Five New Flavonol Glycosides from the Fresh Flowers of *Camellia reticulata*

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Thirty-one phenolic constituents, including 13 flavonol glycosides, 3 dihydroflavonols, 5 flavan-3-ols, 4 hydrolyzable tannins, and 6 phenylpropanoids, were isolated from the fresh flowers of *Camellia reticulata* for the first time. Five of them are new flavonol glycosides. Their structures were elucidated by detailed spectroscopic analyses.

Introduction. – The genus *Camellia* (Theaceae) contains *ca*. 120 species growing mainly in the east and southeast of Asia, of which about 100 species are distributed in China [1]. In this genus, some species are important ornamental plants, *e.g.*, *C. japonica*, *C. sasangua*, and *C. nitidssiam*. The genus *Camellia* is noteworthy also because it includes the origin plant of the economically important 'tea'.

C. reticulata LINDL., a shrub or tree, usually 3–15 m tall, called 'Yunnan Shancha' in Chinese, is a famous Camelliaceous ornamental plant endemic to the southwest of China [2]. The flowers were also used as folk medicine for the treatment of hemostasia, haematemesis, diarrhea, dysentery, and scald by the local people of its growing areas [3]. So far, ten anthocyanins were identified from the red flowers of *C. reticulata* [4], and some triterpenoids, flavan-3-ols, flavonols, and simple phenolic compounds were reported from the flowers of *C. japonica,* another *Camellia* ornamental plant closely related to *C. reticulata* [5–8]. Our detailed chemical investigation on the fresh flowers of *C. reticulata* led to the isolation of five new flavonol glycosides (**1**–**5**), together with 26 known phenolic constituents (**6**–**31**) (see *Figs. 1* and *2*). This article presents the structural determination of these compounds.

Results and Discussion. – The 80% aqueous acetone extract of the fresh flowers of *C. reticulata* was suspended into H_2O, and then partitioned with AcOEt and BuOH, successively. The organic extracts were further chromatographed separately over *Diaion HP20SS*, *Sephadex LH-20*, *MCI*-gel *CHP20P*, *Chromatorex ODS*, and silica gel to afford five new flavonol glycosides (**1**–**5**). In addition, 26 known phenolic compounds, including eight flavonol glycosides (**6**–**13**), three dihydroflavonols (**14**–**16**), five flavan-3-ols (**17**–**21**), four hydrolyzable tannins (**22**–**25**), and six phenylpropanoids (**26**–**31**) were obtained. The known compounds were identified as kaempferol 3-*O*-[α-L-rhamnopyranosyl-(1 → 4)-α-L-rhamnopyranosyl-(1 → 6)]-β-D-glucopyranoside (**6**) [9], kaempferol 3-*O*-[4-*O*-acetyl-α-L-rhamnopyranosyl-(1 → 3)-

