

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**), stigmaterol (**4**), warangalone (**5**), 3-O- β -D-glucopyranoside of β -sitosterol (**6**) and 7-O- β -D-glucopyranoside of daidzein (**7**). Two known compounds (erythrinasinatate (**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], stigmaterol (**4**) [11], warangalone (**5**) [12], β -sitosterol 3-O- β -D-glucopyranoside (**6**) [13] and daidzein 7-O- β -D-glucopyranoside (**7**) [14]. Two known compounds namely erythrinasinatate (**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 ¹H and 125 MHz for ¹³C). 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 μ L 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 F₂₅₄ plates (Merck 0.25 mm thickness). The plates were checked under UV light (254 nm) and developed with H₂SO₄ in EtOH.

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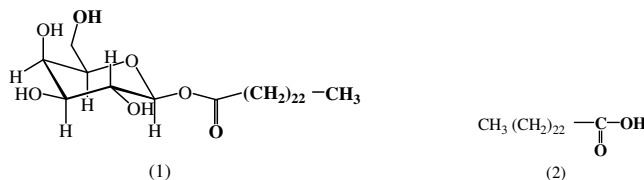
Plant material. The stem barks of *Erythrina addisoniae* and root barks of *Erythrina mildbraedii* were collected respectively in April 1996 at Yaounde (Centre region of Cameroon Republic) and in July 1998 in Buea (South-West region of Cameroon Republic). They were identified at the National Herbarium;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

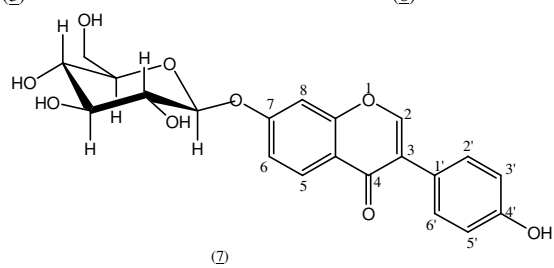
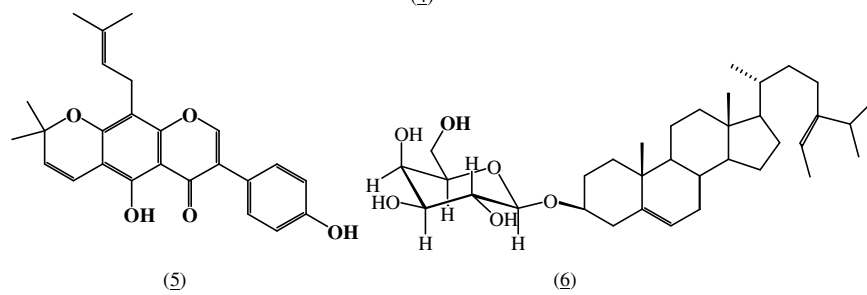
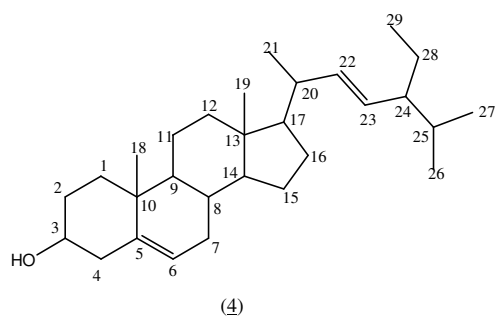
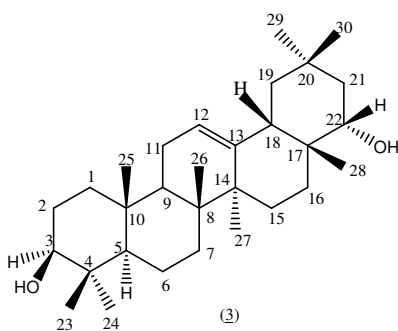
Extraction and isolation. The air-dried root barks of *Erythrina mildbraedii* (5 kg) was exhaustively extracted at room temperature with ethyl acetate to yield 250 g of residue. Part of this residue (150 g) was subjected to column chromatography over silica gel (400 g) using hexane-ethyl acetate of increasing 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-CHCl₃-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 tetracosanoic acid β -D-galactopyranoside (**1**) (25 mg), β -sitosterol 3-O- β -D-glucopyranoside (**6**) (19 mg) and daidzein 7-O- β -D-glucopyranoside (**7**) (8 mg). Series D afforded tetracosanoic acid (**2**) (20 mg).

