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FLAVONOIDS FROM *ABRUS PRECATORIUS*

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Key Word Index—*Abrus precatorius*; Leguminosae; flavonoids; 6,4′-dimethoxy-7,3′-dihydroxyflavone; abrectorin; desmethoxycentaureidin 7-*O*-rutinoside.

Abrus precatorius, having medicinal properties [1], has been examined for its chemical components [2–6]. This communication describes the isolation of a new flavone, abrectorin and a known glycoside, desmethoxycentaureidin 7-*O*-rutinoside.

A. precatorius seed kernels (2 kg) were defatted using petrol and then extracted exhaustively with EtOH. Solvent-free EtOH extract was repeatedly extracted with Et_2O and then EtOAc to separate non-glycosidic and glycosidic components. Combined Et_2O and EtOAc extracts containing non-glycosidic components were concentrated. The solvent-free concentrate was chromatographed on a Si gel column; elutions with C_6H_6–EtOAc (3:1) gave a mixture which was separated into two compounds by preparative TLC (Si gel; C_6H_6–EtOAc; 1:1). One of these was characterized as luteolin by direct comparison with an authentic sample whereas the second compound (**1**) was a new flavone, here named abrectorin. Et_2O- and EtOAc-insoluble fractions containing glycosidic components were combined, concentrated and the resulting solvent-free concentrate was chromatographed on a Si gel column, which was eluted with EtOAc–MeOH (3:1) to give a mixture of three compounds which on preparative-PC using *n*-BuOH–HOAc–H_2O (4:1:5; upper layer) yielded orientin, isoorientin and a flavone glycoside (**2**).

Abrectorin (**1**)

Colour reactions and spectral data indicated **1** to be a polyhydroxyflavone. Methylation of **1** yielded a dimethyl ether identical with 6,7,3′,4′-tetramethoxyflavone (**1a**) [Bhardwaj, D. K. *et al.*, unpublished results] showing that **1** was a 6,7,3′,4′-dihydroxydimethoxyflavone. It gave a negative Quastel test [7] showing the absence of an *ortho*-dihydroxyl in the molecule. On alkali fission **1** yielded isovanillic acid, fixing an OH and an OMe at C-3′ and C-4′ respectively. The solubility of **1** in aqueous Na_2CO_3 (10%) indicated another OH at C-7, so that the other OMe was therefore at C-6. Abrectorin is thus 6,4′-dimethoxy-7,3′-dihydroxyflavone (**1**). This was confirmed by the identity of its diethyl ether with synthetic 6,4′-dimethoxy-7,3′-diethoxyflavone (**1b**) [8].

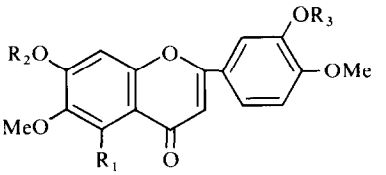
Desmethoxycentaureidin-7-O-rutinoside (**2**)

Colour reactions and spectral data indicated **2** to be a polyhydroxyflavone glycoside. On hydrolysis it yielded an aglycone (**2a**) and two free sugars identified as rhamnose and glucose by PC (*n*-BuOH–Py–H_2O, 6:4:3). Methylation of **2a** yielded a trimethyl ether identical with 5,6,7,3′,4′-pentamethoxyflavone (**2b**) [9] indicating that **2a** was a 5,6,7,3′,4′-trihydroxydimethoxyflavone. On alkali fission **2a** yielded isovanillic acid showing a OH and a OMe at C-3′ and C-4′ respectively. **2a** did not give the Bargellini test) for a 5,6,7-trihydroxy system or the Quastel test [7] characteristic for an *ortho*-dihydroxy system. Consequently, the remaining OMe and OH were at C-6 and C-7 respectively. Bathochromic shifts in UV spectrum of **2a** with $AlCl_3$ confirmed the chelated OH at C-5 and its solubility in aqueous Na_2CO_3 (10%) supported another OH at C-7. The absence of the usual bathochromic shifts in

UV spectrum of **2a** with NaOAc as generally recorded for the 7-hydroxyflavones was attributed to the presence of OMe at C-6 position [9]. The aglycone is thus 5,7,3′-trihydroxy-6,4′-dimethoxyflavone (desmethoxycentaureidin) [10]. Acetylation of **2** gave an acetate **2c**. ^{1}H NMR of **2c** showed two OMe, two phenolic COMe, six alcoholic COMe, sugar protons besides those for five aromatic protons. **2** on complete methylation followed by hydrolysis gave a methyl ether soluble in aqueous Na_2CO_3 (10%) and also identical with 5,6,3′,4′-tetramethoxy-7-hydroxyflavone (**2d**) [9]. Hence, **2** is the 7-*O*-diglycoside of **2a**. Permethylation followed by hydrolysis of **2** gave 2,3,4-tri-*O*-methyl-D-glucopyranose (R_G 0.84) and 2,3,4-tri-*O*-methyl-L-rhamnopyranose (R_G 1.02) indicating it to be a rutinoside [11] as was confirmed by the ^{1}H NMR of its acetate (**2c**) [12]. The glycoside is thus the known desmethoxycentaureidin 7-*O*-rutinoside (**2**) [13].

