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1-EPIZEYLENOL FROM *UVARIA ZEYLANICA* ROOTS

SHIVANAND D. JOLAD, JOSEPH J. HOFFMANN, JACK R. COLE, MICHAEL S. TEMPESTA* and ROBERT B. BATES*

College of Pharmacy and *Department of Chemistry, University of Arizona, Tucson, Arizona, 85721, U.S.A.

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Key Word Index—*Uvaria zeylanica*; Annonaceae; zeylenol; 1-epizeylenol.

Abstract—1-Epizeylenol was isolated from *Uvaria zeylanica* roots and characterized, largely by ^1H and ^{13}C NMR spectral comparisons with zeylenol.

INTRODUCTION

During an investigation of the methanol extract of the roots of *Uvaria zeylanica* L. for tumor inhibitory constituents, two new inactive crystalline compounds, termed zeylena and zeylenol (**1a**), were isolated and characterized [1]. The structure of the latter has been confirmed by biomimetric synthesis from pipoxide (**2**) [2]. We now report the isolation and characterization of a third new inactive constituent, mp 206–207°, isomeric with **1a**, which we have determined to be 1-epizeylenol (**1b**).

RESULTS AND DISCUSSION

The new compound was isolated from the zeylenol-containing fraction [1] by chromatography. Its mass and IR spectra were very similar to those of zeylenol (**1a**), but it had a higher mp, and of the common solvents, was appreciably soluble only in pyridine. The ^1H and ^{13}C NMR spectra were also similar, with some chemical shift differences but almost the same ^1H–^1H coupling constants as zeylenol (**1a**); these coupling constants were measured in the 6-monoacetate (**1c**) and diacetate (**1d**) of the new compound as well. The large magnitudes of $J_{2,3}$ (7.5–8.3 Hz in **1b–d** in various solvents) indicate a *trans* pseudo-diaxial arrangement of H-2 and H-3, while the small values of $J_{3,6}$ (~ 0) and large values of $J_{5,6}$ (4.0–5.0 Hz) indicate that H-6 is pseudoequatorial and thus that the substituents at C-3 and C-6 are *cis*, just as in zeylenol (**1a**) [1]. Since the new compound is neither zeylenol (**1a**) nor its enantiomer, it must be 1-epizeylenol (**1b**) or its enantiomer. This view is supported by the finding that the largest ^1H chemical shift differences between the diacetates of **1a** and the new compound in $CDCl_3$ are for the C-7 protons, which differ by 0.36 and 0.51 ppm.

We favour **1b** over its enantiomer on biogenetic grounds (all of the compounds of this type found to date have the configurations depicted at C-2 and C-3, presumably because they are biosynthesized via 1,6-deoxypipoxide [3] or the corresponding acetate or cinnamate), and because the new compound, like all of the others, has a negative optical rotation. It is not clear whether 1-epizeylenol (**1b**) is biosynthesized from 1,6-deoxypipoxide via pipoxide (**2**) or isomeric epoxide **3**.

We have compared **1b** from *U. zeylanica* with a compound isolated from *U. purpurea* by Prof. Y. Thebtaranonth and co-workers and found them to be identical.

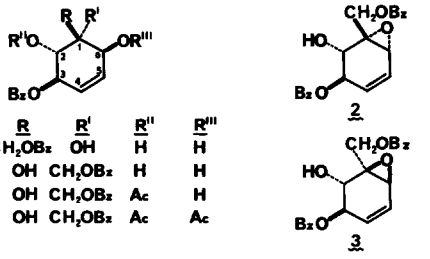
EXPERIMENTAL

For general procedures used, see ref. [1]. ^1H–^1H and ^1H–^{13}C decoupling and our experience with zeylenol (**1a**) and many related substances [1] were used extensively in making NMR assignments. The almost identical benzoate proton absorptions in each compound are not listed.

1-Epizeylenol (**1b**) crystallized from the chromatography fractions preceding zeylena in the zeylena–zeylenol separation [1]. Colorless crystals from hot CH_2Cl_2–MeOH, mp 206–207°. $[M]_D$ −176°, IR and MS almost identical to those of **1a** [1]. ^1H NMR (250 MHz, pyridine-d_5): δ4.98 (H-2), 5.27 and 5.57 (H-7), 5.32 (H-6), 6.02 (H-5), 6.09 (H-4) and 6.60 (H-3); $J_{2,3} = 7.5$, $J_{3,4} = 2.2$, $J_{3,5} = 1.8$, $J_{4,5} = 9.9$, $J_{5,6} = 4.2$, $J_{7,7} = 12.0$ Hz. ^{13}C NMR (62.9 MHz, pyridine-d_5): δ58.2 (C-6), 68.1 (C-7), 69.5 (C-2), 74.6 (C-3), 75.5 (C-1), 127.8 (C-5), 127.9 (C-3'), 128.1 (C-4), 129.1 (C-2'), 130.1 (C-1'), 132.4 (C-4'), 165.8 (C-7'). Anal. Calc. for $C_{21}H_{20}O_7$: C, 65.52; H, 5.24. Found: C, 65.48; H, 5.34.

1-Epizeylenol 6-acetate (**1c**) was formed along with the diacetate **1d** when **1a** was treated with Ac_2O–pyridine overnight. TLC separation gave **1c**, ^1H NMR (250 MHz, $CDCl_3$): δ2.06 (Ac), 4.62 (H-6), 4.63 and 4.73 (H-7), 5.81 (H-2), 5.90 (H-4), 5.91 (H-3), 5.98 (H-5); $J_{2,3} = 7.6$, $J_{3,4} = 2.2$, $J_{3,5} = 1.5$, $J_{4,5} \sim 10$, $J_{5,6} = 4.0$, $J_{7,7} = 12.2$ Hz.

1-Epizeylenol diacetate (**1d**) was prepared as described above. ^1H NMR (250 MHz, $CDCl_3$): δ1.86 and 2.13 (Ac), 4.97 and 4.99 (H-7), 5.54 (H-6), 5.94 (H-4), 5.95 (H-5), 5.95 (H-3), 6.08 (H-2); $J_{2,3} = 8.1$ Hz, others unobserved; in benzene-d_6: δ1.49 and 1.51



	R	R'	R''	R'''
1a	CH_2OBz	OH	H	H
1b	OH	CH_2OBz	H	H
1c	OH	CH_2OBz	Ac	H
1d	OH	CH_2OBz	Ac	Ac

(Ac), 5.15 and 5.45 (H-7), 5.33 (H-5), 5.51 (H-6), 5.63 (H-4), 6.28 (H-3), 6.52 (H-2), $J_{2,3} = 8.3$, $J_{3,4} = 2.4$, $J_{3,5} = 1.8$, $J_{4,5} = 9.7$, $J_{5,6} = 5.0$, $J_{7,7} = 12.3$ Hz.

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