Supplementary Data

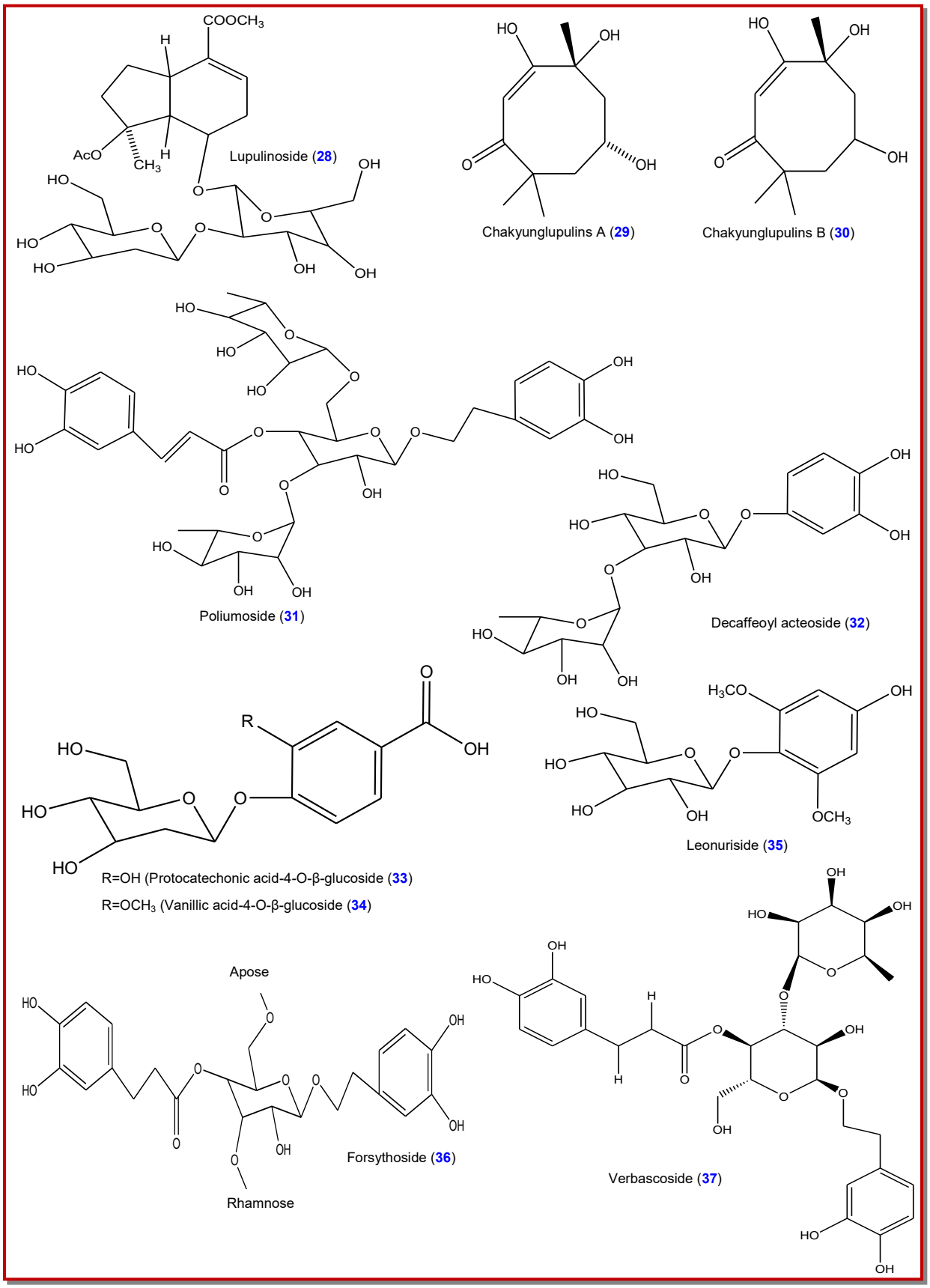
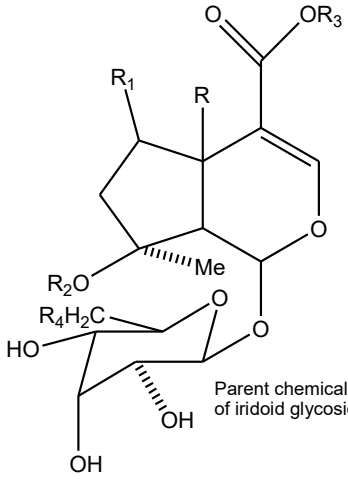
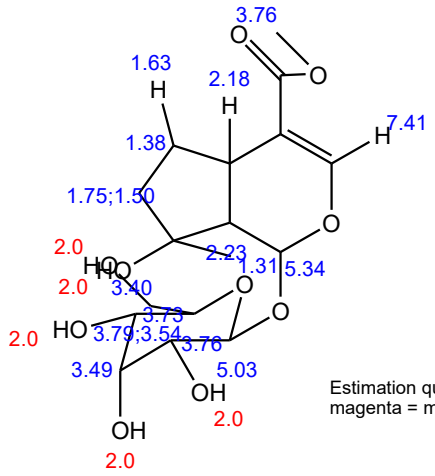


Figure 1: Chemical structures of some compounds isolated from *B. lupulina*



Parent chemical structure A of iridoid glycoside



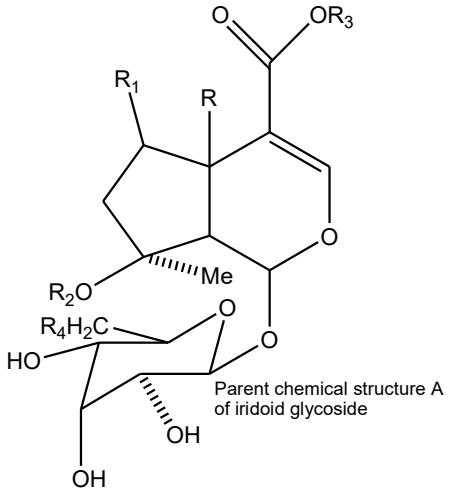
Estimation quality: blue = good; magenta = medium; red = rough

Parent chemical structure A - ^{1}H NMR prediction

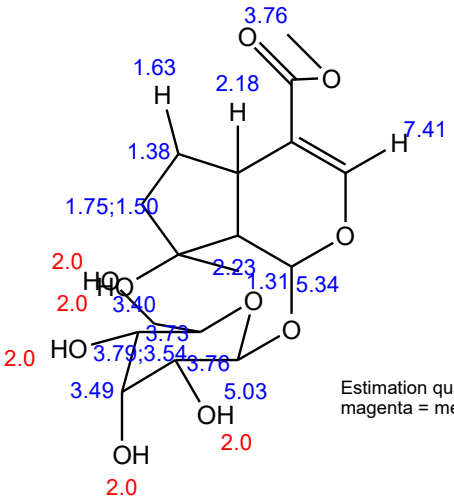
Protocol of the H-1 NMR Prediction:

Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH	2.23	1.51	cyclopentane
		0.03	1 beta -C=C from methine
		0.30	1 beta -O-C=C from methine
		0.32	1 beta -O-C from methine
		0.08	1 beta -O from methine
		-0.01	1 beta -C from methine
CH	5.34	4.00	2,3-dihydro-4H-pyran
		1.35	1 alpha -O-C from methine
		-0.01	1 beta -C from methine
CH2	1.38	1.51	cyclopentane
		0.00	1 beta -C=C from methylene
CH2	1.75;1.50	1.51	cyclopentane
		0.15	1 beta -O from methylene
		-0.04	1 beta -C from methylene
H	2.18	1.51	cyclopentane
		0.68	1 alpha -C=C from methine
		-0.01	1 beta -C from methine
H	1.63	1.51	cyclopentane
		0.00	1 beta -C=C from methylene
CH	5.03	3.60	tetrahydropyran
		1.35	1 alpha -O-C from methine
		0.08	1 beta -O from methine
CH	3.76	3.60	tetrahydropyran
		0.08	1 beta -O from methine
		0.08	1 beta -O from methine
CH	3.40	1.60	tetrahydropyran
		1.73	1 alpha -O from methine
		-0.01	1 beta -C from methine
		0.08	1 beta -O from methine
CH	3.49	1.60	tetrahydropyran
		1.73	1 alpha -O from methine
		0.08	1 beta -O from methine
		0.08	1 beta -O from methine
CH	3.73	1.60	tetrahydropyran
		1.73	1 alpha -O from methine
		0.08	1 beta -O from methine
		0.32	1 beta -O-C from methine

Figure 2: ^{1}H-NMR data for some phytochemicals isolated from *Barleria lupulina*



Parent chemical structure A of iridoid glycoside



Estimation quality: blue = good; magenta = medium; red = rough

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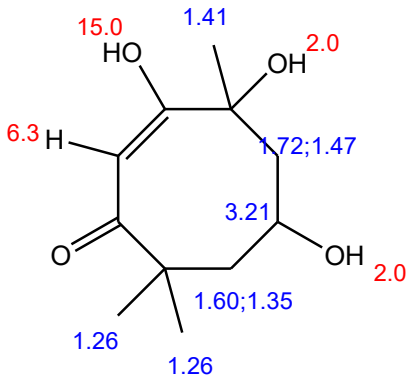
Protocol of the H-1 NMR Prediction:

Node      Shift     Base + Inc.    Comment (ppm rel. to TMS)

  OH       2.0          2.00       alcohol
  OH       2.0          2.00       alcohol
  OH       2.0          2.00       alcohol
  OH       2.0          2.00       alcohol
 CH3       1.31         0.86       methyl
                        0.25       1 beta -O
                        0.20       2 beta -C-R
 CH2  3.79;3.54         1.37       methylene
                        2.20       1 alpha -O
                        0.13       1 beta -O-C
                       -0.04       1 beta -C
  OH       2.0          2.00       alcohol
 CH3       3.76         0.86       methyl
                        2.90       1 alpha -OC(=O)-C=C
   H       7.41         6.40       2,3-dihydro-4H-pyran
                        1.01       1 -C(=O)O-R cis from 1-ethylene
```

Figure 2: ^{1}H-NMR data for some phytochemicals isolated from *Barleria lupulina* (Cont..)

