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TWO NEW PROMELACACINIDIN DIMERS, INCLUDING A NOVEL FLAVANONE-FLAVANOL DIMER CHARACTERIZED BY A UNIQUE C(3)-C(4) LINKAGE, FROM THE HEARTWOOD OF *Acacia nigrescens*

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Two new promelacacinidin biflavonoids, mesquitol-(4α,5)-epimesquitol-4β-ol and a 3′,4′,7,8-tetrahydroxyflavanone(3,4)-ent-epimesquitol, were isolated among others from the heartwood of Acacia nigrescens*. The flavanone derived dimer, characterized by a unique C(3) to C(4) bridge, which links the monomers via two stereogenic and sp^3 hybridized C-atoms, is the prototype of a new subgroup of the flavonoid family. Assessment of the absolute configuration of all five stereogenic centers of this novel flavanone-derived biflavonoid was achieved by correlating the chiroptical properties of the benzoyl chromophore to the absolute configuration of C(2) of the flavanone moiety and hence the absolute stereochemistry of the other four chiral centers.*

Key words: *Acacia nigrescens*, dimeric flavonoids, promelacacinidin, flavanone-flavan-3-ol, CD-spectral properties.

The flavonoids are one of the most prevalent groups of phenolic compounds in nature and display a wide range of biological and pharmacological properties. Biflavonoids, as the simplest members of the polymeric flavonoids, are known to display a variety of biological activities, such as anti-inflammatory activity, the inhibition of cytochrome P450 enzymes, antiviral activity, and neuroprotective effects, the latter suggesting their therapeutic potential against neurodegenerative diseases, including ischemic stroke and Alzheimer's disease [1]. The dimeric procyanidins B1 and B2 demonstrated potent antioxidative activity, whereas grape seed proanthocyanidin extract, containing a mixture of 75–80% oligomeric proanthocyanidin and 3–5% monomeric proanthocyanidin, has proven efficacy against the incidence of ischemia-reperfusion injury and apoptosis of cardiomyocytes and reduced foam cell development [2].

Herein we report on the isolation and characterization of two new biflavonoids, mesquitol-(4$\alpha\rightarrow$5)-epimesquitol-4β-ol **1** and the flavanone-(3$\rightarrow$4)-flavan-3-ol **3** from the heartwoord of *Acacia nigrescens*, belonging to a hitherto small group characterized by the rare pyrogallol A-ring as a structural feature. These are conveniently named promelacacinidins and, together with the related proteracacinidins, were the subject of recent publications demonstrating their occurrence in *Acacia* species [3–7] and in *Prosopsis glandulosa* [8]. To our knowledge, both these compounds are new, whereas the unique carbon-carbon linkage (C-3 to C-4) of the flavanone-flavanol dimer merits special mention since it represents a prototype of a new class of biflavonoids.

The structures of these compounds (as their permethylaryl ether acetate derivatives) were elucidated by spectroscopic methods, including NMR and CD analysis.

The ^{1}H NMR spectrum of the octamethylether triacetate **2** of compound **1** in $(CD_3)_2CO$ (Table 1) exhibited eight *O*-methyl and three *O*-acetyl resonances typical of methylated phenolic groups and acetylated aliphatic hydroxyl groups respectively, which strongly suggested a dimer containing a flavanol unit linked to a flavan-3,4-diol terminal unit.

Dedicated to Prof. E. Malan, who initiated and supervised this research project, for a noteworthy contribution in the flavonoid field, and who has since retired.

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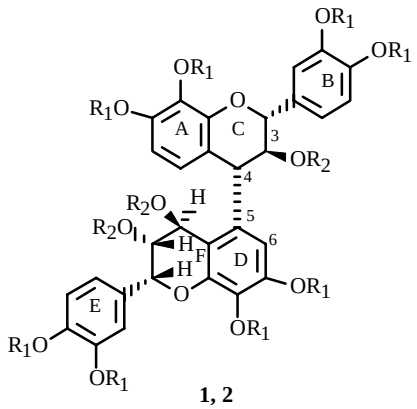
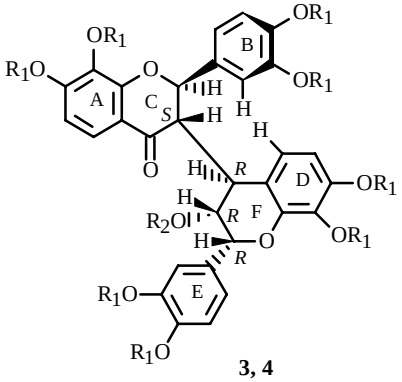
TABLE 1. ^{1}H NMR Peaks (ppm) of **2** and **4** at 300 MHz. Splitting Patterns and J-values (Hz, $(CD_3)_2CO$, 296 K) are Given in Parentheses

