120.3 (C-5″), 129.6 (C-6″), 55.2 (O-CH_3). ^{1}H-NMR ($CDCl_3$, 300.13 MHz): δ = 2.34 (3H, s, N-Me), 1.93 (1H, m, H-2), 1.90 (1H, m, H-3a), 1.45 (1H, m, H-3b), 1.78 (1H, m, H-4a), 1.63 (1H, m, H-4b), 3.10 (1H, ddd, 5.4, 5.4, 5.4, H-5a), 2.14 (1H, q, 10.8, H-5b), 1.63 (1H, m, H-1′a), 1.26 (1H, m, H-1′b), 1.28 (10 H, sl, H-2′ to -6′), 1.35 (2H, m, H-7′), 1.58 (2H, m, H-8′), 2.58 (2H, d, 6.9, H-9′), 7.15 (1H, m, H-6″), 6.87 (1H, m, H-5″), 7.16 (1H, m, H-4″), 6.68 (1H, m, H-3″), 3.63 (O-CH_3).

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Two New Monogalactosylacylglycerols from *Hydrocotyle ramiflora*

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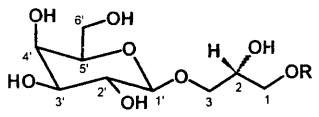
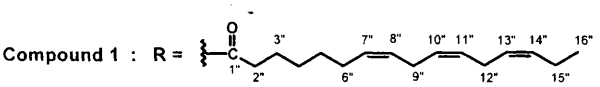
Abstract: **Two new monogalactosylmonoacylglycerols (1, 2) and two known compounds (3, 4) were isolated from *Hydrocotyle ramiflora*. Based on physicochemical evidence and spectral data, the structures of 1, 2, 3, and 4 were determined as (2*S*)-1-*O*-(7*Z*,10*Z*,13*Z*-hexadecatrienoyl)-3-*O*-β-galactopyranosylglycerol, (2*S*)-1-*O*-(9*Z*,12*Z*-octadecadienoly)-3-*O*-β-galactopyranosylglycerol, α-spinasterol, and capsidiol 3-acetate, respectively.**

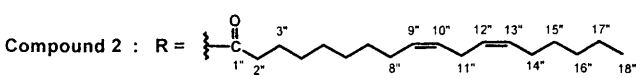
Hydrocotyle ramiflora (Umbelliferae), which is a perennial herb commonly found in Korea, as well as *H. nepalensis*, *H. rotundifolia*, *H. sibthorpioides* var. *batrachium* and *H. wilfodi* have been used in traditional Chinese herbal medicine for the treatment of inflammation, bruise, jaundice, and retention of urine (1, 2). Literature survey of *Hydrocotyle ramiflora* revealed that no phytochemical and pharmacological studies have been reported. Our study on this plant led to the isolation of two previously undescribed monogalactosylmonoacylglycerols (**1**, **2**) and two known compounds, α-spinasterol (**3**) and capsidiol 3-acetate (**4**). Numerous monogalactosyldiacyl and digalactosyldiacylglycerol derivatives have been isolated from algae and higher plants (3–6), but only a few monogalactosylmonoacylglycerol derivatives were reported (7, 8). The anti-inflammatory (9) and platelet aggregation inhibitory activity (10, 11) of galactosylacylglycerol derivatives were studied.

Two known compounds, α-spinasterol (**3**) and capsidiol 3-acetate (**4**) were characterized by comparing their physical and spectroscopic properties with published data (12, 13).

Compound **1** showed a quasimolecular ion peak at *m/z* 509 ($C_{25}H_{42}O_9Na$) in FABMS. Its IR spectrum displayed absorption bands at 3350 and 1720 cm^{-1}, indicating the presence of hydroxy and ester functionalities. Anomeric signals arising