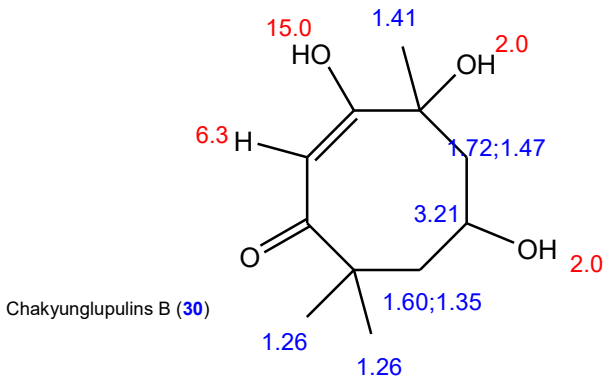


Chakyunglupulins A (**29**)

Estimation quality: blue = good; magenta = medium; red = rough

Protocol of the H-1 NMR Prediction:

Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH2	1.60;1.35	1.37	methylene
		0.07	1 beta -C(=O)C=C
		-0.08	2 beta -C
		0.15	1 beta -O
		-0.04	1 beta -C
CH	3.21	1.50	methine
		1.73	1 alpha -O
		-0.01	1 beta -C
		-0.01	1 beta -C
CH2	1.72;1.47	1.37	methylene
		0.15	1 beta -O
		-0.04	1 beta -C
		0.00	1 beta -C=C
		0.15	1 beta -O
		-0.04	1 beta -C
OH	2.0	2.00	alcohol
CH3	1.41	0.86	methyl
		0.20	1 beta -C=C
		0.25	1 beta -O
		0.10	1 beta -C-R
OH	2.0	2.00	alcohol
CH3	1.26	0.86	methyl
		0.25	1 beta -C(=O)C=C
		0.10	1 beta -C-R
		0.05	1 beta -C
CH3	1.26	0.86	methyl
		0.25	1 beta -C(=O)C=C
		0.10	1 beta -C-R
		0.05	1 beta -C
OH	15.0	15.00	enol
H	6.3	5.25	1-ethylene
		1.10	1 -C(=O)-R gem
		-0.02	1 -C-O trans
		?	1 unknown substituent(s)
			-> 1 increment(s) not found

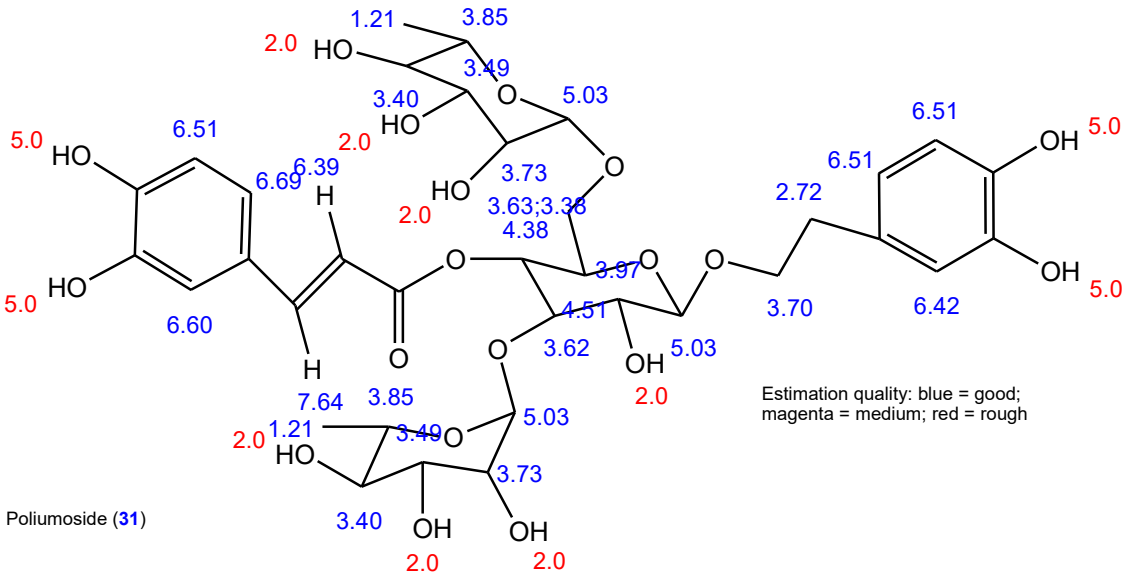


Chakyunglupulins B (**30**)

Estimation quality: blue = good; magenta = medium; red = rough

Protocol of the H-1 NMR Prediction:

Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH2	1.60;1.35	1.37	methylene
		0.07	1 beta -C(=O)C=C
		-0.08	2 beta -C
		0.15	1 beta -O
		-0.04	1 beta -C
CH	3.21	1.50	methine
		1.73	1 alpha -O
		-0.01	1 beta -C
		-0.01	1 beta -C
CH2	1.72;1.47	1.37	methylene
		0.15	1 beta -O
		-0.04	1 beta -C
		0.00	1 beta -C=C
		0.15	1 beta -O
		-0.04	1 beta -C
OH	2.0	2.00	alcohol
CH3	1.41	0.86	methyl
		0.20	1 beta -C=C
		0.25	1 beta -O
		0.10	1 beta -C-R
CH3	1.26	0.86	methyl
		0.25	1 beta -C(=O)C=C
		0.10	1 beta -C-R
		0.05	1 beta -C
CH3	1.26	0.86	methyl
		0.25	1 beta -C(=O)C=C
		0.10	1 beta -C-R
		0.05	1 beta -C
OH	15.0	15.00	enol
OH	2.0	2.00	alcohol
H	6.3	5.25	1-ethylene
		1.10	1 -C(=O)-R gem
		-0.02	1 -C-O trans
		?	1 unknown substituent(s)
			-> 1 increment(s) not found



Protocol of the H-1 NMR Prediction:

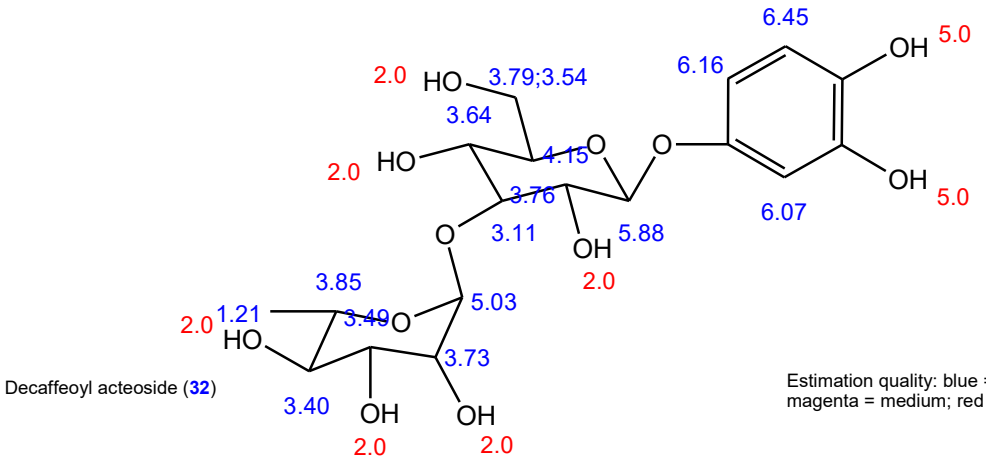
Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH	4.38	1.60	tetrahydropyran
		2.47	1 alpha -O-C=O from methine
		0.32	1 beta -O-C from methine
		-0.01	1 beta -C from methine
CH	3.62	1.60	tetrahydropyran
		1.35	1 alpha -O-C from methine
		0.59	1 beta -O-C=O from methine
		0.08	1 beta -O from methine
CH	3.97	1.60	tetrahydropyran
		1.73	1 alpha -O from methine
		0.32	1 beta -O-C from methine
		0.32	1 beta -O-C from methine
CH	5.03	3.60	tetrahydropyran
		1.35	1 alpha -O-C from methine
		0.08	1 beta -O from methine
CH	4.51	3.60	tetrahydropyran
		0.59	1 beta -O-C=O from methine
		0.32	1 beta -O-C from methine
CH2	3.63;3.38	1.37	methylene
		2.04	1 alpha -O-C
		0.13	1 beta -O-C
		-0.04	1 beta -C
CH	5.03	3.60	tetrahydropyran
		1.35	1 alpha -O-C from methine
		0.08	1 beta -O from methine
CH	3.73	1.60	tetrahydropyran
		1.73	1 alpha -O from methine
		0.32	1 beta -O-C from methine
		0.08	1 beta -O from methine
CH	3.49	1.60	tetrahydropyran
		1.73	1 alpha -O from methine
		0.08	1 beta -O from methine
		0.08	1 beta -O from methine
CH	3.40	1.60	tetrahydropyran
		1.73	1 alpha -O from methine
		0.08	1 beta -O from methine
		-0.01	1 beta -C from methine

Protocol of the H-1 NMR Prediction:

Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH	3.85	3.60	tetrahydropyran
		0.17	1 alpha -C from methine
		0.08	1 beta -O from methine
CH3	1.21	0.86	methyl
		0.25	1 beta -O-C
		0.10	1 beta -C-R
OH	2.0	2.00	alcohol
OH	2.0	2.00	alcohol
OH	2.0	2.00	alcohol
CH	6.69	7.26	1-benzene
