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Structure of an anthocyanin–anthocyanin dimer molecule in anthocyanin-producing cells of a carrot suspension culture

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ABSTRACT

A novel anthocyanin, an anthocyanin–anthocyanin dimer, was isolated from the cells of an anthocyaninproducing carrot cell-line culture, and its structure was elucidated using spectroscopic methods. It consists of two molecules of the anthocyanin, cyanidin 3-[xylosyl-(sinapoyl-glucosyl)-galactoside], with a CH–CH₃ linkage at the 8–8 position. This is the first report of the identification and isolation of an anthocyanin–anthocyanin dimer with a CH–CH₃ linkage from intact plant cells.

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Anthocyanins are one of many subclasses of flavonoids and are responsible for the color of petals, pericarps and of other organs of many plant species,¹ and that of many types of food and beverage.^{2,3} Anthocyanins are the glycosides of anthocyanidins (aglycons), which contain A-, B-, and C-ring moieties.¹ Novel anthocyanins with unique aglycon moieties have recently been identified. A C4-substituted anthocyanin containing an additional pyran ring between C4 and the hydroxyl group at C5 has been isolated from red wine,^{3,4} black carrot juice,⁵ and petals of *Rosa* hybrida cv. M'me Violet.⁶ An ethyl-linked anthocyanin dimer containing anthocyanin and flavonol or two molecules of anthocyanin linked in a CH-CH3 linkage have been isolated from red wine,^{3,7} rosé cider,⁸ and model alcoholic solutions.^{9,10} C4-substituted anthocyanins have been isolated both in vitro and in vivo, but the ethyl-linked anthocyanin dimer has only been identified in vitro.

The carrot (*Daucus carota* L.) produces anthocyanins in intact plants and in cultured cells. Known carrot anthocyanins include

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cyanidin 3-galactoside (Cya 3-Gal), 3-xylosyl-Gal (3-Xyl-Gal), 3-triglycoside (3-Xyl-glucosyl-Gal) (3-Xyl-Glc-Gal), and feruloyl, 4-coumaroyl, sinapoyl, 4-hydroxybenzoyl derivatives of Cya triglycoside.¹¹⁻¹³ The minor component, Cya 3-Glc, was recently isolated,¹⁴ and anthocyanins possessing a peonidin or pelargonidin type of aglycon have been detected using high-performance liquid chromatography/mass spectrometry (HPLC/MS) analysis.¹⁵

Our laboratory has established a variant carrot cell line (*D. carota* L. cv. Kurodagosun).¹⁶ HPLC/MS analysis indicated that the



Figure 1. Structure of anthocyanin 1. The arrows show HMBC correlations.

Abbreviations: Cya, cyanidin; DQF-COSY, double quantum filter correlation spectroscopy; Gal, galactose (galactoside); Glc, glucose (glucoside, glucosyl); HMBC, heteronuclear multiple bond connectivity; HMQC, heteronuclear multiple quantum coherence; HPLC, high-performance liquid chromatography; HR, high-resolution; MS, mass spectrometry; NMR, nuclear magnetic resonance; TFA, trifluoroacetic acid; TOCSY, totally correlated spectroscopy; TOF, time-of-flight; Xyl, xylose (xyosyl).

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Figure 2. Structure of anthocyanin **2.** The arrows show HMBC correlations. The black squares and circles indicate carbons with signals that exhibited isotopic and non-isotopic shifts, respectively, in the H–D exchange experiment.

major anthocyanin of this cell line is Cya 3-Xyl-sinapoyl-Glc-Gal (1, Fig. 1) and that a novel anthocyanin, the anthocyanin–anthocyanin dimer (2, Fig. 2), was present as a minor component (Fig. 3). In this report, we describe the isolation and elucidation of the structures of anthocyanins 1 and 2.

