Journal of the Chinese Chemical Society, **1995**, *42*, 573-577

Chemical Constituents from the Root and Aerial Parts of *Rosa taiwanensis*

Shen-Chyun Yang (楊勝俊), Jim-Min Fang (方俊民) and Yu-Shia Cheng* (鄭玉瑕)
Department of Chemistry, National Taiwan University, Taipei, Taiwan 106, R.O.C.

The root and aerial parts of *Rosa taiwanensis* Nakai contain the chemical constituents phenols, unsaturated acids, loliolide, abscisic acid, flavones, sterols, lupeol, betulin, betulinic acid, oleanolic acid and ursolic acid derivatives. Among them, 2α,3α-dihydroxyurs-12,19-dien-28-oic acid and its C-3 epimer are new compounds.

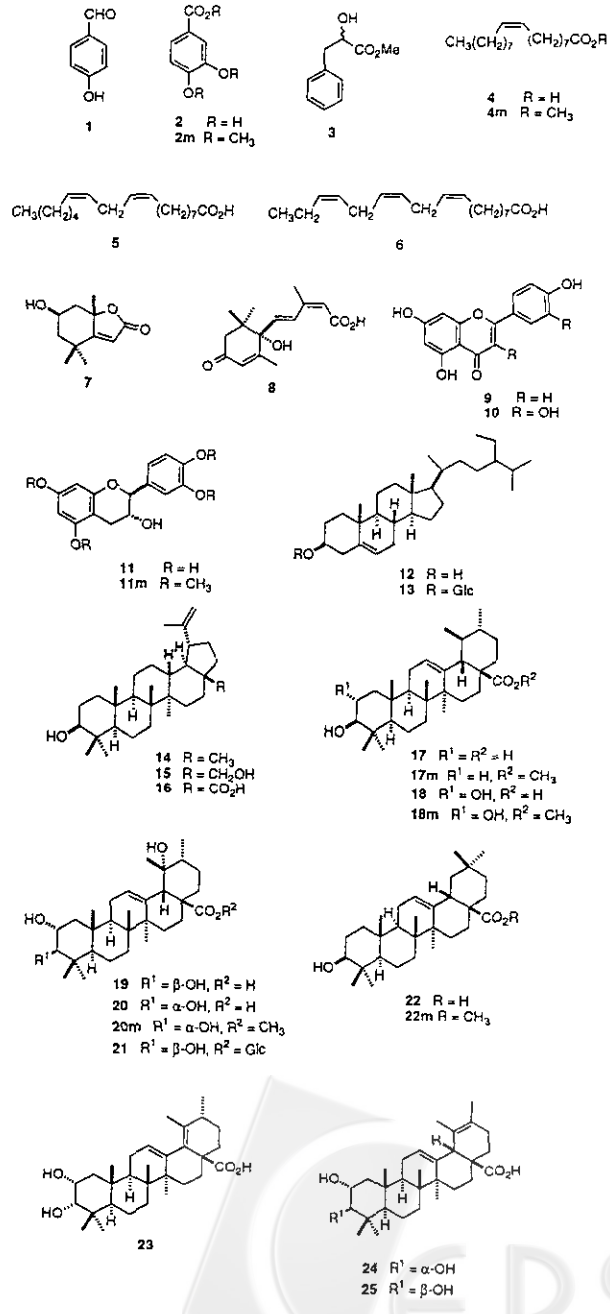
INTRODUCTION

Rosa taiwanensis Nakai (小金櫻), Rosaceae, is an endemic climbing shrub growing at low and medium altitudes throughout Taiwan island.[1] Bioactive compounds are found in plants of Rosa genus.[2] *R. taiwanensis* and *R. laevigata* Michx (大金櫻) are used as traditional folk medicines.[3] Prescriptions made from the extract of the root of *R. multiflora* Thunb. show hypolipidimic activity.[4] We reported chemical constituents of *R. laevigata*[5] and *R. transmorrisonensis* Hayata (高山薔薇),[6] and here report constituents isolated from the root and aerial parts of *R. taiwanensis*.

