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TRITERPENOIDS OF *AMSONIA GRANDIFLORA*

SUBAGUS WAHYUONO, JOSEPH J. HOFFMANN,* SHIVANAND D. JOLAD and STEVEN J. DENTALI

Department of Pharmaceutical Sciences, College of Pharmacy, University of Arizona, Tucson, AZ 85721, U.S.A.; *University of Arizona, Office of Arid Lands Studies, Bioresources Research Facility, 250 E. Valencia Road, Tucson, AZ 85706, U.S.A.

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Key Word Index—*Amsonia grandiflora*; Apocynaceae; stems; leaves; triterpenoids; lupeol β-hydroxyoctadecanoate.

Abstract—Stems and leaves of *Amsonia grandiflora* yielded lupeol β-hydroxyoctadecanoate, betulinic acid, oleanolic acid, lupeol, lupeol acetate and 1-*O*-methyl-*myo*-inositol.

Indigenous desert plants of the genus *Amsonia* have been shown to have potential as new crops for semi-arid lands [1]. With an animal feed potential similar to alfalfa, it is surprising that wild animals do not forage these plants. Therefore, a chemical analysis of *A. grandiflora* was undertaken. From a dichloromethane extract of the stems and leaves of this plant, betulinic acid, oleanolic acid, lupeol and lupeol acetate were isolated along with a new triterpenoid derivative, lupeol β-hydroxyoctadecanoate (**1**). From a methanol extract of the above plant marc, sucrose, 1-D-1-*O*-methyl-*myo*-inositol, glucose and several unidentified flavonoid glycosides were detected [2].

All the known compounds were identified by direct comparison of their IR, ^{1}H NMR and mass spectra with those of authentic samples. The carbohydrates were detected by gas chromatography and confirmed by isolation and identification of their peracetates. **1** was hydrolysed to identify its genin and the location, size and nature of the fatty acid ester moiety. The genin was identified as lupeol by direct comparison with an authentic sample. The acid moiety of **1** was identified as β-hydroxyoctadecanoic acid by comparing the IR, ^{1}H NMR and MS data with the previously reported data [3]. HRMS of the acid moiety confirmed $C_{18}H_{34}O_2$ (found: 282.2550, calculated: 282.2640). The two acids, which comprised more than half of the extract, are considered to render the plant material unpalatable. Also, the high concentration of inositol reduces the nutritional value of this plant.

EXPERIMENTAL

Plant material. Obtained from two harvests (3 May 1984 and 9 July 1984) of observation plots at the Bioresources Research Facility, Office of Arid Lands Studies, College of Agriculture, University of Arizona, Tucson [1].

Extraction and isolation. The ground air-dried stems and leaves (10.35 kg) were extracted with CH_2Cl_2 in a Lloyd-type extractor at room temp. for 48 hr to yield 0.59 kg of an air-dried extract. In a similar manner the marc was extracted with MeOH to yield 2.4 kg of an air-dried syrup. A portion of the CH_2Cl_2 extract (248 g) was extracted with *n*-hexane followed by Et_2O. The hexane soluble fraction was extracted with $(CH_3)_2CO$ and chromatographed over silica gel-60 with a gradient elution of *n*-hexane and EtOAc to give lupeol, its acetate and **1**. The Et_2O-soluble fraction was partitioned between *n*-hexane–H_2O–EtOH (28:1:18) and the upper layer was chromatographed as before to give betulinic and oleanolic acids. Inositol was isolated as its pentaacetate derivative from the EtOAc insoluble fraction of the MeOH extract by reverse phase chromatography and the fraction eluted with H_2O was then acetylated ($ZnCl_2$–Ac_2O/room temp., 24 hr) and chromatographed over silica gel-60 with CH_2Cl_2–EtOAc (20:1) as the eluent.

Hydrolysis of **1** was carried out in refluxing 10% methanolic KOH for 2 hr under N_2. After work up the TLC (hexane–EtOAc, 3:1) analysis indicated only two compounds, lupeol (R_f = 0.66) and β-hydroxydecanoic acid (R_f = 0.25 with tailing).

Lupeol β-hydroxyoctadecanoate (**1**). Amorphous powder (homogeneous by TLC), $[\alpha]_D^{25}$ + 22.98 ($CHCl_3$; *c* 0.97); IR (KBr): 3460, 3080, 1735, 1640, 1465, 1380, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ4.69 (2H), 4.45 (1H, *m*), 2.73 (2H, *d*), 1.73 (3H, *s*), 1.26 (24H), 1.01–0.82 (21H); MS: *m/z* 708 ($M^{+\cdot}$ $C_{48}H_{84}O_3$), 681, 663, 468, 409, 408, 393, 298, 218, 203, 189 (base), 147, 135, 121, 109, 95.

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