EXPERIMENTAL

1: Creamish micro-prisms from MeOH; mp 229–230° (Found: C, 65.2; H, 4.8. $C_{17}H_{14}O_6$; requires: C, 64.96; H, 4.49%); developed yellow–orange colouration with Mg–HCl; was soluble



1 $R_1 = R_2 = R_3 = H$
1a $R_1 = H$; $R_2 = R_3 = Me$
1b $R_1 = H$; $R_2 = R_3 = Et$
2 $R_1 = OH$; R_2 = rutinosyl, $R_3 = H$
2a $R_1 = OH$; $R_2 = R_3 = H$
2b $R_1 = OMe$; $R_2 = R_3 = Me$
2c $R_1 = OAc$; R_2 = hexa-*O*-acetylrutinosyl; $R_3 = Ac$
2d $R_1 = OMe$; $R_2 = H$; $R_3 = Me$

in aq. Na_2CO_3 (10%); IR (KBr) cm^{-1}: 3448 (OH), 1667 (conj. CO); UV (MeOH) nm: 250, 290, 335. No UV spectral shifts with NaOAc. **1a**: Methylation of **1** with Me_2SO_4 (2.2 mol)/K_2CO_3 in Me_2CO gave **1a**, colourless needles from $CHCl_3$–petrol; mp 221–222° (Found: C, 66.40; H, 5.60. $C_{19}H_{18}O_6$ requires: C, 66.66; H, 5.30%); ^{1}H NMR ($CDCl_3$): δ 3.99 (12 H, *s*, 4 × –OMe), 6.60 (1 H, *s*, C-3-H), 6.87 (1 H, *s*, C-8-H), 7.02 (1 H, *d*, J = 9 Hz, C-5′-H), 7.45 (2 H, *m*, C-2′-H and C-6′-H), 7.52 (1 H, *s*, C-5-H). **1b**: Ethylation of **1** with Et_2SO_4 (2.2 mol–K_2CO_3 in Me_2CO gave **1b**, creamish needles from MeOH; mp 176°.

2: Pale-yellow needles from MeOH–EtOAc, mp 183–184°; IR (KBr) cm^{-1}: 3450 (OH), 1640 (conj. CO); UV (MeOH) nm: 275, 335; +$AlCl_3$ 280, 305, 360. **2a**: Hydrolysis of **2** with MeOH–H_2SO_4 (7%) gave rhamnose and glucose as free sugars and an aglycone **2a**, yellow needles from EtOAc, mp 269–270° (Found: C, 62.3; H, 4.6. $C_{17}H_{14}O_7$ requires: C, 61.82; H, 4.24%); UV (MeOH) nm: 275, 335; +$AlCl_3$ 280, 305, 355. **2a** on complete methylation with Me_2SO_4–K_2CO_3 in Me_2CO gave **2b** [9], rectangular plates from EtOH, mp 178°. **2c**: Acetylation (Ac_2O–Py) of **2** gave **2c**, colourless needles from EtOAc–petrol, mp 121–122°. ^{1}H NMR ($CDCl_3$): δ 1.18 (3 H, *br s*, rhamnosyl C-Me), 1.80–2.05 (18 H, *m*, 6 × –OCOMe, alcoholic), 2.34 (3 H, *s*, 1 × –OCOMe, phenolic), 2.47 (3 H, *s*, 1 × OCOMe, phenolic), 3.90 (3 H, *s*, 1 × –OMe), 4.10 (3 H, *s*, 1 × –OMe), 3.47–5.28 (12 H, *m*, sugar-protons), 6.50 (1 H, *s*, C-3-H), 6.70 (1 H, *s*, C-8-H), 7.32 (1 H, *d*, J = 9 Hz, C-5′-H), 7.42 (1 H, *d*, J = 2 Hz, C-2′-H), 7.77 (1 H, *m*, C-6′-H). **2d**: Methylation of **2** with Me_2SO_4–K_2CO_3 in Me_2CO, followed by hydrolysis with MeOH–H_2SO_4 (7%) gave a methyl ether **2d**, pale-yellow needles from MeOH, mp 220–222°, agreed with 5,6,3′,4′-tetramethoxy-7-hydroxyflavone (**2d**) [10].

Permethylation and hydrolysis of **2**. **2** (8 mg) in DMSO (2 ml) and NaH dispersion in oil (50%, 10 mg) was left at 80° for 1 hr, cooled, treated with MeI (1 ml), left overnight, poured into ice-cold H_2O and then extracted with $CHCl_3$. The permethylated product was hydrolysed using Killiani mixture (3 ml). The hydrolysate was found to contain (2,3,4-tri-*O*-methyl-D-glucopyranose (R_G 0.84) and 2,3,4-tri-*O*-methyl-L-rhamnopyranose (R_G 1.02) as shown by direct comparison with authentic samples by PC in *n*-BuOH–EtOH–H_2O (5:1:4).

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