by the condensation of 2,4-dihydroxy-phenylbenzyl ketone with Ac_2O and NaOAc[1] (TLC, mp, mmp, superimposable IR).

Compound B. (30 mg), mp 142–143°, gave colour reactions similar to those of A. λ_{max}^{MeOH} 230, 295; (no shift with $AlCl_3$, NaOAc or NaOMe). ν_{max}^{KBr} 1640 cm^{-1}. *MS.* 266 (M^+), 151, 150, 77.

NMR. (δ, $CDCl_3$) 2·20 (*s*, 3H, −Me), 3·80 (*s*, 3H, −OMe), 6·75, 6·95 (*dd*, 2H, 6-H, 8-H, J_m 2 Hz, J_o 9 Hz; the *m*-coupled signal of 8-H is superposed over the signal at δ 6·95), 7·35 (*m*, 5H, side phenyl protons), 8·10 (*d*, 1H, *J* 9 Hz, 5-H). On alkali hydrolysis B yielded phenylacetic acid. The similarity of B with A in the colour reactions and spectral data indicated it to be 7-methoxy-2-methylisoflavone. It agreed fully with an authentic sample prepared from 7-acetoxy-2-methyl-isoflavone by deacetylation followed by methylation with CH_2N_2 (TLC, mp, mmp, and superimposable I.R.).

Compound C. (5 mg), mp 240°, gave blue colour with $FeCl_3$–K_3 [Fe (CN)$_6$] spray and +ve Na–Hg–HCl test. It was identical with the hydrolysis product of A. Its structure was therefore 7-hydroxy-2-methylisoflavone and this was confirmed by direct comparison with an authentic sample (TLC, mp, mmp).

These three isoflavones seem to be of novel type. The natural occurrence of 2-methylisoflavones has not been noted before in plants and the present results are of biogenetic interest. It has been established that chalcones are the precursors of the naturally occurring isoflavones, but the presence of 2-methyl group cannot be accommodated in such a scheme. The possibility of another biogenetic route has to be visualised for the formation of these compounds, e.g. the linking of a C_2 acetate unit to a desoxybenzoin.

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PHENOLIC COMPOUNDS FROM THE HEARTWOOD OF *DALBERGIA NITIDULA*

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Key Word Index—*Dalbergia nitidula*; Leguminosae; biochanin A; dalbergin, formononetin; (+)3-hydroxy-9-methoxypterocarpan; (s)-4-methoxydalbergione; (±)-liquiritigenin.

Plant and source. Dalbergia nitidula, collected from the Midlands area in Rhodesia by Mr. F. L. Orpen (Forestry Commission, Salisbury) and identified by Mr. R. B. Drummond (Government Herbarium, Salisbury). *Previous work.* None on this species. *Extraction, isolation and identification.* The milled and air-dried heartwood (936 g) was extracted in a Soxhlet with *n*-hexane for 24 hr, followed by Et_2O for 2 days which yielded the bulk of the extractives as a dark red gum (70 g). Preparative scale TLC (Merck GF_{254}, developed with 4% MeOH–$CHCl_3$) of this gum (10 g) gave 7 bands when viewed under UV light. Band 1 (brown gum (0·65 g) with R_f 0·89) and band 5 (dark gum (0·14 g) with R_f 0·42) gave no crystalline products and were not studied further. Further TLC (2% MeOH–$CHCl_3$) of the product from band 2 (brown gum (0·55 g) with R_f 0·67) separated the mixture into 2 crystalline products, viz. (*s*)-4-methoxydalbergione [1] (upper band, 54 mg) mp 115–118°; M^+ *m/e* 254; $[\alpha]_D^{22°}$ −13° ($CHCl_3$), identical with an authentic sample (mmp, IR and NMR), and dalbergin [1] (lower band, 70 mg) mp 212–213°; acetate mp 157–158°; *m/e* 310 (M^+) and 268; NMR* τ 7·74 (*s*, 3H), 6·12 (*s*, 3H), 3·81 (*s*, 1H), 3·10 (*s*, 1H), 2·93 (*s*, 1H), 2·59 (*br.s*, 5H), identical with an authentic sample (mmp IR and TLC). Band 3 produced a buff coloured solid (4·0 g with R_f 0·60) which on repeated TLC and crystallisation gave (+)-3-hydroxy-9-methoxypterocarpan [2] (1·5 g) mp 123–125°; $[\alpha]_D^{21}$ +214° ($CHCl_3$); M^+ *m/e* 270, identical with an authentic sample (mmp, IR, and NMR); methyl ether mp 84–85° (lit. [2] 83–85°). Band 4 yielded a dark gum (0·22 g with R_f 0·45) which on acetylation and TLC gave biochanin-A diacetate [3] (21 mg) mp 191–193°; *m/e* 368 (M^+), 326 and 284; NMR* τ 7·70 (*s*, 3H), 7·61(*s*, 3H), 6·22 (*s*, 3H), 3·18 (*d*, *J* 2·5 Hz, 1H), 3·09 (*d*, *J* 8·5 Hz, 2H), 2·62 (*d*, *J* 8·5 Hz, 2H), 2·20 (*d*, *J* 2·5 Hz, 1H), 2·18 (*s*, 1H); identical (mmp, MS and TLC) with an authentic sample. Band 6 gave a red–brown solid (0·4 g with R_f 0·36) which on further TLC (8% MeOH–$CHCl_3$) and acetylation of the major band gave formononetin acetate [1] (16 mg) mp 171–172°; *m/e* 310 (M^+) and 268; NMR* (recorded in $CDCl_3$ with TMS as internal standard) τ 7·66 (*s*, 3H), 6·20 (*s*, 3H), 3·10 and 2·80 (*dd*, *J* 8·5 Hz, 4H, A_2B_2 system), 2·91 (*q*, *J* 8·5, 2·5 Hz, 1H, H-6), 2·81 (*d*, *J* 2·5 Hz, 1H, H-8), 2·11 (*s*, 1H, H-2), 1·75 (*d*, *J* 8·5 Hz, 1H, H-5); identical (mmp, IR, TLC, MS and NMR) with an acetylated sample of authentic formononetin. Band 7 gave a dark coloured solid (0·41 g with R_f 0·18) which on further TLC (10% MeOH–$CHCl_3$) and acetylation of the major band gave (±)-liquiritigenin diacetate [4] (30 mg) mp 195–198°; $[\alpha]_D^{22}$ 0·0 ($CHCl_3$); *m/e* 340 (M^+), 298 and 256; NMR* τ 7·74 (*s*, 6H), 7·30–6·80 (*m*, 2H, AB of ABX system), 4·59 (*q*, $J_{2,3}$, $J_{2,3}$ 16 Hz, 1H, X of ABX system), 3·32 (*q*, $J_{5,6}$ 9·3 Hz, $J_{6,8}$ 2·5 Hz, 1H, H-6), 3·24 (*d*, *J* 2·5 Hz, 1H, H-8), 2·95 and 2·62 (*dd*, *J* 8·5, 4H,

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].