substantiated by the synthesis through the condensation of cladrastin and tetra-*O*-acetyl-α-D-glucopyranosyl bromide in the presence of Ag_2CO_3 as catalyst followed by deacetylation. Bayin afforded a hexaacetate on acetylation with Ac_2O and NaOAc, but did not yield any sugars on acid hydrolysis. The NMR and UV spectra of the compound and its acetate indicated that the compound might be 7,4′-dihydroxyflavone-8-*C*-glycoside [7]. Ferric chloride oxidation of the glycoside afforded D-glucose by co-PC. The final identification of the compound as bayin, was established on comparison of the acetate with authentic bayin hexaacetate kindly provided by Dr. R. A. Eade. This is the second isolation of bayin, previously found in the wood of *Castanosperum australe* (Fagaceae) [8], from natural source.

Pseudobaptigenin. Colorless needles, mp 295–297° (MeOH) (lit. [6] 290–292°), UV λ_{max}^{MeOH} nm: 241(*sh*), 249, 260(*sh*), 296; $\lambda_{max}^{MeOH+NaOAc}$ nm: 258, 290(*sh*), 334; $\lambda_{max}^{MeOH+AlCl_3}$ nm: 241(*sh*), 249, 260(*sh*), 296, NMR (DMSO-d_6, δ): 8·30(*s*, H-2), 8·02 (*d*, *J* 8 Hz, H-5), 7·10(*m*, H-2′,5′ and 6′), 6·94(*m*, H-6 and 8), 6·06(*s*, OCH_2O) MS *m/e*: 282 (M^+), 281, 268, 146 ($HC{\equiv}C{-}\phi{=}O_2CH_2^+$), 145, 139, 116, 112, 108, 89, 88.

Pseudobaptigenin monoacetate. Colorless needles, mp 166–167° (MeOH), NMR (DMSO-d_6, δ): 8·46(*s*, H-2), 8·14(*d*, *J* 8 Hz, H-5), 7·50(*d*, *J* 2 Hz, H-8), 7·28(*d.d*, *J* 8, 2 Hz, H-6), 7·04(*m*, H-2′,5′ and 6′), 6·02(*s*, OCH_2O), 2·32(*s*, COMe). Double irradiation: Signal H-6 and 8 when signal H-5 was irradiated; H-6 (7·28, *d*, *J* 2 Hz), (7·50, *d*, *J* 2 Hz). MS *m/e*: 324 (M^+), 282, 281, 146, 145, 139, 116, 88.

Cladrastin-7-O-β-D-glucoside. Colorless needles, mp 213–215° (MeOH), UV λ_{max}^{MeOH} nm: 258, 318. NMR Signals after silylation (CCl_4, δ): 7·88(*s*, H-2), 7·58(*s*, H-5), 7·00(*s*, H-8), 7·08(*m*, H-2′,5′ and 6′), 4·94(*d*, *J* 7 Hz, H-1″), 3·94(*s*, OMe), 3·86(*s*, OMe), 3·80(*s*, OMe), 4·04–3·20(*m*, glucosyl 6 H).

Cladrastin. Colorless needles, mp 204–205° (MeOH), NMR (DMSO-d_6 δ): 8·40(*s*, H-2), 7·52(*s*, H-5), 7·28(*s*, H-8), 7·10(*m*, H-2′, 5′ and 6′), 3·92(*s*, OMe), 3·82(*s*, 2 OMe).

Bayin. Pale yellow needles, mp 218–220° (*dec.*) (MeOH) [lit. [8] 220° (*dec.*)], $[\alpha]_D^{18}$ −4·5° (MeOH;*c* 0·20) (lit. [8] −1° [MeOH; *c* 0·19], UV λ_{max}^{MeOH} nm: 256, 315(*sh*), 331; $\lambda_{max}^{MeOH+NaOAc}$ nm: 260, 269, 310, 331; $\lambda_{max}^{MeOH+AlCl_3}$ nm: 255(*sh*), 315(*sh*), 332. NMR (DMSO-d_6, δ): 8·04(*d*, *J* 10 Hz, H-2′ and 6′), 7·58(*d*, *J* 10 Hz, H-5), 7·01 (*d*, *J* 10 Hz, H-6), 6·94 (*d*, *J* 10 Hz, H-3′ and 5′), 6·72 (*s*, H-3), 4·95(*d*, *J* 9 Hz, H-1″), 3·20–4·30(*m*, glucosyl 6 H).

