Biochemical Systematics and Ecology 51 (2013) 4–7

Contents lists available at SciVerse ScienceDirect

Biochemical Systematics and Ecology

journal homepage: www.elsevier.com/locate/biochemsyseco

Diterpenoids and acetylenic lipids from *Aralia racemosa*

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ARTICLE INFO

Article history:
Received 18 March 2013
Accepted 23 June 2013
Available online 31 July 2013

Keywords:
Diterpenoid
Aralia racemosa
ent-kaurane
Araliaceae

ABSTRACT

Phytochemical investigation of *Aralia racemosa* L. afforded three known diterpenoids and two known acetylenic lipids. The presence of these compounds is consistent with the compound classes reported from other members of genus *Aralia*. The structures of these compounds were determined by NMR, IR, and LC-MS spectroscopic methods. This is the first report of acanthoic acid from *A. racemosa*. We present corrected NMR data for (16*R*)-17-hydroxy-*ent*-kauran-19-al, which is also reported from *A. racemosa* for the first time.

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1. Subject and source

Aralia racemosa L. (family Araliaceae) is a perennial herb that is found in much of the eastern and western United States and parts of Canada. It has a variety of traditional uses by the Cherokee of the southeastern United States, including treatment of respiratory problems, as a topical treatment for cuts or burns, (Hamel and Chiltoskey, 1975) and as a treatment for low back pain (Banks, 2004). Like several other members of the Araliaceae, *A. racemosa* has been used as an adaptogen, a substance which promotes dealing with stress (Abascal and Yarnell, 2003). Interestingly, a treatment for cancer was patented in 1869 which involved application of a poultice from *A. racemosa* (Roy and Nesbitt, 1869). Although the medicinal usage of this plant is well-documented and continues to the present, little has been reported on the chemical basis of the medicinal activity. Whole plant material for *A. racemosa* was collected in Buncombe County, North Carolina, in August 2007. The plant was identified by Joshua A. Kelly. A voucher specimen of *A. racemosa* (number JK201010027) was deposited at the herbarium of the Bent Creek Germplasm Repository at the North Carolina Arboretum, Asheville, N.C.

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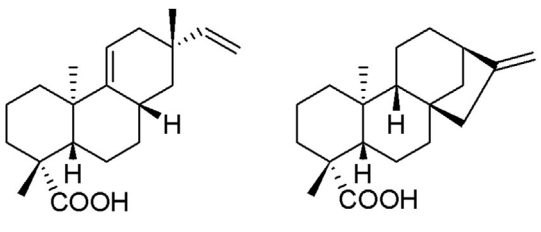
0305-1978/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.bse.2013.06.009

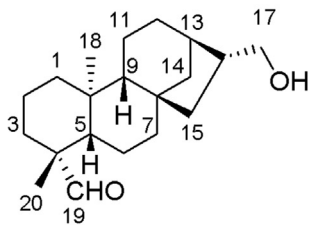
2. Previous work

The genus *Aralia* (Araliaceae) is made up of seventy-one species, eight of which are native to North America (Wen, 2011). Of these species, four are found in the Southern Appalachian Mountains of the United States of America (Natural Resources Conservation Service, 2013). Phytochemical studies of members of genus *Aralia* have reported a number of different compound classes. These include: triterpenoids from *Aralia elata* (Song et al., 2000; Saito et al., 1990), *Aralia dasyphylla* (Xiao et al., 1999), *Aralia armata* (Hu et al., 1995), *Aralia taibaiensis* (Bi et al., 2012), *Aralia spinifolia* (Yu et al., 1994), *Aralia mandshurica* (Kochetkov et al., 1962), *Aralia cordata* (Kawai et al., 1989), *Aralia decaisneana* (Miyase et al., 1996a), *Aralia chinensis* (Miyase et al., 1996b), and *Aralia subcapitata* (Zou et al., 2001); acetylenic lipids from *A. elata*, *A. racemosa*, *Aralia mandschurica*, *Aralia nudicaulis*, *Aralia californica* (Hansen and Boll, 1986); and diterpenoids from *A. cordata* (Yahara et al., 1974; Lee et al., 2006), *Aralia continentalis* (Lim et al., 2009), and *A. racemosa* (Hanson and White, 1970). Additionally, chlorogenic acid is a known component of *A. racemosa* (ANSM, 2009). In this paper, we report the isolation and characterization of three diterpenoids and two acetylenic lipids from *A. racemosa*, which represents a new source for four of these compounds.

