

hardwickiol (4) and sagittariol indicated the need for one more structural change, but probably within the clerodane skeleton. As a consequence a  $^{13}\text{C}$  NMR spectral study of a few selected A-B *cis* clerodanes was undertaken.

A  $^{13}\text{C}$  NMR spectral analysis of the methyl ester (7) and lithium aluminum hydride reduction product (8) of floribundic acid [7] as well as cistodiol (9) [8] yielded the shifts depicted on the formulae. Three interesting facts emanated from these data: (a) the 8-methyl group of cistodiol (9) being equatorial; (b) the three substances maintaining the A-B *cis* steroid conformation in solution; (c) the chemical shifts of the nuclear carbons and one-carbon side-chains of cistodiol (9) being nearly identical with like carbon sites of sagittariol. Thus the relative configuration of sagittariol is as pictured in structure 10a. The carbon shifts of the diol and its derivatives are listed in Table 1.

#### EXPERIMENTAL

The  $^1\text{H}$  NMR spectrum of sagittariol (10a) in  $\text{CDCl}_3$  soln with TMS as int. standard ( $\delta = 0$ ) was recorded on a 360 MHz spectrometer equipped with an Oxford magnet and a computer system. The  $^{13}\text{C}$  NMR spectra were obtained on a wide-bore, broad-band spectrometer, operating with an Oxford magnet at 50.31 MHz in the Fourier transform mode. The carbon shifts on formulas 2-9 are in  $\delta$ -values (ppm) downfield from TMS;  $\delta(\text{TMS}) = \delta(\text{CDCl}_3) + 76.9$  ppm. The asterisked shifts on formula 5 may be interchanged.

*Sagittariol* (10a).  $^1\text{H}$  NMR:  $\delta$  0.73 (3H, *d*,  $J = 7$  Hz, 8-Me), 0.76 (3H, *s*, 9-Me), 1.11 (3H, *s*, 5-Me), 1.29 (3H, *s*, 13-Me), 1.42 (1H, *m*, H-8), 4.06, 4.10, 4.18, 4.21 (2H, AB *dd*, 2H-18), 5.0-5.9 (3H, *m*, vinyl Hs), 5.61 (1H, *br s*, H-3).

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## PHYSCION-8-O-GENTIIOBIOSIDE FROM *RHAMNUS VIRGATA*

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**Key Word Index**—*Rhamnus virgata*; Rhamnaceae; physcion; physcion-8-O-gentiobioside; anthraquinone.

**Abstract**—A new anthraquinone diglucoside isolated from *Rhamnus virgata* has been shown to be physcion-8-O- $\beta$ -gentiobioside on the basis of spectral and other evidence.

#### INTRODUCTION

The stems of *Rhamnus virgata* L. afforded a new compound, the colour reactions and solubility properties of which indicated it to be a quinone glycoside. Its IR spectrum indicated the presence of hydroxyl and chelated and non-chelated carbonyls. On hydrolysis with Kiliani

reagent [1], it gave an aglycone which was identified as physcion from spectral properties and direct comparison with authentic physcion, and glucose as the only identifiable sugar. In the  $^1\text{H}$  NMR spectrum of the peracetate, there were signals for a phenolic acetoxy and an aromatic methyl ( $\delta$  2.45), six alcoholic acetoxy ( $\delta$  2.00) and an alcoholic acetoxy (1.80) indicating the presence of a disaccharide moiety attached to the hydroxyl group at either C-1 or C-8 of the aglycone. The aromatic region had two *meta* coupled doublets ( $\delta$  7.50 and 6.88,  $J = 2.5$  Hz each) arising from the resorcinol ring of the aglycone and two broad singlets ( $\delta$  7.92 and 7.18) assignable to two

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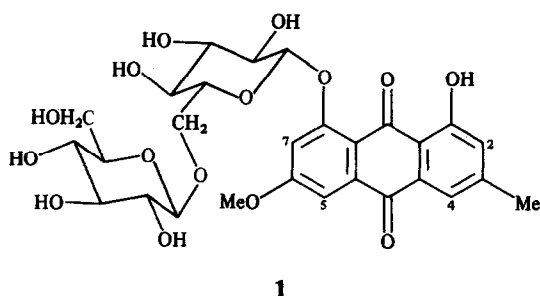
Table 1.