from the sugar moiety appeared at δ = 4.22 (1H, d, J = 7.6 Hz) and δ = 105.33 in the ^{1}H- and ^{13}C-NMR spectra, respectively. The signals at δ = 105.33, 72.59, 74.87, 70.28, 76.78, and 62.49 in the ^{13}C-NMR spectrum and $J_{1'2'}$ (7.6 Hz, diaxial), $J_{3'4'}$ (3.4 Hz, axial-equatorial) in the ^{1}H-NMR spectrum suggested that the sugar in **1** is a β-galactopyranose (14). Analysis of the ^{1}H-^{1}H COSY and HMQC spectra of **1** allowed for the assignments of all the ^{1}H-NMR signals for the sugar and glycerol moieties. In the ^{13}C-NMR spectrum, a carbonyl carbon signal arising from the acyl group was observed at δ = 175.40. In ^{1}H-NMR spectrum, there was a methyl triplet at δ = 0.97 (3H, t, J = 7.6 Hz) and hydrogen signals of doubly allylic methylenes at δ = 2.80 (4H, br. t, J = 5.8 Hz). The geometry of the double bonds in the fatty acid moiety was presumed to be *cis* based on the chemical shift (δ = 26.41 and δ = 26.52) of the adjacent carbons in the ^{13}C-NMR spectrum (5, 15). Alkaline hydrolysis (5, 10) of **1** with NaOMe in MeOH yielded (7*Z*,10*Z*,13*Z*-hexadecatrienoyl methyl ester from the *n*-hexane solubles and β-galactopyranosylglycerol from the MeOH solubles. The fatty acid methyl ester was identified by GC-MS analysis and β-galactopyranosylglycerol by ^{1}H- and ^{13}C-NMR data (5, 14). In the HMBC spectrum, long-range connectivities were observed between the ester carbonyl carbon (δ = 175.40) and the H-1 protons (δ = 4.13 and δ = 4.16), indicating that the compound is acylated at C-1. Regardless of acyl substituents, chemical shifts and coupling constants in the ^{1}H-NMR spectrum were significantly different between (2*R*)- and (2*S*)-1-*O*-acyl-3-*O*-β-galactopyranosylglycerol (16). The ^{1}H-NMR spectrum of **1** was characteristic of the 2*S* type and thus, **1** was assigned the *S*-configuration. The structure of **1** was therefore assigned as (2*S*)-1-*O*-(7*Z*,10*Z*,13*Z*-hexadecatrienoyl)-3-*O*-β-galactopyranosylglycerol.

The FABMS of **2** gave a quasimolecular ion $(M + H)^+$ peak at m/z = 517 ($C_{27}H_{49}O_9$). ^{1}H-NMR and ^{13}C-NMR spectra of **2** closely resembled those of **1** except for the signals due to the fatty acid moiety. In ^{1}H-NMR spectrum, there were hydrogens signals of doubly allylic methylenes at δ = 2.77 (2H, br. t, J = 5.8 Hz). In the ^{13}C-NMR spectrum, four olefinic carbon signals were observed at δ = 129.05, 129.11, 130.95 and 130.88. Treatment of **2** with NaOMe-MeOH furnished β-galactopyranosylglycerol and 9*Z*,12*Z*-octadecadienoyl methyl ester (5, 10). The geometry of the double bonds in the fatty acid moiety was shown to be *cis* based on the chemical shift (δ = 26.53) of the adjacent carbons in the ^{13}C-NMR data (15). On this basis, the structure of **2** was assigned as (2*S*)-1-*O*-(9*Z*,12*Z*-octadecadienoyl)-3-*O*-β-galactopyranosylglycerol.

Materials and Methods

^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AMX-500. IR spectra were measured on Nicolet model 205 FT-IR spectrophotometer. Mass spectra were recorded on a Hewlett-Packard 5890 II GC/Hewlett-Packard 5988 MS system, and fast atom bombardment mass spectrum was obtained on a VG70-VSEQ mass spectrometer (VG Analytical, UK). HPLC was equipped with refective index detector (RI-71), 306 pump with 10SC head (Gilson).

Hydrocotyle ramiflora was collected in Suwon, Korea in September 1996. A voucher specimen (SKK-11-007) is deposited in the College of Pharmacy, Sung Kyun Kwan University.

