Journal of Applied Pharmaceutical Science Vol. 5 (Suppl 2), pp. 001-006, 2015
Available online at http://www.japsonline.com
DOI: 10.7324/JAPS.2015.58.S1
ISSN 2231-3354

Triterpenes and Lignans from *Kigelia africana*

Lazare Sidjui Sidjui[1,2*], Raduis Melong[3,2], Valérie Mahiou-Leddet[4], Gaëtan Herbette[5], Alembert Tiabou Tchinda[1], Evelyne Ollivier[4], Gabriel Ngosong Folefoc[2]

[1]Institute of Medical Research and Medicinal Plant Studies (IMPM), P.O Box 6163 Yaoundé, Cameroon. [2] Laboratory of Natural Products, Department of Organic Chemistry, Faculty of Sciences, University of Yaoundé I, P.O. Box. 812, Yaoundé, Cameroon. [3]Institute for Organic and Biomolecular Chemistry, Georg-August University of Göttingen, Tammannstr. 2, D-37077 Göttingen, Germany. [4]Laboratory of Pharmacognosy and Ethnopharmacology, UMR-MD3, Faculty of Pharmacy, Aix-Marseille University, 27 Bd Jean Moulin, CS 30064, 13385, Marseille cedex 5, France. [5]Spectropole, FR1739, Aix-Marseille University, Campus de St Jérôme - service 511, 13397 Marseille, cedex 20, France.

ARTICLE INFO

Article history:
Received on: 04/05/2015
Revised on: 07/06/2015
Accepted on: 21/06/2015
Available online: 04/09/2015

Key words:
Kigelia africana, Bignonaceae, Isolation, Triterpenes, Lignans.

ABSTRACT

Chemical investigation of the methanol/dichloromethane(1:1 *v/v*) extract of the leaves and fruits of *Kigelia africana* afforded lupeol (**1**), *β*-sitosterol (**2**), *β*-Sitosteryl *β*-D-glucoside (**3**), canophyllol (**4**), fibrarecisin (**5**), pomolic acid (**6**), hydroxy-pomolic acid **7**, *β*-friedelinol (**8**), sesamin (**9**), and paulownin (**10**). Their structures were elucidated on the basis of spectroscopic analysis and identified by comparison of their spectral data with those reported in the literature. Among them, compounds **1** and **5-10** were isolated for the first time from this plant.

INTRODUCTION

Kigelia africana (Lam.) Benth. belongs to the Bignoniaceae family and has a wide geographical distribution in west and central Africa. The tree grows on river banks, wet areas along streams and on floodplains of Nigeria, Cameroon, Kenya, Guinea and Senegal. It is also found in open woodland from KwaZulu-Natal to Tanzania, Chad, Eritrea, South Africa and Namibia (Abioye *et al.*, 2003; Ogbeche *et al.*, 2002; Owolabi *et al.*, 2007; Owolabi and Omogbai, 2007). The tree is widely grown as an ornamental plant in tropical regions for its decorative flowers and unusual fruit hence the name 'sausage tree' (Roodt, 1992). Several species of mammals eat the seeds, e.g., baboons, bush pigs, monkeys, porcupines, savannah elephants, giraffes and hippopotamus (Owolabi and Omogbai, 2007). In Kenya, the roasted seeds mixed with beer cause enlargement of sexual organs (Kokwaro, 1976). In South eastern Nigeria, the fruits and flowers are mixed with alcohol or water and used by traditional healers for fertility treatment among women and men of child bearing age (Ogbeche *et al.*, 2002). Some interesting diverse biological studies on *K. africana* had been reported such as the anti-implantation (Prakash *et al.*, 1985), molluscicidal (Kela *et al.*, 1989), and antimicrobial (Akunyili *et al.*, 1991) activities. The extracts of the stem-bark and fruit were screened for their cytotoxic activities and showed promising results against melanoma and renal carcinoma (Houghton *et al.*, 1994), while the root-bark showed activity against KB cells (Weiss *et al.*, 2000 Previous studies of the fruits showed some anti-inflammatory effects (Picerno *et al.*, 2005; Owolabi and Omogbai, 2007), anticancer activity (Houghton *et al.*, 1994; Jackson *et al.*, 2000; Picerno *et al.*, 2005) and hepatoprotective effect (Olaleye and Rocha, 2007, 2008). The current literature revealed the isolation of naphthoquinons (Inoue *et al.*, 1981; Akunyili and Houghton, 1993; Weiss *et al.*, 2000), coumarins (Govindachari *et al.*, 1971), iridoids (Houghton and Akunyili, 1993) and flavonoids (El-Sayyad, 1982) from *K. africana*.

In the course of phytochemical studies on Cameroonian plants, this study was designed with the objective to identify phytochemicals constituents of the leaves and fruits of *K. africana*.

* *Corresponding Author*
Lazare S Sidjui, Institute of medical research and medicinal plant studies P.O Box 6163 Yaoundé, Cameroon. Laboratory of Natural Product, Department of Organic Chemistry, Faculty of Sciences, University of Yaoundé I, P.O. Box. 812, Yaoundé, Cameroon.
Email: lazaresidjui@yahoo.fr

MATERIALS AND METHODS

General experimental techniques

The structures of isolated compounds were elucidated by means of spectroscopic experiments mainly 1D and 2D NMR performed, on a 600 MHz Bruker Avance III-600 spectrometer equipped with a 5mm BBFO+ probe at 300K and ESIMS / HRESIMS analyses recorded on a SYNAPT G2 HDMS (Waters) mass spectrometer and by comparison with literature data. Fractions were monitored by TLC and performed on precoated silica gel 60 F254 plates (Merck, Dramstadt, Germany). The spots were revealed using both ultra-violet light (254 nm and 366 nm) and 10 % H_2SO_4 spray reagent.

Sample collection

The fruits and leaves of *K. africana* were collected from *Mont Cameroun*, Buea, Cameroon in February 2013 and identified by Mr. Victor NANA (plant taxonomist) of the Cameroon National Herbarium (HNC) where voucher specimens (N° 159/HNC) have been deposited.

