Communications to the Editor

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STRUCTURES OF MAGNOLOSIDES B AND C. NOVEL PHENYLPROPANOID GLYCOSIDES WITH ALLOPYRANOSE AS CORE THE SUGAR UNIT

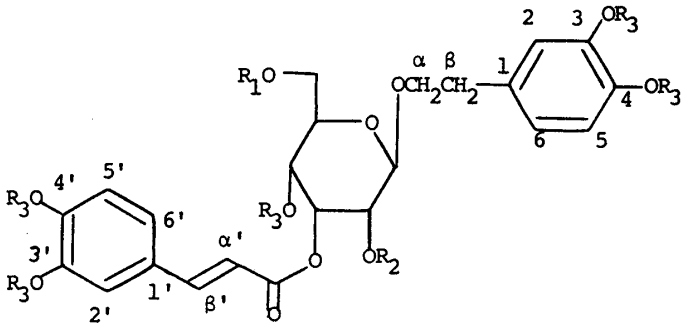
Takashi Hasegawa, Yoshiyasu Fukuyama,* Toshihide Yamada, and Kazuyuki Nakagawa
Tokushima Research Institute, Otsuka Pharmaceutical Co. Ltd., 463-10 Kagasuno, Kawauchi-cho, Tokushima 771-01, Japan

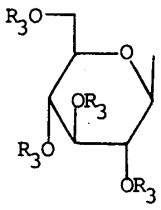
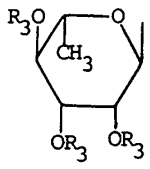
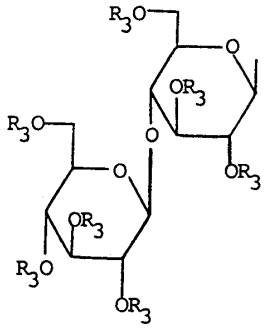
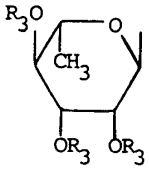
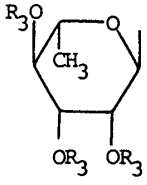
Magnolosides B and C, new phenylpropanoid glycosides have been isolated from the MeOH extract of Magnolia obovata Thunb. on the basis of spectroscopic data and chemical evidence, their structures have been established respectively as 3,4-dihydroxy-β-phenyl-ethyl-O-α-L-rhamnopyranosyl-(1→2)-O-β—D-glucopyranosyl-(1→6)-3-O-caffeoyl-β—D-allopyranoside and 3,4-dihydroxy-β—phenyl-ethyl-O-α—L-rhamnopyranosyl-(1→2)-O-[O-β—D-glucopyranosyl-(1->4)-β—D-glucopyranosyl-(1→6)]-3-O-caffeoyl-β—D-allopyranoside.

KEYWORDS - Magnoliaceae; Magnolia obovata; phenylpropanoid glycoside; magnoloside B; magnoloside C; allopyranose

In a previous paper,[1] we reported the structure of a novel phenylpropanoid glycoside, magnoloside A (3), isolated from the medicinal plant, Magnolia obovata Thunb. Magnoloside A is unique among the phenylpropanoids in having allose as the core sugar unit.[2] Further study of the polar constituents in M. obovata resulted in the isolation of additional phenylpropanoid glycosides 1 and 2 named magnolosides B and C. In this paper, we wish to report the structures of 1 and 2.

Magnoloside B (9.0 g) and C (0.8 g) were obtained as colorless powders by a combination of silica gel, Toyopearl HW-40F, and Sephadex LH-20 chromatographies of the n-BuOH soluble portion (150 g). Compound 1 had the following physical data: $[\alpha]_D$ - 54.1° (c 0.92, EtOH); IR (KBr) 3400 (OH), 1700 (conjugated ester), 1605 and 1520 cm^{-1} (aromatic); UV (EtOH) 218 (ε 18800), 242 (ε 10000), 290 (ε 12400), and 330 (ε 17200) nm. The FABMS exhibited quasi-molecular ion peaks due to $[M + Na]^+$ at m/z 809 and $[M + 2Na - 1]^+$ at m/z 832, giving the molecular formula $C_{35}H_{46}O_{20}$ coupled with the number and kind of the carbons available from the ^{13}C NMR data. The ^1H NMR and ^{13}C NMR spectra[3] of 1 indicated that its structure was closely related to that of magnoloside A (3) except for the presence of an extra sugar moiety. Acetylation of 1 with Ac_2O/pyr. overnight led to a fully acetylated derivative (1a)[4] (R_3 = Ac in 1), the ^1H NMR spectrum of which revealed the presence of eight aliphatic acetyl signals (δ 1.91, 1.93, 1.99, 2.00 x 2, 2.03, 2.08, and 2.13) and four aromatic acetyl signals (δ 2.25, 2.27, 2.31 x 2). Treating of 1 with aqueous 0.1 N HCl under refluxing yielded compound 4, and rhamnose and glucose as the detectable sugars on TLC.[5] This



