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AN ANTHRAQUINONE GLYCOSIDE FROM *RHAMNUS PALLASII**

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Key Word Index—*Rhamnus pallasii*, Rhamnaceae, α-sorinin, anthraquinone glycoside, physcion-8-*O*-β-primeveroside, 1,8-dihydroxy-3-methyl-6-methoxy-anthraquinone-8-*O*-β-primeveroside

Abstract—A new anthraquinone glycoside, together with α-sorinin, has been isolated from the bark of *Rhamnus pallasii* and its structure elucidated as physcion-8-*O*-β-primeveroside

INTRODUCTION

In a previous paper [1], we reported the isolation of a new dihydroflavonol, pallasiin, and seven known flavonoids from the bark of *Rhamnus pallasii* Fisch et May We now report on the isolation of a known naphthalide, α-sorinin (**1**), and a new anthraquinone glycoside, physcion-8-*O*-β-primeveroside (**2**) from the same source

RESULTS AND DISCUSSION

Compound **1** was identified by direct comparison with α-sorinin isolated from the bark of *R japonica* Maxim [2] To the best of our knowledge this is only the second report of the occurrence of α-sorinin in Rhamnaceae

Compound **2** was recrystallized from methanol to give fine orange needles, mp 258–261°, FDMS *m/z* 601 ($[M]^+$ ($C_{27}H_{30}O_{14}$) + ^{23}Na) Its IR spectrum showed absorption bands at 3425, 1635, 1600, 1320, 1265, 1220 and 1080 cm^{-1} in potassium bromide, and its UV spectrum showed maximum absorption at 222 5 (4 52), 269 (4 39), 277 (4 38) and 416 (3 94) nm (log ε) in methanol, and 266 and 442 nm with addition of sodium hydroxide solution

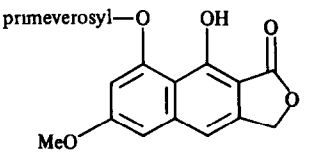
Acetylation of **2** with acetic anhydride–pyridine gave the peracetate **3** as pale yellow fine needles (from ethanol), mp 221–223°, $[\alpha]_D^{20}$ −60 5° ($CHCl_3$) The ^1H NMR spectrum of **3** showed the presence of six alcoholic acetoxy groups (δ2 03, 2 08 and 2 10), a phenolic acetoxy group (δ2 52), an aromatic methoxy group (δ3 97) and an aromatic methyl group (δ2 46)

Acid hydrolysis of **2** gave physcion (**4**), which was identical with an authentic sample The presence of D-glucose and D-xylose in the hydrolysate was shown by TLC and GC

The mass spectrum of **3** contained significant peaks at the *m/z* values shown in Fig 1 Those at *m/z* 547, 259 and 159 suggested the presence of a peracetylxylopyranoglucosyl moiety The location of the *O*-glycosyl substituent in **2** was established as C-8 by correlation of the chemical shifts of the nuclear protons in the ^1H NMR spectrum of **3** with those of physcion-8-*O*-β-glucoside (physcionin) peracetate [3] and physcion-8-*O*-β-gentiobioside peracetate [4] (Table 1)

In the ^{13}C NMR spectrum of **2**, the *ca* 7 ppm downfield chemical shift at C-6 carbon (glc-6) of the glucosyl moiety relative to that of glucose suggested the attachment of the xylosyl moiety at the C-6 carbon of glucose The 1 → 6 linkage in the xylopyrano-glucosyl moiety of **1** had been established by the fact that the physical properties of the disaccharide obtained from **1** by mild hydrolysis and of its phenylosazone were in good agreement with those of synthetic primeverose (xylopyranosyl-(1 → 6)-*O*-β-glucopyranose) [2, 5] The glycosyl moiety of **2** was shown to be primeverose by correlation of the chemical shifts of its carbon atoms in the ^{13}C NMR spectrum of **2** with those of the primeverosyl moiety of **1** (Table 2)

*Part 2 in the series "Studies on Constituents of *Rhamnus pallasii*" For Part 1, see ref [1]



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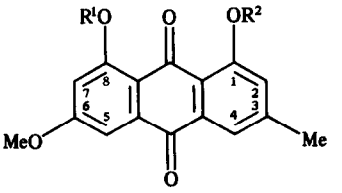
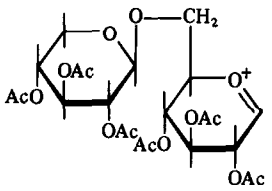
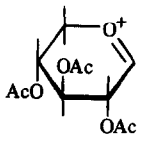


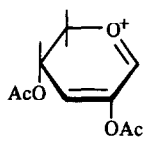
2 R^1 = primeverosyl, R^2 = H
3 R^1 = $(Ac)_6$ primeverosyl, R^2 = Ac
4 $R^1 = R^2$ = H



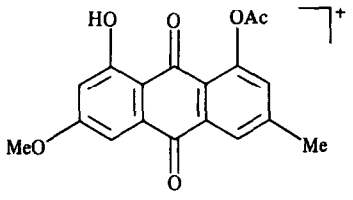
m/z 547 ($C_{23}H_{31}O_{15}$)



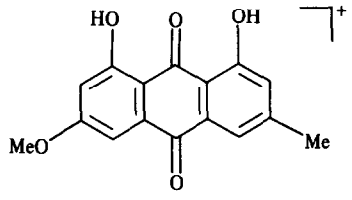
m/z 259 ($C_{11}H_{15}O_7$)



m/z 199 ($C_9H_{11}O_5$)



m/z 326 ($C_{18}H_{14}O_6$)



m/z 284 ($C_{16}H_{12}O_5$)