Extraction and isolation

The air-dried powder leaves (1.5 kgs) and fruits (1.8 kgs) of *K.africana* were separately extracted by maceration at room temperature for 72 h using MeOH/DCM (1:1 *v/v*) mixture. The suspensions were filtered and each filtrate was concentrated under reduced pressure using a rotavapor to give 250 g and 200 g of crude extracts, respectively. The leaves crude extract (200 g) was subjected to flash column chromatography on silica gel (Merck, 230-400mesh) and eluted with hexane/AcOEt(3:1), hexane/AcOEt (1:1), AcOEt, AcOEt/MeOH (9:1) to give four fractions labeled F1 (35 g), F2 (45 g), F3 (55 g), F4 (50 g) respectively. Fractions F1 and F2 were mixed, on the basis of their thin layer chromatography (TLC) profile. The regouped fraction (F, 80 g) was further subjected to column chromatography (CC) on silica gel (Merck, 70-230 mesh) and eluted with hexane/AcOEt mixture of increasing polarity from hexane/AcOEt (9:1) to hexane/AcOEt (1:3). One hundred and twenty fractions of 150 mL each were collected and analyzed by TLC using hexane/AcOEt (7:3) and AcOEt/MeOH (9:1) as mobile phase. Sub-fractions 30-35, 65-68, 75-77, 88-91, 100-103 and 112-14 were left to crystallize at room temperature to afford respectively: lupeol **1** (65 mg), *β*-Sitosterol **2** (20 mg), sitosteryl *β*-D-glucoside **3** (15 mg), canophyllol **4** (12 mg), pomolic acid **6** (13 mg), hydroxy-pomolic acid **7** (15 mg) (Guillermo *et al.,* 1989; Masao *et al.,* 1988;). Similarly, the fruits crude extract (180 g) was also s n'est pas clairubjected to flash column chromatography on silica gel (Merck, 230-400 mesh) and eluted with hexane/AcOEt (3:1), hexane/AcOEt (1:1), AcOEt, AcOEt/MeOH (9:1) to give four fractions labeled A1 (25 g), A2 (36 g), A3 (45 g), A4 (50 g). Fractions A1 and A2 were also pooled, according to their thin layer chromatography (TLC) profile. Fraction A (61 g) obtained was treated as fraction F. One hundred and twenty fractions of 150 mL each were collected and analyzed by TLC using hexane/AcOEt (7:3) and AcOEt/MeOH (9:1) as mobile phase. Sub-fractions 65-71, 88-91 were also left to crystallize at room temperature to afford respectively: *β*-friedelinol **8** (15 mg), fibrarecisin **5** (14 mg). The residues obtained from sub-fractions 112-119 and 125-132 labelled A' and A'' were eluted, each with the mixture Hex/AcOEt (6:4) and afforded sesamin **9** (11 mg) and paulownin **10** (10 mg).

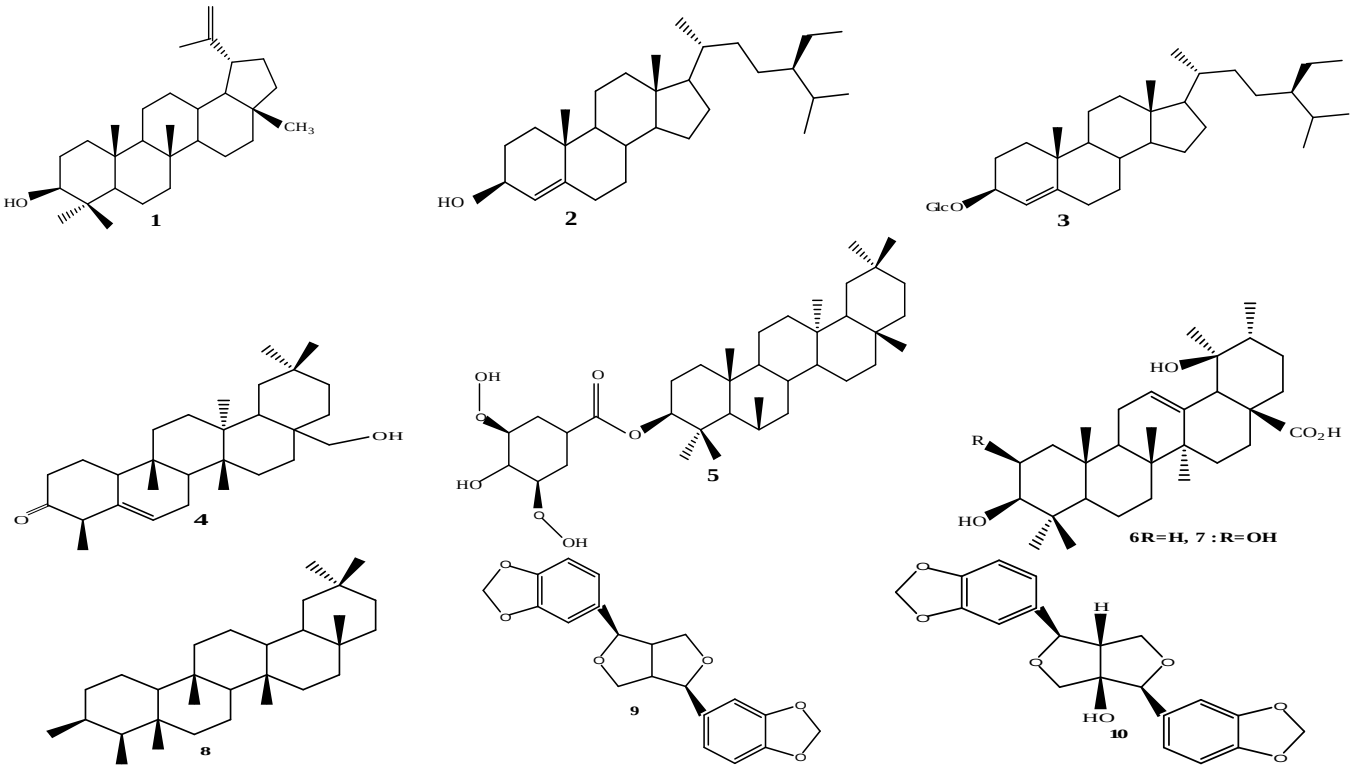

Fig. 1: Chemical structures of compounds **1-10** isolated from the fruits and leaves of *K.africana.*

