Two Acylglycerylgalactosides and a New Sesquiterpene Galactoside from the Flowers of *Hemisteptia lyrata* Bunge

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The flowers of *Hemisteptia lyrata* B. afforded two known acylglycerylgalactosides, 2',3'-di-*O*-(9*Z*,12*Z*,15*Z*-octadecatrienoyl)glyceryl β-D-galactopyranoside (1) and 2'-*O*-(9*Z*,12*Z*,15*Z*-octadecatrienoyl)glyceryl β-D-galactopyranoside (2), and a new sesquiterpene galactopyranoside, 7-eudesmene-1β,4β-diol-1-*O*-β-D-galactopyranoside (3). This is the first time that galactopyranosides (1-3) have been isolated from the genus Hemisteptia. Their structures and stereochemistry were elucidated by 1D and 2D NMR data, including COSY, NOESY and HMBC experiments.

Key words: *Diacylgalactosides, eudesmene, galactopyranoside, Hemisteptia lyrata, Sesquiterpene.*

Hemisteptia lyrata B. (Compositae) is a red-violet flower blooming from May to June throughout Korea, and is placed in only one genus Hemisteptia in many compositae. This plant has been used as traditional folk medicine in China and Korea for its anti-febrile, anti-bleeding, anti-tumor, anti-bacterial and anti-inflammatory remedy.[1)] Additionally, the young plants have been consumed in early spring as herb salads. Recently, we reported the isolation and structural determination of eight sesquiterpene lactones (SQLs), two flavonoids, and four polyacetylenes. And also investigated their medicinal properties such as *in vitro* cytotoxicity, anti-bacterial activities and tyrosinase inhibitory activities.[2-5)] In particular, SQLs has shown a significant cytotoxic and anti-bacterial activity against several human cancer cell lines and bacterial strains.[6-8)] Thus, there has been considerable interest in phytochemical investigations of *H. lyrata*. In the current experiment, our emphasis was placed on the isolation and structural elucidation of three galactopyranosides, 1,2-di-*O*-(9*Z*,12*Z*,15*Z*-octadecatrienoyl)-3-*O*-β-D-galactopyranosyl glycerol (**1**), 2-*O*-9*Z*,12*Z*,15*Z*-octadecatrienoyl-3-*O*-β-D-galactopyranosyl glycerol (**2**), and 7-eudesmene-1β,4β-diol 1-*O*-β-D-galactopyranoside (**3**). This is first report on the isolation of compounds **1-3** from Hemisteptia species.

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Abbreviations: COSY, Correlation Spectroscopy; HMBC, Heteronuclear Multiple Bond Connectivity; NOESY, Nuclear Overhauser Effect Correlation Spectroscopy.

Materials and Methods

Plant material. The sample of *Hemisteptia lyrata* Bunge was collected at Parkjeon, Hamyang, Korea in June 2000. A voucher specimen (Park, K. H. 103) of this raw material is deposited at the herbarium of the Gyeongsang National University (GNUC).

Instruments. Optical rotations were recorded on a PERKIN-ELMER polarimeter. IR spectra were recorded on a Bruker IFS66 infrared Fourier transform spectrophotometer (KBr) and UV spectra were measured in MeOH on a Beckman DU650 spectrophotometer. Low-resolution EIMS was obtained on a JEOL JMS-700 spectrometer. ^{1}H and ^{13}C NMR spectra along with 2D-NMR data were obtained on a Bruker AM 500 (^{1}H-NMR at 500 MHz, ^{13}C-NMR at 125 MHz) spectrometer in CD_3OD solution.

Extraction and isolation. The dried flowers (2.0 kg) were extracted with $CHCl_3$ (30 L) at room temperature for three days. The extracts were washed with brine, dried over anhydrous Na_2SO_4, and then concentrated to give a thickish residue (98.3 g). The residue was diluted with H_2O (0.9 L) to give an aqueous MeOH solution (0.1 L). And successively partitioned with hexane (2.0 L) and $CHCl_3$ (2.0 L). The $CHCl_3$ soluble residue (53.4 g) was chromatographed on a silica gel (1.2 kg, 70-230 mesh) column eluted with a gradient of 100% hexane to 100% EtOAc and then to 20% MeOH to afford twenty fractions (F1-F20). The Fraction F17 (2.3 g) was chromatographed over silica gel (300 g, 230-400 mesh) with a gradient elution starting from $CHCl_3$: MeOH (49 : 1) and then increasing the polarity to the final ratio of 1/1 volume percentage. Fifty fractions (100 m*l* each) were collected and combined to give six major subfractions (F17-1 through F17-

