Chemical constituents of *Treculia acuminata* and *Treculia africana* (Moraceae)

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Received 15 March 2007; accepted 29 June 2007

Keywords: *Treculia acuminata*; *Treculia africana*; Moraceae; Chalcones; Epiphyllocoumarin; Chemotaxonomy

1. Subject and source

Three species of the genus *Treculia* namely, *Treculia acuminata* Baill., *Treculia africana* Decne ex. Trécul and *Treculia obovoidea* N.E.Br. grow in the humid rain forest of southwest Cameroon. They are also widely distributed in tropical Africa. *T. africana* is commonly known as African bread fruit. These three species are commonly used in folk medicine against skin diseases and dental allergies (Berg et al., 1985). The twigs, stem and wood of *T. acuminata* and the leaves of *T. africana*, whose chemical constituents are reported herein, were collected from Kumba, Cameroon, in August 2004, and identified by Mr Victor Nana of the National Herbarium in Yaounde, Cameroon where voucher specimens (N°2921/Srf/CAM and 29053/SRF/Cam, respectively) are deposited.

2. Previous work

3-Prenyl-2′,4,4′-trihydroxychalcone (Licoagrochalcone A) and bergapten were reported from *T. africana* (Moody et al., 2006) in addition to morin (2′,4′,5,7-tetrahydroxyflavonol) and a cyanidin glycoside (Prista and Alves, 1964). *T. africana* has also been subjected to various studies for its nutritional value. The seeds have about 19% protein and 11% fat and, therefore, are potentially valuable as a high protein sources for human food and animal feed in Nigeria. In addition, they are good sources of edible oil, potassium, phosphorus, magnesium, riboflavin and β-carotene (Badihu and Akubor, 2001; Edet et al., 1985; Makinde et al., 1985; Lawal and Bassir, 1987; Sunday et al., 2000; Nwabeze,

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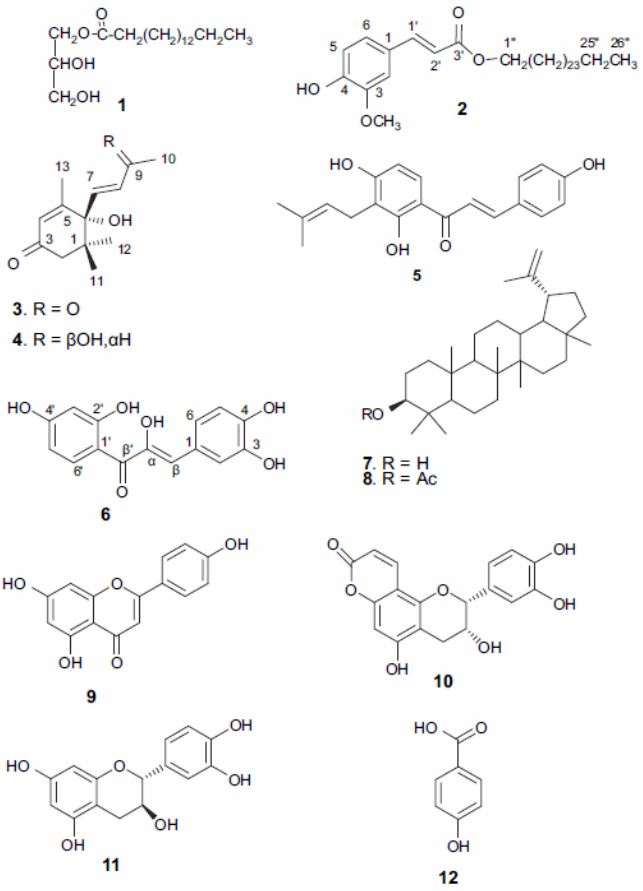

Fig. 1. Structures of compounds **1**–**12**.

2006). *T. obovoidea* contains peptides that are found to act as anti-HIV (Bokesch et al., 2004). To the best of our knowledge there is no previous phytochemical report on *T. acuminata*.