The anthocyanin-producing cells of the variant carrot cell line were grown in modified Lin and Staba liquid medium containing 5×10^{-7} M 2,4-dichlorophenoxyacetic acid and cultured for 14 days as previously reported.¹⁶ The cells were harvested using a Buchner funnel, frozen in liquid N₂, and lyophilized. Anthocyanins were extracted over a period of 12 h from 3 g (dry weight) of cells into 1 L of 70% aqueous ethanol, after which the reddish-purple extracts were filtered and the residual solvent was removed by evaporation. The extracts were dissolved in 20% methanol containing 0.1% trifluoroacetic acid (TFA) and were applied to an ODS column (35 × 180 mm, Wakosil 25C15, Wako Pure Chemical Industries



Figure 3. Elution profile of anthocyanins isolated from the cells of a variant carrot cell line by analytical HPLC using a Synergi 4 μ RP-80 Å (4.6 \times 250 mm, Phenomenex) and 0.1% aqueous formic acid (A) and methanol (B) as a mobile phase. The elution program consisted of a linear gradient from 15% B to 80% B for 30 min at a flow rate of 1.0 mL/min monitored at 530 nm.

Ltd., Osaka, Japan). The anthocyanins were eluted with 20% methanol containing 0.1% TFA followed by 50% methanol containing 0.1% TFA. The solvent was removed from eluates by evaporation. Compound **1** was purified from the 20% methanol containing 0.1% TFA fraction by preparative HPLC on a Synergi 4 μ RP-80 Å (21.2 \times 250 mm, Phenomenex, Torrance, CA, USA) with 0.1% aque-

Table 1

 1H (800 MHz) and ^{13}C (200 MHz) assignments of anthocyanin 1 and 2 in CD_3OD/ CF_3COOD (9:1) at 25 $^\circ C$