RESULTS AND DISCUSSION

The acetone extract of the air-dried root or aerial part of *R. taiwanensis* was subjected to chromatography. The chemical constituents **1-25** were separated and characterized according to spectral methods. Identification of known compounds was based on their physical and spectral properties (mp, [α], IR, MS, ^{1}H and ^{13}C NMR). Aromatic compounds 4-hydroxybenzaldehyde **1**,[7a] 3,4-dihydroxybenzoic acid **2**[7b] and methyl 2-hydroxy-3-phenylpropanoate **3**[7c] were readily recognized. Unsaturated acids oleic acid **4**, linoleic acid **5** and linolenic acid **6** were isolated from the root. Other components include loliolide **7**,[5b,8] abscisic acid **8** (isolated as the methyl ester),[9,10] common flavones kaemferol **9**,[2,11] quercetin **10**[12,13] and catechin **11**,[14-16] as well as β-sitosterol **12**[17,18] and its derivative β-sitosteryl-β-D-glucopyranoside **13**.[19-21] Triterpenoid constituents are abundant in this plant: lupeol **14**,[22-25] betulin **15**,[26] betulinic acid **16**,[27] ursolic acid **17**,[28] 2α,3β-dihydroxyurs-12-en-28-oic acid **18**,[6,29] 2α,3β,19α-trihydroxyurs-12-en-28-oic acid **20**,[31] β-D-glucopyranosyl 2α,3β,19α-trihydroxyurs-12-en-28-oate **21**,[30,33] and oleanolic acid **22**.[28,34,35]

Ursolic acid derivatives **23**, **24** and **25** are isomers hav-



ing the molecular formula $C_{30}H_{46}O_4$ as deduced from tha exact mass measurements. IR absorptions about 3400 and 1700 cm^{-1} indicate the presence of hydroxyl and carboxyl groups in these compounds. The ^{13}C NMR spectrum of each compound showed signals corresponding to one carboxyl carbon (around δ 180) and two carbons (δ 66-85) geminal to the hydroxyl group. According to analyses of ^1H and ^{13}C NMR spectra, **23** was assigned as 2α,3α-dihydroxyurs-12,18-dien-28-oic acid, a component previously isolated from the hydrolysate of a Chinese drug, Daxueteng (*Sargentodoxa cuneata* Oliv.).[36] Compound **23** displayed UV absorption at 230 nm for the moiety of a conjugated diene. A signal in the NMR spectrum of an olefinic proton occurred at δ 5.40 (dd) and for a vinyl methyl group at δ 1.70 (s). The coupling constant between H-2 (axial) and H-3 (equatorial) is 2.7 Hz. The mass spectrum of **23** exhibited a base peak at *m/z* 233 and intense fragments at *m/z* 246, 201 and 187 (Fig. 1).

The mass spectra of **24** and **25** showed fragmentation patterns similar to that of **23**. The structures of **24** and **25** were assigned as 2α,3α-dihydroxyurs-12,19-dien-28-oic acid and 2α,3β-dihydroxyurs-12,19-dien-28-oic acid, respectively, according to their ^1H and ^{13}C NMR spectra. The assigments of proton and carbon signals were based on analyses of their H-H COSY and C-H COSY spectra. As **24** (or **25**) has a $\Delta^{19,20}$-double bond instead of a $\Delta^{18,19}$-double bond, two vinyl methyl groups appeared at δ 1.55 and 1.62. Compounds **24** and **25** are C-3 epimers, the former has a C-3 hydroxyl group at an axial position whereas the latter has a hydroxyl group at an equatorial position. The C-2 protons in **24** (at δ 3.92) and **25** (at δ 3.64) are at axial positions, because they showed ddd splitting patterns with J = 11, 4, 2.5 Hz for H-2 of 24 and J = 12.5, 9.6, 4.5 Hz for H-2 of **25**, in their J-resolved NMR spectra. The coupling constants $J_{2,3}$, 2.5 Hz for **24** and 9.6 Hz for **25**, are consistent with the assigned stereochemistry.

