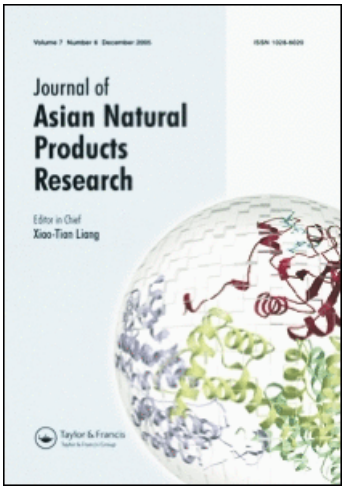

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MONOTERPENOIDS AND THEIR GLYCOSIDES FROM *WINCHIA CALOPHYLLA*

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Three new monoterpenoid compounds have been isolated from extracts of the stem barks of *Winchia calophylla* A. DC. The new compounds include two cyclo-diglycosides, wincaloside A (**2**) and wincaloside B (**3**), and a derivative of tetrahydroxycyclohexane-carboxylic acid, winchiepoxide (**1**). Their structures have been elucidated by spectroscopic and chemical methods.

Keywords: *Winchia calophylla*; Apocynaceae; Monoterpenoids; Wincalosides A and B

INTRODUCTION

Winchia calophylla A. DC. (Apocynaceae), distributed in Yunnan and Hainan provinces of China, India, Myanmar and Indonesia, is a traditional medicinal plant. Its stem barks have been used as a folk medicine to treat chronic tracheitis [1]. Previous research has revealed that this plant mainly contains alkaloids [2,3]. However, the other chemical constituents have not been reported before our work. This paper describes the isolation and structure elucidation of three new monoterpenoid compounds, 2α,3α-epoxy-5α-hydroxy-7-oxa-bicyclo[3.2.1]octan-6-one, winchiepoxide (**1**), wincaloside A (**2**) and wincaloside B (**3**), together with three known compounds, loganin (**4**) [4], loganic acid (**5**) [5] and sweroside (**6**) [6]. Their structures have been elucidated on the basis of spectroscopic analysis, especially 2D NMR experiments, and chemical methods.

RESULTS AND DISCUSSION

Compound **1** has the molecular formula $C_7H_8O_4$, based on its ion peak at *m/z* 156.0428. Owing to cleavage of HO and CO_2, EI-MS exhibits fragment ion peaks at *m/z* 139 [$M^+ - 17$] and 112 [$M^+ - 44$]. Its ^{13}C NMR (DEPT) spectrum shows seven signals for

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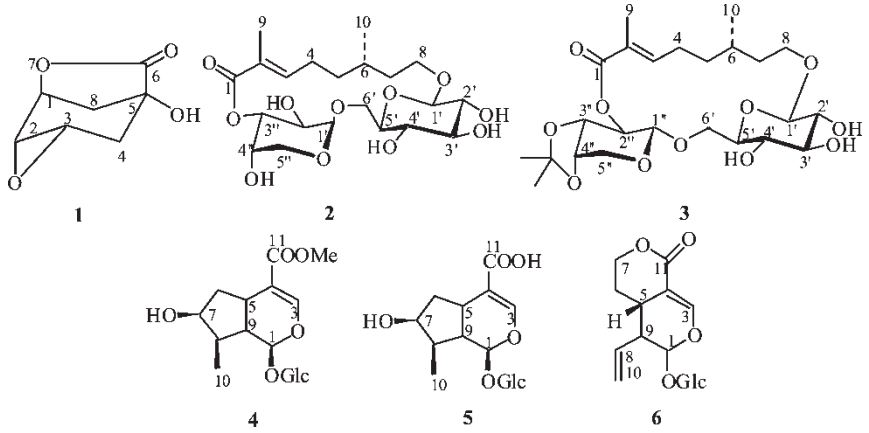

FIGURE 1 Compounds **1**–**6**.

an ester or carboxylic group, a quaternary carbon bearing oxygen, three oxymethines and two methylenes, which are very similar to those of quinide [7], implying that **1** is a derivative of a multi-hydroxyl substituted cyclohexane carboxylic acid. Relative to the ^{13}C NMR spectra of γ-quinide, downfield shifts of C-2, C-3, C-4 and C-8 (+1.4, + 0.8, + 3.1 and + 1.4 ppm, respectively) in **1** are observed. The key HMBC spectra of **1** (Fig. 2 below) shows that 1-hydroxyl and 5-carboxyl form the γ-lactone and that 2- and 3-OH form an epoxide. Thus, the structure of compound **1** was elucidated as 2α,3α-epoxy-5α-hydroxy-7-oxa-bicyclo[3.2.1]octan-6-one (Fig. 1).