	Position	1		2	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		δ^{1} H (ppm)	$\delta^{13}C$ (ppm)	δ^{1} H (ppm)	δ^{13} C (ppm)
CH 5, 19 (q, 8) 28.4 CH 195 (3H, d, 8) 19.3 Cyanidin 2 - 162.3 - 162.4, 164.1 3 - 145.6 - 144.85, 144.92 4 8.34 132.9 8,51', 8,60 133.3, 133.7 4 - 112.4, 124 - 112.3, 113.4 5 - 158,7 - 156.9, 157.3 6 6,61 103.3 6,61,6.63 102.4, 103.1 7 - 169.3 - 156.6, 103.3, 167.7 8 6,39 95.1 - 104, 112.0 8a - 156.6 - 153.1, 155.7 1' - 120.8 - 121.4, 121.7 2' 7,69 118.7 8,06, 8,15 118.5, 119.6 3' - 147.0 - 147.4, 147.6 4' - 156.0 - 155.2, 156.1 5' 6.92 (d, 9) 117.5 7,14 (2H, d, 9) 117.1, 117.9 6' 8,08 (d, 9) 12.9 8, 829 (d, 9), 8.51 ^c 129.1, 130.1 Calactose 1 5,16 (d, 7) 102.3 5,44 (d, 7), 5.50 (d, 7) 101.0, 101.6 2 4,35 (d, 7) 80.6 4.29 (t, 8), 4.35 (t, 8) 80.7, 81.1 3 4,20 (dd, 3,10) 75.6 4.21 -427 (4H) ^d 75.37, 75.44 4 3.99 (d, 3) 70.7 3.98 (2H) 70.6, 77.7, 73.8 6b 4.32 (d, 10) 77.5 4.55 (d, 9), 4.56 (d, 8) 77.3, 77.5 4.48 (d, 10) 77.5 4.55 (d, 9), 4.56 (d, 8) 77.3, 77.5 4.48 (d, 10) 77.5 4.55 (d, 9), 4.56 (d, 8) 77.3, 77.5 64 3.79 (d, 12) 73.6 3.70-3.79 (GH) ^e 73.7, 73.8 6b 4.32 (d, 10) 74.2 3.38 ^{-3.47} (10H) ^f 71.26,71.31 74.327 (4d, 6, 9) 71.2 3.38 ^{-3.47} (10H) ^f 77.87, 77.90 75.34.8 (d, 7) 107.0 4.47 (2H, 17) 107.18, 107.23 75.4 (48 (d, 7)) 77.9 3.38 ^{-3.47} (10H) ^f 77.87, 77.90 75.3 (3.6) (d, 6, 12) 3.70-3.79 (GH) ^e 70.2, 76.3 76.2, 76.3 76.2, 76.3 76.3 (d, 7) 107.0 4.47 (2H, 17) 107.18, 107.23 77.7.3 8 (2H) 107.0 13, 70-3.79 (GH) ^e 70.0 75.3 (3.6) (d, 6, 12) 3.70-3.79 (GH) ^e 77.87, 77.90 75.3 (3.6) (d, 6, 12) 3.70-3.79 (GH) ^e 77.87, 77.90 75.3 (3.6) (d, 6, 12) 3.70-3.79 (GH) ^e 77.87, 77.90 75.3 (3.6) (d, 6, 12) 3.70-3.79 (GH) ^e 77.87, 77.90 75.3 (3.6) (d, 6, 12) 3.70-3.79 (GH) ^e 77.87, 77.90 75.3 (3.6) (d, 6, 12) 3.70-3.79 (GH) ^e 70.0 77.7 (2U, (16) 16.0 14.47, (2H, 12) 6.1.1 6.55 (2U) ^e 77.7 (2U, (16) 16.3 (2H) ^e 105.6 ⁱ 165.6 ⁱ 16.3 (2H) ⁱ 105.6 ⁱ 16.3 (16H) 77.7 (2U, (16) 147.8 7.36 (2H) ⁱ 105.6 ⁱ 163.1 (2H).6 (36 (2H) ⁱ 105.6 ⁱ 163.1 (2H).7 77.20 (d, 16) 147.8 7.36 (d, 16), 74.5 (d, 16) 144.7, 148.1 8 6.07 (d, 16) 16.2 6.26 (d, 16),	Ethvl-linka	192			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	CH	_	_	5.19 (q, 8)	28.4
Cyanidin2-162.3-162.4, 164.13-144.85, 144.9244.85, 144.9248.34132.98.51°, 8.60133.3, 133.74a-112.4-112.3, 113.45-158.7-156.9, 157.366.61103.36.61.6.63102.4, 103.17-169.3-167.3, 167.786.399.5.1-153.1, 155.71'-120.8-153.1, 155.71'-120.8-121.4, 121.72'7.6911.878.06 8.15118.5, 119.63'-147.0-147.4, 147.64'-156.0-155.2, 156.15'6.92 (d, 9)17.57.14 (2H, d, 9)117.1, 117.96'8.08 (d, 9)129.88.29 (d, 9), 