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BENZYL BENZOATES FROM THE ROOT OF *UVARIA PURPUREA*

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Key Word Index—*Uvaria purpurea*, Annonaceae, benzyl benzoates, aromatic esters, biosynthesis

Abstract—Nine benzyl benzoates have been isolated from the root of *Uvaria purpurea*

Previous reports have shown that plants in the *Uvaria* genus possess a number of chemically and biologically interesting compounds which include cyclohexene epoxides [1, 2], *o*-hydroxybenzyl dihydrochalcones and flavanones [3, 4], alkaloids [5, 6], and aromatic constituents [7] including those derived from syncarpic acid [8] In this paper we report the isolation and characterization of nine benzyl benzoate derivatives (**1–9**) from the root of *U purpurea*

Hexane extraction of the root of *purpurea* yielded a crude gummy concentrate which upon standing in the refrigerator yielded pipoxide [1] as colourless crystals The remaining residue was subjected to chromatography on a short column (silica gel) using ethyl acetate–hexane (1 19) as eluant to obtain three fractions (A–C) Upon preparative TLC (silica gel) using ethyl acetate–hexane (1 7) as eluant, fraction A yielded esters **1–3**, fraction B afforded **4–6**, and **8**, and C gave **7**, **9** and (−)-1,6-desoxypipoxide [2] The proposed structures for **1–9** are consistent with their spectroscopic data Direct synthesis from commercially available benzoic acids and benzyl alcohols, together with simple chemical correlations, unambiguously confirmed the structures with regard to their substitution patterns

It has been proposed [9] that benzyl benzoate is probably the biosynthetic origin of the various cyclohexene epoxides as well as the source of the *o*-hydroxybenzyl group in the cytotoxic *o*-hydroxybenzyl dihydrochalcones and flavanones also found in this plant genus The co-isolation of benzyl benzoates **1–9** and pipoxide [1] and (−)-1,6-desoxypipoxide [2] from *U purpurea* is therefore of significance despite their simple structures

EXPERIMENTAL

^{1}H NMR 60 MHz, CCl_4 with TMS as int standard, EIMS probe 70 eV

Extraction and separation procedures Ground, air-dried roots of *U purpurea* (2 kg), collected from Kroab Island, Patalung Province, Thailand, were extracted with hexane (4 l) at room temp for 7 days and the extract was filtered, concd, and left in the refrigerator for 2 days Pipoxide (615 mg) was collected by filtration and washed with cold hexane The residue was concd and chromatographed on a short silica gel column using EtOAc–hexane (1 19) as eluant to afford three fractions, A, B, and C, which were further separated by prep TLC (silica gel) using EtOAc–hexane (1 7) to yield **1**, **2**, **3**, **4**, **5**, **6** and **8**, and **7**, **9** and (−)-1,6-desoxypipoxide (from A, B and C), respectively Esters **1–9** were further purified by bulb-to-bulb distillation (bath temp 120°, 0 1 mm)

Benzyl benzoate (**1**) Colourless oil (220 mg) identical in all respects to the commercial sample

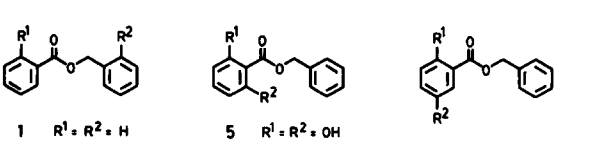
2-Methoxybenzyl benzoate (**2**) Colourless oil (81 mg), IR ν_{max}^{neat} cm^{-1} 1720, 1605, ^{1}H NMR δ 3 87 (3H, *s*), 5 33 (2H, *s*), 6 72–7 50 (7H, *m*), 7 97–8 17 (2H, *m*), MS *m/z* (rel int) 242 $[M]^+$ (8), 137 (57), 121 (21), 91 (100)

Benzyl 2-hydroxybenzoate (**3**) Colourless oil (76 mg), IR ν_{max}^{neat} cm^{-1} 3200, 1685, 1265, ^{1}H NMR δ 5 35 (2H, *s*), 6 81–7 51 (3H, *m*), 7 38 (5H, *s*), 7 86 (1H, *dd*, *J* = 8, 2 Hz), 10 73 (1H, *s*, removed with D_2O), MS *m/z* (rel int) 228 $[M]^+$ (55), 121 (3), 107 (7), 91 (100)

Benzyl 2-methoxybenzoate (**4**) Colourless oil (79 mg), IR ν_{max}^{neat} cm^{-1} 1720, 1260; ^{1}H NMR δ 3 86 (3H, *s*), 5 28 (2H, *s*), 6 78–7 50 (3H, *m*), 7 35 (5H, *s*), 7 72 (1H, *dd*, *J* = 8, 2 Hz), MS *m/z* (rel int) 242 $[M]^+$ (95), 135 (100), 107 (4), 91 (93) (Found C, 74 21, H, 6 06 $C_{15}H_{14}O_3$ requires C, 74 36, H, 5 83%)

Benzyl 2,6-dihydroxybenzoate (**5**) Colourless crystals (93 mg), mp 75–76°, IR ν_{max}^{mull} cm^{-1} 3420, 1680; ^{1}H NMR δ 5 38 (2H, *s*), 6 28 (2H, *d*, *J* = 8 Hz), 7 07 (1H, *t*, *J* = 8 Hz), 7 32 (5H, *s*), 9 40 (2H, *s*, removed with D_2O), MS *m/z* (rel int) 244 $[M]^+$ (26), 137 (3), 107 (4), 91 (100) (Found C, 68 58, H, 5 23 $C_{14}H_{12}O_4$ requires C, 68 85, H, 4 95%)