6), based on the comparison of TLC profiles after examination by shortwave UV light (254 nm) and by spraying with 10% v/v sulfuric acid in water. F17-3 (130 mg) was subjected to silica gel column chromatography using a mixture of $CHCl_3$: EtOH (49 : 1) and then increasing amounts of ethyl alcohol. Sub-subfractions were monitored by TLC using $CHCl_3$-EtOH (9 : 1) to afford 4 fractions (F17-3-1 to F17-3-4). Finally, compound **1** (20 mg) was isolated from F17-3-2 by preparative TLC with $CHCl_3$: EtOH (9 : 1). The purity of compound **1** was determined by TLC using the following developing solvents: $CHCl_3$: MeOH (4 : 1) (R_f 0.77), and $CHCl_3$: EtOH (9 : 1) (R_f 0.31). Fraction F17-5 (100 mg) was subjected to the silica gel column chromatography with a gradient elution of $CHCl_3$: EtOH gradient (49 : 1 → 19 : 1). Forty fractions (10 m*l* each) were collected. Subfraction 31-32 were pooled (30 mg) and subjected to a preparative TLC in $CHCl_3$: EtOH (9 : 1×2 times) solvent condition. Compound **2** (17 mg) was isolated by this chromatographic separation, and the homogeneity of **2** was confirmed by TLC in the following solvent system: $CHCl_3$: MeOH (4 : 1) (R_f 0.45), and chloroform-ethanol (4 : 1) (R_f 0.4). Fraction F18 (970 mg) was chromatographed over silica gel using $CHCl_3$: MeOH gradient (49 : 1 → 1 : 1) to afford 5 subfractions (F18-1 through F18-5). Subfraction F18-4 (140 mg) was purified by repeated silica gel column chromatography using $CHCl_3$: EtOH gradient (49 : 1 → 1 : 1) to afford 4 sub-subfractions (F18-4-1 to F18-4-4). Finally, compound **3** (20 mg) was isolated from F18-4-2 by preparative TLC with $CHCl_3$: MeOH (4 : 1). The purity of compound **3** was checked by TLC using the following developing solvents: $CHCl_3$: MeOH (4 : 1) (R_f 0.37), and $CHCl_3$: EtOH (4 : 1) (R_f 0.33).

Compound 1: Colorless oils; UV, λ_{max} (MeOH) 207 nm; EI/MS (70 eV) *m/z* (intensity, %) 775 (M+H, 2), 757 (0.5), 541 (2), 277 (8), 233 (8), 145 (22), 103 (70), 79 (100); IR ν_{max} 3400, 2920, 1740, and 1650 cm^{-1}; $[\alpha]^{20}$ +2.0° (*c*, 0.17 in MeOH); ^{1}H-NMR (500 MHz, CD_3OD) δ: 0.97 (6H, t, *J* = 7.5 Hz, H-18", 18'"), 1.28-1.38 (16H, m, H-4", 4'", 5", 5'", 6", 6'", 7", 7'"), 1.60 (4H, m, H-3", 3'"), 2.07 (8H, m, H-8", 8'", 17", 17'"), 2.31 (2H, t, *J* = 7.1 Hz, H-2"), 2.32 (2H, t, *J* = 7.1 Hz, H-2'"), 2.81 (8H, t, *J* = 6.0 Hz, H-11", 11'", 14", 14'"), 3.45 (1H, dd, *J* = 9.7, 3.3 Hz, H-3), 3.49 (1H, m, H-2), 3.49-3.52 (1H, m, H-5), 3.71-3.76 (2H, m, H-6), 3.74 (1H, m, H-1'a), 3.82 (1H, dd, *J* = 3.3, 0.8 Hz, H-4), 3.97 (1H, dd, *J* = 10.9, 5.4 Hz, H-1'b), 4.22 (1H, dd, *J* = 12.0, 6.7 Hz, H-3'a), 4.23 (1H, d, *J* = 7.5 Hz, H-1), 4.43 (1H, dd, *J* = 12.0, 3.0 Hz, H-3'b), 5.27 (m, H-2'), 5.31-5.37 (12H, m, H-9", 9'", 10", 10'", 12", 12'", 13", 13'", 15", 5'", 16", 16'"); ^{13}C-NMR (125 MHz, CD_3OD) δ: 15.1 (C-18", 18'"), 21.9 (C-17", 17'"), 26.4 (C-3", 3'"), 26.8 (C-14", 14'"), 26.9 (C-11", 11'"), 28.6 (C-8", 8'"), 30.6 (C-6", 6'", 7", 7'"), 30.8 (C-5", 5'"), 31.1 (C-4", 4'"), 35.4 (C-2"), 35.5 (C-2), 62.9 (C-6), 64.4 (C-3'), 69.1 (C-1'), 70.6 (C-4), 72.2 (C-2'), 77.2 (C-5), 75.3 (C-3), 72.8 (C-2), 105.7 (C-1), 128.7 (C-15",15'"), 129.4 (C-10", 10'"), 129.6 (C-12", 12'", 13", 13'"), 131.3 (C-9", 9'"), 133.2 (C-16", 16'"), 175.1 (C-1"), 175.4 (C-1'").

