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SHORT COMMUNICATION

CHEMICAL CONSTITUENTS FROM ROOT BARKS OF *ERYTHRINA MILDBRAEDII* AND STEM BARKS OF *ERYTHRINA ADDISONIAE*

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ABSTRACT. The β-D-galactopyranoside of the tetracosanoic acid (1) was isolated from the stem barks of *Erythrina addisoniae* along with known tetracosanoic acid (2), α-sophoradiol (3), stigmasterol (4), warangalone (5), 3-*O*β-D-glucopyranoside of β-sitosterol (6) and 7-*O*-β-D-glucopyranoside of daidzein (7). Two known compounds (erythrinasinate (8) and erycristagallin (9)) were also isolated from the root barks of *Erythrina mildbraedii*. Their structures were assigned on the basis of spectroscopic data and chemical transformation.

KEY WORDS: *Erythrina addisoniae*, *Erythrina mildbraedii*, Root barks, Stem barks, Leguminosae, Glucoside acid

INTRODUCTION

The genus *Erythrina* (Leguminosae) has a significant history of folkloric use for treatment of various diseases [1, 2]. Previous chemical studies of Cameroonian *Erythrina* species has resulted in the isolation of flavonoids, alkaloids, cinnamate esters and neutral compounds [3-8]. We here report the isolation and structural elucidation of the new β-D-galactopyranosyl ester of tetracosanoic acid (1) from the EtOAc extract of the stem barks of *Erythrina addisoniae* along with six known compounds, namely tetracosanoic acid (2) [9], α-sophoradiol (3) [10], stigmasterol (4) [11], warangalone (5) [12], β-sitosterol 3-*O*-β-D-glucopyranoside (6) [13] and daidzein7-*O*-β-D-glucopyranoside (7) [14]. Two known compounds namely erythrinasinate (8) [15] and erycristagallin (9) [16] were also isolated from the root barks of *Erythrina mildbraedii*.

EXPERIMENTAL

General procedures. Melting points were determined on a micro-melting point apparatus and are not corrected. IR spectra were run from KBr pallet on a Perkin-Elmer 577 spectrometer. The NMR and two dimensional experiments spectra were recorded with a Bruker AMX 500 (500 MHz for ^{1}H and 125 MHz for ^{13}C). Chemical shifts are given in ppm with tetramethylsilane as internal standard. The HREIMS and EIMS at 70 eV were recorded on a JEOL JMSD-300 mass spectrometer. HPLC was performed by using a system comprised of a CCPM pump, a CCPX-8010 controller, and RI – 8010 detector and a Shodex OR-2 and a Rheodyne injection port with a 20 µL sample loop. Column chromatography was performed using Sephadex LH-20, silica gel Merck 70-230 or 240-400 mesh ASTM. Analytical TLC was carried out on pre-coated silica gel 60 F_{254} plates (Merck 0.25 mm thickness). The plates were checked under UV light (254 nm) and developed with H_2SO_4 in EtOH.

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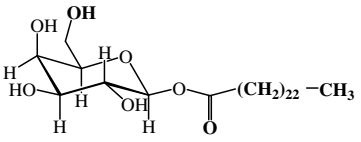
Plant material. The stem barks of *Erythrina addisoniae* and root barks of *Erythrina mildbraedii* were collected respectively in April 1996 at Yaounde (Centre region of Cameroon Republic) and in July 1998 in Buea (South-West region of Cameroon Republic). They were identified at the National Herbarium; Yaounde, Cameroon where voucher specimens have been deposited under the references 41617/HNC and 50452/HNC, respectively.