In summary, ursolic acid derivatives are major components of root and aerial parts of *R. taiwanensis*. Previous work on the chemical constituents of *R. laevigata* and *R. transmorrisonensis* also indicated abundance of ursolic acid derivatives. A related compound 2α-hydroxyurs-12-en-28-oic acid exhibits activity against human colon HCT-8 tumor cell.[38] Further pharmacological tests of ursolic acid derivatives occurring in the plants of *Rosa* genus may provide valuable information.

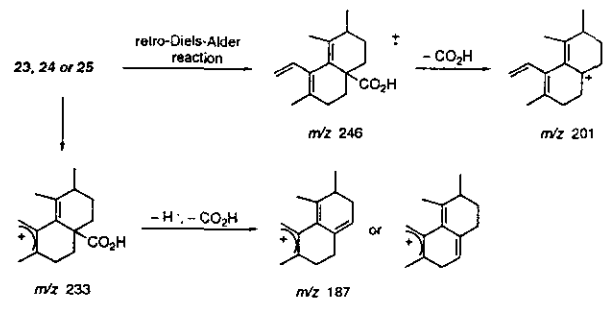


Fig. 1. Possible fragmentation pathways in the mass spectra.

EXPERIMENTAL SECTION

Instrumentation

Yanagimoto (or MP-500D) micro melting point apparatus, JASCO Dip-180 digital polarimeter, Finnigan TSQ-46c mass spectrometer, Perkin-Elmer 983G infrared spectrophotometer, Bruker AM-300 WB (or AC 200) nuclear magnetic resonance spectrometer, and Waters M-45 high-pressure liquid chromatograph with Hibar Lichrosorb Si 60 column (10 μm or 7 μm, 25 cm × 1 cm i.d.) were used.

Plant Material

The root and aerial parts of *Rosa taiwanensis* Nakai (2.3 kg) were collected from Tonshou (通霄) and Shinfon (新豐). Specimens of this plant are deposited in our laboratory. The aerial parts without fruit were exhaustively extracted with acetone (18 L). The extract was concentrated, the precipitates (compound **9**) were filtered, and the filtrate was partitioned between EtOAc and water. The EtOAc-soluble portion was concentrated and chromatographed on a silica-gel (700 g) column eluted with gradients of EtOAc/hexane or EtOAc/$CHCl_3$. The appropriate portions were combined and further separated or purified by HPLC to give **14** (65 mg), **12** (235 mg), **1** (12 mg), **3** (105 mg), **2** (45 mg), **15** (150 mg), **18** (190 mg), **19** (450 mg), **7** (32 mg), **20** (345 mg), **24** (15 mg), **25** (38 mg), **23** (12 mg), **9** (1.2 g), **10** (7.5 g), **11** (100 mg), **13** (1.3 g), and **21** (1.26 g) in order of increasing polarity. Constituents of carboxylic acids, detected according to IR spectra, were dissolved in Et_2O and treated with CH_2N_2 to give the corresponding methyl esters **17m** (120 mg), **22m** (55 mg), **18m** (20 mg) and **8m** (7 mg). Methanolic extracts of roots (45 g) were absorbed with SiO_2 (100 g) and chromatographed on a silica-gel (500 g) column eluted with gradients of EtOAc and hexane. Besides components **12** (45 mg), **1** (12 mg), **16** (121 mg), **22** (42 mg), **20** (50 mg), **19** (25 mg), **21** (206 mg), and **11** (56 mg) found in aerial parts, three fatty acids **4** (15 mg), **5** (37 mg) and **6** (45 mg) were isolated.

Data of new compounds **24** and **25**, and additional data of known compounds are listed as follows.

4-Hydroxybenzaldehyde 1

Solid, mp 115-116 °C. (lit.[7a] mp 117-119 °C).

3,4-Dihydroxybenzoic acid (protocatechuic acid) 2

This compound[7b] was treated with CH_2N_2 in Et_2O to give methyl 3,4-dimethoxybenzoate, $C_{10}H_{12}O_3$ *m/z* 196 (M^+, base peak). ^{13}C NMR ($CDCl_3$) δ 51.9, 55.9, 56.1, 110.2, 111.9, 122.6, 123.5, 146.5, 152.5, 166.8.

