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Highly glycosylated flavonoids from the pods of *Bobgunnia madagascariensis*

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ABSTRACT

Methanolic extracts of the pods of *Bobgunnia madagascariensis* (Leguminosae) yielded four pentaglycosylated flavonoids, including the 3-*O*-α-L-rhamnopyranosyl(1→3)-α-L-rhamnopyranosyl(1→2)[α-L-rhamnopyranosyl(1→6)]-β-D-glucopyranoside-7-*O*-α-L-rhamnopyranosides of 3,5,7-trihydroxy-2-(4-hydroxyphenyl)-4*H*-benzopyran-4-one (kaempferol) and 3,5,7-trihydroxy-2-(3,4-dihydroxyphenyl)-4*H*-benzopyran-4-one (quercetin), which were characterized by a novel O-linked branched tetrasaccharide. Spectroscopic and chemical methods were used to determine the structures of the latter, which co-occurred with the corresponding β-D-galactopyranosyl isomers, and two saponins. Conformational isomerism of quercetin 3-*O*-α-L-rhamnopyranosyl(1→3)-α-L-rhamnopyranosyl(1→2)[α-L-rhamnopyranosyl(1→6)]-β-D-glucopyranoside-7-*O*-α-L-rhamnopyranoside was detected in solution by NMR, a phenomenon previously associated only with *C*-glycosylflavonoids.

Bobgunnia madagascariensis (Desv.) J. H. Kirkbr. & Wiersema (Leguminosae) is a small tree or shrub found in deciduous forests throughout tropical and southern Africa, although it is primarily associated with Miombo woodland.[1] It was previously classified in section *Fistuloides* of the genus *Swartzia*, together with *Bobgunnia fistuloides* (Harms) J. H. Kirkbr. & Wiersema, which occurs in western tropical Africa.[2] Evidence supporting the segregation of both species into the separate genus *Bobgunnia* came initially from differences in morphology and pollen type, compared to neotropical *Swartzia*,[3] and later from DNA sequence analysis.[4] Local uses for *B. madagascariensis* have been documented for most parts of the plant, but those relating to the pods are of particular interest, since in crushed and powdered form they can be effective as fish poisons, insecticides, and molluscicidal agents.[1,5] The latter activity has been associated with saponins,[6] but little is known about other chemical constituents.[7] Herein we report on highly glycosylated flavonoids present in MeOH extracts of the pods, including two new examples characterized by a novel O-linked branched tetrasaccharide, and the first evidence for conformational isomerism of O-glycosylated flavonols in solution.

Pods of *B. madagascariensis* were collected near Mzuzu, northern Malawi, and a voucher specimen deposited in the Herbarium, Royal Botanic Gardens Kew (*STVP 1017*). For initial analyses, 5 g of pods were ground to a powder and extracted in 50 mL of MeOH for 24 h at room temperature. The filtered and evaporated MeOH extract was redissolved in MeOH and analyzed by LC–ESI-MS (Waters Alliance system with ZQ LC–MS detector) using a Phenomenex Luna C18(2) column (150 × 4.0 mm i.d.; 5 μm particle size) operating under gradient conditions (solvents A = MeOH, B = H_2O, C = 1% HCO_2H in MeCN; A = 0%, B = 90% at t = 0 min; A = 90%, B = 0% at t = 20 min; A = 90%, B = 0% at t = 30 min; A = 0%, B = 90% at t = 31 min; Method 1) at a flow rate of 0.5 mL/min at 30 °C. Two pairs of polar constituents eluting between t_R 5–7 min had UV spectra typical of *O*-glycosides of quercetin (**1a** and **1b**; 255, 266 sh, 355 nm) and kaempferol (**2a** and **2b**; 265, 349 nm).[8] In each case, a broad valley observed between bands I and II and the lack of a shoulder at ca. 300 nm indicated that the flavonols were glycosylated at both C-3 and C-7. The earlier eluting quercetin glycosides **1a** and **1b** exhibited identical mass spectra characterized by a protonated molecule at *m/z* 1049 $[M+H]^+$ and fragments generated in-source at *m/z* 903, 757, 611, 449, and 303. Similarly, the kaempferol glycosides **2a** and **2b** gave protonated molecules at *m/z* 1033 $[M+H]^+$ and fragments generated in-source at *m/z* 887, 741, 595, 433, and 287. These results suggested that each flavonol 3,7-di-*O*-glycoside comprised four deoxyhexose residues and one hexose residue. Two less polar constituents that eluted late in the chromatogram and without appreciable absorbance above 210 nm were detected as sodiated molecules $[M+Na]^+$ at *m/z* 1095 (**3**), and 963 (**4**).

