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Chemical Studies of the Bark of *Bauhinia purpurea*

Yueh-Hsiung KUO,*[a,b] Pei-Hung CHU,[a] and Chi-I CHANG[a]

Department of Chemistry, National Taiwan University,[a] Taipei, Taiwan, R.O.C. and National Research Institute of Chinese Medicine,[b] Taipei, Taiwan, R.O.C.

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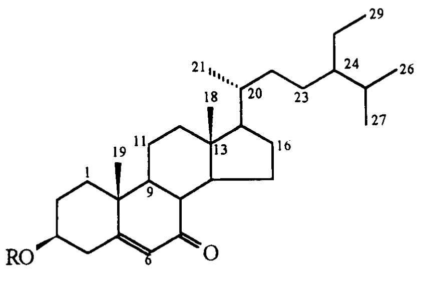
A new compound, 6′-(stigmast-5-en-7-one-3-*O*-β-glucopyranosidyl) hexadecanoate, together with 3β-hydroxystigmast-5-en-7-one, oleanolic acid, 6,8-dimethylchrysin, and chrysin were isolated from the bark of *Bauhinia purpurea* LINN. Their structures were elucidated by spectral and chemical evidence.

Key words *Bauhinia purpurea; Leguminosae*; 6′-(stigmast-5-en-7-one-3-*O*-β-glucopyranosidyl) hexadecanoate

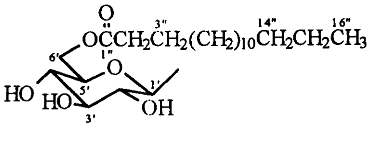
Fourteen species of *Bauhinia* (Leguminosae) are grown in Taiwan, although only one species, *B. championii* B. is indigenous to Taiwan. Chemical studies have been reported, and cyanide and flavonoid compounds were observed.[1,2] The components of the seed of *B. purpurea* LINN.(a popular ornamental tree) have also been reported.[3,4] In our previous report,[5] we investigated the chemical components of the heartwood and found twenty-two crystalline compounds, including steroids, triterpenes, fatty alcohol and ester, glycerols, flavonoid, phenols, chromane, and sugar. In connection with our interest in the chemical components of this plant, chemical studies on the bark were undertaken in our laboratory. In this paper, we present the chemical constituents of a methanol extract of the bark of this plant.

The methanol extract of the bark of *B. purpurea* was concentrated to give a residue which was suspended with water. The suspended aqueous solution was partitioned with *n*-BuOH. The *n*-BuOH extract was repeatedly purified on silica gel to isolate one new compound, 6′-(stigmast-5-en-7-one-3-*O*-β-glucopyranosidyl) hexadecanoate (**1**), together with four known compounds, 3β-hydroxystigmast-5-en-7-one (**2**),[5] oleanolic acid,[6] 6,8-dimethylchrysin,[7] and chrysin.[8] In this paper, we report the structure of this new compound.

Compound **1** was purified by acetylation, so that it was obtained as the triacetate **3**: mp 119—120 °C. The molecular formula of **3** was determined as $C_{57}H_{94}O_{11}$ by FAB-MS. Analysis of the IR spectrum of **3** suggested that it contained an ester group (1738 cm^{-1}), conjugated double bond (1669, 1640, 830 cm^{-1}), and long chain $(CH_2)_n$ rock (721 cm^{-1}). The ^1H-NMR spectrum exhibited signals for seven methyl groups at δ 0.66 (s, H-18), 0.71 and 0.81 (d, J=6.2 Hz, H-26, -27), 0.82 (t, J=7.3 Hz, H-29), 0.90 (d, J=6.5 Hz, H-21), and 1.15 (s, H-19), a methine proton geminal to oxygen at δ 3.57 (1H, m, H-3), and an olefinic proton at δ 5.66 (s). These signals are all similar to 3β-hydroxystigmast-5-en-7-one (**2**).[5] The 2,3,4-triacetyl-6-hexadecanoyl-β-glucopyranosidyl moiety was reaveled by the following spectral signals. Signals at δ 1.98, 2.00 and 2.03 (s, each 3H) were assigned as triacetyl groups (δ_C 169.3, 169.4, 170.3), and signals at δ 4.57 (d, 1H, J=8.0 Hz), 4.94 (dd, 1H, J=9.5, 8.0 Hz), 5.03 (t, 1H, J=9.5 Hz), 5.18 (t, 1H, J=9.5 Hz), and 3.67 (m, 1H) were assigned to H-1′, H-2′, H-3′, H-4′ and H-5′, respectively. H_2-6′ presented at lower field [δ 4.12 (dd, 1H, J=12.3, 2.3 Hz) and a signal 4.20 (dd, 1H, J=12.3, 5.1 Hz)] due to the attached carbon bearing a hexadecanoyloxy group was apparent. Both H-2″ [δ 2.30 (t, 2H, J=8.0 Hz)] and H-6′ showed heteronuclear multiple-bond correlation spectroscopy (HMBC) correlation with C-1″ (δ_C 173.4). Six carbon signals at δ 100.0, 71.4, 71.9, 68.6, 72.8, and 61.9 were assigned to the glucopyranoside moiety carbons C-1′, C-2′, C-3′, C-4′, C-5′ and C-6′, respectively. The above spectral signals for the glucopyroside moiety are similar to those of compound **4** which was isolated from the heartwood of the same plant by acetylation.[5] The characteristic EI-MS molec-

