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PHENOLIC GLUCOSIDES IN *VIBURNUM HENRYI**

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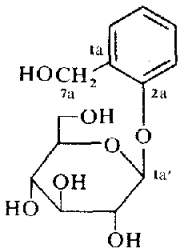
Key Word Index—*Viburnum henryi*; Caprifoliaceae; salicin; henryoside; benzoylhenryoside; 2,6-dihydroxybenzoic acid.

INTRODUCTION

A number of non-flavonoid glycosides have been identified in species of *Viburnum* (Caprifoliaceae). Salicin (**1**) was reported as a constituent of *V. prunifolium* [1], a finding not confirmed by later work, however [2].

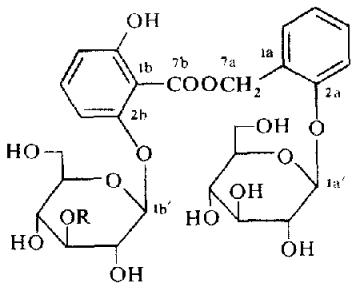


Salicin **1**

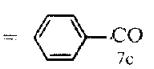
Furcatin was found as a constituent of *V. furcatum* [3]. During our current studies of glycosides in *Viburnum*, we reported the occurrence of dihydrochalcone glycosides in *V. davidii* and *V. lanthanoides* [4], and of iridoid ester allosides in *V. opulus* [5].

RESULTS AND DISCUSSION

An aqueous extract of *V. henryi* Hemsl. has provided salicin together with two novel *bis*-glucosides, henryoside, and benzoylhenryoside, to which we have assigned the structures **2** and **3**, respectively.

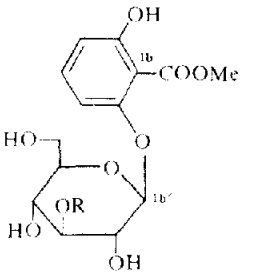


2 R = H



3 R =

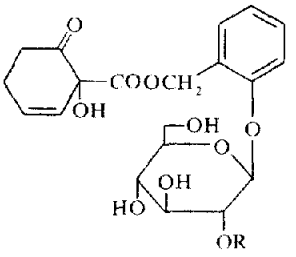
Methanolysis of **3** yielded methyl benzoate, salicin and the known [13] glucoside **4**. Milder conditions resulted in the formation of henryoside (**2**) as an additional product. This suggested the presence in **2** of an ester-linked salicin moiety, and furthermore, that **3** was a



4 R = H
5 R = Bz

benzoate of **2**. Hydrogenolysis (Pd/C) of **3**, followed by treatment of the resulting mixture with CH_2N_2, gave *o*-cresyl-β-D-glucopyranoside, indistinguishable from a synthetic specimen, and **5**, a monobenzoate of **4**. This confirmed that in **2** and **3** the 'b-unit' (**4**) was esterified to C-7a in the salicin moiety, and that the benzoic ester group was attached to the 'b-unit' of **3**.

The ^{1}H NMR spectrum of **3** exhibited a signal at 5.60 ppm, assigned to the methylene group of a benzylic ester, showing a downfield shift (0.89 ppm) when compared with the benzylic group of salicin. In the spectrum of **5**, a doublet (J = 7.5 Hz) at 5.22 ppm was assigned to H-1b′, and a triplet (J = 8 Hz) at 5.47 ppm to a proton located on the carbon atom carrying the benzoyloxy group. No change occurred by irradiation of the H-1b′ signal at 5.22 ppm, leaving H-3b′ and H-4b′ as possibilities. ^{13}C NMR data are compiled in Table 1. In



Salicortin: R = H
Tremulacin: R = Bz

2 the signals from both glucosyl moieties had the expected values [4], while in **3**, one set was abnormal. Here the signals arising from C-1b′, C-5b′ and C-6b′ were seen at the usual frequencies, leaving three signals which

* Part 3 in the series "Glycosides in *Viburnum*". For Part 2 see ref. [5].

