EUROPEAN JOURNAL OF BIOMEDICAL AND PHARMACEUTICAL SCIENCES
http://www.ejbps.com

ISSN 2349-8870
Volume: 5
Issue: 02
71-75
Year: 2018

ISOCOUMARINS DERIVATIVES FROM *DIOSPYROS SOUBREANA* (EBENACEAE)

Boué Guy Blanchard[1], Kabran Aka Faustin[1], Garcia Gabriel[2], Tomi Félix[2] and Tonzibo Zanahi Félix[1]*

[1]Laboratoire De Chimie Organique Biologique, UFR Sciences Des Structures De La Matière et Technologie, Université Félix Houphouët-Boigny, 22 BP 582 Abidjan 22, Côte d'Ivoire.
[2]Laboratoire Sciences pour l'Environnement, UMR CNRS 6134 SPE, Equipe Chimie et Biomasse, Université de Corse, Route des Sanguinaires, 20000 Ajaccio, France.

***Corresponding Author: Tonzibo Zanahi Félix**
Laboratoire De Chimie Organique Biologique, UFR Sciences Des Structures De La Matière et Technologie, Université Félix Houphouët-Boigny, 22 BP 582 Abidjan 22, Côte d'Ivoire.

Article Received on 30/11/2017 **Article Revised on 20/12/2017** **Article Accepted on 10/01/2018**

ABSTRACT
Phytochemical investigation of the leaves and the bark of trunks of *Diospyros soubreana* led to the isolation of three isocoumarins namely 4-*O*-galloylnorbergenin (**1**), norbergenin (**2**) and bergenin (**3**). Their structures were elucidated by spectral analysis including MS, 1D and 2D-NMR spectroscopy. All these compounds were isolated from this plant for the first time.

KEYWORDS: Ebenaceae, *Diospyros soubreana*, isocoumarins, NMR spectroscopy.

INTRODUCTION
Diospyros (Ebenaceae) are deciduous and evergreen trees, shrubs and small bushes of over 700 species (Rashed et al., 2014) widely distributed in the tropical and subtropical regions of the world, notably in central Africa and south east Asia (Ganapaty et al., 2006; Zhong et al., 1984). This genus is the most important, both numerically and economically of the Ebenaceae family (Uc-Cachón et al., 2013). *Diospyros* are known for their richness in bioactive compounds, mainly triterpenoids (Ragasa et al., 2009; Fan et al., 2006; Nareeboon et al., 2006; Mallavadhani et al., 2001), naphthalene derivatives (Matsushita et al., 2010; Salae et al., 2010; Pathak et al., 2004; Gondo et al., 1999), naphtoquinones (Chang et al., 2007; Tangmouo et al., 2006; Ganapaty et al., 2005; Tezuka et al., 1973), flavonoids (Xie et al., 2015; Sahu et al., 2012; Ito et al., 2011) and coumarin derivatives (Akak et al., 2010; Paknikar et al., 1996).

Diospyros soubreana F. White (also named *Maba soubreana* A. Chev.) is shrub or tree to 5 m high in undergrowth of high closed-forest, from Ivory Coast to South Nigeria. The barks are black outside and pale orange-brown inside. The fruits are dark red. Few ethnopharmacological applications have been reported for this species.

Indeed, the leaves are used in Côte d'Ivoire as wound healing (Bouquet and Debray, 1974; Kerharo and Bouquet, 1950). To the best of our knowledge, no phytochemical study has been reported on this plant species. This investigation reports the isolation and structural elucidation of three isocoumarin derivatives.

MATERIAL AND METHODS
The ^{1}H and ^{13}C NMR, as well as 2D spectra (COSY, HSQC, HMBC and NOESY), were recorded on a Bruker Avance 400 Fourier Transform spectrometer operating at 400 MHz for ^{1}H spectra and 100 MHz for ^{13}C using CD_3OD and Me_2CO-d_6 as deuterated solvents. The chemical shift was expressed in ppm from TMS (internal standard). ESIMS was acquired using a Bruker Esquire spectrometer. The chromatography columns were performed on silica gel (Merck, 40-63 µm, 35-70 µm and 60-200 µm) or Sephadex® LH-20 (Pharmacia). Thin-layer chromatographies were carried out on aluminium plates coated with silica gel 60-F_{254} (Merck), and visualized with UV light (254 and 366 nm) then sprayed with vanillin-H_2SO_4 and $FeCl_3$.

