Two new triterpenoid glycosides from the stems of *Camellia oleifera* Abel

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**ABSTRACT**

Two new oleanane-type triterpenoid glycosides, 3-O-\(\beta\)-D-xylopyranosyl-(1\(\rightarrow\)2)-\(\alpha\)-L-arabinopyranosyl-(1\(\rightarrow\)3)[\(\beta\)-D-glucuronopyranosyl-(1\(\rightarrow\)2)]\(\beta\)-D-glucuronopyranosyl-22\(\alpha\)-angeloyloxyolean-12-ene-15\(\alpha\),16\(\alpha\),28-triol(1) and 3-O-\(\beta\)-D-xylopyranosyl-(1\(\rightarrow\)2)-\(\alpha\)-L-arabinopyranosyl-(1\(\rightarrow\)3)-[\(\beta\)-D-glucuronopyranosyl-(1\(\rightarrow\)2)]\(\beta\)-D-glucuronopyranosyl-21\(\beta\)-acetyl-22\(\alpha\)-angeloyloxyolean-12-ene-16\(\alpha\),28-diol (2) were isolated from the stems of *Camellia oleifera* Abel. Their structures were elucidated by means of spectroscopic methods and chemical evidence. The cytotoxic activities of compounds 1–2 were evaluated against five human tumour cell lines (HCT-8, BGC-823, A5049, and A2780). Compounds 1–2 showed cytotoxic activity against five human cancer cell lines, with IC\textsubscript{50} values ranging from 3.15 to 7.32 \(\mu\)M.

**1. Introduction**

*Camellia oleifera* Abel., belonging to the family Theaceae, is widely cultivated as an important oil-bearing crop or garden tree in China (Shanghai Scientific and Technical Publishers 2000). The seeds of *C. oleifera* have been used as an oil material and ointment base, while
the leaves of this plant are used as a Chinese traditional medicine for the treatment of nosebleed, sore carbuncle and itching skin ulcers (Chen et al. 2010). Previous investigation on C. oleifera has led to the isolation of triterpenoid saponins, flavonoids and tannins (Luo et al. 2003; Wang et al. 2006; Li et al. 2014; Tao et al. 2015). Some of them have been shown to exhibit anti-inflammatory, antitumour, antimutation, antibacterial and antiproliferative activities (Wang et al. 2006; Yang et al. 2015; Zong et al. 2015). The crude saponin has been used as a surface-active agent (Chen et al. 2010). Until now, no work has been done on the constituents of the stems of C. oleifera. In our preliminary screening, the n-BuOH part of the 95% EtOH extract of the stems of C. oleifera showed significant anticancer activity (see Table 2). As part of programme to search for bioactive constituents from C. oleifera, a 95% EtOH extract of the stems of C. oleifera has been investigated with two new compounds obtained (1 and 2). Reported herein are the isolation and structure elucidation and biological activity of these compounds.

2. Results and discussion

The 95% EtOH extract of the stems of C. oleifera was partitioned with CHCl₃, EtOAc and n-BuOH, successively. The n-BuOH-soluble portion was separated by a combination of silica gel, D101 macroporous resin chromatography and preparative HPLC (high-performance liquid chromatography) afforded two new compounds (1 and 2) (Figure 1). Their structures were elucidated by extensive NMR techniques including 1D NMR (1H and 13C NMR), 2D NMR (COFSY, NOESY, HSQC and HMBC) and HRESIMS, as well as chemical evidence.}

**Figure 1.** Chemical structures of compounds 1 and 2.
Table 1. $^1$H and $^{13}$C NMR spectral data of compounds 1 and 2 in CSD5N (δ in ppm, J in Hz).

