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A *C*-GLUCOSYLCHALCONE FROM THE WOOD OF *CLADRASTIS PLATYCARPA*[*]

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Key Word Index—*Cladrastis platycarpa*; Leguminosae–Lotoideae; chalcone-*C*-glucoside; *C*-glucosylisoliquiritigenin; di-*C*-glycosylflavone; vicenin 1.

Four flavonoids were earlier isolated from the *n*-butanol soluble fraction of a methanolic extract of wood of *Cladrastis platycarpa*. Two were shown to be bayin (7,4′-dihydroxy-8-*C*-β-glucosylflavone) and cladrastin-7-*O*-β-glucoside (6,3′,4′-trimethoxy-7-*O*-β-glucosyloxyisoflavone) respectively [1]. The other two compounds I, mp 154–157° (dec.) and II, mp 229–230^{c} (dec.), were not identified; we now report on their structures.

Compound I was positive to Pauly's and $FeCl_3$ reactions and gave a reddish orange with 5% aq.NaOH. The UV spectrum was that of a chalcone [2]. The NMR spectrum revealed a chalcone consisting of a β-linked hexosyl, 1,2,3,4-tetrasubstituted and 1,4-disubstituted phenyl nuclei and two vinylenic protons. The linkage of the two protons on the vinylene residue was assigned to be *trans*- by the internuclear double resonance (INDOR) spectrum of the acetate (Fig. 1). The NMR and INDOR spectra of the acetate showed the presence of three aromatic and four aliphatic acetoxyl groups and the relationship of couplings of the aromatic protons (Fig. 1). Acid hydrolysis gave orange polymers but $FeCl_3$ oxidation gave D-glucose, red polymers and a trace of isoliquiritigenin, 4,2′,4′-trihydroxychalcone [3, 4]. The partial methyl ether of compound I with diazomethane underwent $FeCl_3$ oxidation and the aglycone produced was completely methylated with MeI. The permethyl ether was identified as a mixture of trimethylisoliquiritigenin and dimethylliquiritigenin (7,4′-dimethoxyflavanone) by NMR spectroscopy and co-TLC with synthetic specimens. Consequently, the structure of d I appeared to be 4,2′,4′-trihydroxy-3′-*C*-β-glucosylchalcone, i.e. *C*-glucosylisoliquiritigenin. This structure was indirectly confirmed by the TLC comparison of the chalcone methyl ether with the methyl ether prepared from authentic 2′-hydroxy-4,4′-dimethoxy-3′-*C*-β-glucosylchalcone provided by R. A. Eade [5]. This *C*-glucoside was also detected in the *n*-butanol soluble part of fresh bark extracts; its co-occurrence with bayin suggests that bayin could be synthesized from it.

Compound II gave positive Pauly's test but negative $FeCl_3$ and Molisch's reactions. The UV spectral shifts were similar to those of apigenin and the NMR spectra of it and its acetate suggested that the compound was an apigenin diglycoside [6]. It gave no sugars on acid hydrolysis but $FeCl_3$ oxidation yielded D-glucose and L-arabinose and a trace of apigenin. Thus, it was assumed to be 6-*C*-pentosyl-8-*C*-glucosyl- or 6-*C*-glucosyl-8-*C*-pentosyl-apigenin. Its behaviour on PC and TLC suggested it was 6-*C*-xylosyl-8-*C*-glucosyl- or 6-*C*-arabinosyl-8-*C*-glucosyl-apigenins [6]. The final constitution, 5,7,4′-trihydroxy-6-*C*-β-D-xylosyl-8-*C*-β-D-glucosylflavone, was reached by direct comparison with an authentic sample of vicenin 1 (J. Chopin, personal communication).