Table 1. ^{13}C NMR data (recorded at 22.63 and 67.88 MHz) for *Viburnum* phenolic glucosides

Compound (solv.)	Part	C_1	C_2	C_3	C_4	C_5	C_6	C_7	$C_{1'}$	$C_{2'}$	$C_{3'}$	$C_{4'}$	$C_{5'}$	$C_{6'}$
Salicyl alcohol (D_2O/d_6-Me_2CO	a	126.6	153.9	115.1	128.6	119.9	128.6	59.4						
Salicin (**1**) (D_2O)	a	—	155.5	116.3	130.5	124.2	130.5	60.1	101.5	73.9	76.6	70.3	76.9	61.5
2,6-di-OH-benzoic acid (D_2O)*	b	101.1	161.6	108.4	136.7	108.4	161.6							
Henryoside (**2**)	a	125.5	155.8	116.5	131.5	124.1	131.5	64.0	101.6	73.8	76.5	70.3	76.9	61.5
(D_2O)	b	111.1	156.0	108.0	134.2	111.9	156.8	169.4	100.9	73.7	76.4	70.2	76.9	61.5
Benzoylhenryoside (**3**)	a	125.5	155.9	115.9	131.2	123.0	131.2	63.0	101.8	73.9	76.9	70.2	76.9	61.5
(D_2O)	b	109.7	156.9	107.1	133.8	111.2	158.9	169.1	101.2	72.4	78.2	68.4	76.9	61.5
	c	130.0	130.0	128.8	133.8	128.8	130.0	167.4						

* Data from ref. [6].

were assigned to C-2b', C-3b' and C-4b'. The shift differences from the normal values (1.8 ppm downfield for C-3b', 1.3 and 1.8 ppm upfield for C-2b' and C-4b' respectively), prove that the benzoyloxy group is attached to C-3b'.

The tannin contents in a number of *Viburnum* species have recently been studied by Bate-Smith [7], who also found indications for the presence of dihydrochalcone in *V. henryi*. If dihydrochalcones like those in *V. davidii* [4] were present they would probably have been detected by us, whereas, for example, vicinal polyphenols would be lost in the isolation process.

During our screening of some fifty species of *Viburnum*, salicin was isolated from *V. lantana* L. and *V. schensianum* Maxim. together with iridoid glycosides, occurring quite generally within the genus. We were unable to confirm the reported occurrence of salicin in *V. prunifolium* [1], in which we found only arbutin. Salicin is known from many species of Salicaceae, where it often occurs modified by esterification with aromatic acids [8]. The pair of salicin derivatives, salicortin and tremulacin, have some remarkable features in common with the pair **2**/**3**, although in this case only one glucosyl moiety is present and benzoic acid is esterified at C-2'.

Methyl-2,6-dihydroxybenzoate has been detected in cassie oil (*Acacia farnesiana*) [9], and the monomethyl ether of 2,6-dihydroxybenzoic acid in the monocotyledons *Gloriosa superba* [10] and *Colchicum autumnale* [11] (Liliaceae).

EXPERIMENTAL

^1H NMR spectra were recorded at 90 or 270 MHz, ^{13}C NMR spectra at 22.6 or 67.9 MHz. Microanalyses were performed at NOVO Microanalytical Laboratory, Bagsværd, Denmark. *Viburnum henryi* (IOK 24–75), *V. schensianum* (IOK 30–76) and *V. lantana* (IOK 96–72) were collected in June or July at the Botanical Garden of The University of Copenhagen. Vouchers have been deposited at the Botanical Museum, Copenhagen (C).