| Position | δ$_H$ (1H, m) | δ$_C$ | δ$_H$ (1H, m) | δ$_C$ |
|----------|----------------|-------|----------------|-------|
| 1        | 1.30           | 39.1  | 1.27           | 39.2  |
|          | 0.80           |       | 0.74           |       |
| 2        | 2.08           | 26.6  | 2.08           | 27.0  |
|          | 1.79           |       | 1.78           |       |
| 3        | 3.20 (1H, dd, 12.6, 4.8 Hz) | 89.7  | 3.24 (1H, dd, 12.0, 4.0 Hz) | 89.9  |
| 4        | 39.6           |       | 40.0           |       |
| 5        | 0.76 (1H, brd, 12.0 Hz) | 55.6  | 0.73           | 56.1  |
| 6        | 1.52           | 18.8  | 1.57           | 18.8  |
|          | 1.36           |       | 1.35           |       |
| 7        | 2.07           | 37.0  | 1.31 (1H, m)   | 35.3  |
|          | 2.00           |       | 1.61 (1H, m)   |       |
| 8        |                | 44.4  |                | 40.5  |
| 9        | 1.68           | 47.1  | 1.61 (1H, m)   | 47.5  |
| 10       |                | 36.6  |                | 36.7  |
| 11       | 1.85           | 24.1  | 1.81           | 24.2  |
|          | 1.80           |       | 1.78           |       |
| 12       | 5.49 (1H, br s) | 124.9 | 5.40 (1H, br s) | 123.5 |
| 13       | 144.4          |       | 143.2          |       |
| 14       | 48.1           |       | 40.5           |       |
| 15       | 4.31 (1H, m)   | 67.6  | 1.59 (1H, m)   | 33.5  |
|          |                |       | 2.12 (1H, m)   |       |
| 16       | 4.42 (1H, m)   | 78.3  | 4.49 (1H, m)   | 69.1  |
| 17       |                | 46.1  |                | 47.3  |
| 18       | 2.76 (1H, m)   | 41.5  | 3.04 (1H, brd, 12.0 Hz) | 42.1  |
| 19       | 2.87 (1H, m)   | 47.3  | 3.03 (1H, m)   | 48.4  |
|          | 1.28 (1H, m)   |       | 1.40 (1H, m)   |       |
| 20       |                | 31.8  |                | 37.2  |
| 21       | 2.88 (1H, m)   | 42.5  | 6.58 (1H, d, 10.5 Hz) | 79.8  |
|          | 2.74 (1H, m)   |       |                |       |
| 22       | 4.31 (1H, dd)  | 72.9  | 6.30 (1H, d, 10.5 Hz) | 73.1  |
| 23       | 1.16 (3H, s)   | 28.0  | 1.21 (3H, s)   | 28.3  |
| 24       | 1.03 (3H, s)   | 16.8  | 1.07 (3H, s)   | 17.1  |
| 25       | 0.79 (3H, s)   | 15.8  | 0.79 (3H, s)   | 16.1  |
| 26       | 1.12 (3H, s)   | 17.8  | 0.83 (3H, s)   | 17.3  |
| 27       | 1.83 (3H, s)   | 21.3  | 1.84 (3H, s)   | 28.0  |
| 28       | 4.30 (1H, d, 10.2 Hz) | 63.7  | 3.65 (1H, d, 10.0 Hz) | 63.9  |
|          | 4.48 (1H, d, 10.2 Hz) |       | 3.41 (1H, d, 10.0 Hz) |       |
| 29       | 1.04 (3H, s)   | 33.7  | 1.07 (3H, s)   | 29.9  |
| 30       | 1.14 (3H, s)   | 25.3  | 1.31 (3H, s)   | 20.5  |
| 1’       |                | 167.7 |                | 168.6 |
| 2’       |                | 128.3 |                | 129.5 |
| 3’       | 5.90 (1H, q, 6.6 Hz) | 138.3 | 5.91 (1H, q, 7.0 Hz) | 137.5 |
| 4’       | 1.98 (3H, d, 6.6 Hz) | 15.9  | 2.08 (3H, d, 7.0 Hz) | 16.3  |
| 5’       | 1.91 (3H, s)   | 20.9  | 1.95 (3H, s)   | 21.5  |
| OAc      |                |       |                |       |
| 1        |                |       |                | 171.6 |
| 2        |                |       | 2.02 (3H, s)   | 21.3  |
| Sugar (C-3) | GlcA 1          | 4.81 (1H, d, 7.8 Hz) | 105.6  | 4.91 (1H, d, 7.0 Hz) | 106.1 |
|          | 2              | 4.63 (1H, m) | 78.4  | 4.68 (1H, m) | 79.1  |
|          | 3              | 4.42 (1H, m) | 84.8  | 4.42 (1H, m) | 84.2  |
|          | 4              | 4.48 (1H, m) | 71.1  | 4.51 (1H, m) | 71.6  |
|          | 5              | 4.47 (1H, m) | 172.1 | 4.57 (1H, m) | 172.2 |
| Ara(1→3)GlcA | 1              | 5.69 (1H, d, 7.8 Hz) | 101.9  | 5.78 (1H, d, 7.0 Hz) | 102.3 |
|          | 2              | 4.50 (1H, m) | 83.8  | 4.57 (1H, m) | 82.7  |
|          | 3              | 4.71 (1H, m) | 73.5  | 4.30 (1H, m) | 74.1  |
|          | 4              | 4.33 (1H, m) | 68.9  | 4.33 (1H, m) | 68.7  |
The 13C NMR spectrum of 1 displayed 57 carbon signals, of which 30 were attributed to the aglycone. Signals at $\delta_C 124.9$ and $144.4$ were assigned to a pair of typical olefinic carbons. Acid hydrolysis of 1 with 2 M HCl afforded monosaccharides, which were identified by GC analysis of their trimethylsilyl L-cysteine derivatives (Zhang et al. 1996) and the coupling constants of the anomeric protons, as $\beta$-D-glucuronic acid, $\alpha$-L-arabinose, $\beta$-D-xylose and $\beta$-D-glucose. These data demonstrated that 1 is a glycoside of an oxygenated 28-hydroxy-olean-12-ene aglycone (Table 1). The NMR data analysis of 1 indicated that 1 was almost identical with gordonoside J, which has been reported previously (Fu et al. 2011). The only difference between 1 and gordonoside J is that the galactose in gordonoside J was replaced by a glucose in 1. In the HMBC spectrum of 1 (Figure 2), a long-range correlation between H-22 and C-1’ indicated unambiguously that the angeloyloxy ester group is attached to C-22 of the aglycone. In addition, a HMBC correlation between GlcA-H-1 ($\delta_H 4.81$) and C-3 ($\delta_C 89.7$)