Lupeol (***1***): colorless solid; ^{1}H- NMR (600 MHz, $CDCl_3$): δ 4.68 (H-29b), 4.55 (H-29a), 3.18 (H-3), 1.68 (s, H_3-30), 0.96 (s, H_3-23), 0.78 (s, H_3-24), 0.83 (s, H3-25), 0.94 (s, H_3-26), 1.06 (s, H_3-27), 0.91 (s, H_3-28), 1.68 (s, H_3-30). *β*-Sitosterol (**2**): white powder; ^{1}H-NMR (600 MHz; Pyridine-d_5) δ 5.38 (1H, brdt, *J* = 5.0; 2.4 Hz, H-6), 3.96 (1H, m, H-3), 2.76 (1H, ddd, *J* =12.9; 4.5; 2.1 Hz; Ha-4), 2.50 (1H, td, *J* = 12.4; 3.1 Hz; H-4b), 2.16 (1H, brd, *J* = 11.8 Hz; H-2a), 2.00 (1H, dt, *J* = 12.4; 3.5 Hz; H-12a), 1.96 (1H, m, H-7a), 1.86 (1H, m, H-16a), 1.77 (1H, m, H-2b), 1.71 (1H, m, H-25), 1.58 (1H, m, H-15a), 1.56 (1H, m, H-7b), 1.46 (1H, m, H-11a), 1.43 (1H, m, H-22a), 1.42 (1H, m, H-20), 1.41 (1H, m, H-11b), 1.40 (1H, m, H-8), 1.33 (2H, m, H-28), 1.28 (3H, m, H-16b/23b), 1.13 (2H, m, H-12b/H-17 b), 1.12 (1H, m, H-22 b), 1.06 (1H, m, H-15b), 1.03 (1H, m, H-24), 1.01 (1H, d, *J* = 6.7 Hz, H-21), 1.33 (1H, m, H-2b), 0.96 (1H, m, H-14), 0.96 (3H, s, H-19), 0.93 (1H, m, H-9), 0.92 (3H, t, *J* = 7.4 Hz, H-29), 0.91 (3H, d, *J* = 6.7 Hz, H-27), 0.89 (3H, d, J = 6.7 Hz, H-26), 0.69 (3H, s, H-18).^{13}C-NMR (150 MHz; Pyridine-d_5) δ 38.0 (C-1), 30.8 (C-2), 78.6 (C-3), 39.8 (C-4), 141.4 (C- 5), 122.4 (C-6), 32.7 (C-7), 32.6 (C-8), 50.9 (C-9), 37.4 (C-10), 21.8 (C-11), 40.5 (C-12), 43.0 (C-13), 57.3 (C-14), 25.0 (C-15), 29.0 (C-16), 56.7 (C-17), 12.5 (C-18), 19.9 (C-19), 36.9 (C-20), 19.5 (C-21), 34.7 (C-22), 26.9 (C-23), 46.5 (C-24), 30.0 (C-25), 19.7 (C- 26), 20.5 (C-27), 23.9 (C-28), 12.7 (C-29).

β-Sitosteryl -D-glucoside (***3***): white powder; ^{1}H-NMR (600 MHz; Pyridine-d_5) δ 5.38 (1H, brdt, *J* = 5.0; 2.4 Hz, H-6), 5.08 (1H, d, J = 7.7 Hz, H-1'), 4.59 (1H, dd, *J* = 11.8; 2.1 Hz, Ha-6'), 4.44 (1H, dd, *J* = 11.8; 5.1 Hz, Hb-6'), 4.32 (1H, t, *J* = 8.7 Hz, H-3'), 4.30 (1H, t, *J* = 8.7 Hz, H-4'), 4.08 (1H, dd, *J* = 8.7;7.7 Hz, H-2'), 4.01 (1H, m, H-5'), 3.96 (1H, m, H-3), 2.76 (1H, ddd, *J* =12.9; 4.5; 2.1 Hz; H-4a), 2.50 (1H, td, *J* =12.4; 3.1 Hz; H-4b), 2.16 (1H, brd, *J* = 11.8 Hz; H-2a), 2.00 (1H, dt, *J* =12.4; 3.5 Hz; H-12a), 1.96 (1H, m, H-7a), 1.86 (1H, m, H-16a), 1.77 (1H, m, H-2b), 1.71 (1H, m, H-25), 1.58 (1H, m, H-15a), 1.56 (1H, m, H-7b), 1.46 (1H, m, H-11a), 1.43 (1H, m, H-22a), 1.42 (1H, m, H-20), 1.41 (1H, m, H-11b), 1.40 (1H, m, H-8), 1.33 (2H, m, H-28), 1.28 (3H, m, H-16 b /23b), 1.13 (2H, m, H-12 b /H-17b), 1.12 (1H, m, H-22b), 1.06 (1H, m, H-15b), 1.03 (1H, m, H-24), 1.01 (1H, d, *J* = 6.7 Hz, H-21), 1.33 (1H, m, H-2b), 0.96 (1H, m, H-14), 0.96 (3H, s, H-19), 0.93 (1H, m, H-9), 0.92 (3H, t, J = 7.4 Hz, H-29), 0.91 (3H, d, J = 6.7 Hz, H-27), 0.89 (3H, d, J = 6.7 Hz, H-26), 0.69 (3H, s, H-18).