Methyl 2-hydroxy-3-phenylpropanoate 3

Oil, $[\alpha]_D^{25}$ -51.2° ($CHCl_3$, *c* 1.8). ^{13}C NMR ($CDCl_3$) δ 40.4, 52.2, 71.2, 126.7, 128.2, 128.2, 129.3, 129.3, 136.2, 174.4.

9Z-Octadecenoic acid (oleic acid) 4

Oil. IR (neat) 3380-2850, 1710 cm^{-1}.

9Z,12Z-Octadecadienoic acid (linoleic acid) 5

Oil. ^{13}C NMR ($CDCl_3$) δ 14.0, 22.5, 24.6, 25.6, 27.1, 29.0, 29.0, 29.1, 29.3, 29.4, 29.5, 31.5, 33.9, 127.8, 128.0, 130.0, 130.2, 180.0.

9Z,12Z,15Z-Octadecatrienoic acid (linolenic acid) 6

Oil. ^{13}C NMR ($CDCl_3$) δ 14.2, 20.5, 24.6, 25.4, 25.5, 27.1, 28.9, 29.0, 29.1, 29.5, 34.0, 127.0, 127.7, 128.2, 128.2, 130.2, 131.9, 180.2.

Loliolide 7[5b,8]

Solid, mp 148-150 °C (lit.[5b] 151-152 °C), $[\alpha]_D^{28}$ -5.55° ($CHCl_3$, *c* 0.18). ^{13}C NMR ($CDCl_3$) δ 26.4 (q), 26.9 (q), 30.6 (q), 35.9 (s), 45.5 (t), 47.2 (t), 66.6 (d), 86.9 (s), 112.7 (d), 142.1 (s), 182.7 (s).

Abscisic acid 8

This compound was treated with CH_2N_2 in Et_2O to give methyl ester **8m**.[9,10] Oil, $[\alpha]_D^{28}$ +57.1° ($CHCl_3$, *c* 0.7). ^{13}C NMR ($CDCl_3$) δ 18.8, 21.1, 23.0, 24.3, 42.2, 49.7, 51.1, 68.1, 118.1, 126.5, 128.0, 136.3, 137.2, 150.0, 172.3, 201.0.

Kaemferol 9[2,11]

Yellow needles (from MeOH), mp 274-276 °C (lit.[2] 276-277 °C). ^{13}C NMR (C_5D_5N) δ 94.2, 99.2, 104.3, 116.2, 116.2, 123.2, 130.4, 130.4, 137.7, 148.5, 157.3, 160.6, 162.3, 165.5, 177.2.

Quercetin 10[12,13]

Yellow needles (from MeOH), mp 289-290 °C (lit.[13] 290 °C). ^{13}C NMR (CD_3COCD_3) δ 94.4, 99.1, 104.0, 115.6, 116.1, 121.3, 123.6, 136.6, 145.8, 146.2, 148.3, 157.6, 162.1, 165.0, 176.5.

Catechin 11[14-16]

This compound was treated with CH_2N_2 to give **11m** as yellow crystals (from MeOH), mp 174-175 °C (lit.[14] 175-178 °C), $[\alpha]_D^{28}$ -4.8° (Me_2CO, *c* 3.0; lit.[14] -4.1°).

β-Sitosterol 12[17,18]

Needles (from $CHCl_3$), mp 135-138 °C (lit.[17] 137.5-138 °C), $[\alpha]_D^{25}$ -33.5° ($CHCl_3$, *c* 1.03; lit.[14] -34.3°).

β-Sitosteryl-β-D-glucopyranoside 13[19-21]

This compound was treated with Ac_2O in pyridine to give peracetate **13a**, mp 168-170 °C (lit.[19] 169-170 °C), $[\alpha]_D^{28}$ -30.1° ($CHCl_3$, *c* 2.5).

