ELSEVIER

Fitoterapia 75 (2004) 795–798

FITOTERAPIA

www.elsevier.com/locate/fitote

Phytochemical communication

A new sesquiterpene from the fruits of *Allophylus laevigatus*

Juceni P. David[a,*], Ihanmarck D. dos Santos[b], Jorge M. David[b]

[a]*Faculdade de Farmácia, Universidade Federal da Bahia, Campus Ondina, 40170-290, Salvador, Bahia, Brazil*
[b]*Instituto de Química, Universidade Federal da Bahia, 40170-290, Salvador, Bahia, Brazil*

Received 26 November 2003; accepted in revised form 9 September 2004

Abstract

From the fruits of *Allophylus laevigatus* a new sesquiterpene, 11-acetoxy-4α-methoxyeudesmane, was isolated alongwith the known compounds carissone and apigenin-8-C-β-rhamnopyranoside. The flavone showed no antioxidant activity in the autoxidation of β-carotene assay.

Keywords: Eudesmane sesquiterpenes; *Allophylus laevigatus*; Apigenin-8-C-β-rhamnopyranoside

1. Plant

Allophylus laevigatus, fruits collected in January 1998 in the "restinga" of Parque Metropolitano de Pituaçu, Salvador (Bahia), Brazil. The plant material was identified by Prof. Germano Guarim Neto of Universidade Federal do Mato Grosso (UFMT) and a voucher was deposited under number 042618 in Herbarium Alexandre Leal Costa, Instituto de Biologia, Universidade Federal da Bahia.

A. laevigatus Radlk is a tree belonging to the family Sapindaceae, which possesses 140 genera distributed in the tropical and subtropical areas [1]. In Brazil the species of this family are distributed in 22 different genera, most of them in the Amazon region

* Corresponding author. Tel.: +55 71 3321580; fax: +55 71 2355166.
E-mail address: juceni@ufba.br (J.P. David).

0367-326X/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.fitote.2004.09.018

(especially the genera *Sapindus*, *Serjania*, *Cardiospermum* and *Paullinia* [2]). The genus *Allophylus* is represented in the northwest of Brazil where were reported the occurrence of *A. dioicus* Radlk, *A. laevigatus* Radlk, *A. semidentatus* Radlk, *A. puberulus* Radlk, *A. quercifolius* (Mart.) Radlk, *A. edulis* (A. St.-Hil.) Radlk, *A. petiolulatus* Radlk and *A. sericeus* Radlk.

2. Uses in traditional medicine and other reported activities

Many species of the genera *Allophylus* and *Sapindus* are used in Brazil in folk medicine [1]. Only *A. edulis* was reported to contain sesquiterpenes [3], flavonoids and phenolic compounds [4].

3. Previous isolated constituents

No constituents described from this species.

4. New-isolated constituents

Carissone (**1**, 11.8 mg, from 826 g of dried fruits) [5], the new compound (**2**, 15.3 mg) and 3-β-*O*-glycopyranosylsitosterol (49.7 mg) were isolated from the $CHCl_3$ phase obtained from MeOH extract (118 g) after Si-Gel CC and PTLC.

Compound **2** showed spectral data consistent with an eudesmane skeleton carrying a methoxy and an acetoxyl groups (δ 3.12 and 1.97 in the ^{1}H-NMR spectrum). The quasi molecular ion at *m*/*z* 314 [M+NH_4^+] detected by CI-MS permitted to assign the molecular formula $C_{18}H_{32}O_3$ to this compound. Inspection of the NMR spectra allowed to identify compound 2 as a methyl ether of 11-acetoxyeudesman-4α-ol [6]. The correlations between the hydrogens (H-14) of methyl group at δ 1.04 with C-4 (δ 76.1), C-3 (δ 44.8) and C-5 (50.1) and the correlation between the methoxyl group (δ 3.12) and C-4 at δ 76.1 were conclusive of the presence of methoxyl group at C-4 position. On the other hand, the correlations observed for hydrogens of the two methyl groups (δ 1.42 and 1.45) and C-7 (δ 47.2) and C-11 (δ 85.1) indicated C-11 as bearing the acetoxy group.

Besides these compounds, apigenin-8-C-β-rhamnopyranoside **3**, (19.2 mg) [7] was isolated from the methanolic extract (Fig. 1) alongwith the known sitosterol (24.4 mg), stigmasterol (23.9 mg) and stigmast-4-en-3-one (14.4 mg). A mixture of fatty acids (555.7 mg), found by GC-MS analysis to contain tetradecanoic, hexadecanoic and 9-hexadecenoic acids, was also isolated.