Extraction and isolation. The air-dried root barks of *Erythrina mildbraedii* (5 kg) was exhaustively extracted at room temperature with ethyl acetate to yield 250 g of residue. Part of this residue (150 g) was subjected to column chromatography over silica gel (400 g) using hexane-ethyl acetate of increasing polarity as solvent. A total of 210 fractions of 250 mL each were collected and combined on the basis of their TLC analysis leading to four major series A (5 g, hexane-EtOAc 9:1), B (3 g, hexane-EtOAc, 8:2), C (17 g, hexane-EtOAc, 2:8) and D (2 g, EtOAc). Further purification of series A, B, C and D were achieved by column chromatography followed by PTLC (MeOH-$CHCl_3$-toluene: 1:4:5) and/or by permeation through Sephadex LH-20 with MeOH as solvent. Series A afforded α-sophoradiol (3) (17 mg) and stigmasterol (4) (13 mg). Series B afforded warangalone (5) (15 mg). Series C afforded of tetracosanoic acid β-D-galactopyranoside (1) (25 mg), β-sitosterol 3-*O*-β-D-glucopyranoside (6) (19 mg) and daidzein7-*O*-β-D-glucopyranoside (7) (8 mg). Series D afforded tetracosanoic acid (2) (20 mg).

The air-dried stem barks of *Erythrina addisoniae* (7 kg) was exhaustively extracted with EtOAc at room temperature yielding (200 g) of residue. Part of this residue (100 g) was subjected to column chromatography over silica gel eluted with hexane-EtOAc gradient system. Elution with hexane-EtOAc (6:4) gave erythrinasinate (8) (21 mg). Erycristagallin (9) (15 mg) was obtained with hexane-EtOAc (6:4).

Physical and spectral data of the compound (1). Amorphous solid. R_f 0.6 (MeOH-CH_2Cl_2-cyclohexane 1:4:5). HREIMS M^+/z = 530.5308 (calcd. for $C_{30}H_{58}O_{7,}$ 530.7880); EIMS: m/z (%) = 530 [M+], 367 (69.2), 163 (30.7), 145 (27.3), 127 (23.9), 109 (20.5), 91 (17.1). IR: ν_{max} 1730 and 3450 cm^{-1}. ^1H and ^{13}C-NMR (see Table 1).

Acid hydrolysis of (1). Compound (1) (10.5 mg) was refluxed with 12 mL of 15% HCl/MeOH at 80 °C for 4 h. After cooling, the reaction mixture was concentrated and the residue partitioned with $CHCl_3/H_2O$. The organic layer was concentrated to dryness to yield 8 mg of a white material. Purification of this material by PTLC using silica gel and MeOH-CH_2Cl_2 (0.25:9.75) as eluent yielded 3 mg of aglicone (2) identified as tetracosanoic acid by comparison of its physical and spectral data with the previously isolated compound (2). The aqueous layer was evaporated and the residue analyzed by HPLC under the following conditions: column HPX – 87 H (7.8 mm i.d. x 300 mm); solvent 5 μm H_2SO_4; flow rate 0.6 mL/min; detection, refractive, index and optical rotation. The sugar was confirmed as D–galactose by comparison of its retention time and optical rotation with those of an authentic sample retention time (min) of D–galactose 9.62 (positive optical rotation).



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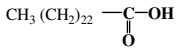

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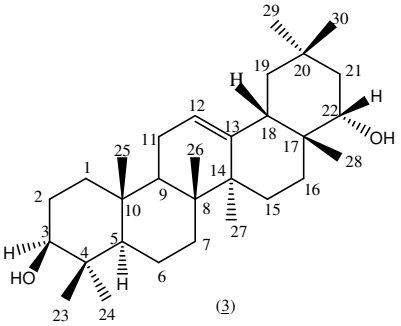

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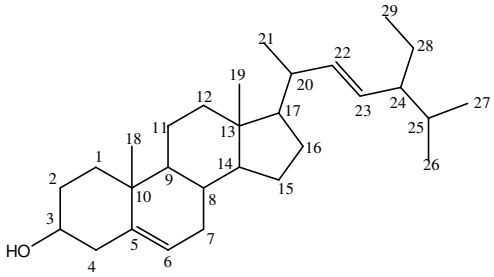