	R_1	R_2	R_3
1			H
2			H
3	H		H
4	H	H	H

suggests that the extra sugar was glucose and that both sugars were the terminal units. Further evidence for the terminal glucose and rhamnose was obtained from the observation of pertinent fragment ion peaks at m/z 331 $[Ac_4\ Glc]^+$ and at m/z 273 $[Ac_3\ Rham]^+$ in the EIMS of 1a. Pertrifluoroacetate (1b) (R_3 = $COCF_3$) readily prepared in an NMR tube was measured by ^1H NMR. Detailed proton decoupling experiments of 1b[6] disclosed the presence of allopyranoside as the core sugar unit, and rhamnose and an additional glucose as the terminal sugar moieties as well as 3,4-dihydroxy phenylethyl and caffeoyl groups. This spectral and chemical evidence implied that the structure of 1

Table I. ^{13}C NMR Data for Sugar Carbons of 1, 2, and 3

	C	1[a]	2[a]	3[b]	δ (1)-δ (3)	δ (2)-δ (1)
Allo	1	98.32	98.34	98.59	-0.27	+0.02
	2	70.99	71.02	71.39	-0.40	+0.03
	3	73.55	73.58	74.05	-0.50	+0.03
	4	66.85	66.83	67.54	-0.69	-0.02
	5	75.15	75.18	76.09	-0.94*	+0.03
	6	69.68	69.69	62.96	+6.72*	+0.01
Rham	1	100.78	100.75	100.93	-0.15	-0.03
	2	71.92	71.92	71.98	-0.06	0.00
	3	71.92	72.18	72.09	-0.17	+0.26
	4	73.79	73.79	78.95	-0.16	0.00
	5	69.87	69.87	69.97	-0.10	0.00
	6	17.93	17.95	17.84	+0.09	+0.02
Glc	1	104.82	104.58			-0.24
	2	75.04	74.81			-0.23
	3	77.86	76.18			-1.68*
	4	71.50	80.54			+9.04*
	5	77.86	76.41			-1.45*
	6	62.66	61.79			-0.87

a) 62.9 MHz in methanol-d_4; b) 100 MHz in methanol-d_4.

should correspond to that of 3 bearing the extra terminal glucose. The linkage position of the extra glucose could be reasonably clarified by comparison of the ^{13}C NMR data of 1 and 3 (Table I). Namely, the allose C-5 and C-6 signals appeared at higher and lower fields, by -0.94 and +6.72 ppms, respectively, than the corresponding ones in 3. But the remaining signals were found to be in good accordance with each other. The glycosylation shifts clearly indicated that the extra terminal glucose must be connected at C-6 on the inner allose, and also its anomeric configuration was assigned to β considering the large J value (7.9 Hz) for H-1 on the glucose part. Thus, the structure of magnoloside B (1) was found to be 3,4-dihydroxy-β—phenyl-ethyl-O-α—L-rhamnopyranosyl-(1→2)-O-β—D-glucopyranosyl-(1→6)-3-O-caffeoyl-β—D-allopyranoside.

Magnoloside C (2),[7] $[\alpha]_D$ -73.2° (c 0.41, EtOH), contained 3,4-dihydroxyphenethyl and caffeoyl groups as its IR and UV spectra showed absorptions similar to the magnolosides. The FABMS of 2 not only exhibited quasi-molecular ion peaks at m/z 971 $[M + Na]^+$ and m/z 949 $[M + H]^+$, but also its ^{13}C NMR spectrum contained the signals due to the twenty-four sugar carbons, suggesting that 2 has an additional sugar moiety on magnoloside B (1). Acetylation of 2 furnished a fully acetylated compound (2a) (R_3 = Ac in 2), the ^1H NMR spectrum of which had eleven aliphatic acetyl and four aromatic acetyl signals. Mild hydrolysis of 2 in refluxing aqueous 0.1 N HCl again yielded compound 4 and rhamnose and glucose. These chemical and spectral data disclosed that the extra glucose in 2 was a terminal unit and was bonded elsewhere at C-OH on the glucose unit in 1 through

an ether linkage. This extra terminal glucose was reasonably rationalized to be connected to C-4 on the inner glucose unit, since the C-3, C-5, and C-4 carbon signals due to the inner glucose in 2 appeared at higher and lower fields by -1.68 and -1.45 ppms, and +9.04 ppm, respectively, than the corresponding ones in 1, and the other carbon signals[9] revealed no large shift values (Table I). Finally, it was evident from the J value [7.4 Hz for H-1 in 2c (R_3 = $COCF_3$ in 2)] that the anomeric configuration of the additional glucose moiety was β.
Accordingly, the structure proposed for 2 was 3,4-dihydroxy-β-phenyl-ethyl-O-α-L-rhamnopyranosyl-(1→2)-O-[O-β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl-(1->6)]-3-O-caffeoyl-β-D-allopyranoside.