Half-dried and chopped whole plant materials (1.5 kg) were extracted with MeOH for 7 days at room temperature twice and for 5 hours at 50 °C. The concentrated MeOH extract (70 g) was suspended in H_2O (800 ml) and successively partitioned with CH_2Cl_2, EtOAc and BuOH (each 800 ml). The concentrated extract (40 g) of the CH_2Cl_2 soluble portion was subjected to column chromatography over silica gel (600 g) eluted sequentially with hexane/EtOAc/MeOH (20 : 20 : 1, 1.5 L; 10 : 10 : 1, 2 L; 2 : 5 : 1, 2 L; 1 : 2 : 2, 1.5 L). Eluents were fractionated by TLC to yield fractions designated as HR1 - HR8: void volume (400 ml), HR1 (360 ml), HR2 (480 ml), HR3 (420 ml), HR4 (1.9 L), HR5 (1.2 L), HR6 (1.2 L), HR7 (360 ml) and HR8 (680 ml). The HR7 fraction (2 g) was further separated by column chromatography on silica gel (250 g) eluted with CH_2Cl_2 : MeOH : H_2O (50 : 10 : 1) to yield three subfractions (HR71 - HR73, each 150 ml). HR73 fraction was rechromatographed over Sephadex LH-20 (30 g) with CH_2Cl_2 : MeOH (1 : 3) to yield HR730 fraction (30 ml), HR730 fraction was further purified with reverse phase Lobar®-A column (RP-18, 40 - 63 μm, 1.0 × 24 cm, 90% MeOH/H_2O) to afford compounds **1** (30 mg) and **2** (5 mg). The HR3 fraction (1.2 g) was chromatographed with silica gel column (100 g, CH_2Cl_2 : EtOAc = 7 : 1) to give six subfractions (HR31 - HR36; each 100 ml). The HR33 (150 mg) fraction was further subjected to repeated column chromatography on silica gel (50 g, *n*-hexane : EtOAc, 3 : 1), sephadex LH-20 (30 g, CH_2Cl_2 : MeOH, 1 : 1) and HPLC (*n*-hexane : EtOAc, 4 : 1, silica gel column, 1.0 × 25 cm) to afford compound **3** (12 mg, t_R = 12 min). The HR35 (110 mg) was rechromatographed over silica gel (45 g, *n*-hexane : EtOAc, 3 : 1) to yield two subfractions (HR351 and HR352, 30 ml each). HR351 fraction was further purified with Sephadex LH-20 column chromatography (10 g, MeOH only) to afford compound **4** (10 mg).

Compound **1**: colorless oil; FAB-MS: m/z = 509 $[M + Na]^+$; $[\alpha]_D^{23}$: −24° (c 0.6, MeOH); IR (film): ν_{max} = 3350 (OH), 2900, 2800, 1720 (C=O) cm^{-1}; ^{1}H-NMR (CD_3OD): δ = 0.97 (3H, t, J = 7.6 Hz, H-16″), 1.37 (4H, m, H-4″,5″), 1.62 (2H, m, H-3″), 2.09 (4H, m, H-6″,15″), 2.35 (2H, t, J = 7.4 Hz, H-2″), 2.80 (3H, br. t, J = 5.8 Hz, H-9″,12″), 3.46 (1H, dd, J = 9.7, 3.4 Hz, H-3′), 3.51 (1H, m, H-5′), 3.53 (1H, dd, J = 9.7, 7.6 Hz, H-2′), 3.65 (1H, dd, J = 10.5, 4.6 Hz, H-3a), 3.71 (1H, dd, J = 11.5, 5.3 Hz, H-6′a), 3.76 (1H, dd, J = 11.5, 6.9 Hz, H-6′b), 3.82 (1H, dd, J = 3.4, 0.9 Hz, H-4′), 3.90 (1H, dd, J = 10.5, 5.2 Hz, H-3b), 3.98 (1H, m, H-2), 4.13 (1H, dd, J = 11.4, 5.9 Hz, H-1a), 4.16 (1H, dd, J = 11.4, 4.6 Hz, H-1b), 4.22 (1H, d, J = 7.6 Hz, H-1′), 5.34 (6H, m, H-7″, 8″, 10″, 11″, 13″, 14″); ^{13}C-NMR (CD_3OD): δ = 14.64 (C-16″), 21.48 (C-15″), 25.88 (C-3″), 26.41, 26.52 (C-9″, 12″), 28.02 (C-6″), 29.83, 30.39 (C-4″, 5″), 33.92 (C-2″), 62.49 (C-6′), 66.59 (C-1), 69.66 (C-2), 70.28 (C-4′), 71.91 (C-3), 72.59 (C-2′), 74.87 (C-3′), 76.78 (C-5′), 105.33 (C-1′), 128.24, 129.04, 129.19, 129.26, 130.94, 132.77 (C-7″, 8″, 10″, 11″, 13″, 14″), 175.40 (C-1″).

Compound **2**: colorless oil: FAB-MS: m/z = 517 $[M + H]^+$; $[\alpha]_D^{23}$: −24° (c 0.1, MeOH); IR (film): ν_{max} = 3350, 2950, 2850, 1730 cm^{-1}; ^{1}H-NMR (CD_3OD): δ = 0.90 (3H, t, J = 7.1 Hz, H-18″), 1.28 - 1.37 (14H, m, H-4″-7″, H-15″-17″), 1.61 (2H, m, H-3″), 2.06 (4H, m, H-8″, 14″), 2.34 (2H, t, J = 7.4 Hz, H-2″), 2.77 (2H, br. t, J = 6.5 Hz, H-11″), 3.46 (1H, dd, J = 9.7, 3.3 Hz, H-3′), 3.51 (1H, m, H-5′), 3.53 (1H, dd, J = 9.7, 7.6 Hz, H-2′), 3.65 (1H, dd, J = 10.5, 4.6 Hz, H-3a), 3.71 (1H, dd, J = 11.3, 5.3 Hz, H-6′a), 3.76 (1H, dd, J = 11.3, 6.9 Hz, H-6′b), 3.82 (1H, dd, J = 3.3, 1.0 Hz, H-4′), 3.90 (1H, dd, J = 10.5, 5.2 Hz, H-3b), 3.98 (1H, m, H-2), 4.13 (1H, dd, J = 10.3, 5.7 Hz, H-1a), 4.16 (1H, dd, J = 10.3,