Compound 2: Colorless oils; UV, λ_{max} (MeOH) 205 nm; EI/MS (70 eV) *m/z* (intensity, %) 514 (M^+, 5), 496 (0.5), 478 (4), 352 (28), 278 (10), 233 (15), 103 (70), 79 (100); IR ν_{max}

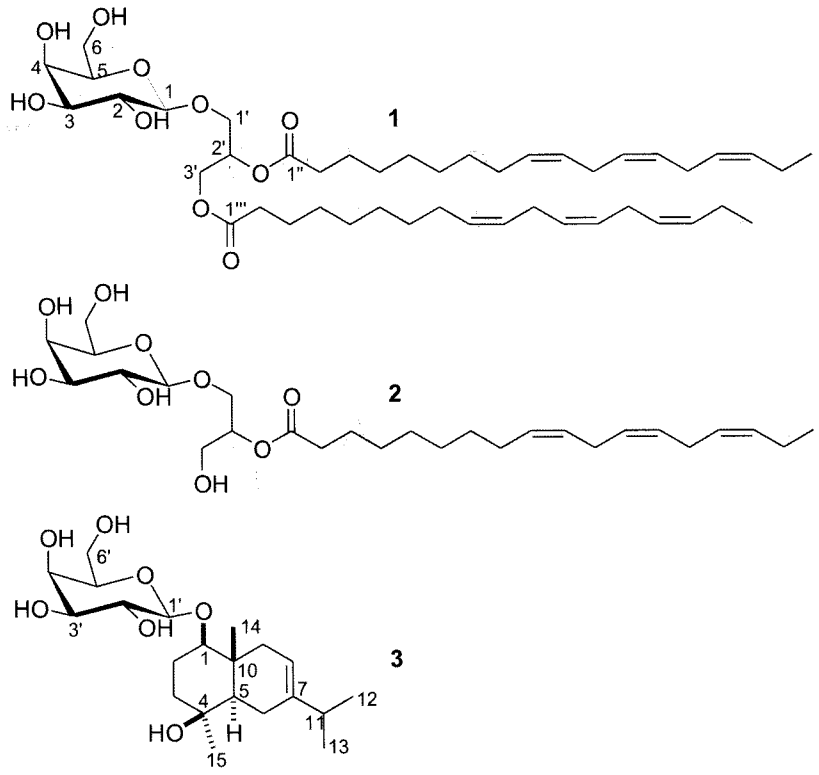

Fig. 1. Structures of compounds 1-3.

3400, 2920, 1740, and 1650 cm^{-1}; $[\alpha]^{20}$ +2.0° (*c*, 0.16 in MeOH); ^{1}H-NMR (500 MHz, CD_3OD) δ: 0.97 (3H, t, *J* = 7.5 Hz, H-18"), 1.28-1.38 (8H, m, H-4", 5", 6", 7"), 1.62 (2H, m, H-3"), 2.07 (4H, m, H-8", 17"), 2.35 (2H, t, *J* = 7.4 Hz, H-2"), 2.80 (4H, t, *J* = 6.0 Hz, H-11", 14"), 3.46 (1H, dd, *J* = 9.7, 3.3 Hz, H-3), 3.53 (1H, m, H-2), 3.49-3.55 (1H, m, H-5), 3.65 (1H, dd, *J* = 10.5, 4.6 Hz, H-1'a), 3.73 (2H, m, H-6), 3.82 (1H, brd, *J* = 2.8 Hz, H-4), 3.90 (1H, dd, *J* = 10.5, 5.2 Hz, H-1'b), 3.98 (1H, quint, *J* = 5.3 Hz, H-2'), 4.15 (2H, m, H-3'), 4.23 (1H, d, *J* = 7.6 Hz, H-1), 5.30-5.38 (6H, m, H-9", 10", 12", 13", 15", 16"); ^{13}C-NMR (125 MHz, CD_3OD) δ: 14.7 (C-18"), 21.5 (C-17"), 26.0 (C-3"), 26.4 (C-14"), 26.6 (C-11"), 28.2 (C-8"), 30.2 (C-7"), 30.3 (C-6"), 30.5 (C-5"), 30.7 (C-4"), 35.0 (C-2"), 62.5 (C-6), 66.6 (C-3'), 69.7 (C-2'), 70.3 (C-3), 71.9 (C-1'), 72.6 (C-2), 75.0 (C-4), 76.8(C-5), 105.4 (C-1), 128.3 (C-15"), 128.9 (C-10"), 129.3 (C-12", 13"), 131.1 (C-9"), 132.7 (C-16"), 175.5 (C-1").

