.7 (C-4''), 77.1 (C-5''), 60.7 (C-6'').

© 2024 ACG Publications. All rights reserved.

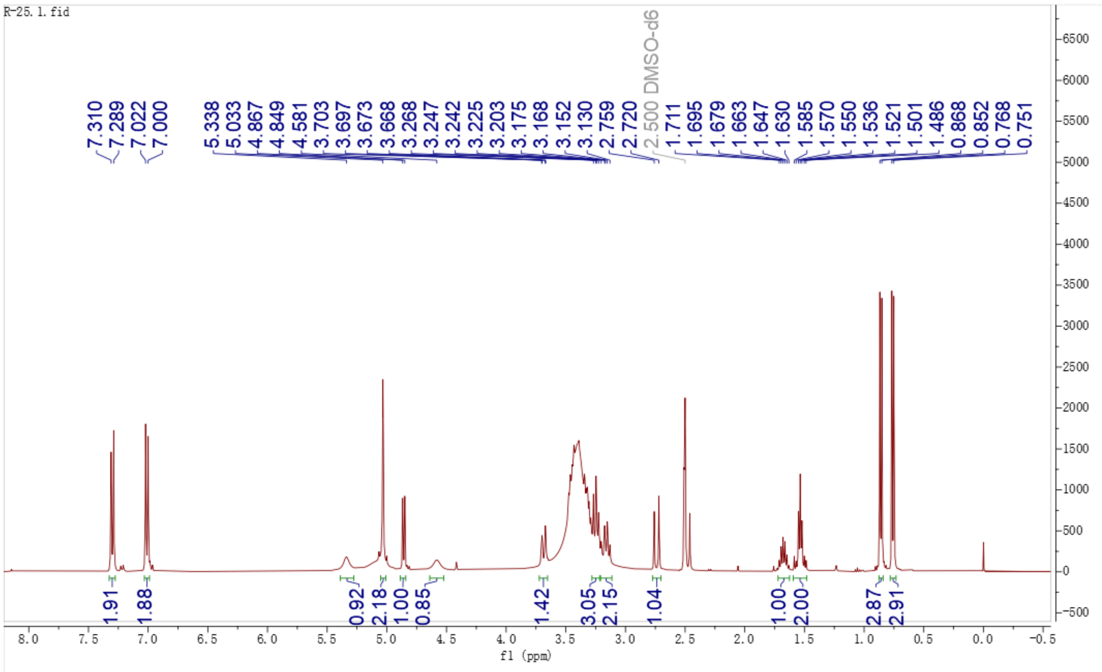

Figure S13: ^{1}H-NMR (400 MHz, DMSO-d_6) spectrum of **7** (gymnoside II)

^{1}H-NMR (400 MHz, DMSO-d_6): 7.30 (2H, d, J = 8.4 Hz, H-2',6'), 7.01 (2H, d, J = 8.8 Hz, H-3', 5'), 5.03 (2H, s, H-7'), 4.86 (1H, d, J = 7.2 Hz, H-1"), 3.67 (1H, dd, J = 12.0, 2.4 Hz, H-6″a), 3.25 (1H, dd, J = 10.4, 8.4 Hz, H-6″b), 3.24 ~ 3.16 (4H, m, H-2", 3", 4", 5"), 2.74 (1H, d, J = 15.6 Hz, H-3a), 2.46 (1H, d, J = 16.0 Hz,H-3b), 1.67 (1H, m, H-6), 1.55 (1H, m, H-5a), 1.49 (1H, m, H-5b), 0.86 (3H, d, J = 6.4 Hz, H-7), 0.76 (3H, d, J = 6.8 Hz, H-8).

© 2024 ACG Publications. All rights reserved.

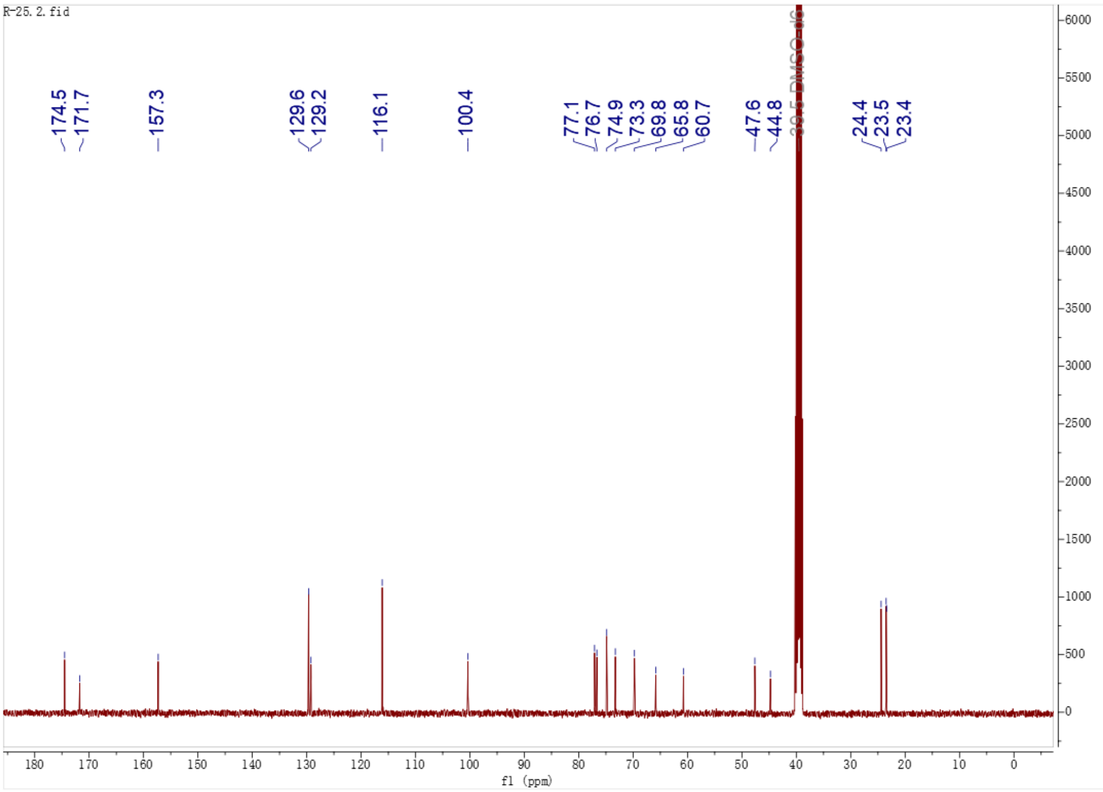

Figure **S14**: ^{13}C-NMR (100 MHz, DMSO-d_6) spectrum of **7** (gymnoside II)

^{13}C-NMR (100 MHz, DMSO-d_6) δ: 171.7 (C-1), 74.9 (C-2), 44.8 (C-3), 174.5 (C-4), 47.6 (C-5), 24.4 (C-6), 23.5 (C-7), 23.4 (C-8), 129.2 (C-1'), 129.6 (C-2', 6'), 116.1 (C-3', 5'), 157.3 (C-4'), 65.8 (C-7'), 100.4 (C-1''), 73.3 (C-2''), 76.7 (C-3''), 69.8 (C-4''), 77.1 (C-5''), 60.7 (C-6'').

© 2024 ACG Publications. All rights reserved.