A_2B_2 system), 2·14 (*d*, *J* 9·3, 1H, H-5); identical (mmp, TLC and MS) with a sample prepared by acetylating authentic liquiritigenin.

The co-occurrence of (S)-4-methoxydalbergione, dalbergin, (+)-3-hydroxy-9-methoxypterocarpan, biochanin-A, formononetin, and (+)-liquiritigenin, which have all been previously found to occur in *Dalbergia* [1,5] species, further emphasises the biosynthetic relationship between these classes of compounds. *Dalbergia nitidula* is the first example of an African *Dalbergia* species producing a pterocarpan [6]. In this connection it is relevant that *Dalbergia ecastophyllum* a species indigenous to Africa and America, was found to contain [7] (+)-demethylhomoptercarpin only in a specimen from the latter source. Furthermore, (+)-3-hydroxy-9-methoxypterocarpan was found to be the major constituent, present in the comparatively large yield of 1·1% of the dry heartwood weight.

Our study of *Dalbergia nitidula* is a continuation of our interest in termite resistant central African timbers [8], a property exhibited by this species.

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FLAVONOIDS FROM THE WOOD OF *CLADRASTIS PLATYCARPA**

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Key Word Index—*Cladrastis platycarpa*; Leguminosae; isoflavone; pseudobaptigenin; isoflavone-*O*-glucoside; cladrastin-7-*O*-β-D-glucoside; fujikinin; platycarpanetin-7-*O*-β-D-glucoside; flavone-*C*-glucoside; bayin.

Plant. Cladrastis platycarpa Makino (Japanese name: fujiki), tree, Leguminosae (subfamily Lotoideae). *Source.* Yamato-mura, Gifu Prefecture, Japan. *Previous work.* On barks [1,2] and wood [3] of this species, wood of *C. lutea* [4] and *C. amurensis* [5].

Present work. The powdered wood (*ca* 6 kg) was extracted with hot MeOH and then the concentrated extract was successively fractionated with *n*-hexane, Et_2O, EtOAc and *n*-BuOH. The ether and ethyl acetate soluble portions were respectively chromatographed on silica followed by fractional recrystallizations, affording a known isoflavone, pseudobaptigenin (7-hydroxy-3′,4′-methylenedioxyisoflavone), and 2 known isoflavone glucosides fujikinin (6-methoxy-3′,4′-methylenedioxy-7-*O*-β-D-glucosyloxyisoflavone) and platycarpanetin-7-*O*-β-D-glucoside (5,8-dimethoxy-3′,4′-methylenedioxy-7-*O*-β-D-glucosyloxyisoflavone), in addition to the isoflavonoids described in the previous paper [3]. The *n*-butanol soluble part was chromatographed on silica and polyamide followed by fractional recrystallizations from MeOH, giving a new isoflavone glucoside, cladrastin-7-*O*-β-D-glucoside (6,3′,4′-trimethoxy-7-*O*-β-D-glucosyloxyisoflavone), a rare flavone-C-glucoside, bayin (7,4′-dihydroxy-8-*C*-β-D-glucosylflavone) and two unknown yellow compounds, mp 229–230° (*dec.*) and mp 154–157° (*dec.*) which are probably *C*-glycosides and whose characterization is still in progress.

The structure of pseudobaptigenin was confirmed on the basis of alkaline degradation (product: piperonylacetic acid, mp 125–127°) and instrumental analyses of it and its acetate [6]. Fujikinin, colorless needles (MeOH), mp and mmp 228–230° and platycarpanetin-7-*O*-β-D-glucoside, colorless needles (MeOH), mp and mmp 142–144°, were identified by direct comparisons with the authentic specimens isolated from the bark of this tree [1,2]. The new isoflavone glucoside, negative to Pauly's reagent but positive to Molisch's test, yielded an aglycone and sugar in equimolar ratio on acid hydrolysis. The aglycone was identified as cladrastin in comparison of the IR and NMR spectra with authentic specimen. The sugar moiety was shown to be D-glucose by co-PC with the authentic sugar and the β-linkage was revealed by the coupling constant (7 Hz) of glucose H-1 in the NMR spectrum. Thus, the structure of the new compound was deduced to be cladrastin-7-*O*-β-D-glucoside, which was

* Part 4 in the series The Extractives of Japanese *Cladrastis* Species. For Part 3 see *ref.* [2].

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); $\nu_{max}^{CHCl_3}$