this could not be crystallised. It was acetylated (Ac_2O–Py) and the product gave colourless crystals, mp 133°. UV: λ_{max}^{MeOH}: 326 (*sh*), 312, 302, 236 (*sh*), 228 (*sh*) nm. IR ν_{max}^{KBr}: 692, 745, 755, 817, 850, 870, 900, 1010, 1080, 1140, 1200, 1270, 1300, 1340, 1370, 1420, 1450, 1470, 1500, 1600, 1770, 300 cm^{-1}. PMR (250 MHz, CCl_4, TMS) δ: 2.21 (6 H, *s*), 3.85 (3 H, *s*), 6.85 (2 H, *s*), 6.94 (2 H, *s*), 7–7.45 (5 H, *m*) ppm. MS 70 eV *m/e* (rel. int.): 326 (11), 284 (36), 242 (100; 242.0944, calc. 242.0943), 227 (0.5), 223 (1), 209 (4), 181 (8), 165 (3), 153 (4), 152 (5), 141 (4), 115 (3), 91 (3), 84 (7), 69 (5), 58 (7), 65 (7), *m** 247.4 (326–284), 206.2 (284–242), 156.8 (209–181), 129.3 (181–153), 93.8 (141–115). Reduction by hydrogenation with Pd–C catalyst in EtOH and purification by Si gel column chromatography with $CHCl_3$ as eluent. PMR δ: 2.20 (6 H, *s*), 2.88 (4 H, *s*), 3.73 (3 H, *s*), 6.44 (1 H, *d*, J = 2.5 Hz), 6.53 (1 H, *d*, J = 2.5 Hz), 7.04–7.30 (5 H, *m*) ppm. MS *m/e*: 328 (8), 286 (30), 244 (56), 195 (4), 153 (100), 138 (2), 91 (38), 71 (8), 57 (16). *m* 249.4 (328–286), 208.2 (286–244), 95.9 (244–153), 124.5 (153–138).

Acknowledgements—We wish to thank Prof. Dr K. Egger (Heidelberg) for supplying the bud material and Miss Noailly (CILAMPAG, Marseille) for assistance with 250 MHz PMR.

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Phytochemistry, 1978, Vol 17, pp 822–823 Pergamon Press Printed in England

A NEW CHALCONE GLUCOSIDE AND ISOSALIPURPOSIDE FROM *ACACIA CYANOPHYLLA*

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(*Received* 24 *October* 1977)

Key Word Index—*Acacia cyanophylla*; Leguminosae; 4,2′,4′,6′-tetrahydroxychalcone 4-glucoside; isosalipurposide.

Quercetin 3-*O*-glucoside has previously been reported from the leaves of *Acacia cyanophylla* [1]. The present paper describes the isolation of two anthochlor pigments, isosalipurposide and chalcononaringenin 4-glucoside, from the flowers of this plant. These pigments are primarily responsible for the yellow flower colour.

Prep PC of an ethanolic extract of the flowers of *Acacia cyanophylla* afforded two anthochlor pigments (C_1 and C_2). C_1 was identified as isosalipurposide (4,2′,4′,6′-tetrahydroxychalcone 2′-glucoside) by UV spectral analysis in the presence of usual shift reagents [2, 3] and paper co-chromatography with authentic material (5 solvents). The above identification was confirmed by controlled acid hydrolysis, total acid hydrolysis and treatment with β-glucosidase to give naringenin and D-glucose, and by conversion (by heating in a NaOAc soln [4]) to naringenin 5-*O*-glucoside. This is the first report of isosalipurposide in the Leguminosae.

