Journal of Pharmacognosy and Phytochemistry

Available online at www.phytojournal.com

J P P Journal of Pharmacognosy and Phytochemistry

E-ISSN: 2278-4136
P-ISSN: 2349-8234
JPP 2015; 4(1): 55-56
Received: 01-02-2015
Accepted: 12-03-2015

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Secondary metabolites of *Phellolophium madagascariensis*

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Abstract
A new fatty alcohol 1-icos-17-en-1-ol (**1**), 1-octacosanol (**2**), 1-triacontanol (**3**), Umbelliferone (**4**) and skimmin (**5**), were isolated from the aerial parts of *Phellolophium madagascariensis* (Apiaceae), an endemic species of Madagascar. Structure elucidations of the compounds were performed by using spectroscopic methods (1-D and 2-D NMR, EI-MS) and comparison with literature data. To the best of our knowledge, all of the compounds have been isolated for the first time from *Phellolophium madagascariensis.*

Keywords: *Phellolophium madagascariensis*, Fatty alcohol, Coumarin, NMR, EI-MS

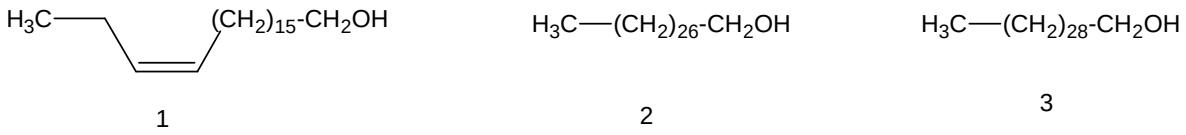
1. Introduction
Plant source
The genus *Phellolophium*, endemic to Madagascar, belongs to the Apiaceae family. The genus contains two species, *P. madagascariensis* and *P. sp.* It has been discovered and described for the first time in 2004 by F. Sales *et al.* [1]. *Phellolophium madagascariensis* is known Tongotramboabe as a vernacular name. The aerial part of the plant is used as an infusion to treat problems of indigestion, gastralgic pain, intestinal disturbances [2], and externally to treat skin diseases such as scabies, acne, and leprosy. The steam is utilized to the treatment of nervous disorders (hysteria, chlorosis) and spasmodic affections [3].
The leaves of *Phellolophium madagascariensis* were collected in September 2012 in Andramasina, a village not far from the capital of Madagascar. The plant was authenticated at the botanical and zoological park of Tsimbazaza Antananarivo Madagascar where a voucher specimen is deposited.

2. Previous Studies
Chemical and pharmacological study of essential oil from *Phellolophium madagascariensis* has been described by H. Andriamanantoanina *et al.* in 2006. They reported the identification of 33 chemical compounds. Limonene (58.5%) and sabinene (30.25%) were the major products [3].
C. Rivière *et al.* revealed the presence of three antiproliferative coumarins in the *Phellolophium madagascariensis*: Osthol, Murraol and Meranzin [2].

3. Present Study
The dried leaves powder (100 g) of *Phellolophium madagascariensis* were macerated with hexane, dichloromethane, ethyl acetate and methanol thrice for each solvent at room temperature. The extracts of each solvent were filtrated and evaporated under reduced pressure to afford 2,2 g of hexane crude extract, 6,54 g of dichloromethane crude extract, 8,9 g of ethyl acetate crude extract and 7,05 g of methanol extract.
The CH_2Cl_2 extract was subjected to column chromatography over silica gel (Merck), using Petrol ether, EtOAc with increasing polarity. Three compounds **1** (5mg), **2** (9mg) and **3** (13mg) were isolated. The ^1H NMR and ^{13}C NMR spectra of **1-3** showed the presence of fatty alcohols compounds. On their mass spectrum EI-MS, the loss of a water molecule is observed before the appearance of the first peak. The compound **3** is recognized as 1-triancontanol from the given spectral and by comparison with the literature data [4]. The comparison of the EIMS spectra of **2** and **3** allowed concluding that compound **2** is an 1- octacosanol. The ^1H NMR spectrum of **1** showed the presence of two signals at δ 7.55 ppm (d) and 7.75 ppm (d) with a coupling constant J = 8 Hz, indicated the presence of cis olefinic protons. This is confirmed by

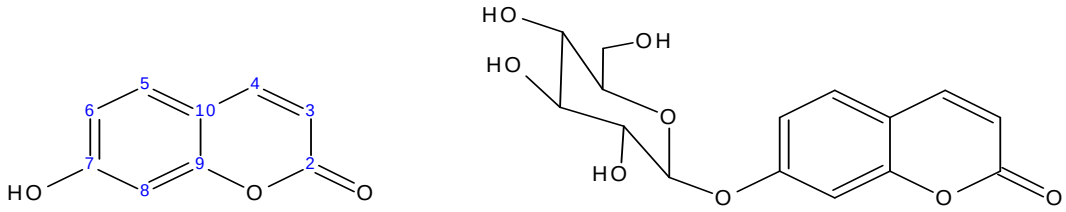
the signals at δ 129.2 ppm and 131.2 ppm observed in the ^{13}C NMR spectrum. The presence of the alcohol function is indicated by the peak at 63.5 ppm. The first peak of its EI-MS appeared at m/z 278, indicating a molecular weight of 296. The peak at m / z 223 is attributed to the loss of m/z 55 and determined the position of the double bond at C-17. **1** is identified as a 1-icos-17- enol. To the best of our knowledge it is the first time that this compound is discovered from natural resource.

