protons, respectively. The remaining aromatic signals at 6.72. 6.96 and 7.16δ appeared very similar to those of the catechol ring of (−)-epicatechin gallate. The fact that the non-aromatic signals showed only small coupling constants indicates that both flavanol moieties possess the epi configuration. This appears to be the first report of the occurrence of a gallyl proanthocyanidin. Further material must be isolated before a final structure is presented, however.

EXPERIMENTAL

Air-dried leaves of *D. pruriens* F. Muell were kindly supplied by B. P. M. Hyland, Forestry and Timber Bureau, Australian Department of Agriculture, Atherton, Queensland. Plant material was extracted and the neutral flavonoid clycosides isolated by methods described elsewhere [6]. The sulfate derivatives, after normal chromatography on Sephadex LH-20 and cellulose partition columns [6], were purified by preparative TLC on cellulose with BAW (4:1:5). The three compounds showed the same electrophoretic mobility on Eastman cellulose chromagrams: 3.8 cm at 400 V, 8 mA for 1 hr. After the normal sugar analysis [6] the aqueous portion of the hydrolysate was evaporated to dryness, taken up in a few drops of 0.1 M nitric acid and tested with $BaCl_2$. A white precipitate confirmed the presence of sulfate ion. R_f values in BAW and 20% acetic acid for the kaempferol, quercetin and myricetin compounds were 86, 74; 83, 69; and 81, 65, respectively. R_f values (× 100) for the flavanols on polyamide 6.6 in Me_2CO–MeOH–HOAc (5:5:1) were: (−)-epicatechin gallate, 50; (−)-epigallocatechin gallate, 37; compound C, 26; and compound D, 10.

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TWO NEW SULPHATED FLAVONOL GLUCOSIDES FROM LEAVES OF *MALVA SYLVESTRIS*

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Fresh leaves were extracted with 25%EtOH, followed by column chromatography (cellulose). Two successive fractions, eluted with H_2O, were found to contain two new anionic flavonol glycosides (G, mp 320° decomp.) and (H, mp 332° decomp.), respectively. Both G and H showed chromatographic properties of highly glycosylated flavonols and migrated towards the anode on electrophorograms (Table 1).

Compound G on acid hydrolysis (N HCl) gave glucose and gossypetin (mmp, colour reactions[1], co-chromatography and UV data [2] Table 1); The hydrolysate gave also a white ppt. with $BaCl_2$.

On treatment with β-glucosidase, G gave a single positively charged product (G_1, dark brown on PC under UV, Table 1) which on acidification (0.05N HCl) gave gossypetin and a white ppt. with $BaCl_2$, but no sugar. Controlled acid hydrolysis of G with 0.05N HCl gave rise to only one intermediate G_{II} beside gossypetin. G_{II} (yellow spot on chromatograms under UV) which started to appear immediately after acidification of G was identified as gossypetin-8-*O*-β-D-glucoside (gossypin) through enzymic hydrolysis, co-chromatography and UV data (Table 1).

The above data prove that G (dark brown spot changing to brownish–yellow with NH_3 on chromatograms under UV) is a gossypin-mono-sulphate ester with its sulphate group (presented as $KHSO_3$) most probably at C-3 (Found: S: 5.4%, Calc. for $C_{21}H_{20}O_{16}SK$, S: 5.34%). K was detected by flame spectrophotometer and by a ppt. obtained with Na cobaltinitrite. Esterification at position 3 was confirmed through the hypsochromic shift observed on comparing the UV spectra of both G and gossypin (Table 1).

Compound H, on acid hydrolysis gave glucose and 8-hydroxyluteolin (hypolaetin, mp 295°–296°, lit. [3] 296°) the hydrolysate gave a white ppt. with $BaCl_2$. R_f-values, colour reactions and UV spectral analysis (Table 1) confirmed hypolaetin [3]; this was confirmed through the prolonged heating of the aglycone with N HCl–EtOH (1:1), whereby the corresponding 6-OH isomer was formed and by alkali fusion which yielded pyrogallol and protocatechuic acid. Glycoside H on treatment with β-glucosidase gave a positively charged product H_1 (bluish–black colour on PC and electrophorograms under UV, Table 1) which on acidification with 0.05N HCl gave hypolaetin and a white ppt. with

Table 1. Properties of new sulphated flavonols and their partial hydrolysis products.

	Chromatographic properties						λ_{max} (nm) in MeOH	*H* UV spectral data				
	Electrophoresis (distance travelled cm)	R_f-values (× 100)						Δλ (nm)				
		H_2O	15% HOAc	BAW	50% HOAc	Forestal		NaOAc†	NaOAc–H_3BO_4‡	NaOMe‡	$AlCl_3$‡	$AlCl_3$*‡ HCl
G	4.7	64	59	31			260(*sh*), 274 370	20	20	57	18	33
G_i	2.0	38		33			260, 275, 382	19	10	60 (dec)	68	63
Gossypetin				48	24	33	260, 278, 338, 366	20	6	39 (dec)		
H	4.5	63	54	44			260 (*sh*), 275, 355	22	0	75	50	50
H_I	2.5	20		35								
H_{II}	0.0	6	17	50			255, 270, 350	16	25	50	55	45
Hypolaetin				52	33	48	256, 280, 342	4	17	38	44	

*pH 2.2, 2.5% HCO_2H + 8% HOAc (1:1), 50 V/cm, 30, 90 min. †Band II; ‡band I; (*sh*) shoulder.

$BaCl_2$. Controlled acid hydrolysis of H with 0.05N HCl released a single intermediate (H_{11}, dull black on chromatograms under UV) together with hypolaetin. The intermediate H_{11} was hydrolysed with either N HCl to yield hypolaetin and glucose or β-glucosidase.

From the spectra (Table 1) H_{11} is obviously hypolaetin-8-*O*-β-D-glucoside and H is a mono-sulphated derivative (Found: S: 5.5%, Calc. for $C_{21}H_{19}O_{15}SK$, S: 5.4%). The UV spectra of H (Table 1) showed that the sulphate esterified position 3′ and glycoside H is, therefore, hypolaetin-8-*O*-β-D-glucoside-3′-sulphate (K salt).

This is the first report of both gossypin-3-sulphate and hypolaetin-8-*O*-β-D-glucoside-3′-sulphate. Hypolaetin itself, which is quite a rare flavone of restricted occurrence, was first reported by Harborne [3] in 1966, its 7-glucoside was reported in 1971 by Siddiqui and Sen [4] and its 8-sulphate described in 1975 by Harborne [5].

Plant source. Malva sylvestris Collected from Giza farms, Egypt, and identified by Prof. Dr. Vivi Tackholm, Department of Botany, Cairo University.

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