^{13}C-NMR (150 MHz; Pyridine-d_5) δ 38.0 (C-1), 30.8 (C-2), 78.6 (C-3), 39.8 (C-4), 141.4 (C- 5), 122.4 (C-6), 32.7 (C-7), 32.6 (C-8), 50.9 (C-9), 37.4 (C-10), 21.8 (C-11), 40.5 (C-12), 43.0 (C-13), 57.3 (C-14), 25.0 (C-15), 29.0 (C-16), 56.7 (C-17), 12.5 (C-18), 19.9 (C-19), 36.9 (C-20), 19.5 (C-21), 34.7 (C-22), 26.9 (C-23), 46.5 (C-24), 30.0 (C-25), 19.7 (C- 26), 20.5 (C-27), 23.9 (C-28), 12.7 (C-29), 103.1 (C-1'), 75.8 (C-2'), 79.1 (C-3'), 72.2 (C-4'), 79.0 (C- 5'),63.4 (C-6'), Canophyllol (**4**): white powder; ^{1}H-NMR (600 MHz; $CDCl_3$) δ 3.64 (1H, d, *J* = 11.0 Hz, H-28a), 3.62 (1H, d, *J* = 11.0 Hz, H-28b), 2.39 (1H, ddd, *J* = 13.9 ; 5.1 ; 1.8 Hz, H-2a), 2.29 (1H, dddd, *J* = 13.9 ; 13.0 ; 7.3 ; 1.1 Hz, H-2b), 2.25 (1H, brq, *J* = 6.6 Hz, H-4), 1.96 (1H, ddt, *J* = 13.2 ; 7.3 ; 2.5 Hz, Ha-1), 1.86 (1H, t, *J* = 9.5 Hz, H-16a), 1.76 (1H, dt, *J* = 12.8 ; 3.0 Hz, H-6a), 1.69 (1H, qd, *J* = 13.1 ; 5.0 Hz, Hb-1), 1.54 (1H, m, H-10), 1.49 (1H, m, H-7a), 1.48 (1H, m, H-15a), 1.47 (2H, m, H-11a/19 a), 1.42 (1H, m, H-8), 1.41 (1H, m, H-15b), 1.36 (2H, m, H-12), 1.35 (1H, m, Hb-7), 1.33 (2H, m, H-22),1.32 (1H, m, H-16b), 1.30 (2H, m, Hb-6/11), 1.30 (1H, m, H-18a), 1.30 (2H, m, H-21),1.27 (1H, m, H-19b), 1.13 (3H, s, H-27), 0.99 (3H, s, H-30), 0.98 (3H, s, H-29), 0.91 (3H, s, H-26), 0.88 (3H, d, J = 6.0 Hz, H-23), 0.87 (3H, s, H-25), 0.72 (3H, s, H-24). ^{13}C-NMR (150 MHz; Pyridine-d_5) δ 22.4 (C-1), 41.7 (C-2), 213.3 (C-3), 58.4 (C-4), 42.3 (C- 5), 41.4 (C-6), 18.4 (C-7), 52.6 (C-8), 37.6 (C-9), 59.6 (C-10), 35.6 (C-11), 30.3 (C-12), 39.5 (C-13), 38.3 (C-14), 31.6 (C-15), 29.3 (C-16), 35.3 (C-17), 39.6 (C-18), 34.7 (C-19), 28.3 (C-20), 33.5 (C-21), 31.4 (C-22), 7.0 (C-23), 14.8 (C-24), 18.2 (C-25), 19.2 (C- 26), 19.3 (C-27), 68.2 (C-28), 33.0 (C-29), 34.4 (C-30). Fibrarecisin (***5***): white powder; ^{1}H-NMR (600 MHz; Pyridine-d_5) δ 7.33 (2H, s, H-3'/7'), 5.55 (1H, dd, *J* = 8.2 ; 3.1 Hz, H-15), 4.96 (1H, dd, *J* = 11.4; 5.0 Hz, H-3), 3.94 (2xOMe, s), 2.06 (2H, dt, *J* = 12.8; 2.9 Hz, Ha-7), 1.93 (1H, dd, *J* = 14.7; 2.7 Hz, H-16a), 1.78 (1H, m, H-2a), 1.67 (1H, m, H-11a), 1.66 (1H, m, H-1a), 1.65 (1H, m, H-16b), 1.65 (2H, m, H-6a), 1.64 (2H, m, H-12a), 1.57 (1H, m, H-12b), 1.53 (1H, m, H-6b), 1.50 (1H, m, H-11b), 1.49 (1H, m, H-9), 1.47 (1H, m, H-2b), 1.39 (1H, td, *J* = 13.6; 3.3, H-7b), 1.38 (1H, m, H-22a), 1.35 (1H, m, H-21a), 1.33 (1H, m, H-19a), 1.26 (1H, m, H-21b), 1.12 (1H, td, *J* = 12.6; 4.4 Hz, H-1b), 1.12 (3H, s, H-26), 1.03 (3H, m, H-24), 1.02 (3H, m, H-22b), 1.01 (3H, m, H-25), 0.98 (1H, m, H-5), 0.98 (1H, m, H-19b), 0.97 (1H, m, H-18), 0.96 (3H, m, H-29), 0.93 (3H, s, H-23/27), 0.92 (3H, s, H-30), 0.83 (3H, s, H-28).). ^{13}C-NMR (150 MHz; Pyridine-d5) δ 37.6 (C-1), 23.8 (C-2), 81.7 (C-3), 38.3 (C-4), 55.8 (C- 5), 18.9 (C-6), 41.4 (C-7), 39.2 (C-8), 49.4 (C-9), 38.1 (C-10), 17.7 (C-11), 33.9 (C-12), 37.7 (C-13), 158.1 (C-14), 117.1 (C-15), 37.9 (C-16), 36.0 (C-17), 48.9 (C-18), 36.0 (C-19), 29.0 (C-20), 33.3 (C-21), 35.3 (C-22), 28.3 (C-23), 17.1 (C-24), 15.7 (C-25), 26.1 (C- 26), 21.1 (C-27), 30.0 (C-28), 33.5 (C-29), 30.1 (C-30), 166.2 (C-1'), 122.1 (C-2'), 106.8 (C-3'/7'), 146.8 (C-4'/6'), 139.2 (C-5'), 56.5 (2xOMe)

Pomolic acid (***6***): white powder; ^{1}H-NMR (600 MHz; C_5D_5N) δ 5.64 (1H, t, *J* = 3.20 Hz, H-12), 3.46 (1H, dd, *J* = 11.1; 4.5 Hz, H-3), 3.16 (1H, td, *J* = 13.3; 4.6 Hz, H-16a), 3.08 (1H, s, H-18), 2.37 (1H, m, H-15a), 2.20 (2H, m, H_a-22), 2.12 (2H, m, H-21a), 2.10 (1H, m, H-11a, H-16b, H-22b), 2.06 (1H, m, H_b-11),1.92 (1H, m, H_a-2), 1.88 (1H, m, H-9), 1.85 (1H, m, H-2b), 1.78 (1H, m, H-7a), 1.76 (3H, s, H-27), 1.75 (1H, m, H-15b), 1.61 (1H, m, H-6a), 1.60 (1H, m, H-1a), 1.53 (1H, m, H-20), 1.48 (3H, s, H-29), 1.43 (1H, m, H-6,7b), 1.37 (1H, m, H-21b), 1.26 (3H, s, H-23), 1.15 (3H, s, H-26), 1.14 (3H, d, *J* = 4.5Hz, H-30), 1.05 (3H, s, H-24), 0.95 (3H, s, H-25). ^{13}C-NMR (150 MHz; C_5D_5N,) δ 39.5 (C-1), 28.6 (C-2), 78.7 (C-3), 39.9 (C-4), 56.3 (C- 5), 19.4 (C-6), 34.1 (C-7), 40.8 (C-8), 48.3 (C-9), 37.8 (C-10), 24.5 (C-11), 128.5 (C-12), 140.4 (C-13), 42.6 (C-14), 29.8 (C-15), 26.9 (C-16), 48.8 (C-17), 55.1 (C-18), 73.2 (C-19), 42.8 (C-20), 27.4 (C-21), 39.0 (C-22), 17.0 (C-23), 29.3 (C-24), 16.0 (C-25), 17.2 (C- 26), 25.2 (C-27), 181.1 (C-28), 27.6 (C-29), 17.4 (C-30).