Compound **2** has the molecular formula $C_{21}H_{34}O_{11}$, based on its HR-FABMS peak at *m/z* 461.1939. The EI-MS fragment ion peaks at *m/z* 462 [M^+], 330 (462 − 132), 301 (462 − 161) and 169 (301 − 132 or 330 − 161) imply that there is a pentose and a hexose in this molecule, and the fragment ion peaks at *m/z* 197 (330 − 161 + 18 or 301 − 132 + 18) indicate that two glycose moieties form a ring with the aglycone of composition $C_{10}H_{18}O_3$ (M 196). The fragment ion peaks at *m/z* 179 (197 − 18), 151 (169 − 18) and 123 (169 − 46) show the aglycone to be a hydroxyl carboxylic acid. Except for the characteristic signals of glucoses, the ^{1}H NMR spectrum shows a vinyl proton (δ 6.82, 1H, dd, $J = 7.3$ Hz), an oxymethylene (δ 3.71, 1H, dd, $J = 4.1$, 4.9 Hz & 3.76, 1H, dd, $J = 4.1$, 7.9 Hz), a tertiary methyl (δ 1.90, 3H, s) and a secondary methyl (δ 0.91, 3H, d, $J = 6.5$ Hz). These data indicate that **2** is a lonitoside-type compound [8]. The ^{13}C NMR (DEPT) spectrum shows the signals of two methyls, four ethylenes, one of which bears an oxygen, a methine, a vinyl methine, a vinyl quaternary carbon and an ester carbonyl, indicating that the aglycone of **2** is

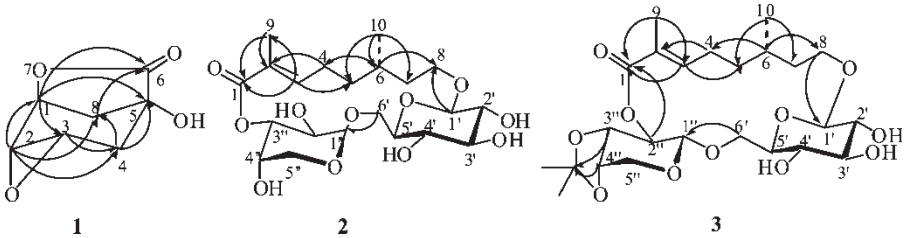

FIGURE 2 Selected HMBC correlations of **1**–**3**.