		0.04	1 -C=C
		-0.17	1 -O
		-0.44	1 -O
CH	6.51	7.26	1-benzene
		-0.05	1 -C=C
		-0.53	1 -O
		-0.17	1 -O
CH	6.60	7.26	1-benzene
		0.04	1 -C=C
		-0.17	1 -O
		-0.53	1 -O
OH	5.0	5.00	aromatic C-OH
OH	5.0	5.00	aromatic C-OH
CH	5.03	3.60	tetrahydropyran
		1.35	1 alpha -O-C from methine
		0.08	1 beta -O from methine
CH	3.73	1.60	tetrahydropyran
		1.73	1 alpha -O from methine
		0.32	1 beta -O-C from methine
		0.08	1 beta -O from methine
CH	3.49	1.60	tetrahydropyran
		1.73	1 alpha -O from methine
		0.08	1 beta -O from methine
		0.08	1 beta -O from methine
CH	3.40	1.60	tetrahydropyran
		1.73	1 alpha -O from methine
		0.08	1 beta -O from methine
		-0.01	1 beta -C from methine
CH	3.85	3.60	tetrahydropyran
		0.17	1 alpha -C from methine
		0.08	1 beta -O from methine
OH	2.0	2.00	alcohol
OH	2.0	2.00	alcohol
OH	2.0	2.00	alcohol
CH3	1.21	0.86	methyl
		0.25	1 beta -O-C
		0.10	1 beta -C-R
OH	2.0	2.00	alcohol
CH2	3.70	1.37	methylene
		2.04	1 alpha -O-C
		0.29	1 beta -1:C*C*C*C*C*C*1
CH2	2.72	1.37	methylene
		1.22	1 alpha -1:C*C*C*C*C*C*1
		0.13	1 beta -O-C
CH	6.42	7.26	1-benzene
		-0.14	1 -CC
		-0.53	1 -O
		-0.17	1 -O

Protocol of the H-1 NMR Prediction:

Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH	6.51	7.26	1-benzene
		-0.05	1 -CC
		-0.17	1 -O
		-0.53	1 -O
CH	6.51	7.26	1-benzene
		-0.14	1 -CC
		-0.44	1 -O
		-0.17	1 -O
OH	5.0	5.00	aromatic C-OH
OH	5.0	5.00	aromatic C-OH
H	6.39	5.25	1-ethylene
		0.78	1 -C(=O)O-R gem
		0.36	1 -1:C*C*C*C*C*C*1 cis
H	7.64	5.25	1-ethylene
		1.01	1 -C(=O)O-R cis
		1.38	1 -1:C*C*C*C*C*C*1 gem



Decaffeoyl acteoside (**32**)

Estimation quality: blue = good; magenta = medium; red = rough

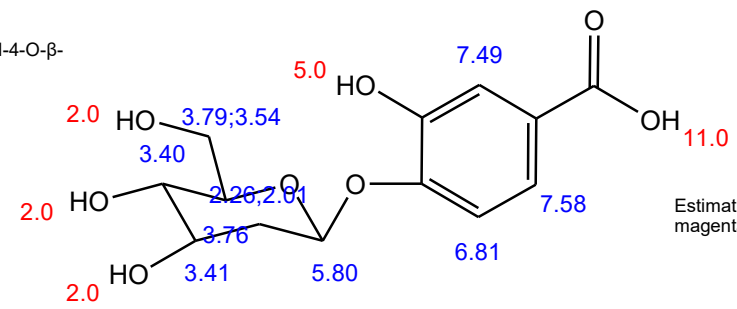
Protocol of the H-1 NMR Prediction:

Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH	3.64	1.60	tetrahydropyran
		1.73	1 alpha -O from methine
		0.32	1 beta -O-C from methine
		-0.01	1 beta -C from methine
CH	3.11	1.60	tetrahydropyran
		1.35	1 alpha -O-C from methine
		0.08	1 beta -O from methine
		0.08	1 beta -O from methine
CH	4.15	1.60	tetrahydropyran
		1.73	1 alpha -O from methine
		0.32	1 beta -O-C from methine
		0.50	1 beta -O-1:C*C*C*C*C*C*1 from methine
CH	5.88	3.60	tetrahydropyran
		2.20	1 alpha -O-1:C*C*C*C*C*C*1 from methine
		0.08	1 beta -O from methine
CH	3.76	3.60	tetrahydropyran
		0.08	1 beta -O from methine
		0.08	1 beta -O from methine
CH2	3.79;3.54	1.37	methylene
		2.20	1 alpha -O
		0.13	1 beta -O-C
		-0.04	1 beta -C
CH	5.03	3.60	tetrahydropyran
		1.35	1 alpha -O-C from methine
		0.08	1 beta -O from methine
CH	3.73	1.60	tetrahydropyran
		1.73	1 alpha -O from methine
		0.32	1 beta -O-C from methine
		0.08	1 beta -O from methine
CH	3.49	1.60	tetrahydropyran
		1.73	1 alpha -O from methine
		0.08	1 beta -O from methine
		0.08	1 beta -O from methine
CH	3.40	1.60	tetrahydropyran
		1.73	1 alpha -O from methine
		0.08	1 beta -O from methine
		-0.01	1 beta -C from methine

Protocol of the H-1 NMR Prediction:

Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH	3.85	3.60	tetrahydropyran
		0.17	1 alpha -C from methine
		0.08	1 beta -O from methine
OH	2.0	2.00	alcohol
OH	2.0	2.00	alcohol
OH	2.0	2.00	alcohol
CH3	1.21	0.86	methyl
		0.25	1 beta -O-C
		0.10	1 beta -C-R
OH	2.0	2.00	alcohol
OH	2.0	2.00	alcohol
OH	2.0	2.00	alcohol
CH	6.07	7.26	1-benzene
		-0.49	1 -O-C
		-0.53	1 -O
		-0.17	1 -O
CH	6.45	7.26	1-benzene
		-0.11	1 -O-C
		-0.17	1 -O
		-0.53	1 -O
CH	6.16	7.26	1-benzene
		-0.49	1 -O-C
		-0.44	1 -O
		-0.17	1 -O