Compounds **1a**, **1b**, **2a**, **2b**, **3,** and **4** were purified by semi-preparative HPLC using a Waters system (LC600 pump and controller, 996 photodiode array detector, and 717 Plus autosampler). A dried

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MeOH extract derived from 10 g of powdered pods of *B. madagascariensis* was redissolved in 2 mL of MeOH, and aliquots (100 μL) injected successively onto a LiChrospher 100 RP-18 column (250 × 10.0 mm i.d.; 10 μm particle size). Gradient conditions were selected to give baseline separation of the four flavonol glycosides (A = MeOH, B = H_2O; A = 20% at t = 0 min; A = 44% at t = 16 min; A = 100% at t = 20 min; flow rate of 4.7 mL/min at 30 °C; Method 2), which were obtained in yields of 3.4 mg (**1a**, t_R = 11.3 min), 1.4 mg (**1b**, t_R = 11.9 min), 25.0 mg (**2a**, t_R = 12.7 min), and 2.6 mg (**2b**, t_R = 13.4 min). Additional constituents isolated using the same column but with method 1 above and a flow rate of 4.7 mL/min comprised a mixture of **3** and **4** (4.3 mg, t_R = 20.2 min), and **4** (8.0 mg, t_R = 20.7 min), as white amorphous solids, and the common flavonoid aglycones, eriodictyol (1.6 mg), and luteolin (1.3 mg).[9] The structures of the compounds were determined by NMR, MS, and in the case of the flavonoid glycosides, by sugar analysis. NMR spectra were acquired in MeOH-d_4 at 30 °C on a Bruker Avance II+ 700 MHz instrument equipped with a TCI-cryoprobe or on a Bruker Avance 400 MHz instrument. Standard pulse sequences and parameters were used to obtain 1D ^{1}H, 1D ^{13}C, 1D selective NOE, COSY, TOCSY, HSQC, and HMBC spectra. Chemical shift referencing was carried out using the internal solvent resonances at δ_H 3.31 and δ_C 49.1 (calibrated to TMS at 0.00 ppm). The absolute configurations of the constituent monosaccharides of **1a**, **1b**, **2a,** and **2b** released by acid hydrolysis (0.1–0.5 mg in 0.5 mL of 2 M HCl; 100 °C, 1.5 h) were determined by GC–MS of their trimethylsilylated thiazolidine derivatives prepared using an established method.[10] Conditions for GC were: capillary column, DB5-MS (30 m × 0.25 mm × 0.25 μm), oven temp. programme, 180–300 °C at 6 °C/min; injection temp., 350 °C; carrier gas, He at 1 mL/min. The acid hydrolysates of **1a** and **2a** each gave L-rhamnose and D-galactose, whereas **1b** and **2b** gave L-rhamnose and D-glucose (L-rhamnose, D-galactose and D-glucose at t_R = 10.3, 12.4 and 12.2 min, respectively; identical to authentic standards).

