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PSORALIDIN OXIDE, A COUMESTAN FROM THE SEEDS OF *PSORALEA CORYLIFOLIA*

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Key Word Index—*Psoralea corylifolia*; Leguminosae; coumestan; psoralidin-2′, 3′-oxide.

In our earlier communication we reported [1] the isolation and characterization of a new coumestan from the seeds of *Psoralea corylifolia*. We now describe the isolation and characterization of a new coumestan. Due to difficulty in isolating the pure compound the crude residue obtained from the mother liquor remaining after the removal of corylidin was acetylated to yield a diacetate which was separated by Si gel column chromatography.

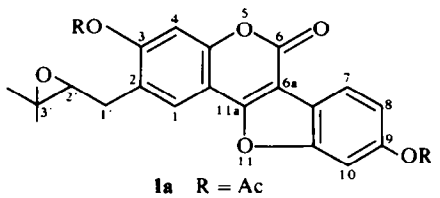
Compound **1a** crystallized from EtOH as colourless needles, mp 232–234°, M^+ at *m/e* 436, and analysed for $C_{24}H_{20}O_8$. Its UV spectrum showed absorptions at 233, 260 sh, 288 sh, 299, 329, 336 sh and 344 nm. Its IR (KBr) spectrum showed characteristic absorptions at 1755 due to carbonyl of the acetyl groups, at 1700 due to coumestan carbonyl and at 1378 and 1362 cm^{-1} due to gem-dimethyl. ^1H NMR ($CDCl_3$) of compound **1a** gave two sharp singlets at δ 1.40 and 1.44 for gem-dimethyl protons. Two singlets at 2.39 and 2.43 showed the presence of six acetoxy protons. A multiplet centred at 2.95 integrating for three protons was assigned to two benzylic protons and a methine proton attached to a carbon bearing an exirane group. The methine proton present in the above multiplet, in conformity with its assigned character, shifted to 5.40 in the ^1H NMR ($CDCl_3$) spectrum of the tetraacetate (**3b**), obtained by opening of the oxarine ring after refluxing the compound with Ac_2O and NaOAc. Also, there was an *ortho*- and *meta* coupled double-doublet at 7.26 (1 H, C-8) and a singlet at 7.33 (1 H, C-4), a *meta*-coupled doublet at 7.46 (1 H; C-10), a downfield singlet at 8.01 (1 H, C-1) and an *ortho*-coupled doublet appeared further downfield at 8.13 (1 H, C-7). Based on the above spectral data, compound **1a** was assigned the structure psoralidin-2′,3′- oxide diacetate. This has been further confirmed by its partial synthesis from psoralidin diacetate which on epoxidation with *m*-chloroperbenzoic acid gave a product identical to the natural psoralidin oxide diacetate.

EXPERIMENTAL

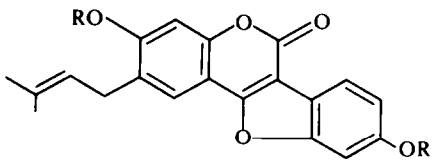
The whole dried seeds of *Psoralea corylifolia* (5 kg) were extracted with Et_2O. The dried Et_2O extract (800 g) was chromatographed on a Si gel column. The elution was carried out with petrol (40–60°), petrol–C_6H_6 (1:1), C_6H_6, C_6H_6–Et_2O (with increasing polarity) and MeOH.

The C_6H_6–Et_2O (1:3) eluate yielded corylidin (60 mg). The mother liquor showed the presence of one violet fluorescent compound on TLC (R_f 0.76; C_6H_6–Me_2CO, 4:1) in addition to other compounds. Due to difficulty in isolating the pure compound, the crude residue obtained from the mother liquor (after the removal of corylidin) was acetylated with Py–Ac_2O at room temp. The reaction product (3.5 g) was chromatographed over Si gel and the column was eluted with C_6H_6 and C_6H_6–EtOAc (with increasing polarity).