Lupeol 14[22-25]

Solid (from EtOAc), mp 214-215 °C (lit.[22] 215 °C), $[\alpha]_D^{25}$ +25° ($CHCl_3$, *c* 1.2; lit.[22] +22°). ^{13}C NMR ($CDCl_3$) δ 14.4, 15.3, 16.0, 17.9, 18.2, 19.2, 20.9, 25.0, 27.3, 27.4, 27.9, 29.6, 29.8, 34.2, 35.5, 37.1, 38.0, 38.6, 38.7, 39.9, 40.7, 42.7,42.9, 47.9, 48.2, 50.3, 55.2, 78.9, 109.3, 150.8.

Betulin 15[26]

Solid (from MeOH), mp 252-255 °C (lit.[26] 255-256 °C), $[\alpha]_D^{24}$ +15.8° (pyridine, *c* 1.0; lit.[26] +20.1°). ^{13}C NMR (C_5D_5N) δ 15.0, 16.2, 16.3, 18.8, 19.3, 21.1, 25.8, 27.8, 28.3, 28.7, 30.1, 30.4, 34.7, 34.9, 37.5, 37.6, 39.3, 39.5, 41.3, 43.0, 48.3, 48.5, 49.2, 49.7, 50.8, 55.9, 59.5, 78.1, 109.9, 151.2.

Betulinic acid 16[27]

Solid (from MeOH), mp 288-290 °C (lit.[27] 290-292 °C), $[\alpha]_D^{26}$ +19° (pyridine, *c* 2.5; lit.[27] +32°). ^{13}C NMR ($CDCl_3$) δ 14.8, 16.2, 16.3, 18.7, 19.4, 21.1, 26.0, 28.2, 28.6, 29.5, 30.2, 32.0, 32.8, 34.7, 37.4, 37.5, 38.5, 39.2, 39.4, 41.0, 42.7, 47.7, 49.7, 50.9, 55.8, 56.5, 78.0, 109.8, 151.2, 178.8.

Ursolic acid 17

This compound was treated with CH_2N_2 in Et_2O to give the methyl ester **17m** as needles (from MeOH), mp 110-113 °C (lit.[28] 111-114 °C), $[\alpha]_D^{24}$ +65.6° ($CHCl_3$, *c* 2.0; lit.[28] +66.5°). ^{13}C NMR ($CDCl_3$) δ 15.3, 15.5, 16.8, 16.9, 18.2, 21.1, 23.2, 23.5, 24.1, 27.1, 27.9, 28.0, 30.6, 32.8, 35.6, 36.8, 38.5, 38.5, 38.7, 38.8, 39.8, 41.9, 47.7, 48.0, 51.3, 52.7, 55.1, 78.9, 125.4, 138.0, 178.0.

2α,3β-Dihydroxyurs-12-en-28-oic acid 18[6,29]

This compound was treated with CH_2N_2 in Et_2O to give the methyl ester **18m**, mp 200-203 °C (lit.[29] 203-206

°C), $[\alpha]_D^{24}$ +39.8° ($CHCl_3$, *c* 3.0; lit.[6] +40.2°). ^{13}C NMR ($CDCl_3$) δ 15.6, 15.7, 16.8, 16.9, 18.2, 21.0, 23.2, 23.5, 24.3, 27.8, 28.6, 32.7, 35.5, 38.0, 38.7, 38.9, 39.1, 39.4, 40.5, 41.5, 46.5, 47.3, 47.9, 51.3, 52.7, 55.2, 68.7, 83.5, 125.2, 138.0, 177.9.

2α,3β,19α-Trihydroxyurs-12-en-28-oic acid 19[30]

Solid (from MeOH), mp 259-261 °C (lit.[30] 260-262 °C), $[\alpha]_D^{25}$ +32° (pyridine, *c* 3.0; lit.[30] +30°). ^{13}C NMR (C_5D_5N) δ 16.7, 16.7, 17.1, 17.5, 18.9, 22.3, 24.0, 24.6, 26.2, 26.8, 27.0, 29.1, 29.2, 30.1, 33.4, 38.3, 39.7, 40.3, 42.0, 42.2, 47.7, 48.1, 54.4, 55.8, 68.5, 72.5, 83.7, 127.8, 138.8, 180.6.

