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FLAVONOIDS OF *ALBIZIA ADIANTHIFOLIA*

H. Arthur Candy*, K. Bridget Brookes*, James R. Bull†, Errol J. McGarry‡ and Joan M. McGarry

*Department of Chemistry, University of Natal, Durban 4001, Republic of South Africa; †National Chemical Research Laboratories, C.S.I.R., Box 395, Pretoria 0001, Republic of South Africa; ‡Imperial Chemical Industries Ltd, Pharmaceuticals Division, Mereside, Alderley Park, Macclesfield, Cheshire SK10 4TG, U K.

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INTRODUCTION

Eleven trees of the *Albizia* genus (Leguminosae) are indigenous to South Africa [1]. Of these *A. adianthifolia* (Schumach) W. F. Wight, with its umbrella-like crown, is characteristic of the Natal coastal bush. The golden-yellow wood is of little industrial importance, while the toxic bark is used by some of the African population in a 'love potion'. It was observed during milling that the wood dust caused considerable respiratory discomfort, a property shared with *A. suluensis* and *A. tanganicensis* [2].

A sample of the wood of *A. adianthifolia* was examined and three flavonoids, 3,4,2′,3′,4′-pentahydroxychalcone (okanin), 3,7,8,3′,4′-tetrahydroxyflavone (melanoxetin) and a dihydroflavonol (**1**), were isolated, the last being in greatest abundance. The properties of **1** were similar in several respects to those of 3,7,8,3′,4′-tetrahydroxyflavanone, originally isolated from *Acacia excelsa* and characterized by Clark-Lewis *et al.* [3, 4]. The reported occurrence of the dihydroflavonol **1** in the heartwood of *Albizia odoratissima* [5] was disputed [4] since its identification was based not upon the isolation of the compound but upon the formation of the pentamethyl ether on methylation of a brown gum. Such methylation of a dihydroflavonol to a 3-methoxyflavanone is without precedent. Under normal methylating conditions dihydroflavonols undergo dehydrogenation and subsequent methylation to give 3-methoxyflavones [6]. This communication reports the results of investigations to establish the identity of **1** and the fact that in our hands one of the products obtained on methylation of the dihydroflavonol **1** was indeed the 3-methoxyflavanone.

RESULTS

From colour tests (violet with either MgHCl or Zn–HCl [7, 8] and a +ve Pacheco reaction [7]) and from the appearance and behaviour of the UV spectrum in various media [9], it was inferred that **1** was a 5-deoxydihydroflavonol. In support of this, the PMR spectrum exhibited 1H signals as doublets at δ(DMSO-d_6) 4.39 and 4.98, $J = 11$ Hz each, assigned to C-3 and C-2 respectively, and at 6.56 and 7.18, $J = 9.0$ Hz each, assigned to C-6 and C-5 respectively. A mass ion of *m/e* 304 (M^+ 16%) was consistent with $C_{15}H_{12}O_7$. The PMR spectrum of the acetate revealed the presence of 5 × —OCOMe thus defining the degree of hydroxylation in the parent compound. In the same spectrum, 1H signals at δ($CDCl_3$) 5.40 and 5.70, each a doublet with $J = 12$ Hz, confirmed the reduced state of the C-2, C-3 bond.

Methylation of **1** (DMS–Me_2CO–K_2CO_3) under N_2 on a steam bath for 6 hr, provided a mixture of 5 compounds. Of these, 3 were predominant, each displaying a different colour when sprayed with *p*-anisaldehyde–H_2SO_4 on TLC. Two of these components were isolated by PLC. The most abundant was identified as 3,7,8,3′,4′-tetramethoxyflavanone on the basis of its spectral data (UV, PMR, MS), which agreed closely with published data [10, 11], notwithstanding the marked difference in mp with that published [10, 12] (our value 174°: lit. 166°).

The second methylation product was recovered as colourless needles, mp 149°. Apart from small differences the PMR spectrum was consistent with that reported for 3,7,8,3′,4′-pentamethoxyflavanone [10] obtained as needles mp 138.5° [11]. The UV spectrum (MeOH) displayed inflections at 232, 259 nm and a maximum at 286 nm, while the MS gave a mass ion at *m/e* 374 (M^+ 18%) with a base peak at *m/e* 194.

