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*Phytochemistry*, 1977, Vol. 16, pp. 1126-1127. Pergamon Press. Printed in England.

### 5-HYDROXYCANTHIN-6-ONE FROM *SIMAROUBA AMARA*

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(Received 14 January 1977)

**Key Word Index**—*Simarouba amara*; Simaroubaceae; alkaloid; 5-hydroxycanthin-6-one.

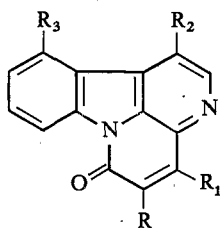
Earlier work on the constituents of *Simarouba amara* Aubl. of two different origins has yielded the quassinoid simarolide [1] and two derivatives of  $\Delta^7$ -tirucallol [2]. We now wish to report the isolation of a new naturally occurring alkaloid, 5-hydroxycanthin-6-one (1) from the root bark of trees growing in Guyana.

5-Hydroxycanthin-6-one was obtained as a very insoluble, bright yellow precipitate at the  $H_2O$ - $CHCl_3$  interface of the alkalised acid layer, obtained during a routine search for alkaloids in the  $CHCl_3$  extract of the dried and defatted plant material. It crystallises as orange-

yellow platelets from MeOH, mp 256-8° (decomp.), gives a green colour with alcoholic  $FeCl_3$  and exhibits a pronounced blue-green fluorescence in very dilute methanolic solution.

Its empirical formula,  $C_{14}H_8N_2O_2$ , as well as its UV spectrum, which resembles that of 5-methoxycanthin-6-one 2 [3], ( $C_{15}H_{10}N_2O_2$ ), suggests that this new compound might be 5- or 4-hydroxycanthin-6-one. An important peak at M-56 ( $m/e$  180) in its MS, corresponding to the loss of  $2 \times CO$  and supported by the presence of an appropriate metastable ion at  $m/e$  137.3, provides evidence that the OH is adjacent to the carbonyl of the amide function and thus supports our structure assignment. Final proof of the structure was obtained by converting 1 into 5-methoxycanthin-6-one (2) by means of  $CH_2N_2$  and direct comparison with authentic 2, a naturally occurring alkaloid first described from *Pentaceras australis* Hook. F. (Rutaceae) by Nelson and Price [3]. These authors were able to demethylate 2 to 1 by means of  $HBr$ - $HOAc$ . However, Si gel TLC of an alcoholic extract of our plant material still indicated the presence of a substantial amount of 1, thus ruling out any likelihood of artefact formation.

All alkaloids so far reported from the family Simaroubaceae belong to the structurally related classes of canthin-6-one and harmane. Derivatives of the former have been reported from *Aeschrion crenata* Vell. (= *Picrasma crenata* Vell.) 3 [4] *Picrasma ailanthoides* Planchon 4, 5 [5, 6] and *Soulamea pancheri* Brongn, et Gris 3, 6, 7 [7]. Harmane derivatives have been found in *Aeschrion crenata* Vell. 8, 9, 10 [8], *Picrasma javanica* Bl. 11 [9], *Picrasma ailanthoides* Planchon 8, 12 [10] and *Perriera madagascariensis* Courchet 13 and possibly a dimer of 13 [11].



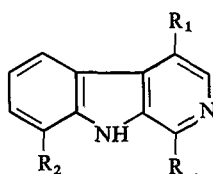
R	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>
1 —OH	—H	—H	—H
2 —OMe	—H	—H	—H
3 —H	—H	—H	—H
4 —OH	—OMe	—H	—H
5 —OMe	—OMe	—H	—H
6 —H	—H	—OMe	—H
7 —H	—H	—OMe	—OH

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R	R <sub>1</sub>	R <sub>2</sub>
8 —COOMe	—H	—H
9 —CH <sub>2</sub> Me	—OMe	—H
10 —CH <sub>2</sub> Me	—OMe	—OMe
11 —CH=CH <sub>2</sub>	—OMe	—H
12 —CH <sub>2</sub> OH	—H	—H
13 —CH=CH <sub>2</sub>	—OMe	—OMe

## EXPERIMENTAL

Mps are uncorr. UV spectra were determined in EtOH (95%) and MS at 70 eV. Microanalyses were performed by the Service Central de Microanalyse du CNRS (Gif sur Yvette).