2α,3α,19α-Trihydroxyurs-12-en-28-oic acid 20[31]

This compound was treated with CH_2N_2 in Et_2O to give the methyl ester **20m** as needles (from MeOH), mp 124-126 °C (lit.[31] 125-130 °C), $[\alpha]_D^{25}$ +22.8° ($CHCl_3$, *c* 5.3). ^{13}C NMR ($CDCl_3$) δ 15.7, 16.0, 16.1, 16.6, 18.0, 21.7, 23.3, 24.6, 25.3, 25.9, 27.3, 28.0, 28.4, 32.4, 37.3, 38.1, 38.2, 41.0, 41.1, 41.6, 46.8, 47.8, 47.0, 51.5, 53.1, 66.4, 73.0, 78.8, 128.9, 138.0, 178.6.

β-D-Glucopyranosyl 2α,3β,19α-trihydroxyurs-12-en-28-oate 21[32,33]

Solid (from Me_2CO), mp 206-208 °C (lit.[32] 208-210 °C), $[\alpha]_D^{25}$ +14° (pyridine, *c* 1.1). ^{13}C NMR (C_5D_5N) δ 16.6, 16.9, 17.4, 17.5, 19.7, 24.1, 24.3, 26.0, 26.7, 29.1, 29.3, 29.3, 33.4, 37.6, 38.4, 38.6, 39.8, 40.5, 42.1, 47.8, 47.9, 49.6, 54.3, 55.9, 62.2, 68,5, 71.1, 72.6, 74.0, 78.9, 89.2, 83.8, 95.7, 128.3, 139.2, 176.9.

Oleanolic acid 22[28,34,35]

This compound was treated with CH_2N_2 in Et_2O to give the methyl ester **22m**, mp 199-201 °C (lit.[28] 200-203 °C), $[\alpha]_D^{26}$ +60.1° ($CHCl_3$, *c* 2.0; lit.[28] +66.7°).

2α,3α-Dihydroxyurs-12,18-dien-28-oic acid 23[36,37]

Oil, $[\alpha]_D^{28}$ +89° ($CHCl_3$, *c* 0.5). IR (neat) 3434, 1697 cm^{-1}. UV (MeOH) 230 nm (log ε, 3.81). MS *m/z* (rel intensity) 470 (30, M^+), 455 (5), 437 (6), 246 (19), 233 (100), 201 (82), 187 (70). ^1H NMR ($CDCl_3$) δ 0.84 (3 H, s), 0.86 (3 H, s), 0.95 (3 H, s), 0.99 (3 H, s), 1.00 (3 H, s), 1.06 (3 H, d, *J* = 7.2 Hz), 1.70 (3 H, s), 3.41 (1 H, d, *J* = 2.7 Hz, H-3), 3.99 (1 H, m, H-2), 5.40 (1 H, dd, *J* = 7.5, 3.6 Hz, H-12). ^{13}C NMR ($CDCl_3$) δ 17.1, 17.8, 17.9, 18.6, 19.4, 21.6, 21.7, 23.1, 26.5, 28.5, 31.1, 32.2, 34.3, 34.4, 34.8, 37.7, 38.2, 39.1, 42.7, 44.7, 47.5, 48.2, 49.7, 66.5, 78.8, 126.3, 132.0, 138.0, 138.90, 179.8.

2α,3α-Dihydroxyurs-12,19-dien-28-oic acid 24

Oil, $[\alpha]_D^{28}$ +93.2° (MeOH, *c* 0.59). IR (neat) 3425, 1698 cm^{-1}. MS *m/z* (rel intensity) 470 (34, M^+), 424 (35), 246 (12), 233 (100), 201 (653, 187 (57). ^1H NMR (CD_3COCD_3) δ 0.84 (3 H, s), 0.86 (3 H, s), 0.98 (3 H, s), 1.00 (6 H, s), 1.55 (3 H, s), 1.62 (3 H, s), 3.20 (1 H, s), 3.30 (1 H, d, *J* = 2.5 Hz, H-3), 3.92 (1 H, ddd, *J* = 11.0, 4.0, 2.5 Hz, H-2), 5.47 (1 H, dd, *J* = 7.0, 3.6 Hz, H-12). ^{13}C NMR ($CDCl_3$) δ 16,8, 17.4, 17.8, 17.9, 20.3, 21.9, 21.9, 23.2, 27.9, 28.2, 28.5, 32.6, 33.4, 38.2, 39.2, 42.0, 43.7, 46.7, 47.4. 48.1, 4g.6, 51.9, 55.8, 66.5, 78.7, 123.6, 127.3, 129.2, 138.6, 182.8. HRMS for $C_{30}H_{46}O_4$ calcd. 470.3387, found *m/z* 470.3384.

