Cyclopentenoid Cyanohydrin Glycosides with Unusual Sugar Residues*

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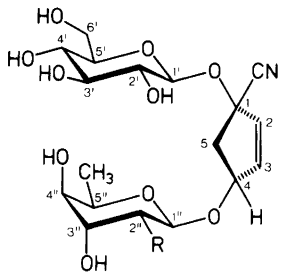
The cyclopentenoid cyanohydrin glycosides passicapsin and passibiflorin have been identified as (1*S*, 4*R*)-1-(β-D-glucopyranosyloxy)-4-(2,6-dideoxy-β-D-*xylo*-hexo pyranosyloxy)-2-cyclopentene-1-carbonitrile and (1*S*, 4*R*)-1-(β-D-glucopyranosyloxy)-4-(6-deoxy-β-D-gulopyranosyloxy)-2-cyclopentene-1-carbonitrile, respectively, using one- and two-dimensional NMR spectroscopy, selective acid-catalysed cleavage of the glycosidic linkages of the deoxy sugars, and optical rotation data.

Deoxyaldohexoses other than hexomethyloses (6-deoxyhexoses) are relatively rare in nature, being encountered especially in antibiotics, bacterial polysaccharides, and cardiac glycosides.[2–4] In this paper we describe the structure of a cyclopentenoid cyanohydrin glycoside[5–7] from *Passiflora capsularis* L. (Passifloraceae) bearing a 2,6-dideoxy-β-D-*xylo*-hexopyranosyl (boivinosyl) residue, otherwise found only as a constituent of cardenolides.[8] A related species, *P. biflora* Lam., contains the corresponding 6-deoxy-β-D-gulopyranoside (antiaroside), i.e., a hydroxylated derivative of the former glycoside.

Results and discussion

Passicapsin,[9] the principal cyanogenic constituent of *P. capsularis*, has been tentatively assigned[9,10] the structure 1-(β-D-glucopyranosyloxy)-4-(2,6-dideoxy-*xylo*-hexopyranosyloxy)-2-cyclopentene-1-carbonitrile, the stereochemistry of the cyclopentene ring and the absolute configuration of the deoxy sugar moiety being left unspecified. The site of attachment of the latter seemed to need confirmation as well. Passibiflorin[11] was isolated from *P. biflora*; no satisfactory proposal as to the nature and arrangement of sugar residues has been made for this compound.[1]



1 R = H (passicapsin)
2 R = OH (passibiflorin)

We have reisolated the glycosides from these *Passiflora* species and purified them by reverse-phase HPLC. According to spectral data, each of the glycosides was present as a single isomer, in contrast with simple cyclopentenoid cyanohydrin glycosides, which usually occur as pairs derived from enantiomeric aglycones.[5–7] One such a pair, epivolkenin and taraktophyllin,[7] was present in *P. capsularis* as a minor component.

The ^{1}H NMR spectrum of passicapsin in CD_3OD contains three sets of resonances; the spin connectivity patterns are readily distinguishable in a COSY spectrum. The spin systems of the β-D-glucopyranosyloxy unit and of the cyclopentene ring (Table 1) are closely similar to those found for other representatives of the group.[6,7] The chemical shifts and couplings of the second sugar moiety correspond to boivinose;[9] in particular, the observed couplings agree well with those calculated using the Altona–Haasnoot relationship.[12]

In the absence of data on glycosidation-induced shifts for the boivinosyl group and on the stereochemistry of the linked sites,[13,14] it is difficult to infer the point of attachment of the boivinosyl residue from the ^{1}H data alone. Thus although the resonance of the allylic hydrogen of passicapsin (δ 4.87, Table 1) is displaced relative to unsubstituted counterparts,[6,7] the attachment of the boivinopyranosyl group to the glucosyl residue cannot be rigorously excluded.