table 1 (continued)

| Position | $\delta_H$ | $\delta_C$ | $\delta_H$ | $\delta_C$ |
|----------|------------|------------|------------|------------|
| **5**    | 4.54 (1H, m) | 66.2       | 3.76 (1H, d, 11.5 H) | 66.3       |
|          | 4.36 (1H, m) |            | 4.42 (1H, m)       |            |
| **Xyl(1→3)Ara** |            |            |            |            |
| 1        | 5.01 (1H, d, 8.4 Hz) | 107.7       | 5.00 (1H, d, 6.5 Hz) | 107.5       |
| 2        | 4.22 (1H, m) | 75.1       | 4.11 (1H, m) | 76.1       |
| 3        | 4.42 (1H, m) | 78.3       | 3.99 (1H, m) | 78.7       |
| 4        | 4.44 (1H, m) | 70.6       | 4.24 (1H, m) | 71.1       |
| 5        | 3.40 (1H, t, 11.4 Hz) | 67.6       | 3.47 (1H, t, 11.5 Hz) | 68.0       |
|          | 4.38 (1H, m) |            | 4.40 (1H, m)       |            |
| **Glc(1→2) GlcA** |            |            |            |            |
| 1        | 5.98 (1H, d, 8.4 Hz) | 102.4       | 5.91 (1H, d, 5.5 Hz) | 103.1       |
| 2        | 4.29 (1H, m) | 76.0       | 4.30 (1H, m) | 76.9       |
| 3        | 4.30 (1H, m) | 77.1       | 4.35 (1H, m) | 77.9       |
| 4        | 4.45 (1H, m) | 69.8       | 4.42 (1H, m) | 73.1       |
| 5        | 4.07 (1H,m) | 76.5       | 4.38 (1H,m) | 78.7       |
| 6        | 4.34 (1H,m) | 61.9       | 4.13 (1H,m) | 63.9       |

*a*Measured in C5D5N at 600MHz for $^1$H NMR, and 125 MHz for $^{13}$C NMR, respectively.