OH	5.0	5.00	aromatic C-OH
OH	5.0	5.00	aromatic C-OH

Protocatechonic acid-4-O-β-glucoside (**33**)

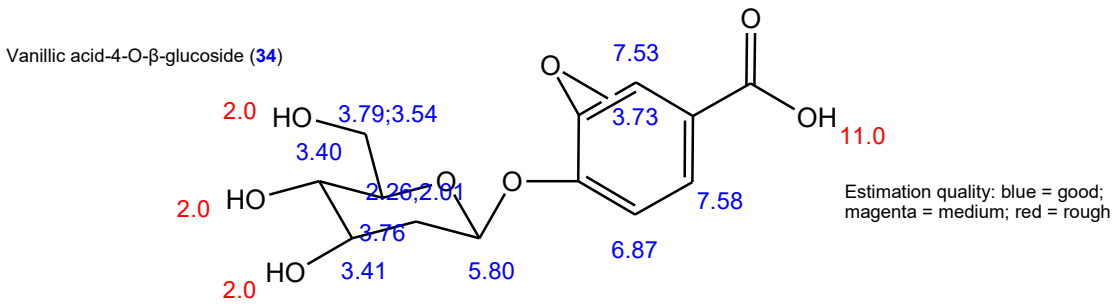


Estimation quality: blue = good; magenta = medium; red = rough

Protocol of the H-1 NMR Prediction:

Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH	3.40	1.60	tetrahydropyran
		1.73	1 alpha -O from methine
		0.08	1 beta -O from methine
		-0.01	1 beta -C from methine
CH	3.41	1.60	tetrahydropyran
		1.73	1 alpha -O from methine
		0.08	1 beta -O from methine
CH2	2.26;2.01	1.60	tetrahydropyran
		0.15	1 beta -O from methylene
		0.38	1 beta -O-1:C*C*C*C*C*C*1 from methylene
CH	5.80	3.60	tetrahydropyran
		2.20	1 alpha -O-1:C*C*C*C*C*C*1 from methine
CH	3.76	3.60	tetrahydropyran
		0.08	1 beta -O from methine
		0.08	1 beta -O from methine
CH2	3.79;3.54	1.37	methylene
		2.20	1 alpha -O
		0.13	1 beta -O-C
		-0.04	1 beta -C
OH	2.0	2.00	alcohol
OH	2.0	2.00	alcohol
OH	2.0	2.00	alcohol
CH	6.81	7.26	1-benzene
		-0.49	1 -O-C
		0.21	1 -C(=O)O
		-0.17	1 -O
CH	7.58	7.26	1-benzene
		-0.11	1 -O-C
		0.87	1 -C(=O)O
		-0.44	1 -O
CH	7.49	7.26	1-benzene
		-0.11	1 -O-C
		0.87	1 -C(=O)O
		-0.53	1 -O
OH	5.0	5.00	aromatic C-OH
OH	11.0	11.00	carboxylic acid

Vanillic acid-4-O-β-glucoside (**34**)

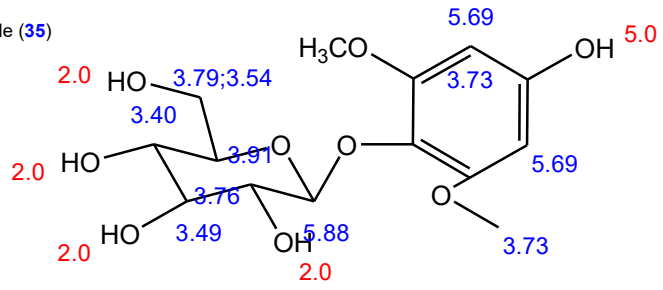


Estimation quality: blue = good; magenta = medium; red = rough

Protocol of the H-1 NMR Prediction:

Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH	3.40	1.60	tetrahydropyran
		1.73	1 alpha -O from methine
		0.08	1 beta -O from methine
		-0.01	1 beta -C from methine
CH	3.41	1.60	tetrahydropyran
		1.73	1 alpha -O from methine
		0.08	1 beta -O from methine
CH2	2.26;2.01	1.60	tetrahydropyran
		0.15	1 beta -O from methylene
		0.38	1 beta -O-1:C*C*C*C*C*C*1 from methylene
CH	5.80	3.60	tetrahydropyran
		2.20	1 alpha -O-1:C*C*C*C*C*C*1 from methine
CH	3.76	3.60	tetrahydropyran
		0.08	1 beta -O from methine
		0.08	1 beta -O from methine
CH2	3.79;3.54	1.37	methylene
		2.20	1 alpha -O
		0.13	1 beta -O-C
		-0.04	1 beta -C
OH	2.0	2.00	alcohol
OH	2.0	2.00	alcohol
OH	2.0	2.00	alcohol
CH	6.87	7.26	1-benzene
		-0.49	1 -O-C
		0.21	1 -C(=O)O
		-0.11	1 -O-C
CH	7.58	7.26	1-benzene
		-0.11	1 -O-C
		0.87	1 -C(=O)O
		-0.44	1 -O-C
CH	7.53	7.26	1-benzene
		-0.11	1 -O-C
		0.87	1 -C(=O)O
		-0.49	1 -O-C
OH	11.0	11.00	carboxylic acid
CH3	3.73	0.86	methyl
		2.87	1 alpha -O-1:C*C*C*C*C*C*1

Leoonuriside (**35**)



Estimation quality: blue = good; magenta = medium; red = rough

Protocol of the H-1 NMR Prediction:

Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH	3.40	1.60	tetrahydropyran
		1.73	1 alpha -O from methine
		0.08	1 beta -O from methine
		-0.01	1 beta -C from methine
CH	3.49	1.60	tetrahydropyran
		1.73	1 alpha -O from methine
		0.08	1 beta -O from methine
		0.08	1 beta -O from methine
CH	3.91	1.60	tetrahydropyran
		1.73	1 alpha -O from methine
		0.08	1 beta -O from methine
		0.50	1 beta -O-1:C*C*C*C*C*C*1 from methine
CH	5.88	3.60	tetrahydropyran
		2.20	1 alpha -O-1:C*C*C*C*C*C*1 from methine
		0.08	1 beta -O from methine
CH	3.76	3.60	tetrahydropyran
		0.08	1 beta -O from methine
		0.08	1 beta -O from methine
CH2	3.79;3.54	1.37	methylene
		2.20	1 alpha -O
		0.13	1 beta -O-C
		-0.04	1 beta -C
OH	2.0	2.00	alcohol
OH	2.0	2.00	alcohol
OH	2.0	2.00	alcohol
CH	5.69	7.26	1-benzene
		-0.11	1 -O-C
		-0.49	1 -O-C
		-0.53	1 -O
		-0.44	1 -O-C
CH	5.69	7.26	1-benzene
		-0.11	1 -O-C
		-0.44	1 -O-C
		-0.53	1 -O
		-0.49	1 -O-C
OH	2.0	2.00	alcohol