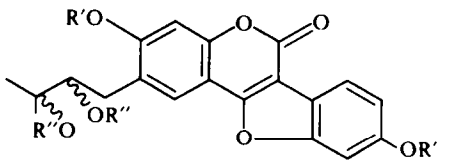
The C_6H_6–EtOAc (19:1) eluate (violet fluorescent) gave colourless crystalline needles from EtOH (20 mg), mp 232–234° R_f 0.28 (C_6H_6–Me_2CO, 19:1), UV λ_{max}^{MeOH} log ε) nm: 233 (4.45, sh), 260 (4.04, sh), 288 (4.05, sh), 299 (4.21), 329 (4.43), 336 (4.36, sh), 344 (4.36). IR ν_{max}^{KBr} cm^{-1}: 1755, 1700, 1642, 1378, 1362, 1200, 955, 920, 852 and 830. ^1H NMR (60 MHz, $CDCl_3$): δ 1.40 and 1.44 (3 H each, 2 *s*, Me_2C–), 2.39 and 2.43 (3 H each, 2 *s*, 2 × O–$COCH_3$), 2.95 (3 H, *m*, Ar–CH_2–$\underset{\diagdown\,\diagup}{O}$CH–$CMe_2$), 7.26 (1 H, *dd*,



1a R = Ac
1b R = Bz



2a R = Ac
2b R = Bz



3a R′ = R″ = H
3b R′ = R″ = Ac

J = 2.5, 8 Hz, C-8), 7.33 (1 H, *s*, C-4), 7.46 (1 H, *d*, J = 2.5 Hz, C-10), 8.01 (1 H, *s*, C-1), 8.13 (1 H, *d*, J = 8 Hz, C-7). (Found: C, 66.15; H, 4.61. $C_{24}H_{20}O_8$ requires C, 66.05, H, 4.58%).

Synthesis of psoralidin oxide diacetate (**1a**). To a soln of psoralidin diacetate (**2a**) (50 mg) in 5 ml $CHCl_3$ was added a soln of *m*-chloroperbenzoic acid (22 mg) in 5 ml $CHCl_3$ and the mixture kept at 10° for 18 hr. The $CHCl_3$ soln was washed free of acid, first with 2% $NaHCO_3$ soln (10 ml) and then with H_2O, and dried (Na_2SO_4). The solvent was removed and the residue purified on a Si gel column and crystallized from EtOH to yield colourless needles (35 mg), mp 233–235°. It was found to be identical with natural psoralidin oxide diacetate (co-TLC, mmp, IR and ^{1}H NMR).

2′,3′-*Dihydro*-3,9,2′,3′-*tetraacetyl psoralidin* (**3b**). Compound **1a** (30 mg) was refluxed for 2 hr with Ac_2O–NaOAc. The reaction product was worked up as usual and found to be a mixture of two compounds by TLC (R_f 0.33, 0.17; C_6H_6–Me_2CO, 19:1). These were separated on a Si gel column by eluting with C_6H_6–EtOAc (with incresing polarity). The compound with higher R_f (0.33) on TLC was eluted first by C_6H_6–EtOAc (19:1) and crystallized as fine needles from Me_2CO–petrol (11 mg), mp 210–212°. This compound could not be characterized. Compound **3b** was eluted with C_6H_6–EtOAc (19:1) in later fractions and crystallized from EtOH as fine needles (11 mg), mp 244–246°, R_f (0.17). UV λ_{max}^{MeOH} nm: 208, 224 sh, 237 sh, 260 sh, 288 sh, 299, 328, 344. IR ν_{max}^{KBr} cm^{-1}: 1765, 1740, 1735, 1635, 1365. ^{1}H NMR (100 MHz, $CDCl_3$): δ 1.54 and 1.58 (3 H each, 2*s*, Me_2C–), 1.88 (3 H, *s*, *O*–Ac), 1.98 (3 H, *s*, O–Ac), 2.35 (3 H, *s*, O–Ac), 2.40 (3 H, *s*, *O*–Ac), 2.96 (2 H, *m*, Ar–CH_2 at C-1′), 5.40 (1 H, *m*, C-2′), 7.20 (1 H, *s*, C-4), 7.26 (1 H, *dd*, J = 2, 8 Hz, C-8), 7.48 (1 H, *d*, J = 2 Hz, C-10), 7.88 (1 H, *s*, C-1), 8.08 (1 H, *d*, J = 8 Hz, C-7).