*b*Measured in C5D5N at 500MHz for $^1$H NMR, and 100 MHz for $^{13}$C NMR, respectively.

The $^{13}$C NMR spectrum of 1 displayed 57 carbon signals, of which 30 were attributed to the aglycone. Signals at $\delta_C 124.9$ and 144.4 were assigned to a pair of typical olefinic carbons. Acid hydrolysis of 1 with 2 M HCl afforded monosaccharides, which were identified by GC analysis of their trimethylsilyl L-cysteine derivatives (Zhang et al. 1996) and the coupling constants of the anomeric protons, as $\beta$-D-glucuronic acid, $\alpha$-L-arabinose, $\beta$-D-xylose and $\beta$-D-glucose. These data demonstrated that 1 is a glycoside of an oxygenated 28-hydroxy-olean-12-ene aglycone (Table 1). The NMR data analysis of 1 indicated that 1 was almost identical with gordonoside J, which has been reported previously (Fu et al. 2011). The only difference between 1 and gordonoside J is that the galactose in gordonoside J was replaced by a glucose in 1. In the HMBC spectrum of 1 (Figure 2), a long-range correlation between H-22 and C-1’ indicated unambiguously that the angeloyloxy ester group is attached to C-22 of the aglycone. In addition, a HMBC correlation between GlcA-H-1 ($\delta_H 4.81$) and C-3 ($\delta_C 89.7$)

Figure 2. Key HMBC (H→C) and NOESY(H→H) correlations of compound 1.
confirmed that the $\beta$-D-glucuronopyranosyl unit is located at C-3. The long-range correlations observed between the $^1$H NMR resonances at $\delta_H$ 5.98 (Glc-H-1) and the $^{13}$C NMR resonance at $\delta_C$ 78.4 (GlcA-C-2), between $\delta_H$ 5.69 (Ara-H-1) and $\delta_C$ 84.8 (GlcA-C-3), and between $\delta_H$ 5.01 (Xyl-H-1) and $\delta_C$ 83.8 (Ara-C-2) indicated that the tetrasaccharide residue at C-3 of aglycone as $\beta$-D-xylopyranosyl-(1→2)$\alpha$-L-arabinopyranosyl-(1→3)$\beta$-D-glucuronopyranosyl-(1→2)$\beta$-D-glucuronopyranoside. The relative configuration of 1 was indicated by the NOESY spectrum, which showed NOESY correlations between the following proton pairs: H-3/H-5, H-15/H3–26, H-16/H 3–26 and H-22/H-18. Therefore, compound 1 was determined as 3-O-$\beta$-D-xylopyranosyl-(1→2)$\alpha$-L-arabinopyranosyl-(1→3)$\beta$-D-glucuronopyranosyl-22$\alpha$-angeloyloxyolean-12-ene-15$\alpha$,16$\alpha$,28-triol.

