Supporting Information for NP030241V

Antitumor Agents 228. Five New Agarofurans, Reissantins A-E, and Cytotoxic Principles from *Reissantia buchananii*

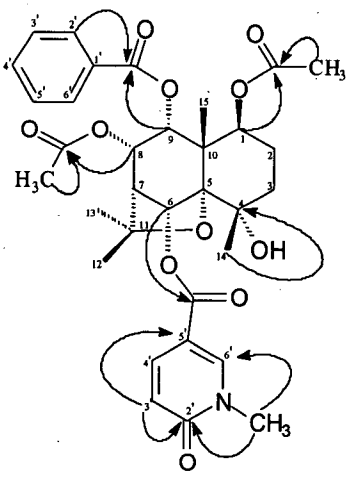


Figure 1. HMBC spectral correlations of **1**.

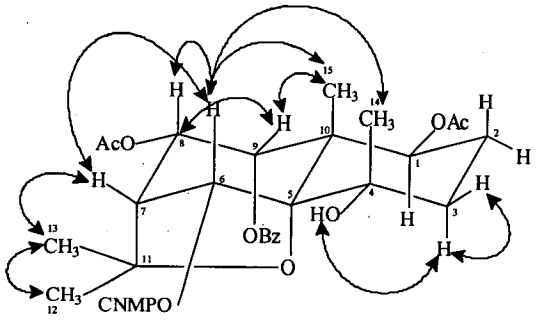


Figure 2. NOESY spectral correlations of **1**.

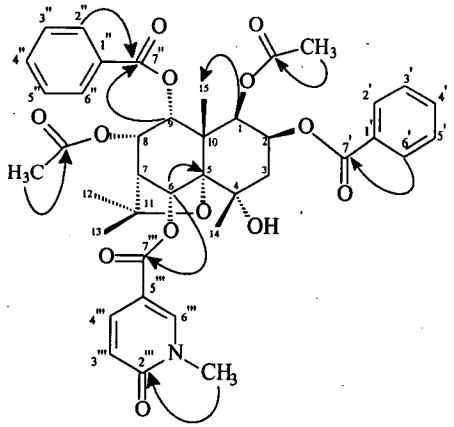


Figure 3. HMBC spectral correlations of **2**.

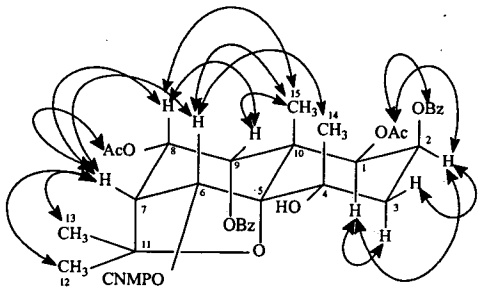


Figure 4. NOESY spectral correlations of **2**.

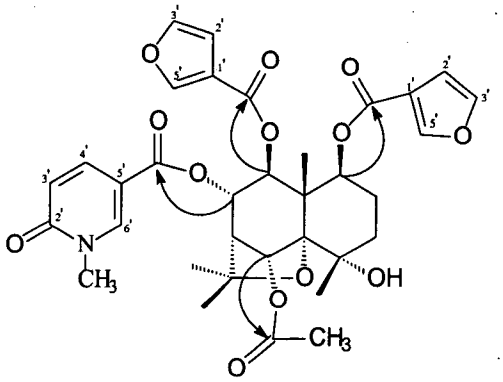


Figure 5. HMBC spectral correlations of **3**.

