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SECOIRIDOID GLUCOSIDES FROM *FRAXINUS MALACOPHYLLA*

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Key Word Index—*Fraxinus malacophylla*; Oleaceae; leaves; secoiridoid glucosides; bis-secoiridoid glucoside; butyl isoligustrosidate; fraximalacoside.

Abstract—Two new secoiridoid glucosides, butyl isoligustrosidate and fraximalacoside, were isolated from the leaves of *Fraxinus malacophylla*, together with the known constituents, isoligustroside, fraxiformoside, isoligustrosidic acid, 1‴-*O*-β-D-glucosylfraxiformoside, verbascoside, cosmosiin, sitosterol-β-D-glucoside and tyrosol. Their structures have been elucidated by chemical and spectroscopic methods.

INTRODUCTION

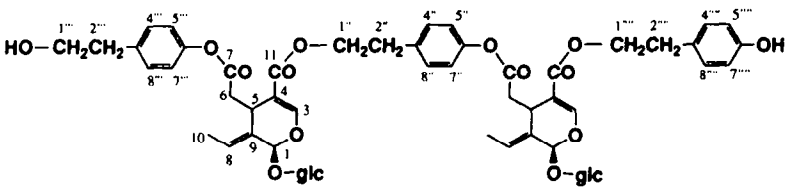
Fraxinus malacophylla Hemsl. in Hook., an oleaceous plant, has long been used as a folk medicine in south-western China. For example, the Bai tribe uses the whole plant in treating stomatitis, haemostatic and urinary organ infection; Li-shu, Miao and Wa tribes use its root as an antipyretic, antimalaria, antirhinitis and antiinflammatory agent as well as a remedy for excretory organ infection; the Han tribe uses its bark in treating stomatitis, toothache, pyrexia and urinary organ infection, etc. [1]. In continuation of our investigations on the oleaceous secoiridoids [2], and ethnobotanical and ethnopharmaceutical studies on medicinal plants in Yunnan province of China [3], we have isolated the chemical constituents of *F. malacophylla*. This paper describes the isolation of two new secoiridoid glucosides, butyl isoligustrosidate and fraximalacoside along with eight known constituents from the leaves of *F. malacophylla* and the structure elucidation of the new secoiridoid glucosides.

RESULTS AND DISCUSSION

The methanolic extract of the fresh leaves of *F. malacophylla* was fractionated as described in the Experimental section to give two new secoiridoid glucosides, butyl isoligustrosidate (**1**) and fraximalacoside (**4**) together with four known secoiridoid glucosides, isoligustroside (**2**), fraxiformoside (**3**), isoligustrosidic acid (**5**), and 1‴-*O*-β-D-glucosylfraxiformoside (**6**) [4], as well as four known compounds, 2-(4-hydroxy-phenyl) ethanol (tyrosol), verbascoside, sitosterol-β-D-glucoside and cosmosiin (**7**) [2].

Glucoside **1**, a powder, was analysed for $C_{28}H_{38}O_{12}$ from its FAB mass spectrum (*m/z* 567 $[M+H]^+$). The ^1H and ^{13}C NMR spectra of compound **1** are very similar to those of isoligustrosidic acid (**5**) except for the appearance of a set of signals arising from a *n*-butyl group in **1** (Tables 1 and 2). By comparison of ^{13}C NMR signals of **1** with those of **5**, the chemical shift assignable to C-7 of **5** shifted upfield from δ175.2 to δ173.3. On the other hand, the long range (C-H) COSY experiment of **1** showed a two ^3J interaction between H-1 of the *n*-butyl group (δ4.06) and C-7 (δ 173.3) as well as H-1″ (δ4.28) and C-11 (δ168.1). The butyl group should be conjugated at C-7 with compound **5**, thus the structure of **1** was characterized as butyl isoligustrosidate. As *n*-butanol was added as a defoaming agent during concentration of the ethyl acetate and water extracts, it was open to question whether compound **1** is an artifact or not. This problem was solved in the following way: a 3.83 g aliquot of the concentrated methanol extract of the fresh leaves of *F. malacophylla* was suspended in 30 ml of water. The suspension was extracted with hexane (4 × 20 ml) and ethyl acetate (4 × 20 ml), respectively. The hexane, ethyl acetate and water extracts were concentrated without adding butanol to give 0.14 g, 1.67 g and 1.05 g of the residues, respectively. The ethyl acetate extract was chromatographed on silica gel column and PTLC to give pure **1** (6.9 mg) which was characterized by TLC, IR and ^1H NMR. To our knowledge, this is the first example of the isolation of secoiridoid glucoside comprising a *n*-butyl ester moiety in the molecule.