The ^{13}C NMR spectra of the four isomeric 1-(β-D-glucopyranosyloxy)-4-hydroxy-2-cyclopentene-1-carbonitriles are quite similar and contain two closely spaced signals at about δ 75.0, corresponding to C4 and C2′.[6,7,15] In passicapsin one of these signals is shifted to δ 81.7 (Table 2), which must be caused by attachment of the second sugar

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Table 1. ^{1}H NMR spectra of passicapsin (**1**) and passibiflorin (**2**) and their derivatives.[a]

Compound	H2 and H3	H4	H5	H1′	H2′	H3′	H4′	H5′
Passicapsin	6.12 (dd,1.3,5.5) 6.36 (dd,2.1,5.5)	4.87 (m)	2.34 (dd,4.7,14.8) 3.04 (dd,7.1,14.8)	4.59 (d,7.7)	[c]	[c]	[c]	[c]
Passicapsin[b]	6.25 (dd,1.1,5.5) 6.46 (dd,2.2,5.5)	5.09 (m)	2.39 (dd,3.5,15.2) 3.04 (dd,7.0,15.2)	4.80 (d,7.7)	3.32 (dd, 7.7,9.2)	[e]	[e]	[e]
Passibiflorin	6.16 (dd,1.2,5.5) 6.38 (dd,2.2,5.5)	4.89 (m)	2.50 (dd,4.2,15.0) 3.01 (dd,7.1,15.0)	4.62 (d,7.7)	3.22 (dd, 7.7,8.8)	[g]	[g]	[g]
Passicapsin hexaacetate[i]	5.94 (dd,1.3,5.5) 6.41 (dd,2.0,5.5)	4.86[d] (m)	2.27 (dd,5.0,14.5) 2.99 (dd,7.0,14.5)	4.89 (d,7.9)	5.01 (dd, 7.9,9.3)	5.22 (t,9.3)	5.07 (t,9.3)	3.77(dq, 2.9,4.8,9.3)
Passibiflorin heptaacetate[j]	5.96 (dd,1.4,5.5) 6.34 (dd,2.0,5.5)	4.85[d] (m)	2.24 (dd,5.0,14.6) 3.05 (dd,7.1,14.6)	4.88 (d,8.0)	4.98[d]	5.26 (t,9.3)	5.05[d]	3.78(dq, 2.6,5.1,ca.10)
Hexa-*O*-trimethylsilylpassicapsin	5.98 (dd,1.6,5.6) 6.36 (dd,1.9,5.6)	4.89 (m)	2.26 (dd,5.9,14.2) 3.06 (dd,6.9,14.2)	4.55 (d,7.3)	3.28[d]	3.40[d]	3.40[d]	3.20[d] (m)
Hepta-*O*-trimethylsilylpassibiflorin	6.01 (dd,1.8,5.6) 6.36 (dd,1.6,5.6)	4.83 (m)	2.21 (dd,6.3,14.1) 3.11 (dd,6.9,14.1)	4.47 (d,7.3)	3.30[d]	[h]	[h]	3.20 (m)

Compound	H6′	H1″	H2″	H3″	H4″	H5″	CH_3
Passicapsin	3.67 (dd,5.2,12.0) 3.86 (dd,2.0,12.0)	4.89 (dd, 2.5,9.5)	1.70 (dq,2.5,13.5) 1.83 (ddd,3.2,9.5,13.5)	3.96 (br q,3.5)	3.20[d]	4.00 (qd,1.5,6.6)	1.25 (d,6.6)
Passicapsin[b]	3.75 (dd,5.3,12.5) 3.92 (dd,2.1,12.5)	4.97 (dd, 4.0,8.3)	1.79[f]	4.10 (br q,3.5)	3.40 (dd, 1.3,3.3)	4.07 (qd,1.3,6.6)	1.25 (d,6.6)
Passibiflorin	3.67 (dd,5.2,12.0) 3.86 (dd,2.0,12.0)	4.70 (d,8.2)	3.56 (dd,3.5,8.2)	3.97 (t,3.5)	3.48 (dd, 1.3,3.7)	4.05 (dq,1.3,6.6)	1.24 (d,6.6)
Passicapsin hexaacetate[i]	4.19 (dd,2.9,12.2) 4.23 (dd,4.8,12.2)	4.80 (dd, 4.0,8.2)	1.88[f]	5.04[d]	4.68 (dd, 1.4,3.1)	4.02 (dq,1.5,6.4)	1.21 (d,6.5)
Passibiflorin heptaacetate[j]	4.18 (dd,2.6,12.3) 4.25 (dd,5.1,12.3)	4.83 (d,8.4)	4.95[d]	5.34 (t,3.6)	4.85[d]	4.12[d] (m)	1.21 (d,6.5)
Hexa-*O*-trimethylsilylpassicapsin	3.64[d] 3.75[d]	4.80 (dd, 2.2,9.7)	1.54 (dm,13.1) 1.88 (ddd,2.7,10.1,12.8)	3.85 (q,3.0)	3.14 (d,3.4)	3.94 (dq)	1.18 (d,6.5)
Hepta-*O*-trimethylsilylpassibiflorin	[h]	4.63 (d,7.8)	3.70[d]	[h]	[h]	4.02 (dq)	1.16 (d,6.5)