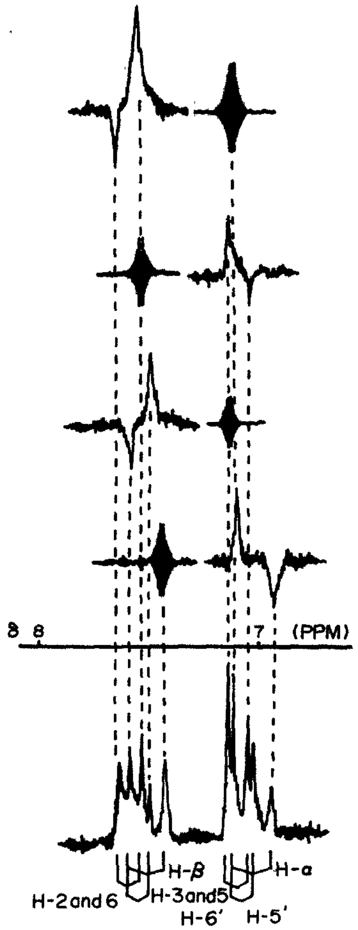

Fig. 1.

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[*] Part 7 in the series 'The Extractives of Japanese *Cladrastis* Species.' For Part 6 see ref. [1].

EXPERIMENTAL

Compound I. Yellow amorphous (MeOH), mp 154–157° (dec.). UV λ_{max}^{MeOH} (nm): 225(*sh*), 310(*sh*), 371; $\lambda_{max}^{MeOH+NaOAc}$: 283, 336(*sh*), 407; $\lambda_{max}^{MeOH+NaOAc+H_3BO_3}$: 286, 379, 420, 445, 470(*sh*); $\lambda_{max}^{MeOH+AlCl_3}$: 234(*sh*), 320(*sh*), 385(*sh*), 422; $\lambda_{max}^{MeOH+AlCl_3+HCl}$: 235(*sh*), 320(*sh*), 385(*sh*), 422. NMR (DMSO-d_6) δ: 8.20 (1H, *d*, *J* 9 Hz), 7.82 (2H, *d*, *J* 9 Hz), 7.80 (2H, *s*), 6.86 (2H, *d*, *J* 9 Hz), 6.50 (1H, *d*, *J* 9 Hz), 4.70 (1H, *d*, *J* 9 Hz), 4.20–3.00 (6H, *m*). The partial methyl ether (from CH_2N_2 treatment) was oxidized with $FeCl_3$ and the product methylated with MeI to give a mixture of isoliquiritigenin and liquiritigenin permethyl ethers (as pale yellow oils). NMR of the product ($CDCl_3$) δ: (1) trimethylisoliquiritigenin portion 7.86 (H-6′, *d*, *J* 9 Hz), 7.64 (H-β, *d*, *J* 18 Hz), 7.42 (H-2 and 6, *d*, *J* 9 Hz), 6.96 (H-3 and 5, *d*, *J* 9 Hz), 6.84 (H-α, *d*, *J* 18 Hz), 6.50 (H-3′ and 5′, *m*). (2) dimethylliquiritigenin portion 7.84(H-5, *d*, *J* 9 Hz), 7.44(H-2′ and 6′, *d*, *J* 9 Hz), 6.92(H-3′ and 5′, *d*, *J* 9 Hz), 6.50(H-6 and 8, *m*), 5.44(H-2, *dd*, *J* 5 and 12 Hz), 2.94(H-3 *trans*, *d*, *J* 12 Hz), 2.88(H-3 *cis*, *d*, *J* 5 Hz). The chalcone methyl ether (1) was compared by TLC in $CHCl_3$–MeOH (6:1) with material prepared from 2′-hydroxy-4′,4-dimethoxy-3′-C-β-glucosylchalcone. *Pentaacetate* (prepared with $(AcO)_2O$ and a drop of H_2SO_4) triangular needles (MeOH), mp 111–112° (93–95° softness), M^+ 712. NMR (CD_2Cl_2) δ: 7.62(H-6′, *d*, *J* 9 Hz), 7.56(H-2 and 6, *d*, *J* 9 Hz), 7.52(H-β, *d*, *J* 18 Hz), 7.08(H-3 and 5, *d*, *J* 9 Hz), 7.04(H-5′, *d*, *J* 9 Hz), 7.02(H-α, *d*, *J* 18 Hz), 5.60–3.40(glucosyl 7H, *m*), 2.26, 2.14, 2.12(3 aromatic OAc), 1.88, 1.84, 1.64 (4 aliphatic OAc) (See Fig. 1).