Hydroxy-pomolic acid (**7**): white powder; ^{1}H-NMR (600 MHz; Pyridine) δ 5.30 (1H, t, *J* = 3.9 Hz, H-12), 4.01 (1H, m, H-2), 3.14 (1H, d, *J* = 4.0 Hz, H-3), 2.56 (2H, m, H-15), 2.50 (1H, brs, H-18), 2.06 (1H, dd, *J* = 14.3; 2.9 Hz, H-3a), 2.02 (1H, m, Ha-11),1.94 (1H, m, H-11b), 1.80 (2H, m, H-15), 1.72 (2H, m, H-21a, H-22a), 1.63 (2H, m, H-16), 1.61 (1H, m, H-22b), 1.55 (2H, m, H-6a, H-7a), 1.50 (1H, m, H-6b), 1.45 (1H, m, H-6b), 1.33 (3H, s, H-26), 1.31 (1H, m, H-7b), 1.25 (3H, s, H-25), 1.45 (1H, m, H-6b), 1.23 (2H, m, H-21), 1.19 (1H, s, H-29), 1.16 (1H, m, H-1b), 1.01 (3H, s, H-24), 1.00 (3H, s, H-623), 0.93 (3H, d, *J* = 6.6 Hz, H-30), 0.86 (1H, m, H-5), 0.81 (3H, s, H-26). ^{13}C-NMR (150 MHz; C_5D_5N) δ 45.5 (C-1), 72. (C-2), 79.7 (C-3), 39.2 (C-4), 56.8 (C- 5), 19.4 (C-6), 34.2 (C-7), 41.1 (C-8), 49.2 (C-9), 38.0 (C-10), 24.8 (C-11), 129.6 (C-12), 140.0 (C-13), 42.6 (C-14), 29.5 (C-15), 26.2 (C-16), 48.7 (C-17), 55.1 (C-18), 73.6 (C-19), 43.1 (C-20), 27.3 (C-21), 39.0 (C-22), 30.3 (C-23), 17.9 (C-24), 16.6 (C-25), 17.5 (C- 26), 24.9 (C-27), 182.3 (C-28), 27.1 (C-29), 16.6 (C-30).

β-Friedelinol (**8**): white powder; ^{1}H-NMR (600 MHz; Pyridine-d_5) δ 5.02 (3-OH, s), 4.00 (1H, sl, H-3), 2.17 (1H, dq, *J* = 13.2, 2.9 Hz, Ha-2), 1.93 (1H, qd, *J* = 12.8; 3.1 Hz, Ha-1), 1.92 (1H, qd, *J* = 13.1, 3.3 Hz, Ha-7), 1.86 (1H, dt, *J* = 12.6; 3.0 Hz, Ha-6), 1.69 (1H, tdd, *J* = 13.2; 4.0, 3.5 Hz, H-2b), 1.59 (1H, m, H-18), 1.58 (1H, m, Ha-16), 1.53 (1H, m, Hb-7), 1.52 (2H, m, Ha-21, Hb-1), 1.51 (1H, m, H-22a), 1.49 (1H, m, H-11a), 1.48 (1H, m, H-15a), 1.44 (1H, m, Ha-19), 1.37 (1H, m, H-16b), 1.36 (1H, m, H-8), 1.32 (2H, m, H-12), 1.31 (1H, m, H-21b), 1.31 (3H, s, H-24), 1.31 (1H, m, H-4), 1.30 (1H, m, H-15b), 1.27 (1H, m, H-19b), 1.21 (1H, m, H-11b), 1.21 (3H, s, H-28), 1.19 (3H, d, *J* = 7.2 Hz, H-23), 1.08 (3H, s, H-30), 1.06 (1H, m, H-6b), 1.06 (3H, s, H-27), 1.03 (1H, m, H-10), 1.02 (3H, s, H-29), 1.01 (3H, s, H-26), 0.95 (1H, dd, *J* = 11.0; 2.6 Hz, Hb-22), 0.95 (3H, s, H-25). ^{13}C-NMR (150 MHz; C_5D_5N,) δ 17.1 (C-1), 37.1 (C-2), 71.9 (C-3), 50.5 (C-4), 39.1 (C- 5), 42.8 (C-6), 17.1 (C-7), 54.0 (C-8), 37.9 (C-9), 62.4 (C-10), 36.5 (C-11), 31.4 (C-12), 39.1 (C-13), 40.5 (C-14), 33.0 (C-15), 36.9 (C-16), 30.7 (C-17), 43.6 (C-18), 36.0 (C-19), 28.8 (C-20), 33.6 (C-21), 39.9 (C-22), 13.0 (C-23), 17.5 (C-24), 19.1 (C-25), 20.8 (C- 26), 19.3 (C-27), 33.0 (C-28), 35.5 (C-29), 32.5 (C-30).

Sesamin (**9**): Pink needle crystals. EIMS: *m/z* 354 $[M]^+$,

^{1}H-NMR (500 MHz, $CDCl_3$), δ: 2.98 (2H, m, H-1/5), 3.80 (2H, dd, H-4/8), 4.16 (2H, dd, H-4/8), 4.64 (2H, d, H-2/6), 5.88 (4H, s, [(-O-CH_2-O)-2]), 6.70 *d* (2H, d, H-5'/5"), 6.72 (2H, dd, H-6'/6"), 6.77 (d, 2H, H-2'/2"). ^{13}H-NMR (150 MHz, $CDCl_3$), δ: 54.3 (C-1/5), 85.7 (C-2/6), 71.7 (C-4/8), 101.0 (C-[(-O-CH_2-O)-2]), 135.0 (C-1'/1"), 106.4 (C-2'/2"), 147.9 (C-3'/3"), 147.1 (C-4'/4"), 108.1 (C-5'/5"), 119.3 (C-6'/6"

Paulownin (***10***): Pink needle crystals. EIMS: *m/z* = 370 $[M]^+$ for formula $C_{20}H_{18}O_7$; ^{1}H-NMR (500 MHz, $CDCl_3$), δ: 1.5 (1H, s, OH), 3.06 (1H, ddd, H-1), 3.86 *dd* (1H, dd, H-8b), 3.93 (1H, d, H-4b), 4.06 (1H, d, H-4a), 4.53 (1H, dd, H-8a), 4.83 (1H, s, H-6), 4.86 (1H, d, H-2), 5.97 (2H, s, CH_2 (a)), 6.00 (2H, s, CH_2 (b)), 6.81 (1H, d, H-5'), 6.86 (1H, d, H-5"), 6.88 (1H, dd, H-6'), 6.89 (1H, dd, H-6"), 6.93 (1H, d, H-2'), 6.96 (1H, d, H-2"). ^{13}C-NMR (150 MHz, $CDCl_3$), δ: 59.4 (C-1), 84.8 (C-2), 73.8 (C-4), 90.7 (C-5), 86.5 (C-6), 70.6 (C-8), 100.1 (CH_2 (a)), 100.2 (CH_2 (b)), 128.1 (C-1'), 133.6 (C-1"), 105.9 (C-2'), 106.4 (C-2"), 147.0 (C-3'), 147.2 (C-3"), 146.3 (C-4'), 146.9 (C-4"), 118.8 (C-5'), 119.0 (C-5"), 107.2 (C-6'), 107.6 (C-6").