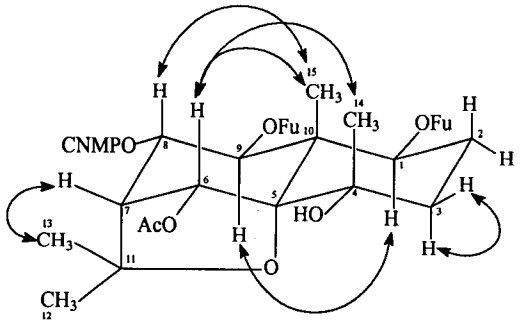
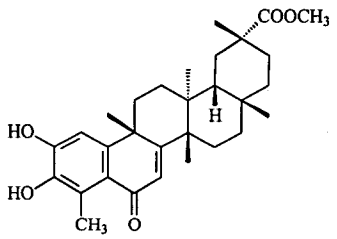
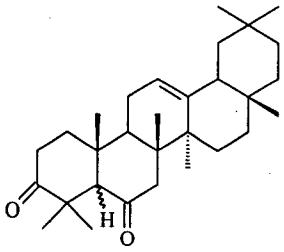


Figure 6. NOESY spectral correlations of **3**.

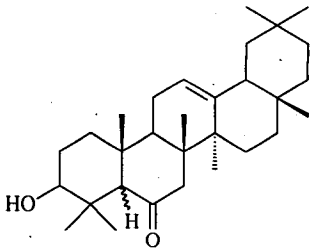
The structures of known compounds:



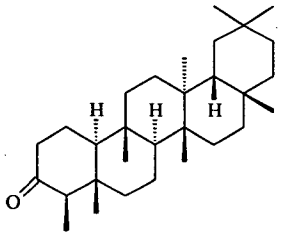
8



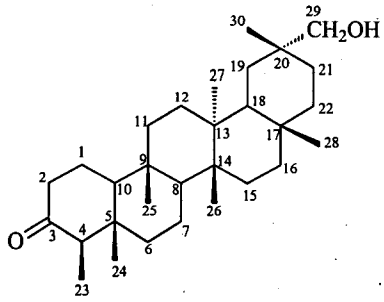
9 and 10



11 and 12



13



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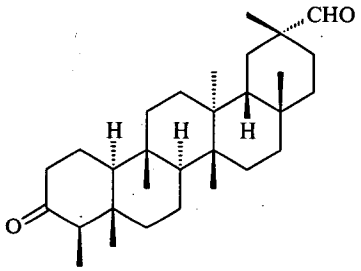

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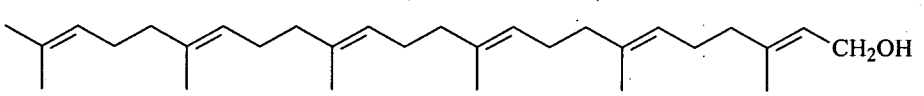

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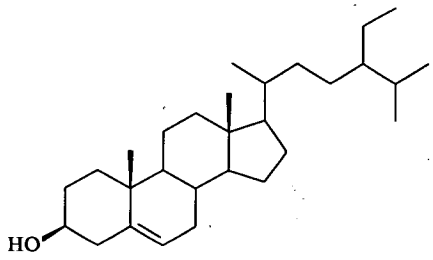

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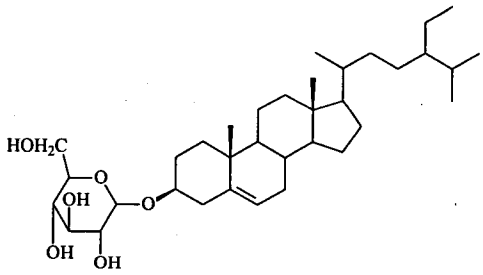

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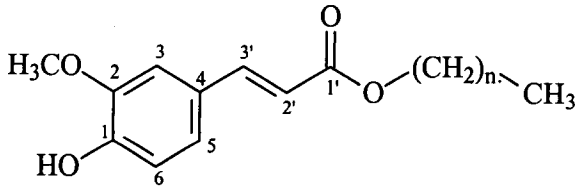
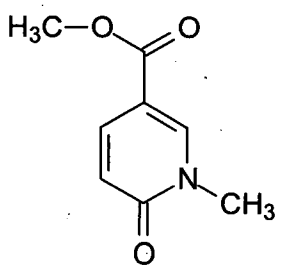


19 and **20**



21

Data of known compounds.