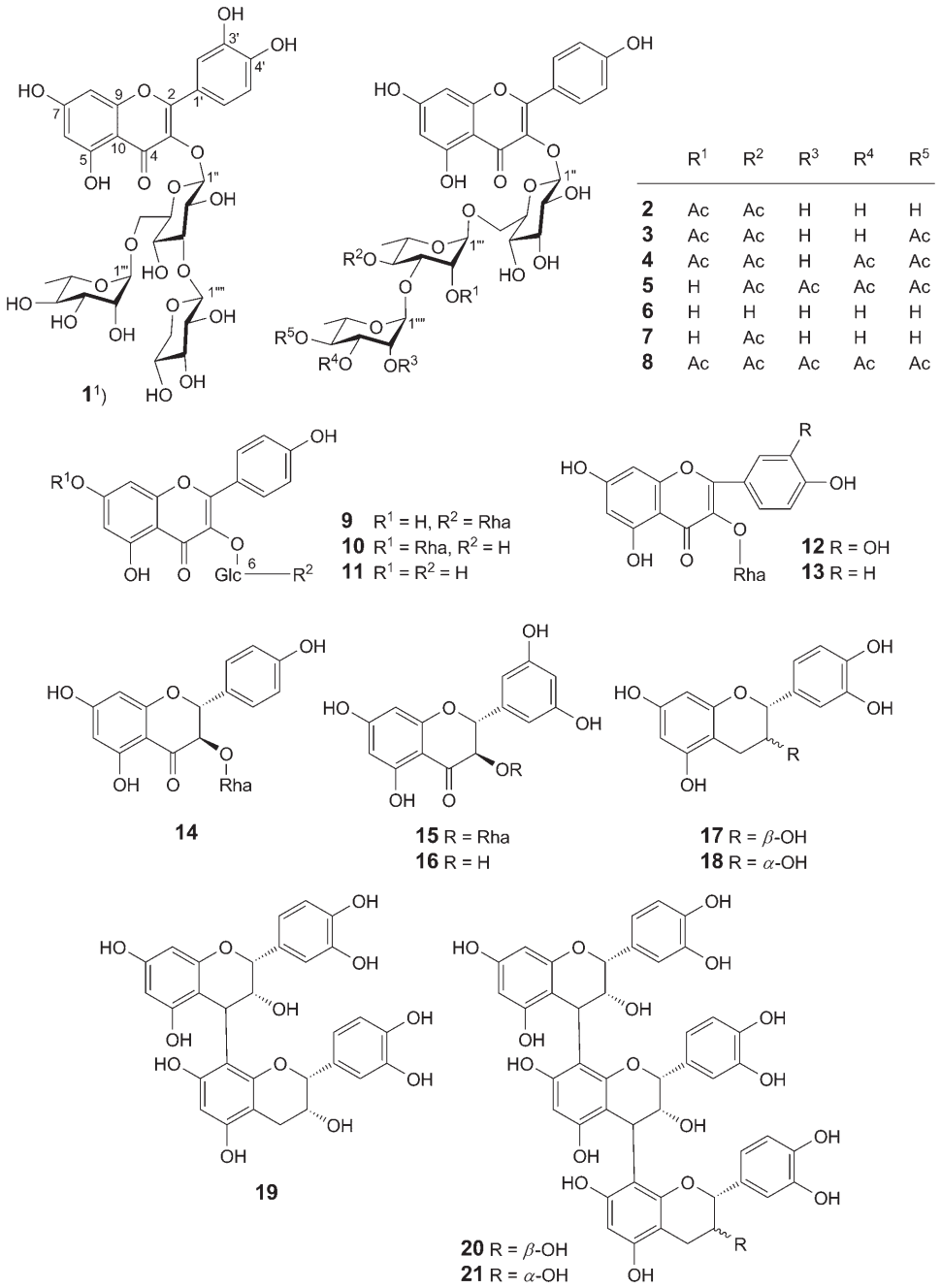

Fig. 1. *Compounds* **1**–**21** *isolated from the fresh flowers of* C. reticulata

[1]) Arbitrary numbering. For systematic names, see *Exper. Part*.

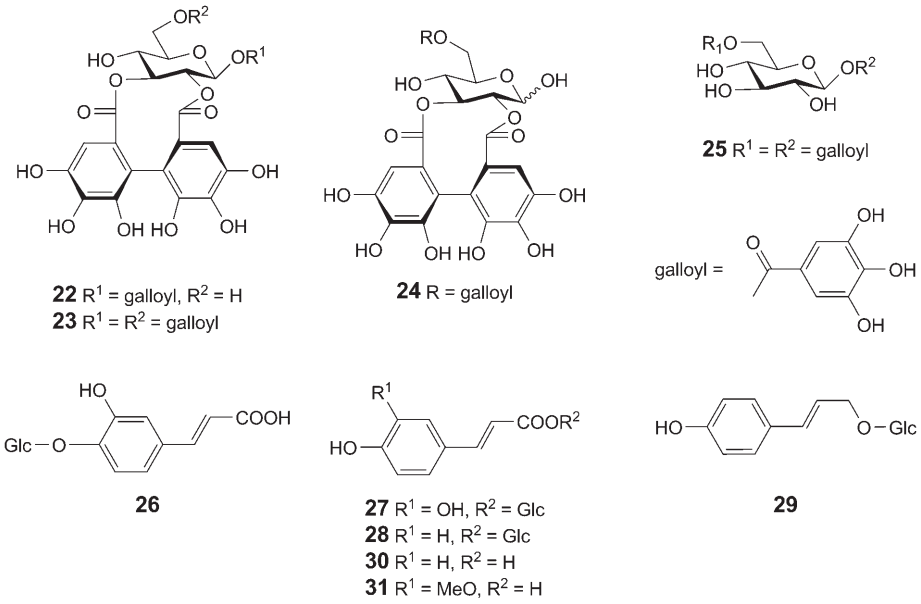

Fig. 2. *Compounds* **22**–**31** *isolated from the fresh flowers of* C. reticulata

α-L-rhamnopyranosyl-(1 → 6)]-β-D-glucopyranoside (**7**) [9], kaempferol 3-*O*-[2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl-(1 → 3)-2,4-di-*O*-acetyl-α-L-rhamnopyranosyl-(1 → 6)]-β-D-glucopyranoside (**8**) [10], nicotiflorin (**9**) [11], kaempferol 3-*O*-β-D-glucosyl-7-*O*-α-L-rhamnoside (**10**) [12], astragalin (**11**) [13], quercitrin (**12**) [14], afzelin (**13**) [15], engelitin (**14**) [16], smitilbin (**15**) [17], 3,3′,5,5′,7-pentahydroxyflavanone (**16**) [18], (+)-catechin (**17**) [12], (−)-epicatechin (**18**) [12], procyanidin B-2 (**19**) [12], arecatannin A1 (**20**) [19], procyanidin C-1 (**21**) [19], isostrictinin (**22**) [20], nobotanin D (**23**) [21], sanguiin H4 (**24**) [22], 1,6-*O*-digalloyl-β-D-glucose (**25**) [23], linocaffein (**26**) [24], 1-*O*-caffeoyl-β-D-glucose (**27**) [25], 1-*O*-*p*-coumaroyl-β-D-glucose (**28**) [13], triandrin (**29**) [26], *p*-coumaric acid (**30**) [27], and ferulic acid (**31**) [28], respectively, by comparison of the physical and spectral data with literature values. All of these known compounds were reported from the title plant for the first time, and compounds **8**, **10**, **13**–**16**, **20**, **22**, **24**, **26**, **28**, and **29** were firstly obtained from the genus *Camellia*.