Flavonol glycosides **1a** and **2a** were identified from NMR and MS data as the known 3-*O*-α-L-rhamnopyranosyl(1→3)-α-L-rhamnopyranosyl(1→2)[α-L-rhamnopyranosyl(1→6)]-β-D-galactopyranoside-7-*O*-α-L-rhamnopyranosides of quercetin (cordylasin A), and kaempferol (cordylasin B), respectively (Fig. 1).[11] Compounds **1b** and **2b** were thus hexosyl isomers of the latter; they had UV and MS spectra identical to those of **1a** and **2a**, respectively, but on hydrolysis afforded D-glucose and L-rhamnose rather than D-galactose and L-rhamnose. For **1b**, a yellow amorphous solid ($[\alpha]_D^{22}$ −88.0 (*c* 0.038, MeOH)), the molecular formula $C_{45}H_{60}O_{28}$ was established by HRESIMS (*m*/*z* 1049.3336 $[M+H]^+$, calcd for $C_{45}H_{61}O_{28}$, 1049.3344). The ^{1}H NMR spectrum of **1b** included resonances for anomeric protons of O-linked sugars at δ_H 5.62 (d, J = 7.7 Hz, δ_C 100.5), corresponding to D-glucose, and 5.55 (d, J = 1.9 Hz, δ_C 100.0), 5.22 (d, J = 1.8 Hz, δ_C 102.6), 5.03 (d, J = 1.8 Hz, δ_C 104.1), and 4.50 (d, J = 1.8 Hz, δ_C 102.2), corresponding to four L-rhamnose residues. Full assignment of the ^{1}H and ^{13}C resonances of each sugar was achieved using standard 2D NMR datasets (Table 1), and their anomeric configurations defined from the magnitudes of $^3J_{H\text{-}1,H\text{-}2}$ coupling constants.[12] The sites of glycosylation of the quercetin aglycone of **1b** were determined from long range connectivities detected in the HMBC spectrum between δ_H 5.62 (H-1 of Glc) and C-3 (δ_C 134.7), and δ_H 5.55 (H-1 of 7-*O*-Rha) and C-7 (δ_C 163.4). The β-D-glucopyranosyl residue was therefore the primary sugar O-linked at C-3. Both C-2 and C-6 of the latter were shifted downfield in the ^{13}C NMR spectrum, and glycosylated by α-L-rhamnopyranosyl residues (Rha I and Rha III, respectively), according to the HMBC connectivities detected from Glc H-2 to C-1 of Rha I at δ_C 102.6, H-1 of Rha I to Glc C-2 at δ_C 80.1, Glc 6-CH_2 to C-1 of Rha III at δ_C 102.2, and H-1 of Rha III to Glc C-6 at δ_C 68.2. An additional site of glycosylation was suggested by the

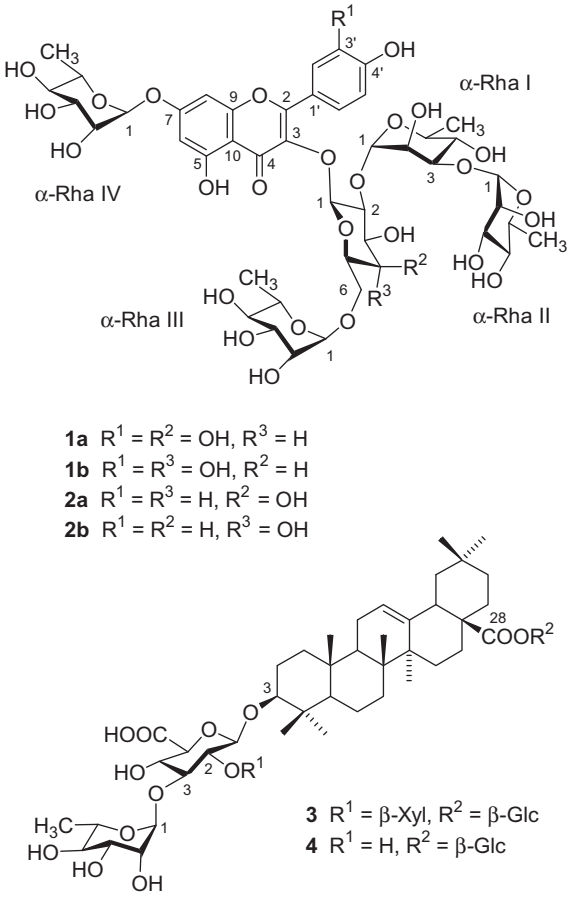

Figure 1. Flavonol pentaglycosides and saponins from the pods of *Bobgunnia madagascariensis* (β-Glc = β-glucopyranosyl, α-Rha = α-rhamnopyranosyl, β-Xyl = β-xylopyranosyl).

downfield shift to C-3 of Rha I, and confirmed by connectivities detected from H-3 of Rha I to C-1 of Rha II at δ_C 104.1, and H-1 of Rha II to C-3 of Rha I at δ_C 80.2. Thus a branched tetrasaccharide was O-linked at C-3, and a single α-L-rhamnopyranosyl residue (Rha IV) O-linked at C-7. Compound **1b** was therefore quercetin 3-*O*-α-L-rhamnopyranosyl(1→3)-α-L-rhamnopyranosyl(1→2)[α-L-rhamnopyranosyl(1→6)]-β-D-glucopyranoside-7-*O*-α-L-rhamnopyranoside (Fig. 1).