Fig 1

Table 1 Chemical shifts of nuclear protons in ^1H NMR spectra of physcion glycoside peracetates

Peracetates	H-2 (*s, br*)	H-4 (*s, br*)	H-5 (*d, J* = 2 5 Hz)	H-7 (*d, J* = 2 5 Hz)
Physcion-8-*O*-β-primeveroside (**2**)	7 13	7 88	7 45	6 97
Physcion-8-*O*-β-glucoside*	7 13	7 90	7 43	6 92
Physcion-8-*O*-β-gentiobioside†	7 19	7 95	7 50	7 00

*Synthesised from physcion and α-acetobromglucose, mp 164–165°, $[\alpha]_D^{20}$ – 37 2° ($CHCl_3$)
†From ref [4]

Table 2 ^{13}C NMR data

Physcion moiety of **2**		Primeverosyl moiety		
C		C	**2**	**1**
1	164 7	glc-1	100 4	99 8
2	119 2	glc-2	73 2	73 2
3	147 0	glc-3	75 8	76 0
4	124 1	glc-4	69 4	69 7
5	108 3	glc-5	75 8	76 0
6	160 5	glc-6	67 8	67 8
7	107 0	xyl-1	104 0	104 1
8	161 6	xyl-2	73 2	73 2
9	186 3	xyl-3	76 2	76 3
10	181 7	xyl-4	69 4	69 3
11	136 3	xyl-5	65 5	65 5
12	106 9			
13	114 4			
14	131 9			
OMe	56 0			
Me	21 2			

Consequently, the structure of **2** has been established as physcion-8-*O*-β-primeveroside (1,8-dihydroxy-3-methyl-6-methoxy-anthraquinone-8-*O*-β-primeveroside) This is the first report of the occurrence of a physcion diglycoside in Rhamnaceae

EXPERIMENTAL

^1H NMR 90 MHz, $CDCl_3$ with TMS as int standard, ^{13}C NMR 15 MHz, DMSO-d_6, MS direct inlet, 70 eV, ion source temp 200°, GC glass column (3 mm × 1 m), 1 5% OV-1 on shimalite-W (80–100 mesh), column temp 140–190° (3°/min), injection and detector temp 280°, carrier gas N_2 (20 ml/min)

Plant material R pallasii was collected on Sept 1980 at Artvin near Ardanuç, Turkey A voucher specimen is retained in 'Ankara Universitesi Eczacilik Fakultesi Herbaryume' (AEF No 7173)

Isolation Dry powdered bark (100 g) was extracted (× 3) with MeOH The concentrated extract plus H_2O was extracted successively with Et_2O, $CHCl_3$, EtOAc and BuOH, and the BuOH extract chromatographed on a silica gel column developed with a $CHCl_3$–MeOH gradient The fractions were monitored by TLC developed with $CH_3COC_2H_5$–EtOAc–HCOOH–H_2O–C_6H_6 (4 3 1 1 2, upper layer) The fractions showing a TLC spot

at R_f 0 26 were concentrated to afford crude **2**, whilst those showing a TLC spot at R_f 0 09 were concentrated to afford crude **1**

α-Sorinin (**1**) Colourless fine needles from EtOH, mp 159–163° IR ν_{max}^{KBr} cm^{-1} 3300 (OH), 1720 (chelated CO), 1630, 1610 (arom C=C), 1060, 1030; UV λ_{max}^{EtOH} nm (log ε) 219 (3 55), 250 (4 09) sh, 257 (4 24), 348 (3 36), UV $\lambda_{max}^{EtOH+NaOH}$ nm 241, 264, 365, ^{1}H NMR (DMSO-d_6) δ 3 84 (3H, *s*, MeO), 4 16 (1H, *d*, *J* = 7 Hz, anomeric H), 5 06 (1H, *d*, *J* = 7 Hz, anomeric H), 5 26 (2H, *s*, lactone CH_2), 7 00 (1H, *d*, *J* = 3 Hz, arom H), 7 03 (1H, *d*, *J* = 3 Hz, arom H), 7 22 (1H, *s*, arom H)

Acid hydrolysis of physcion-8-O-β-primeveroside (**2**) Compound **2**, in 10% H_2SO_4 soln, was heated on a water bath for 1 hr then cooled The mixture was extracted with $CHCl_3$ The $CHCl_3$ layer was washed and evaporated to dryness The residue was purified by prep TLC (C_6H_6) to give **4** The aq layer was neutralized with $BaCO_3$ and the precipitate was filtered off The filtrate was evaporated to dryness, and the residue was examined by TLC and GC for the presence of D-glucose and D-xylose

Physcion (**4**) Dark orange needles from $CHCl_3$, mp 207–210° (Found $[M]^+$ at *m/z* 284 0678, $C_{16}H_{12}O_5$ requires 284 0683) IR ν_{max}^{KBr} cm^{-1} 1625, 1490, 1370, 1320, 1275, 1220, 1160, UV λ_{max}^{EtOH} nm (log ε) 223 5 (4 41), 254 (4 14), 264 (4 16), 286 (4 14), 433 (3 99), UV $\lambda_{max}^{EtOH+NaOH}$ nm 212, 229, 255, 304, 503, ^{1}H NMR ($CDCl_3$) δ 2 42 (3H, *s*, Me), 3 87 (3H, *s*, MeO), 6 57 (1H, *d*, *J* = 2 5 Hz, H-7), 7 00 (1H, *s* (*br*), H-2), 7 26 (1H, *d*, *J* = 2 5 Hz, H-5), 7 53 (1H, *s* (*br*), H-4)

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