304, 342, 381; NaOAc 280, 304 *sh*, 364; NaOH 280, 329 *sh*, 400. The eluted compound co-chromatographed with vitexin and, on heating for 3 hr with 4 N HCl–MeOH (1:1), gave a mixture of vitexin and isovitexin which co-chromatographed with authentic samples.

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# OCCURRENCE OF 2-METHYLISOFLAVONES IN *GLYCYRRHIZA GLABRA*

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**Key Word Index**—*Glycyrrhiza glabra*; Leguminosae; liquorice root; 7-hydroxy-2-methylisoflavone; 7-acetyl and 7-methyl derivatives.

A number of flavonoids have been reported from time to time from the roots of *Glycyrrhiza glabra*. Samples examined in different countries seem to vary in composition. Recently, the plant has been cultivated in India for the first time. The Indian grown *Glycyrrhiza glabra* has not been studied in detail before. The sample used in the present work has been obtained from the experimental gardens of Govt. Ayurvedic College, Jammu, kindly supplied by Dr. S. C. Sankhyadhar.

The air dried roots have yielded as ether soluble components 3 new compounds. The air dried powdered roots (1·2 kg) were extracted with hot EtOH and the extract concentrated. The solvent-free residue was repeatedly extracted with $Et_2O$ and the combined $Et_2O$ extract was evaporated and the residue chromatographed over Si gel. $C_6H_6$–EtOAc (3:1) eluted compounds A–C which were further purified by preparative TLC and crystallisation from light petrol. In other fractions quercetin, kaempferol, apigenin, liquiritigenin and isoliquiritigenin were also identified, confirming that the roots are liquorice.

*Compound A.* (20 mg), mp 161–162°, gave −ve $FeCl_3$, −ve Mg–HCl, −ve Zn–HCl but +ve Na–Hg–HCl tests. $\lambda_{max}^{MeOH}$ 230, 295 nm (no shift with $AlCl_3$, NaOAc or NaOMe). $\nu_{max}^{KBr}$ 1750, 1640, 1245 $cm^{-1}$. The colour reactions and UV spectrum indicated A to be an isoflavone.

*MS.* 294 ($M^+$), 252, 137, 136, 77. *NMR* (TMS internal standard) ($\delta$, $CDCl_3$): 2·30, 2·40 (6H, OCOMe and Me), 7·20, 7·35 (*dd*, 2H, 6-H, 8-H, $J_m$ 2 Hz, $J_o$ 8 Hz; the *m* coupled signal of 8-H is superposed over the signal at $\delta$ 7·35), 7·50 (*m*, 5H side phenyl protons), 8·50 (*d*, 1H, *J* 8 Hz, 5-H). The IR and NMR indicated the presence of an acetoxyl function in the compound. Hydrolysis of A with methanolic HCl gave a phenol identical with compound C. The NMR spectrum of A further indicated the presence of (i) mono-substituted phenyl system, (ii) unsubstituted resacetophenone system and (iii) an aromatic methyl or a methyl attached to a C–C double bond. Mass spectrum also supported the conclusions (i) and (ii). Further, alkali hydrolysis of A gave phenylacetic acid. Thus the possibilities of the *C*-methyl being in the rings A or B of the isoflavone unit are eliminated. Hence it must be in the pyrone ring; thus, compound A is 7-acetoxy-2-methylisoflavone. The above structure was confirmed by comparison with an authentic sample prepared

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. $\lambda_{max}^{MeOH}$ 230, 295; (no shift with $AlCl_3$, NaOAc or NaOMe). $\nu_{max}^{KBr}$ 1640 $cm^{-1}$. *MS.* 266 ($M^+$), 151, 150, 77.

*NMR.* ($\delta$, $CDCl_3$) 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 $\delta$ 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* $\tau$ 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* $\tau$ 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) $\tau$ 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* $\tau$ 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,