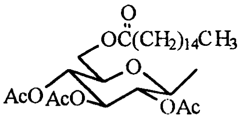


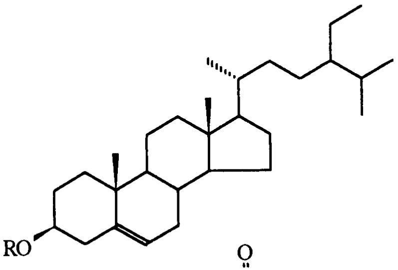
1 R=



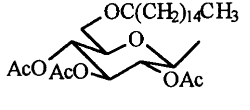
2 R= H

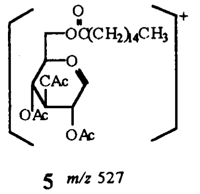
3 R=



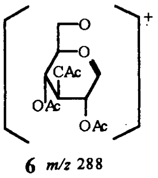


4 R=





5 *m/z* 527



6 *m/z* 288

$[CH_3(CH_2)_{14}C\equiv O]$

7 *m/z* 239

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* To whom correspondence should be addressed.

ular ion peaks at *m/z* 527 (**5**), 288 (**6**) and 239 (**7**) in compound **4** were also present in compound **3**. Compound **3** was readily degraded in 1 N HCl methanol solution at room temperature and the products were identified as methyl hexadecanoate,[5] 3β-hydroxystigmast-5-en-7-one (**2**), and a mixture of 1α- and 1β-methylglucopyranoside. From the above evidence, compound **1** was deduced to be 6′-(stigmast-5-en-7-one-3-*O*-β-glucopyranosidyl) hexadecanoate.

Experimental

General Procedures Melting points were determined with a Yanagimoto micromelting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 781 spectrophotometer. EI-MS, FAB-MS, UV, and specific rotations were taken on a JEOL JMS-HX 300, a JOEL JMS-HX 110, a Hitachi S-3200 spectrometer, and a JASCO DIP-180 digital polarimeter, respectively. ^{1}H- and ^{13}C-NMR, heteronuclear multiple quantum coherence (HMQC) and HMBC spectra were obtained on a Bruker AM-300 spectrometer. Chemical shifts are given in δ-values and coupling constants (J) in Hertz (Hz).

Plant Material The bark of *B. purpurea* were collected in September 1993 on the campus of the National Taiwan University. The plant material was identified by Mr. Muh-Tsuen Gun, formerly a technician of the Department of Botany, National Taiwan University, and a voucher specimen has been deposited at the National Research Institute of Chinese Medicine, Taipei, Taiwan, R.O.C.

Extraction and Isolation The pieces of bark of *B. purpurea* (4.2 kg) were extracted with MeOH (30 l) at room temperature three times (6 d each time). The crude extract was evaporated *in vacuo* to leave a black syrup (350 g), and water was added to a total volume of 1 l. The aqueous layer was partitioned with *n*-BuOH (1 l×3). The upper layer was then evaporated *in vacuo* to yield a residue (75 g) which was subjected to chromatography on silica gel repeatedly. Oleanolic acid (35 mg) (30% EtOAc in hexane), 6,8-dimethylchrysin (2 mg) (50% EtOAc in hexane), **2** (33 mg) (50% EtOAc in hexane), chrysin (2 mg) (50% EtOAc in hexane), and crude **1** (36 mg) (70% EtOAc in hexane; no acetyl group was observed) were obtained and the isolated crude **1** was converted to its pure triacetate **3** (36 mg) by acetylation with Ac_2O in pyridine.

6′-(Stigmast-5-en-7-one-3-*O*-β-glucopyranosidyl) hexadecanoate triacetate (3) Colorless needles, mp 119—120 °C, $[\alpha]_D^{25}=-41.2°$ (c=0.6, $CHCl_3$); UV λ_{max}^{MeOH} (log ε) 235 (3.82) nm; IR (KBr) ν_{max} 3030, 1738, 1669, 1640, 1170, 830, 721 cm^{-1}; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 36.2 (C-1), 28.5 (C-2), 78.7 (C-3), 38.6 (C-4), 164.3 (C-5), 126.3 (C-6), 202.2 (C-7), 45.4 (C-8), 49.9 (C-9), 38.4 (C-10), 22.7 (C-11), 38.7 (C-12), 43.1(C-13), 49.9 (C-14), 21.2 (C-15), 26.3 (C-16), 54.7 (C-17), 11.9 (C-18), 17.2 (C-19), 36.0 (C-20), 18.9 (C-21), 33.9 (C-22), 26.1 (C-23), 45.8 (C-24), 29.1 (C-25), 19.8 (C-26), 19.0 (C-27), 23.0 (C-28), 11.9 (C-29), 99.9 (C-1′), 71.4 (C-2′), 72.8 (C-3′), 68.5 (C-4′), 71.8 (C-5′), 61.9 (C-6′), 173.4 (C-1″), 34.1 (C-2″), 24.8 (C-3″), 29.2—29.7 (C-4″—13″), 31.9 (C-14″), 22.7 (C-15″), 14.1 (C-16″), 20.6, 20.6, 20.7 ($3\times\underline{C}H_3COO$), 169.2, 169.3, 170.2, 173.0 ($4\times CH_3\underline{C}OO$); FAB-MS *m/z* (rel. int.) 955 $(M+1)^+$ (3), 819 (3), 527(7), 411 (100), 288(7), 239 (38). HR-FAB-MS *m/z* $[M+H]^+$ Calcd for $C_{57}H_{95}O_{11}$: 955.6878; Found 955.6869.

Acidic Methanolysis of 3 Compound **3** (25 mg) and 2,2-dimethoxypropane (2 drops) were added to 1 N methalolic HCl (2 ml) and stirred for 2 d at room temperature. The products were purified by preparative TLC, and three compounds, methyl hexadecanoate (6 mg),[5] **2** (10 mg), and a mixture of methyl 1α- and 1β-D-glucopyranoside (4 mg)[9] were identified by comparisons with authentic samples.

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