OH	5.0	5.00	aromatic C-OH
CH3	3.73	0.86	methyl
		2.87	1 alpha -O-1:C*C*C*C*C*C*1
CH3	3.73	0.86	methyl
		2.87	1 alpha -O-1:C*C*C*C*C*C*1

^{1}H-NMR and ^{13}C-NMR data for some iridoid glycosides from *Barleria lupulina*

[1] Shanzhiside methyl ester (Boros and Stermitz, 1990)

$C_{17}H_{26}O_{11}$: 406.39 ; [α]$_D$ -115° (MeOH), UV 234 (EtOH); ^{1}H-NMR (250 *MHz* CD_3OD) 5.57(H-1, d, 3), 7.41 (H-3, d, 11, 2.99 (H-5, m, 10, 3.5, 1),4.03(H-6,m,6.5,6,3.5),2.01(H-7,dd,13,6.5), 10, s), 3.72 (OMe), 4.61 (H-l', d, 8), 3.91 (H-6', dd,1.83 (H-7, dd, 13, 6), 2.61 (H-9, dd, 10, 3), 1.26 (H-12, 2), 3.64 (H-6', dd, 12, 6); ^{13}C-NMR (CD_3OD): 94.9 (C- l), 152.9(C-3), 111.4(C-4), 41.5 (C-5),78.O(C-6Y, 51.9(C-7), 79.1 (C-8), 51.7 (C-9), 24.7 (C-lo), 169.8 (C-11), 49.1 (OMe), 99.9(C-l'), 74.6(C-2'), 78.3(C-3'), 71.6 (C-4'), 77.5 (C-5')a, 62.9 (C-6').

[2] 8-O-acetyl shanzhiside methyl ester (barlerin) (Boros and Stermitz, 1990)

$C_{19}H_{28}O_{12}$: 448.42 , mp 180°, [α]$_D$ -85° (MeOH), UV235 (EtOH), 1H-NMR (250MHz $D_2$0): 5.98 (H- 1, d, 1.5), 7.6 1(H-3, s), 3.02 (H-5, H-9, m), 2.16(H-7, m), 1.50(H-10, s), 3.72(OMe), 2.00(OAc), 4.70(H-l', d, 7), 3.40(H-6', m); 13C-NMR(D_2O) 95.4 (C-l), 153.5 (C-3), 109.2(C-4), 41.0(C-5), 75.3(C-6), 46.7(C-7), 89.8 (C-8),48.8(C-9), 22.5 (C-lo), 61.5 (C-6').

[3] 6, 8-Di-O-acetyl shanzhiside methyl ester (Acetyl barlerin) (Boros and Stermitz, 1990)

$C_{21}H_{30}O_{13}$: 490.46, [α]$_D$ -99° (MeOH), UV 235(EtOH); ^{1}H-NMR (250MHz, D_2O): 5.90 (H-I, d, 2), 7.61 (H-3, s), 5.20 (H-6, m), 1.50 (H-10, s), 3.72 (OMe), 2.10,2.05(OAC), 4.70 (H-l', d, 7); 13C-NMR (D_2O): 95.1 (C-l), 154.3 (C-3), 108.0 (C-4), 38.7 (C-5), 78.8 (C-6), 44.3 (C-7), 89.5 (C-8), 48.9 (C-9), 22.4 (C-10), 61.5 (C-6')

[4] 6-O-acetyl shanzhiside methyl ester (Boros and Stermitz, 1990)

$C_{19}H_{28}0_{12}$: 448.42 mp 227-228^{0}, [α]$_D$ -118.7° uv 233 (MeOH); X -ray (80 MHz D_2O) , 5.56(H-l, d, 4). 7.58(H-3, s), 3.40(H-5,m), 5.14 (H-6, m), 2.31 (H-7, dd, 14, 7), 1.91 (H-7, dd, 14,4.5), 2.64 (H-9, dd, 9.5, 4), 1.38 (H-10, s), 3.75 (OMe), 2.17 (OAc), 4.87 (H-l', d, 7.51, 4.20-3.45(H-2'-H-6'); ^{13}C-NMR (D2O) 94.2 (C-1), 152.8 (C-3), 108.5 (C-4), 37.3 (C-5). 78.3 (C-6), 45.6 (C-7), 78.3 (C-8), 49.8(C-9), 24.1 (C-lo), 169.1 (C-11), 51.9 (OMe), 173.6(O=CMe), 20.7 (O=CMe), 98.4 (C-l'), 72.8 (C-2'),75.8 (C-3')^{a}, 69.7 (C-4'), 76.4 (C-5')^{a}, 60.9 (C-6').

[6] 6-*O*-*p*-Methoxy-*cis*-cinnamoyl-8-*O*-acetylshanzhiside methyl ester (Dinda et al., 2007a)

$C_{29}H_{36}O_{14}$: 608.2104; colorless powder; [α]$_D$ -129.7° (*c*=0.35, MeOH); UV (?): 227 (4.36), 297 sh (4.25), 307(4.27); IR (?): 3400, 1700, 1640, 1600, 1270, 1180, 1080, 1020; 1H-NMR (400 MHz, $CDCl_3$–DMSO-*d*6): 5.95 (d, 1.5, H-1), 7.48 (s, H-3), 3.25 (d, 9.0, H-5), 5.41 (d, 4.5, H-6), 2.01 (dd, 15.0, 4.5, H_a-7), 2.38 (d, 15.0, H_b-7), 3.00 (dd, 1.0, 1.5, H-9), 1.57 (s, H_3-10), 3.70 (s, MeO-11), 4.66 (d, 7.5, H-1′), 7.73 (d, 9.0, H-2′, 6′), 6.88 (d, 9.0, H-3′, 5′), 6.84 (d, 12.0, H-7′′), 5.79 (d, 12.0, H-8′′), 3.84 (s, MeO-4′′), 1.90 (s, Ac); ^{13}C-NMR (100 MHz, $CDCl_3$–DMSO-*d*6):92.4 (C-1), 151.5 (C-3), 105.3 (C-4), 37.1 (C-5), 75.2 (C-6), 42.5 (C-7), 86.4 (C-8), 47.2 (C-9), 20.2 (C-10), 49.8 (MeO-11), 97.4 (C-1′), 71.6 (C-2′), 75.6 (C-3′), 68.7 (C-4′), 77.2 (C-5′), 60.2 (C-6′), 125.2 (C-1′′), 128.4 (C-2′′, 6′′), 113.0 (C-3′′, 5′′), 159.8 (C-4′′), 142.0 (C-7′′), 114.0 (C-8′′), 164.6, 165.0, 169.2 (C-11, C-9′, C=O), 53.9 (MeO-4′′), 19.8 (Ac).