The third methylation product exhibited TLC properties (R_f and colour) identical with those of the pentamethoxyflavone derived from 3,7,8,3′,4′-tetrahydroxyflavone.

From the above evidence, it is concluded that the dihydroflavonol, **1**, is identical with 3,7,8,3′,4′-tetrahydroxyflavanone. The formation of the pentamethoxy derivative during methylation, was unexpected [4].

EXPERIMENTAL

Mps (uncorrected) were determined on a Kofler microscope hotstage. PMR spectra were recorded at 60 MHz with TMS as internal standard, unless otherwise stated. Acetylation was carried out by adding 2 drops of a soln of $HClO_4$–Ac_2O (2 drops, 70%: 0.5 ml) to a suspension of the substrate in 1.0 ml Ac_2O, shaking for a few min and then pouring onto ice. Methylation was achieved by heating the substrate with DMS in Me_2CO over K_2CO_3 on a steam bath for 6 hr. TLC was performed on Si gel plates and zones were located by spraying with *p*-anisaldehyde–H_2SO_4–EtOH (1:1:18). Paper chromatograms were sprayed with $K_3Fe(CN)_6$ (1% aq.)–$FeCl_3$ (1% aq), 1:1

Isolation of 3,4,2′,3′,4′-*pentahydroxychalcone and* 3,7,8,3′,4′-*tetrahydroxyflavone*. Finely milled wood (2.5 kg) was defatted with petrol (bp 60–80°) and then extracted with hot EtOAc (35 hr). Removal of the solvent furnished a brown gum (126 g) which was triturated with Et_2O. The insoluble residue dried to a tan coloured powder (X), while evaporation of the ethereal solution gave a brown gum (Y). Most of Y dissolved in warm water. This solution, after standing at 10° for 12 hr, deposited a yellow solid (1 g) which crystallized from H_2O–MeOH in yellow needles, mp 239–242°, similar in all respects (mp, mmp, PC and UV) to a sample of 3,4,2′,3′,4′-pentahydroxychalcone, synthesized according to Kurth [13].

The residue remaining after exhaustive EtOAc extraction of the powder X, was mainly one compound which was purified by repeated recrystallization from EtOH giving yellow crystals of 3,7,8,3′,4′-tetrahydroxyflavone, mp *ca* 300° (dec) (lit. [14], 312–320° (dec), R_f 0.36 (PC, *n*-BuOH–HOAc–H_2O, 4:1:5); UV absorption agreed with lit. [15]; MS: *m/e* 302 (M^+ 100%), 301(21), 286(16), 153(14), 137(11), 122(12). The pentaacetate crystallized from EtOH in colourless needles, mp 181–3 (lit. [3], 176°), R_f 0.59 (C_6H_6–EtOH, 95:5); MS: *m/e* ($M^+ + 1$), 512 (M^+) both low intensity, 470 (69%), 428(55), 386(83), 302(100); λ_{max}^{MeOH} 250, 301 nm; PMR($CDCl_3$): δ 2.32 (15H, *m*, 5 × —OCOMe); (80 MHz, $CDCl_3$): 7.29 (1H, *d*, $J_{6,5} = 8.9$ Hz, C-6), 7.35 (1H, *d*, $J_{5',6'} = 9.0$ Hz, C-5′), 7.68 (1H, *dd*, $J_{6',5'} =$ 9.0 Hz and $J_{6',2'} = 2.1$ Hz, C-6′), 7.70 (1H, *d*, $J_{2',6'} = 2.1$ Hz, C-2′), 8.15 (1H, *d*, $J_{5,6} = 8.9$ Hz, C-5). The pentamethoxy derivative, colourless crystals (MeOH), mp 153–154°, agreed in mp and UV absorption with published data [4]. R_f 0.29 (C_6H_{12}–EtOAc, 1:1), yellow with spray reagent, MS: *m/e* 372 (M^+, 100%), 371(75) 358(12), 357(49), 341(16), 329(19), PMR ($CDCl_3$): δ 3.90 (3H, *s*, —OMe), 3.98 (6H, *s*, 2 × —OMe), 4.00 (3H, *s*, —OMe), 4.03 (3H, *s*, —OMe), 7.02 (2H, *2d*, $J_{6,5}$ and $J_{5',6'}$ each 9.0 Hz, C-6, C-5′).