Isolation of salicin (**1**), **2** *and* **3**. Foliage of *V. henryi* (405 g) collected in July 1975 and stored at ÷23° was homogenized in EtOH and worked up as previously described [12] to give an Me_2CO-eluate (9.4 g). Chromatography of an aliquot (4.9 g) on Si gel with $CHCl_3$–MeOH (8:1, 6:1, 4:1) as eluents yielded 3 fractions. The first consisted of **3** (1.7 g, 0.8%), crystallized from EtOH to give the pure compound, mp 139.0–140.0; $[\alpha]_D^{22}$ −17° (*c*, 1·0; MeOH); ^1H NMR (Me_2CO-d_6/TMS): δ 5.05 (*d*, J = 7.0 Hz, H-1b'), 5.33 (*t*, J = 8.0 Hz, H-3b'), 5.60 (2H, *s*, H-7a), 6.78 (*d*, J = 8.0 Hz, H-3b or H-5b), 6.96 (*d*, J = 9.0 Hz, H-3b or H-5b), 8.26 (H-2c and H-6c). (Found: C, 55.78; H, 5.42. $C_{33}H_{36}O_{16}$, H_2O requires: C, 55.95; H, 5.43%). The next fraction was salicin (**1**, 0.31 g, 0.6%), identical (^1H NMR, mp and mmp) with an authentic sample. The last fraction consisted of **2** (0.55 g, 0.2%), crystallized from EtOH, mp 128–130°, $[\alpha]_D^{26}$ − 47° (*c* 0.4; MeOH); ^1H NMR (D_2O/DSS): δ 5.05 (H-1a' and H-1b'), 5.50 (2H, *s*, H-7a), 6.69 (*d*, J = 8.0 Hz, H-3b or H-5b), 6.74 (*d*, J = 8.5 Hz, H-3b or H-5b). (Found: C, 51.38; H, 5.89. $C_{26}H_{30}O_{15}$, $1\frac{1}{2}$ H_2O requires: C, 51.30; H, 5.48%).

Methanolysis of **3**. A soln of **3** (180 mg) in NaOMe/MeOH (2%, 6 ml) was heated under reflux for 40 min, and after neutralization with aq. HOAc, extracted with Et_2O. Separation of the aq. fraction by prep. TLC with $CHCl_3$–MeOH (3:1) gave salicin (55 mg) and **4** (51 mg), mp 171–171.5°; $[\alpha]_D^{26}$ − 40° (*c* 0.7; MeOH) (rep. mp 173–176°, $[\alpha]_D$ − 50° [13]); ^1H NMR (D_2O/DSS): δ 3.96 (*s*, COOMe), 5.17 (*d*, J = 7.0 Hz, H-1b'), 6.78 (*d*, J = 8.5 Hz, H-3b or H-5b), 6.87 (*d*, J = 8.5 Hz, H-3b or H-5b), 7.50 (*t*, J = 8.5 Hz, H-4b). The Et_2O fraction, after concn and saponification with 2N NaOH, gave benzoic acid (6 mg), mp 116–117°.

Partial methanolysis of **3**. A soln of **3** (300 mg) in NaOMe/MeOH (1%, 10 ml) was left at room temp. for 15 min and worked up as above by prep. TLC to yield **4** (44 mg), salicin (40 mg) and **2** (73 mg).

Hydrogenolysis of **3**. A methanolic soln of **3** (180 mg) containing Pd/C (5%, 40 mg) was treated with H_2 at atm. pres. After filtration, CH_2N_2 in Et_2O was added in excess. TLC ($CHCl_3$–MeOH (4:1)) of the crude product yielded as the faster running band **5** (80 mg), hygroscopic crystals from MeOH, mp 171.5–173.5°; $[\alpha]_D^{20}$ − 74° (*c*, 0.7; MeOH); ^1H NMR (Me_2CO-d_6/TMS): δ 3.95 (*s*, COOMe), 5.22 (*d*, J = 7.5 Hz, H-1b'), 5.47 (*t*, J = 8.0 Hz, H-3b'), 6.73 (*d*, J = 8.5 Hz, H-3b or H-5b), 6.93 (*d*, J = 8.5 Hz, H-3b or H-5b), 7.44 (*t*, J = 8.5 Hz, H-4b), 8.20 (H-2c and H-6c). (Found: C, 55.01; H, 5.29. $C_{21}H_{22}O_{10}$, $1\frac{1}{2}$ H_2O requires: C, 54.67; H, 5.47%). The slower moving band was *o*-cresyl β-D-glucopyranoside (46 mg), mp 160–161°; $[\alpha]_D^{20}$ − 88° (*c*, 0.4, MeOH), rep. mp 162–163° [14]); ^1H NMR (D_2O/DSS): δ 2.28 (*s*, CH_3), 5.10 (*dd*, J = 6.5 and 1.5 Hz, H-1'). The compound was identical with an authentic sample, prepared from salicin pentaacetate by catalytic hydrogenation (Pd/C) followed by deacetylation (NH_3/MeOH).