Bayin hexaacetate. Colorless plates, mp 128–129° (MeOH), NMR ($CDCl_3$, δ): 8·25(*d*, *J* 10 Hz H-2′ and 6′), 8·15(*d*, *J* 9 Hz, H-6), 7·42(*d*, *J* 9 Hz, H-5), 7·24(*d*, *J* 10 Hz, H-3′ and 5′), 6·86(*s*, H-3), 5·02(*d*, *J* 9 Hz, H-1″), 4·24(*m*, glucosyl 6 H), 2·42(*s*, COMe), 2·34(*s*, COMe), 2·08(*s*, COMe), 1·98(*s*, COMe), 1·86(*s*, COMe), 1·72(*s*, COMe).

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12,13-DIHYDRO-12-HYDROXYAUSTAMIDE, A NEW DIOXOPIPERAZINE FROM *ASPERGILLUS USTUS*

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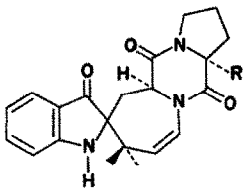
Key Word Index—*Aspergillus ustus*; Aspergillaceae; 12,13-dihydro-12-hydroxyaustamide; dioxopiperazine.

We have previously described[1] the characterization of 5 biogenetically related dioxopiperazines from maize meal infected with *Aspergillus ustus* (Bainier) Thom and Church. The proposed structure and absolute configuration of 12S-tetrahydroaustamide was subsequently confirmed by X-ray crystallography[2].

In the present investigation toxic material was obtained from maize meal (10 kg) infected with *A. ustus* and separated by chromatography on formamide-impregnated cellulose powder. A fraction was obtained which contained prolyl-2-(1′,1′-dimethylallyl) tryptophyl-dioxopiperazine (100 mg), austamide (1·7 g) and the new minor metabolite (10 mg) which we have assigned 2S, 9S,12R-12,13-dihydro-12-hydroxyaustamide (**1**) by comparison with spectral data of the known austamides.

The new compound was purified by extensive column chromatography and TLC on silica gel and aluminium oxide. It had mp 164–5° (from MeOH) and *m/e* 381·1685 (M^+, $C_{21}H_{23}N_3O_4$ requires 381·1688); λ_{max}^{MeOH} 231, 255 and 390 nm (log ε 4·48, 4·04 and 3·47, respectively); $\nu_{max}^{CHCl_3}$

3430–3350 (*br.* band), 1670 and 1618 cm^{-1}. The NMR spectrum ($CDCl_3$) showed 2 singlets at τ8·48 (3H) and τ9·16 (3H) which were assigned to the 2 geminal Me groups. The *cis*-olefinic protons appeared as an AB-pattern at τ3·29 and τ4·98 (J_{AB} 10 Hz). The protons at C_8 and C_9 appeared as an ABX system, H_A being H_{seq}, τ7·13 (*q*, J_{AB} 15, J_{AX} 6 Hz); H_B being H_{8ax}, τ7·86 (*q*, J_{AB} 15, J_{BX} 12 Hz) and H_X represented by a pair of doublets at τ5·16 (J_{AX} 6 and J_{BX} 12 Hz). A complex pattern centred around τ6·36 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 τ7·6 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 τ5·80–5·90[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, $C_{21}H_{21}N_3O_3$ (40%) due to the loss of H_2O from the molecular ion and subsequent fragmentation virtually identical to that of austamide with the base peak at *m/e* 218, $C_{12}H_{14}N_2O_2$.



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

The C.D. properties of (**1**) in MeOH: λ/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**): λ/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 (ψ-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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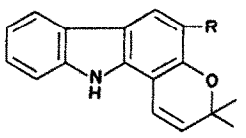
Key Word Index—*Clausena heptaphylla*; Rutaceae; murrayacine; carbazole alkaloid.

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 dentatin. 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, $C_{18}H_{15}NO_2$, mp 244–45° which readily gave a 2:4 DNPH derivative. The IR spectrum of the compound showed the presence of –NH– and aldehyde functions on an aromatic system [ν_{max}^{KBr} 3250, (NH–); 1675 (–CHO); 1640, 1600 (unsaturation and aromatic group) and 895, 865, 740 cm^{-1}]. Its UV spectrum λ_{max}^{EtOH} 226, 282, 301 nm; log ϵ 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.

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

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