Compound **1** was obtained as a brown amorphous powder and gave a positive reaction with the $FeCl_3$ reagent. The IR spectrum showed absorption bands due to OH groups (3443, 1064 cm^{-1}), aromatic rings (1451 cm^{-1}), and CO groups (1640 cm^{-1}). The molecular formula of **1** was determined to be $C_{32}H_{38}O_{20}$ by HR-FAB-MS (*m*/*z* 741.1861, $[M-H]^-$). The ^{1}H- and ^{13}C-NMR (*Table*) spectra showed the presence of a set of H-atom signals[1]) (δ(H) 6.18 (*s*, H−C(6)), 6.41 (*s*, H−C(8)), 7.60 (br. *s*, H−C(2′)), 6.90 (*d*, *J* = 8.3, H−C(5′)), 7.60 (br. *d*, *J* = 8.3, H−C(6′))), together with a CO group (C(4), δ(C) 178.4) and 14 aromatic C-atom signals at δ(C) 94.6–164.9 arising from a quercetin moiety. In addition, three anomeric H-atoms (δ(H) 5.30 (*d*, *J* = 7.4), 4.39 (br. *s*), and 4.73 (*d*, *J* = 7.1)), and a Me group (δ(H) 0.97 (*d*, *J* = 6.1)) were observed.

Table. *^{13}C-NMR Data of* **1**–**5**[1]). At 125 MHz, δ in ppm.

	1[a])	**2**[b])	**3**[b])	**4**[b])	**5**[b])		**1**[a])	**2**[b])	**3**[b])	**4**[b])	**5**[b])
C(2)	157.8	158.6	158.8	158.5	159.0	C(5″)	76.8	78.1	77.9	77.9	78.1
C(3)	133.8	135.1	135.0	134.8	134.9	C(6″)	66.9	68.0	67.8	67.2	67.4
C(4)	178.4	179.3	179.2	179.4	179.4	C(1‴)	101.0	98.9	98.9	98.8	100.4
C(5)	161.4	163.1	162.9	163.1	163.1	C(2‴)	71.0	73.2	72.8	72.8	71.8
C(6)	99.4	100.0	99.9	100.0	100.0	*Ac*O–C(2‴)		171.8	171.5	172.1	
								20.8	20.6	21.0	
C(7)	164.9	166.6	165.8	166.0	166.0	C(3‴)	70.7	76.1	75.4	75.8	78.6
C(8)	94.6	94.9	94.7	94.8	9 4.8	C(4‴)	72.5	74.0	74.0	73.6	73.6
C(9)	157.3	158.8	158.4	158.9	158.5	*Ac*O–C(4‴)		171.9	171.8	172.0	172.3
								20.9	21.0	20.9	20.6
C(10)	104.7	105.7	105.6	105.6	105.7	C(5‴)	68.8	67.6	67.4	67.5	67.7
C(1′)	122.2	122.9	122.7	122.8	122.8	C(6‴)	17.2	17.4	17.1	17.2	17.3
C(2′)	116.9	132.2	132.1	132.2	132.3	C(1⁗)	104.2	103.6	103.3	100.4	101.9
C(3′)	144.8	116.2	116.1	116.2	116.1	C(2⁗)	73.9	72.4	72.2	71.1	70.4
C(4′)	148.7	161.5	161.3	161.4	161.5	*Ac*O–C(2⁗)					171.6
											20.7
C(5′)	115.8	116.2	116.1	116.2	116.1	C(3⁗)	75.9	72.1	69.9	71.2	71.1
C(6′)	123.0	132.2	132.1	132.2	132.3	*Ac*O–C(3⁗)				172.2	171.8
										20.8	21.0
C(1″)	99.6	103.9	103.5	103.1	103.2	C(4⁗)	69.8	73.6	75.1	72.6	72.5
C(2″)	75.6	75.8	75.7	75.0	75.9	*Ac*O–C(4⁗)			172.5	172.3	172.3
									20.7	20.8	20.8
C(3″)	81.2	76.9	76.7	76.6	76.6	C(5⁗)	65.6	70.6	68.3	70.7	67.9
C(4″)	69.9	71.0	70.9	70.9	71.2	C(6⁗)		17.9	17.6	17.7	17.7

[a]) Measured in (D_6)acetone. [b]) Measured in CD_3OD.