Compound 3: Colorless oils: UV, λ_{max} (MeOH) 220 nm; EI/MS (70 eV) *m/z* (intensity, %) 400 (M^+, 11), 382 (4), 364 (4), 352 (16), 221 (82), 202 (78), 149 (100), 105 (76); HREIMS *m/z* 400.2461 (calcd. for $C_{21}H_{32}O_7$, 400.2462); IR ν_{max} 3410, 2900, 1640, and 1220 cm^{-1}; $[\alpha]^{20}$ +40.6° (*c*, 0.42 in MeOH); ^{1}H-NMR (500 MHz, CD_3OD) δ: 0.99 (3H, s, H-14), 1.01 (3H, d, *J* = 2.4 Hz, H-12), 1.03 (3H, d, *J* = 2.4 Hz, H-13), 1.14 (3H, s, H-15), 1.28 (1H, dd, *J* = 12.2, 5.1 Hz, H-5), 1.47 (1H, ddd, *J* = 14.0, 14.0, 3.8 Hz, H-3a), 1.69 (1H, m, H-2a), 1.75 (1H, dt, *J* = 14.0, 3.2, 3.2 Hz, H-3b), 1.87 (1H, m, H-2b), 1.89 (1H, d, *J* = 19.5Hz, H-9a), 1.98 (1H, dd, *J* = 17.0, 2.5 Hz, m, H-6a), 2.12 (1H, dd, *J* = 18.1, 5.6 Hz, H-9b), 2.15 (1H, m, H-6b), 2.19 (1H, quint, *J* = 6.6 Hz, H-11), 3.16 (1H, dd, *J* = 9.0, 7.8 Hz, H-2'), 3.22 (1H, m, H-5'), 3.28 (1H, m, H-4'), 3.34 (1H, dd, *J* = 4.4, 4.4 Hz, H-3'), 3.40 (1H, dd, *J* = 11.9, 3.8 Hz, H-1), 3.66 (1H, dd, *J* = 11.8, 5.7 Hz, H-6'a), 3.85 (1H, dd, *J* = 11.8, 2.3 Hz, H-6'b), 4.32 (1H, d, *J* = 7.7 Hz, H-1'), 5.31 (1H, d, *J* = 5.4 Hz, H-8); ^{13}C-NMR (125 MHz, CD_3OD) δ: 13.4 (C-14), 22.1 (C-12), 22.7 (C-13), 24.2 (C-2), 24.5 (C-6), 30.3 (C-15), 36.7 (C-11), 38.7 (C-10), 40.6 (C-3), 42.3 (C-9), 48.9 (C-5), 63.5 (C-6'), 71.8 (C-4), 72.4 (C-4'), 75.5 (C-2'), 78.2 (C-5'), 78.7 (C-3'), 87.3 (C-1), 102.3 (C-1'), 118.3 (C-8), 143.2 (C-7).

Results and Discussions

Dried flowers of *H. lyrata* were extracted with $CHCl_3$ and then defatted with *n*-hexane. Silica gel column chromatography of the dried $CHCl_3$-soluble fraction led to the isolation of the galactopyranosides **1**, **2**, and **3** (Fig. 1).

