petrol–C_6H_6 (1:3) eluates, and 10-methoxyvellosimine (**1**) occurring in the C_6H_6–$CHCl_3$ (1:1) eluates have been reported earlier [2]. The C_6H_6 eluate from the same column contained a mixture of bases, which on careful rechromatography over Al_2O_3 furnished majvinine (yield: 15 mg; 0.0002%). Majvinine (**4**) crystallised as needles, mp 195–97° (dec) from C_6H_6. MS: M^+ 336.1818 (70%) ($C_{21}H_{24}N_2O_2$: calc. 336.1836), *m/e* 335.1765 (39%) ($C_{21}H_{23}N_2O_2$, calc. 335.1761), 321.1621 (8%) ($C_{20}H_{21}N_2O_2$, calc. 321.1605), 307.1831 (100%) ($C_{20}H_{23}N_2O$, calc. 307.1811), 293.1618 (17%) ($C_{19}H_{21}N_2O$, calc. 293.1654), 226.1118 (10%) ($C_{14}H_{14}N_2O$, calc. 226.1108), 198.0805 (12%) ($C_{12}H_{10}N_2O$, calc. 198.0795). IR (Nujol, cm^{-1}): 2700, 1718 (—CHO); 1620, 1585, 853, 837, 800 (1,2,4-tri-substituted C_6H_6). NMR (60 MHz, $CDCl_3$) (δ): 9.73 (1H, *d*, *J* 1.5 Hz, $C\underline{H}O$), 7.17 (1H, *d*, J_o 8 Hz, C-12-H), 6.93 (1H, *d*, J_m 2.5 Hz, C-9-H), 6.80 (1H, *dd*, J_o 8 Hz, J_m 2.5 Hz, C-11-H), 5.36 (1H, *q* with further fine splitting, *J* 7 Hz, $=C\underline{H}—Me$), 3.84 (3H, *s*, Ar—OCH_3), 3.60 (3H, *s*, $N_{(a)}—C\underline{H}_3$), 1.61 (3H, double triplet, J_1 7 Hz, J_2 2 Hz, $=CH—CH_3$). The dihydroderivative **6**, obtained by $NaBH_4$ reduction of **4**, was obtained as an amorphous powder. MS: M^+ 338.1980 (calc. for $C_{21}H_{26}N_2O_2$, 338.1994) (72%), 337 (M—H) (70%), 323 (M—Me) (7%), 307 (M—CH_2OH) (36%), 293 (12%), 226 (11%), 213 (100%), 212 (85%), 198 (12%), 197 (16%).

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FUROQUINOLINE ALKALOIDS FROM *TYLOPHORA ASTHMATICA*

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Key Word Index—*Tylophora asthmatica*; Asclepiadaceae; furoquinoline alkaloids; γ-fagarine and skimmianine.

Furoquinoline alkaloids, *e.g.* γ-fagarine and skimmianine, have so far been found only in plants of the Rutaceae, [1] with one exception: skimmianine has been found as a minor alkaloid of *Vinca herbaceae* (Apocynaceae) [2] It is thus of some interest that we now report the isolation of two such alkaloids from *Tylophora asthmatica* of the Asclepiadaceae. We separately isolated basic material from the roots and aerial parts of the plant. The major alkaloids were the phenanthroindolizidine alkaloids reported previously [3, 4] One of the minor alkaloids of the roots, however, proved to be γ-fagarine and a minor base of the aerial parts was shown to be skimmianine.

This is a surprising observation since the Rutaceae and Asclepiadaceae are taxonomically unrelated (although the latter family is closely allied to the Apocynaceae). [5] Moreover, the biosynthesis of furoquinoline [6] and phenanthroindolizidine [7] alkaloids is quite different. The validity of our results is strengthened by the isolation of different furoquinoline bases from roots and aerial parts.

EXPERIMENTAL

Plant Source. *Tylophora asthmatica*, Wight et Arn, obtained originally through Dr. T. R. Govindachari, Ciba Research Centre, Bombay, India; greenhouse grown in Leeds.

Alkaloids were isolated as reported previously [3] except that initial fractionation by column chromatography was carried out on Kieselgel G nach Stahl [8] using MeOH in $CHCl_3$. The furoquinoline alkaloids appeared in front of tylophorine. Skimmianine was purified on Woelm Al_2O_3 (neutral; grade 1; benzene–chloroform) (yield: 9×10^{-4}% of dried plant material) and γ-fagarine by preparative TLC (Kieselgel G, 5% MeOH in $CHCl_3$) (yield: 8×10^{-4}%). The NMR and MS (including accurate mass determination on the molecular ions) corresponded to the authentic alkaloids [9]. In addition, direct comparison established identity on TLC (3 solvent systems) and HPLC; in the case of γ-fagarine further proof of identity was obtained by mp mmp and IR spectra.

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

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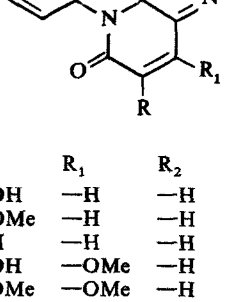
Key Word Index—*Simarouba amara*; Simaroubaceae; alkaloid; 5-hydroxycanthin-6-one.

Earlier work on the constituents of *Simarouba amara* Aubl. of two different origins has yielded the quassinoid simarolide [1] and two derivatives of Δ^7-tirucallol [2]. We now wish to report the isolation of a new naturally occurring alkaloïd, 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 alkalinised acid layer, obtained during a routine search for alkaloïds 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.



	R	R₁	R₂	R₃
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

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 × 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 alkaloïd 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 ailanthoïdes* Planchon **8**, **12** [10] and *Perriera madagascariensis* Courchet **13** and possibly a dimer of **13** [11].

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