[a]250 MHz spectra (δ values relative to internal tetramethylsilane) in CD_3OD (free glycosides) or $CDCl_3$ (derivatives); multiplicities and coupling constants (apparent splittings of lines, accurate to 0.2 Hz) are given in parentheses (d doublet, t triplet, q quartet, m multiplet, br broad). [b]In deuterium oxide with methanol (δ 3.35) as an internal standard. [c]Complex pattern at δ 3.18–3.37. [d]Approximate value from COSY spectrum. [e]Complex pattern at δ 3.33–3.51. [f]Center of multiplet. [g]Complex pattern at δ 3.28–3.43. [h]Complex pattern at δ 3.25–3.85. [i]Acetyl groups at δ 2.00, 2.03, 2.04, 2.09, 2.10 and 2.14. [j]Acetyl groups at δ 2.00, 2.03 (two), 2.04, 2.09, 2.14 and 2.18.

group.[16] We have assigned the δ 81.7 resonance to C4 from a ^{1}H–^{13}C shift-correlated spectrum, which proves that the originally proposed[9] gross structure of passicapsin is correct. The ^{13}C resonances of the boivinosyl moiety of passicapsin are closely similar to those reported for isobutyl β-DL-boivinopyranoside (Table 2).[17] Since the glycosidation-induced shift[13,14] of H4 can hardly be negative (upfield), passicapsin (δ 4.87 of H4) may be immediately considered to be a *cis*-1,4-dioxygenated[7,18] cyclopentene, the chemical shift of the corresponding alcohols[7] being δ 4.81 (*trans* alcohols[6] have δ 4.98).

The ^{1}H and ^{13}C NMR spectra of passibiflorin (Tables 1 and 2) show correspondingly that it is a *cis*-1,4-dioxygenated cyclopentene similar to passicapsin, but having a different sugar residue attached to the allylic hydroxy group. Thus a ^{1}H–^{13}C shift-correlated spectrum connects the resonance of C4 at δ 82.2 to that of H4 at δ 4.89 (Fig. 1). The nature of the second sugar residue is apparent from the ^{1}H NMR data (Table 1), which show that passibiflorin differs from passicapsin by the presence of an equatorial hydroxy group attached to C2″ ($^3J_{1,2}$ 8.2, $^3J_{2,3}$ 3.5 Hz; the respective values for β-D-gulopyranose in water are 8.3–8.4 and 3.2–3.6 Hz[15,19]). The observed ^{13}C chemical shifts (Table 2) match those of methyl 6-deoxy-β-L-gulopyranoside.[20] Passibiflorin hence contains a 6-deoxygulopyranosyl (antiarosyl) group.