6-Oxopristimerol (8) was obtained as yellow solid: mp 225-227 °C; $[\alpha]^{24.6}_{D}$ -33.02°(*c* 0.321, MeOH); IR (neat) ν_{max} 3371 and 1705 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.79 (H-1), 6.18 (H-7), 1.56 (H-25), 0.46 (H-26), 1.18 (H-27), 1.03 (H-28), 3.49 (-$COOCH_3$), 1.22 (H-30). EIMS *m/z* 218 (19), 121 (18), 109 (19), 107 (25), 95 (35), 81 (36), 69 (49), 67 (26), 59 (44), 57 (44), 55 (90).

5α-Daturadione (**9**) and **5β-daturadione** (**10**) was obtained as white amorphous solid: mp 198-200 °C; $[\alpha]^{25.2}_{D}$ +46.73°(*c* 0.104, $CHCl_3$); IR (neat) ν_{max} 1707 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.11 (1H, s, H-5α), 2.41 (1H, d, *J*=12, H-7α) (**9**), δ 1.94 (1H, s, H-5β), 2.36 (1H, d, *J*=12, H-7α) (**10**); ESIMS *m/z* 461 $[M+Na]^+$ (100).

5α-3β-Hydroxyolean-12-en-one (**11**) and **5β-3β-hydroxyolean-12-en-one** (**12**) was obtained as colorless needle crystals: mp 228-230 °C; $[\alpha]^{25.2}_{D}$ +37.80°(*c* 0.209, $CHCl_3$); UV (MeOH) λ_{max} 266 nm; IR (neat) ν_{max} 3407, 1699 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.06

(1H, s, H-5α), 2.48 (1H, d, *J*=12, H-7α) (**11**); δ 1.99 (1H, s, H-5β), 2.46 (1H, d, *J*=12, H-7α) (**12**); ESIMS *m/z* 463 $[M+Na]^+$ (100).

Friedelan (13) was obtained as needle crystals: mp 256-258 °C; $[\alpha]^{25.2}_D$ -18.45°(*c* 0.104, $CHCl_3$); UV (MeOH) λ_{max} 243, 268, 274 nm; IR (neat) ν_{max} 1638 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 0.83 (H-23), 0.66 (H-24), 0.81 (H-25), 0.94 (H-26), 0.99 (H-27), 1.12 (H-28), 0.89 (H-29), 0.94 (H-30); ESIMS *m/z* 449 $[M+Na]^+$ (100), 300.4 (15), 248.5 (25).

29-Hydroxy-friedelan-3-one (14) was obtained as white amorphous solid: mp 262-265 °C; $[\alpha]^{25.4}_D$ -19.00°(*c* 0.123, $CHCl_3$); UV (MeOH) λ_{max} 277, 285, 344 nm; IR (neat) ν_{max} 3430, 1704 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.66, 0.81, 0.83, 0.97, 0.99, 1.16 (18H, s, six Me groups); ESIMS *m/z* 465 $[M+Na]^+$ (100).

3-Oxofriedo-olean-29-al (15) was obtained as white needles: mp 253-255 °C; $[\alpha]^{25.5}_D$ +3.79°(*c* 0.132, $CHCl_3$); UV (MeOH) λ_{max} 274, 341, 308 nm; ^1H NMR ($CDCl_3$, 300 MHz): δ 0.65, 0.80, 0.81, 0.82, 0.92, 1.04 (18H, s, six Me groups), 9.34 (1H, d, *J*=1.5, CHO); ESIMS *m/z* 463 $[M+Na]^+$ (100).