With the HSQC-TOCSY experiment, the three sugar moieties were determined to be each a β-glucopyranosyl, a α-rhamnopyranosyl, and a β-xylopyranosyl unit. The fragment ion peaks at m/z 609 $[M-132-H]^-$ and 595 $[M-146-H]^-$ in the FAB-MS indicated that both the xylopyranosyl and rhamnopyranosyl unit were located at terminal positions.

The sugar linkages were further determined by the HMBC spectrum, in which correlations of H–C(1″) (δ(H) 5.30) of the glucopyranosyl unit with C(3) (δ(C) 133.8) of the aglycone, H–C(1‴) (δ(H) 4.39) of the rhamnopyranosyl unit with C(6″) (δ(C) 66.9) of the glucopyranosyl unit, and H–C(1⁗) (δ(H) 4.73) of the xylopyranosyl unit with C(3″) (δ(C) 81.2) of the glucopyranosyl unit were observed. Therefore, compound **1** was determined to be quercetin 3-*O*-[β-D-xylopyranosyl-(1 → 3)]-[α-L-rhamnopyranosyl-(1 → 6)]-β-D-glucopyranoside[2]).

The molecular formulae of compounds **2**–**5** were assigned to be $C_{37}H_{44}O_{21}$, $C_{39}H_{46}O_{22}$, $C_{41}H_{48}O_{23}$, and $C_{41}H_{48}O_{23}$, respectively, on the basis of the HR-FAB-MS analyses. All of them possessed kaempferol as aglycone and one glucopyranosyl and two rhamnopyranosyl units as sugar moieties. In addition, two to four acetyl groups

[2]) The absolute configurations of glucose and xylose were assumed to be D, and of rhamnose to be L, based on biogenetic considerations.

were attached on the sugar moiety. The NMR data of the sugar moiety for compounds **2**–**5** were fully assigned by HSQC-TOCSY experiments.

Compound **2** had similar ^{1}H- and ^{13}C-NMR spectral data as **7**, except for the signals due to an additional acetyl group (δ(C) 20.8 and 171.8, δ(H) 2.06). Compared to the signals of **7**, the downfield shift of C(2‴) (δ(C) 73.2) and H–C(2‴) (δ(H) 5.04) of the inner rhamnopyranosyl unit suggested that the additional AcO group was located at C(2‴) of the inner rhamnopyranosyl unit. This was further confirmed by HMBC experiments, in which both of the inner rhamnopyranosyl H–C(2‴) (δ(H) 5.04) and the Me group (δ(H) 2.06) of one AcO group were correlated with the Ac CO group at δ(C) 171.8. Moreover, HMBC correlations of δ(H) 4.81 (inner rhamnopyranosyl H–C(4‴)) and δ(H) 1.96 (Me of another AcO group) with δ(C) 171.9 (CO group of this AcO group), H–C(1″) (δ(H) 5.34) with C(3) (δ(C) 135.1), H–C(1‴) (δ(H) 4.60) with C(6″) (δ(C) 68.0), and H–C(1⁗) (δ(H) 4.70) with C(3‴) (δ(C) 76.1) were also observed. Therefore, compound **2** was elucidated to be kaempferol 3-*O*-[α-L-rhamnopyranosyl-(1 → 3)-2,4-di-*O*-acetyl-α-L-rhamnopyranosyl-(1 → 6)]-β-D-glucopyranoside[2]).

The NMR spectra of **3** showed a difference from **2** only in the addition of an AcO group (δ(C) 172.5 and 20.7; δ(H) 2.07). The significant acetylation shift effects occurred for the signal of terminal rhamnopyranosyl C(4⁗) (δ(C) 75.1), which suggested that the additional AcO group was linked to the C(4⁗)-position of the terminal rhamnopyranosyl unit. This deduction was unambiguously confirmed by the HMBC correlations of the terminal rhamnopyranosyl H–C(4⁗) (δ(H) 4.82–4.88) and the AcO Me group (δ(H) 1.97) with the Ac CO group (δ(C) 171.8). Thus, the structure of **3** was established as kaempferol 3-*O*-[4-*O*-acetyl-α-L-rhamnopyranosyl-(1 → 3)-2,4-di-*O*-acetyl-α-L-rhamnopyranosyl-(1 → 6)]-β-D-glucopyranoside[2]).