Isolation of 3,7,8,3′,4′-*tetrahydroxyflavanone*. A further sample of defatted wood was extracted with hot Me_2CO and provided a brown semi-solid mass. The water soluble components of this material were separated on a cellulose column (HOAc–H_2O, 1:50) furnishing 3,7,8,3′,4′-tetrahydroxyflavanone which crystallized from HOAc–H_2O, 1:4, as a colourless microcrystalline solid, melting at 214° (dec) (lit. [4] dec above 200°) and giving a violet colour with Mg–HCl and with Zn–HCl (lit. [3] red colour). R_f (PC) and UV agree with reported data [4, 15 respectively]. MS: *m/e* 304 (M^+, 16%), 302(7), 286(5), 153(100), 137(11), 123(31): PMR(DMSO-d_6): δ 4.39 (1H, *d*, $J_{3,2} =$ 11 Hz, C-3), 4.98 (1H, *d*, $J_{2,3} = 11$ Hz, C-2), 6.56 (1H, *d*, $J_{6,5} =$ 9 Hz, C-6), 6.78 (2H, *s*, aromatic), 6.93 (1H, *m*, aromatic), 7.18 (1H, *d*, $J_{5,6} = 9$ Hz, C-5). The pentaacetate, colourless crystals (EtOH–H_2O), melted at 200–205° (dec). λ_{max}^{MeOH} 261, 314 nm; MS: *m/e* 514 (M^+, 2%), 472(13), 454(3), 430(18), 370(15), 328(11), 286(11), 278(26), 237(24), 236(47), 195(44), 194(48), 153(55), 152(100), 123(22); PMR($CDCl_3$): δ 2.05 (3H, *s*, —OCOMe), 2.23 (3H, *s*, —OCOMe), 2.30 (9H, *s*, 3 × —OCOMe), 5.40 (1H, *d*, $J_{3,2} = 12.0$ Hz, C-3), 5.70 (1H, *d*, $J_{2,3} = 12$ Hz, C-2), 6.9 (1H, *d*, $J_{6,5} = 9.0$ Hz, C-6), 7.79 (1H, *d*, $J_{5,6} = 9.0$ Hz, C-5).

Methylation of 3,7,8,3′,4′-*tetrahydroxyflavanone*. Methylation of the dihydroflavanol under N_2, gave a mixture which on TLC revealed the presence of two minor components (not examined further) and 3 major components. One of these displayed TLC properties (R_f and colour) identical with 3,7,8,3′,4′-pentamethoxyflavone (already referred to in this communication). The remaining two compounds were separated on PLC (Si gel, C_6H_6–EtOH, 95:5). The first (brown with spray reagent), mp 174°, R_f 0.38 (C_6H_{12}–EtOAc, 1:1) showed physical properties (UV, PMR, MS) in close agreement with published data for 3-hydroxy-7,8,3′,4′-tetramethoxyflavanone [10, 11]. In addition, we observed 1H signals at δ ($CDCl_3$) 6.68 (1H, *d*, $J_{6,5} =$ 9.0 Hz, C-6) and 7.66 (1H, *d*, $J_{5,6} = 9.0$ Hz, C-5). The second component separated as colourless crystals, mp 149°, R_f 0.51 (C_6H_{12}–EtOAc, 1:1): λ_{max}^{EtOH} 232(*sh*), 259(*sh*), 286 nm, MS: *m/e* 374 (M^+, 18%), 195(13), 194(100), 179(18), 151(14). The PMR spectrum corresponded closely with that published for 3,7,8,3′,4′-pentamethoxyflavanone [10].

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