8.51°129.1, 130.1Calactore15.16 (4, 7)102.35.44 (d, 7), 5.50 (d, 7)101.0, 101.624.35 (d, 7)80.64.29 (t, 8), 4.35 (t, 8)80.7, 81.134.20 (dd, 3, 10)7.64.21-4.27 (4H) ^d 7.53.7, 75.4443.99 (d, 3)70.73.98 (2H)70.6, 70.754.48 (d, 10)77.54.55 (d, 9), 4.56 (d, 8)77.3, 75.56a3.79 (d, 12)7.623.32'76.2, 76.333.40 (t, 9)7.823.38-3.47 (10H) ^f 71.26, 71.315a3.63 (dd, 6, 12)3.79-3.9 (6H)	CH ₃	_	_	1.95 (3H, d, 8)	19.3
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cyanidin				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2	-	162.3	-	162.4, 164.1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	-	145.6	-	144.85, 144.92
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4	8.34	132.9	8.51, 8.60	133.3, 133.7
6 6.661 103.3 6.61,6.63 102.4, 103.1 7 - 169.3 - 167.3, 167.7 8 6.39 95.1 - 110.4, 112.0 8a - 156.6 - 153.1, 155.7 1' - 120.8 - 121.4, 121.7 2' 7.69 118.7 8.06, 8.15 118.5, 119.6 3' - 147.0 - 147.4, 147.6 4' - 156.0 - 155.2, 156.1 5' 6.92 (d, 9) 117.5 7.14 (2H, d, 9) 117.1, 117.9 6' 8.08 (d, 9) 129.8 8.29 (d, 9), 8.51c 129.1, 130.1 Galactose - - 101.0, 101.6 12 4.35 (d, 7) 80.6 4.29 (t, 8), 4.35 (t, 8) 80.7, 81.1 3 4.20 (d, 3.10) 75.5 4.41 -4.27 (4H) ^d 75.37, 75.44 3.99 (d, 3) 70.7 3.98 (2H) 706.70.7 5 5 4.48 (d, 10) 77.5 4.55 (d, 9), 4.56 (d, 8) <td< td=""><td>4a 5</td><td>_</td><td>158.7</td><td>_</td><td>1569 1573</td></td<>	4a 5	_	158.7	_	1569 1573
7 - 169.3 - 167.3, 167.7 8 6.39 95.1 - 110.4, 112.0 8a - 156.6 - 153.1, 155.7 1' - 120.8 - 121.4, 121.7 2' 7.69 118.7 8.06, 8.15 118.5, 119.6 3' - 147.0 - 147.4, 147.6 4' - 156.0 - 155.2, 156.1 5' 6.92 (d, 9) 117.5 7.14 (2H, d, 9) 117.1, 117.9 6' 8.08 (d, 9) 129.8 8.29 (d, 9), 8.51c 129.1, 130.1 <i>Galactose</i> - 153.7, 75.44 3.99 (d, 3) 70.7 3.98 (2H) 70.6, 70.7 5 4.48 (d, 10) 75.6 4.29 (t, 8), 4.35 (t, 8) 80.7, 81.1 3.420 (dd, 3, 10) 7.42 (3.79 (GH)c 73.7, 73.8 6b 4.32 (d, 10) 73.6 3.70 (A), 55 (d, 9) 70.7, 73.77.5 4.32 (d, 10) 4.21 ~ 4.27 (4H)d 74.43 (7, 73.8 Xylose - 1 4.88 (d, 8) 105.9 4.89 (d, 8), 4.95 ¹ 106.1, 106.2 76.3 3.247 (10H)f	6	6.61	103.3	6.61.6.63	102.4. 103.1
8 6.39 95.1 - 110.4, 112.0 8a - 156.6 - 153.1, 155.7 1' - 120.8 - 121.4, 121.7 2' 7.69 118.7 8.06, 8.15 118.5, 119.6 3' - 147.0 - 147.4, 147.6 4' - 156.0 - 155.2, 156.1 5' 6.92 (d, 9) 117.5 7.14 (2H, d, 9) 117.1, 117.9 6' 8.08 (d, 9) 129.8 8.29 (d, 9), 8.51° 129.1, 130.1 <i>Calactose</i> - - 101.0, 101.6 2 4.35 (d, 7) 80.6 4.21 (4, 7), 5.50 (d, 7) 101.0, 101.6 2 4.35 (d, 7) 102.3 5.44 (d, 7), 5.50 (d, 7) 101.0, 101.6 2 4.35 (d, 7) 107.5 4.55 (d, 9), 4.56 (d, 8) 77.3, 77.5, 44 4 3.99 (d, 3) 70.7 3.98 (2H) 706.7 (76, 76.3) 5 4.48 (d, 10) 77.5 4.55 (d, 9), 4.56 (d, 8) 77.3, 77.5 6a 3.79 (d, 12) 76.2 3.21' 762.76.3 7.4 3.2	7	_	169.3	-	167.3, 167.7