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ANTHRAQUINONE RHAMNOSIDES FROM *CASSIA JAVANICA* ROOT BARK

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Key Word Index—*Cassia javanica*; Leguminosae; root bark; anthraquinone pigments; emodin 8-rhamnoside; 5-hydroxyemodin 8-rhamnoside.

Two anthraquinones and their glycosides have been isolated from the root bark of *Cassia javanica*. The aglycones were identified as emodin and 5-hydroxyemodin by mp, mmp, colour reactions and IR, UV, NMR and mass spectral data. These compounds have been reported from many plant sources [1, 2].

The other two pigments (**1**, **2**) gave characteristic colour reactions of hydroxyanthraquinones and on acid hydrolysis, gave emodin and 5-hydroxyemodin respectively together with rhamnose. The attachment of the sugar moiety at position-8 in both cases was established by colour reactions [3] and UV spectra [4]. Both glycosides consumed 2 mol of periodate per mol liberating one mol of formic acid showing that the sugar is in the pyranose form. Hydrolysis of the glycosides by diastase indicated the α-nature of sugar linkage in both cases. On the basis of these results, the glycosides are 1,6-dihydroxy-3-methylanthraquinone 8-*O*-α-L-rhamnopyranoside (**1**) and 1,5,6-trihydroxy-3-methylanthraquinone 8-*O*-α-L-rhamnopyranoside (**2**). These glycosides have not been reported earlier from any plant source.

EXPERIMENTAL

Acetone-extracted root bark of *Cassia javanica* was extracted with hot EtOH. The conc extract was diluted with H_2O giving an aq. soln (fraction I) and coloured residue (fraction II).

Fraction (I) on extraction with EtOAc and chromatography over Si gel with EtOAc gave the glycoside **1**, mp 200(d.). Further elution with EtOAc–MeOH (1:1) gave glycoside (**2**), mp 310°.

Compound (**1**). IR ν_{max}^{KBr} cm^{-1}: 3380, 2900, 1670, 1620, 1595, 1470, 1320, 1100, 1065, 1035, 830 and 770. λ_{max}^{EtOH} nm: 220, 280 and 415. *Acetate* (Py/Ac_2O), colourless plates, mp 185°. ^1H NMR (60 Hz, $CDCl_3$) δ: 7.28 (*br*, 1-H, C-2), 7.95 (*br*, 1-H, C-4), 7.75 (*d*, 1-H, C-5), 7.38 (*d*, 1-H, C-7), 2.45 (C-CH_3), 2.30 (*s*, —$COCH_3$), 5.10 (H-1, rhamnosyl) and 3.10–5.10 (*m*, 5 sugar protons), 0.95 (CH_3 of rhamnosyl).

Compound (**2**). IR ν_{max}^{KBr} cm^{-1}: 3420, 3300, 2920, 1640, 1550, 1475, 1450, 1375, 1360, 1300, 1230, 1220, 1100, 1030, 990, 890, 870, 835 and 770. λ_{max}^{EtOH} nm: 235, 255, 300 and 470. *Acetate* (**2**) colourless crystals, mp 130°. ^1H NMR (60 Hz, $CDCl_3$) :δ 7.25 (*br*, 1-H, C-2), 7.75 (*br*, 1-H, C-4), 7.00 (*s*, 1-H, C-7), 2.47 (C—CH_3), 2.35 (—$COCH_3$), 5.15 (H-1 rhamnosyl), 3.00–5.15 (*m*, 5 protons of rhamnose) and 0.90 (CH_3 of rhamnose).

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