a hydroxycarboxylic acid of a monoterpene. HMBC experiments show long-range correlations between H-3 (δ 6.82, 1H, t, $J = 7.3$ Hz) and C-1 (δ 169.2, s), C-2 (δ 128.5, s), C-4 (δ 26.7, t), C-5 (δ 35.8, t) and C-9 (δ 12.8, q); H-9 (δ 1.19, 1H, s) and C-1, C-2 and C-3 (δ 145.1, d); H-10 (δ 0.91,1H, d, $J = 6.5$ Hz) and C-5, C-6 (δ 28.9, d), and C-7 (δ 36.7, t); H-6 (δ 1.52, 1H, and C-4, C-5, C-10 and C-8 (δ 68.2, t) (Fig. 2). In addition, ^{1}H–^{1}H COSY spectra show connectivities between H-4 and H-5, H-5 and H-6, H-6 and H-7 and H-10, H-7 and H-8. Its NOESY spectra show no long-range correlation between H-3 and H-9. All the above evidence supports the aglycone of **2** as 2,6-dimethyl-8-hydroxy-(2*E*)-octenoic acid. The anomeric protons at δ 4.25 (1H, d, $J = 7.5$ Hz) and 4.68 (1H, s), and anomeric carbons at δ 103.7 (d) and 101.7 (d), indicate a β-configuration for glucopyranose and arabinopyranose, which is supported by comparison of the acid hydrolysis products with authentic samples. Also, the HMBC experiments show ^{1}H–^{13}C long-range correlations between H-1′ (δ 4.25, 1H, d, $J = 7.5$ Hz) and C-8 (δ 68.2, t); H-8 (δ 3.71, 1H, dd, $J = 4.1$, 4.9 Hz & 3.76, 1H, dd, $J = 4.1$, 7.9 Hz) and C-1′ (δ 103.7, d); H-6′ (δ 3.96, 1H, dd, $J = 5.2$, 5.8 Hz) and C-1″ (δ 101.7, d); H-1″ (δ 4.68, 1H, s) and C-6′(δ 67.4, t) (Fig. 2). This observation indicates the biose is 6′-*O*-β-L-arabinopyranosyl-β-D-glucopyranose and that C-1′ of glycose is linked to C-8 of the monoterpenoid acid. Hence, relative to those of β-L-arabinopyranose [9] and methyl β-L-arabinopyranose [10] (δ 3.6 and 70.7, respectively), the downfield shifts of H-3″ and C-3″ (δ 5.07 and 73.1, respectively) show that the 3″-OH forms an ester with −COOH of the monoterpenoid acid. The absolute configuration of the monoterpenoid acid was determined by the Iwagawa's method [11]; on hydrolysis with 10% HCl, and **2**, 6-dimethyl-8-hydroxy-2*E*-octenoic acid was produced, which shows a negative optical rotation ($[\alpha]_D^{22} - 6.7$), in agreement with that of (2*E*,6*S*)-dimethyl-8-hydroxy-2*E*-octenoic acid [11], and is opposite to that of (2*E*,6*R*)-dimethyl-8-hydroxy-(2*E*)-octenoic acid [12]. Thus, the monoterpenoid acid in compound **2** is (2*E*,6*S*)-dimethyl-8-hydroxy-(2*E*)-octenoic acid. The structure of wincaloside A (**2**) was thus elucidated as shown in Fig. 1.

Compound **3** has the molecular formula $C_{24}H_{38}O_{11}$, based on its HREIMS peak at *m*/*z* 502.2420. Apart from being 40 units larger than **2** in molecular weight, the EIMS, ^{1}H, ^{13}C NMR, HMBC, ^{1}H–^{1}H COSY and NOSEY spectra of **3** are very similar to those of **2**, implying that they are the same type of compound. The ^{1}H and ^{13}C NMR data of the anomeric protons and carbons at δ 4.11 (1H, d, $J = 7.8$ Hz) and 103.5 (d), δ 4.41 (1H, d, $J = 7.6$ Hz) and 102.3 (d) indicate a β-configuration for glucopyranose and α-configuration for arabinopyranose. On comparison of spectral data of **3** with those of **2**, an isopropylidene unit in the pentose moiety on the framework of **3** was proved by the fragment ion signals of EI-MS of **3** at *m*/*z* 369 (502 − 133), 340 (502 − 162), 329 (369 − 40), 312 (502 − 150 − 40) and 169 (340 − 131 − 40); additionally two tertiary methyls at δ 1.32 (3H, s) and 1.52 (3H, s) and two methyls at δ 26.3 (q) and 26.5 (q) and a quaternary carbon at δ 111.3 (s) appear in the ^{1}H and ^{13}C NMR spectra, respectively; and ^{1}H–^{13}C long-range correlations between H-3″ (δ 4.26, 1H, m), H-4″ (δ 4.25, 1H, m) and C-2‴(δ 111.3, d) have been observed in HMBC experiments. The spectral data indicate that the 3-OH and 4-OH form an acetal with acetone in α-L-arabinopyranose. In addition, ^{1}H–^{13}C long-range correlations between H-6′ (3.86, 1H, dd, $J = 2.0$, 13.2 Hz & 4.24, 1H, dd, $J = 4.5$, 13.2 Hz) and C-1″ (δ 102.3, d); H-1″ (δ 4.41, 1H, d, $J = 7.6$ Hz) and C-6′ (δ 70.9, t) show the biose to be a 6′-*O*-α-L-arabinopyranosyl-β-D-glucopyranose. The ^{1}H–^{13}C long-range correlations between H-1′ (δ 4.11, 1H, d, $J = 7.8$ Hz) and C-8 (δ 70.2, t); H-8 (3.59, 2H, m, $J = 5.7$, 6.8 Hz) and C-1′ (δ 103.5, *d*); H-2″ (δ 5.00, 1H, t, $J = 7.6$ Hz) and C-1 (δ 168.6, s) indicate that 8-OH and carboxyl of (2*E*,6*S*)-dimethyl-8-hydroxy-(2*E*)-octenoic acid form the glycoside and ester with the anomeric hydroxyl and 2″-OH of the biose, respectively. Thus, the structure of wincaloside A (**3**) is elucidated as shown in Fig. 1.