The MeOH extract was similarly chromatographed on silica gel using the system MeOH/ CH_2Cl_2 (8:2; v:v) as an elution. Three fractions (A-C) were obtained. Fraction B was submitted on reverse phase column chromatography over RP8 using MeOH - Water (8:2) as an elution. Two coumarins, **4** (17 mg) and **5** (15 mg), were isolated. The NMR spectra of **4** and **5** are similar and showed coumarin skeleton. The only difference was the presence of glucosyl moiety in **5**. They are identified respectively as Umbelliferone [5] and skimmin [6] by means of 1-D and 2-D NMR spectra and comparison with literature data.



1 2 3

Fig 1: Fatty alcohols isolated from *Phellolophium madagascariensis*



4 5

Fig 2: Coumarins isolated from *Phellolophium madagascariensis*

1-icos-17-en-1-ol (1): $C_{20}H_{39}OH$, white powder; EIMS: 278, 223, 149, 137, 123, 111, 97, 83, 69, 55; ^{13}C NMR (400 MHz in $CDCl_3$): δ (ppm) 14.5 (-CH_3, C-1), 23.0 (-CH_2), 26.1 (-CH_2), 29.9 (-CH_2), 30.0 (-CH_2x11), 32.5 (-CH_2), 33.3 (-CH_2), 63.5 (-CH_2OH), 129.2 (-CH, C-17), 131.2 (-CH, C-18).

1- octacosanol (2): $C_{28}H_{57}OH$, white powder; EIMS: 392, 279, 167, 149, 139, 125, 111, 97, 83, 71, 57; ^{13}C NMR (400 MHz in $CDCl_3$): δ (ppm) 14.5 (-CH_3, C-1), 23.0 (-CH_2), 26.1 (-CH_2), 29.9 (-CH_2), 30.0 (-CH_2x21), 32.5 (-CH_2), 33.3 (-CH_2), 63.5 (-CH_2OH).

1-triacontanol (3): $C_{30}H_{61}OH$, white powder; EIMS: 420, 392, 181, 167, 153, 139, 125, 111, 97, 83, 69, 57; ^{1}H NMR (400 MHz in $CDCl_3$): δ (ppm) 0.9 (t, 3H), 1.25 (s, 54 H), 1.55 (m, 4H), 3.64 (t, 2H); ^{13}C NMR (400 MHz in $CDCl_3$): δ (ppm) 14.5 (-CH_3, C-1), 23.1 (-CH_2), 26.1 (-CH_2), 29.9 (-CH_2), 30.1 (-CH_2x23), 32.3 (-CH_2), 33.2 (-CH_2), 63.5 (-CH_2OH).

Umbelliferone (4): white - yellow crystals: ^{1}H NMR (400 MHz in $CDCl_3$): δ (ppm) 6,30 (1H, d, J=10Hz, H-3), 7.1 (1H, s, H-8), 7.2 (1H, d, J=8 Hz, H-6), 7.50 (1H, d, J=10 Hz, H-5), 7.90 (1H,d,9,3Hz, H-4); ^{13}C NMR (400 MHz in $CDCl_3$): δ (ppm) 102.0 (-CH, C-6), 112.9 (-CH, C-3), 114.0 (-Cq, C-8), 114.3 (-CH, C-10), 129.4 (-CH, C-5), 144.6 (-CH, C-4), 155.8 (-Cq, C-9), 161.1 (-Cq, C-7), 162.1 (Cq,C-2).

Skimmin (5) white crystals: ^{1}H NMR (400 MHz in $CDCl_3$)): δ (ppm) 3.45 (1H, m, H-4'), 3.5 (2H, m, H-2', H-3'), 3.52 (1H, m, H-5'), 3.72 (1H, q, H-6'), 3.94 (1H, d, H-6'), 5.06 (1H, d, J=7.5 Hz, H-1'), 6.31 (1H, d, J=10 Hz, H-3), 7.1 (1H, s, H-8), 7.2 (1H, d, J=8 Hz, H-6), 7.58 (1H, d, J=10 Hz, H-5), 7.92 (1H, d, J=10 Hz,H-4); ^{13}C NMR (400 MHz in $CDCl_3$): δ (ppm) 61.3 (-CH_2OH, C-6'), 70.2 (-CHOH,C-4'), 73.7(-CHOH, C-2'), 76.8 (-CHOH, C-3'), 77.5 (-CHOH, c-5'), 100.9 (-CH,C-1'), 103 .9 (-CH, C-6), 113.3(-CH, C-3), 114.2 (-CH, C-8), 114.3 (-CH, C-10), 129.4 (-CH, C-5), 144.6 (-CH, C-4), 155.8 (-Cq, C-9), 161.1 (-Cq, C-7), 162.1 (-Cq, C-2).

4. Acknowledgments

The authors are grateful to the financial support of D.A.A.D (Deutscher Akademischer Austauschdienst) for its re-invitation program to Dr Rivoarison Randrianasolo and to the Organic Chemistry Faculty of the University of Hanover for EIMS and NMR spectra.

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