Compound 2 was isolated as a white amorphous powder. The molecular formula, C$_{59}$H$_{92}$O$_{26}$, was determined by HRESIMS ($m/z$ 1215.5789 [M−H]$^-$, calcd for 1215.5804). The $^1$H NMR and $^{13}$C NMR spectroscopic data of 2 were similar to those of 1 (see Table 1), indicated that contained the same aglycone, the structure of sugar chain, and angeloyloxy ester group as 1, except for additional signals [$\delta_H$ 1.95 (3H, s); $\delta_C$ 171.6 and 21.3] assignable to an acetyl group in the NMR spectrum of 2. These data suggested that 2 is an acetyl derivative of 1, which was confirmed by appropriate 2D NMR experiments on 2. Acid hydrolysis of 2 afforded $\beta$-D-glucuronic acid, $\alpha$-L-arabinose, $\beta$-D-xylose and $\beta$-D-glucose in a ratio of 1:1:1:1 through GC analysis. In the HMBC spectrum of 2 (Figure 3), long-range correlations were observed between H-21 ($\delta_H$ 6.58) and acetyl carbonyl carbon ($\delta_C$ 171.6), and between H-22 ($\delta_H$ 6.30) and angeloyl carbonyl carbon ($\delta_C$ 168.6) indicated the acetyl groups and the angeloyloxy ester group are attached to C-21 and C-22, respectively. The vicinal coupling constant (10.5 Hz) between H-21 and H-22 indicated their trans-diaxial orientation, which was confirmed by NOESY cross peaks of H-22/H$_{2-28}$/H$_{3-30}$ and H-21/H-19$\alpha$/H$_{3-27}$. Therefore, compound 2 was determined as 3-O-$\beta$-D-xylopyranosyl-(1→2)$\alpha$-L-arabinopyranosyl-(1→3)-[\beta$-D-glucuronopyranosyl-(1→2)]$\beta$-D-glucuronopyranosyl-21$\beta$-acetyl-22$\alpha$-angeloyloxyolean-12-ene-16$\alpha$,28-diol.

Compounds 1–2 were evaluated for cytotoxic activities against five human cell lines (HCT-8, Bel-7402, BGC-823, A549 and A2780) with paclitaxel as a positive control. As shown in Table 2, compounds 1–2 showed cytotoxic activity against five human cancer cell lines, with IC$_{50}$ values ranging from 3.15 to 7.32 $\mu$M.
Table 2. Cytotoxicity of the extract and compounds 1-2.

| Compound | HCT-8 (μM) | Bel-7402 (μM) | BGC-823 (μM) | A-549 (μM) | A2780 (μM) |
|----------|------------|---------------|--------------|------------|-------------|
| The extract\(^a\) | 7.10 ± 1.02*** | 9.18 ± 1.42*** | 9.23 ± 1.34*** | 9.23 ± 1.52*** | 7.88 ± 1.42*** |
| 1        | 12.02 ± 1.89*** | 5.50 ± 0.73*** | 5.81 ± 0.45*** | 6.24 ± 1.03*** | 7.27 ± 1.23*** |
| 2        | 7.32 ± 0.93*** | 3.15 ± 0.78*** | 4.68 ± 0.75*** | 5.93 ± 0.64*** | 3.36 ± 0.47*** |
| Paclitaxel\(^b\) | (5.15 ± 0.25) × 10\(^{-2}\) | (6.06 ± 0.89) × 10\(^{-3}\) | (3.43 ± 0.23) × 10\(^{-3}\) | (4.40 ± 0.41) × 10\(^{-3}\) | (8.05 ± 1.02) × 10\(^{-3}\) |

\(^a\)The \(n\)-BuOH part of the 95% EtOH extract of the stems of \(C.\) oleifera;
\(^b\)Positive control, \(n=3\).
***\(P<0.001\) vs Paclitaxel.
3. Experimental

3.1. General experimental procedures

Optical rotations were measured on an Autopol IV-T/V (Rudolph Research Analytical, New Jersey, USA). UV spectra were recorded in MeOH on a Jasco V650 spectrophotometer (JASCO, Inc., Easton, Maryland, USA). The $^1$H (600 MHz), $^{13}$C (150 MHz) and 2D NMR spectra were recorded on a Bruker AVANCE → 600 instrument using TMS (Tetramethylsilane) as an internal reference (Bruker Company, Massachusetts, USA). 1D and 2D NMR spectra were obtained at 500 and 125 MHz for $^1$H and $^{13}$C, respectively, on an INOVA 500 MHz spectrometer in pyridine-$d_5$ with solvent peaks as references. HRESIMS data were obtained on an Agilent 7890–7000A mass spectrometer (Agilent Technologies, Santa Clara, USA). Preparative HPLC was conducted with an Agilent Technologies 1200 series instrument with a MWD detector using a YMC-pack ODS (Octadecylsilyl)-A column (5 μm, 250 × 20 mm). Column chromatography (CC) was performed with silica gel (200–300 mesh, Qingdao Marine Chemical Ltd., Qingdao, China), Developol ODS (50 μm, Nomura Chemical Co. Ltd., Osaka, Japan), Sephadex LH-20 (GE Healthcare Bio-Sciences AB, Uppsala, Sweden). TLC (thin-layer chromatography) was carried out with glass precoated with silica gel GF$_{254}$'. Spots were visualised under UV light or by spraying with 10% sulphuric acid in EtOH followed by heating.