3. Present study

3.1. T. acuminata

Dried and ground twigs, stem and wood of *T. acuminata* (2.5 kg) were macerated twice with methanol (10 l) at room temperature. The solvent was removed at reduced pressure ($T < 40$ °C) to give a brown extract (57 g). This crude extract was subjected to vacuum liquid chromatography (VLC) on silica gel 60 (250 g) and eluted with petroleum ether 40–60 °C, petroleum ether–EtOAc mixtures and EtOAc, successively to give 46 fractions of 250 ml each. Fractions 1–6 (10 g) were examined on TLC (petroleum ether–EtOAc, 9:1). These were found to contain mainly stigmasterol (comparison with authentic sample) and were not investigated further. Fractions 7–9 (4 g) were treated with acetone and the formation of a precipitate was noted and identified as glycerol-1-hexadecanoate (**1**, 2 mg, amorphous white crystals, Sultana et al., 1999). The mother liquor was subjected to column chromatography over silica gel,

Table 1
^{1}H (δ, $CDCl_3$, 600 MHz) and ^{13}C (δ, $CDCl_3$, 150 MHz) NMR data of compounds **2** and **3**

Position	**2**		Position	**3**	
	^{1}H	^{13}C		^{1}H	^{13}C
1		127.1 (s)	1		41.8 (s)
2	7.05 (d, 1.8)	109.3 (s)	2	2.38/2.48 (d, 17.2)	49.9 (t)
3		146.7 (s)	3		199.4 (s)
4		147.9 (s)	4	5.97 (d,1.0)	128.1 (d)
5	6.93 (d, 8.1)	114.7 (d)	5		160.7 (s)
6	7.09 (dd, 8.1, 1.8)	123.0 (d)	6		79.7 (s)
1′	7.62 (d, 15.6)	144.6 (d)	7	6.85 (d, 15.7)	145.4 (d)
2′	6.31 (d, 15.6)	115.7 (d)	8	6.48 (d, 15.7)	130.8 (d)
3′		167.3 (s)	9		197.8 (s)
1″	4.20 (t, 6.9)	64.1 (t)	10	2.13 (s)	28.8 (q)
2″	1.40 (d, 7.2)	31.9 (t)	11	1.12 (s)	18.5 (q)
3″–24″	1.27 (br s)	26.0–29.7 (t)	12	1.04 (s)	23.4 (q)
25″	1.26 (br s)	22.7 (t)	13	1.90 (d, 1.0)	19.1 (q)
26″	0.89 (t, 6.7)	14.0 (q)	6-OH	2.15	
3-OCH_3	3.95 (s)	55.9 (q)			
4-OH	6.98 (s)				

Chemical shifts are in ppm from TMS; multiplicities and coupling constants (in Hz) are given in parentheses.

followed by preparative TLC (petroleum ether–$CHCl_3$, 1:4) to give 9 mg of an aliphatic long chain ester of ferulic acid (**2**, white crystals, Wandji et al., 1990; Achenbach et al., 1986). Fractions 10–25 (8 g) were passed through a Sephadex LH-20 column and eluted with $CHCl_3$–MeOH (2:1); preparative TLC on the post chlorophyll fractions (CH_2Cl_2–Me_2CO, 4:1) gave 11 mg of 6-hydroxy-4,7-megastigmadiene-3,9-dione (**3**, yellow oil, Tadahiro et al., 1977) and 3 mg of isobavachalcone (**5**, yellow crystals, Ngadjui et al., 2005). Fractions 26–38 (6 g) were also passed through column chromatography over silica gel followed by preparative TLC (CH_2Cl_2–Ac_2O–acetic acid, 92:6:2), to give 5 mg of 6,9-dihydroxymegastigmane-3-one (**4**, yellow oil, Ting-Ting and Meei-Yueh, 1993; Gonzalez et al., 1994; Siddiqui et al., 2003), and 3 mg of 2′,4′,3,4,α-pentahydroxychalcone (**6**, yellow crystals, Malan and Roux, 1974; Van der Merwe et al., 1972). Fractions 39–46 (8 g), subjected to column chromatography over silica gel, yielded mainly β-stigmasterol glucoside (compared with authentic sample).

Table 2
^{1}H (δ, $CDCl_3$, 600 MHz) and ^{13}C (δ, $CDCl_3$, 150 MHz) NMR data together with important HMBC correlation observed for compound **6**

Position	^{1}H	^{13}C	^{2}J-and ^{3}J correlated carbons
1		113.8 (s)	
2	7.53 (d, 1.9)	117.9 (d)	C-4, C-6
3		145.7 (s)	
4		148.4 (s)	
5	6.85 (d, 8.2)	115.7 (d)	C-3
6	7.26 (dd, 8.2, 1.9)	125.4 (d)	C-1, C-4
α		146.7 (s)	
β	6.71 (s)	98.4 (d)	C-1, C-2, C-α, C-β′
β′		183.4 (s)	
1′		124.5 (s)	
2′		168.8 (s)	
3′	6.69 (d, 1.9)	113.6 (d)	C-2′, C-4′
4′		167.4 (s)	
5′	6.70 (dd, 8.3, 1.9)	113.1 (d)	C-4′, C-6′
6′	7.60 (d, 8.3)	125.8 (d)	C-4′, C-β′

Chemical shifts are in ppm from TMS. Multiplicities and coupling constants (in Hz) are given in parentheses.