All of the magnolosides so far isolated from M. obovata contain a rarely occurring allopyranose.

REFERENCES AND NOTES

1) T. Hasegawa, Y. Fukuyama, T. Yamada, and K. Nakagawa, Chem. Lett., 1988, 167.
2) M. F. Lahloub, G. -A. Gross, O. Sticher, T. Winkler, and H. -R. Schulten, Planta Med., 1986, 352.
3) ^{13}C NMR data of 1 except for the sugar carbons listed in Table I: δ 36.64 (β), 72.18 (α), 115.06 (2'), 115.25 (α'), 116.38 (5'), 116.51 (2), 117.13 (5), 121.37 (6), 123.07 (6'), 127.72 (1'), 131.52 (1), 144.51 (3), 145.91 (4), 146.70 (3'), 147.27(β'), 149.55 (4'), 168.82 (CO).
4) 1a: IR (KBr) 1750, 1640, and 1510 cm^{-1}.
5) The sugars were detected in the free form by TLC [silica gel, iPrOH : EtOAc : H_2O (7 : 2 : 1), rhamnose : Rf = 0.65; glucose : Rf = 0.44].
6) For 1b (R_3 = $COCF_3$) ^1H NMR data (400 MHz, pyridine-d_5): δ 1.39 (3 H, d, 6.4 Hz, rham-6-H), 3.11 (2 H, t, 6.4 Hz, β-H), 3.95 (1 H, dt, 9.8, 6.4 Hz, α-H), 4.35 (1 H, dt, 9.8, 6.4 Hz, α-H), 4.21 (1 H, dd, 11.3, 4.9 Hz, allo-6-H), 4.42 (1 H, dd, 7.9, 3.5 Hz, allo-2-H), 4.57 (1 H, dd, 11.3, 2.5 Hz, allo-6-H), 4.82 (1 H, m, allo-5-H), 4.82 (1 H, dq, 9.8, 6.4 Hz, rham-5-H), 4.99 (1 H, dd, 12.8, 4.4 Hz, glc-6-H), 5.06 (1 H, dd, 12.8, 3.5 Hz, glc-6-H), 5.11 (1 H, ddd, 9.4, 4.4, 3.5 Hz, glc-5-H), 5.45 (1 H, d, 7.9 Hz, allo-1-H), 5.71 (1 H, dd, 9.8, 3.5 Hz, allo-4-H), 5.69 (1 H, t, 9.8 Hz, rham-4-H), 5.78 (1 H, d, 2.0 Hz, rham-1-H), 5.80 (1 H, d, 7.9 Hz, glc-1-H), 6.08 (1 H, dd, 9.4, 7.9 Hz, glc-2-H), 6.16 (1 H, dd, 9.8, 3.5 Hz, rham-3-H), 6.20 (1 H, dd, 3.5, 2.0 Hz, rham-2-H), 6.25 (1 H, t, 9.4 Hz, glc-4-H), 6.48 (1 H, t, 3.5 Hz, allo-3-H), 6.69 (1 H, t, 9.4 Hz, glc-3-H), 7.00 (1 H, d, 15.8 Hz, α'-H), 7.42 (1 H, dd, 8.4, 1.5 Hz, 5-H), 7.59 (1 H, d, 1.5 Hz, 2-H), 7.60 (1 H, d, 8.4 Hz, 5-H), 7.69 (1 H, d, 8.4 Hz, 5'-H), 7.74 (1 H, dd, 8.4, 1.5 Hz, 6'-H), 8.02 (1 H, d, 1.5 Hz, 2'-H), 8.08 (1 H, d, 15.8 Hz, β'-H).
7) 2: IR (KBr) 3400 (OH), 1690 (conjugated ester), 1600 and 1520 cm^{-1} (aromatic); UV (EtOH) 218 (ε 16500), 244 (ε 8900), 290 (ε 10700), 330 (ε 15000) nm.
8) 2a (R_3 = Ac): IR (KBr) 1750, 1640, and 1510 cm^{-1}; EIMS (20 eV) m/z 331 [Ac_4 Glc]$^+$, 289 [Ac_3 Glc]$^+$, 273 [Ac_3 Rham]$^+$, and 247 [$(AcO)_2PhCH=CHCO\cdot$].
9) ^{13}C NMR data of the terminal glucose carbons in 2: δ 104.49 (1), 74.81 (2), 77.95 (3), 71.27 (4), 77.74 (5), 62.36 (6).

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