2′,3′-*Dihydro*-2′-3′-*dihydroxy psoralidin* (**3a**). Compound **3b** (30 mg) was deacetylated in alcoholic KOH (4 g KOH in 50 ml EtOH, refluxed for 4 hr) and the reaction mixture separated on a Si gel column with C_6H_6–EtOAc (with increasing polarity). The C_6H_6–EtOAc (7:3) eluate gave **3a**, crystallized from EtOH as fine needles (9.5 mg), mp 261–263°, R_f 0.06 (C_6H_6–Me_2CO, 4:1). MS *m/e* 370, M^+, UV λ_{max}^{MeOH} nm: 207, 225 sh, 244, 266 sh, 293 sh, 305, 314 sh, 348, 362. IR ν_{max}^{KBr} cm^{-1}: 3320, 1708, 1630, 1392, 1378. ^{1}H NMR (220 MHz, DMSO-d_6): δ 1.10 and 1.13 (3 H each, 2*s*, Me_2C–), 3.0 (2 H, *d*, J = 13.2 Hz, –CH_2 at C-1′), 3.40 (1 H, *m*, C-2′), 6.88 (1 H, *d*, *C*-4), 6.92 (1 H, *dd*, J = 2.5, 10 Hz, C-8), 7.15 (1 H, *d*, J = 2.5 Hz, C-10), 7.65 (1 H, *d*, J = 10 Hz, C-7), 7.76 (1 H, *s*, C-1).

3,9-*Dibenzyloxy psoralidin* (**2b**). Psoralidin (200 mg) was benzylated ($C_6H_5CH_2Cl$, 1 ml; K_2CO_3, 1.5 gm; NaI, 0.3 g; Me_2CO, 10 ml; DMF, 10 ml; refluxed for 8 hr), 3,9-Dibenxyloxy psoralidin was crystallized from EtOH as needles, mp 147–148°, R_f 0.81 (C_6H_6–Me_2CO, 19:1). Yield 220 mg.

3,9-*Dibenzyloxy psoralidin* -2′,3′-*oxide* (**1b**). To a soln of compound **2b** (185 mg) in 5 ml $CHCl_3$ was added a soln of *m*-chloroperbenzoic acid (70 mg) in 5 ml $CHCl_3$ and the mixture kept at 10° for 48 hr. The reaction product processed as for **1a** and **1b** was crystallized from EtOH to yield colourless needles (120 mg), mp 159–161° R_f, 0.64 (C_6H_6–Me_2CO, 19:1). UV λ_{max}^{MeOH} nm: 210, 243, 265 sh, 292 sh, 304, 342, 360 sh. IR ν_{max}^{KBr} cm^{-1}: 1742, 1735, 1638, 1630, 1378, 1355, 1265, 955, 820. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.33 and 1.40 (3 H each, 2*s*, Me_2C–), 3.00 (3 H, *m*, AR–CH_2–$\underset{\diagdown O \diagup}{CH}$–$CMe_2$), 5.10 and 5.13 (2 H each, 2*s*, –*O*–CH_2–Ar), 6.90 (1 H, *s*, C-4), 7.13 (1 H, *dd*, J = 2.5, 8 Hz, C-8), 7.23 (1 H, *d*, J = 2.5 Hz, C-10), 7.41 (10 H, *s*, 2 × O-$CH_2C_6H_5$), 7.70 (1 H, *s*, C-1), 7.90 (1 H, *d*, J = 8 Hz, C-7).

REFERENCE

1. Gupta, G. K., Dhar, K. L. and Atal, C. K. (1977) *Phytochemistry* **16**, 403.

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LAMPROLOBINE AND OTHER QUINOLIZIDINE DERIVATIVES FROM *LUPINUS HOLOSERICEUS*

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INTRODUCTION

Several species of the legume genus *Lupinus* are reported to be toxic to grazing animals in the Rocky Mountain region of the United States [1]. It is generally acknowledged that the quinolizidine alkaloids from these lupines are responsible for acute toxicoses and death in livestock [2, 3]. The Kellogg's spurred lupine, *L. caudatus* Kell., has caused cattle loss in Nevada and Utah [4] and a number of chemical studies [5–7] have shown this plant to contain anagyrine, α-isosparteine, α-isolupanine, lupanine, sparteine, and thermopsine. More recently, hydroxylupanine and three unidentified dehydrolupanine isomers have also been detected [8].

Presently, *L. holosericeus* Nutt. and *L. caudatus* are viewed as being taxonomically distinct ([9, 10]; D. B. Dunn, personal communication), although they have been