[7] 6-*O*-*p*-Methoxy-*trans*-cinnamoyl-8-*O*-acetylshanzhiside methyl ester (Dinda et al., 2007a)

$C_{29}H_{36}O_{14}$: 608.2104; colorless powder; [α]$_D$ -103.0° (*c*_0.26, MeOH); UV (?): 227 (4.36), 297 sh (4.35), 310 (4.38); IR (?): 3400 (br), 1715, 1645, 1602, 1260, 1190, 1030; ^{1}H-NMR (400 MHz, $CDCl_3$–DMSO-*d*6): 6.03 (d, 1.5, H-1), 7.50 (s, H-3), 3.31 (d, 9.0, H-5), 5.46 (d, 4.5, H-6), 2.04 (dd, 15.0, 4.5, H_a-7), 2.41 (d, 15.0, H_b-7), 3.09 (dd, 9.0, 1.5, H-9), 1.53 (s, H_3-10), 3.71 (s, MeO-11), 1.96 (s, AcO-8), 4.69 (d, 7.5, H-1′), 7.49 (d, 9.0, H-2′′, 6′′), 6.97 (d, 9.0, H-3′′, 5′′), 7.61 (d, 15.0, H-7′′), 6.29 (d, 15.0, H-8′′), 3.86 (s, MeO-4′′); ^{13}C-NMR (100 MHz, $CDCl_3$–DMSO-*d*6): 93.4(C-1), 152.5 (C-3), 106.1 (C-4), 37.8 (C-5), 76.3 (C-6), 43.5 (C-7), 87.2 (C-8), 48.1 (C-9), 21.4 (C-10), 98.5 (C-1′), 72.5 (C-2′), 76.1 (C-3′), 69.8 (C-4′), 76.3 (C-5′), 61.3 (C-6′), 126.5 (C-1′′), 131.6 (C-2′′, 6′′), 113.8 (C-3′′, 5′′), 159.7(C-4′′), 142.6 (C-7′′), 116.3 (C-8′′), 164.8, 165.9, 170.2 (C-9′′, C-11, C=O), 50.6, 54.7 (2×OMe), 20.8 (Ac).

[8] 6-*O*-*cis*-*p*-Coumaroyl-8-*O*-acetylshanzhiside methyl ester (Dinda et al., 2007a)

$C_{28}H_{34}O_{14}$: 594.1948; amorphous solid; [α]$_D$ -19.5° (*c*=0.04, MeOH); UV (MeOH): 228 (4.08), 309 (3.93); IR (KBr):3422 (br), 2924, 1715, 1634, 1605, 1514, 1440, 1372, 1161, 1084, 1010, 654; ^{1}H-NMR (400 MHz, CD3OD): 5.87 (d, 3.3,H-1), 7.52 (d, 1.6, H-3), 3.26 (ddd, 8.0, 2.0, 1.6, H-5), 5.37 (dd, 5.3, 2.0, H-6), 2.40 (br d, 15.0, H-7), 2.10 (dd, 15.0, 5.3,H-7), 2.92 (dd, 8.0, 3.3, H-9), 1.55 (s, H3-10), 1.89 (s, AcO-8), 3.70 (s, MeO-11), 4.66 (d, 7.8, H-1′), 3.21 (dd, 9.0, 7.8,H-2′), 3.37 (dd, 9.0, 8.8, H-3′), 3.28 (dd, 9.5, 8.8, H-4′), 3.34 (ddd, 9.5, 6.2, 2.0, H-5′), 3.91 (dd, 12.1, 2.0, H-6′), 3.67(dd, 12.1, 6.2, H-6′), 7.63 (d, 8.4, H-2′′, 6′′), 6.76 (d, 8.4, H-3′′, 5′′), 6.90 (d, 12.7, H-7′′), 5.78 (d, 12.7, H-8′′); ^{13}C-NMR (100 MHz, CD_3OD): 95.4 (C-1), 154.6 (C-3), 108.6 (C-4), 39.9 (C-5), 78.7 (C-6), 45.1 (C-7), 89.6 (C-8), 50.3 (C-9), 21.9(C-10), 168.5 (C-11), 100.4 (C-1′), 74.6 (C-2′), 77.9 (C-3′), 71.6 (C-4′), 78.4 (C-5′), 62.9 (C-6′), 127.6 (C-1′′), 133.6 (C-2′′, 6′′), 115.9 (C-3′′, 5′′), 160.1 (C-4′′), 144.9 (C-7′′), 116.9 (C-8′′), 167.6 (C-9′′), 51.9 (OMe), 22.1, 172.9 (Ac).

[9] 6-*O*-*trans*-*p*-Coumaroyl-8-*O*-acetylshanzhiside methyl ester (Dinda et al., 2007a)

C28H34O14: 594.1948; white amorphous powder; [α]$_D$ -52.0° (*c*=0.152, MeOH); UV (MeOH): 229 (4.17), 313 (4.23);IR (KBr): 3430 (br), 2952, 2918, 1714, 1634, 1606, 1516, 1442, 1373, 1279, 1169, 1082, 1056, 862, 835; 1H-NMR(400 MHz, CD3OD): 5.91 (d, 3.3, H-1), 7.53 (d, 1.4, H-3), 3.34 (ddd, 8.6, 2.0, 1.4, H-5), 5.39 (br dd, 5.4, 2.0, H-6), 2.42 (br d, 15.2, H-7), 2.13 (dd, 15.2, 5.4, H-7), 3.05 (dd, 8.6, 3.3, H-9), 1.58 (s, H3-10), 3.70 (s, MeO-11), 1.98 (s, AcO-8), 4.68 (d, 8.0, H-1′), 3.20 (dd, 9.0, 8.0, H-2_), 3.38 (dd, 9.0, 8.8, H-3′), 3.27 (dd, 9.5, 8.8, H-4′), 3.35 (ddd, 9.5, 6.2, 2.0, H-5′), 3.92 (dd, 11.9, 2.0, H-6_), 3.67 (dd, 11.9, 6.2, H-6′), 7.47 (d, 8.6, H-2′′, 6′′), 6.81 (d, 8.6, H-3′′, 5′), 7.62 (d, 16.0, H-7′′), 6.34 (d, 16.0, H-8′′); 13C-NMR (100 MHz, CD_3OD): 95.5 (C-1), 154.5 (C-3), 108.6 (C-4), 40.0 (C-5), 78.9 (C-6),45.2 (C-7), 89.6 (C-8), 50.4 (C-9), 21.8 (C-10), 168.4 (C-11, 9_), 100.4 (C-1′), 74.7 (C-2′), 78.0 (C-3′), 71.7 (C-4′), 78.4(C-5′), 63.0 (C-6′), 127.1 (C-1′′), 131.2 (C-2′′, 6′′), 116.9 (C-3′′, 5′′), 161.4 (C-4′′), 146.6 (C-7′′), 115.4 (C-8′′), 51.9 (OMe), 22.2, 172.9 (Ac).

[10] 8-*O*-Acetyl-6-*O*-*trans*-*p*-coumaroylshanzhiside (Dinda et al., 2007a)

$C_{27}H_{32}O_{14}$: 580.1791; amorphous powder[α]$_D$ -75.6° (*c*=1.58, MeOH); ^{1}H-NMR (400 MHz, CD_3OD): 5.89 (d, 2.7, H-1), 7.49 (d, 1.5, H-3), 3.33 (H-5), 5.40 (m, H-6), 2.37 (br d, 15.4, H_a-7), 2.05 (dd, 15.4, 5.3, H_b-7), 3.01 (dd, 8.5, 2.7, H-9),1.51 (s, H_3-10), 4.65 (d, 7.8, H-1′), 3.18 (dd, 9.0, 7.8, H-2′), 3.37 (dd, 9.0, 9.0, H-3′), 3.26 (dd, 9.0, 9.0, H-4′), 3.31 (m, H-5′), 3.88 (dd, 12.2, 2.2, H-6′), 3.66 (dd, 12.2, 6.1, H-6′), 7.40 (d, 8.6, H-2′′, 6′′), 6.77 (d, 8.6, H-3′′, 5′′), 7.56 (d, 15.9, H-7′′),6.28 (d, 15.9, H-8′′); ^{13}C-NMR (100 MHz, CD_3OD): 95.3 (C-1), 154.6 (C-3), 108.4 (C-4), 39.8 (C-5), 78.8 (C-6), 45.2 (C-7), 89.6 (C-8), 50.3 (C-9), 21.9 (C-10), 169.7 (C-11), 22.2, 173.0 (Ac), 100.3 (C-1′), 74.6 (C-2′), 77.8 (C-3′), 71.5 (C-4′),78.2 (C-5′), 62.9 (C-6′), 127.0 (C-1′′), 131.1 (C-2′′, 6′′), 115.4 (C-3′′, 5′′), 161.1 (C-4′′), 146.5 (C-7′′), 116.8 (C-8′′), 168.5(C-9′′).