Compounds **4** and **5** had the same molecular formula $C_{41}H_{48}O_{23}$ as determined by HR-FAB-MS. Detailed analyses of their NMR data indicated that both compounds possessed the same basic structure of acetylated kaempferol glycosides, which were closely related to those of compounds **2**, **3**, and **7**. However, the number of acetyl groups and their location was different from those of **2**, **3**, and **7**. Both compounds **4** and **5** contained four AcO groups, and their positions were elucidated on the basis of 2D-NMR spectral data. In the case of compound **4**, the long range correlations of H–C(2‴) (δ(H) 4.93–5.08) and H–C(4‴) (δ(H) 4.80–4.86) of the inner rhamnopyranosyl unit with AcO CO groups at δ(C) 172.1 and 172.0, as well as H–C(3⁗) (δ(H) 4.93–5.08) and H–C(4⁗) (δ(H) 4.80–4.86) of the terminal rhamnopyranosyl unit with AcO CO groups at δ(C) 172.2 and 172.3, were observed, respectively. The other HMBC correlations confirmed the structure of **4**. Accordingly, **4** was characterized as kaempferol 3-*O*-[3,4-di-*O*-acetyl-α-L-rhamnopyranosyl-(1 → 3)-2,4-di-*O*-acetyl-α-L-rhamnopyranosyl-(1 → 6)]-β-D-glucopyranoside[2]).

Similarly, the long range correlations of the inner rhamnopyranosyl H–C(4‴) (δ(H) 4.90–5.04) with the AcO CO group at δ(C) 172.3, as well as the terminal rhamnopyranosyl H–C(2⁗) (δ(H) 4.90–5.04), H–C(3⁗) (δ(H) 5.26), and H–C(4⁗) (δ(H) 4.90–5.04) with the AcO CO groups at δ(C) 171.6, 171.8 and 171.9, observed respectively in the HMBC spectra of **5**, allowed the assignment of the four acetyl groups located at C(4‴), C(2⁗), C(3⁗), and C(4⁗) of the sugar moiety in **5**. Consequently, compound **5** was assigned to be kaempferol 3-*O*-[2,3,4-tri-*O*-acetyl-α-

L-rhamnopyranosyl-(1 → 3)-4-*O*-acetyl-α-L-rhamnopyranosyl-(1 → 6)]-β-D-glucopyranoside[2]).

In this study, 31 phenolic compounds, including 13 flavonol glycosides (**1**–**13**), 3 dihydroflavonols (**14**–**16**), 5 flavan-3-ols (**17**–**21**), 4 hydrolyzable tannins (**22**–**25**), and 6 phenylpropanoids (**26**–**31**), were isolated from the fresh flowers of *C. reticulata* for the first time. Thereof, compounds **1**–**5** are new flavonol glycosides, while six compounds, **2**–**5**, **7**, and **8**, are acetylated flavonol glycosides. The latter are typical constituents from the genus *Camellia*.

Experimental Part

General. TLC: silica gel precoated plates (*Qingdao Haiyang Chemical Co. Ltd.*), eluting with benzene/ethyl formate/formic acid 1:7:1 or $CHCl_3$/MeOH/H_2O 7:3:0.5; detection by spraying with ferric chloride ($FeCl_3$) and 10% sulfuric acid reagents. Column chromatography (CC): *Diaion HP20SS* (*Mitsubishi Chemical Co.*), *MCI-gel CHP20P* (75–150 μm, *Mitsubishi Chemical Co.*), *Sephadex LH-20* (25–100 μm, *Pharmacia Fine Chemical Co. Ltd.*), and *Chromatorex ODS* (100–200 mesh, *Fuji Silysia Chemical Co. Ltd.*), silica gel (SiO_2, 200–300 mesh, *Qingdao Haiyang Chemical Co. Ltd.*). Optical rotations: *JASCO-20* polarimeter. UV Spectra: *UV 210A Shimadzu* spectrometer; λ_{max} (log ε). IR Spectra: *Bio-Rad FTS-135* spectrometer. NMR Spectra: *Bruker AM-400* and *DRX-500* instruments, with Me_4Si as internal standard. FAB-MS and HR-FAB-MS: *VG Auto Spec3000* spectrometer with glycerol as matrix.

