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NIRURIN: A NEW PRENYLATED FLAVANONE GLYCOSIDE FROM *PHYLLANTHUS NIRURII*

D.R. GUPTA and BAHAR AHMED

Department of Chemistry, University of Roorkee, Roorkee (U.P.) India

ABSTRACT.—A new prenylated flavanone glycoside, nirurin, has been isolated from *Phyllanthus nirurii*. On the basis of chemical and spectral studies, its structure is proposed as 5,6,7,4′-tetrahydroxy-8-(3-methylbut-2-enyl) flavanone-5-O-rutinoside (**1**). The aglycone, also a new flavanone, has been characterized as 5,6,7,4′-tetrahydroxy-8-(3-methylbut-2-enyl) flavanone, which may be designated as nirurinetin (**2**).

Phyllanthus nirurii L. (Euphorbiaceae), a small herb, has been reported to possess medicinal properties against jaundice, dropsy, and genitourinary infections (1). Earlier work on this plant showed the occurrence of phyllanthin, hypophyllanthin (2), quercetin, quercitrin, isoquercitrin, astragalin, rutin (3), kaempferol-4′-rhamnopyranoside, eriodictyol-7-rhamnopyranoside (4), and lup-20 (29)-en-3β-ol (5). On reinvestigation, a new glycoside of fisetin, characterized as the 4′-O-glucoside, has been reported from this laboratory (6). This communication reports the isolation and characterization of a new prenylated flavanone glycoside. This flavanone has been characterized as 5,6,7,4′-tetrahydroxy-8-(3-methylbut-2-enyl) flavanone-5-O-rhamnoglucoside, **1**, on the basis of specific color reactions and chemical and spectral data and is named nirurin. Besides nirurin; quercetin, quercitrin, isoquercitrin, astragalin, and rutin have also been isolated and characterized.

Compound **1** (nirurin) gave characteristic colors, i.e., red with Mg-HCl and Na-Hg/HCl, orange changing immediately to deep red with aqueous NaOH and NaOMe, orange with H_2SO_4 and $NaBH_4$ (7), an orange-red precipitate with 2,4-dinitrophenylhydrazine (8), and blue with $FeCl_3$. It gave a positive Molisch test, reduced Tollen's reagent (reducing sugar), and exhibited a major absorption band in uv at 283 nm (9) indicating that it was a flavanone glycoside. Its ir spectrum showed the presence of polyhydroxy alcoholic groups (3450 cm^{-1}), phenolic groups (3250 cm^{-1}), and a flavanone carbonyl group (1690, 1510 cm^{-1}).

Its uv spectrum exhibited a bathochromic shift in the major absorption band (band II) of 36 nm with NaOAc relative to its spectrum in MeOH, which indicated the presence of a hydroxyl group at the 7-position (9). This was further evidenced by its solubility in Na_2CO_3 solution (10). The compound produced a yellow-orange precipitate with neutral lead acetate solution, indicating the presence of an *ortho*-dihydroxyl system. This was supported by bathochromic shifts of 18 nm in band II and 15 nm in band I, with the addition of $AlCl_3$, and 16 nm in band II with $NaOAc/H_3BO_3$, which clearly established the presence of an *ortho*-dihydroxyl system in the ring A at 6,7, or 7,8 positions (9). The spectrum with NaOMe exhibited a major absorption band (band I) at 419 nm when observed after 5 min; this was caused by the isomerization of the flavanone to a chalcone, indicating the absence of a free 5-hydroxyl group (11).

A high resolution ^{1}H-nmr spectrum of the compound displayed signals at δ 1.0 (3H, d, J=5.5Hz, rhamnosyl CH_3), 3.9 (10H, sugar protons), 4.3 (1H, d, J=2Hz, rhamnosyl H-1, α-linkage), and 5.0 (1H, d, J=7Hz, glucosyl H-1, β-linkage) indicating the presence of two sugar moieties in the molecule. The signals at δ 1.72, 1.82 (6H, 2s, 2×CH_3), 3.22 (2H, d, J=6.0Hz, benzylic protons), and 5.22 (1H, m, olefinic proton) indicated the presence of a γ,γ-dimethylallyl group in the compound. The aromatic protons appeared as two doublets at δ 6.72 (2H, J=9Hz) assignable to H-3′ and H-5′ and at δ 7.21 (2H, J=9Hz) attributed to H-2′ and H-6′. The compound was