The UV spectrum of C_2 showed λ_{max}^{MeOH} 368 nm and a bathochromic shift (50 nm) with both $AlCl_3$ and $AlCl_3$/HCl which is consistent with a chalcone skeleton with a hydroxyl group at position 2′. Since the UV spectrum showed a bathochromic shift (50 nm) in the presence of NaOMe without any increase in peak intensity [3], this chalcone lacks a free 4-hydroxyl group. The presence of a 4′-hydroxyl group was indicated by a bathochromic shift (10 nm) with NaOAc [3]. When heated in NaOAc [4] soln C_2 easily isomerized to the corresponding flavanone (F). The UV spectrum of F showed λ_{max}^{MeOH} 289 and 324 nm (*sh*) and bathochromic shifts with NaOAc (37 nm), $AlCl_3$ (21 nm) and $AlCl_3$/HCl (21 nm). The above spectral data are consistent [3] with those of a 5,7-dihydroxy flavanone. Treatment with β-glucosidase, controlled acid hydrolysis and total acid hydrolysis of F gave naringenin and D-glucose. The aglycone: sugar ratio was 1:1.09. Methylation of F followed by acid hydrolysis gave naringenin 5,7-dimethyl ether (characterized by alkaline degradation which gave *p*-coumaric acid and di-*O*-methylphloroglucinol) and 2,3,4,6-tetra-*O*-methyl-D-glucose. The PMR spectrum [3] of F (TMS ether, 60 MHz, CCl_4) showed a typical four peaks pattern of two doublets (each J = 8.5 Hz) at δ 7.12 (C-2′ and C-6′ protons) and 6.78 (C-3′ and C-5′ protons) for a 4′-oxygenated B ring, an ABX pattern characteristic of the protons at C-3 (AB) and C-2 (X) of a flavanone nucleus [3], two doublets (δ-5.95 and 6.05; each J = 2.5 Hz) for C-6 and C-8 protons, a doublet (δ 5.0; J = 7 Hz) for C-1″ proton and a signal between 3.8 and 3.0 δ (glucosyl 6 protons). Thus F is the flavanone naringenin 4′-*O*-glucoside and C_2 must be 4,2′,4′,6′-tetrahydroxychalcone 4-glucoside which has not been previously described. The occurrence of 2′,6′-dihydroxychalcones in nature is somewhat rare, possibly because of their ready conversion to the corresponding flavanones which are stabilized due to the hydrogen bonding between the 5-hydroxyl and the 4-carbonyl groups.

EXPERIMENTAL

Isolation of the pigments. Fr. flowers of *Acacia cyanophylla*, collected in Catania, were homogenized and extracted 3 × with

hot 95% EtOH. The combined extracts were filtered, concd to a small vol. *in vacuo* and re-filtered. The two pigments, C_1 and C_2, were purified by prep PC in BAW, 5% HOAc and BEW. R_f data for C_1 and C_2 are: BAW 0.64, 0.64; 5% HOAc 0.06, 0.16 and BEW 0.66, 0.66. Two other yellow pigments were isolated but were not present in sufficient amount for analysis. Their UV spectra suggested that they may be chalcones. When paper strips of C_2 bands were kept for one to two days before elution with EtOH the eluate showed a complete absence of C_2 and contained instead the corresponding flavanone (R_f 0.65 in BAW; 0.66 in BEW; 0.54 in H_2O; 0.59 in 5% HOAc; 0.64 in 30% HOAc).

Hydrolysis of the pigments. Controlled acid hydrolysis was carried with 10% aq. HOAc (3.5 hr under reflux); total acid hydrolysis was carried with 2 N HCl (2 hr at 100°). Naringenin was identified by CO-PC with an authentic sample (5 solvents) and UV spectral analysis with usual shift reagents. D-Glucose was identified by the use of glucose oxidase, CO-PC (4 solvents) and GLC of its TMS ether [5]. The aglycone: sugar ratio was determined according to ref. [6].

Methylation of F. The flavanone was methylated (Me_2SO_4–K_2CO_3–Me_2CO) and hydrolysed as in ref. [3]. Alkaline degradation of the partially methylated aglycone was achieved as in ref. [7]; *p*-coumaric acid was identified by PC (3 solvents), TLC on Si gel (C_6H_6–HOAc–H_2O, 2:1:1, upper phase) and paper electrophoresis at pH 4.5 and 8.7; di-*O*-methylphloroglucinol was identified by comparison with an authentic sample (TLC on Si gel; 3 solvents); 2,3,4,6-tetra-*O*-methyl-D-glucose was identified by TLC on Si gel ($CHCl_3$–EtOAc. 1:1) and PC [8].