RESULTS AND DISCUSSION

Fractionation of *K. africana* fruits and leaves extracts by column chromatography led to the isolation and purification of five triterpenoids (**1, 4-8**), two sterols (**2-3**) and two lignans (**9-10**). Silica gel chromatography of the different fractions of leaves of *Kigelia africana* afforded lupeol **1** (Prakash and Garg, 1980), *β*-Sitosterol **2** (Shaleen *et al.*, 2001), sitosteryl *β*-D-glucoside **3** (Shaleen *et al.*, 2001), canophyllol **4** (Mahato and Kundu, 1994), pomolic acid **6** (Masao *et al.*, 1988; Guillermo *et al.*, 1989), hydroxy-pomolic acid **7** (Nchu *et al.*, 2010; Masao *et al.*, 1988; Guillermo *et al.*, 1989). Similarly, the different fractions of the fruits of *Kigelia africana* afforded *β*-friedelinol **8** (Salazar *et al.*, 2000), fibrarecisin **5**, (Jiao-longfu *et al.*, 2007), sesamin **9** (Alvarez *et al.*, 2007; Li *et al.*, 2000; Laggoune *et al.*, 2011), and paulownin **10** (Angel *et al.*, 2008; Laggoune *et al.*, 2011). The structures of the isolated compounds were determined by spectroscopic analysis, especially, MS, ^{1}H, and ^{13}C NMR spectra in conjunction with 2D experiments (COSY, HSQC, HMBC) and direct comparison with reference data from available literature.

Compound **5** was obtained as a white amorphous powder. Its EI-MS showed the molecular ion peak at *m/z* 606, corresponding to the molecular formula $C_{39}H_{58}O_5$, which was in agreement with ^{1}H and ^{13}C NMR data. The ^{1}H NMR spectrum displayed proton signals for eight methyls (δ 0.83, 0.91, 0.92, 0.93, 0.95, 1.00, 1.03 and 1.11, eachs, 3H), two methoxyles (δ 3.94, s, 6H),one oxygen-bearing methylene (δ 4.69, dd, *J* = 11.3, 5.5 Hz, 1H), one pair of tri-substituted double bond (δ 5.55, dd, *J* = 3.5, 1.3 Hz,1H), and asymmetric 1,3,4,5-tetrasubstituted aromatic ring (7.32, s, 2H), suggesting an oleanane-type triterpenoid derivative. The ^{13}C NMR of **5** showed 8 methyls, 10 methylenes, 3 methines, one hydroxy-bearing methine, a pair of double bond, and six quaternary carbons for the triterpenoid moiety. The remaining signals at 166.0 (s), 121.9 (s), 106.5 (d, 2C), 146.6 (s, 2C), 139.0 (s), 55.6 (t, 2C) were attributed to a syringyl group (Jiao-Longfu *et al.*, 2007). The position of the oxygen-bearing methylene and double bonds were assigned to be C-3, C14 and C-15, respectively, according to the significant HMBC cross-peaks of H-3 with C-23 and C-24, and C-10 H-15/C-16, H3 C-26/C-14, and H3 C-27/C-14) The *β*-configuration (axial) of H-3 was determined by the coupling constants of 11.3 and 5.5 Hz.Thus, fibrarecisin (**5**) was structurally elucidated to be 3-*O*-syringyl-3-*β*-oleanol-14-ene. Although bioassays were not conducted on the isolated compounds, previous studies reported on their biological activities. Lupeol (**1**) exhibited antiurolithiatic and diuretic activity (Vidya *et al.*, 2002). It prevented the formation of vesical calculi and reduced the size of the preformed stones in rats (Anand *et al.*, 1994). *β*-Sitosterol (**2**) and *β* sitosteryl -D-glucoside (**3**) have shown growth inhibitory effects on human breast MCF-7 and

MDA-MB-231 adenocarcinoma cells (Awad *et al.,* 2007). It was shown to be effective for the treatment of benign prostatic hyperplasia (Jayaprakasha *et al.,* 2007). It was also reported to attenuate β-catenin and PCNA expression, as well as quench radical *in vitro*, making it a potential anticancer drug for colon carcinogenesis (Baskar *et al.,* 2010). It can inhibit the expression of NPC1L1 in the enterocytes to reduce intestinal cholesterol uptake (Jesch *et al.,* 2009). It was reported to induce apoptosis mediated by the activation of ERK and the down regulation of Akt in MCA-102 murine fibrosarcoma cells (Moon *et al.,* 2007).

An earlier study reported that pomolic acid (**6**) and hydroxy-pomolic acid (**7**) exhibited anti-tumor activity against human colon carcinoma cell line HCT15 with pomolic acid acid showing stronger activity than hydroxy-pomolic acid (Chang *et al.,* 2010). It exhibited anti-inflammatory effects by inhibiting hyperpermeability, the expression of CAMs, and the adhesion and migration of leukocytes (Li *et al.,* 2012). hydroxy-pomolic acid was observed to have anti- microbial, and analgesic effect (Leitao *et al.,* 2011). Canophyllol (**4**) exhibited anti-AGEs activity through various mechanisms such as radical scavenging, chelation of divalent metal ions as well as catching of dicarbonylated species (Pashikanti *et al.,* 2010) Fibrarecisin (**5**) exhibited anti-tumor activity against human colon carcinoma cell line HCT15 (Fu *et al.,* 2007).

β-Friedelinol(**8**) exhibited antiurolithiatic, antimicrobial and anti-inflammatory activity. It prevented the formation of vesical calculi and reduced the size of the preformed stones in rats (Corrêa *et al.,* 2014). Sesamin (**9**) and *paulownin* (**10**) exhibited anti-inflammatory activity by inhibiting del-ta5-desaturase, a key enzyme in arachidonic acid biosynthesis that leads to a reduction in the formation of pro-inflammatory mediators. It increases the production of ketone bodies, when glucose is low in the brain tissue. It also significantly quenches the excess generation of nitric oxide induced by lipopolysaccharide in the murine microglial cell line BV-2 and rat primary microglia cells (Ahmed and Neelakantan, 2013).