Glucoside **4**, a powder, $[\alpha]_D^{27}-123°$ (MeOH), was analysed for $C_{56}H_{66}O_{24}$ from its mass spectrum. It showed UV maxima at 220, 228, 236 (sh), 244 (sh) and 276 (sh) nm. IR bands appeared at 3400, 1740, 1700, 1630 and 1515 cm^{-1}. Its ^1H NMR spectrum (Table 1) exhibited a broad signal characteristic of H-3 of secoiridoid glucosides at δ 7.51 (2H, *d*), two signals for a vinyl methyl group at δ 1.73 (6H, *m*), anomeric protons at δ 4.83 (2H, *d*), allylic acetal proton at δ 6.00 (2H, *br s*), olefinic protons at δ 6.16



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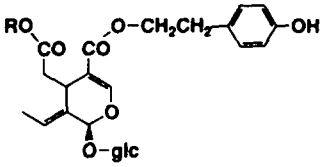
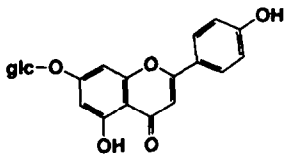


1 R=$CH_3CH_2CH_2CH_2$-
2 R=Me
3 R=$HOCH_2CH_2$-Ph-
5 R=H
6 R=glc-O-CH_2CH_2-Ph-



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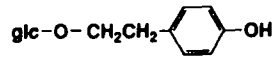

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(2H, *br q*), and three aromatic AA'BB' spin systems at δ 6.71–7.28. These signals together with the ^{13}C NMR spectrum of **4** (Table 2) suggested that the structure of this compound (**4**) could be composed of two molecules of **5**-type and an extra 2-(4-hydroxyphenyl) ethyl alcohol unit. By comparison of the ^{13}C NMR spectrum of **4** with that of **5**, the chemical shift assignable to C-7 and 6″ of **4** shifted upfield from δ 175.2 to δ 171.7 and from δ 157.0 to δ 150.5, respectively. Accordingly, glucoside **4** was considered to be formed through the attachment of a molecule of **5** and a 2-(4-hydroxyphenyl) ethyl alcohol unit at 6″ hydroxy and 7 carboxy moieties, respectively. Furthermore, the COLOC experiment of **4** showed two ^3J interactions between H-1″ (δ 4.36) and C-11 (δ 168.1) as well as H-1‴″ (δ 4.29) and C-11 (δ 168.0). Methanolysis of **4** gave two compounds. Their spectral and physical data were in good accordance with those of isoligustroside (**2**) and fraxiformoside (**3**). The structure of this glucoside was thus concluded to be as shown in **4**. This novel bis-secoiridoidic glucoside is designated as fraximalacoside.

EXPERIMENTAL

^1H (200 MHz and 300 MHz) and ^{13}C (50 MHz and 75 MHz) NMR; TMS as int. standard; FAB-MS: glycerol as the matrix; CC and TLC: silica gel, Si 60 (Lobar, 40–63 μm, length: 250 mm, diameter: 25 mm, Merck), Rp-18 (Lobar, 40–63 μm, length: 250 mm, diameter: 25 mm, Merck) and Diaion HP-20 (Mitsubishi Kasei).

Plant material. Leaves of *Fraximus malacophylla* grown in the Botanical Garden, Kunming Institute of Botany, Chinese Academy of Sciences were collected in October 1990.