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	8	6.39	95.1	_	110.4, 112.0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	8a	-	156.6	_	153.1, 155.7
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1'	-	120.8	-	121.4, 121.7
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2'	7.69	118.7	8.06, 8.15	118.5, 119.6
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3' 1/	-	147.0	-	147.4, 147.6
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4' 5/	- 6 02 (d 0)	100.0	- 714(2Hd0)	155.2, 150.1
Galactose 1 5.16 (d, 7) 102.3 5.44 (d, 7), 5.50 (d, 7) 101.0, 101.6 2 4.35 (d, 7) 80.6 4.29 (t, 8), 4.35 (t, 8) 80.7, 81.1 3 4.20 (dd, 3,10) 75.6 4.21–4.27 (4H) ^d 75.37, 75.44 4 3.99 (d, 3) 70.7 3.98 (2H) 70.6, 70.7 5 4.48 (d, 10) 77.5 4.55 (d, 9), 4.56 (d, 8) 77.3, 77.5 6a 3.79 (d, 12) 73.6 3.70–3.79 (6H) ^e 73.7, 73.8 6b 4.32 (d, 10) 4.21~4.27 (4H) ^d 76.2, 76.3 76.2 3.21 (t, 9) 76.2 3.32 ¹ 76.2, 76.3 3 3.40 (t, 9) 71.2 3.38–3.47 (10H) ^f 71.26,71.31 5a 3.19 (d, 12) 67.2 3.17 (t, 11), 3.27 (t, 11) 67.4, 67.5 5b 3.63 (dd, 6, 12) 3.70–3.79 (6H) ^e 70.4 7.82, 78.3 2 3.52 (d, 7) ^a 77.9 3.38–3.47 (10H) ^f 71.8, 107.23 2 3.52 (d, 7) ^a 77.9 3.38–3.47 (10H) ^f 74.7 3 3.52 (d, 7) ^a 74.7 3.8–3.47 (10H) ^f 74.7	5 6'	8 08 (d, 9)	129.8	$829(d 9) 851^{\circ}$	129.1 130.1
Sinterior5.16 (d, 7)102.35.44 (d, 7), 5.50 (d, 7)101.0, 101.624.35 (d, 7)80.64.29 (t, 8), 4.35 (t, 8)80.7, 81.134.20 (dd, 3,10)75.64.21-4.27 (4H) ^d 75.37, 75.4443.99 (d, 3)70.73.98 (2H)70.6, 70.754.48 (d, 10)77.54.55 (d, 9), 4.56 (d, 8)77.3, 77.56a3.79 (d, 12)73.63.70-3.79 (6H) ^e 73.7, 73.86b4.32 (d, 10)4.21~4.27 (4H) ^d 76.2, 76.373.21 (t, 9)76.23.32 ¹ 76.2, 76.333.40 (t, 9)78.23.38-3.47 (10H) ^f 78.2, 78.343.27 (dd, 6, 9)71.23.38-3.47 (10H) ^f 71.26,71.315a3.19 (d, 12)67.23.17 (t, 11), 3.27 (t, 11)67.4, 67.55b3.63 (dd, 6, 12)3.70-3.79 (6H) ^e 70.0Clucose14.53 (d, 7)107.04.47 (2H,t, 7)107.18, 107.2323.52 (d, 7) ^a 74.73.38-3.47 (10H) ^f 74.743.74 (t,9)70.13.70-3.79 (6H) ^e 70.053.46 (4.10)75.33.38-3.47 (10H) ^f 75.66a4.12 (d, 11)61.04.14 (2H, t, 12)61.16b5.33 (d,10)5.37 (2H,t, 11)53.66.31 (2H) ^s 53.60 (42H) ^b 105.0 ^h 6.31 (2H), 6.36 (2H) ^g 105.6 ^j 3-125.4-125.826.04 (2H) ^b 105.0 ^h 6.31 (2H), 6.36 (2H) ^g	o Galactose	0.00 (u, 5)	125.0	0.23 (d, 3), 0.31	125.1, 150.1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1	5.16 (d, 7)	102.3	5.44 (d, 7), 5.50 (d, 7)	101.0, 101.6
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2	4.35 (d, 7)	80.6	4.29 (t, 8), 4.35 (t, 8)	80.7, 81.1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	4.20 (dd, 3,10)	75.6	4.21-4.27 (4H) ^d	75.37, 75.44