Plant Material. The fresh flowers of *Camellia reticulata* LINDL. were collected in Kunming Botany Garden in February 2005. The plant material was identified by Prof. *C.-R. Yang*, Kunming Institute of Botany, Chinese Academy of Sciences. A voucher specimen (NO: KY040212) is deposited with the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and Isolation. The fresh flowers of *Camellia reticulata* (20 kg) were extracted with 80% aq. acetone (3 × 5 l, 7 d each) at r.t. The combined extracts were concentrated *in vacuo* to afford a residue, which was suspended into H_2O (6 l) and then partitioned successively with $CHCl_3$ (3 × 2 l), AcOEt (3 × 2 l), and BuOH (3 × 2 l). The AcOEt extract (80 g) was applied to a *Sephadex LH-20* column, eluting with H_2O/MeOH (1:0–0:1), to give fractions *1–8*. *Fr. 4* (13.8 g) was further separated by CC over *Sephadex LH-20*, *Chromatorex ODS*, *MCI*-gel *CHP20P*, and SiO_2 to give **2** (20 mg), **3** (34 mg), **4** (27 mg), **5** (51 mg), **8** (43 mg), **11** (2 mg), **14** (15 mg), **15** (4 mg), **30** (60 mg), and **31** (7 mg). Similarly, compound **16** (11 mg) was obtained from *Fr. 7* (17.2 g) by repeated CC over *Sephadex LH-20*, *Chromatorex ODS*, *MCI*-gel *CHP20P*, and SiO_2. The BuOH extract (420 g) was chromatographed over a *Sephadex LH-20* column with H_2O/MeOH (1:0–0:1) to give *Fractions 1–8*. Repeated CC over *Sephadex LH-20*, *Chromatorex ODS*, *MCI*-gel *CHP20P*, and SiO_2 afforded **1** (22 mg), **6** (10 mg), **9** (14 mg), **26** (4 mg), **27** (373 mg), **28** (25 mg), and **29** (2 mg) from *Fr. 4* (14.0 g), **7** (31 mg), **10** (8 mg), **12** (200 mg), **22** (10 mg), and **24** (22 mg) from *Fr. 5* (86.0 g), **13** (22 mg), **17** (10 mg), **18** (25 mg), **20** (30 mg), and **21** (120 mg) from *Fr. 6* (47 g), **19** (38 mg) and **25** (7 mg) from *Fr. 7* (60 g), and compound **23** (7 g) from *Fr. 8* (65 g), resp.

*Quercetin 3-*O*-[β-*D*-Xylopyranosyl-(1 → 3)]-[α-*L*-rhamnopyranosyl-(1 → 6)]-β-*D*-glucopyranoside* (= *3-{[*O*-6-Deoxy-α-*L*-mannopyranosyl-(1 → 6)-*O*-[β-*D*-xylopyranosyl-(1 → 3)]-β-*D*-glucopyranosyl]oxy}-2-(3,4-dihydroxyphenyl)-5,7-dihydroxy-4*H*-1-benzopyran-4-one*; **1**). Brown amorphous powder. $[\alpha]_D^{22}$ = +21.7 (*c* = 0.31, MeOH). UV (MeOH): 358 (4.11), 256 (4.33), 203 (4.78). IR (KBr): 3443, 2925, 1640, 1451, 1364, 1271, 1202, 1166, 1064. ^{1}H-NMR (500 MHz, (D_6)acetone): 0.97 (*d*, *J* = 6.1, Me(6‴)); 3.18–3.24 (*m*, H_b–C(5⁗), H–C(4‴), H–C(4″)); 3.32–3.46 (*m*, H–C(2″), H_b–C(6″), H–C(3⁗), H–C(5‴), H–C(2⁗), H–C(2‴), H–C(4⁗)); 3.60–3.66 (*m*, H–C(3‴), H–C(5″), H–C(3″), H_a–C(6″)); 3.82–3.88 (*m*, H_a–C(5⁗)); 4.39 (br. *s*, H–C(1‴)); 4.73 (*d*, *J* = 7.1, H–C(1⁗)); 5.30 (*d*, *J* = 7.4, H–C(1″)); 6.18 (*s*, H–C(6)); 6.41 (*s*, H–C(8)); 6.90 (*d*, *J* = 8.3, H–C(5′)); 7.60 (br. *s*, H–C(2′)); 7.60 (br. *d*, *J* = 8.3, H–C(6′)). ^{13}C-NMR (125 MHz, (D_6)acetone): *Table*. FAB-MS (neg.): 741

([$M-H$]$^-$), 609 ([$M-132-H$]$^-$), 595 ([$M-146-H$]$^-$). HR-FAB-MS (neg.): 741.1861 ([$M-H$]$^-$, $C_{32}H_{37}O_{20}^-$; calc. 741.1878).