Isolation of glucosides. The fresh leaves (5.23 kg) of *F. malacophylla* were extracted with hot MeOH (20 l × 4). The MeOH extract was concd *in vacuo* to give a residue (733.0 g), which was dissolved in H_2O (1 l). The aq. suspension was extracted with hexane and EtOAc, successively. The hexane, EtOAc and H_2O layers were concd *in vacuo* to give residues, 3.40 g, 107.34 g and 350.18 g, respectively. The EtOAc extract (107.34 g) was fractionated with CC on silica gel, eluted with $CHCl_3$–MeOH with increasing MeOH content to afford frs A–G. The following frs were further purified by LC on Si 60 (Lobar, 40–63 μm, Merck) and Rp-18 (Lobar, 40–63 μm, Merck): fr. A yielded 2-(4-hydroxyphenyl) ethanol (tyrosol, 979.5 mg), fr. B: sitosterol-β-D-glucoside (36 mg), fr. C: **1** (45 mg), fr. D: **2** (2080 mg) and **3** (648 mg), fr. E: **4** (210 mg), fr. F: **5** (45.2 mg), fr. G: verbascoside (178 mg). The H_2O extract (350.18 g) was fractionated by CC on Diaion HP-20 eluting with aq. MeOH to afford fr. H_2O, fr. 50% MeOH and fr. MeOH. Fr. 50% MeOH (90.20 g) and fr. MeOH (3.45 g) were subjected to silica gel CC with $CHCl_3$–MeOH (8:2) and purified by LC on Si 60 (Lobar, 40–63 μm, Merck) and Rp-18 (Lobar, 40–63 μm, Merck). Fr. 50% MeOH yielded verbascoside (81.92 g) and **7** (17 mg), fr. MeOH: **2** (320 mg), **3** (380 mg) and **6** (306 mg).

Butyl isoligustrosidate (**1**). Powder, $[\alpha]_D^{27}$ −148° (MeOH; *c* 0.17). UV λ_{max}^{EtOH} nm (log ε): 226 (3.89), 238 (3.79), 246 (3.60). IR ν_{max}^{KBr} cm^{-1}: 3400, 2950, 1710, 1630, 1515, 1075, 810, 770. ^1H and ^{13}C NMR: see Tables 1 and 2. Positive ion FAB-MS, *m/z*: 567 $[M+H]^+$, 387 $[M-O$-Glc$]^+$. (Found: C, 59.5; H, 6.7. $C_{28}H_{38}O_{12}$ requires: C, 59.4; H, 6.7%.)

Isoligustroside (**2**). Powder, $[\alpha]_D^{27}$ −137° (MeOH; *c* 0.14). UV λ_{max}^{EtOH} nm (log ε): 228 (4.03), 278 (3.12). IR