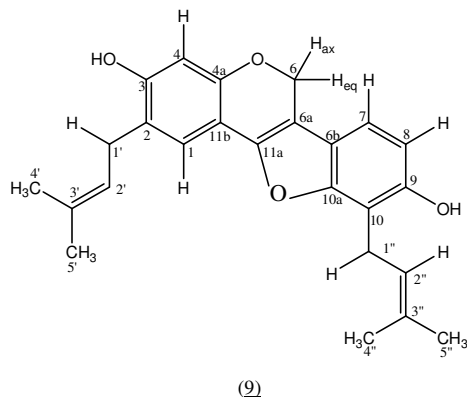
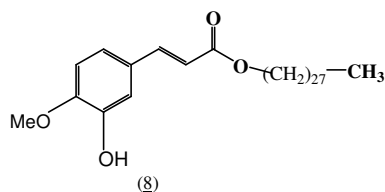
The air-dried stem barks of *Erythrina addisoniae* (7 kg) was exhaustively extracted with EtOAc at room temperature yielding (200 g) of residue. Part of this residue (100 g) was subjected to column chromatography over silica gel eluted with hexane-EtOAc gradient system. Elution with hexane-EtOAc (6:4) gave erythrinasinat (**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-CH₂Cl₂-cyclohexane 1:4:5). HREIMS M^+/z = 530.5308 (calcd. for C₃₀H₅₈O₇, 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 ¹³C-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 CHCl₃/H₂O. 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-CH₂Cl₂ (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 μ m H₂SO₄; 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).







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 tetracosanoxyloxy moiety. The presence of an anomeric carbon signal at $\delta = 100.5\text{ ppm}$ 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 $J = 7.8\text{ Hz}$ 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)

REFERENCES

1. Kouam, J.; Etoa, F.X.; Mabeku, L.B.K.; Fomum, Z.T. *Nat. Prod. Com.* **2007**, 2, 1105.
2. Mitscher, L.A.; Drake, S.; Golapudi, S.R.; Okwute, S.K. *J. Nat. Prod.* **1987**, 50, 1025.
3. Fomum, Z.T.; Ayafor, J.F.; Wandji, J.; Fomban, W.G.; Nkengfack, A.E. *Phytochemistry* **1986**, 25, 757.
4. Mitscher, L.A.; Gollapudi, S.R.; Gerlach, D.C.; Drake, S.D.; Veliz, E.A.; Ward, J.A. *Phytochemistry* **1988**, 27, 381.
5. Fomum, Z.T.; Ayafor, J.F.; Mbafor, T.J. *Tetrahedron Lett.* **1983**, 24, 4127.
6. Fomum, Z.T.; Ayafor, J.F.; Mbafor, T.J.; Mbi, C.M. *J. Chem. Soc. Perkin Trans. I* **1986**, 33.
7. Fomum, Z.T.; Ayafor, J.F.; Wandji, J. *Phytochemistry* **1985**, 24, 3075.
8. El-Olemy, M.M.; Ali, A.A.; El-Mottaleb, M.A. *Lloydia* **1978**, 41, 342.
9. Mitscher, L.A.; Ward, J.A.; Drake, S.; Rao, G.S. *Heterocycles* **1984**, 22, 1673.
10. Ndom, J.C.; Kouam, Vardamides, J.C.; Wansi, J.D.; Kamdem, A.W.; Mbafor, T.J.; Fomum, Z.T. *Bull. Chem. Soc. Ethiop.* **2001**, 15, 151.
11. Fukuya, T.; Orihara, Y.; Hyaschi, C. *Photochemistry* **1987**, 26, 715.
12. Pelter, A.; Stainton, P. *J. Chem. Soc.* **1966**, 701.
13. Mallavadhani, U.V.; Anita, R.K.; Rao, Y.R. *Phytochemistry* **1998**, 49, 901.
14. Ingham, J.L.; Markam, K.R. *Phytochemistry* **1980**, 19, 1203.
15. Nkengfack, A.E.; Sanson, D.R.; Tempesta, M.S.; Fomum, Z.T. *J. Nat. Prod.* **1989**, 52, 320.
16. Telikepalli, H.; Gollapudi, S.R.; Keshavarz-Shokri, A.; Velazquez, L.; Sandmann, R.A.; Veliz, E.A.; Rao, K.V.J.; Madhvi, A.S.; Mitscher, L.A. *Phytochemistry* **1990**, 29, 2005.
17. Tori, K.; Yohko, Y.; Sco, S.; Sakurawi, K.; Tomita, Y.; Ishi, H. *Tetrahedron Lett.* **1976**, 4163.
18. Arriva, F.; Wollenweber, E.; Shoher, I.; Sostal, P.; Braun, S. *Phytochemistry* **1986**, 25, 719.

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