The EIMS of compound **1** exhibited a molecular ion peak at *m/z* 775 $[M+H]^+$ and a molecular formula $C_{45}H_{74}O_{10}$ with nine index of hydrogen deficiency, as deduced from its molecular formula. The IR spectrum of **1** showed absorption at 3400 and 1740 cm^{-1}, suggesting the presence of hydroxyl and carbonyl moiety. The ^{1}H-NMR spectrum of compound **1** revealed a broad signal at δ 1.28-1.38, two methyl groups at δ 0.97 (t, *J* = 7.5 Hz), and anomeric proton signal at δ 4.23 (d, *J* = 7.5 Hz) which were indicative to the presence of an aliphatic long-chain and sugar moiety. Sugar conformation was assumed to be a β form from the chemical shift and coupling constant value of anomeric proton signal.[9] The chemical shifts at δ 105.7, 72.8, 75.3, 70.6, 77.2, and 62.9 in the ^{13}C NMR spectrum, and coupling constants at $J_{1,2}$ (7.5 Hz, diaxial) and $J_{3,4}$ (3.3 Hz, axial-aquatorial) in the ^{1}H NMR spectrum clearly pointed out that compound **1** had a β-galactopyranose group.[10,11] And three oxygenated carbons (72.2, 69.1, and 64.4 ppm) originated from glycerol moiety were detected. The methylene signals, together with the integration of the olefinic hydrogen signals and the fragment ion peak at *m/z* 277 produced by α-cleavage to the carbonyl group, indicated the presence of two moles of octadeca-9, 12, 15-trienoic acid in the molecule. The stereochemistry of double bond in fatty acid were identified as *cis* configuration, because chemical shift value in allylic carbons (C-11", 14", 8", 11"', 14"', and 8"') were in 26-28 ppm range.[12] β-Galactopyranose should be linked to the C-1' of the glycerol, as indicated by the HMBC correlation between the anomeric proton H-1 and C-1', while the HMBC cross peaks H-2'/C-1", H-2"/C-1", H-3'/C-1"', and H-2"'/C-1"' indicated the attachment of acyl groups at the positions 2' and 3' of the glycerol moiety (Fig. 2). Based on all the above obtained evidences, the structure of **1** was established as 2',3'-di-*O*-(9Z,12Z,15Z-octadecatrienoyl)glyceryl β-D-galactopyranoside (**1**). This compound have been isolated from *Armoracia rusticana*,[13] *Rosa canina*,[14] and *Spinacia oleracea*,[12] however, it is the first report from genus Hemistepta.

The ^{1}H NMR spectral data for **2** were almost the same as those for **1**, except for the integration of the overlapped methylene signals of fatty acid residues. Therefore **2** were postulated to have one aliphatic long-chain moiety having

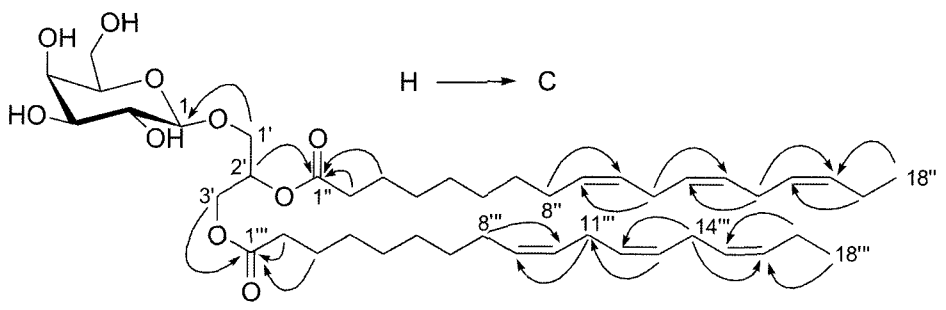

Fig. 2. Important HMBC correlations of 1.

three double bonds. The stereochemistry of double bonds in **2** were also identified as *cis*-configuration by the same reason in **1**. From the above obtained evidences, the structure of **2** was established as 2'-*O*-(9*Z*,12*Z*,15*Z*-octadecatrienoyl)glyceryl 1-*O*-β-D-galactopyranoside (**2**). This compound have been isolated from *Citrus hystrix*,[15] however, it is the first report from genus Hemistepta.