The antioxidant activity of **3** was determined by the method described by Hidalgo [8], based on the inhibition of autoxidation reaction of β-carotene/linoleic acid system. Compound **3** had little pro-oxidant activity (AA=19.4) when compared to the propyl gallate (AA=55.7), BHT (AA=72.5) and α-tocopherol (AA=43.5).

11-Acetoxy-4α-methoxyeudesmane (**2**). $C_{18}H_{32}O_3$, oil; IR bands (film): 2930, 2851, 1731, 1458, 1384, 1367, 1256, 1126 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.89 (3H, *s*, H-

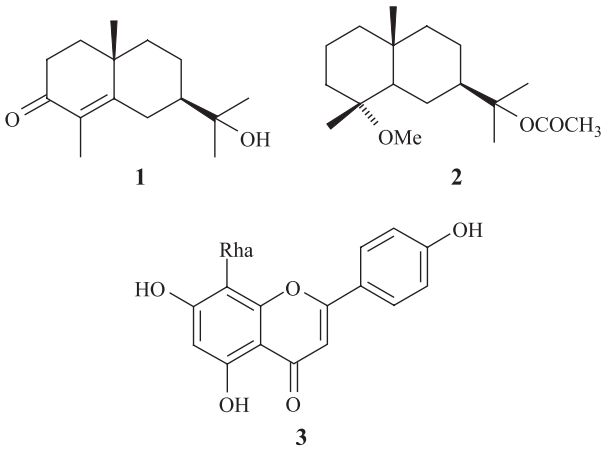

Fig. 1. Isolates from *A. laevigatus*.

15), 1.05 (3H, *s*, H-14), 1.42 (3H, *s*, H-12), 1.45 (3H, *s*, H-13), 1.97 (3H, *s*, Ac), 3.12 (3H, *s*, OMe); CI-MS *m/z* (rel. int.): 314 $[(M+NH_4)^+(56)]$, 237 (30), 205 (100); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 19.1 (C-14), 19.2 (C-15), 19.7 (C-2), 21.1 (C-6), 22.1 (C-8), 22.5 (OOCMe), 23.5 (C-13), 23.7 (C-12), 34.5 (C-10), 36.1 (C-10), 40.8 (C-1), 44.8 (C-3), 47.1 (C-7), 47.6 (OMe), 50.1 (C-5), 76.1 (C-4), 85.1 (C-11), 170.5 (COO).

Apigenin-8-C-β-rhamnopyranoside (**3**). Yellow powder; UV max (MeOH): 276 (15380) and 330 (11355) nm, (MeOH+$AlCl_3$): 278 and 373 nm, (MeOH+NaOMe): 279 and 389 nm, (MeOH+NaOAc): 280 and 382 nm; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.28 (3H, *d*, 5.4 Hz, H-6″), 4.53 (1H, *d*, 8.9 Hz, H-1″), 6.64 (1H, *s*, H-6), 6.77 (1H, *s*, H-3), 6.92 (2H, *d*, 8.0 Hz, H-3′ and H-5′), 7.91 (2H, *d*, 8.0 Hz, H-2′ and H-6′); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 163.9 (C-2), 102.8 (C-3), 182.3 (C-4), 156.8 (C-5), 99.2 (C-6), 163.8 (C-7), 103.8 (C-8), 156.3 (C-9), 102.9 (C-10), 121.2 (C-1′), 128.1 (C-2′ , C-6′), 116.2 (C-3′ , C-5′), 161.2 (C-4′), 78.5 (C-1″), 73.6 (C-2″), 73.1 (C-3″), 71.4 (C-4″), 70.5 (C-5″), 18.5 (C-6″).

Acknowledgements

The authors are grateful to the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Fundação Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for grants and fellowship supports. We are in debt with Dr. G.A. Cordell for MS data and Dr. G. Guarim Neto for the plant identification.

References

[1] Hegnauer W. Sapindaceae. Chemotaxonomie Pflanz 1970;6:271.
[2] Joly AB. Botânica: Introdução à Taxonomia Vegetal, Companhia Ed. Nacional 11ª ed., 1993.
[3] Fester GA, Retamar JA, Ricciardi AI. Bol Acad Nac Cienc (Cordoba, Rep Arg) 1960;42:13.

[4] Arisawa M, Morinaga Y, Nishi Y, Ueno H. Shoyakugaku Zasshi 1989;43:78.
[5] Maatoog GT, Stumpf DK, Hoffmann JJ, Hutter LK, Timmermann BN. Phytochemistry 1996;41:519.
[6] Su W-C, Fang J-M, Cheng Y-S. Phytochemistry 1995;39:603.
[7] Haggag EG, Mahmoud II, Abou-Moustafa EA, Mabry TJ. Asian J Chem 1999;11:707.
[8] Hidalgo ME, Fernández E, Quilhot W, Lissi E. Phytochemistry 1994;37:1585.