*Kaempferol 3-*O*-[α-*L*-Rhamnopyranosyl-(1→3)-2,4-di-*O*-acetyl-α-*L*-rhamnopyranosyl-(1→6)]-β-*D*-glucopyranoside* (= *3-[[*O*-6-Deoxy-α-*L*-mannopyranosyl-(1→3)-*O*-2,4-di-*O*-acetyl-6-deoxy-α-*L*-mannopyranosyl-(1→6)-β-*D*-glucopyranosyl]oxy}-5,7-dihydroxy-2-(4-hydroxyphenyl)-4*H*-1-benzopyran-4-one*; **2**). Yellow amorphous powder. $[\alpha]_D^{22} = -27.7$ ($c = 0.96$, MeOH). UV (MeOH): 204 (4.85), 266 (4.53), 301 (4.31), 345 (4.43). IR (KBr): 3425, 2926, 1729, 1654, 1608, 1508, 1451, 1362, 1239 1179, 1047. ^{1}H-NMR (500 MHz, CD_3OD): 0.82 (*d*, $J = 6.2$, Me(6‴)); 1.16 (*d*, $J = 6.2$, Me(6‴)); 1.96 (*s*, MeCO–O–C(4‴)); 2.06 (*s*, MeCO–O–C(2‴)); 3.32–3.36 (*m*, H–C(4‴)); 3.45–3.50 (*m*, H–C(3″), H–C(4″), H–C(2″), H–C(5″)); 3.60–3.70 (*m*, H_b–C(6″), H–C(5‴), H–C(2‴), H–C(3‴), H–C(5‴)); 3.80 (br. *d*, $J = 10.7$, H_a–C(6″)); 3.89 (*dd*, $J = 4.5$, 12.5, H–C(3‴)); 4.60 (br. *s*, H–C(1″)); 4.70 (br. *s*, H–C(1‴)); 4.81 (*m*, H–C(4‴)); 5.04 (br. *s*, H–C(2‴)); 5.34 (*d*, $J = 7.2$, H–C(1′)); 6.18 (*d*, $J = 1.6$, H–C(6)); 6.35 (*d*, $J = 1.6$, H–C(8)); 8.01 (*d*, $J = 8.7$, H–C(2′), H–C(6′)); 6.90 (*d*, $J = 8.7$, H–C(3′), H–C(5′)). ^{13}C-NMR (125 MHz, CD_3OD): *Table*. FAB-MS (neg.): 823 ([$M-H$]$^-$). HR-FAB-MS (neg.): 823.2289 ([$M-H$]$^-$, $C_{37}H_{43}O_{21}^-$; calc. 823.2296).

*Kaempferol 3-*O*-[4-*O*-Acetyl-α-*L*-rhamnopyranosyl-(1→3)-2,4-di-*O*-acetyl-α-*L*-rhamnopyranosyl-(1→6)]-β-*D*-glucopyranoside* (= *3-[[*O*-4-O-Acetyl-6-deoxy-α-*L*-mannopyranosyl-(1→3)-*O*-2,4-di-*O*-acetyl-6-deoxy-α-*L*-mannopyranosyl-(1→6)-β-*D*-glucopyranosyl]oxy}-5,7-dihydroxy-2-(4-hydroxyphenyl)-4*H*-1-benzopyran-4-one*; **3**). Yellow amorphous powder. $[\alpha]_D^{22} = -25.4$ ($c = 0.66$, MeOH). UV (MeOH): 204 (4.81), 266 (4.56), 300 (4.35), 348 (4.46). IR (KBr): 3430, 2925, 1728, 1655, 1608, 1364, 1235, 1178, 1043. ^{1}H-NMR (500 MHz, CD_3OD): 0.84 (*d*, $J = 6.2$, Me(6‴)); 1.04 (*d*, $J = 6.2$, Me(6‴)); 1.97 (*s*, MeCO–O–C(4‴)); 2.06 (*s*, MeCO–O–C(2‴))); 2.07 (*s*, MeCO–O–C(4‴)); 3.38–3.58 (*m*, H–C(3″), H–C(4″), H–C(2″), H–C(5″), H_b–C(6″)); 3.60 (*d*, $J = 3.1$, H–C(3‴)); 3.62–3.79 (*m*, H–C(5‴), H–C(2‴), H–C(5‴), H_a–C(6″)); 3.94 (*dd*, $J = 4.5$, 12.5, H–C(3‴)); 4.57 (br. *s*, H–C(1‴)); 4.82–4.88 (*m*, H–C(4‴), H–C(4‴)); 5.05 (*d*, $J = 1.8$, H–C(2‴)); 5.36 (*d*, $J = 7.1$, H–C(1″)); 6.19 (*d*, $J = 1.4$, H–C(6)); 6.36 (*d*, $J = 1.4$, H–C(8)); 6.90 (*d*, $J = 8.7$, H–C(3′), H–C(5′)); 8.00 (*d*, $J = 8.7$, H–C(2′), H–C(6′)). ^{13}C-NMR (125 MHz, CD_3OD): *Table*. FAB-MS (neg.): 865 ([$M-H$]$^-$). HR-FAB-MS (neg.): 865.2405 ([$M-H$]$^-$, $C_{39}H_{45}O_{22}^-$; calc. 825.2402).