The EIMS of compound **3** exhibited a molecular ion peak at *m/z* 400 $[M]^+$. The molecular formula $C_{21}H_{36}O_7$ was deduced from its HREIMS and NMR. The structure of **3** was deduced from the ^1H and ^{13}C NMR spectral data including DEPT and 2D NMR experiments (^1H-^1H COSY, HMQC, and HMBC). The ^1H-NMR spectrum revealed the four tertiary methyl signal at δ 0.99, 1.01, 1.03, and 1.14, while six oxymethine proton signals appeared at δ 3.16, 3.22, 3.28, 3.34, 3.40, and 4.32. Twenty one carbon atoms were observed in ^{13}C NMR spectrum. Four methyl signal, five sp^3 methylene signals, nine methine signals, and three quaternary carbon signals were detected in DEPT analysis. Anomeric proton signal at δ 4.32 (d, J = 7.7 Hz) and signals at δ 102.3, 78.7, 78.2, 75.5, 72.4, and 63.5 in the ^{13}C NMR spectrum, and $J_{1,2}$ (7.7 Hz, diaxial), $J_{3,4}$ (4.4 Hz, axial-aquatorial) in the ^1H spectrum suggesting the presence of β-galactopyranose group.[9] ^1H-^1H COSY NMR spectrum of **3** showed five spin-systems for this compound. Thus, H-1 at δ 3.40 (dd, J = 11.9, 3.8 Hz) was coupled to H-2a/b at δ 1.69 and δ 1.87, which was in turn coupled to H-3a/b at δ 1.47 (ddd, J = 14.0, 14.0, 3.8 Hz) and δ 1.75 (dt, J = 14.0, 3.2 Hz). A second spin-system, H-5 at δ 1.28 (dd, J = 12.2, 5.1 Hz) showed vicinal coupling to H-6a/b at δ 1.98 and δ 2.15. A third spin-system was observed with H-8 at δ 5.31 (δ, J = 5.4 Hz) which exhibited a vicinal coupling with H-9a/b at δ1.89 and δ 2.12. A fourth spin-system was observed with δ 2.19 (H-11) which exhibited a vicinal coupling with H-12 (δ, J = 2.4 Hz) and H-13 (d, J = 2.4 Hz). The other spin system was identified as β-galactopyranose group. The connectivity between C-14 and H-1, C-1 and H-1', C-15 and H-3, C-15 and H-5, C-7 and H-12/13, C-14 and H-9 were determined on the basis of HMBC correlations (Fig. 3). Additionally, the ^1H and ^{13}C NMR signals of aglycone moiety was almost identical to those in published data.[16,17] And the relative stereochemistry of **3** was determined by 2D-NOESY experiments. Strong NOE cross peaks were observed between H-1 and H-3a, H-1 and H-9a,

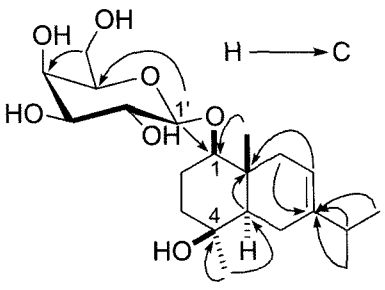

Fig. 3. Important HMBC correlations of 3.

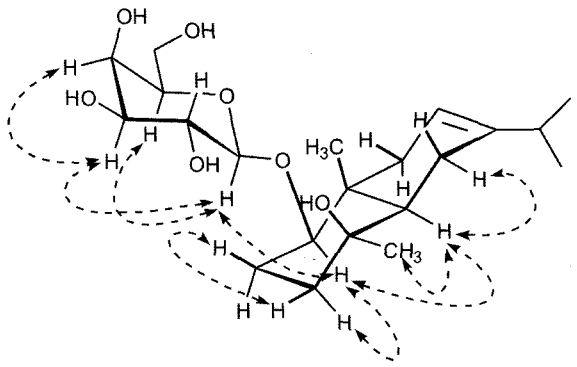

Fig. 4. Selected NOESY correlations of 3.

H-1 and H-5, H-5 and H-6a, H-15 and H-6a, H-1 and H-1' (Fig. 4). Thus, the structure of the new compound **3** was elucidated as 7-eudesmene-1β,4β-diol 1-*O*-β-D-galactopyranoside.

In summary, three galactopyranosides, 1,2-di-*O*-(9*Z*,12*Z*,15*Z*-octadecatrienoyl)-3-*O*-β-D-galactopyranosyl glycerol (**1**), 2-*O*-9*Z*,12*Z*,15*Z*-octadecatrienoyl-3-*O*-β-D-galactopyranosyl glycerol (**2**), and 7-eudesmene-1β,4β-diol 1-*O*-β-D-galactopyranoside (**3**) were isolated from the flowers of *H. lyrata*. Among the isolated compounds, **3** is a new sesquiterpene galactoside, and the others are the first isolation from this plant.

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