

DITERPENOIDS OF *CONYZA COULTERI*

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Abstract—Four furanoditerpenoids, including three furanoclerodanes, have been identified in the extract of the aerial parts of *Conyza Coulteri*. One of the terpenoids, 2 β -hydroxyhardwickiic acid, was found as a natural product for the first time.

INTRODUCTION

The genus *Conyza* is known to produce acetylenes, di- and triterpenoids, flavones and coumarins [1–7]. This note reports our examination of the chemical constituents of *Conyza Coulteri* Gray, an annual herb of the southwestern United States and Mexico that is known to be toxic to livestock [8].

From the methylene chloride extract of *C. Coulteri*, four furanoditerpenoids (1–4), including three furanoclerodanes (2–4) were isolated and characterized mainly by spectral (NMR and MS) methods and comparisons with literature data. The furanoditerpenoid (1) was identified [IR $\lambda_{\text{max}}^{\text{CHCl}_3}$: 3000–2500 and 1690 (COOH), 1500 and 870 (furan), 3040, 1645, 1635 (C=C) cm^{-1} ; EIMS m/z : 316 (M^+), 81 (furan-CH₂), 69 (>=CH-CH_2 , base); $^1\text{H NMR}$ as reported] as centipedic acid, a constituent of *Centipeda orbicularis* (Asteraceae) [9]. The three furanoclerodanes include, hardwickiic acid (2), bacchotricuneatin A (3) and 2 β -hydroxyhardwickiic acid (4). Compound 2, previously reported from plants of different genera [7,10], was identified by direct comparison with an authentic sample. Compound 3, previously isolated from *Baccharis tricuneata* var. *tricuneata* [11, 12] and *B. articulata* [13], was characterized on the basis of

its spectral data [IR $\lambda_{\text{max}}^{\text{CHCl}_3}$: 1770 and 1750 (-C=O-), 3015 and 1660 (C=C), 1500 and 868 (furan) 1380 (Me) cm^{-1} ; EIMS m/z : 342 (M^+), 312 (base), 95 (furan-CH₂-CH₂), 94 (furan-CH=CH₂); HRMS m/z 342.1540 (+5.3 mmu), C₂₀H₂₂O₅ and $^1\text{H NMR}$ as previously reported].

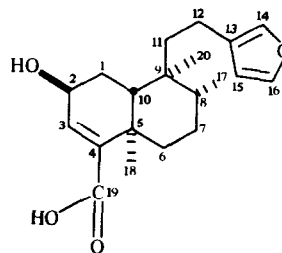
2 β -Hydroxyhardwickiic acid (4) was previously prepared (i) by the saponification of 2 β -succinyloxyhardwickiic acid present in the acidic fraction of *Dodonaea boronifolia* and characterized as its methyl ester derivative and (ii) by synthesis, along with its C-2 epimer, from *ent*-15,16-epoxycleroda-3,13(16),14-triene-2 α ,19-diol isolated from the neutral fraction of the same species [14]. Recently, Pandey, *et al.* [7] reported the C-2 epimer of 4, characterized as its methyl ester derivative, from *Conyza japonica* and synthesized both epimers from methyl hard-

wickiic acid. Our isolation of 4 is the first report of the free acid from a natural source. Its spectral data [IR $\lambda_{\text{max}}^{\text{CHCl}_3}$: 3600 and 1020 (OH), 3000–2500 and 1700 (COOH), 1500 and 870 (furan), 3010, 1635 and 840 (C=C) cm^{-1} ; EIMS m/z : 332 (M^+), 314 ($M-\text{H}_2\text{O}$), 95 (furan-CH₂-CH₂), 81 (furan-CH₂), $^1\text{H NMR}$ (δ , CDCl₃) 0.75 (H-20), 0.84 d (J = 5.8 Hz, H-17), 1.20 (H-19), 4.34 $br s$ (H-2), 6.26 $br s$ (H-14), 6.63 d (J = 4.1 Hz, H-3), 7.20 $br s$ (H-16), 7.31 $br s$ (H-15)] parameters are in accord with those given for its methyl ester derivative [14]. In particular, the signal for H-2 as a doublet (J = 4.1 Hz) rather than as a doublet of doublets (J = 2.5, 1.5 Hz) defines the configuration at C-2 [7]. The $^{13}\text{C NMR}$ parameters for 4 (see Experimental), hitherto unreported, support the structure.

EXPERIMENTAL

Plant material. The collection of *C. Coulteri* was made on 30 August 1985 in the Santa Rita and Huachuca mountains in Southern Arizona. A voucher specimen (SPM 3039) was deposited in the Herbarium of the University of Arizona. All plant material was air-dried, ground to 3 mm particle size and stored at 5° prior to extraction.

Extraction and isolation. The solvent-free CH₂Cl₂ extract (48 g) of the ground plant (Soxhlet) was stirred with Et₂O (800 ml,



4

2 hr), left in the refrigerator overnight, filtered and solvent removed. A small portion of the Et₂O-soluble fraction when submitted to TLC [*n*-hexane-Et₂O (2:1), 2 developments] gave **1** which was purified by further TLC (same solvent system). Another portion of the Et₂O-soluble fraction when submitted to Silica gel CC (120 g packed in *n*-hexane) gave nine fractions: 1 [*n*-hexane-Et₂O (2:1)], 2-4 [*n*-hexane-Et₂O (1:1)], 5-8 (Et₂O) and 9 [CH₂Cl₂-MeOH (1:1)], from which 2-4 were isolated as follows.

Fraction I, which contained **2**, was initially submitted to Silica gel CC and the fraction eluted with *n*-hexane-Et₂O (4:1) gave **2** on further TLC [*n*-hexane-Et₂O-AcOH (25:10:1)].

Fractions 6-7 gave **3** when submitted to TLC [*n*-hexane-CHCl₃-AcOH (10:10:3), 1 development].

TLC of Fr. 2 [*n*-hexane-Et₂O-AcOH (15:9:1), 2 developments] gave **4**, ¹³C NMR (δ, CDCl₃) (for C-1 to C-20, in order): 27.1, 64.1, 135.8, 144.4, 37.9 or 38.3, 35.2, 27.1, 36.0, 37.9 or 38.3, 41.1, 38.6, 17.4, 125.6, 142.4, 111.0, 138.3, 172.2, 18.6 or 18.8, 15.7 and 18.6 or 18.8, in accord with the structure.

The spectral properties of **1-4** are described in the text.

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A NEW CLERODANE DERIVATIVE FROM *TINOSPORA CORDIFOLIA*

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Key Word Index—*Tinospora cordifolia*, Menispermaceae, new clerodane diterpenoid.

Abstract—A new clerodane diterpenoid has been isolated from the stems of *Tinospora cordifolia*. Its structure was established by spectroscopic means and by comparison with closely related clerodane derivatives.

INTRODUCTION

Chemical investigation of *Tinospora cordifolia* has led to the isolation of a phenolic lignan and one diterpenic furano lactone which were reported earlier [1, 2]. In the

present paper the isolation and structure of a new clerodane derivative, isolated from the same plant, is reported. The structure (**1**) was deduced mainly with the help of ¹H NMR, spin-decoupling and ¹³C NMR studies along with the comparison of the spectral data of closely related clerodane diterpenoids such as 6-hydroxy arcangelisin (**2**) [3], fibraurin (**3a**) [4], 6-hydroxy fibraurin (**3b**) [3, 4], palmarin (**4**) [5-7] and 8-hydroxy columbin (**5**) [8].

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