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Phytochemistry, 1977, Vol. 16, pp. 1300–1301. Pergamon Press Printed in England.

IRIDOID GLUCOSIDES OF *WENDLANDIA FORMOSANA*

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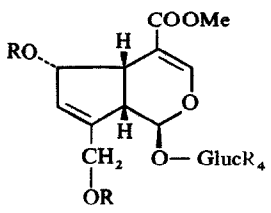
(*Revised received* 28 *February* 1977)

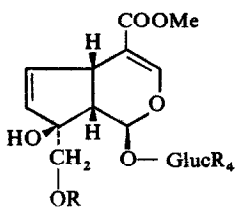
Key Word Index—*Wendlandia formosana*; Rubiaceae; iridoid glucosides; gardenoside; methyl deacetylasperulosidate; tarennoside; geniposidic acid.

Wendlandia formosana Cowan was collected in Ishigaki Island (Okinawa Pref.) on Aug. 27, 1974 and identified by Mr. G. Murata of Faculty of Science, Kyoto University. A voucher sample (Y. Takeda, Y. Ikeshiro & H. Nishimura No. 8) is deposited in the herbarium of the Institute of Botany, Faculty of Science, Kyoto University (KYO), Kitashirakawaoiwake-cho, Sakyo-ku, Kyoto, Japan.

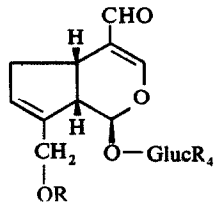
Air dried leaves (875 g) were extracted with hot MeOH. The extract was evaporated *in vacuo* and extracted with H_2O. After washing with EtOAc, the aq. extract was chromatographed on charcoal with H_2O–MeOH as eluent with increasing MeOH content. The 50% MeOH eluate gave upon TLC (Si gel, $CHCl_3$–MeOH 8:2) spots corresponding to methyl deacetylasperulosidate (1) (R_f 0.29), tarennoside (3) (R_f 0.17) and gardenoside (2) (R_f 0.13). Geniposidic acid (4) was also detected by TLC (Si gel containing 0.25% H_3PO_4, $CHCl_3$–MeOH 8:2, R_f 0.26). This eluate gave, on evaporation, 9.3 g of residue. A portion (0.92 g) of this residue was acetylated (Ac_2O–Py) and the product was chromatographed on Si gel with $CHCl_3$–MeOH as eluent. Fractions eluted with $CHCl_3$–MeOH (99.5:0.5) gave Acetate-1 and Acetate-3, while fraction eluted with $CHCl_3$–MeOH (99:1) Acetate-2: (a) Acetate-1 (47 mg), an amorphous powder, $[\alpha]_D^{30}$ + 34.8° ($CHCl_3$, c = 1.09) (lit. [1], $[\alpha]_D^{24}$ + 38.1° ($CHCl_3$, c = 0.84); lit. [2], $[\alpha]_D^{16}$ + 51.3° (EtOH, c = 0.78)); ν_{max}^{KBr} cm^{-1}: 1740, 1710, 1630; PMR ($CDCl_3$) δ: 1.93–2.10 (6 × OCOMe), 2.63 (1H, *m*, 9-H), 3.24 (1H, *m*, 5-H), 3.73 (3H, *s*, COOMe), 6.07 (1H, *m*, 7-H), 7.57 (1H, *d*, J = 1.5 Hz, 3-H). (Found: C, 53.04; H, 5.66. Cacld. for $C_{29}H_{36}O_{17}$: C, 53.04; H, 5.52%). Acetate-1 was identical to an authentic sample of methyl deacetylasperulosidate hexaacetate (= daphylloside pentaacetate) [1, 2] according to their IR and PMR spectra.



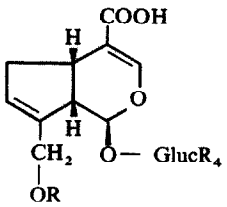
1: R=H
Acetate-1: R=COMe



2: R=H
Acetate-2: R=COMe



3: R=H
Acetate-3: R=COMe



4: R=H
Acetate-4: R=COMe

(b) Acetate-2 (232 mg), an amorphous powder, $[\alpha]_D^{30}$ − 97.6° ($CHCl_3$, c = 0.82) (lit. [1], $[\alpha]_D^{23}$ − 104.5° (MeOH, c = 0.22)); ν_{max}^{KBr} cm^{-1}: 3450, 1745, 1710; PMR ($CDCl_3$) δ: 1.91–2.11 (5 × OCOMe), 4.35 (1H, *d*, J = 2.0 Hz, 1-H), 5.70 (1H, *dd*, J = 6.0, 1.0 Hz, 7-H), 6.27 (1H, *dd*, J = 6.0, 2.5 Hz, 6-H), 7.32 (1H, *d*, J = 1.5 Hz, 3-H). (Found: C, 52.57; H, 5.52. Calcd. for $C_{27}H_{34}O_{16}$: C, 52.77; H, 5.58%). Acetate-2 was identical to an

