(1 H, *m*, C-3), 3.65 (2 H, *s*, C-8), 3.4 (3 H, *s*, –OMe), 2.33–3.23 (5 H, *m*, C-10, 11, 12), 1.66–1.93 (2 H, *m*, C-4).

Identification of β-erythroidine (**2**). R_f 0.35 (0.133 g), mp 100° [7]; MS (*m/z*): 273.1359 M^+; UV λ_{max}^{EtOH} 235 nm (log ε 4.15); IR ν_{max}^{KBr} cm^{-1}: 2810, 1720, 1090, 810, 645; ^{1}H NMR (60 MHz, $CDCl_3$): δ 6.43 (1 H, *q*, $J_{2,1}$ = 10 Hz, $J_{2,3}$ = 2 Hz, C-2), 5.85 (1 H, *q*, $J_{1,2}$ = 10 Hz, C-1), 5.71 (1 H, *m*, C-7), 4.63 (2 H, *s*, C-17), 4.1 (1 H, *m*, C-3), 3.58 (2 H, *m*, C-8), 3.38 (3 H, *s*, –OMe), 2.35–3.23 (6 H, *m*, C-14, 10, 11), 1.58–1.96 (2 H, *m*, C-4). The methiodide of β-erythroidine which we prepared [8] had the following constants: mp 219–220°, IR ν_{max}^{KBr} cm^{-1}: 2820, 1740, 1110, 840, 810. As it was not possible to obtain α-erythroidine in a pure crystalline form, it was converted to the β-isomer [9] and compared with an authentic sample.

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1-HYDROXYCANTHIN-6-ONE, AN ALKALOID FROM *AILANTHUS GIRALDII*

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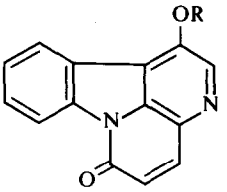
Key Word Index—*Ailanthus giraldii*; Simaroubaceae; 1-hydroxycanthin-6-one; alkaloid.

Abstract—A new alkaloid has been isolated from the heartwood of *Ailanthus giraldii* and its structure determined as 1-hydroxycanthin-6-one.

The reported presence of 4-methoxy-1-methyl-3(3,3-dimethyl-allyl)-2(1 H)quinone [1], alkaloids [2,3] and quassinoids [4] in simaroubaceous plants and the anti-cancer activity associated with several of these compounds [5,6] prompted this investigation. The MeOH extract of the heartwood of *Ailanthus giraldii* on work-up yielded a yellow solid (**1a**), mp 220°. Positive reactions towards both Dragendorff's and Mayer's reagents as well as its acid solubility revealed the alkaloid nature of **1a**, making it possible to assign the band appearing in its IR spectrum at 1655 cm^{-1} to a lactam function. Absorptions characteristic of its aromatic and hydroxylic nature were also discernible in the spectrum (3350, 1585, 1545, 770 and 720 cm^{-1}). The UV spectrum of **1a** (263, 287.8, 336, 364, 370 and 385 nm) was entirely compatible with those reported for canthinones [7]. The mass spectral fragmentation pattern also resembled that reported for canthinones, the M^+ appearing at *m/z* 236 ($C_{14}H_8O_2N_2$) and a metastable ion at *m/z* 183.32 corresponding to the loss of CO from the M^+ (236–208). **1a** is thus a hydroxycanthinone. The ^{1}H NMR of **1a**, signals of which integrated for the correct number of protons by the appearance of a pair of doublets at δ 6.89 and 8.09 (1 H each, J = 10 Hz), indicated that ring D was unsubstituted. Evidence for the location of the OH function on either C-1 or C-2 could also be obtained from the ^{1}H NMR by the absence of the *ortho*-coupled doublets characteristic of H-1 and H-2, in place of which appeared a singlet at 8.48.

1a was acetylated to yield a monoacetate (**1b**), mp 205°.



1a R = H
1b R = Ac
1c R = Me

In the ^{1}H NMR of **1b** two protons were deshielded relative to **1a**. The OH, therefore, should be located on C-1, the protons undergoing deshielding being located on C-2 (δ 8.48–8.68) and C-11 (δ 8.23–8.7).

Methylation of **1a** with Me_2SO_4–K_2CO_3–Me_2CO afforded a methyl ether, **1c**, mp 246° which was identical with 1-methoxycanthin-6-one by comparison with an authentic sample [3].

EXPERIMENTAL

Extraction. Dried pieces of the heartwood of *A. giraldii* Dode (5 kg) were exhaustively extracted with petrol (60–80°) and then repeatedly extracted with MeOH. The MeOH extract was concd and chromatographed on a Si gel column using C_6H_6 containing increasing quantities of EtOAc as eluant.

1a. Fractions (100 ml each) eluted with C_6H_6–EtOAc (2:3) were combined and processed to yield a solid homogeneous on TLC (800 mg). It was crystallized from MeOH–Me_2CO, mp 220°. UV λ_{max}^{MeOH} nm: 263, 287.8, 336, 364, 370, 385; IR ν_{max}^{mujol} cm^{-1}: 3350, 1655, 1620, 1585, 1545, 815, 770, 270: ^{1}H NMR (100 MHz; DMSO-d_6): δ 6.89 (1 H, *d*, J = 10 Hz, H-5), 7.8 (2 H, *m*, H-9 and H-10), 8.09 (1 H, *d*, J = 10 Hz, H-4), 8.23 (1 H, *dd*, J_1 = 7 and J_2 = 1.5 Hz, H-11), 8.48 (1 H, *s*, H-2) and 8.57, (1 H, *dd*, J_1 = 7 and J_2 = 1.5 Hz, H-8); MS *m/z* (rel. int.): 236 (M^+, 100), 235 (32), 208 (76), 183.32 (m*), 181 (8), 180 (2.6).

1b. To a soln of **1a** (100 mg) in pyridine (3 ml) was added Ac_2O (3 ml) and the mixture kept in the dark overnight. The product isolated on precipitation in ice was crystallized from MeOH, mp 205°. ^{1}H NMR (60 MHz, $CDCl_3$): δ 2.56 (3 H, *s*, OAc), 6.95 (1 H, *d*, J = 9.5 Hz, H-5), 7.35–7.85 (2 H, *m*, H-10 and H-9), 7.95 (1 H, *dd*, J_1 = 2, J_2 = 8 Hz, H-8), 8.03 (1 H, *d*, J = 9.5 Hz, H-4), 8.68 (1 H, *s*, H-2) and 8.7 (1 H, *dd*, J_1 = 2.0 and J_2 = 8 Hz, H-11).

1c. **1a** (100 mg) was dissolved in Me_2CO (dry, 50 ml) and refluxed in the presence of K_2CO_3 (dry, 2 g) and Me_2SO_4 (neutral, freshly dist., 0.4 ml) until methylation was completed as revealed by TLC (20 hr). The crude product isolated by pouring into H_2O and extraction with Et_2O was chromatographed over Si gel. The portion eluted with $CHCl_3$–MeOH (49:1) was crystallized from MeOH, mp 246° (mp with authentic sample, 246–247°).

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