Plant material
Leaves and bark of trunks of *D. soubreana* were collected in July 2014 in « Petit Yapo » forest, Agboville Department, south-east of Côte d'Ivoire. The plant samples were identified by a botanist of Centre National de Floristique (CNF), University Félix Houphouët-Boigny of Cocody-Abidjan, where voucher specimens are deposited. The samples were dried at room temperature, then ground.

Isolation
100 g of leaves powder were extracted by maceration with the mixture water/ethanol (70: 30) for 24 h at room temperature. After filtration and the removal of the solvent under reduced pressure, a residue of 25.5 g was obtained. 15 g of this residue was suspended in ethanol

70% and extracted sequentially with increasing polarity solvents to give after evaporation 0.88 g of *n*-hexane (DSFH), 1.82 g of dichloromethane (DSFD) and 2.39 g of ethyl acetate (DSFA) extracts.

Powdered bark of trunks (120 g) were extracted in a Soxhlet apparatus, firstly with petroleum ether and then with dichloromethane, followed by maceration in ethyl acetate at room temperature. Extracts were filtered and concentrated under reduced pressure to give 0.8 g of petroleum ether (DSTPE), 1.2 g of dichloromethane (DSTD) and 9.7 g of ethyl acetate (DSTA) extracts.

An other part of the dried leaves (100 g) was treated as above (in a Soxhlet apparatus followed by maceration at room temperature) with petroleum ether, ethyl acetate and methanol to give 2.7 g, 6 g and 15.9 g of the corresponding extracts (DSFPE, DSFA1 and DSFM respectively).

The leaves ethyl acetate extract (DSFA) (401.7 mg) was subjected to a silica gel CC (40-63 µm) eluting with a gradient elution of hexane/ethyl acetate (50: 50 → 0: 100) then ethyl acetate/methanol (95: 5) to give two fractions (F1 and F2). The fraction F2 (160.9 mg) was successively subjected to a Sephadex® LH-20 column ($CHCl_3$/MeOH, 1: 1) and a silica gel (35-70 µm) column (EtOAc/MeOH, 80: 20) to yield 28 mg of 4-*O*-galloylnorbergenin (**1**).

3 g of the extract DSTA were chromatographed on a silica gel (60-200 µm) column (CH_2Cl_2/EtOAc, 100: 0 → 0: 100) to give six fractions (T1-T6). Fraction T5 (791 mg) was treated on a silica gel (60-200 µm) using EtOAc/MeOH (90: 10) as eluent to provide 98 mg of Bergenin (**3**).

A part of the extract DSFM (2 g) was subjected to a vacuum chromatography eluted with EtOAc/MeOH (100: 0 → 70: 30) to give four fractions (M1-M4). The fraction M3 (593.9 mg) was purified by silica gel chromatography (35-70 µm) with $CHCl_3$/MeOH (70: 30) to give two major fractions (M3A and M3B). The fraction M3B (215.4 mg) was treated on Sephadex® LH-20 column ($CHCl_3$/MeOH, 70: 30) and preparative thin layer chromatography (Merck $60F_{254}$, 20 x 20 x 0.5 cm, $CHCl_3$/MeOH, 70: 30) to yield 16.3 mg of Norbergenin (**2**).

Identification of compounds 1, 2 and 3

4-O-galloylnorbergenin (1): Brown amorphous powder; ^1H and ^{13}C NMR (400 MHz, Me_2CO-d_6) data in **Table 1**; ESI-MS (*m/z*): 465 $[M-H]^-$, 489 $[M+Na]^+$, 955 $[2M+Na]^+$ (molecular formula $C_{20}H_{18}O_{13}$).

