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FLAVONOIDS OF *POLYGONUM SENEGALENSE* (MEISN) PART II[1] : MORE SURFACE AND INTERNAL TISSUE FLAVONOID AGLYCONES

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ABSTRACT. Apart from the eight surface flavonoids already reported from *Polygonum senegalense* [1], four more methylated flavonoids are further described. Furthermore the cell vacuole flavonoids are glycosides based on the three common aglycones.

INTRODUCTION

We have reported earlier that the aerial surface of *Polygonum senegalense* (Meisn) is covered with an exudate which consists of mostly non-polar methylated flavonoids (chalcones and flavanones) [1]. These deposits can reach up to 17% on the young leaves but the quantity reduces with age. In fact we indicated that the surface mileau is a very good anti-feedant towards the ravenous insect, *Schistocerca gregaria* [1].

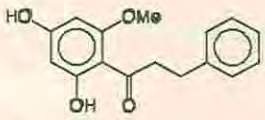
In this paper we report four further methoxylated flavonoids in the surface exudate of the plant. Prior to our first report, other workers reported the occurrence of quercetin-3-(2"-galloylglucoside) from the same plant [2]. The internal tissue flavonoids of *P. sengalense* are presumed to be glycosides based on the aglycones quercetin, kaemferol and luteolin.

RESULTS AND DISCUSSION

Extraction of the surface compounds was accomplished by washing with acetone as described before [1]. The acetone concentrate was separated on silica gel into petroleum ether (Fp), benzene (Fb), chloroform (Fc) and methanol (Fm) fractions. 2',4'-dihydroxy-6'-methoxydihydrochalcone (**1**) and 3,7-dihydroxy-5,8-dimethoxy-flavanone (**2**) were isolated as minor components from Fc while 7-hydroxy-5,8-dimethoxyflavone (**3**) was found in Fm of both forms, *P. senegalense forma senegalense* and *P. senegalense forma albomentosum*. On the other hand 3',6'-dihydroxy-2',4',5'-trimethoxychalcone (**4**), was only found in the glabrous *forma senegalense*. It is not known what the unique physiological implication of this compound is *vis.à.vis* the transformation from tomentose to glabrous form but it is clearly a chemical character distinguishing the two forms.

The NMR data of compounds (**1-4**) are given in Table 1. Structural assignments were done through extensive use of NOE experiments and comparison with literature data where available. When the pre-washed leaves and flower heads were dried,

ground, extracted with aqueous methanol, then hydrolysed with 2N HCl, the resultant hydrolysate gave the common flavone aglycones, mainly quercetin, together with kaempferol and luteolin in trace amounts. These compounds were identified by comparison with authentic samples.



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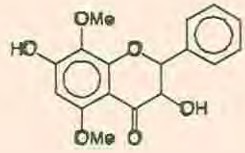

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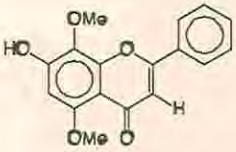

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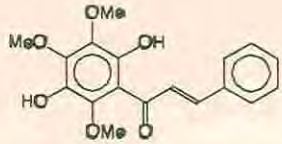

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Table 1. ^{13}C and (^{1}H) NMR data for surface flavonoid aglycones **1-4**.

Chalcone carbon	1	4	Flavone and Flavonone carbon	2	3
1'	104.4	106.4	2	72.7(5.0*d*)	158.1
2'	164.8	152.0	3	68.1(4.1*d*)	137.4
3'	95.7(5.88*d*)	135.2	4	199.1	185.9
4'	163.0	143.0	5	154.7	157.5
5'	91.4(5.98)	134.2	6	94.4(6.05)	94.3(6.05)
6'		147.0	7	158.9	157.3
7	30.1 (2.87*t*)	126.3(7.8*bd*)	8	158.1	157.5
8	45.0(3.22*t*)	143.7(7.92*bd*)	9	139.8	155.3
9	203.7	193.5	10	102.7	103.5
1	128.2	128.4	1'	128.8	129.8
2	128.3	128.9(7.41*m*)	2'	126.7(7.4*m*)	126.1(7.49*m*)
3	125.8	128.4(7.41*m*)	3'	128.7(7.4*m*)	128.8(7.45*m*)
4	128.4	130.4(7.41*m*)	4'	128.7(7.4*m*)	129.7(7.45*m*)
5	125.8	128.4(7.41*m*)	5'	128.7(7.4*m*)	128.8(7.49*m*)
6	128.3	128.9(7.63*m*)	6'	128.7(7.4*m*)	126.1(7.49*m*)
2'-OH	-	(12.88*m*)	5-OCH_3	61.0(3.93*s*)	61.0(3.96*s*)
3'-OCH_3	-	61.9(4-14*s*)	8-OCH_3	51.2(3.92*s*)	55.7(3.76*s*)
4'-OCH_3	-	61.2(3.90*s*)			
6'-OCH_3	55.9(3.80*s*)	60.9(3.84*s*)			