Benzyl 2-hydroxy-6-methoxybenzoate (**6**) Colourless oil (220 mg), IR ν_{max}^{neat} cm^{-1} 3100, 1665, 1250, ^{1}H NMR δ 3 88 (3H, *s*), 5 32 (2H, *s*), 6 27 (1H, *dd*, *J* = 8, 2 Hz), 6 47 (1H, *dd*, *J* = 8, 2 Hz), 7 06–7 42 (6H, *m*), 11 28 (1H, *s*, removed with D_2O), MS *m/z* (rel int) 258 $[M]^+$ (11), 151 (23), 107 (4), 91 (100) (Found C, 69 65, H, 5 59 $C_{15}H_{14}O_4$ requires C, 69 76, H, 5 46%)



1 $R^1 = R^2 = H$
2 $R^1 = H$, $R^2 = OMe$
3 $R^1 = OH$ $R^2 = H$
4 $R^1 = OMe$ $R^2 = H$
5 $R^1 = R^2 = OH$
6 $R^1 = OH$ $R^2 = OMe$
7 $R^1 = R^2 = OMe$
8 $R^1 = OH$ $R^2 = OMe$
9 $R^1 = R^2 = OMe$

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Benzyl 2,6-dimethoxybenzoate (7) Colourless crystals (1 05 g), mp 64–65°, IR ν_{max}^{mull} cm^{-1} 1730, 1255, ^1H NMR δ 3 70 (6H, *s*), 5 25 (2H, *s*), 6 40 (2H, *d*, *J* = 8 Hz), 6 99–7 39 (6H, *m*), MS *m/z* (rel int) 272 $[M]^+$ (30), 165 (100), 107 (15), 91 (80) (Found C, 70 56, H, 6 08 Calc for $C_{16}H_{16}O_4$ C, 70 58, H, 5 92%)

Benzyl 2-hydroxy-5-methoxybenzoate (8) Colourless oil (105 mg), IR ν_{max}^{neat} cm^{-1} 1680, 1280; ^1H NMR δ 3 67 (3H, *s*), 5 26 (2H, *s*), 6 66–7 40 (3H, *m*), 7 30 (5H, *s*), 10 18 (1H, *s*, removed with D_2O), MS *m/z* (rel int) 258 $[M]^+$ (23), 151 (57), 107 (34), 91 (100) (Found C, 69 53, H, 5 70 $C_{15}H_{14}O_4$ requires C, 69 76, 5 46%)

Benzyl 2,5-dimethoxybenzoate (9) Colourless oil (75 mg), IR ν_{max}^{neat} cm^{-1} 1730, 1250; ^1H NMR δ 3 73 (3H, *s*), 3 76 (3H, *s*), 5 24 (2H, *s*), 6 65–6 98 (2H, *m*), 7 13–7 42 (6H, *m*), MS *m/z* (rel int) 272 $[M]^+$ (100), 165 (40), 107 (6), 91 (44) (Found C, 70 41, H, 6 11 $C_{16}H_{16}O_4$ requires C, 70 58, H, 5 92%)

Methylation of **3**, **5**, **6** *and* **8** These compounds were methylated using Me_2SO_4–K_2CO_3–Me_2CO and the products were purified by bulb-to-bulb distillation to yield **4**, **7** (from both **5** and **6**) and **9**, respectively

Syntheses of **2**–**5** *and* **7**–**9** The reaction of benzoyl chlorides (prepared from benzoic acids) with benzyl alcohols in C_6H_6 directly yielded the corresponding benzyl benzoates

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1-*N*-METHYL-(6*E*)-(2-METHYLPROPYLIDENE)-(3*Z*)-3-(PHENYLMETHYLENE)-2,5-PIPERAZINEDIONE, A METABOLITE FROM *STREPTOMYCES ALBUS*

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Key Word Index—*Streptomyces albus*, 2,5-piperazinedione derivatives

Abstract—The structure and stereochemistry of a new piperazinedione, isolated from the cells of *Streptomyces albus*, are assigned on the basis of spectroscopic data, including comparison with related 2,5-piperazinediones

In the course of our work [1] on the biosynthesis of bacterial menaquinones (vitamins K_2), the menaquinones were isolated from the non-polar lipid extract of cells of *Streptomyces albus* Further fractionation of the non-polar constituents from the bacterial cell paste afforded a hitherto unreported crystalline compound in 0 1% yield

Mass spectral analysis (found $[M]^+$, 270 1375 $C_{16}H_{18}N_2O_2$ requires 270 1368) indicated a molecular formula of $C_{16}H_{18}N_2O_2$ for the new metabolite (**1**) The UV spectrum of **1** closely resembled that of the *Streptomyces* metabolite albonoursin (**3**), [2, 3] which has a molecular formula of $C_{15}H_{16}N_2O_2$ The ^1H NMR spectrum of the metabolite (**1**) showed the presence of the 2-methylpropylidene and phenylmethylene groups The remaining signals, a three-proton singlet at δ3 27 and a one-proton multiplet at δ8 00, exchangeable with D_2O, were attributable to NMe and NH groups, respectively Thus, the gross structure of the new metabolite (**1**) differs