Norbergenin (2): White needles; ^1H and ^{13}C NMR (400 MHz, CD_3OD) data in **Table 1**; molecular formula $C_{13}H_{14}O_9$.

Bergenin (3): White shiny crystals; ^1H and ^{13}C NMR (400 MHz, CD_3OD) data in **Table 1**; ESI-MS (*m/z*): 329 $[M+H]^+$ (molecular formula $C_{14}H_{16}O_9$).

RESULTS AND DISCUSSION

Purification of the bark of trunks ethyl acetate extract and the leaves methanol extract by chromatography on various stationary phases (silica, Sephadex® LH-20 and preparative thin layer) led to compounds **1**, **2** and **3**. This paper deals with their structural elucidation.

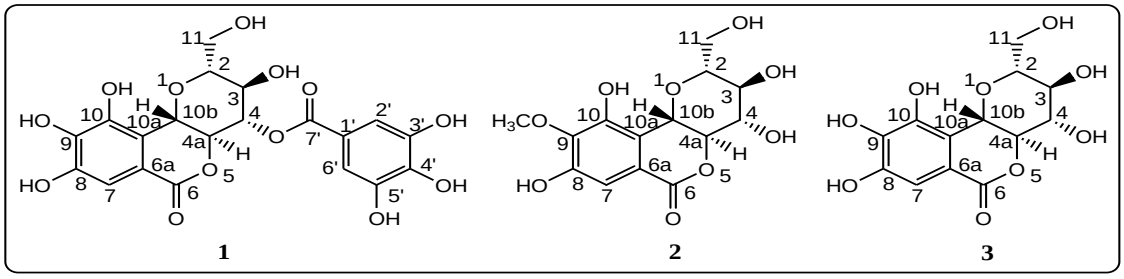

Figure 1: Structures of compounds 1, 2 and 3.

Compound **1** (**Fig. 1**) was isolated as a brown amorphous powder. In thin-layer chromatography, **1** was detected using a UV lamp at 254 nm as a dark brown spot by spraying with $FeCl_3$ solution indicating its phenolic nature. Its ESI mass spectrum showed a pseudo-molecular ion at *m/z* 465.2 $[M-H]^-$ in agreement with the molecular formula $C_{20}H_{18}O_{13}$.

The ^1H and ^{13}C NMR spectra of **1** (**Table 1**) showed a galloyl group in the aromatic region [δ_H 7.14 (2H, s, galloyl-2', 6')] and [δ_C 166.3 (C-7'), 146.2 (C-3', 5'), 139.0 (C-4'), 121.6 (C-1'), 110.3 (C-2', 6')] (Subeki et al., 2005; Li et al., 2015), along with a norbergenin nucleus [δ_H 7.08 (1H, s, H-7), 5.56 (1H, dd, *J* = 8.5, 9.8 Hz, H-4), 5.13 (1H, d, *J* = 10.5 Hz, H-10b), 4.39 (1H, dd, *J* = 9.8, 10.5 Hz, H-4a), 3.82 (1H, m, H-2), 3.78 (1H, m, H-3), 3.76 (2H, m, H-11)] and [δ_C 163.6 (C-6), 146.8 (C-8), 143.3 (C-10), 140.0 (C-9), 114.7 (C-10a), 116.6 (C-6a), 110.7 (C-7), 82.7 (C-2), 78.4 (C-4a), 75.9 (C-4), 73.9 (C-10b), 70.1 (C-3), 62.4 (C-11)] (Saijo et al., 1990; Taneyama et al., 1983). The linkage of norbergenin nucleus and galloyl moieties was determined to be between the C-4 of the norbergenin nucleus and the C-7' of the galloyl moiety (in *J*-3) because of the cross-peak observed in HMBC spectrum between the H-4 (norbergenin nucleus) and C-7' (galloyl moiety) (**Fig. 2**).