4.8 Hz, H-1b), 4.22 (1H, d, J = 7.6 Hz, H-1′), 5.33 (4H, m, H-9″, 10″, 12″, 13″); ^{13}C-NMR (CD_3OD): δ = 14.39 (C-18″), 23.59 (C-17″), 30.18 (×2), 30.26, 30.45, 30.69, 32.65 (C-4″-7″, C-15″-16″), 25.97 (C-3″), 26.53 (C-11″), 28.14 (×2) (C-8″, 14″), 34.94 (C-2″), 62.49 (C-6′), 66.57 (C-1), 69.65 (C-2), 70.29 (C-4′), 71.90 (C-3), 72.58 (C-2′), 74.87 (C-3′), 76.79 (C-5′), 105.34 (C-1′), 129.05, 129.11, 130.88, 130.95 (C-9″, 10″, 12″, 13″), 175.46 (C-1″).

α-Spinasterol (**3**): white powder, m.p. 168 °C, $[\alpha]_D^{23}$: −4.27° (*c* 0.075, $CHCl_3$); EI-MS, ^{1}H-NMR, and ^{13}C-NMR data were in good agreement with those of α-spinasterol (12).

Capsidiol 3-acetate (**4**): colorless oil; IR, EI-MS, ^{1}H-NMR and ^{13}C-NMR data were in good agreement with those of capsidiol 3-acetate (13).

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Bioassay Guided Isolation of a New C_{18}-Polyacetylene, (+)-9(*Z*),17-Octadecadiene-12,14-diyne-1,11,16-triol, from *Cussonia barteri*

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Abstract: **A novel C_{18}-polyacetylene, (+)-9(*Z*),17-octadecadiene-12,14-diyne-1,11,16-triol (3), has been isolated from the ethyl acetate extract of *Cussonia barteri* (Araliaceae) leaves collected in Cameroon. The structure determination was achieved by NMR, mass, IR, and UV spectroscopy. The new polyenyne shows antibacterial activity against *Bacillus subtilis* and *Pseudomonas fluorescens*, antifungal activity against *Cladosporium cucumerinum*, molluscicidal activity against *Biomphalaria glabrata* at low concentrations, and in addition it possesses haemolytic activity.**

Polyacetylenes are common constituents of Araliaceae, and of interest to plant physiologists and pharmacologists because of their antibacterial, antifungal, and other biological activities (1). The C_{18}-polyacetylenes isolated so far are either carboxy- or hydroxymethyl-derivatives of falcarinol (**1**) or derivatives of falcarindiol (**2**) (1–3). We report on the isolation of a novel C_{18}-polyacetylene, (+)-9(*Z*),17-octadecadiene-12,14-diyne-1,11,16-triol (**3**, Fig. **1**), from the ethyl acetate extract of *Cussonia barteri* (Araliaceae) leaves.

Materials and Methods

Plant material: The plant material was collected in Cameroon in 1995, and identified by Dr. S. Yonkeu, Institute de Recherche Zoo Veterinaire, Wakwa, Cameroon. A specimen is deposited in the Herbarium of the Regional Research Centre of Wakwa, Ngaoundere Cameroon (voucher: W.150).

Isolation: The air-dried material (2.4 kg) was successively extracted with petrol ether (15 l), ethyl acetate (4 × 15 l), and methanol (2 × 15 l) to give 3 fractions F1 (18 g), F2 (149 g), and F3 (290 g), respectively. The crude extracts were tested against *Bacillus subtilis*, *Pseudomonas fluorescens* and *Cladosporium cucumerinum* at 50 μg and 250 μg by direct bioautographic TLC assays (4, 5). In addition haemolytic activity was examined in a modified way by direct bioautographic TLC assays: Fresh pig's blood in PBS-buffer [PBS-buffer/pig's blood/sodium citrate solution, 150 : 9 : 1] was sprayed onto analytical TLC plates [Merck, 20 cm × 20 cm, silica gel 60 F_{254}]. The activity was qualified by the inhibition or agglutination zones. As mobile phase petrol ether/ethyl acetate (3 : 7) was used. The water-soluble fractions were tested against