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Phytochemistry, 1978, Vol. 17, pp 823–824. Pergamon Press Printed in England

A NEW CHALCONE AS A NATURAL MOLLUSCICIDE FROM *POLYGONUM SENEGALENSE*

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(*Received* 21 *September* 1977)

Key Word Index—*Polygonum senegalense*; Polygonaceae; molluscicide; 2′,4′-dihydroxy-3′,6′-dimethoxychalcone.

There is a pressing need in the tropical world for cheap and simple molluscicides to control vector snails of parasites responsible for schistosomiasis and other snail-borne diseases. Of the numerous molluscicides available, few [1] are from botanical sources. We now report the structure of a molluscicide from an East African plant.

Crude aqueous extracts of seeds and leaves of *Polygonum senegalense* were found [2] to have molluscidal activity against *Biomphalaria pfeifferi* and *B. sudanica* snails. One of the active principles is the chalcone **1**, (2′,4′-dihydroxy-3′,6′-dimethoxychalcone). At 40 ppm concentration, **1** is 100% lethal to *B. pfeifferi* and *B. sudanica* in less than six hours.

Hydrophilic and hydrophobic fractions of a methanolic extract of seeds and leaves of the plant both contain molluscicides. A hydrophobic fraction in benzene gives, after chromatography on silica gel, the chalcone **1** as orange crystals mp 124–125° (CH_2Cl_2–*n*-hexane) M^+ 300, $C_{17}H_{16}O_5$. The UV spectrum of **1** in MeOH has bands at λ_{max} 211 nm (ε 31 500) and 348 nm (ε 27 000). Addition of NaOMe, $AlCl_3$, $AlCl_3$–HCl, NaOAc, NaOAc–H_3BO_3 to **1** in MeOH, cause bathochromic shifts of 44, 36, 32, 44 and 48 nm resp. of the long wavelength band with no increase in intensity. These shifts suggest that **1** is a flavonoid [3–5] with hydroxyl groups located at C-2′ and C-4′. 2′-Hydroxy-4′,6′-dimethoxychalcone [6] which is also present in *P. senagalense* extracts does not give a bathochromic shift with NaOAc but gives one of 38 nm with $AlCl_3$. That **1** has phenolic hydroxyl groups is confirmed by the presence of a sharp band at ν ($CHCl_3$) 3455 cm^{-1} in the IR spectrum and the appearance of acetoxyl singlets at δ 2.23, and 2.4 in the PMR spectrum (recorded in $CDCl_3$) of the acetylated product of **1**. The α,β-unsaturated C=O group absorbs at 1628 cm^{-1}.

In the 60 MHz PMR spectrum of **1** in $CDCl_3$ methoxyl signals appear at δ 4.04 and 4.06. A singlet appears at δ 6.17 (1 H). Aromatic, α, and β, protons (7 H) resonate between 7.38 and 8.12 ppm. Hydroxyl protons resonate at 14.42 (O<u>H</u>-2′ [6] and 6.57 ppm (O<u>H</u>-4′). The α and β-protons of **1** are well resolved in the spectrum of the di-*O*-trimethylsilyl derivative in CCl_4 and C_6D_6; thus in CCl_4 the α-proton resonates at 6.86 ppm $J_{\alpha,\beta}$ = 17 Hz while in C_6D_6 the β-proton signal is at 7.74 ppm. $J_{\beta,\alpha}$ = 17 Hz. In the MS of **1** (see below) ring B is unsubstituted; therefore the singlet at δ 6.17 arises from Ar.<u>H</u> of ring A and is typical of H-3′ or H-5′ signals in 2′, 4′, 6′-trioxygenated chalcones and other similarly constituted flavonoids [4, 6]. Furthermore, H-5′, moves downfield by 0.51 ppm in the spectrum of the diacetate of **1** in $CDCl_3$ and suggests [7] that in this derivative H-5′ is *ortho* or alternatively *para* to an acetoxyl group. Again, in