Preparation of methyl 17-desoxyadirubine (**2d**). Methyl anhydroadirubine (1 mg) in MeOH (2 ml) was hydrogenated over Pd black (1 mg) for 3 hr. Filtration and evaporation afforded the 2 epimers of methyl desoxyadirubine; UV (MeOH): λ_{max} 289, 282, 273, 225 nm; MS, *m/e* 398 (M$^+$), 397, 340, 339, 337, 311, 309, 269, 251, 242, 183, 182, 169, 168, 156. TLC on Sil with CHCl$_3$–EtOAc (2:1) showed 2 overlapping spots.

Preparation of methyl anhydroadirubine. Methyl adirubine acetate (**2c**) (10 mg), prepared by methylation and acetylation of adirubine, was heated under reflux with NaOMe in dry MeOH for 45 min. After addition of a small lump of solid CO$_2$, solvent was removed under red pres the residue taken up in CHCl$_3$ and separated by TLC on silica with CHCl$_3$–EtOAc (2:1). In addition to methyl adirubine (2·6 mg), methyl anhydroadirubine (3·5 mg) was obtained and proved to be identical with the previously isolated material by MS, IR, NMR, CD spectra and TLC in several systems.

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REFERENCES

1. Brown, R. T., Chapple, C. L. and Lee, G. K. (1972) *Chem. Commun.* 1007.
2. Brown, R. T. and Charalambides, A. A. (1974) *Tetrahedron Letters* 1649, 3429.
3. Brown, R. T. and Chapple, C. L. (1973) *J.C.S. Chem. Commun.* 886.

Phytochemistry, 1975, Vol. 14, p. 2529. Pergamon Press. Printed in England.

CALYCANTHINE FROM *PALICOUREA ALPINA*

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Key Word Index—*Palicourea alpina*; Rubiaceae; alkaloid; calycanthine.

Plant. Palicourea alpina (Sw.) DC. *Source.* Newcastle, St. Andrew, Jamaica, collected in October 1970 (Herbarium No. 27,179, Botany Department, University of the West Indies). *Previous work.* Plant material from Hardwar Gap, St. Andrew collected in July 1973 was shown to contain vomifoliol [1], indole alkaloids palinine, palidimine and harman [2].

Present work. Stems and leaves were dried and powdered (150 g). Extraction with 2% tartaric acid followed by the usual work up for basic material [1] yielded 0·275 g of crude material. PLC on silica plates using CHCl$_3$–MeOH (1:1) afforded 12 mg of a chromatographically homogeneous solid which had identical physical properties (UV, IR [3], NMR [4] to calycanthine. High resolution MS showed that the base peak was the parent ion (*m/e* 346·2113; Calculated for $C_{22}H_{26}N_4$, 346·2157) and the fragmentation pattern observed was very similar to that reported earlier for calycanthine [5].

Calycanthine has previously been shown to be the principal poisonous constituent of *Calycanthus glaucus* Willd. [6] and was also reported from *C. floridus* L. [7] and *C. occidentalis* Hook. and Arn. [8] (Calycanthaceae). *Chimonanthus praecox* (L.) Link (= *Meratia praecox* Rehder and Wilson) Calycanthaceae [9] and *Bhesa archboldiana* (Merr. and Perry) Ding Hou (Celastraceae) [10] have also been shown to contain this alkaloid, but this is the first report of its isolation from the Rubiaceae. It is noteworthy that specimens of *Palicourea alpina* growing at Hardwar Gap, only 2 km from the location of the plants used in this study, did not yield this alkaloid, but other indole types were shown to be present [2].

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REFERENCES

1. Stuart, K. L. and Woo-Ming, R. B. (1975) *Phytochemistry* **14**, 594.
2. Stuart, K. L. and Woo-Ming, R. B. (1974) *Tetrahedron Letters* 3853.
3. *Physical Data of Indole and Dihydroindole Alkaloids*, Vol. 1, 1961, Lilly Research Laboratories, Eli Lilly, Indiana, U.S.A.
4. Woodward, R. B., Yang, N. C., Katz, T. J., Clark, V. M., Harley-Mason, J, Ingleby, R. F. J and Sheppard, N. (1960) *Proc. Chem. Soc.* 76.
5. Clayton, E., Reed, R. I., and Wilson, J. M. (1962) *Tetrahedron* **18**, 1495.
6. Eccles, G. R. (1888) *Proc. Am. Pharm. Assoc.* **84**, 382.
7. Späth, E. and Stroh, W. (1925) *Ber. Deut. Chem. Ges.* **58**, 2131.
8. Manske, R. H. F. and Marion, L. (1939) *Can. J. Res.* B17, 293.
9. Manske R. H. F. (1929) *J. Am. Chem. Soc.* **51**, 1836.
10. Culvenor, C. C. J., Johns, S. R., Lamberton, J. A. and Smith, L. W. (1970) *Aust. J. Chem.* **23**, 1279.