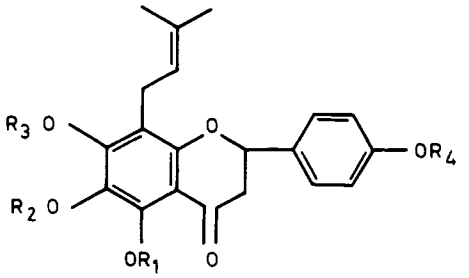
further confirmed to be a flavanone by ABX system, diagnostic for the C-2 and C-3 protons of a flavanone molecule (12). The C-2 proton, the X part, appeared as a double doublet at δ 5.41 (1H, J_{AX}=11.5, J_{BX}=3.5Hz), while the C-3 protons, the AB part, appeared as double quartet at 2.82 and 3.05 (2H, J_{AB}=17.0, J_{AX}=11.5, J_{BX}=3.5Hz). A high value of J (11.5Hz) for the coupling constant J_{AX} clearly indicated an axial-axial coupling, thereby concluding that the C-2 hydrogen was axial and the ring B was equatorial (13).

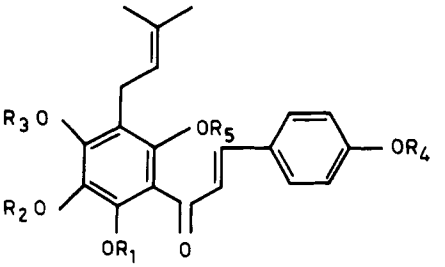
Compound **1**, on hydrolysis with dilute HCl, afforded an aglycone, **2**, nirurinetin, and in the filtrate, the sugars were identified as glucose and rhamnose. The ratio of the aglycone to the glycoside was found to be 42.6%, which indicated the presence of two moles of sugar per mole of aglycone (14), i.e., one mole each of glucose and rhamnose.

The elemental analysis and molecular ion peak in the mass spectrum of the aglycone **2** at *m/z* 356 gave the molecular formula $C_{20}H_{20}O_6$. Its uv spectrum in the presence of $AlCl_3$/HCl exhibited a bathochromic shift in band II by 23 nm relative to MeOH spectrum which established the presence of a hydroxyl group at 5-position. The hypsochromic shift in band II by 14 nm with $AlCl_3$/HCl relative to the $AlCl_3$ spectrum and a bathochromic shift in band II by 9 nm with NaOAc/H_3BO_3 relative to the MeOH spectrum indicated an *ortho*-dihydroxyl system in ring A (9). The spectra in the presence of NaOMe and NaOAc degenerated when observed after 5 and 10 min, which gave strong evidence for the presence of an alkali sensitive hydroxyl system, i.e., a 5,6,7 or 6,7,8 hydroxylation pattern (11). It did not become red-brown or precipitate with *p*-benzoquinone (gossypetone reaction), which ruled out the presence of an 8-hydroxyl group (15). A 5,6,7 hydroxylation pattern must, therefore, be present in compound **2**.

Compound **2** formed a tetraacetate, **3**, with Ac_2O/H_2SO_4 and a pentaacetate, **4**, with Ac_2O/NaOAc which did not exhibit absorption bands in the ir spectra in the region 3450-3350 cm^{-1}, indicating the complete acetylation of compound **2**. Sharp absorption bands in the region 1760-1800 (C=O) and 1180-1200 cm^{-1} (C-O ester) were, however, observed. The ^{1}H-nmr spectra also displayed overlapping singlets between δ 2.3-2.45 (12H) assignable to four acetoxyl protons in the tetraacetate, **3**, and between 2.3-2.46 (15H) attributable to five acetoxy groups in the pentaacetate, **4**. The pentaacetate was obtained through the chalcone formation in the presence of NaOAc which is a characteristic property of a flavanone. It was also evidenced by the disappearance of the signals at δ 5.39 due to the C-2 proton and 3.05-2.82 due to C-3 protons and the appearance of a broad signal between δ 6.62-7.69 assignable to H-α centered at 6.75 (d, J=17Hz), H-β centered at 7.35 (d, J=17Hz), H-3 and H-5 at 7.12 (d, J=9Hz), and H-2 and H-6 at 7.56 (d, J=9Hz). It was thus concluded that only four hydroxyl groups were present in compound **2**, three of which have been assigned to the 5,6,7-positions on the basis of uv and ^{1}H-nmr spectral data of compounds **1** and **2**. Thus, the fourth one must be present in ring B. On the basis of ^{1}H-nmr spectral data of compounds **1-4**, it may be assigned to the 4′-position. This conclusion was further substantiated by alkaline degradation of compound **2** (9), which afforded *p*-hydroxycinnamic acid, thus, strongly supporting the above assignments.