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4	3.99 (d, 3)	70.7	3.98 (2H)	70.6, 70.7
6a $3.79 (d, 12)$ 73.6 $3.70-3.79 (6H)^e$ $73.7, 73.8$ 6b $4.32 (d, 10)$ $4.21 \sim 4.27 (4H)^d$ $4.21 \sim 4.27 (4H)^d$ Xylose 1 $4.88 (d, 8)$ 105.9 $4.89 (d, 8), 4.95^1$ $106.1, 106.2$ 2 $3.21 (t, 9)$ 76.2 3.32^1 $76.2, 76.3$ 3 $3.40 (t, 9)$ 78.2 $3.38-3.47 (10H)^f$ $78.2, 78.3$ 4 $3.27 (dd, 6, 9)$ 71.2 $3.370-3.79 (6H)^e$ $71.26, 71.31$ 5a $3.19 (d, 12)$ 67.2 $3.17 (t, 11), 3.27 (t, 11)$ $67.4, 67.5$ 5b $3.63 (dd, 6, 12)$ $3.70-3.79 (6H)^e$ $61.4, 67.5$ 75.5 <i>Clucose</i> 1 $4.53 (d, 7)$ 107.0 $4.47 (2H, t, 7)$ $107.18, 107.23$ 2 $3.52 (d, 7)^a$ 74.7 $3.38-3.47 (10H)^f$ 74.7 3 $3.52 (d, 7)^a$ 74.7 $3.38-3.47 (10H)^f$ 75.6 6a $4.12 (d, 11)$ 61.0 $4.14 (2H, t, 12)$ 61.1 6b $5.33 (d, 10)$ $5.37 (2H, t, 11)$ 5.6^i Sinapic acid 11	5	4.48 (d, 10)	77.5	4.55 (d, 9), 4.56 (d, 8)	77.3, 77.5
6b 4.32 (d, 10) $4.21 \sim 4.27$ (4H) ⁴ Xylose 1 4.88 (d, 8) 105.9 4.89 (d, 8), 4.95 ¹ 106.1, 106.2 2 3.21 (t, 9) 76.2 3.32 ¹ 76.2, 76.3 3 3.40 (t, 9) 78.2 3.38–3.47 (10H) ^f 78.2, 78.3 4 3.27 (dd, 6, 9) 71.2 3.38–3.47 (10H) ^f 71.26,71.31 5a 3.19 (d, 12) 67.2 3.17 (t, 11), 3.27 (t, 11) 67.4, 67.5 5b 3.63 (dd, 6, 12) $3.70-3.79$ (6H) ^e $71.26,71.31$ <i>Clucose</i> 1 4.53 (d, 7) 107.0 4.47 (2H,t, 7) 107.18, 107.23 2 3.52 (d, 7) ^a 77.9 3.38–3.47 (10H) ^f 74.7 4 3.74 (t,9) 70.1 3.70–3.79 (6H) ^e 70.0 5 3.46 (d,10) 75.3 3.38–3.47 (10H) ^f 75.6 6a 4.12 (d, 11) 61.0 4.14, (2H, t, 12) 61.1 6b 5.33 (d,10) 5.37 (2H, t, 11) 57.6 7 105.0 ^h 6.31 (2H), 6.36 (2H) ^g 105.6 ⁱ 7 125.4 - 125.8 <th< td=""><td>6a</td><td>3.79 (d, 12)</td><td>73.6</td><td>3.70–3.79 (6H)^e</td><td>73.7, 73.8</td></th<>	6a	3.79 (d, 12)	73.6	3.70–3.79 (6H) ^e	73.7, 73.8
Xylose14.88 (d, 8)105.94.89 (d, 8), 4.95 ¹ 106.1, 106.2,23.21 (t, 9)76.2 3.32^1 76.2, 76.333.40 (t, 9)78.2 3.38 –3.47 (10H) ^f 78.2, 78.343.27 (dd, 6, 9)71.2 3.38 –3.47 (10H) ^f 71.26,71.315a3.19 (d, 12)67.2 3.17 (t, 11), 3.27 (t,11)67.4, 67.55b3.63 (dd, 6, 12) 3.70 –3.79 (6H) ^e 67.2 3.70 –3.79 (6H) ^e Clucose14.53 (d, 7)107.04.47 (2H,t, 7)107.18, 107.232 3.52 (d, 7) ^a 77.9 3.38 –3.47 (10H) ^f 77.87, 77.903 3.52 (d, 7) ^a 74.7 3.38 –3.47 (10H) ^f 74.74 3.74 (t,9)70.1 3.70 –3.79 (6H) ^e 70.05 3.46 (d,10)75.3 3.38 –3.47 (10H) ^f 75.66a4.12 (d, 11)61.04.14, (2H, t, 12)61.16b5.33 (d,10)5.37 (2H,t, 11)5.6Sinapic acid1 $-$ 125.4 $-$ 1 $-$ 125.4 $-$ 26.04 (2H) ^b 105.0 ^h 6.31 (2H), 6.36 (2H) ^g 105.6 ^j 3 $-$ 148.9 ⁱ $-$ 149.1 ^k 4 $-$ 139.2 $-$ 139.35 $-$ 148.9 ⁱ $-$ 149.1 ^k 66.04 (2H) ^b 105.0 ^h 6.31 (2H), 6.36 (2H) ^g }105.6 ^j 77.20 (d, 16)147.87.36 (d, 16), 7.45 (d, 16) <td>6D</td> <td>4.32 (d, 10)</td> <td></td> <td>4.21~4.27 (4H)^a</td> <td></td>	6D	4.32 (d, 10)		4.21~4.27 (4H) ^a	