Table 1. ^{1}H NMR spectral data of glucosides **1**–**6** in CD_3OD

H	1	2	3	4	5	6
Aglucone						
1	5.91 (1H, *s*)	5.90 (1H, *s*)	6.01 (1H, *s*)	6.00 (2H, *br s*)	5.93 (1H, *s*)	6.00 (1H, *br s*)
3	7.47 (1H, *s*)	7.46 (1H, *s*)	7.51 (1H, *s*)	7.51 (2H, *d*, 1.8)	7.48 (1H, *s*)	7.51 (1H, *s*)
5	3.98 (1H, *dd*, 9.5, 4.3)	3.96 (1H, *dd*, 9.5, 4.3)	4.08 (1H, *dd*, 9.5, 4.5)	4.07 (2H, *dd*, 9.1, 4.5)	4.02 (1H, *dd*, 9.5, 4.3)	4.06 (1H, *dd*, 9.6, 3.8)
6	2.40 (1H, *dd*, 14.0, 9.5)	2.39 (1H, *dd*, 14.1, 9.5)	2.65 (1H, *dd*, 15.0, 9.5)	2.65 (1H, *dd*, 14.4, 9.3)	2.32 (1H, *dd*, 14.0, 9.5)	2.64 (1H, *dd*, 14.4, 9.5)
	2.65 (1H, *dd*, 14.0, 4.3)	2.62 (1H, *dd*, 14.1, 4.3)	2.89 (1H, *dd*, 15.0, 4.5)	2.64 (1H, *dd*, 14.4, 9.3)	2.69 (1H, *dd*, 14.0, 4.3)	2.85 (1H, *dd*, 14.4, 4.5)
				2.83 (1H, *dd*, 14.4, 4.6)		
				2.89 (1H, *dd*, 14.4, 4.6)		
8	6.09 (1H, *q*, 6.5)	6.11 (1H, *q*, 7.3)	6.18 (1H, *q*, 5.9)	6.16 (1H, *br q*, 5.7)	6.12 (1H, *q*, 7.3)	6.16 (1H, *q*, 6.9)
10	1.72 (3H, *d*, 6.5)	1.72 (3H, *d*, 7.3)	1.74 (3H, *d*, 5.9)	1.73 (6H, *m*)	1.76 (3H, *d*, 7.3)	1.73 (3H, *d*, 6.9)
OMe		3.63 (3H, *s*)				
Glucose						
1′	4.83 (1H, *d*, 7.7)	4.79 (1H, *d*, 7.7)	4.82 (1H, *d*, 7.3)	4.83 (2H, *d*, 7.7)	4.81 (1H, *d*, 7.8)	4.32 (1H, *d*, 8.0)
						4.82 (1H, *d*, 7.7)
Tyrosol						
1″	4.28 (2H, *m*)	4.27 (2H, *t*, 6.6)	4.29 (2H, *t*, 6.8)	4.36 (2H, *t*, 6.5)	4.29 (2H, *m*)	4.28 (2H, *dt*, 11.1, 6.5)
2″	2.86 (2H, *t*, 6.6)	2.86 (2H, *t*, 6.6)	2.82 (*m*)	2.97 (2H, *t*, 6.5)	2.86 (2H, *t*, 6.6)	2.85 (2H, *t*, 6.6)
4″, 8″	7.06 (2H, *d*, 8.4)	7.06 (2H, *d*, 8.6)	7.06 (2H, *d*, 8.6)	7.28 (2H, *d*, 8.6)	7.09 (2H, *d*, 8.6)	7.05 (2H, *d*, 8.3)
5″, 7″	6.71 (2H, *d*, 8.4)	6.71 (2H, *d*, 8.6)	6.71 (2H, *d*, 8.6)	7.00 (2H, *d*, 8.6)	6.72 (2H, *d*, 8.6)	6.71 (2H, *d*, 8.3)
1‴			3.75 (2H, *t*, 6.8)	3.75 (2H, *t*, 7.0)		3.76 (1H, *dt*, 9.4, 7.0)
2‴			2.82 (*m*)	2.81 (2H, *t*, 7.0)		2.93 (2H, *t*, 7.0)
4‴, 8‴			7.25 (2H, *d*, 8.5)	6.99 (2H, *d*, 8.6)		7.28 (2H, *d*, 8.3)
5‴, 7‴			6.99 (2H, *d*, 8.5)	7.24 (2H, *d*, 8.6)		6.98 (2H, *d*, 8.3)
1⁗				4.29 (2H, *dt*, 6.7, 1.6)		
2⁗				2.83 (2H, *t*, 6.7)		
4⁗, 8⁗				7.05 (2H, *d*, 8.6)		
5⁗, 7⁗				6.71 (2H, *d*, 8.6)		
Butanol						
1	4.06 (2H, *t*, 7.3)					
2	1.60 (2H, five, 7.3)					
3	1.38 (2H, six, 7.3)					
4	0.93 (3H, *t*, 7.3)					

Coupling constants (J values in Hz) are shown in parentheses.