EXPERIMENTAL

General Experimental Procedures

Optical rotations were determined on a Jasco-20C digital polarimeter. HREIMS and HR-FABMS were performed on an Autospec-3000 spectrometer. 1D NMR spectra were recorded on a Brucker AM-400 and a Brucker DRX-500 spectrometer. 2D NMR spectra were recorded on a Brucker DRX-500 spectrometer.

Plant Material

Stem barks of *Winchia calophylla* A. DC were collected in Xishuangbanna, Yunnan province of China in July 2000. The plant was identified by Professor Hong Mao Liu and Mr Jing Yun Cui, and a voucher specimen has been deposited in the Xishuangbanna Garden of Tropical Plants, Chinese Academy of Sciences.

Extraction and Isolation

The dried and ground stem barks (10.5 kg) of *W. calophylla* were extracted four times with 95% EtOH under reflux. Removal of the solvents *in vacuo* produced a concentrated syrup (600 g) that was dissolved in 2% HCl (4 × 500 mL). The pH was then adjusted to 9–10 with concentrated ammonia and the obtained basic solution was extracted with light petroleum, chloroform, and n-butanol successively. The *n*-butanol fraction (180 g) was subjected to flash column chromatography over silica gel H, eluting with ethyl acetate and a gradient of EtOAc–MeOH, to afford six fractions. Fraction 2 (8 g) was then further isolated by flash column chromatography over silica gel H, eluting with $CHCl_3$–MeOH (40:1), to yield **1** (14 mg). Fraction 6 (30 g) was separated into three further parts, 61, 62 and 63. Compounds **4** (1.25 g) and **6** (274 mg) were isolated from part 61 (2.3 g), compounds **2** (26 mg) and **3** (31 mg) from part 62 (1 g), and **5** (22 mg) from part 63 (6.9 g) through flash column chromatography over silica gel H, eluting with $CHCl_3$–MeOH–HCO_2H (900:100:0.5), AcOEt–EtOH (9:1) and $CHCl_3$–MeOH–HCO_2H (900:100:1), respectively.

Acidic Hydrolysis

Compound **2** (10 mg) was hydrolyzed with 10% HCl in MeOH by Iwagawa's method [11] to furnish an oil, i.e. (2*E*,6*S*)-2,6-dimethyl-8-hydroxyoctenoic acid (3 mg). $[\alpha]_D^{22}$ − 6.7 (*c* 0.30, $CHCl_3$); ^{1}H NMR (400 MHz, in $CDCl_3$) δ (ppm): 6.85 (t, 1H, J = 7.1 Hz, H-3), 2.26 (m, 2H, H-4), 1.38 (m, 2H, H-5), 1.43 (m, 2H, H-6), 1.59 (m, 2H, H-7), 3.72 (m, 2H, H-8), 1.87 (s, 3H, H-9) and 0.93 (s, 3H, H-10). After neutralization with 10% Na_2CO_3 and concentration under reduced pressure, D-glucose and L-arabinose were qualitatively identified in the aqueous layer by comparison of their TLC behavior on a silica gel plate with that of authentic samples. Upon development with the solvent system $CHCl_3$–MeOH–HOAc–H_2O (7:3:1:0.5) and the upper layer of *n*-BuOH–HOAc–H_2O (4:1:5), D-glucose and L-arabinose gave R_f values of 0.185 and 0.283, 0.145 and 0.193, respectively.