The mass spectrum also supported the proposed structure of compound **2**, which exhibited a prominent peak at *m/z* 301 due to the tropolium ion, showing that the γ,γ-dimethylallyl group was attached to ring A and not to C (16). A prominent peak at *m/z* 120 supported the structure of ring B. It was, therefore, evident that the prenylated side-chain should be attached to the 8 position, since the 5,6, and 7 positions have already been assigned from uv and ^{1}H-nmr spectral studies. Had the side-chain been present at the 6 position, compound **2**, on treatment with mineral acid, would give a cyclized product, which on subsequent fusion with alkali, would yield a 2,2-dimethyl-





1 R_1=Rhamnoglucosyl; R_2,R_3,R_4=H
2 R_1,R_2,R_3,R_4=H
3 R_1,R_2,R_3,R_4=$-COCH_3$
5 R_1=H; R_2,R_3,R_4=$-CH_3$
6 R_1=Glucosyl; R_2,R_3,R_4=H

4 R_1,R_2,R_3,R_4,R_5=$-COCH_3$
7 R_1=Rhamnoglucosyl (6x-$COCH_3$); R_2,R_3,R_4,R_5=$-COCH_3$

chroman derivative, as in the case of pomiferin and osajin (17). As no such product could be obtained from compound **2**, the side-chain must be present at the 8 position. The prominent peaks at *m/z* 247 (with H· transfer) and 246 (without H· transfer) confirmed the structure of ring A. The structure of the new flavanone designated as nirurinetin was thus assigned as 5,6,7,4′-tetrahydroxy-8-(3-methylbut-2-enyl) flavanone **2**.

It was apparent from the uv and ^{1}H-nmr spectral studies that the sugar moiety was linked with the 5-hydroxyl group of the flavanone unit, which was further substantiated by complete methylation of compound **1** with CH_2N_2 (18) which on hydrolysis with dilute acid gave an aglycone, **5**. The ^{1}H-nmr spectrum displayed overlapping singlets at δ 3.92 (9H) assignable to three methoxyl groups in compound **5**. The uv spectrum in the presence of $AlCl_3$/HCl exhibited a bathochromic shift in band II by 24 nm relative to MeOH spectrum, which indicated the presence of a free 5-hydroxyl group. The significant bathochromic shifts in the presence of NaOMe, NaOAc, and NaOAc/H_3BO_3 and a hypsochromic shift with $AlCl_3$/HCl relative to the $AlCl_3$ spectrum could not be observed, indicating the absence of a free 7 position and *ortho*-dihydroxyl groups in compound **5**. Compound **5** was, therefore, characterized as 5-hydroxy-6,7,4′-trimethoxy-8-(3-methylbut-2-enyl) flavanone **5**, which strongly confirmed that the 5-hydroxyl group in compound **1** was engaged in glycosidic linkage with the sugar moiety.

The stepwise hydrolysis of compound **1** with 2% H_2SO_4 showed that the rhamnose moiety was removed first and the glucose unit afterwards, suggesting that the glucose unit was involved in the glycosidic linkage with the aglycone. It was also supported, further, by a partial hydrolysis of glycoside **1**, by treating it with HCOOH in boiling cyclohexanol (19) followed by pc examination of the hydrolysate confirming the presence of rhamnose, glucose, nirurinetin (**2**), and nirurinetin-5-O-glucoside (**6**). The enzymatic hydrolysis with β-glucosidase of compound **6** and a one proton doublet at δ 5.0 (J=7.0Hz) due to diaxial coupling of C-1 proton with C-2 proton of glucose in the ^{1}H-nmr spectrum of compound **1** confirmed the β-linkage of glucose in compound **1** (9). Further, a one proton doublet at δ 4.3 (J=2.0Hz) due to equatorial-equatorial coupling of C-1 proton with C-2 proton of the rhamnose unit indicated the α-linkage with the glucose moiety (9).