3.2. Plant material

The stems of *C. oleifera* were collected from Guangfeng, Jiangxi, China, in May 2014 and identified by Prof. Guiping Yuan at Jiangxi Provincial Institute for Drug Control, China. A voucher specimen (No. 20140515) has been deposited in the Herbarium of Jiangxi Provincial Institute for Drug Control. The 95% EtOH extract of the stems of *C. oleifera* was partitioned with CHCl$_3$, EtOAc and n-BuOH, successively.

3.3. Extraction and isolation

The air-dried stems of *C. oleifera* (15.5 kg) were extracted three times with 95% EtOH at reflux for 3 × 2 h. The extracting solution was evaporated under reduced pressure to yield a dark brown residue (700 g). The residue was suspended in water (10 L) and then successively partitioned with CHCl$_3$ (3 × 10 L), EtOAc (3 × 10 L) and n-BuOH (3 × 10 L). After removing the solvent, the n-BuOH extract (100 g) was passed through a D101 macroporous resin column eluted with H$_2$O, H$_2$O-EtOH (9:1, v/v), H$_2$O-EtOH (7:3, v/v), H$_2$O-EtOH (1:1, v/v) and H$_2$O-EtOH (3:7, v/v), respectively. The H$_2$O-EtOH (3:7, v/v) fraction (5 g) was separated by silica gel column chromatography using CHCl$_3$–MeOH–H$_2$O gradient mixtures (8:2:0.2–6:4:0.5, v/v) to afford 14 fractions (A1–A14) on the basis of TLC analysis. Subfraction 6 (53 mg) was further separated by preparative HPLC (YMC-ODS-A 5 μm, 250 mm × 20 mm, detection at 210 nm) using 60% CH$_3$OH–H$_2$O (7 mL/min) containing 0.01%TFA as mobile phase to yield compounds 1 (16.2 mg, $t_R$ 92 min) and 2 (5.7 mg, $t_R$ 97 min).
3.3.1. 3-O-β-D-xylopyranosyl-(1→2)-α-L-arabinopyranosyl-(1→3)-[β-D-glucuronopyranosyl-(1→2)]-β-D-glucuronopyranosyl-22α-angeloyloxyolean-12-ene-15α,16α,28-triol (1)
White amorphous powder; mp 253–254 °C; [α]_{D}^{20} -10.8 (c 0.08, MeOH); UV (MeOH) λ_{max} (log ε): 204 (4.35) nm; 1H NMR (600 MHz, pyridine-d$_5$) and 13C NMR (150 MHz, pyridine-d$_5$) spectral data see Table 1; HRESIMS m/z 1197.5668 [M + Na]$^+$ (calcd for C$_{57}$H$_{90}$NaO$_{25}$, 1197.5663).

3.3.2. 3-O-β-D-xylopyranosyl-(1→2)-α-L-arabinopyranosyl-(1→3)-[β-D-glucuronopyranosyl-(1→2)]-β-D-glucuronopyranosyl-21β-acetyl-22α-angeloyloxyolean-12-ene-16α,28-diol (2)
White amorphous powder; mp 240–241 °C; [α]_{D}^{20} -17.2 (c 0.09, MeOH); UV (MeOH) λ_{max} (log ε): 206 (4.29) nm; 1H NMR (500 MHz, pyridine-d$_5$) and 13C NMR (100 MHz, pyridine-d$_5$) spectral data see Table 1; HRToFMS: m/z 1215.5789 [M−H]$^-$ (calcd for C$_{59}$H$_{91}$O$_{26}$, 1215.5804).