The absolute stereochemistry of the cyclopentene ring of passibiflorin and passicapsin and of the deoxy sugar moieties were elucidated by taking advantage of the fact that rates of acid-catalysed hydrolysis of glycosidic linkages of deoxy sugars are appreciably higher than those of the hydroxylated analogues.[21–23] Thus the boivinosyl residue of

Table 2. ^{13}C NMR spectra of passicapsin (**1**) and passibiflorin (**2**) and their derivatives.[a]

Compound	C1	C2, C3	C4	C5	CN	C1′	C1″	Remaining resonances
Passicapsin	82.1	132.7, 142.4	81.7	46.9	120.4	101.0	99.7	17.2, 34.9, 62.9, 70.6 (two), 71.3, 71.7, 74.9, 78.3, 78.4
Passicapsin[b]	81.5	132.1, 141.5	80.9	44.6	120.3	99.9	98.4	16.4, 33.7, 61.4, 69.2, 69.9, 70.2, 70.5, 73.6, 76.3, 77.0
Passibiflorin	82.2	132.9, 142.2	82.2	46.3	120.5	102.0	100.8	16.6, 62.8, 69.6, 70.5, 71.7, 73.6, 73.7, 74.9, 78.2, 78.3
Passicapsin hexaacetate	80.3[c]	130.3, 141.4	80.3	45.2	117.9	97.9[d]	97.5[d]	16.4, 31.7, 61.7, 67.9, 68.2, 68.6, 68.7, 70.9, 72.2, 72.7[e]
Passibiflorin heptaacetate	80.1	130.7, 140.7	80.5	45.3	117.9	97.9[d]	97.5[d]	15.9, 61.7, 68.1, 68.2 (two), 68.9, 70.3, 71.0, 72.3, 72.7[e]
Hexa-*O*-trimethylsilylpassicapsin	79.8[c]	130.7, 141.1	79.8	46.5	118.6	99.7[d]	97.8[d]	17.0, 34.3, 62.0, 69.0, 70.5, 71.4, 71.5, 75.0, 77.8, 78.4[f]
Hepta-*O*-trimethylsilylpassibiflorin	79.7	130.5, 141.9	80.4	46.1	118.6	99.8[d]	99.3[d]	16.4, 62.0, 68.7, 69.4, 71.5, 74.6, 74.9, 75.1, 77.8, 78.3[f]

[a]62.9 MHz spectra (δ values relative to internal tetramethylsilane) in CD_3OD (free glycosides) or $CDCl_3$ (derivatives). [b]In deuterium oxide with dioxane (δ 67.4) as an internal standard. [c]Not observed as a separate resonance, assumed to coincide with C4 resonance. [d]Assignments may be interchanged. [e]Acetate resonances at δ 20.5–21.0 and 169.0–170.5. [f]Trimethylsilyl groups at δ −0.3–1.7.

passicapsin was smoothly split off within 15 min at 95–100 °C and pH 2 (0.01 M HCl), to leave epivolkenin, which has the (1*S*, 4*R*) configuration.[7] Epivolkenin was isolated by HPLC and identified by ^1H NMR spectroscopy. Passibiflorin was stable under these conditions, but the glycosidic bond of the antiarosyl group was selectively cleaved in 0.1 M HCl. The relative rates of partial hydrolysis of passicapsin and passibiflorin are as expected from the location of the deoxygenated sites.[21–23] The hydrolysis product obtained from passibiflorin was also epivolkenin, isolated and identified as above. The sugars liberated during these reactions, boivinose and antiarose, were purified and identified by ^1H and ^{13}C NMR spectroscopy, and were shown to belong to the D series by the sign of their optical rotations.[20,24–27]