The point of attachment of rhamnose to glucose was mentioned as (1↦6, rutinoside) on the basis of ^{1}H-nmr spectral analysis of compound **1** and its acetyl derivative, **7**. The three-proton doublet of the rhamnosyl methyl group of **1** appeared at δ 1.0, whereas the C-1 protons of rhamnose and glucose were exhibited at 4.3 (d, J=2Hz) and 5.0 (d, J=7Hz), respectively, indicating the rutinose moiety in the

molecule (9). The decaacetate, **7**, of compound **1** displayed a signal at δ 1.77 assignable to the 2-acetoxyl group of the glucose unit, while other aliphatic acetoxyl singlets were observed between 2.0 and 2.15. The singlets between 1.90-1.95 due to the 6-acetoxyl group of the glucose unit could not be observed, which strongly supported that the 6-hydroxyl group of the glucose moiety was engaged in a glucosidic linkage with the rhamnose moiety (20).

On the basis of above chemical and spectral studies the structure of nirurin (**1**) has been characterized as 5,6,7,4′-tetrahydroxy-8-(3-methylbut-2-enyl) flavanone-5-O-rutinoside.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Column chromatography was performed on silica gel (deactivated with 2N HCl) 60-120 mesh (BDH, India) and pc on Whatman no. 3 chromatographic paper for flavonoids and Whatman no. 1 for sugars. The ir spectra in KBr were recorded on a Beckmann spectrophotometer, uv on a C.Z. Specord uv-viz spectrophotometer, and ^{1}H-nmr at 60 and 90 MHZ on a F-16 Varian nmr spectrophotometer in DMSO-d_6 and $CDCl_3$ solution using TMS as internal standard. The elemental analysis was carried out on Hosli's Micro Combustion Apparatus type CHA, and mass spectra were taken on a JEOL-JMS D-300 instrument.

ISOLATION OF THE NEW FLAVANONE GLYCOSIDE.—The plant *Phyllanthus nirurii* L. (2.0 kg) authenticated and a voucher specimen deposited at the Horticultural Institute, Saharanpur, and collected from the Saharanpur region in the month of September, was extracted three times with petroleum ether (60-80°) and subsequently with EtOH. The ethanolic extract, on concentration, was dissolved in H_2O and fractionated into petroleum ether, EtOAc, and *n*-BuOH soluble fractions. The latter two fractions, giving the same pattern on tlc, were combined and redissolved into Et_2O and MeOH soluble fractions. The MeOH soluble portion was chromatographed over silica gel using $CHCl_3$, EtOAc, and MeOH as eluents. The MeOH fraction afforded the crude sample of compound **1**, which was purified by repeated column and thin layer chromatography.

CHARACTERIZATION OF NIRURIN (**1**).—Crystallized from MeOH in light yellow crystals (800 mg), mp 298-299° (dec); Rf 0.82 (TBA=*t*-BuOH-HOAc-H_2O, 3:1:1 v/v), 0.76 (BAW=*n*-BuOH-HOAc-H_2O, 4:1:5), 0.68 (Forestal=HOAc-HCl-H_2O, 10:3:30), 0.60 (HOAc=15% aqueous acetic acid); uv blue-green spot; uv/NH_3 yellow-green spot; ir (KBr) ν max 3450, 3250, 2960, 2920, 1690, 1600, 1510, 1450, 1390, 1360, 1300, 1250, 1210, 1180, 1130, 1100, 1040, 1020, 925, 870, 820, 780, 770 cm^{-1}; uv λ max (MeOH) 255 sh, 283 (band II), 369 (band I), λ max (MeOH+NaOMe) 263 sh, 330, 419, λ max (MeOH+$AlCl_3$) 245 sh, 301, 384, λ max (MeOH+$AlCl_3$/HCl) 255 sh, 284, 370, λ max (MeOH+NaOAc) 250 sh, 319, 390, λ max (MeOH+NaOAc/H_3BO_3) 250 sh, 299, 380; ^{1}H-nmr (DMSO-d_6) δ 1.0 (3H, d, J=5.5Hz, rhamnosyl-CH_3), 1.72 (3H, bs, vinylic CH_3), 1.82 (3H, bs, vinylic CH_3), 2.81, 3.05 (2H, dq, J=17.0, 11.5, 3.5Hz, 2H-3), 3.22 (2H, d, J=6Hz, benzylic CH_2), 3.9 (10H, bs, sugar protons), 4.3 (1H, d, J=2Hz, rhamnosyl H-1), 5.0 (1H, d, J=7Hz, glucosyl H-1), 5.22 (1H, m, vinylic H), 5.41 (1H, q, J=11.5, 3.5Hz, H-2), 6.72 (2H, d, J=9Hz, H-3′ and H-5′), 7.21 (2H, d, J=9Hz, H-2′ and H-6′).