The previous work on *K. africana* leaded the isolation of iridoids (Gouda *et al.,* 2003), limonoids (Bushra *et al.,* 2013), naphtho-quinones (Weiss *et al.,* 2000), flavonoids (El-Sayyad, 1982), steroids (Sidjui *et al.,* 2014), coumarins (Sidjui *et al.,* 2014) and caffeic acid (Sidjui *et al.,* 2014). The present study reports the identification of two steroids (**2-3**), six triterpenes (**1**, **4-8**) and two lignans (**9-10**). Compounds **2-3**, are common steroids present in many plants. From the six triterpènes described there, compounds **4-5** were identified for the first time from Bignoniaceae family while compounds **1** and **6-8** was already identified from other (Sidjui *et al.,* 2014). Lignans were described here or the first time from Bignoniaceae family. Therefore, it is clear that compounds **9-10** could also be used as chemotaxonomic markers of *K. africana*.

REFERENCES

Abioye AIR, Duru FIO, Noronha CC, Okanlawon AO. Aqueous extract of the bark of *Kigelia africana* reverses early testicular damage induced by methanol extract of *Carica papaya*. Niger J Health BiomedSci 2003; 2:87-89.

Ahmad DA, Neelakantan A. Lignans of sesame: Purification methods, biological activities and biosynthesis–A review. Bioorg Chem 2013; 50:1–10.

Akunyili DN, Houghton PJ, Roman A. Antimicrobial activities of the stem bark of Kigelia pinnata. J Ethnopharmacol 1991; 35:173–177.

Akunyili DN, Houghton PJ. Monoterpenoids and naphthaquinones from *Kigelia pinnata*. Phytochemistry 1993; 32:1015–1018.

Alvarez JK, Aislamieto. Purificatione identification de sesamina a partir de lodos de microfiltrado en la fabricacion del aceite virgin de Sesamum indicum L. (ajonjoli), Rev. Col. Cienc Quim Farm 2007; 36:5-10.

Anand R, Patnaik GK, Kulshreshtha DK, Dhawan N. Antiurolithiatic activity of lupeol, the active constituent of *Crateva nuriala*. Phytother Res 1994; 8(7):417-421

Angel SR, Choi I, Tham FS. Stereoselective synthesis of 3-alkyl-2-aryltetrahydrofuran-4-ols: total synthesis of (±)-paulownin, J Org Chem 2008; 73:6268-6278.

Asekun OT, Olusegun E, Adebola O. The volatile constituents of the leaves and flowers of *Kigelia africana* Benth. Flav Fragr J 2007; 22:21-23.

Awad AB, Chinnman M, Fink CS, Bradford PG. *β*-Sitosterol activates Fas signaling in human breast cancer cells. Phytomedicine 2007; 14:747–754.

Baskar AA, Ignacimuthu S, Paulraj G, Numair K. Chemopreventive potential of β-sitosterol in experimental colon cancer model - an I *in vitro* and *in vivo* study. BMC Compl Alt Med 2010; 10: 24.

Bharti N, Singh S, Naqvi F, Azam A. Isolation and *in vitro* antiamoeboic activity of iridoids isolated from Kigelia pinnata. General Papers ARKIVOC 2006 69-76.

Bushra J, Naheed R, Muhammad S, Akram N M, Maqsood A, Nawaz TM, Gennaro P, Muhammad A, Abida ES, Irshad A, Jabbar A. Isolation and characterization of limonoids from Kigelia africana. Z. Naturforschung, B: J Chem Soc 2013; 68:1041-1048.

Corrêa GM, Da Costa AVG, De abreu MDA, Takahashi J A, DE Souza fontoura H, Cara DC, Piló-veloso D, De carvalho alcântara A F. Anti-Inflammatory and antimicrobial activities of steroids and triterpenes isolated from aerial parts of *Justicia acuminatissima* (Acanthaceae). Int J Pharm Pharm Sci 2014; 6 (6):75-81.

Del Hoyo J, Elliot A, Sargatal J eds. 1997. Handbook of the birds of the world 4: 415. Lynx Edicions.

Delgado G, Hernandez J, Pereda-Miranda R. Triterpenoid acids from *Cunila lythrifolia*. Phytochemistry 1989; 28:1483-1485.

El-Sayyad, SM. Flavonoids of the leaves and fruits of *Kigelia pinnata*. Fitoterapia 1982; 52: 189–191.

Faizi S, Ali M, Irfanullah SR, Bibi S. Complete ^{1}H and ^{13}C NMR assignments of stigma-5-en-3-O-β-glucosideanditsacetyl derivative. Magn Reson Chem. 2001; 39:399–405.

Fu J-L, Tan C-H, Lin L-P, Huang J Z, Da-Y. Fibrarecisin, a novel triterpenoid from *Fibraurea recisa* with antitumor activity. Nat Prod Res 2007; 21(4):351-353

Gouda Y G, Abdel-Baky AM, Darwish FM, Mohamed KM, Kasai R, Yamasaki K. Iridoids from *Kigelia pinnata* DC. fruits. Phytochemistry 2003; 63:887–892.

Govindachari TR, Patankar SJ,Viswanathan N. Isolation and structure of two new dihydroisocoumarins from *Kigelia pinnata*. Phytochemistry 1971; 10:1603–1606.

Houghton PJ, Photiou A, Uddin S, Shah P, Browning M, Jackson SJ, Retsas S. Activity of extracts of *Kigelia pinnata* against melanoma and renal carcinoma cell lines. Planta med 1994; 60:430–433.

Inoue K, Inouye H, Chen C. A naphthoquinone a lignan from the wood of *Kigelia pinnata*. Phytochemistry 1981; 20:2271–2276.

Jackson SJ, Houghton PJ, Restsas S, Photiou A. In vitro cytotoxicity of norvibutinal and isopinnatal from Kigelia pinnata against cancer cell lines. Planta med 2000; 66:758-761.

Jayaprakasha GK, Mandadi KK, Poulose SM, Jadegoud Y, Gowda GA, Patil BS. Inhibition of colon cancer growth and antioxidant

activity of bioactive compounds from *Poncirus trifoliate* (L.) Raf. Bioorg Med Chem 2007; 15:4923-4932.