*Isolation of 5-hydroxycanthin-6-one (1).* The dried, finely ground and hexane defatted root bark of *S. amara* (260 g) (Herbarium voucher n° H.J. 1804) was CHCl<sub>3</sub> extracted for 24 hr in a Soxhlet apparatus. The dark brown residue (6.9 g) obtained on evaporation of solvent was redissolved in CHCl<sub>3</sub> and shaken with dil. HCl (2%, 3 × 250 ml). The combined acid layers were basified with a slight excess of ice-cold 5% aq. KOH and shaken with CHCl<sub>3</sub>. A viscous yellow emulsion which had formed at the interface of the two layers was separated, filtered through a sintered glass crucible, the residue thoroughly washed and dried yielding crude 5-hydroxycanthin-6-one **1** (460 mg). Recrystallisation from MeOH gave orange-yellow platelets, mp 256–258° (decomp. with sublimation from 220°) (lit. [3]: 259–261°, decomp.); (Found: C 71.7; H 3.5; N 11.9; C<sub>14</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub> requires C 71.2; H 3.4; N 11.9). UV  $\lambda_{\text{max}}^{\text{EtOH}}$  (log.  $\epsilon$ ) 288 (3.96), 325 (3.62), 341 (3.79), 358 (3.96), 376 (4.00), 412 nm (3.66);  $\lambda_{\text{min}}^{\text{EtOH}}$  275 (3.91), 321 (3.60), 328 (3.61), 347 (3.74), 368 (3.79), 389 nm (3.56);  $\lambda_{\text{max}}^{\text{EtOH/H}^+}$  263 sh (4.00), 312 (3.96), 320 sh (3.92), 362 sh (4.05), 376 (4.13); 388 nm (4.09);  $\lambda_{\text{min}}^{\text{EtOH}}$  278 (3.57), 337 (3.74), 384 nm (4.08);  $\lambda_{\text{max}}^{\text{EtOH/OH}^-}$  286 (4.06), 324 sh (3.59), 338 (3.56), 410 nm (4.02);  $\lambda_{\text{min}}^{\text{EtOH/OH}^-}$  277 (4.04), 332 (3.54), 351 nm (3.29). MS (peaks > 5% m/e (%)): 237 (11), 236 (M<sup>+</sup>, 100), 181 (6), 180 (40), 179 (34), 154 (12), 153 (38), 152 (22), 151 (8), 150 (6), 140 (10), 129 (5), 128 (8),

127 (18), 126 (20), 125 (12), 118 (20), 114 (8), 113 (11), 102 (8), 101 (14), 100 (8), 99 (7), 90 (16), 88 (8), 87 (10), 86 (6), 77 (11), 76 (18), 75 (19), 74 (12), 64 (5), 63 (22), 62 (13); metastable peaks at m/e 183.8, 155.7, 137.2, 130.1, 129.1, 103.8, 102.9, 91.7, 77.9, 65.0, 56.6 and 55.7. The compound fluoresces bright yellow-green on Si gel under UV light of  $\lambda$  366 nm.

*5-Methoxycanthin-6-one (2).* 5-Hydroxycanthin-6-one (15 mg) in dioxane (1 ml) containing a few drops of MeOH was methylated during 5 days at 5° with a slight excess of CH<sub>2</sub>N<sub>2</sub>-Et<sub>2</sub>O. After evaporation of solvents, the crude reaction product was dissolved in CHCl<sub>3</sub> and separated from traces of unchanged starting material by elution with CHCl<sub>3</sub> from a short Si gel column (20 g, Merck Kieselgel 60). After evaporation of solvent and recrystallisation from 95% EtOH, 5-methoxycanthin-6-one was obtained as colourless needles, mp and mmp 243–244° (decomp.); the UV spectrum had maxima at  $\lambda$  242, 247, 263 sh, 296, 306 sh, 324 sh, 339.5, 355 and 373 nm and was superimposable upon that of authentic 5-methoxycanthin-6-one [3].

*Acknowledgements*—We are greatly indebted to Dr. J. A. Lambertson, C.S.I.R.O., Melbourne, for a sample of 5-methoxycanthin-6-one. One of us (E.V.L.) thanks the French Government for the award of a scholarship.

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