The kaempferol pentaglycoside **2b** was a yellow amorphous solid ($[\alpha]_D^{22}$ −121.2 (*c* 0.085, MeOH)) for which a molecular formula of $C_{45}H_{60}O_{27}$ was obtained by HRESIMS (*m*/*z* 1033.3389 $[M+H]^+$, calcd for $C_{45}H_{61}O_{27}$, 1033.3395). It had a glycosylation profile identical to that of **1b**. In comparison with the latter, the same pattern of connectivities defining linkages between the glycosyl residues and the aglycone, and between the glycosyl residues themselves, was observed in HMBC data. NMR assignments for the ^{1}H and ^{13}C resonances of the glycosyl residues of **2b** were almost identical to those of **1b** (Table 1). Compound **2b** was therefore kaempferol 3-*O*-α-L-rhamnopyranosyl(1→3)-α-L-rhamnopyranosyl(1→2)[α-L-rhamnopyranosyl(1→6)]-β-D-glucopyranoside-7-*O*-α-L-rhamnopyranoside (Fig. 1).

Two sets of resonances corresponding to the protons of the quercetin B-ring of **1b** were observed in the ^{1}H NMR spectrum acquired in MeOH-d_4, and duplication of other resonances, including those of the 3-*O*-β-D-glucopyranosyl and 6^{Glc}-*O*-α-L-rhamnopyranosyl (Rha III) residues, was detectable, although with less differentiation in chemical shift between the two forms. The extent of the differences noted for the ^{13}C resonances of **1b** was greatest

Table 1
^{1}H and ^{13}C NMR spectroscopic data for **1b**, **1b**‡[a] and **2b** (700 MHz, CD_3OD, 30 °C)