1 4.88 (d, 8) 105.9 4.89 (d, 8), 4.95 106.1, 106.2 2 3.21 (t, 9) 76.2 3.32^1 76.2, 76.3 3 3.40 (t, 9) 78.2 $3.38^{-3.47}$ (10H) ^f 78.2, 78.3 4 3.27 (dd, 6, 9) 71.2 $3.38^{-3.47}$ (10H) ^f 71.26, 71.31 5a 3.19 (d, 12) 67.2 3.17 (t, 11), 3.27 (t, 11) 67.4, 67.5 5b 3.63 (dd, 6, 12) $3.70^{-3.79}$ (6H) ^e 67.4 67.7 <i>Glucose</i> - 107.0 4.47 (2H,t, 7) 107.18, 107.23 2 3.52 (d, 7) ^a 77.9 $3.38^{-3.47}$ (10H) ^f 77.87, 77.90 3 3.52 (d, 7) ^a 74.7 $3.38^{-3.47}$ (10H) ^f 75.6 6a 4.12 (d, 11) 61.0 75.3 $3.38^{-3.47}$ (10H) ^f 75.6 6a 4.12 (d, 11) 61.0 5.37 (2H,t, 12) 61.1 6b 5.33 (d,10) 5.37 (2H,t, 12) 61.1 6b 5.33 (d,10) 5.37 (2H,t, 11) 5.6 ⁱ 7 2.0 (A (2H) ^b) 105.0 ^b 6.31 (2H), 6.36 (2H) ^g 105.6 ⁱ	Xylose	400(10)	105.0	400 (4.0) 405	100 1 100 2
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1	4.88 (0, 8) 3 21 († 9)	76.2	4.89(0, 8), 4.95	76.2 76.3
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2	3.21(t, 9) 3.40(t, 9)	78.2	3 38-3 47 (10H) ^f	78.2, 78.3
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	4	3.27 (dd. 6, 9)	71.2	$3.38 - 3.47 (10H)^{f}$	71.26.71.31
5b $3.63 (dd, 6, 12)$ $3.70-3.79 (6H)^e$ Glucose 1 $4.53 (d, 7)$ 107.0 $4.47 (2H,t, 7)$ $107.18, 107.23$ 2 $3.52 (d, 7)^a$ 77.9 $3.38-3.47 (10H)^f$ $77.87, 77.90$ 3 $3.52 (d, 7)^a$ 74.7 $3.38-3.47 (10H)^f$ 74.7 4 $3.74 (t,9)$ 70.1 $3.70-3.79 (6H)^e$ 70.0 5 $3.46 (d,10)$ 75.3 $3.38-3.47 (10H)^f$ 75.6 6a $4.12 (d, 11)$ 61.0 $4.14, (2H, t, 12)$ 61.1 6b $5.33 (d,10)$ $5.37 (2H,t, 11)$ $5.37 (2H,t, 11)$ Sinapic acid 1 $ 125.4$ $ 125.8$ 2 $6.04 (2H)^b$ 105.0^h $6.31 (2H), 6.36 (2H)^g$ 105.6^i 3 $ 148.9^i$ $ 149.1^k$ 4 $ 139.2$ $ 149.1^k$ 6 $6.04 (2H)^b$ 105.0^h $6.31 (2H), 6.36 (2H)^g$ 105.6^i 7 $7.20 (d, 16)$ 147.8 $7.36 (d, 16), 7.45 (d, 16)$	5a	3.19 (d, 12)	67.2	3.17 (t, 11), 3.27 (t,11)	67.4, 67.5
Clucose 1 4.53 (d, 7) 107.0 4.47 (2H,t, 7) 107.18, 107.23 2 3.52 (d, 7) ^a 77.9 3.38–3.47 (10H) ^f 77.87, 77.90 3 3.52 (d, 7) ^a 74.7 3.38–3.47 (10H) ^f 74.7 4 3.74 (t,9) 70.1 3.70–3.79 (6H) ^e 70.0 5 3.46 (d,10) 75.3 3.38–3.47 (10H) ^f 75.6 6a 4.12 (d, 11) 61.0 4.14, (2H, t, 12) 61.1 6b 5.33 (d,10) 5.37 (2H,t, 11) 5.6 5.3 2 6.04 (2H) ^b 105.0 ^h 6.31 (2H), 6.36 (2H) ^g 105.6 ⁱ 3 - 148.9 ⁱ - 149.1 ^k 4 - 139.2 - 139.3 5 - 148.9 ⁱ - 149.1 ^k 6 6.04 (2H) ^b 105.0 ^h 6.31 (2H), 6.36 (2H) ^g 105.6 ^j 7 7.20 (d, 16) 147.8 7.36 (d, 16), 7.45 (d, 16) 144.7, 148.1 8 6.07 (d, 16) 147.8 </td <td>5b</td> <td>3.63 (dd, 6, 12)</td> <td></td> <td>3.70–3.79 (6H)^e</td> <td></td>	5b	3.63 (dd, 6, 12)		3.70–3.79 (6H) ^e	