2α,3β-Dihydroxyurs-12,19-dien-28-oic acid 25

Oil, $[\alpha]_D^{28}$ +56.7° (MeOH, *c* 2.8). IR (neat) 3390, 1694 cm^{-1}. MS *m/z* (rel intensity) 470 (18, M^+), 424 (22), 246 (15), 233 (83), 201 (68), 187 (73), 43 (100). ^1H NMR (CD_3OD) δ 0.80 (3 H, s), 0.88 (3 H, s), 0.99 (3 H, s), 1.00 (3 H, s), 1.03 (3 H, s), 1.55 (3 H, s), 1.62 (3 H, s), 2.90 (1 H, d, *J* = 9.6 Hz, H-3), 3.12 (1 H, s), 3.64 (1 H, ddd, *J* = 12.5, 9.6, 4.5 Hz, H-2), 5.46 (1 H, dd, *J* = 7.0, 3.5 Hz, H-12). ^{13}C NMR (CD_3OD) δ 17.8, 18.1, 18.7, 19.9, 20.9, 21.0, 22.9, 24.7, 25.0, 29.0, 29.7, 29.6, 29.7, 29.8, 34.5, 35.4, 39.7, 40.0, 45.0, 48.6, 49.6, 51.8, 57.3, 70.0, 84.9, 125.4, 128.7, 129.9, 139.5, 181.6. HRMS for $C_{30}H_{46}O_4$ calcd. 470.3387, found *m/z* 470.3385.

ACKNOWLEDGMENT

We thank the National Science Council of the Republic of China for financial support.

Received October 12, 1994.

Key Words

Rosa taiwanensis; Rosaceae; Aerial part; Root; Flavones; Ursolic acid derivatives; Lupeol; Betulin; Oleanolic acid.

REFERENCES

1. Huang, T.-C. Ed. *Flora of Taiwan*, 2nd ed.; Dept. Botany, National Taiwan Univ.: Taipei, **1993**, Vol. 3, pp 118-119.
2. Hsu, H.-Y.; Chen, Y.-P.; Hong, M. *The Chemical Con-*