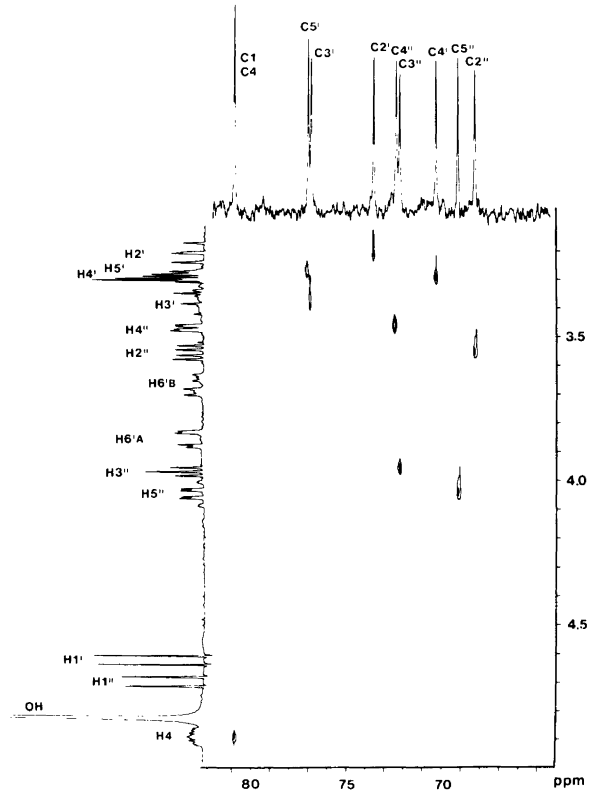

Fig. 1. Fragment of a ^1H–^{13}C shift-correlated NMR spectrum of passibiflorin showing proton connectivities of the ^{13}C resonances in the 65–80 ppm region (250 MHz, CD_3OD), see Tables 1 and 2.

Passicapsin ($[M]_D$ +33°) and passibiflorin ($[M]_D$ −30°) are more levorotatory than epivolkenin ($[M]_D$ +127°). The levorotation of the additional sugar residues present indirectly confirms their β-D configuration.[17,20,28,29] The change in molecular rotation between passicapsin and passibiflorin corresponds well to that between D-boivinose[24,25] and D-antiarose[20,26,27] of about −70° (equilibrium rotations in water, presumably corresponding largely to the β-anomers). The increased levorotation on going from β-D-boivinose to β-D-antiarose or from passicapsin to passibiflorin is in good agreement with the expected levorotatory effect of the hydroxy group introduced at C2″; assuming that the overall conformation of the system remains unchanged, the skew interactions of this hydroxy group with the oxygen functions at C1″ and C3″ should change the molecular rotation by −90°.[30,31]

Experimental[1,6]

Isolation of passicapsin. Fresh leaves (51 g) of *P. capsularis* L. (Botanical Garden, University of Copenhagen) were extracted and fractionated initially in the general way described elsewhere.[1,7] The cyanogenic fractions from the silica gel column were purified by HPLC (1.6×25 cm column of Lichrosorb RP-18, 5 μm) using 4 ml min^{-1} of water–methanol (7:3), to give 68 mg of passicapsin

(k' 0.72; yield 0.13% of fresh weight) and about 5 mg (0.01 %) of a mixture of epivolkenin and taraktophyllin in a ratio of 5:1 (identified by 250 MHz ^{1}H NMR spectra[7] recorded before and after acetylation of the sample with pyridine–acetic anhydride). Passicapsin was authenticated by comparison of ^{1}H and ^{13}C NMR spectra in D_2O (Tables 1 and 2) with literature[9] data. The glycoside was recrystallized from ethyl acetate; m.p. 124–126 °C (corr.), literature[9] m.p. 116–119 °C; $[\alpha]_D^{24}$ +8° (*c* 0.56, methanol); IR (KBr) 3570–3160 (s), 2232 (w) cm^{-1}.

Isolation of passibiflorin. Fresh leaves and branches (203 g) of *P. biflora* Lam. (Botanical Garden, University of Copenhagen) were extracted and the extract was fractionated as above to give 270 mg (k' 0.71; yield 0.13% of fresh weight) of passibiflorin, authenticated by comparison of the ^{1}H NMR spectrum of its per-*O*-trimethylsilyl ether (Table 1) with literature[11] data. A crystalline sample was not obtained; $[\alpha]_D^{20}$ −7° (*c* 0.5, methanol); IR (KBr pellet obtained after evaporation of a methanolic solution of the glycoside with KBr and desiccation) 3585–3200 (s), 2245 (w) cm^{-1}.