It is clear that surface flavonoid differentiation is greater than the corresponding cell vacuole compounds. These results are in line with the findings of Wollenweber *et al.* [3,4], who claim that the surface flavonoids can be of great utility for chemotaxonomic purposes because of their diversity. Again it must be true that the few internal tissue flavonoids give rise to the plethora of surface flavonoids. The functional utilities of these surface flavonoids are not established even though we have determined anti-feedant activity for the acetone leaf wash and some of its components [1].

EXPERIMENTAL

General: See Ref. 1

Extraction: Aerial parts of *P. senegalense forma senegalense*, were washed with acetone before drying. Removal of the solvent gave 11.4 g of dark brown gummy residue. The acetone washed aerial parts on drying weighed 205 g.

Isolation and characterisation: The residue from the acetone extract was chromatographed as before on silica gel into petroleum ether (Fp), benzene (Fb), chloroform (Fc) and methanol (Fm) eluant concentrates. Further column chromatography and TLC on silica gel of Fc gave compounds **1-4**. Similar treatment of Fm as for Fc above yielded compound **3**.

2',4'-dihydroxy-6'-methoxydihydrochalcone (**1**, 45 mg). M.P. 178-179° (lit [6] M.P. 177-178°); UV λ_{max} (MeOH) nm: 286, 222, the former shifted with NaOMe, NaOAc and $AlCl_3$ (unchanged with HCl); IR ν_{max} cm^{-1} (KBr): 1620 (C=O); MS m/z (rel. int.): 272 (58), 167 (100), 141 (78), 91 (39), 69 (38).

3,7-dihydroxy-5,8-dimethoxyflavanone (**2**, 120 mg). M.P. 134-135°; UV λ_{max} (MeOH) nm: 288, 330, the latter shifted with NaOMe (degenerates), NaOAc, $AlCl_3$ (unchanged with HCl); IR ν_{max} cm^{-1} (KBr) 1660 (C=O); MS m/z (rel. int.): 316, M^+, (100), 210 (100), 167 (32), 105 (23), 79 (77), 77 (69), 69 (93), 55 (55).

7-hydroxy-5,8-dimethoxyflavone (**3**, 15 mg). M.P. 194-196°; UV λ_{max} (MeOH) nm: 284, 290, 340, the latter shifts with NaOMe, NaOAc and $AlCl_3$ (changes with HCl); IR ν_{max} cm^{-1} (KBr): 1635 (C=O); MS m/z (rel. int.): 298, M^+, (12.5), 167 (44.9), 115 (2.0), 69 (100.0); Elemental analysis: found, C 68.4, H 4.75. $C_{17}H_{14}O_5$ requires, C 68.45, H 4.73.

3',6'-dihydroxy-2',4',5'-trimethoxychalcone (**4**, 30 mg). M.P. 126-127°); UV λ_{max} (MeOH) nm: 317, one peak only which shifts with NaOMe, $AlCl_3$ (unchanged with HCl); IR ν_{max} cm^{-1} (KBr): 1615 (C=O); MS m/z (rel. int): 330, M^+, (84.5), 226 (96.2), 212 (24.4), 211 (100), 90 (15.0), 77 (20.1).

The surface extracts of *P. senegalense forma albomentosum* gave the above compounds except for compound **4**, in about the same yields. The dried, ground acetone-washed material of either plant, was extracted in the cold using 70% MeOH and the solvent removed under vacuum. The resulting aqueous solution was hydrolysed with approximately 2N HCl by refluxing for 1 hr. The organic fraction was partitioned into ethyl acetate and silica gel chromatography gave quercetin (1.3 g), kaempferol (70 mg) and luteolin (12 mg) which were identified by comparison with authentic samples.

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