Compound	$\delta$				Steglich acylation shift ( $\Delta$ ) $\ddagger$			
	H-2 (s, br)	H-4 (s, br)	H-5 (d)*	H-7 (d)*	H-2	H-4	H-5	H-7
Emodin pertrimethylsilyl ether [2]	6.80	7.53	7.18	6.46	—	—	—	—
Emodin-1- <i>O</i> - $\beta$ -glucoside peracetate [2]	7.35	7.88	7.97	7.29	-0.45	-0.35	-0.79	-0.83
Emodin-8- <i>O</i> - $\beta$ -glucoside peracetate [2]	7.23	7.97	7.76	7.31	-0.43	-0.44	-0.58	-0.85
Emodin-8- <i>O</i> - $\beta$ -gentiobioside peracetate [3]	7.19 $\ddagger$	7.97 $\ddagger$	7.78	7.29	-0.39	-0.44	-0.60	-0.83
Physcion pertrimethylsilyl ether [2]	6.84	7.53	7.21	6.50	—	—	—	—
Physcion-8- <i>O</i> - $\beta$ -glucoside peracetate [2]	7.15	7.90	7.42	6.94	-0.31	-0.37	-0.21	-0.44
Physcion-8- <i>O</i> - $\beta$ -gentiobioside peracetate (1)	7.18	7.92	7.50	6.88	-0.34	-0.39	-0.29	-0.38

\* $J = 2.5$  Hz.

$\ddagger d$  (br).

$\ddagger \Delta = \delta$  values of the aromatic proton in permethylsilylaglycone minus that in peracetyl glycoside.



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protons of the other ring. On the basis of Steglich acylation shifts [2] and the observation that in emodin 1-*O*-glucoside peracetate, the doublet signal H-5 is more downfield than the singlet signal H-4 whereas the reverse is seen for the corresponding signals of the isomeric 8-*O*-glucoside peracetate (Table 1), it was concluded that the new compound was a physcion-8-*O*-glycoside. Enzymatic hydrolysis and permethylation studies suggested the compound was physcion-8-*O*- $\beta$ -gentiobioside (1). This is the first report of its isolation.

#### EXPERIMENTAL

Stems of *R. virgata* (3 kg), obtained from Solan, Himachal Pradesh, India were chopped into small pieces and extracted with hot EtOH. After removal of the solvent, the extract was subjected to CC over silica gel when the new compound was obtained with MeOH-EtOAc (1:9).

Physcion-8-*O*- $\beta$ -gentiobioside (1) (100 mg) was obtained as orange yellow crystals (EtOH) mp 358–360°. Red colour with Mg(OAc)<sub>2</sub> and also with NaOH. Sparingly soluble in EtOH (Found: C, 55.5; H, 5.7. C<sub>28</sub>H<sub>32</sub>O<sub>15</sub> requires: C, 55.3; H, 5.3%) UV  $\lambda_{\text{max}}^{\text{EtOH}}$  nm: 220, 256, 350, 380, 414; IR  $\nu_{\text{max}}^{\text{nujol}}$  cm<sup>-1</sup>: 3410, 2900,

1705, 1665, 1640, 1595, 1455, 1378, 1315, 1260, 1240, 1180, 1160, 1085, 1068, 1030, 990, 895.

Physcion-8-*O*- $\beta$ -gentiobioside peracetate was prepared by treatment of 1 with C<sub>5</sub>H<sub>5</sub>N-Ac<sub>2</sub>O. Crystals (EtOAc-petrol) mp 198–200°. (Found: C, 55.4; H, 4.9. C<sub>44</sub>H<sub>48</sub>O<sub>23</sub>, requires: C, 55.9; H, 5.1%) UV  $\lambda_{\text{max}}^{\text{EtOH}}$  nm: 257, 332; IR  $\nu_{\text{max}}^{\text{KBr}}$  cm<sup>-1</sup>: 1745; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.92 (s (br), 1H, H-4), 7.50 (d, 1H, H-5), 7.18 (s (br), 1H, H-2), 6.88 (d, 1H, H-7), 5.50–3.70 (m, 14H, sugar protons), 3.90 (s, 3H, aromatic methoxyl), 2.45 (d, 6H, a phenolic acetoxyl and an aromatic methyl), 2.00 (s, 18H, six sugar acetoxyls), 1.80 (s, 3H, sugar acetoxyl).

Hydrolysis of 1. Compound 1 (30 mg) and 0.5 ml of Kiliani mixture were heated on a boiling water bath for 6 hr. The aglycone, which separated was collected mp and mmp with physcion 208–210°. The aq. mother liquor was concd and then examined for sugar by descending PC (*n*-BuOH-C<sub>5</sub>H<sub>5</sub>N-H<sub>2</sub>O, 6:4:3). Glucose was identifiable as the only sugar.

Permethylation of 1. Compound 1 was permethylated by Hakomori's procedure, and the permethylated product hydrolysed with Kiliani mixture. The hydrolysate was concd and shown to contain a mixture of 2,3,4,6-*O*-methylglucose ( $R_G$  1) and 2,3,4-tri-*O*-methylglucose ( $R_G$  0.85) by descending PC (*n*-BuOH-EtOH-H<sub>2</sub>O, 5:1:4).

Enzymatic hydrolysis. Compound 1 and a soln of emulsion were incubated for 10 days at 37°. The hydrolysate on direct comparison showed the presence of physcion and glucose.

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