From these spectral data, the structure of compound **1** was elucidated as 4-*O*-galloylnorbergenin (**Fig. 1**) (Tangmouo et al., 2009; Saijo et al., 1990).

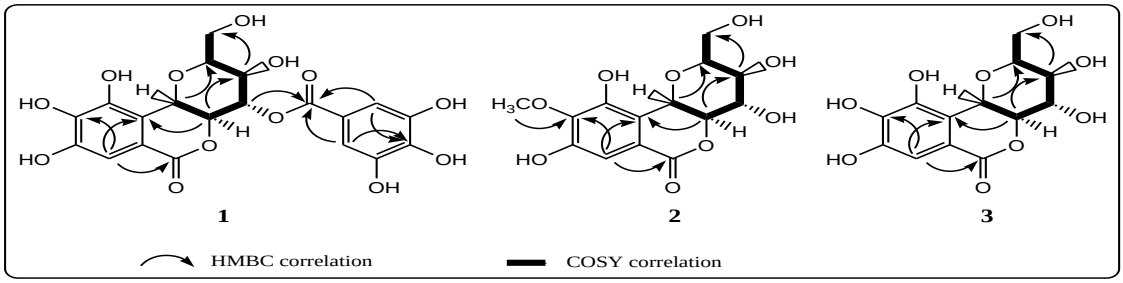

Figure 2: Important COSY and HMBC correlations for compounds 1, 2 and 3.

Compound **2** obtained as white needles, gave a positve result for the ferric chloride reaction, revealing its phenolic nature. ^{1}H and ^{13}C NMR spectra of **2** (**Table 1**) were quite similar to those of **1** except the lack of the galloyl group. Analysis of these spectra indicated that compound **2** was norbergenin (Nazir et al., 2011). Indeed, the ^{1}H spectrum of **2** exhibited one aromatic proton at δ 7.09 (1H, s) and a *C*-glycosyl moiety at δ 3.42-4.94. The ^{13}C spectrum of **2** exhibited 13 carbon signals including a *C*-glycosyl moiety at δ 83.0 (C-2), 81.5 (C-4a), 75.7 (C-4), 74.4 (C-10b), 72.0 (C-3) and 62.8 (C-11), one substituted benzene moiety at δ 147.4 (C-8), 143.8 (C-10), 141.5 (C-9), 117.4 (C-6a), 114.2 (C-10a) and 111.0 (C-7), and one ester carbonyl carbon at δ 166.6 (C-6) characteristics of norbergenin (**Fig. 1**) (Taneyama et al., 1983).

Compound **3** was isolated as white shiny crystals. It also gave a positive test with ferric chloride indicating its phenolic nature. ^{1}H and ^{13}C NMR spectra of **3** which were very similar to those of **2** indicated that the two compounds had in common the norbergenin nucleus with the presence of one supplementary methoxyl group in the structure of **3**. Indeed, the norbergenin nucleus was perceptible at [δ_H 7.08 (1H, s, H-7), 3.81 (1H, dd, *J* = 8.8, 9.4 Hz, H-4), 4.95 (1H, d, *J* = 10.4 Hz, H-10b), 4.06 (1H, dd, *J* = 9.4, 10.4 Hz, H-4a), 3.66 (1H, dd, *J* = 6.0, 8.8 Hz, H-2), 3.43 (1H, dd, *J* = 8.8, 9.5 Hz, H-3), 3.69 (2H, m, H-11)] and [δ_C 165.8 (C-6), 152.4 (C-8), 149.5 (C-10), 142.3 (C-9), 117.3 (C-10a), 119.5 (C-6a), 111.1 (C-7), 83.1 (C-2), 81.5 (C-4a), 75.7 (C-4), 74.3 (C-10b), 71.9 (C-3), 62.7 (C-11)] (Saijo et al., 1990; Taneyama et al., 1983). In addition, the additional methoxyl group was observable at δ 3.90 (1H, s) ppm on the ^{1}H NMR spectrum, and at δ 60.9 ppm on the ^{13}C NMR spectrum. The position of the hydroxyl group on carbon C-9 (δ_C 142.3) was specified by the correlation between protons at δ 3.90 ppm and that carbon on the HMBC spectrum. Based on the above evidence and according to the literature (Saijo et al., 1990; Nazir et al., 2011), the structure of **3** was determined to be bergenin (**Fig. 1**).