[**11**] Saletpangponoside A [6-*O*-(4-*O*-β–glucopyranosyl)-*trans*-*p*-coumaroyl-8-*O*-acetylshanzhiside methyl ester] (Dinda et al., 2007a)

$C_{34}H_{44}O_{19}$: 756.2476; amorphous powder; [α]$_D$ -90.3^0 (*c*=1.79, MeOH); ^{1}H-NMR (400 MHz, CD_3OD): 5.85 (d,3.2, H-1), 7.48 (d, 1.5, H-3), 3.30 (H-5), 5.34 (m, H-6), 2.38 (br d, 15.4, H_a-7), 2.09 (dd, 15.4, 5.3, H_b-7), 3.00 (dd,8.6, 3.2, H-9), 1.53 (s, H_3-10), 3.65 (s, MeO-11), 4.63 (d, 8.1, H-1′), 3.16 (dd, 9.0, 8.1, H-2′), 3.34 (H-3′), 3.23 (dd,9.5, 9.5, H-4′), 3.31 (m, H-5′), 3.88 (dd, 11.9, 2.2, H-6′), 3.66 (dd, 11.9, 6.1, H-6′′), 7.53 (d, 8.8, H-2′′, 6′′), 7.08 (d, 8.8, H-3′′, 5′′), 7.61 (d, 15.9, H-7′′), 6.37 (d, 15.9, H-′′ 4.93 (d, 7.6, H-1′′′), 3.42 (H-2′′′), 3.34 (H-3′′′), 3.40 (H-4′′′),3.26 (H-5_), 3.81 (dd, 12.0, 2.0, H-6′′′), 3.64 (dd, 12.0, 6.4, H-′′′ 1.92 (s, OAc); ^{13}C-NMR (100 MHz, CD3OD): 95.4(C-1), 154.5 (C-3), 108.5 (C-4), 39.9 (C-5), 78.9 (C-6), 45.1 (C-7), 89.6 (C-8), 50.3 (C-9), 21.8 (C-10), 168.4 (C-11),51.9 (OMe), 100.3 (C-1′), 74.6 (C-2′), 77.9 (C-3′), 71.6 (C-4′), 78.3 (C-5′), 62.9 (C-6′), 129.8 (C-1′′), 130.8 (C-2′′, 6′′), 118.0 (C-3′′, 5′′), 160.9 (C-4′′), 145.9 (C-7′′), 117.2 (C-8′′), 168.1 (C-9′′), 101.8 (C-1′′), 74.8 (C-2′′), 77.9 (C-3′′),71.2 (C-4′′), 78.1 (C-5′′), 62.4 (C-6′′), 22.3, 172.9 (OAc).

[**12**] Saletpangponoside B (Dinda et al., 2007a)

C34H44O19: 756.2476; amorphous powder[α]$_D$ -104.8° (*c*=2.43, MeOH); ^{1}H-NMR (400 MHz, CD3OD): 5.85 (d, 3.2, H-1), 7.50 (d, 1.5, H-3), 3.25 (H-5), 5.34 (m, H-6), 2.38 (br d, 15.6, H_a-7), 2.09 (dd, 15.6, 5.4, H_b-7), 2.90 (dd, 8.6, 3.2, H-9), 1.53 (s, H3-10), 3.68 (s, MeO-11), 4.66 (d, 7.8, H-1′), 3.22 (dd, 9.0, 7.8, H-2′), 3.34 (H-3′), 3.26 (H-4′), 3.31 (m, H-5′), 3.90 (dd, 12.0, 2.0, H-6′), 3.71 (dd, 12.0, 5.6, H-6′′), 7.65 (d, 8.8, H-2′′, 6′′), 7.07 (d, 8.8, H-3′′, 5′′), 6.94 (d, 12.9, H-7′′), 5.86 (d, 12.9, H-8′′), 4.96 (d, 7.6, H-1′′′), 3.48 (H-2′′′), 3.34 (H-3′′′), 3.45 (H-4′′′), 3.28 (H-5′′′), 3.87 (dd, 12.0, 1.7, H-6′′′), 3.71 (dd, 12.0, 5.6, H-6′′′), 1.89 (s, AcO); ^{13}C-NMR (100 MHz, CD_3OD): 95.4 (C-1), 154.5(C-3), 108.4 (C-4), 39.8 (C-5), 78.8 (C-6), 45.0 (C-7), 89.6 (C-8), 50.3 (C-9), 21.8 (C-10), 168.4 (C-11), 51.9 (OMe), 100.3 (C-1′), 74.5 (C-2′′), 77.8 (C-3′′), 71.6 (C-4′′), 78.3 (C-5′′), 62.9 (C-6′′), 130.3 (C-1′′′), 132.9 (C-2′′, 6′′), 117.1 (C 3′′, 5′′), 159.7 (C-4′′), 144.0 (C-7′′), 118.8 (C-8′′), 167.4 (C-9′′), 101.9 (C-1′′′), 74.8 (C-2′′′), 77.8 (C-3′′′), 71.2 (C-4′′′), 78.1 (C-5′′′), 62.4 (C-6′′′), 22.2, 172.9 (OAc).

[**13**] Saletpangponoside C (Dinda et al., 2007a)

$C_{26}H_{34}O_{13}$: 554.1999; amorphous powder; [α]$_D$ -58.9° (*c*=2.86, MeOH); ^{1}H-NMR (400 MHz, CD_3OD): 5.82 (d, 2.4, H-1), 7.38 (d, 1.5, H-3), 2.94 (H-5), 4.25 (m, H-6), 2.11 (br d, 14.9, H_a-7), 1.97 (dd, 14.9, 5.4, H_b-7), 2.94 (H-9),1.38 (s, H3-10), 3.66 (s, MeO-11), 4.59 (d, 7.8, H-1′), 3.14 (dd, 9.0, 7.8, H-2′), 3.32 (dd, 9.0, 8.8, H-3′), 3.22 (dd, 9.5, 8.8, H-4′), 3.26 (m, H-5′), 3.85 (dd, 12.2, 2.2, H-6′), 3.61 (dd, 12.2, 6.4, H-6′), 6.98 (d, 8.5, H-2′′, 6′′), 6.64 (d, 8.5, H-3′′, 5′′), 2.76 (m, H-7′′), 2.49 (m, H-8′′); ^{13}C-NMR (100 MHz, CD3OD): 95.7 (C-1), 153.6 (C-3), 109.8 (C-4), 42.2 (C-5), 76.0 (C-6), 47.7 (C-7), 89.7 (C-8), 49.9 (C-9), 22.2 (C-10), 169.0 (C-11), 51.8 (OMe), 100.4 (C-1′), 74.7 (C-2′),78.0 (C-3′), 71.4 (C-4′), 78.2 (C-5′), 63.0 (C-′), 132.6 (C-1′′), 130.3 (C-2′′, 6′′), 116.2 (C-3′′, 5′′), 156.7 (C-4′′), 31.2(C-7′′), 38.2 (C-8′′), 175.0 (C-9′′).