Winepoxide (**1**) was obtained as a white, amorphous powder, $[\alpha]_D^{26}$ − 20.0 (*c* 2.20, MeOH). ^{1}H NMR (pyridine-d_5, 400 MHz) δ (ppm): 5.03 (dd, 1H, J = 4.5, 6.4 Hz, H-1), 4.50 (dd, 1H, J = 4.5, 4.6 Hz, H-2), 4.40 (ddd, 1H, J = 4.5, 4.6, 6.4 Hz, H-3), 2.58 (dd, 1H, J = 4.5, 10.5 Hz, H-4β), 2.75 (dd, 1H, J = 6.4, 10.5 Hz, H-4α), 2.60 (dd, 1H, J = 6.4, 11.4 Hz, H-8α), 3.04 (br.d, 1H, J = 11.4 Hz, H-8β). ^{13}C NMR (pyridine-d_5, 100 MHz)

δ (ppm): 77.3 (d, C-1), 66.9 (d, C-2), 67.2 (d, C-3), 41.4 (t, C-4), 72.9 (s, C-5), 179.0 (s, C-6), 38.3 (t, C-8). EIMS *m/z* $[M]^+$ 156 (13), 139 (5), 118 (27), 112 (78), 100(27), 89 (17), 84 (36), 71 (100), 60 (88). HREIMS *m/z* 156.0428 (calcd for $C_7H_8O_8$ 156.0423).

Wincaloside A (**2**) was obtained as a white, amorphous powder, $[\alpha]_D^{22}$ − 29.5 (*c* 2.00, C_5H_5N). ^{1}H NMR (MeOH-d_4, 400 MHz) δ (ppm): 6.82 (t, 1H, J = 7.3 Hz, H-3), 2.35 (ddd, 2H, J = 6.7, 7.3, 13.0 Hz, H-4), 1.39 (m, 2H, H-5), 1.52 (m, 1H, J = 6.5 Hz, H-6), 1.64 (ddd, 2H, J = 4.1, 6.4, 6.5 Hz, H-7), 3.71 (dd, 1H, J = 4.9, 6.4 Hz) and 3.76 (dd, 1H, J = 4.1, 6.4 Hz) (H-8), 1.90 (s, 3H, H-9), 0.91 (d, 3H, J = 6.5 Hz, H-10), 4.25 (d, 1H, J = 7.5 Hz, H-1′), 3.14 (dd, 1H, J = 7.5, 8.4 Hz, H-2′), 3.30 (dd, 1H, J = 8.4, 8.9 Hz, H-3′), 3.28 (dd, 1H, J = 4.6, 8.9 Hz, H-4′), 3.32 (t, 1H, J = 4.6 Hz, H-5′), 3.96 (dd, 2H, J = 4.6, 11.0 Hz, H-6′), 4.68 (br.s, 1H, H-1″), 3.85 (d, 1H, J = 2.8 Hz, H-2″), 5.07 (br.s, 1H, H-3″), 4.12 (m, 1H, H-4″), 3.50 (dd, 1H, J = 4.9, 5.7 Hz) and 3.94 (dd, 1H, J = 4.8 Hz) (H-5″). ^{13}C NMR (MeOH-d_4, 100 MHz) δ (ppm): 169.2 (s, C-1), 128.5 (s, C-2), 145.1 (d, C-3), 26.7 (t, C-4), 35.8 (t, C-5), 28.9 (d, C-6), 36.6 (t, C-7), 68.2 (t, C-8), 12.8 (q, C-9), 20.5 (q, C-10), 103.7 (d, C-1′), 75.2 (d, C-2′), 78.3 (d, C-3′), 71.1 (d, C-4′), 76.8 (d, C-5′), 67.2 (t, C-6′), 101.7 (d, C-1″), 69.0 (d, C-2″), 73.1 (d, C-3″), 63.9 (d, C-4″), 60.4 (t, C-5″). EIMS *m/z* $[M]^+$ 462 (0.4), 360 (8), 330 (34), 301 (23), 197 (97), 169 (56), 151 (14), 123 (52), 95 (69), 81 (63), 69 (100). Negative HR-FABMS *m/z* 461.1939 (calcd. for $C_{21}H_{33}O_{11}$ 461.2022).