$ \begin{array}{ccccccccccccccccccccccccc$	Glucose				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1	4.53 (d, 7)	107.0	4.47 (2H,t, 7)	107.18, 107.23
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2	3.52 (d, 7) ^a	77.9	3.38–3.47 (10H) ⁴	77.87, 77.90
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	$3.52 (d, 7)^{\circ}$	/4./	3.38-3.47 (10H) ⁴	74.7
	4	3.74 (1,9) 3.46 (d.10)	70.1	3.70-3.79 (0H) ⁻ 3.38-3.77 (10H) ^f	70.0
Gb Gb	5 6a	4 12 (d. 11)	61.0	4 14 (2H t 12)	61.1
Sinapic acid 1 – 125.4 – 125.8 2 $6.04 (2H)^{b}$ 105.0 ^h $6.31 (2H), 6.36 (2H)^{g}$ 105.6 ^j 3 – 148.9 ⁱ – 149.1 ^k 4 – 139.2 – 139.3 5 – 148.9 ⁱ – 149.1 ^k 6 $6.04 (2H)^{b}$ 105.0 ^h $6.31 (2H), 6.36 (2H)^{g}$ 105.6 ^j 7 $7.20 (d, 16)$ 147.8 $7.36 (d, 16), 7.45 (d, 16)$ 144.7, 148.1 8 $6.07 (d, 16)$ 116.2 $6.26 (d, 16), 6.32 (d, 16)$ 116.3, 116.5 9 – 169.2 – 169.3 (d, 16), 56.4, 56.5	6b	5.33 (d,10)	01.0	5.37 (2H,t, 11)	01.1
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Sinapic ac	id			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1	-	125.4	-	125.8
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2	6.04 (2H) ^b	105.0 ^h	6.31 (2H), 6.36 (2H) ^g	105.6 ^j
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3	-	148.9 ⁱ	-	149.1 ^k
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	4	-	139.2	-	139.3
b 6.04 (2H) ⁻ 105.0 ⁻ 6.31 (2H), 6.36 (2H) ^o 105.6 ^o 7 7.20 (d, 16) 147.8 7.36 (d, 16), 7.45 (d, 16) 144.7, 148.1 8 6.07 (d, 16) 116.2 6.26 (d, 16), 6.32 (d, 16) 116.3, 116.5 9 - 169.2 - 169.3, 169.4 OMe 3.37 (6H) 56.2 3.52 (6H), 3.60 (6H) 56.4, 56.5	5		148.9 ⁴		149.1* 105.cl
7 7.26 (d, 16) 147.8 7.36 (d, 16), 7.43 (d, 16) 144.7, 148.1 8 6.07 (d, 16) 116.2 6.26 (d, 16), 6.32 (d, 16) 116.3, 116.5 9 - 169.2 - 169.3, 169.4 OMe 3.37 (6H) 56.2 3.52 (6H), 3.60 (6H) 56.4, 56.5	0 7	0.04 (2H) ^o 7.20 (d. 16)	147.9	0.31 (2H), 0.36 (2H) ⁸ 7.36 (d. 16), 7.45 (d. 16)	105.6'
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	8	6.07 (d. 16)	147.0	626(d, 16), 7.45(u, 16)	144.7, 140.1
OMe 3.37 (6H) 56.2 3.52 (6H), 3.60 (6H) 56.4, 56.5	9	_ (u, 10)	169.2		169.3, 169.4
	OMe	3.37 (6H)	56.2	3.52 (6H), 3.60 (6H)	56.4, 56.5

TMS was used as internal standard. Values in parentheses indicate integral, multiplicity and coupling constants (*J* in Hz).

^{a-g} Overlapped with each other.

^{h-k} Assignments with the same letters are interchangeable.

¹ Overlapped with solvent peak. Signals were detected by HMQC and HMBC analyses.

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