3.2. *T. africana*

The air-dried and powdered leaves of *T. africana* (1.5 kg) were successively soaked in 5 l of CH_2Cl_2–MeOH (1:1) mixtures and 3 l of MeOH for 24 and 2 h, respectively, at room temperature. Solvents were removed under reduced pressure and the two extracts which were similar in composition as judged by TLC were combined to give a dark green residue (300 g). Part of this residue (49 g) was subjected to vacuum liquid chromatography (VLC) on silica gel 60 (180 g) and eluted with petroleum ether–EtOAc (2:3) mixtures and EtOAc to give 34 fractions of 250 ml each. These were further combined on the basis of their TLC profiles. Fractions 1–4 (3 g) eluted with petroleum ether–EtOAc (9:1) were treated with acetone to yield 5 mg of lupeol (**7**, white powder, Burns et al., 2000). Fractions 5–11 (5 g) obtained from petroleum ether–EtOAc (3:1) were treated in acetone to give 5 mg of lupeol acetate (**8**, white powder, Rao, 1962). The mother liquor after column chromatography over silica gel, gave 2 mg of apigenin (**9**, yellow powder, Aquil et al., 1993). Combined fractions 12–30 (25 g) and 31–34 (3 g) eluted with 70% petroleum ether–EtOAc and EtOAc, respectively, were passed through a Sephadex LH-20 column and subjected successively to silica gel CC and preparative TLC to give 4 mg of epiphyllocoumarin (**10**, white solid, Foo, 1989), 3 mg of catechin (**11**, yellow powder, comparison with authentic sample), 39 mg of 4-hydroxybenzoic acid (**12**, yellow powder, Klick and Herrmann, 1988) and 15 mg of 6,9-dihydroxymegastigmane-3-one (**4**).

The structures of these secondary metabolites (Fig. 1) were established using spectroscopic analysis, especially, 1D NMR in conjunction with 2D experiments (COSY, HMQC and HMBC), and physical data compared with those published. Although compounds **2** (Wandji et al., 1990; Achenbach et al., 1986), **3** (Tadahiro et al., 1977) and **6** (Malan and Roux, 1974; Van der Merwe et al., 1972) are listed in the literature, this is the first complete report on their full ^{1}H and ^{13}C NMR assignments (Tables 1 and 2).

4. Chemotaxonomic significance

A recent study on the phylogenetic relationships of plants belonging to the Moraceae family resulted in the reclassification of tribes and a revision of the limits of the tribes Artocarpeae, Moreae and Castilleae to reflect evolutionary relationships (Datwyler and Weiblen, 2004). The genus *Treculia* was placed in the revised tribe Artocarpeae on the basis of morphology by these authors in conformity with earlier classifications (Rohwer, 1993; Takhtajan, 1997). According to Rohwer (1993) the genus *Treculia* consists of three species namely, *T. africana*, *T. obovoidea* and *T. acuminata*. Phytochemical information on the genus *Treculia* is scanty. There is no previous report on *T. acuminata* and only one compound, a peptide, is reported from *T. obovoidea* (Bokesch et al., 2004). Through this work, two chalcones and four flavonoid derivatives are identified from *T. acuminata* and *T. africana*, respectively. This observation, together with the earlier report of a chalcone and a coumarin from *T. africana* (Moody et al., 2006) suggests that polyphenols may be the major constituents of the genus *Treculia*. 6,9-Dihydro-megastigmane-3-one is isolated from both *T. africana* and *T. acuminata*. This compound may tentatively be considered as a marker of the *Treculia* genus. Isobavachalcone (**5**), previously isolated from several species of the genus *Dorstenia* (Watchueng, 2004; Dongo, 2001; Ngadjui et al., 1998; Abegaz et al., 1998, 2000), can be used to establish intertribal relationship between the two genera *Treculia* and *Dorstenia*. The isolation of six compounds from *T. acuminata* and seven from *T. africana* is the first significant phytochemical report and may be used as foundation for further chemotaxonomic studies on the genus.

Acknowledgements

F.N. and B.T.N. are grateful to the Third World Academic of Science (TWAS) for travel grant and to the Network of Analytical and Bioassay Services in Africa (NABSA) for a 3-months maintenance grant to the University of Botswana. The Chemistry Department of the University of Botswana is acknowledged for providing research facilities.

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