Passicapsin hexaacetate. The glycoside (8 mg) was acetylated by overnight treatment with an excess of pyridine–acetic anhydride (1:1) at room temperature, and the product was recrystallized from ether–petroleum ether; m.p. 160–161 °C; $[\alpha]_D^{20}$ +19.5° (*c* 0.13, chloroform); IR (KBr) 1750 (s), 1635 (m) cm^{-1}.

Passibiflorin heptaacetate. Acetylation of the glycoside (30 mg) as described above gave a non-crystalline acetate; $[\alpha]_D^{20}$ +21° (*c* 1.6, chloroform).

Hydrolysis of passicapsin. The glycoside (40 mg) in 0.01 M HCl (40 ml) was heated at 95–100 °C for 15 min, and the solution was neutralized with Amberlite IR-45 (OH^-) and evaporated. The residue was chromatographed (1.6×25 cm column of Lichrosorb RP-18, 5 μm, 4 ml min^{-1} of 13 % aqueous methanol), to give 18 mg of epivolkenin (65 %) and 7.8 mg (55 %) of boivinose. Epivolkenin was identified by 250 MHz ^{1}H NMR spectra[7] recorded before and after acetylation. Boivinose: $[\alpha]_D^{20}$ +2.5° (*c* 0.26, water) or +15° (*c* 0.6, acetone), in agreement with literature [24,25,28] data for D-boivinose;* ^{1}H NMR (250 MHz, CD_3OD) δ 1.22 (d, *J* 6.6 Hz, CH_3), 1.80 (m, CH_2), 3.20 (d, *J* 3.2 Hz, H4), 3.96 (m, H3 and H5), 4.98 (dd, *J* 3.2 and 9.1 Hz, H1) (minor signals attributable to the α-anomer were present); ^{13}C NMR (62.9 MHz, CD_3OD) δ 17.0 (C6), 35.9 (C2), 70.3, 70.6 and 71.0 (C3, C4 and C5), 93.4 (C1), spectrum in D_2O as reported.[25,32]

Hydrolysis of passibiflorin. The glycoside remained unchanged (TLC) on attempted hydrolysis in 0.01 M HCl as described for passicapsin, but was smoothly cleaved in 0.1 M HCl (15 min, reflux); two portions of 17 mg and 18 mg of passibiflorin yielded a total of 10 mg (43 %) of epivolkenin (^{1}H NMR of the free glycoside and its acetate[7]) and 8.7 mg (66 %) of the deoxy sugar, isolated as described above.

Antiarose: $[\alpha]_D^{20}$ −34° (*c* 0.4, water), in agreement with literature[20,26,27] data for D-antiarose; ^{1}H NMR (250 MHz, CD_3OD) δ 1.21 (d, *J* 6.6 Hz, CH_3), 3.46 (dd, *J* 1.5 and 3.5 Hz; H4), 3.50 (dd, *J* 3.4 and 8.2 Hz, H2), 3.95 (t, *J* 3.5 Hz, H3), 4.02 (dq, *J* 1.5 and 6.6 Hz, H5), 4.77 (d, *J* 8.2, H1) (minor signals attributable to the α-anomer were present). In D_2O the corresponding figures were 4.81 (H1), 3.53 (H2), 4.03 (H3), 3.58 (H4), 4.06 (H5) and 1.18 (CH_3); ^{13}C NMR (62.9 MHz, CD_3OD) δ 16.4 (C6), 70.2, 70.9, 73.5 and 73.8 (C2–C5), 95.8 (C1), in D_2O δ 15.5, 69.3, 69.7, 71.7, 72.3 and 94.0.

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*D-Boivinose recrystallized from acetone is levorotatory in acetone[24] ($[\alpha]_D$ −13°) and exhibits mutarotation in water (−4° → +4°).[24,25] The material obtained here was not recrystallized and must thus correspond approximately to the anomeric equilibrium for the aqueous solution. We confirmed, with authentic[25] D-boivinose, that the rotation in acetone of material obtained by evaporation of an aqueous solution is the opposite of that of the crystalline material. Since the crystalline, levorotatory D-boivinose becomes dextrorotatory upon anomeric equilibration it can be concluded that it is the β form.[30,31]

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