CHARACTERIZATION OF NIRURINETIN (**2**).—Obtained on hydrolysis of compound **1** by dilute HCl, crystallized from MeOH in light yellow crystals, mp 320-322° (dec); Rf 0.76 (TBA), 0.23 (HOAc); uv and uv/NH_3 purple spot; ir (KBr) ν max 3450, 3250, 2920, 1640, 1620, 1513, 1400, 1320, 1190, 1090, 1050, 1020, 920, 970 cm^{-1}; uv λ max (MeOH) 255 sh, 293 (band II), 370 (band I), λ max (MeOH+NaOMe) 278 sh, 300 sh, 407, λ max (MeOH+$AlCl_3$) 251 sh, 330, 385, λ max (MeOH+$AlCl_3$/HCl) 250 sh, 316, 374, λ max (MeOH+NaOAc) 295 sh 312, 390, λ max (MeOH+NaOAc/H_3BO_3) 248 sh, 302, 380; ^{1}H-nmr (DMSO-d_6) δ 1.71 (3H, s, vinylic CH_3), 1.81 (3H, s, vinylic CH_3), 2.82 and 3.05 (2H, dq, J=17.0, 11.5, 3.5Hz, 2H-3), 3.23 (2H, d, J=6.0Hz, benzylic CH_2), 5.23 (1H, m, vinylic H), 5.39 (1H, q, J=11.5, 3.5Hz, H-2), 6.71 (2H, d, J=9Hz, H-3′ and H-5′), 7.20 (2H, d, J=9Hz, H-2′ and H-6′); *m/z* 356 (M^+), 355, 341, 301, (100%), 287, 273, 247, 246, 218, 217, 191, 177, 163, 120; found C, 67.34; H, 5.73; $C_{20}H_{20}O_6$ requires: C, 67.42, H, 5.62%.

ACETYLATION OF NIRURINETIN WITH Ac_2O/H_2SO_4 (**3**).—Compound **2** (30 mg) was dissolved in Ac_2O (1 ml) and H_2SO_4 (0.5 ml) and was gently refluxed on a water-bath, which afforded straw-colored needles (25.0 mg) of compound **3** upon crystallization from $CHCl_3$-MeOH (1:1); mp 250-253°; ^{1}H-nmr ($CDCl_3$) δ 1.70 (3H, s, vinylic CH_3), 1.80 (3H, s, vinylic CH_3), 2.3-2.45 (12H, 4×OCOCH$_3$), 3.35 (2H, d, J=6.0Hz, benzylic CH_2), 2.81, 3.05 (2H, dq, J=17, 11.5, 3.5Hz, 2H-3), 5.22 (1H, q,

J=11.5, 3.5 Hz, H-2), 5.40 (1H, m, vinylic H), 7.0 (2H, d, J=9Hz, H-3′ and H-5′), 7.35 (2H, d, J=9Hz, H-2′ and H-6′).

ACETYLATION OF NIRURINETIN WITH Ac_2O/NaOAc (**4**).—Compound **2** (30 mg) on treatment with Ac_2O (1 ml) and fused NaOAc (0.3 g) afforded orange needles (25 mg) from $CHCl_3$-MeOH, compound **4**; mp 230-233°; ir (KBr) ν max 3080 (aromatic CH), 2940, 1800-1760 (C=O), 1630, 1480, 1420, 1350, 1180-1200 (C-O ester), 1140, 1100, 1070, 1010, 920, 880 cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ 1.70, 180 (6H, d, two vinylic CH_3), 2.3-2.45 (15H, 5×OCOCH_3), 3.35 (2H, d, J=6 Hz, benzylic CH_2), 6.75 (1H, d, J=17 Hz, H-α), 7.12 (2H, d, J=9 Hz, H-3 and H-5), 7.35 (1H, d, J=17 Hz, H-β), 7.56 (2H, d, J=9 Hz, H-2 and H-6).