[**14**] Ipolamiide (Boros and Stermitz, 1990)

$C_{17}H_{26}O_{11}$: 406.39, mp 142-143^{o}C, [α]$_D$ -139^o (MeOH); UV 231 (EtOH); 1H-NMR (90MHzD_2O): 5.81(H-l, d, 1.8), 7.52 (H-3, s), 2.49(H-9, d, 0.8). 1.15 (H-10, s), 3.74 (OMe); 13C-NMR (D_2O): 94 .4(C-1), 153.0 (C-3), 113.8 (C-4), 71.3 (C-5), 37.9 (C-6), 39.4 (C-7), 79.0 (C-8), 60.6 (C-9), 22.7 (C-lo), 169.0 (C-11), 52.6 (OMe), 99.2 (C-1'), 73.2 (C-2'), 76.1 (C-3'), 70.4 (C-4'), 77.1(C-5'), 61.5 (C-6').

[**15**] Phlorigidoside B (8-*O*-acetyl-6b-hydroxyipolamiide) (Dinda et al., 2007a)

$C_{19}H_{28}O_{13}$: 464.1529; amorphous powder[α]$_D$ -88.0° (*c*=0.63, MeOH; UV (MeOH): 231 (3.86); IR (dry film): 3386, 1708,1628, 1294, 1078; ^{1}H-NMR (400 MHz, CD_3OD): 6.15 (s, H-1), 7.58 (s, H-3), 4.34 (t, 4.9, H-6), 2.12 (d, 4.9, H2-7), 2.90 (s, H-9), 1.40 (s, H3-10), 3.72 (s, MeO-11), 2.02 (s, AcO-8), 4.59 (d, 8.0, H-1′), 3.19 (dd, 8.8, 7.8, H-2′), 3.69 (dd, 12.1, 5.9, H-6′), 3.90 (dd, 12.2, 2.0, H-6′); ^{13}C-NMR(100 MHz, CD_3OD): 95.3 (C-1), 155.5 (C-3), 112.3 (C-4), 72.7 (C-5), 74.9 (C-6), 45.8 (C-7), 86.0(C-8), 57.6 (C-9), 22.0 (C-10), 167.8 (C-11), 51.8 (OMe), 100.2 (C-1′), 74.3 (C-2′), 77.5 (C-3′), 71.6 (C-4′), 78.3 (C-5′), 62.8 (C-6′).

[**16**] 8-*O*-Acetylmussaenoside (Dinda et al., 2007a)

$C_{19}H_{28}O_{11}$: 432.1631; amorphous powder; [α]$_D$ -53.2° (*c*=1.84, MeOH); ^{1}H-NMR (400 MHz, CD_3OD): 5.71 (d, 3.4, H-1), 7.43(d, 1.0, H-3), 3.12 (m, H-5), 1.75 (m, H2-6), 2.05 (m, H2-7), 2.68 (dd, 8.5, 3.4, H-9), 1.54 (s, H3-10), 3.69 (s, MeO-11), 4.59 (d, 7.8, H-1′), 3.14 (dd, 9.0, 7.8, H-2′), 3.32 (dd, 9.0, 8.8, H-3′), 3.22 (dd, 9.5, 8.8, H-4′), 3.26 (m, H-5′), 3.85 (dd, 12.2, 2.2, H-6′), 3.61(dd, 12.2, 6.4, H-6′); 13C-NMR (100 MHz, CD_3OD): 95.5 (C-1), 153.0 (C-3), 112.2 (C-4), 32.9 (C-5), 29.7 (C-6), 39.6 (C-7), 91.0(C-8), 51.0 (C-9), 21.2 (C-10), 169.0 (C-11), 51.7 (OMe), 100.2 (C-1′), 74.7 (C-2′), 78.0 (C-3′), 71.6 (C-4′), 78.3 (C-5′), 62.9 (C-6′).

[**17**] Mussaenosidic acid (Boros and Stermitz, 1990)

$C_{16}H_{24}O_{10}$: 376.36, , [α]$_D$ -118^o, (MeOH) UV 238 (MeOH), 1H-NMR (90 MHz D_2O) 5.55 (H-1, d, 3), 7.44(H-3, s); ^{13}C-NMR (D_2O): 95.2 (C- l), 152.2(C-3), 113.0 (C-4), 30.4 (C-5), 29.6 (C-6),40.3 (C-7), 80.4 (C-8), 51.4 (C-9), 23.8 (C-10), 171.6(C-11), 99.1 (C-1'), 73.4 (C-2'), 76.5 (C- 3'), 70.4 (C-4'), 77.1 (C-5'), 61.5 (C-6').

[**18**] 8-*O*-Acetylshanzhiside (Dinda et al., 2007a)

$C_{18}H_{26}O_{12}$: 434.1424; white amorphous powder; [α]$_D$ -42.0° (*c*=0.1, MeOH); UV (MeOH): 205 (2.88); IR (KBr): 3450, 1739,1695, 1400, 1250, 1100; ^{1}H-NMR (500 MHz, CD_3OD): 5.62 (d, 3.8, H-1), 7.10 (br s, H-3), 3.01 (dd, 9.3, 3.5, H-5), 4.13 (m, H-6),2.24 (dd, 14.4, 6.2, H_a-7), 2.17 (dd, 14.4, 5.3, H_b-7), 2.85 (dd, 9.3, 3.8, H-9), 1.55 (s, H_3-10), 2.00 (s, Ac), 4.65 (d, 7.9, H-1′), 3.13 (dd, 9.0, 7.9, H-2′), 3.38 (t, 9.0, H-3′), 3.30 (m, H-4′), 3.32 (m, H-5′), 3.90 (dd, 12.0, 2.1, H-6′), 3.66 (dd, 12.0, 6.2, H-6′); ^{13}C-NMR (125 MHz, CD_3OD): 94.9 (C-1), 147.9 (C-3), 111.0 (C-4), 43.6 (C-

5), 77.6 (C-6), 46.9 (C-7), 90.1 (C-8), 48.6 (C-9), 22.1(C-10), 181.0 (C-11), 22.3, 172.9 (Ac), 100.6 (C-1′), 74.8 (C-2′), 77.9 (C-3′), 71.7 (C-4′), 78.3 (C-5′), 62.9 (C-6′).

[28] Lupulinoside (Dinda et al., 2007a)

$C_{25}H_{38}O_{16}$: 594.2159; colorless amorphous solid; $[\alpha]_D$ -41.6° (*c*=0.125, MeOH); IR (KBr): 3405, 2923, 1706, 1636, 1438, 1382, 1284, 1075, 1027; ^{1}H-NMR (500 MHz, D_2O+CD_3OD, 50 : 1): 5.73 (d, 1.1, H-1), 7.38 (d, 0.8, H-3), 2.96 (m, H-5, 2′, 4′), 1.93, 1.65 (each m, H2-6, 7), 2.66 (dd, 9.2, 1.5, H-9), 1.38 (s, H3-10), 3.65 (s, MeO-11), 4.78 (d, 8.0, H-1′), 3.49 (dd, 8.0, 7.7, H-2′), 3.58 (dd, 9.2, 7.7, H-3′), 3.29 (dd, 9.9, 9.2, H-4′), 3.39 (ddd, 9.9, 5.9, 2.1, H-5′), 3.82 (dd, 12.5, 2.1, H-6′), 3.63 (dd, 12.5, 5.9, H-‘ 4.59 (d, 7.8, H-1′′), 3.33 (t, 9.2, H-3′′), 3.20 (m, H-5′′), 3.76 (dd, 12.2, 2.1, H-6′′), 3.48 (dd, 12.2, 7.7, H-6′′); ^{13}C-NMR (125 MHz, D_2O+CD_3OD, 50 : 1): 95.5 (C-1), 153.2 (C-3), 112.1 (C-4), 31.6 (C-5), 28.7 (C-6), 39.6 (C-7), 90.6 (C-8), 50.3 (C-9), 20.8 (C-10), 170.2 (C-11), 52.7 (MeO-11), 22.5, 175.2 (Ac), 97.5 (C-1′),77.8 (C-2′), 77.2 (C-3′, 5′, 5′′), 70.3 (C-4′), 61.6 (C-6′), 102.4 (C-1′′), 74.6 (C-2′′), 76.5 (C-3′′), 71.2 (C-4′′), 62.4 (C-6′′).