3,7,11,15,19,23-Hexamethyl-tetracosa-2,6,10,14,18,22-hexaen-1-ol (16) was obtained as yellow oil; $[\alpha]^{24.7}_D$ -8.06°(*c* 0.186, $CHCl_3$); UV (MeOH) λ_{max} 242, 276 nm; IR (neat) ν_{max} 3401 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 5.05 (1H, t, *J*=6.9; H-2), 5.12 (5H, t, *J*=6.9; H-6, H-10, H-11, H-18, H-22), 3.93 (2H, d, *J*=4.5; H-1), 1.99 (10H, m) and 1.95 (10H, m) (H-4,

H-5, H-8, H-9, H-12, H-13, H-16, H-17, H-20, H-21), 1.72 (3H, s, Me-24), 1.63 (18H, s, C-3-Me, C-7-Me, C-11-Me, C-15-Me, C-19-Me, C-23-Me); ESIMS *m/z* 449.1 $[M+Na]^+$ (100).

***β*-Sitosterol (17)** was obtained as white solid: mp 135-137 °C, $[\alpha]^{25.1}_D$ -23.2°(*c* 0.173, $CHCl_3$); UV (MeOH) λ_{max} 256 (sh), 289, 340 nm; IR (neat) ν_{max} 3417 (brs), 1635, 1430 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.55 (1H, m, H-3), 5.54 (1H, d, *J*=5.0 Hz, H-6); EIMS *m/z* 414 $[M]^+$ (15), 161 (17), 145 (23).

***β*-Sitosteryl-*β*-D-glycoside (18)** was obtained as white powder: mp 272-275 °C; $[\alpha]^{25.1}_D$ -56°(*c* 0.23, pyridine); UV ($CHCl_3$) λ_{max} 245, 268, 274 nm; IR (neat) ν_{max} 3433, 2663.53, 1635.06, 1450 cm^{-1}; ^1H NMR (Pyridine, 300 MHz) δ 5.35 (1H, m, H-6), 5.17 (1H, m, H-23), 5.05 (1H, m, H-22), 3.91 (1H, m, H-3), 0.98 (3H, s, H-19), 0.93 (3H, d, *J*=6.3), 0.86 (3H, t, *J*=7.0, H-29), 0.83 (3H, s, H-27), 0.68 (3H, s, H-18).

***Trans*-docosanyl-ferulate (19)** and ***trans*-lignoceryl-ferulate (20)** was obtained as white amorphous solid: mp 54-56 °C; $[\alpha]^{25.4}_D$ -9.86°(*c* 0.071, $CHCl_3$); UV ($CHCl_3$) λ_{max} 217, 220, 325 nm; IR (neat) ν_{max} 3410 (brs), 1712 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.60 (1H, d, *J*=16.0; H-3′), 6.29 (1H, d, *J*=16.0; H-2′), 6.91 (1H, d, *J*=8.0; H-6), 7.03 (1H, d, *J*=2.0; H-3), 7.07 (1H, dd, *J*=2.0 and 8.0; H-5), 3.93 (3H, s, C-2 OMe), 4.18 (2H, t, *J*=7.0, $-CH_2O-$), 1.7 (2H, q, *J*=7, $-CH_2-$), 1.26 (38H, s, $19\times CH_2$), 0.87 (3H, t, *J*=7, Me); ESIMS *m/z* 525.2 $[M+Na]^+$ (95) and 554.9 $[M+Na]^+$ (100).

Methyl *N*-methyl-2-oxohydropyridine-5-carboxylate (21) was obtained as white powder: mp 115-118 °C; $[\alpha]^{23.9}_{D}$ +7.68°(*c* 0.23, $CHCl_3$); UV (MeOH) λ_{max} 208, 260, 294 nm; IR (neat) ν_{max} 1712 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.56 (1H, d, *J*=9.50), 7.86 (1H, dd, *J*=9.50, 2.50), 8.20 (1H, d, *J*=2.50), *N*-methyl: δ 3.61 (3H, s), OCH_3: 3.87 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.97 (s; C-2), 119.45 (d; C-3), 138.69 (d; C-4), 109.65 (s; C-5), 143.57 (d; C-6), 164.70 ($OCOCH_3$), 52.09 (OCH_3); ESIMS *m/z* 167 (100), 136 (80), 108 (76), 95 (27), 80 (16), 51 (18).