stituents of Oriental Herbs, Oriental Healing Arts Institute: Los Angeles, California, **1982**.
3. Ma, D.; Wang, S.; Sun, B.; Liu, X.; Zhang, N. *Zhongcaoyao* **1985**, *16*, 244; *Chem. Abstr. 103*, 129180h.
4. Du, H.; Zhao, X.; Zhao, T.; Wang, M.; Zhang, Z.; Yao, M.; Yu, S. *Yaoxue Xuebao* **1983**, *18*, 314; *Chem. Abstr. 100*, 48578e.
5. (a) Fang, J.-M.; Wang, K.-C.; Cheng, Y.-S. *Phytochemistry* **1991**, *30*, 3383. (b) Fang, J.-M.; Wang, K.-C.; Cheng, Y.-S. *J. Chin. Chem. Soc. (Taipei)* **1991**, *38*, 297.
6. Kao, S.-F.; Fang, J.-M.; Cheng, Y.-S. *J. Chin. Chem. Soc. (Taipei)* **1993**, *40*, 597.
7. (a) *The Aldrich Library of NMR Spectra*, Aldrich Chemical Company, Inc., New York, **1983**, Vol. 2, 110C. (b) *ibid.* 195A. (c) Yoshida, M.; Asano, M.; Yamanaka, H. *Eur. Polym. J.* **1990**, *26*, 1273.
8. Hodges, R.; Porte, A. L. *Tetrahedron* **1964**, *20*, 1463.
9. Findlay, J. A.; Mackay, W. D. *Can. J. Chem.* **1971**, *49*, 2369.
10. Ohkuma, K.; Addicott, F. T. *Tetrahedron Lett.* **1965**, 29, 2529.
11. Agrawal, P. K. *Carbon-13 NMR of Flavonoids*, Elsevier: Amsterdam, **1989**, pp 152-155.
12. Chen, R.-S.; Lai, J.-S.; Wu, T.-S. *J. Chin. Chem. Soc. (Taipei)* **1986**, *33*, 329.
13. Chen, M.-T.; Wan, C.-H.; Chen, C.-M. *J. Chin. Chem. Soc. (Taipei)* **1988**, *35*, 167.
14. Nonaka, G. 1.; Ezaki, E.; Hayashi, K.; Nishioka, I. *Phytochemistry* **1983**, *22*, 1659.
15. Foo, L. Y.; Dorter, L. J. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1535.
16. Singh, J.; Ralhan, N. K. *J. Ind. Chem. Soc.* **1984**, 1044.
17. Jain, T. C.; Banks, C. M. *Can. J. Chem.* **1968**, *46*, 2325.
18. Wright, J. L. C.; Mcinnes, A. G.; Shimizu, S.; Smith, D. G. *Can. J. Chem.* **1978**, *56*, 1898.
19. Ramiah, P. A.; Lavie, D. L.; Budhivaja, R. D.; Garg, K. N. *Phytochemistry* **1984**, *23*, 143.
20. Rubinstein, I.; Goad, L. J.; Mulheirn, L. J. *Phytochemistry* **1976**, *15*, 195.
21. Kuo, Y.-H.; Chen, W.-C.; Lin, Y.-T. *J. Chin. Chem. Soc. (Taipei)* **1984**, *31*, 159.
22. Appleton, R. A.; Enzell, C. R. *Phytochemistry* **1971**, *10*, 447.
23. Budzikiewicz, H.; Wilson, J. M.; Djerassi, C. *J. Am. Chem. Soc.* **1963**, *85*, 3688.
24. Chin, W.-J.; Corbett R. E. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1437.
25. Bhattacharyya, J.; Cymone, B. B. *Phytochemistry* **1986**, *25*, 274.
26. Tanaka, R.; Tabuse, M.; Matsunago, S. *Phytochemistry* **1988**, *27*, 3563.
27. Chen, C. M.; Chen, M. T. *Phytochemistry* **1976**, *15*, 1997.
28. Furuya, T.; Orihara, Y.; Hayashi, C. *Phytochemistry* **1987**, *26*, 715.
29. Yamagishi, T.; Chang, J. J.; Antrew, T. *Phytochemistry* **1988**, *27*, 3213.
30. Numata, A.; Yang, P.; Fujita, E. *Chem. Pharm. Bull.* **1989**, *37*, 648.
31. Takahashi, K.; Kawaguchi, S.; Takan, M. *Chem. Pharm. Bull.* **1974**, *22*, 650.
32. Qin, W.; Wu, X.; Zhao, J.; Yamada, T.; Nakagawa, K. *Phytochemistry* **1986**, *25*, 913.
33. Seto, T.; Tanaka, T.; Tanaka, O.; Naruhashi, N. *Phytochemistry* **1984**, *23*, 2829.
34. Doddrell, D. M.; Khong, P. W.; Lewis, K. G. *Tetrahedron Lett.* **1974**, *27*, 2381.
35. Seo, S.; Tomita, Y.; Tori, K. *J. Am. Chem. Soc.* **1981**, *103*, 2075.
36. Rücker, G.; Mayer, R.; Shin-Kim J.-S. *Planta Med.* **1991**, *57*, 468.
37. Numata, A.; Takahashi, C.; Miyamoto, T.; Yang, P. *Chem. Pharm. Bull.* **1990**, *38*, 942.
38. Yamagishi, T.; Zhang, D. C.; Chang, J. J.; McPhail, D. R.; McPhail, A. T.; Lee, K. H. *Phytochemistry* **1988**, *27*, 3213.