Table 2. ^{13}C-^{1}H NMR spectral data of glucosides **1**–**6** in CD_3OD

C	1	2	3	4	5	6	
Aglucone							
1	95.2	95.2	95.4	95.4	95.3	95.4	
3	155.1	155.1	155.2	155.4	155.3	155.3	
4	109.5	109.5	109.5	109.4	109.3	109.3	
5	31.8	31.7	31.7	31.7	31.7	31.8	31.7
6	41.2	40.9	41.0	41.0	41.0	41.2	41.0
7	173.3	173.5	171.6	171.7	171.5	175.2	171.6
8	124.7	124.8	125.1	125.2	125.2	124.9	125.1
9	130.6	130.4	130.6	130.5	130.5	130.5	130.4
10	13.7	13.6	13.8	13.9	13.9	13.8	13.9
11	168.1	168.1	168.1	168.1	168.0	168.2	168.1
OMe		52.2					
Glucose							
1′	100.8	100.9	101.1	101.0	101.0	100.9	101.0	104.3
2′	74.8	74.8	74.8	74.7	74.7	74.8	74.7	75.0
3′	77.9	77.9	77.9	77.9	77.9	77.9	77.8	77.8
4′	71.5	71.5	71.4	71.4	71.4	71.4	71.5	71.5
5′	78.4	78.4	78.4	78.3	78.3	78.3	78.2	78.0
6′	62.8	62.7	62.7	62.6	62.6	62.7	62.7	62.6
Tyrosol							
1″	66.6	66.4	66.4	66.0		66.4	66.4	
2″	35.3	35.3	35.3	35.3		35.3	35.2	
3″	130.2	130.2	130.2	137.4		130.3	130.2	
4″,8″	131.0	130.9	130.9	131.0		131.0	131.0	
5″,7″	116.3	116.3	116.3	122.7		116.3	116.3	
6″	157.0	157.0	157.0	150.5		157.0	156.9	
1‴			64.1	64.1			71.3	
2‴			39 6	39.5			36.5	
3‴			138.2	138.2			137.9	
4‴,8‴			130.9	131.0			131.0	
5‴,7‴			122.5	122.5			122.5	
6‴			150.5	150.7			150.4	
1⁗				66.5				
2⁗				35.5				
3⁗				130.2				
4⁗,8⁗				131.0				
5⁗,7⁗				116.3				
6⁗				157.0				
Butanol								
1	65.7							
2	31.8							
3	20.2							
4	14.1							

ν_{max}^{KBr} cm^{-1}: 3400, 2950, 1700, 1630, 1520, 1080, 920, 820, 770. ^{1}H and ^{13}C NMR: see Tables 1 and 2. Positive ion FAB-MS, *m/z*: 525 $[M+H]^+$, 345 $[M-O\text{-Glc}]^+$. (Found: C, 57.2; H, 5.9. Calcd for $C_{25}H_{32}O_{12}$: C, 57.3; H, 6.1%.)

Fraxiformoside (**3**). Powder, $[\alpha]_D^{27}$ −111° (MeOH; *c* 0.42). UV λ_{max}^{EtOH} nm (log ε): 201 (4.62), 222 (4.40), 270 (3.09), 279 (3.15), 286 (3.16). IR ν_{max}^{KBr} cm^{-1}: 3400, 2950, 1740, 1700, 1630, 1515, 1080, 920, 830, 770. ^{1}H and ^{13}C NMR: see Tables 1 and 2. Positive ion FAB-MS, *m/z*: 631 $[M+H]^+$, 451 $[M-O\text{-Glc}]^+$. (Found: C, 61.2; H, 5.9. Calcd for $C_{32}H_{38}O_{13}$: C, 61.0; H, 6.0%.)

Fraximalacoside (**4**). Powder, $[\alpha]_D^{27}$ −123° (MeOH; *c* 0.41). UV λ_{max}^{EtOH} nm (log ε): 204 (3.99), 220 (4.03), 228 (4.03), 236 (3.99), 244 (3.90), 276 (3.14). IR ν_{max}^{KBr} cm^{-1}: 3400, 2950, 1740, 1700, 1630, 1515, 1080, 920, 830, 770. ^{1}H and ^{13}C NMR: see Tables 1 and 2. Positive ion FAB-MS, *m/z*: 1123 $[M+H]^+$, 943 $[M-O\text{-Glc}]^+$, 764 $[M-(O\text{-Glc})_2]^+$. (Found: C, 60.1; H, 6.0. $C_{56}H_{66}O_{24}$ requires: C, 59.9; H, 5.9%.)

Isoligustrosidic acid (**5**). Powder, $[\alpha]_D^{27}$ −139° (MeOH; *c* 0.23). UV λ_{max}^{EtOH} nm (log ε): 202 (4.30), 226 (4.30), 226 (4.64), 280 (3.23). IR ν_{max}^{KBr} cm^{-1}: 3400, 2900, 1700, 1630, 1518, 1080, 920, 800, 770. ^{1}H and ^{13}C NMR: see Tables 1 and 2. Positive ion FAB-MS, *m/z*: 511 $[M+H]^+$, 331 $[M-O\text{-Glc}]^+$. (Found: C, 56.6; H, 6.0. Calcd for $C_{24}H_{30}O_{12}$: C, 56.5; H, 5.9%.)