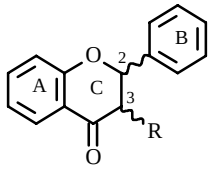
Ring, Atom C	**2**	**4**	Ring, Atom C	**2**	**4**
A 5	6.21 (d, 8.5)	7.60 (d, 8.5)	E 2′	7.20 (br.d, 2.0)	7.07 (d, 2.0)
6	6.56 (d, 8.5)	6.82 (d, 8.5)	5′	6.99 (d, 8.5)	6.98 (d, 8.5)
B 2′	7.22 (d, 2.0)	7.08 (d, 2.0)	6′	7.1 (dd, 2.0, 8.5)	7.03 (dd, 2.0, 8.5)
5′	6.96 (d, 8.5)	6.83 (d, 8.5)	F 2	5.46 (br.s, 1.5)	5.65 (d, 2.0)
6′	7.10 (dd, 2.0, 8.5)	6.89 (dd, 2.0, 8.5)	3	5.42 (br.s)	5.42 (dd, 2.0, 2.5)
C 2	5.06 (d, 9.0)	5.91 (d, 3.5)	4	6.10 (d, 3.5)	3.43 (dd, 2.5, 10.0)
3	5.94 (dd, 9.0 & 10.0)	3.59 (dd, 3.5, 10.0)	OMe	3.85, 3.84, 3.83 (×3),	3.95, 3.91, 3.89, 3.83
4	4.50 (d, 10.0)	-		3.79, 3.76, 3.75 (all s)	(×3), 3.74, 3.72 (all s)
D 5	-	7.15 (d, 8.5)	OAc	2.24, 1.98, 1.66 (s)	1.70 (s)
6	6.70 (s)	6.76 (d, 8.5)			



1, 2



3, 4



5

C(2) = if CE negative

C(2) = if CE positive

1: $R_1 = R_2 = H$; **2**: R_1 = Me, R_2 = Ac; **3**: $R_1 = R_2 = H$

4: R_1 = Me, R_2 = Ac; R = H/OH

Furthermore, the two ABX-systems and an AB-system in the aromatic region are in harmony with two 3,4-dihydroxybenzene (catechol) B-ring and also a pyrogallol A-ring. These discernible spin systems are associated with a broad singlet at δ 6.70 which is indicative of an interflavanyl linkage between C(4) of the "upper" unit and either C(5) or C(6) of the D-ring of the "lower" unit. This structural data, considered together with the presence of two AMX-systems in the heterocyclic region, is in accordance with a dimer comprised of two mesquitol moieties, one being a terminal flavan-3,4-diol.

By utilizing the shielded proton H-4 (F)(δ 6.10, d) and H-4 (C) (δ 4.50, d) as references [8, 9], it was possible to correlate each of the two heterocyclic AMX-systems with the two monomeric units (i.e., the F- and C-rings respectively).

The broad aromatic singlet showed no $^4J_{HH}$ coupling to the H-4 (F), but significant coupling to H-4 (C) and the OMe at δ 3.75 (D-ring), which is a clear justification that this singlet belongs to H-6 (D) and hence the interflavanyl linkage is between C-4 (C) and C-5 (D).

From the benzylic coupling between H-4 (C) (δ 4.50, d, 10.0 Hz) and H-5 (A) (δ 6.21,d, 8.5 Hz) it was possible to establish the AB-system belonging to the A-ring.

The heterocyclic AMX-system of the C-ring showed coupling constants ($J_{2,3}$ = 9.0; $J_{3,4}$ = 10.0 Hz) typical of a 2,3-*trans*-3,4-*trans* relative stereochemistry [10], which was confirmed by the n.O.e-association between H-2 (C) and H-4(C), placing these protons on the same side of the heterocyclic ring.

The coupling constants ($J_{2,3}$ = 1.5; $J_{3,4}$ = 3.5 Hz) of the F-ring are in accordance with a 2,3-*cis*-3,4-*trans* relative stereochemistry [8, 9].

The negative Cotton effect of [θ] – 15580 near 246 nm is reminiscent of a 4α-substituted C-ring [3, 10]. This observation, when taken in conjunction with the 2,3-*trans*-3,4-*trans* relative stereochemistry already established for the C-ring, permits assignment of the absolute stereochemistry of the top unit as 2*R*,3*S*,4*R*.

The prominent occurrence of epimesquitol-4β-ol in the same extract of the plant makes it highly likely that it is the logical monomeric precursor for the dimer **1**, hence permitting assessment of the absolute stereochemistry of the F-ring of the lower unit as 2*R*,3*R*,4*S*.

The 3′,4′,7,8-tetrahydroxyflavanone-(3→4)-3′,4′,7,8-tetrahydroxylflavan-3-ol **3** was isolated and characterized as the methyl ether acetate derivative **4**.