Table 1. ^{1}H and ^{13}C NMR data for compounds 1, 2 and 3.

Position	1[a]		2[b]		3[b]	
	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
2	3.82, 1H, m	82.7	3.68, 1H, m	83.0	3.66, 1H, dd (8.8, 6)	83.1
3	3.78, 1H, m	70.1	3.42, 1H, m	72.0	3.43, 1H, dd (9.5, 8.8)	71.9
4	5.56, 1H, dd (9.80, 8.5)	75.9	3.81, 1H, dd (9.2, 8.8)	75.7	3.81, 1H, dd (9.4, 8.8)	75.7
4a	4.39, 1H, dd (10.5, 9.8)	78.4	4.03, 1H, dd (10.4, 9.2)	81.5	4.06, 1H, dd (10.4, 9.4)	81.5
6	-	163.6	-	166.6	-	165.8
6a	-	116.6	-	117.4	-	119.5
7	7.08, 1H, s	110.7	7.09, 1H, s	111.0	7.08, 1H, s	111.1
8	-	146.8	-	147.4	-	152.4
9	-	140.0	-	141.5	-	142.3
10	-	143.3	-	143.8	-	149.5
10a	-	114.7	-	114.2	-	117.3
10b	5.13, 1H, d (10.5)	73.9	4.94, 1H, d (10.4)	74.4	4.95, 1H (10.4)	74.3
11	3.76, 2H, m	62.4	3.68, 2H, m	62.8	3.69, 2H, m	62.7
1’	-	121.6	-	-	-	-
2’, 6’	7.14, 2H, s	110.3	-	-	-	-
3’, 5’	-	146.2	-	-	-	-
4’	-	139.0	-	-	-	-
7’	-	166.3	-	-	-	-
OCH_3	-	-	-	-	3.90, 3H, s	60.9

a: In Me_2CO-d_6
b: In CD_3OD

Isocoumarins are a class of compounds distributed sporadically but broadly in nature. They have been isolated from microorganisms, insects and plants. In Angiosperms, they are frequently found in the families Fabaceae, Asteraceae, Apiaceae and Rutaceae (Bruneton, 2009). Moreover, they are to a small extent represented in Euphorbiaceae and in their sister taxon, Phyllanthaceae (*Flueggea* genus) (Seigler, 1994). These compounds possess various biological activities such as anti-inflammatory, antifungal, antimicrobial, antibacterial, phytotoxic, cytotoxic and antiviral properties (Saddiqa et al., 2017; Pal et al., 2011; Hill, 1986).

CONCLUSION

This present study investigated for the first time the isolation and structural determination of compounds from *Diospyros soubreana*. It led to the isolation and characterization of three isocoumarins derivatives: bergenin, norbergenin and 4-*O*-galloylnorbergenin, all isolated for the first time from this species. This work thus contributes to the chemical characterization of this species.

To provide scientific evidence of traditional medicine uses of *D. soubreana*, biological assessments will be carried out.