1‴-O-β-D-*Glucosylfraxiformoside* (**6**). Powder, $[\alpha]_D^{27}$ −130° (MeOH; *c* 0.38). UV λ_{max}^{EtOH} nm (log ε): 202 (4.64), 222 (4.40), 271 (3.11), 280 (3.15), 284 (3.15). IR ν_{max}^{KBr} cm^{-1}:

3400, 2900, 1740, 1700, 1630, 1515, 1080, 920, 830, 770. ^{1}H and ^{13}C NMR: see Tables 1 and 2. Positive ion FAB-MS, *m/z*: 793 $[M+H]^+$, 613 $[M-O\text{-Glc}]^+$, 434 $(M-(O\text{-Glc})_2]^+$. (Found: C, 57.4; H, 5.9. Calcd for $C_{38}H_{48}O_{18}$: C, 57.5; H, 6.1%.)

Cosmosiin (7). Yellow powder, UV λ_{max}^{EtOH} nm (log ε): 204 (4.08), 268 (3.86), 337 (4.00). IR ν_{max}^{KBr} cm^{-1}: 3400, 2900, 1650, 1600, 1580, 1480, 1140, 1290, 1178, 830. ^{1}H NMR (300 MHz, DMSO): δ 6.47 (1H, *s*, H-3), 6.81 (1H, *s*, H-6), 6.85 (1H, *s*, H-8), 7.95 (2H, *d*, $J=8.8$ Hz, H_2-2′, H_2-6′), 6.90 (2H, *d*, $J=8.8$ Hz, H_2-3′, H_2-5′), 5.06 (1H, *d*, $J=7.1$ Hz, GlcH-1). ^{13}C NMR (75 MHz, DMSO): δ 164.6 (C-2), 103.3 (C-3), 182.2 (C-4), 161.3 (C-5), 99.8 (C-6), 163.2 (C-7), 95.2 (C-8), 157.2 (C-9), 105.5 (C-10), 121.3 (C-1′), 129.8 (C-2′), 116.3 (C-3′), 161.5 (C-4′), 116.3 (C-5′), 129.8 (C-6′), 100.2 (GlcC-1), 73.3 (GlcC-2), 77.3 (GlcC-3), 69.9 (GlcC-4), 76.6 (GlcC-5), 61.0 (GlcC-6) [1]. Positive ion FAB-MS, *m/z*: 433 $[M+H]^+$, 253 $[M-O\text{-Glc}]^+$.

Methanolysis of glucoside **4**. A soln of **4** (102.3 mg) in MeOH (10 ml) was heated for 36 hr under reflux. After concn *in vacuo*, the residue was purified by CC on silica gel ($CHCl_3$–MeOH, 9:2) to give **2** (30.6 mg) and **3** (25.1 mg).

Methanolysis of glucoside **6**. A soln of 6 (90.9 mg) in MeOH (10 ml) was heated for 56 hr under reflux. After concn *in vacuo*, the residue was purified by CC on silica gel ($CHCl_3$–MeOH, 9:2) to give **2** (44.5 mg) and salidroside **8** (22.2 mg).

Salidroside (**8**). Powder, UV λ_{max}^{EtOH} nm (log ε): 222.6 (3.58), 278 (2.87). IR ν_{max}^{KBr} cm^{-1}: 3400, 1600, 1512, 1235, 1045, 810, 560. ^{1}H NMR (200 MHz, CD_3OD): δ 3.71 (2H, *t*, $J=7.2$ Hz, H_2-1), 2.83 (2H, *t*, $J=7.2$ Hz, H_2-2), 7.06 (2H, *d*, $J=8.1$ Hz, H_2-4, 8), 6.69 (2H, *d*, $J=8.1$ Hz, H_2-5,7), 4.29 (1H, *d*, $J=7.8$ Hz, GlcH-1). ^{13}C NMR (50 MHz, CD_3OD): δ 72.1 (C-1), 36.3 (C-2), 130.7 (C-3), 130.9 (C-4), 116.1 (C-5), 156.8 (C-6), 116.1 (C-7), 130.9 (C-8), 104.3 (GlcC-1), 75.1 (GlcC-2), 78.0 (GlcC-3), 71.6 (GlcC-4), 77.9 (GlcC-5), 62.7 (GlcC-6) [5].

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