METHYLATION OF NIRURIN (**5**).—A solution of compound **1** (60 mg) in MeOH (250 ml) was treated with an ethereal solution of CH_2N_2 to give an oil (18). The oil was acid hydrolyzed to afford the aglycone **5** (25 mg) on Et_2O extraction and was crystallized from $CHCl_3$-MeOH (1:1) in yellow needles, mp 240-245°; uv λ max (MeOH) 250 sh, 290, 368, λ max (MeOH+NaOMe) 255 sh, 290, 330, λ max (MeOH+$AlCl_3$) 253, 315, 375, λ max (MeOH+$AlCl_3$/HCl) 252 sh, 314, 371, λ max (MeOH+NaOAc) 292, 369, λ max (MeOH+NaOAc/H_3BO_3) 291, 368; ^{1}H-nmr ($CDCl_3$) δ 1.69, 1.79 (6H, d, two vinylic CH_3), 3.22 (2H, d, J=6 Hz, vinylic CH_2), 2.82, 3.05 (2H, dq, J=17, 11.5, 3.5 Hz, 2H-3), 3.92 (9H, 3×OCH_3), 5.25 (1H, m, vinylic H), 5.40 (1H, q, J=11.5, 3.5 Hz, H-2), 6.72 (2H, d, J=9 Hz, H-3′ and H-5′), 7.21 (2H, d, J=9 Hz, H-2′ and H-6′).

ALKALINE DEGRADATION OF NIRURINETIN.—Compound **2** (40 mg) was refluxed with 50% aqueous KOH (3 ml) containing a few drops of MeOH (9), which afforded *p*-hydroxycinnamic acid, mp 208-210° (mmp, co-ir).

MILD HYDROLYSIS OF NIRURIN.—Compound **1** (10 mg) was dissolved in 2% H_2SO_4 with addition of a few drops of MeOH and heated gently on a water-bath for an hour. The hydrolysates were examined after each interval of 5 min by paper chromatography for sugars and flavonoids. The first sugar obtained on hydrolysis was rhamnose while glucose was detected later.

PARTIAL HYDROLYSIS OF NIRURIN.—Compound **1** (30 mg) was added to cyclohexanol (2 ml) and HCOOH (1 ml), and the contents were refluxed at 100-110° for 10 h. The hydrolysed product was examined by paper chromatography revealing the presence of rhamnose, glucose, nirurinetin (**2**) and compound **6**. Compound **6** was dissolved in aqueous EtOH (5 ml) and mixed with emulsin (5 ml, isolated from almond seeds). The mixture was incubated for 6 h at 40° and left for 72 h at room temperature. The resulting reaction mixture was extracted with EtOAc which gave compound **2**. Upon examining the aqueous layer for sugars, only glucose was detected.

ACETYLATION OF NIRURIN (**7**).—Compound **1** (30 mg) was treated with Ac_2O (1.5 ml) and fused NaOAc (0.3 g), by usual methods, which afforded orange needles (25 mg) from $CHCl_3$-MeOH (1:1), mp 158-160°; ir (KBr) ν max 3080 (aromatic CH), 2920, 2850, 1780, 1710, (C=O), 1660, 1610, 1580, 1470, 1410, 1365, 1340, 1320, 1180 (C-O ester), 1130, 1100, 1000, 920, 838 cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ 1.05 (3H, d, J=5.5 Hz, rhamnosyl CH_3), 1.70, 1.80 (6H, d, two vinylic CH_3), 1.77, 2.05-2.15 (18H, 6×OCOCH_3, aliphatic), 2.3-2.40 (12H, 4×OCOCH_3, aromatic), 3.36 (2H, d, J=6.0 Hz, benzylic CH_2), 3.52 (4H, m, H-5, 2H-6 glucosyl and H-5 rhamnosyl), 4.48 (1H, d, J=2 Hz, rhamnosyl H-1), 5.0 (7H, m, H-1,2,3,4, of glucosyl and H-2,3,4, of rhamnosyl), 5.41 (1H, m, vinylic H), 6.74 (1H, d, J=17 Hz, H-α), 7.12 (2H, d, J=9 Hz, H-3 and H-5), 7.34 (1H, d, J=17 Hz, H-β), 7.56 (2H, d, J=9 Hz, H-2 and H-6).

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