3.4. Determination of absolute configurations of the sugar moieties in 1–2
The determination of the absolute configuration of the sugars in compounds 1–2 was conducted as described previously (Zhong et al. 2013).

3.5. Cytotoxicity assay
Compounds 1–2 were tested for cytotoxicity against HCT-8 (human colon cancer cell line), Bel-7402 (human hepatoma cancer cell line), BGC-823 (human gastric cancer cell line), A549 (human lung cancer cell line) and A2780 (human ovarian cancer cell line) by MTT assay (Li et al. 2008).

3.6. Statistical analysis
The results of the cytotoxicity were expressed as means ± SD. Student’s t test was used to determine statistical comparisons between the data-sets. p < 0.05 was considered to be significant.

Supplementary material
Supplementary material relating to this article is available online, alongside Figures S1–S16.

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Disclosure statement
No potential conflict of interest was reported by the authors.
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**References**

Chen YL, Feng BM, Tang L, Li HB, Shi LY, Wang YQ. 2010. Chemical constituents of leaves from *Camellia Oleifera* Abel. J Shenyang Pharm Univ. 27:292–301.

Fu HZ, Li CJ, Yang JZ, Shen ZF, Zhang DM. 2011. Potential anti-inflammatory constituents of the stems of *Gordonia chrysandra*. J Nat Prod. 74:1066–1072.

Li XI, Zhao JP, Peng CP, Chen Z, Liu YL, Xu QM, Khan IA, Yang SL. 2014. Cytotoxic triterpenoid glycosides from the roots of *Camellia oleifera*. Planta Med. 80:590–598.

Li CL, Zhang DM, Luo YM, Yu SS, Li Y, Lu Y. 2008. Bis-sesquiterpenes and diterpenes from Chloranthus henryi. Phytochem. 69:2867–2875.

Luo YM, Li B, Xie YH. 2003. Studies on the Chemical Constituents of Callicarpa nudiflora *Camellia Oleifera* Abel. Chin Tradit Herb Drugs. 34:117–122.

Shanghai Scientific and Technical Publishers Shanghai, China. 2000. Jiangsu New Medical College. Dictionary of Chinese traditional drugs. pp. 1603–1613.

Tao MK, Xu M, Zhang H, Chen H, Liu C, Zhu HT, Wang D, Yang CR, Zhang YJ. 2015. Methylenebisnicotiflorin: a rare methylene-bridged bisflavonoid glycoside from ripe Pu-er tea. Nat Prod Res. 26:1–7. doi:10.1080/14786419.2015.1065491

Wang YQ, Wu XJ, Li HB, Pang Y, Tang L, Feng BM. 2006. Research of medicinal plants of the genus *camellia*. J Dalian Univ. 27:47–55.

Yang P, Li X, Liu YL, Xu QM, Li YQ, Yang SL. 2015. Two triterpenoid glycosides from the roots of *Camellia Oleifera* and their cytotoxic activity. J Asian Nat Prod Res. 28:1–8.

Yoshikawa M, Morikawa T, Li N, Nagatomo A, Li X, Matsuda H. 2005. Bioactive saponins and glycosides. XXIII. Triterpene saponins with gastroprotective effect from the seeds of *Camellia sinensis*-theasaponins E3, E4, E5, E6, and E7. Chem Pharm Bull. 53:1559–1563.

Zhang DM, Miyase I, Kuroyanagi M, Umehara K, Ueno A. 1996. Five new triterpene saponins, polygalasaponins XXVIII–XXXII from the root of *Polygala japonica* Houtt. Chem Pharm Bull. 44:810–815.

Zhong RJ, Yuan H, Fu HZ, Zhou GP, Wu X, Zhang CH, Yuan MM. 2013. Three new compounds from the leaves of *Liquidambar formosana*. J Asia Nat Prod Res. 15:1249–1253.

Zong J, Wang RL, Bao GH, Ling TJ, Zhang L, Zhang XF, Hou R. 2015. Novel triterpenoid saponins from residual seed cake of *Camellia oleifera* Abel. show anti-proliferative activity against tumor cells. Fitoterapia. 104:7–13.