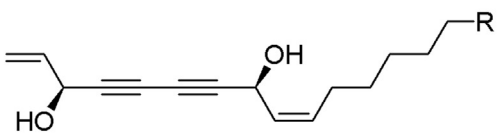


1

2



5 R = CHO
6 R = COOH



3 R = CH_2CH_3
4 R = $CH{=}CH_2$

3. Present study

The dried whole plant (75 g) of *A. racemosa* was milled, and the powder was extracted with 80% $MeOH_{(aq)}$ at room temperature overnight. An acid-base extraction was applied to the crude extract as follows. From the 80% $MeOH_{(aq)}$ extraction, the methanol was removed by rotary evaporation, and the aqueous phase was acidified to pH 2 with addition of HCl. The acidic solution was extracted with CH_2Cl_2, and the CH_2Cl_2 phase was concentrated to dryness by rotary evaporation to afford 1.5 g of oil (fraction A). The aqueous phase was basified to pH 9 and extracted with CH_2Cl_2, which was dried to afford 13.1 mg of fraction B.

In an initial fractionation, fraction A (250 mg) was further purified by C_{18} open column chromatography (step gradient, 50%–100%, followed by CH_2Cl_2) to afford seven fractions (A-i – A-vii). The 90% $MeOH_{(aq)}$ wash (A-v, 112 mg), was further purified by silica gel open column chromatography, followed by C_{18} HPLC (isocratic, 90% $MeOH_{(aq)}$). Purification of 12 mg of A-v afforded **1** (6.5 mg) and **2** (4.0 mg). The compounds were identified based on comparisons with literature data (Kim et al., 1988).

In a second separation, fraction A (1.1 g) was fractionated by the same open column C_{18} method above to afford seven fractions (fractions A-1 through A-7), three of which were found to contain primarily acetylenic lipids and diterpenoids: A-3 (117 mg) and A-4 (134 mg), and A-5 (524 mg). Fraction A-5 was found to contain **1** and **2** based on NMR analysis.

Fraction A-3, the 70% $MeOH_{(aq)}$ wash (58 mg), was purified by preparative C_{18} HPLC (isocratic, 84% $MeOH_{(aq)}$) to afford six fractions, two of which were purified further: A-3-1 (15.8 mg) and A-3-3 (3.3 mg). A-3-1 was purified further by SiO_2 HPLC (95:5 hexane:2-propanol) to afford **3** (6.7 mg). A-3-3 was purified by that same SiO_2 HPLC method to yield **4** (1.1 mg). Compounds **3** and **4** were identified based on comparisons with literature data (Kern and Cardellina, 1982).

Fraction A-4, the 80% $MeOH_{(aq)}$ fraction, was purified by repeated preparative C_{18} HPLC (isocratic, 83% $MeOH_{(aq)}$) to afford **5** (2.7 mg), although **3** and **4** appeared to be components of A-4. Although **5** was able to be characterized by 1D and 2D NMR methods, the compound apparently auto-oxidized during attempts to recrystallize the compound. From the product mixture, **6** was isolated by C_{18} HPLC (isocratic, 83% $MeOH_{(aq)}$).

Compound **5** ($[\alpha]_D^{25} = -63$, *c* 0.61, $CHCl_3$) was isolated as a colorless solid. High-resolution MS analysis of **5** indicated a molecular formula of $C_{20}H_{32}O_2$ (observed *m/z* $[M + H]^+ = 305.2461$, calculated for $C_{20}H_{33}O_2$, 305.2480), suggesting the

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