Compound II. Pale yellow amorphous powder (MeOH), mp 229–230° (dec.). UV λ_{max}^{MeOH} (nm): 272, 331; $\lambda_{max}^{MeOH+NaOAc}$: 280, 300(*sh*), 350; $\lambda_{max}^{MeOH+NaOAc+H_3BO_3}$: 273, 328; $\lambda_{max}^{MeOH+AlCl_3}$: 278, 304, 346, 390(*sh*); $\lambda_{max}^{MeOH+AlCl_3+HCl}$: 278, 303, 244, 380(*sh*). NMR (TMS Et_2O in CCl_4) δ: 7.77(2H, *d*, *J* 8.5 Hz), 6.78(2H, *d*, *J* 8.5 Hz), 6.25(1H, *s*), 4.55(1H, *d*, *J* 9 Hz), 4.35(1H, *d*, *J* 3.5 Hz), 4.40–3.10(12H, *m*). IR ν_{max}^{KBr} (cm^{-1}): 3450–3250, 1645, 1625, 1570, 1510, 1470, 1435, 1360, 1285, 1250, 1215, 1180, 1110, 1080, 1050, 1005, 960, 930, 895, 825. Chromatography of II. PC in 15% HOAc vitexin (0.38), 6,8-di-*C*-glucosylapigenin (0.53), compound II (0.41); in BAW vitexin (0.54), 6,8-di-*C*-glycosylapigenin (0.22), compound II (0.24). TLC EtOAc–pyridine–H_2O–MeOH (80:20:10:5) vitexin (0.54), 6,8-di-*C*-glucosylapigenin (0.11), compound II (0.23). *Deca-acetate* (prepared with $(AcO)_2O$ and a drop of H_2SO_4) triangular (MeOH), mp 171–173°. NMR (CD_2Cl_2) δ: 8.15(H-2′ and 6′, *d*, *J* 8.5 Hz), 7.45(H-3′ and 5′, *d*, *J* 8.5 Hz), 6.70(H-3, *s*), 6.20–3.40(glucosyl 14H, *m*), 2.46, 2.44, 2.30 (3 aromatic OAc), 2.04, 2.00, 1.98, 1.94, 1.88, 1.84, 1.74 (7 aliphatic OAc).

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FLAVONOIDS FROM THE LEAVES OF *CASSIA OCCIDENTALIS*

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Key Word Index—*Cassia occidentalis*; Leguminosae; matteucinol 7-rhamnoside; jaceidin 7-rhamnoside; flavonoids.

From the ethanolic extract of the leaves of *Cassia occidentalis* two flavonoid glycosides A and B have been isolated. Homogeneity and purity of both compounds were established by paper and thin layer chromatography.

Compound A, mp 170°(d), molecular formula $C_{24}H_{28}O_9$, gave all the characteristic colour reactions of flavonoids and was found to be glycosidic in nature. On acid hydrolysis, it gave rhamnose (PC, osazone) and an aglycone mp 186°, $C_{18}H_{18}O_5$, which showed colour reactions characteristic of flavanones. The compound analysed for two hydroxyl groups (acetate, IR 3355 cm^{-1}) two C-methyl groups (NMR signal at 7.60 τ corresponding to 6-protons of two CH—Me [1]) and one methoxyl group (Zeisel, IR 2865 cm^{-1}, 1185 cm^{-1}, NMR signal at 6.2 τ corresponding to 3-protons of one —OMe group. Spectral studies of the aglycone (λ_{max} 290 nm, 325 nm) indicated the presence of free hydroxyl groups at positions -5 and -7 (bathochromic shifts with aluminium chloride [2] and fused sodium acetate [3] respectively). On permanganate oxidation the aglycone gave anisic acid as one of the oxidation products which fixed the