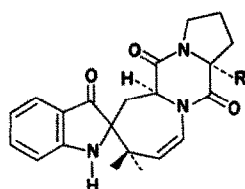


3430–3350 (*br.* band), 1670 and 1618  $\text{cm}^{-1}$ . The NMR spectrum ( $\text{CDCl}_3$ ) showed 2 singlets at  $\tau$ 8.48 (3H) and  $\tau$ 9.16 (3H) which were assigned to the 2 geminal Me groups. The *cis*-olefinic protons appeared as an AB-pattern at  $\tau$ 3.29 and  $\tau$ 4.98 ( $J_{AB}$  10 Hz). The protons at  $C_8$  and  $C_9$  appeared as an ABX system,  $H_A$  being  $H_{\text{seq}}$ ,  $\tau$ 7.13 ( $q$ ,  $J_{AB}$  15,  $J_{AX}$  6 Hz);  $H_B$  being  $H_{8ax}$ ,  $\tau$ 7.86 ( $q$ ,  $J_{AB}$  15,  $J_{BX}$  12 Hz) and  $H_X$  represented by a pair of doublets at  $\tau$ 5.16 ( $J_{AX}$  6 and  $J_{BX}$  12 Hz). A complex pattern centred around  $\tau$ 6.36 was assigned to the methylene protons adjacent to the proline *N*-atom, the remaining 4 methylene protons which comprised the proline ring appeared as an unresolved multiplet between  $\tau$ 7.6 and 8.1. The splitting pattern of the aromatic region was identical to that of dihydroaustamide. In both 12R- and 12S-dihydroaustamide and in the 12R- and 12S-tetrahydroaustamide, the proton at  $C_{12}$  resonated between



(1) R = OH  
(2) R = H

$\tau$ 5.80–5.90[1]. The lack of any absorption in this region strongly supports the location of the OH group at  $C_{12}$ . The mass spectrum of (1) showed a strong peak at  $m/e$  363,  $\text{C}_{21}\text{H}_{21}\text{N}_3\text{O}_3$  (40%) due to the loss of  $\text{H}_2\text{O}$  from the molecular ion and subsequent fragmentation virtually identical to that of austamide with the base peak at  $m/e$  218,  $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_2$ .

The C.D. properties of (1) in MeOH:  $\lambda/\text{nm}$   $\Delta\epsilon$  420(0), 374 (–2.0), 355(0), 341 (+2.35), 314(0), 305 (–0.34) and 290(0) resembled those of 2S,9S,12S-dihydroaustamide (2):  $\lambda/\text{nm}$   $\Delta\epsilon$  420(0), 376 (–0.66), 366(0), 346 (+2.4), 322(0), 305 (–0.73) and 278(0). It is known[1] that conformational changes (stereochemistry at  $C_{12}$ ) remote from the chiral spiro atom ( $\psi$ -indoxyl chromophore) do have a marked influence on the sign of the observed Cotton effects for these compounds between 300 and 400 nm. The close similarity in C.D. spectra of the two compounds established the *cis*-relationship of the  $C_9$ -H and  $C_{12}$ -OH groups and the S-configuration at  $C_2$  and  $C_9$ . On the contrary, 12R-dihydroaustamide exhibited  $\Delta\epsilon$  383 nm + 3.0 and  $\Delta\epsilon$  320 nm – 4.60[1].

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### MURRAYACINE FROM *CLAUSENA HEPTAPHYLLA*\*

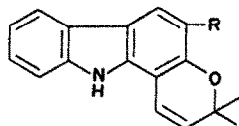
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**Key Word Index**—*Clausena heptaphylla*; Rutaceae; murrayacine; carbazole alkaloid.

From taxonomic interest, we undertook the examination of *Clausena heptaphylla* (Rutaceae, Sub. Fam. Aurantiae) from which we reported the isolation and structure proof of two new carbazole alkaloids, heptazoline [1], and heptazolidine [2], besides murrayanine and denatatin. We now report the isolation of another carbazole alkaloid which has been identified as murrayacine [3] (1).



(1) R = CHO  
(2) R = Me

The neutral fraction of the petrol (40–60°) extract of roots of *Clausena heptaphylla*, on repeated chromatography, furnished a crystalline nitrogenous constituent,  $\text{C}_{18}\text{H}_{15}\text{NO}_2$ , mp 244–45° which readily gave a 2:4 DNPH derivative. The IR spectrum of the compound

showed the presence of  $-\text{NH}-$  and aldehyde functions on an aromatic system [ $\nu_{\text{max}}^{\text{KBr}}$  3250, (NH–); 1675 (–CHO); 1640, 1600 (unsaturation and aromatic group) and 895, 865, 740  $\text{cm}^{-1}$ ]. Its UV spectrum  $\lambda_{\text{max}}^{\text{EtOH}}$  226, 282, 301 nm;  $\log \epsilon$  4.60, 4.57, 4.58 and the other physical and analytical data were suggestive of the identity of the isolated compound with murrayacine and this was confirmed by direct comparison with a pure sample (mmp, TLC and UV, IR).

The presence of (1) in *Clausena heptaphylla* is taxonomically and biogenetically rational since the plant has been shown [4] to contain girinimbine (2) and is taxonomically related to *Murraya koenigii* Spreng in which both (1) and (2) were reported.

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\* Part 37 in the series of Chemical Taxonomy. Part 36, Chakraborty, D. P., Bhattacharyya, P., Islam, A., and Ray, S. (1974) *Chem. Ind.* 303.