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‡ The reported value of opposite sign [2] was found to be erroneous.

authentic sample of gardenoside pentaacetate [1] by IR and PMR spectroscopy (c) Acetate-3 (24 mg), colourless needles, mp 127–129°, $[\alpha]_D^{25}$ + 5.6° ($CHCl_3$, c = 0.90‡; ν_{max}^{KBr} cm^{-1}: 1740, 1660, 1630; PMR ($CDCl_3$) δ: 1.97–2.08 (5 × OCOMe), 4.71 (2H, *br. s*, 10-H), 5.83 (1H, *m*, 7-H), 7.17 (1H, *d*, J = 1.0 Hz, 3-H), 9.30 (1H, *s*, 11-H). (Found: C, 54.68; H, 5.91. Calcd. for $C_{26}H_{32}O_{14}$: C, 54.93; H, 5.67%). Acetate-3 was identical to an authentic sample of tarennoside pentaacetate [3] by IR and PMR spectroscopy.

Another portion (1.6 g) of the above residue was chromatographed on Amberlite IRA-410 (OH-type) with H_2O–AcOH with increasing AcOH content. On evaporation, the eluate with 0.6 M AcOH gave a residue (260 mg), which was then acetylated (Ac_2O–Py) and the product was purified by chromatography on Si gel with Et_2O as eluent to give Acetate-4 (46 mg) as an amorphous powder, $[\alpha]_D^{25}$ + 9.5° ($CHCl_3$, c = 1.04) lit. [4], $[\alpha]_D^{23}$ + 14.9° ($CHCl_3$, c = 1.61)); ν_{max}^{KBr} cm^{-1}: 1740, 1630; PMR ($CDCl_3$) δ: 2.02–2.08 (5 × OCOMe), 4.73 (2H, *br. s*, 10-H), 5.87 (1H, *m*, 7-H), 7.55 (1H, *s*, 3-H); (Found: C, 53.37; H, 5.62. Calcd. for $C_{26}H_{32}O_{15}$: C, 53.43; H, 5.52%). This substance was identical to an authentic sample of geniposidic acid pentaacetate [4, 5] by IR and PMR spectroscopy.

Although Briggs and Nicholls recorded a negative test for asperuloside in *Wendlandia luzoniensis* [6], we have now succeeded in isolation of four asperuloside-type iridoids from a plant of the same genus.

Acknowledgements—The authors wish to thank Mr. G. Murata for the identification of plant material and Dr. Y. Ikeshiro for his collaboration in collecting plant material. We are also indebted to Mrs. M. Uobe for measurements of PMR spectra and the members of Microanalytical Center of this University for microanalyses.

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Phytochemistry, 1977, Vol. 16, pp. 1301–1302. Pergamon Press. Printed in England.

TERPENES OF *SCHINUS TEREBINTHIFOLIUS*

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(*Received* 15 *February* 1977)

Key Word Index—*Schinus terebinthifolius*; Anacardiaceae; mono-, sesqui- and triterpenes.

Schinus terebinthifolius Raddi, which is native to Central and South America, was introduced to Florida 50 years ago as a shade and ornamental tree and spread rapidly to thousands of acres [1]. The suspected cause of allergies and respiratory afflictions, it is now considered a noxious species. Previous studies on fruits [2–4], leaves [5], and bark [5, 6] have revealed the presence of triterpene alcohols [5, 6], ketones [6] and acids [2–6]. However, the monoterpenes and sesquiterpenes have not been investigated; we now report on these and other terpenoid constituents.

Exhaustive hexane and ether extraction of crushed berries furnished two previously reported [2–5] triterpenes: masticadienoic and hydroxymasticadienoic acids, also a small amount of ursolic acid (comparison with authentic sample) and of an unidentified acid (MW 502). The neutral oily portion was examined by GLC (2 columns: 180 cm 1% OV-17 and 360 cm 10% SP-1000) and by GC–MS (same column packings). The bulk of the material (*ca* 80%) consisted of a mixture of 9 monoterpene hydrocarbons which were identified unambiguously by comparison with GLC R_t and MS spectra of authentic samples: α-pinene (25% of total monoterpenes), β-pinene (1%), sabinene (0.7%), Δ^3-carene (26%), α-phellandrene (16%), limonene (11%), β-phellandrene (8%), *p*-cymene (10%) and terpinolene (1%). The remainder of the oil, a complex mixture of over 50 components, consisted of monoterpene alcohols and ketones, sesquiterpene hydrocarbons, alcohols and ketones, and triterpene alcohols and ketones. *Cis*-sabinol, carvotanacetone, β-caryophyllene, α- and β-cubebene were identified by comparison with reported MS spectra. Simiarenol, simiarenone, α-amyrin and α-amyrenone were also identified by comparison with authentic samples. The large concentration of volatile monoterpenes (over 10% of the weight of air dried berries) may

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