	1b		**1b**‡		**2b**	
	δ ^{1}H (*J* in Hz)	δ ^{13}C	δ ^{1}H (*J* in Hz)	δ ^{13}C	δ ^{1}H (*J* in Hz)	δ ^{13}C
Aglycone						
2		159.5		161.2		159.7
3		134.7		134.0		134.7
4		179.5		179.3		179.6
5		162.9		163.1		163.1
6	6.46 (d, 2.1)	100.5	6.45 (d, 2.1)	100.3	6.47 (d, 2.2)	100.6
7		163.4		163.3		163.5
8	6.72 (d, 2.2)	95.6	6.72 (d, 2.1)	95.6	6.73 (d, 2.2)	95.8
9		158.0		158.0		158.2
10		107.6		107.5		107.7
1′		123.1		121.0		122.8
2′	7.61 (d, 2.1)	117.3	7.44 (d, 2.0)	110.0	8.05 (d, 8.9)	132.4
3′		146.2		153.2	6.90 (d, 8.9)	116.5
4′		150.2		157.2		161.9
5′	6.88 (d, 8.4)	116.2	6.69 (d, 8.2)	109.1	6.90 (d, 8.9)	116.5
6′	7.64 (dd, 8.4, 2.1)	123.6	7.52 (dd, 8.2, 2.1)	122.8	8.05 (d, 8.9)	132.4
3-O-β-Glc						
1	5.62 (d, 7.7)	100.5	5.66 (d, 7.7)	100.3	5.65 (d, 7.6)	100.5
2	3.67 (dd, 9.4, 7.8)	80.1	3.74 (dd, 9.2, 7.7)	79.6	3.62 (dd, 9.4, 7.6)	80.1
3	3.56 (t, 9.1)	79.0	3.55 (m)	79.0	3.56 (t, 9.0)	79.0
4	3.28 (m)	71.9	3.37 (t, 9.3)	71.7	3.25 (t, 9.3)	72.1
5	3.34 (ddd, 9.7, 6.3, 1.8)	77.1	3.33 (m)	77.1	3.35 (ddd, 9.6, 6.4, 1.9)	77.3
6	3.81 (m)	68.2	3.81 (m)	67.9	3.82 (dd, 11.4, 1.7)	68.3
	3.40 (m)		3.42 (m)		3.39 (m)	
2^{Glc}-O-α-Rha (I)						
1	5.22 (d, 1.8)	102.6	5.23 (d, 1.7)	102.4	5.22 (d, 1.7)	102.7
2	4.11 (dd, 3.4, 1.8)	72.2	4.10 (m)	72.3	4.10 (dd, 3.4, 1.8)	72.3
3	3.88 (dd, 9.7, 3.4)	80.2	3.88 (dd, 9.6, 3.2)	80.2	3.87 (dd, 9.7, 3.3)	80.2
4	3.47 (t, 9.5)	73.3	3.46 (m)	73.2	3.46 (t, 9.7)	73.3
5	4.11 (m)	70.2	4.10 (m)	70.1	4.09 (dd, 9.7, 6.2)	70.3
6	1.01 (d, 6.2)	17.5	0.95 (d, 6.2)	17.5	0.98 (d, 6.2)	17.7
3^{Rhal}-O-α-Rha (II)						
1	5.03 (d, 1.8)	104.1	5.02 (d, 1.8)	104.1	5.03 (d, 1.8)	104.2
2	3.97 (dd, 3.4, 1.8)	72.2	3.96 (dd, 3.3, 1.8)	72.2	3.97 (dd, 3.4, 1.8)	72.3
3	3.77 (dd, 9.6, 3.4)	72.3	3.77 (dd, 9.6, 3.4)	72.3	3.77 (dd, 9.5, 3.4)	72.4
4	3.40 (t, 9.5)	74.2	3.40 (t, 9.5)	74.2	3.40 (t, 9.5)	74.3
5	3.84 (dd, 9.7, 6.2)	70.1	3.84 (dd, 9.7, 6.2)	70.1	3.83 (dd, 9.5, 6.2)	70.2
6	1.30 (d, 6.3)	18.0	1.30 (d, 6.3)	18.0	1.31 (d, 6.3)	18.1
6^{Glc}-O-α-Rha (III)						
1	4.50 (d, 1.8)	102.2	4.52 (d, 1.7)	102.1	4.49 (d, 1.7)	102.3
2	3.55 (dd, 3.4, 1.8)	72.1	3.61 (dd, 3.4, 1.7)	72.2	3.55 (dd, 3.4, 1.7)	72.2
3	3.47 (m)	72.3	3.52 (dd, 9.4, 3.4)	72.1	3.46 (dd, 9.5, 3.4)	72.4
4	3.22 (t, 9.5)	73.9	3.20 (t, 9.6)	73.9	3.22 (t, 9.5)	74.0
5	3.41 (m)	69.7	3.40 (m)	69.7	3.41 (m)	69.8
6	1.07 (d, 6.2)	17.8	1.06 (d, 6.2)	17.8	1.07 (d, 6.2)	17.9
7-O-α-Rha (IV)						
1	5.55 (d, 1.9)	100.0	5.55 (d, 1.9)	100.0	5.56 (d, 1.8)	100.1
2	4.01 (dd, 3.4, 1.8)	71.8	4.01 (dd, 3.4, 1.8)	71.8	4.01 (dd, 3.5, 1.8)	71.8
3	3.82 (dd, 9.5, 3.5)	72.1	3.82 (dd, 9.5, 3.5)	72.1	3.83 (dd, 9.5, 3.4)	72.2
4	3.48 (t, 9.5)	73.7	3.48 (t, 9.5)	73.7	3.48 (t, 9.5)	73.7
5	3.62 (dd, 9.5, 6.2)	71.3	3.62 (dd, 9.5, 6.2)	71.3	3.61 (dd, 9.6, 6.2)	71.3
6	1.26 (d, 6.2)	18.1	1.26 (d, 6.2)	18.1	1.26 (d, 6.2)	18.2

[a] Rotameric form of **1b**.