REFERENCES

1. Akak, C.M., Djama, C.M., Nkengfack, A.E., Tu, P-F., Lei, L-D. New coumarin glycosides from the leaves of *Diospyros crassiflora* (Hiern). *Fitoterapia*, 2010; 81: 873-877.
2. Bouquet, A., Debray, M. Plantes médicinales de la Côte d'Ivoire. Travaux et documents de l'ORSTOM. ORSTOM, Paris, 1974; 232.
3. Bruneton, J. Pharmacognosie, Phytochimie, Plantes médicinales. 4e Ed, 2009; 1269p.
4. Chang, C-I., Huan, S-L., Kuo, Y.H. Two new naphthoquinones from the stem of *Diospyros maritima*. *J. Asian Nat. Prod. Res*, 2007; 9: 153-158.
5. Fan, J-P., He, C-H. Simultaneous quantification of three major bioactive triterpene acids in the leaves of *Diospyros kaki* by high-performance liquid chromatography method. *J. Pharm. Biomed. Anal*, 2006; 41: 950-956.
6. Ganapaty, S., Thomas, S.P., Karagianis, G., Waterman, P.G. Mono and dimeric naphthalene derivatives from the roots of *Diospyros assimilis*. *Nat. Prod. Res*, 2006; 20: 783-787.
7. Ganapaty, S., Thomas, P.S., Mallika, B.N., Balaji, S., Karagianis, G., Waterman, P.G. Dimeric naphthoquinones from *Diospyros discolor*. *Biochem. Syst. Ecol*, 2005; 33: 313-315.
8. Gondo, M., Tanaka, N., Tanaka, T., Shimomura, K., Nakanishi, F., Ishimaru, K. A naphthalene glycoside from callus cultures of *Diospyros kaki*. *Phytochemistry*, 1999; 51: 879-881.
9. Hill, R.A. Naturally occurring isocoumarins. In: Progress in the Chemistry of Organic Natural Products, 49, Wien, New York: Springer Verlag, 1986; 1-78.
10. Ito, T., Ohguchi, K., Nakajima, C., Oyama, M., Linuma, M., Nozawa, Y., Akao, Y., Ito, M. Inhybitory effects of flavonoid glycosides isolated from the peel of Japanese persimmon (*Diospyros kaki Fuyu*) on antigen-stimulated degranulation in rat basophilic leukaemia RBL-2H3 cells. *Food Chem*, 2011; 126: 289-294.
11. Kerharo, J., Bouquet, A. Plantes médicinales et toxiques de la Côte d'Ivoire - Haute-Volta: mission d'étude de la pharmacopée indigène en A.O.F. Vigot Frères, Paris, 1950; 297.
12. Li, C-W., Dong, H-J., Cui, C-B. The synthesis and antitumor activity of twelve galloyl glucosides. *Molecules*, 2015; 20: 2034-2060.
13. Mallavadhani, U.V., Panda, A.K., Rao, Y.R. *Diospyros melanoxylon* leaves: A rich source of pentacyclic triterpenes. *Pharm. Biol*, 2001; 39: 20-24.
14. Matsushita, Y., Jang, I-C., Imai, T., Fukushima, K., Lee, S-C. Naphthalene derivatives from *Diospyros kaki*. *J. Wood Sci*, 2010; 56: 418-421.
15. Nareeboon, P., Kraus, W., Beifuss, U., Conrad, J., Klaiber, I., Sutthivaiyakit, S. Novel 24-nor-, 24-nor-2,3-*seco*-, and 3,24-dinor-2,4-*seco*-ursane triterpene from *Diospyros decandra:* evidences for ring A biosynthetic transformations. *Tetrahedron*, 2006; 62: 5519-5526.
16. Nazir, N., Koul, S., Qurishi, A.M., Najar, M.H., Zargar, M.I. Evaluation of antioxidant and antimicrobial activities of bergenin and its derivatives obtained by chemoenzymatic synthesis. *Eur. J. Med. Chem*, 2011; 46: 2415-2420.
17. Pathak, A., Kulshreshtha, D.K., Maurya, R. Coumaroyl triterpene lactone, phenolic and naphthalene glycoside from stem bark of *Diospyros angustifolia*. *Phytochemistry*, 2004; 65: 2153-2158.
18. Paknikar, S.K., Pai, Fondekar, K.P., Kirtany, J.K., Natori, S. 4-hydroxy-5-methylcoumarin derivatives from *Diospyros kaki* Thunb and *D. kaki* Var. *Sylvestris* Makino; structure and synthesis of 11-methylgerberinol. *Phytochemistry*, 1996; 41: 931-933.
19. Pal,S., Chatare, V., Pal, M. Isocoumarin and its derivatives: An overview on their synthesis and applications. *Curr. Org. Chem*, 2011; 15(5): 782-800.
20. Ragasa, C.Y., Puno, M.R.A., Sengson, J.M.A.P., Shen, C-C., Rideout, J.A., Raga, D.D. Bioactive triterpenes from *Diospyros blancoi*. *Nat. Prod. Res*, 2009; 23: 1252-1258.
21. Rashed, K., Ciric, A., Glamoclija, J., Sokovic, M. Antibacterial and antifungal activities of methanol extract and phenolic compounds from *Diospyros virginiana* L. *Ind. Crops Prod*, 2014; 59: 210-215.
22. Saddiqa, A., Usman, M., Cakmak, O. Isocoumarins and 3,4-dihydroisocoumarins, amazing natural products: a review.*Turk. J. Chem*, 2017; 41: 153-178.