Wincaloside B (**3**) was obtained as a white, amorphous powder, $[\alpha]_D^{22}$ − 34.0 (*c* 1.00, C_5H_5N). ^{1}H NMR (MeOH-d_4, 400 MHz) δ (ppm): 6.85 (t, 1H, J = 7.2 Hz, H-3), 2.18 (m) and 2.37 (m) (H-4), 1.41 (m) and 1.54 (m) (H-5), 1.50 (m, 1H, J = 5.9 Hz, H-6), 1.45 (m, 2H, H-7), 3.59 (m, 2H, J = 5.7, 6.8 Hz, H-8), 1.83 (s, 3H, H-9), 0.98 (d, 3H, J = 5.9 Hz, H-10), 4.11 (d, 1H, J = 7.8 Hz, H-1′), 3.10 (t, 1H, J = 7.8, 9.2 Hz, H-2′), 3.29 (dd, 1H, J = 9.2 Hz, H-3′), 3.00 (t, 1H, J = 9.2 Hz, H-4′), 3.33 (t, 1H, J = 4.5, 9.2 Hz, H-5′), 3.86 (dd, 1H, J = 2.0, 13.2 Hz) and 4.24 (dd, 1H, J = 4.5, 13.2 Hz) (H-6′), 4.41 (d, 1H, J = 7.6 Hz, H-1″), 5.00 (t, 1H, J = 7.6 Hz, H-2″), 4.26 (m, 1H, H-3″), 4.25 (m, H-4″), 3.87 (br.d, 1H, J = 13.0 Hz) and 4.19 (br.d, 1H, J = 13.0 Hz) (H-5″), 1.32 (s, 3H, H-1‴) and 1.52 (s, 3H, H-3‴). ^{13}C NMR (MeOH-d_4, 100 MHz) δ (ppm): 168.7 (s, C-1), 128.5 (s, C-2), 144.7 (d, C-3), 26.3 (t, C-4), 36.0 (t, C-5), 31.0 (d, C-6), 36.4 (t, C-7), 70.2 (t, C-8), 12.7 (q, C-9), 22.7 (q, C-10), 103.5 (d, C-1′), 75.3 (d, C-2′), 78.2 (d, C-3′), 72.4 (d, C-4′), 76.9 (d, C-5′), 70.9 (t, C-6′), 102.3 (d, C-1″), 75.0 (d, C-2″), 78.1 (d, C-3″), 75.2 (d, C-4″), 64.3 (t, C-5″), 26.3 (q, C-1‴), 111.3 (s, C-2‴), 28.1 (q, C-3‴). EIMS *m/z* $[M]^+$ 502 (8), 487 (23), 472 (2), 369 (50), 340 (19), 329 (8), 312 (17), 300 (3), 241 (5), 197 (100), 169 (42), 151 (14), 123 (56), 109 (30), 95 (73), 81 (80), 69 (78). HR-EIMS *m/z* 502.2420 (calcd. for $C_{24}H_{38}O_{11}$ 502.2414).

Loganin (**4**) was obtained as a white, amorphous powder, $[\alpha]_D^{22}$ − 37.5 (*c* 1.10, MeOH). ^{1}H (MeOH-d_4, 400 MHz) and ^{13}C NMR (MeOH-d_4, 100 MHz) spectral data accord with those reported [4].

Loganic acid (**5**) was obtained as a white, amorphous powder. ^{1}H (MeOH-d_4, 400 MHz) and ^{13}C NMR (MeOH-d_4, 100 MHz) accord with those reported [5].

Sweroside (**6**) was also obtained as a white, amorphous powder. ^{1}H (MeOH-d_4, 400 MHz) and ^{13}C NMR (MeOH-d_4, 100 MHz) spectral data are in accord with those reported [6].

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