*Kaempferol 3-*O*-[3,4-Di-*O*-acetyl-α-*L*-rhamnopyranosyl-(1→3)-2,4-di-*O*-acetyl-α-*L*-rhamnopyranosyl-(1→6)]-β-*D*-glucopyranoside* (= *3-[[*O*-3,4-Di-*O*-acetyl-6-deoxy-α-*L*-mannopyranosyl-(1→3)-*O*-2,4-di-*O*-acetyl-6-deoxy-α-*L*-mannopyranosyl-(1→6)-β-*D*-glucopyranosyl]oxy}-5,7-dihydroxy-2-(4-hydroxyphenyl)-4*H*-1-benzopyran-4-one*; **4**). Yellow amorphous powder. $[\alpha]_D^{22} = -44.8$ ($c = 0.73$, MeOH). UV (MeOH): 204 (4.90), 265 (4.56), 345 (4.46). IR (KBr): 3432, 2927, 1746, 1731, 1655, 1608, 1508, 1367, 1236, 1179, 1137, 1065, 1049. ^{1}H-NMR (500 MHz, CD_3OD): 0.77 (*d*, $J = 6.2$, Me(6‴)); 1.23 (*d*, $J = 6.2$, Me(6″)); 1.95 (*s*, MeCO–O–C(4‴)); 2.03 (*s*, MeCO–O–C(3‴)); 2.09 (*s*, MeCO–O–C(2‴)); 2.11 (*s*, MeCO–O–C(4‴)); 3.43–3.60 (*m*, H–C(3″), H–C(5″), H–C(4″), H–C(2″), H_b–C(6″), H–C(5‴)); 3.70–3.74 (*m*, H–C(2‴), H–C(5‴)); 3.79 (*dd*, $J = 1.1$, 10.2, H_a–C(6″)); 3.89 (*dd*, $J = 4.5$, 12.5, H–C(3‴)); 4.61 (*s*, H–C(1‴)); 4.62 (br. *s*, H–C(1‴)); 4.80–4.86 (*m*, H–C(4‴), H–C(4‴)); 4.93–5.08 (*m*, H–C(3‴), H–C(2‴)); 5.44 (*d*, $J = 7.2$, H–C(1″)); 6.18 (*d*, $J = 1.8$, H–C(6), 6.35 (*d*, $J = 1.8$, H–C(8)); 6.88 (*d*, $J = 8.7$, H–C(3′), H–C(5′)); 8.00 (*d*, $J = 8.7$, H–C(2′), H–C(6′)). ^{13}C-NMR (125 MHz, CD_3OD): *Table*. FAB-MS (neg.): 907 ([$M-H$]$^-$). HR-FAB-MS (neg.): 907.2502 ([$M-H$]$^-$, $C_{41}H_{47}O_{23}^-$; calc. 907.2508).

*Kaempferol 3-*O*-[2,3,4-Tri-*O*-acetyl-α-*L*-rhamnopyranosyl-(1→3)-4-*O*-acetyl-α-*L*-rhamnopyranosyl-(1→6)]-β-*D*-glucopyranoside* (= *5,7-Dihydroxy-2-(4-hydroxyphenyl)-3-[[*O*-2,3,4-tri-*O*-acetyl-6-deoxy-α-*L*-mannopyranosyl-(1→3)-*O*-4-O-acetyl-6-deoxy-α-*L*-mannopyranosyl-(1→6)-β-*L*-glucopyranosyl]oxy}-4*H*-1-benzopyran-4-one*; **5**). Yellow amorphous poweder. $[\alpha]_D^{22} = -5.2$ ($c = 0.51$, MeOH). UV (MeOH): 203 (4.87), 266 (4.55), 345 (4.43). IR (KBr): 3430, 2925, 1746, 1654, 1608, 1508, 1367, 1228, 1178, 1078, 1047. ^{1}H-NMR (500 MHz, CD_3OD): 0.76 (*d*, $J = 6.3$, Me(6‴)); 1.14 (*d*, $J = 6.3$, Me(6‴)); 1.93 (*s*, MeCO–O–C(4‴), MeCO–O–C(2‴)); 2.03 (*s*, MeCO–O–C(4‴)); 2.17 (*s*, MeCO–O–C(3‴)); 3.44–3.58 (*m*, H–C(3″), H–C(4″), H–C(5″), H–C(2″), H_b–C(6″), H–C(5‴)); 3.73 (*dd*, $J = 4.5$, 9.0, H–C(3‴)); 3.88–4.05 (*m*, H_a–C(6″), H–C(2‴), H–C(5‴)); 4.58 (*s*, H–C(1‴)); 4.66 (br. *s*, H–C(1‴)); 4.90–5.04 (*m*, H–C(4‴), H–C(4‴), H–C(2‴)); 5.26 (*m*, H–C(3‴)); 5.47 (*d*, $J = 7.2$, H–C(1″)); 6.20 (*d*, $J = 1.8$, H–C(6)); 6.36 (*d*, $J = 1.8$, H–C(8)); 6.89 (*d*, $J = 8.7$, H–C(3′), H–C(5′));

8.00 (*d*, $J = 8.7$, H–C(2′), H–C(6′)). ^{13}C-NMR (125 MHz, CD_3OD): *Table*. FAB-MS (neg.): 907 ($[M - H]^-$). HR-FAB-MS (neg.): 907.2501 ($[M - H]^-$, $C_{41}H_{47}O_{23}^-$; calc. 907.2508).

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