Jiao L,Chang H, Li P, Jihuangand DY. Fibrarecisin, a novel triterpenoid from *Fibraurea recisa* with antitumor activity. Nat Prod Res 2007; 21:351–353

Kela SL, Ogunsusi RA, Ogbogu VC, Nwude N. Screening of some Nigerian plants for molluscicidal activity. Rev Elev Med Vet Pays Trop 1989; 42:20–195.

Laggoune S, Brouard I, Leon F, Calliste CA, Duroux JL, Bermejo J, Kabouche Z, Kabouche A. Lignans and an abundant flavone glycoside with free-radical scavenging activity from the roots of the endemic species *Stachys mialhesi* de Noé. Rec Nat Prod 2011; 5(3):238-241.

Leitao SG, dos Santos TC, Delle Monache F, Matheus ME Fernandes PD, Marinho BG. Phytochemical profile and analgesic evaluation of *Vitex cymosa* leaf extracts. Rev Bras Farmacog 2011 ; 21(5) : 874-883

Li X, Zhang J, Gao W, Wang H. Study on chemical composition, anti-inflammatory and anti-microbial activities of extracts from Chinese pear fruit (*Pyrus bretschneideri* Rehd.). F Chem Toxicol 2012; 50(10):3673-3679.

Li Y, Ye M, Liu HW, Ji XH, Yan YN. Identification and determination of (+)-sesamin in Semen cuscutae by capillary GC and GC-MS. Chin Chem Lett 2000; 11:1076-1076.

Mahato SB, Kundu AP.^{13}C NMR Spectra of pentacyclic triterpenoids - a compilation and some salient features. Phytochemistry 1994; 37(6):1517-1575.

Masao H, Kue-Ping K, Yue-Zhong S, Yasuhiro T, Tohru K, Tsuneo N. A triterpene from the fruits of *Rubus chingii*. Phytochemistry 1988; 27:3975-3976.

Moiden SV, Houghton PJ, Rock P, Croft SL, Aboagye-Nyame F. Activity of extracts and naphthoquinones from *Kigelia pinnata* against *Trypanosoma brucei brucei* and *Trypanosoma brucei rhodesiense*. Planta med 1999; 65:536-40.

Moon DO, Kyeong Jun L, Yung HC, Gi-Young K. Moon DO, Kyeong Jun L, Yung HC, Gi-Young K. β-Sitosterol-induced-apoptosis is mediated by the activation of ERK and the downregulation of Akt in MCA-102 murine fibrosarcoma cells. Int Immunopharmacol 2007; 7:1044-1053.

Nchu F, Aderogba MA, Mdee LK, Eloff JN. Isolation of anti-Candida albicans compounds from *Markhamia obtusifolia* (Baker) Sprague (Bignoniaceae). South Afr J Bot 2010; 76(1):54-57.

Ogbeche KA, Ogunbiyi YO, Duru FIO. Effect of methanol extract of *Kigelia africana* on sperm motility and fertility in rats. Niger J Health Biomedical Sci 2002; 2:113-116.

Olaleye MT, Rocha BT. Acetaminophen-induced liver damage in mice: Effects of some medicinal plants on the oxidative defence system. Exp Toxicol Pathol 2008; 59:319-327.

Olaleye MT, Rocha JB. Commonly used tropical medicinal plants exhibit distinct in vitro antioxidant activities against hepatotoxins in rat liver. Exp Toxicol Pathol 2007; 58: 433-8.

Owolabi OJ, Omogbai EKI, Obasuyi O. Antifungal and antibacterial activities of ethanolic and aqueous extract of *Kigelia africana* (Bignoniaceae) stem bark. Afr J Biotechnol 2007; 6:1677-1680.

Owolabi OJ, Omogbai EKI. Analgesic and anti-inflammatory activities of the ethanolic stem bark extract of *Kigelia africana* (Bignoniaceae). Afr J Biotechnol 2007; 6:582-585.

Pashikanti S, De Alba DR, Boissonneault GA, Cervantes-Laurean D. Rutin metabolites: novel inhibitors of nonoxidative advanced glycation end products. Free Radic Biol Med 2014; 8:656–663

Picerno P, Autore G, Marzocco S, Meloni M, Sanogo R, Aquino RP . Anti-inflammatory activity of verminoside from *Kigelia africana* and evaluation of cutaneous irritation in cell cultures and reconstituted human epidermis. J Nat Prod 2005; 68:1610-4.

Prakash L, Garg G. Chemical examination of the root barks of *Jacaranda mimosifolia* D. Don and *Tabebuia pentaphylla* (Linn) Hemsl. Pharmazie 1980; 35:649-655.

Prakash, AO, Saxena V, Shukla S,Tewari RK, Mathur S, Gupta A, Sharma S, Mathur R. Anti-implantation activity of some indigenous plants in rats. ACTA Eur Fertil 1985; 16:441–448.

Roodt V (1992). Kigelia africana in: The Shell Field Guide to the Common Trees of the Okavango Delta and Moremi Game Reserve. Gaborone, Botswana: Shell Oil Botswana.

Salazar GCM, Silva GDF, Duarte LP, Vieira Filho SA, Lula IS. Two epimeric friedelane triterpenes isolated from *Maytenus truncata* Reiss: ^{1}H and ^{13}C chemical shift assignments. Mag Res Chem 2000; 38:977-980.

Sidjui SL, Zeuko'o M E, Toghueo K R M, Noté PO, Mahiou-Leddet V, Herbette G Fekam, B F, Ollivier E, Folefoc N G. Secondary metabolites from *Jacaranda mimosifolia* and *Kigelia Africana* (Bignoniaceae) and their anticandidal activity. Rec Nat Prod 2014; 8:3307-311

Vidya L, Leni M, Varalakshmi P. Evaluation of the effect of triterpenes on urinary risk factors of stone formation in pyridoxine hyperoxaluric rats. Phytother Res 2002 ; 16 (6):514-518.

Weiss CR, Moideen SVK, Croft SL, Houghton PJ. Activity of extracts and isolated naphthaquinones from *Kigelia pinnata* against *Plasmodium falciparm*. J Nat Prod 2000; 63:1306–1309.

How to cite this article:

Lazare S Sidjui, Raduis Raduis Melong, Valérie Mahiou-Leddet, Gaëtan Herbette, Alembert T Tchinda, Evelyne Ollivier, Gabriel Ngosong Folefoc. Triterpenes and Lignans From *Kigelia Africana*. J App Pharm Sci, 2015; 5 (Suppl 2): 001-006.