23. Sahu, R., Dewanjee, S., Dua, T.K., Gangopadhyay, M., Das, A.K., Dey, S.P. Dereplication coupled with *in vitro* antioxidant assay of two flavonoid glycosides from *Diospyros peregrina* fruit. *Nat. Prod. Res*, 2012; 26: 454-459.
24. Saijo, R., Nonaka, G-I., Nishioka, I. Gallic acid esters of bergenin and norbergenin from *Mallotus japonicus*. *Phytochemistry*, 1990; 29: 267-270.
25. Salae, A-W., Karalai, C., Ponglimamont, C., Kanjana-Opas, A., Yuenyongsawad. Naphthalene derivatives from *Diospyros wallichii*. *Can. J. Chem*, 2010; 88: 922-927.
26. Seigler, D.S. Phytochemistry and systematic of the Euphorbiaceae. *Ann. Mo. Bot. Gard*, 1994; 81: 380-401.
27. Subeki, S., Matsuura, H., Takahashi, K., Yamasaki, M., Yamato, O., Maede, Y., Katakura, K., Kobayashi, S., Trimurningsih, T., Chairul, C., Yoshihara, T. Anti-babesial and anti-plasmodial compounds from *Phyllanthus niruri*. *J. Nat. Prod*, 2005; 68: 537-539.
28. Taneyama, M., Yoshida, S., Kobayashi, M., Hasegawa, M. Isolation of norbergenin from *Saxifraga stolonifera*. *Phytochemistry*, 1983; 22: 1053-1054.
29. Tangmouo, J.G., Ho, R., Lannang, A.M., Komguem, J., Lontsi, A.T. Norbergenin derivatives from the stem bark of *Diospyros sanza-minika* (Ebenaceae) and their radical scavenging activity. *Phytochem. Lett*, 2009; 2: 192-195.
30. Tangmouo, J.G., Meli, A.L., Komguem, J., Kuete, V., Ngounou, F.N., Lontsi, D., Beng, V.P., Choudhary, I.M., Sondengam, B.L. Crassiflorone, a new naphthoquinone from *Diospyros crassiflora* (Hien). *Tetrahedron Lett*, 2006; 47: 3067-3070.
31. Tezuka, M., Takahashi, C., Kuroyanagi, M., Satake, M., Yoshihira, K., Natori, S. New naphthoquinones from *Diospyros*. *Phytochemistry*, 1973; 12: 175-183.
32. Uc-Cachón, A.H., Molina-Salinas, G.M., Said-Fernández, S., Méndez-González, M., Cáceres-Farfán, M., Borges-Argáez, R. A new naphthoquinone from *Diospyros anisandra*. *Nat. Prod. Res*, 2013; 27: 1174-1178.
33. Xie, C., Xie, Z., Xu, X., Yang, D. Persimmon (*Diospyros kaki* L.) leaves: A review on traditional uses, phytochemistry and pharmacological properties. *J. Ethnopharmacol*, 2015; 163: 229-240.
34. Zhong, S-M., Waterman, P.G., Jeffreys, A.D. Naphthoquinones and triterpenes from african *Diospyros* species. *Phytochemistry*, 1984; 23: 1067-1072.