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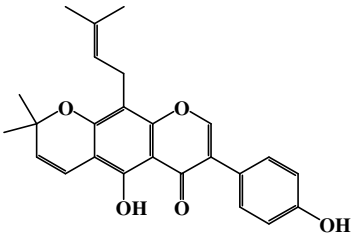

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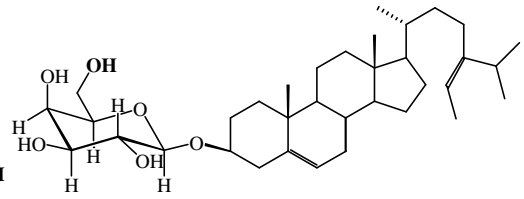

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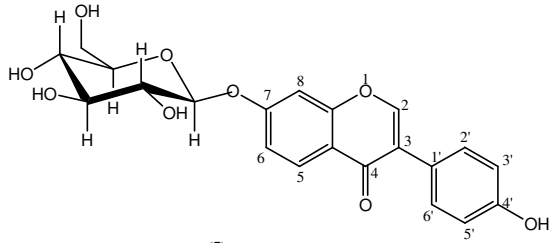

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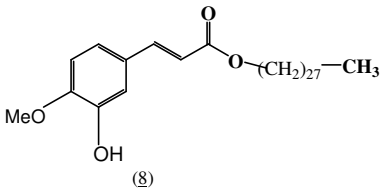

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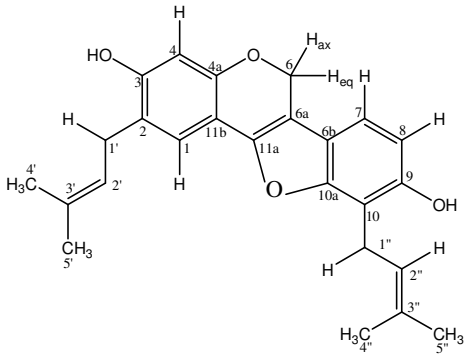

(9)

RESULTS AND DISCUSSION

Compound (1) was obtained as a white amorphous solid. Its molecular formula $C_{30}H_{58}O_7$ was deduced from HRMS. The IR spectrum disclosed absorption bands at 3430 cm^{-1} due to hydroxyl group and at 1735 cm^{-1} due to an ester carbonyl. The ^1H and ^{13}C spectroscopic spectral data (Table 1) revealed the presence of a sugar residue and chemical shifts sequence of tetracosanoyloxy moiety. The presence of an anomeric carbon signal at δ = 100.5 ppm indicated (1) to be a tetracosanoic acid glycoside [17]. Upon acid hydrolysis (1) afforded the aglycone (2) and D-galactose. The β-configuration of D-galactopyranosyl moiety was deduced from the coupling constant J = 7.8 Hz of anomeric proton signal 4.81 ppm in the ^1H-NMR spectrum [18]. On the basis of the above evidence, the structure of (1) was determinate as β-D-galactopyranoside of tetracosanoic acid.

Table 1. ^1H-NMR (500 MHz, DMSO-d_6) and ^{13}C-NMR (125 MHz, DMSO-d_6) data of compound (1).

N°	δ_H (mult, J)	δ_C (DEPT)
1		175.3 (C)
2	2.48 (2H, t, 6.9)	34.7 (CH_2)
3	1.65 (2H; m)	22.68-31.90 (CH_2)
4-23	1.26 (40H, m)	22.68-31.90 (CH_2)
24	0.91 (3H, t, 7.0)	14.10 (CH_3)
1’	4.81 (1H, d, 7.0)	100.10 (CH)
2’	3.22 (1H, dd, 8.6, 7.9)	73.60 (CH)
3’	3.40 (1H, m)	76.90 (CH)
4’	3.40 (1H, dd, 3.6, 3.5)	70.20 (CH)
5’	3.32 (1H, 1H, m)	76.70 (CH)
6’	3.75 (1H, dd, 11.4, 5.6) 3.51 (1H, dd, 11.4, 2.4)	61.30 (CH_2)

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