for B-ring carbons (C-1′–C-6′), C-2, and C-3. Correlations between the duplicated resonances of B-ring protons were observed in selective 1D NOE experiments; thus excitation of δ_H 7.61 (H-2′), 6.88 (H-5′), and 7.64 (H-6′) of **1b** elicited responses at δ_H 7.44 (H-2′), 6.69 (H-5′), and 7.52 (H-6′), respectively, of **1b**‡, and vice versa (Table 1). These exchange phenomena were consistent with the presence of conformational isomers (rotamers). However, no evidence for conformational isomerism was detected for the kaempferol analog **2b**. Rotamer formation in **1b** appears to originate from restricted rotation about the C-2 to C-1′ bond of the aglycone due to steric hindrance between the bulky O-linked branched tetrasaccharide at C-3, and the disubstituted flavonol B-ring (3′,4′-diOH). Although conformational isomerism is a well-known solution property of C-glycosylated flavonoids,[13] it has not been reported previously for O-linked flavonoid glycosides.

Compounds **3** and **4** were identified from spectroscopic data and literature comparisons as the known saponins, 3-*O*-β-xylopyranosyl(1→2)[α-rhamnopyranosyl(1→3)]-β-glucuronopyranosyl-28-*O*-β-glucopyranosyl-oleanolic acid, and 3-*O*-α-rhamnopyranosyl(1→3)-β-glucuronopyranosyl-28-*O*-β-glucopyranosyl-oleanolic acid (putranoside C), respectively (Fig. 1).[14] Neither compound has been reported previously as a constituent of *B. madagascariensis* (including work published using the synonym, *Swartzia madagascariensis*), although saponins with similar structures occur in the pods.[6] Other sources of both **3** and **4** in the Leguminosae include the aerial parts of *Sesbania sesban* (L.) Merr.[15], and the leaves of

Swartzia simplex (Sw.) Spreng.,[14] while **4** was also reported from the fruits of *Swartzia langsdorffii* Raddi.[16]

Pentaglycosides represent fewer than 1% of the known flavonol glycosides, which number more than 1500.[17] There are no previous reports of the O-linked branched tetrasaccharide that characterizes **1b** and **2b**, although the corresponding β-D-galactopyranosyl isomer has been found as a component of mildbraedin, a kaempferol tetraglycoside from the leaves of *Mildbraediodendron excelsum* Harms (Leguminosae), and four species of *Cordyla* (Leguminosae).[11,18] It was also present in cordylasins A (**1a**) and B (**2a**), flavonol pentaglycosides that accumulate in the leaves of three species of *Cordyla*.[11] The occurrence of flavonol pentaglycosides in MeOH extracts of the leaves of *B. madagascariensis* and *B. fistuloides* (sourced from herbarium specimen *Le Testu 8983*, Royal Botanic Gardens Kew) was also investigated in the present study, using LC–ESI-MS as above. Both species contained **1a**, **1b**, **2a,** and **2b**, but in the case of dried leaves of *B. madagascariensis*, at levels 10 times less than in the mature pods. The kaempferol pentaglycosides **2a** and **2b** were more abundant than their quercetin analogs (**1a** and **1b)** in the pod and together represented up to 20% of the pod weight. Saponins **3** and **4** were not detected in the leaf extracts of either species.

Bobgunnia, *Cordyla,* and *Mildbraediodendron* have traditionally been assigned to the tribe Swartzieae of the Leguminosae. However, DNA sequence analyses indicate that the tribe is polyphyletic, and in need of reclassification.[19] Although *Bobgunnia* has been placed in the so-called 'swartzioid' clade, a relatively well-defined group of seven genera,[4] both *Cordyla* and *Mildbraediodendron* fall within the 'aldinoid' clade, a closely related but more diverse assembly that includes genera not only of the Swartzieae, but also of two other Leguminosae tribes, the Sophoreae and Dipterygeae.[19] The distinctive flavonoid chemistry shared by *Bobgunnia*, *Cordyla,* and *Mildbraediodendron* is represented in both the 'swartzioid' and 'aldinoid' clades, suggesting that wider surveys for flavonol glycosides that incorporate the unique branched tetrasaccharide, *O*-α-L-Rha(1→3)-α-L-Rha(1→2)[α-L-Rha(1→6)]-β-D-Gal/Glc, are merited.

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