The ^{1}H NMR spectrum of **4**, which was free from the effects of rotational isomerism, exhibited eight clearly defined *O*-methyl resonances and one *O*-acetyl resonance, which is indicative of a dimeric compound. This deduction was corroborated by FAB-MS with a molecular ion of *m/z* 730 and a molecular formula of $C_{40}H_{42}O_{13}$.

The H-4 (F) (δ 3.43) was identified and correlated to the aromatic AB-system, establishing the D-ring as a pyrogallol type, and hence the flavanol as either a mesquitol or oritinol analogue. The same H-4 was also correlated to H-3 (F, δ 5.42, dd, $^3J_{HH}$ = 2.5 and 2.0 Hz), while the latter proton was conveniently correlated to H-2 (F, δ 5.65, d, $^3J_{HH}$ = 2.0 Hz), hence revealing the presence of the heterocyclic AMX-system. A COSY experiment showed the coupling of H-2 (F) to the 2′,6′-protons of the E-ring (δ 7.07 and 7.03) which, in turn, assisted the identification of the ABX-system of the E-ring of compound **4** and hence the flavan-3-ol as a mesquitol type, while the coupling constants ($J_{2,3}$ = 2.0 and $J_{3,4}$ = 2.5 Hz) are reminiscent of a 2,3-*cis*-3,4-*trans* relative stereochemistry [10].

Notable in the unidentified part of the NMR spectrum of **4** was the presence of a low field doublet at δ 7.60 (J = 8.5 Hz) coupled to a signal at δ 6.82 (d, J = 8.5 Hz), which was not only a clear indication of an aromatic AB-system (pyrogallol type), but also that this ring is conjugated with the carbonyl functionality.

The flavanone skeleton of the "upper" unit was confirmed unequivocally by the exposure of the remaining two coupled heterocyclic protons at δ 5.91 (d, 3.5 Hz) and at δ 3.59 (dd, J = 3.5 and 10.0 Hz) as H-2(C) and H-3(C) respectively, while the proton at δ 3.59 is also coupled to H-4(F) at δ 3.43 with a coupling constant of 10.0 Hz, hence establishing the novel link between the H-3(C) and H-4(F) of the constituent flavanone and flavanol monomers.

The aromatic ABX-system of the B-ring was revealed by a COSY experiment and by the utilization of H-2(C) as a reference, while the coupling constant between H-2(C) and H-3(C) of J = 3.5 Hz is in harmony with a 2,3-*cis* or 2,3-*trans* (placement of the bulky C(2) and C(3) substituents diaxial) relative stereochemistry [10].

An HMBC experiment showed couplings between H-3 (C, δ 3.59) to C-3 (F, δ_C 69.6, $^2J_{CH}$), C-4 (F, δ_C 38.7, $^2J_{CH}$), and to C-4 (C, δ_C 191.7, $^2J_{CH}$), all of which are in full agreement with the inference (*vide supra*) that the C(3) of the "upper" flavanone unit is indeed uniquely linked to the C(4) of the flavanol "lower" unit.

Moreover, this bridge between two sp^3-hybridized and stereogenic carbon atoms is, to the best of our knowledge, the prototype of a new subgroup in the biflavonoid family.

It is conceivable that the unique electronic/steric properties entrenched in the pyrogallol A-ring of both monomeric units of **3** played a pivotal role in the formation of this rare interflavanyl bridge. Furthermore, it is likely that the isolation and identification of dimer **3** could give rise to the isolation of more members of this type of oligomeric flavonoids.

A perusal of the literature has revealed that the presence of the benzoyl chromophore in compound **4** and its known chiroptical properties offers the most tangible leverage to unravel the absolute stereochemistry of all the stereogenic centers [11–14].

Despite a lengthy and ostensibly successful utilization of circular dichroism (CD) to establish absolute configuration in monomeric and oligomeric flavonoids, some uncertainty as to the direct extrapolation of the empirical rules has arisen over the years. Although this ambiguity was addressed recently [14], it is noteworthy to mention the contemporary and authoritative article [15] in which the authors persuasively reported the results of an investigation into the non-empirical assignment of the absolute configuration of the C(2) stereogenic center of flavanones. They concluded that flavanones with the C(2)-aryl group equatorially oriented and with the 2*S* (2α, *vide infra*) configuration will exhibit a negative CE at the n→π* absorption band (285 nm) and a negative CE at the π→π*(330 nm) band [15].The authors have succeeded elegantly not only in establishing a firm and uncompromising correlation between the chiroptical properties of flavanones and the absolute configuration of C(2), but also in erasing the prevailing uncertainty in this regard. It is worthwhile mentioning that this configurational/chiroptical correlation established (*vide supra*) is in full agreement with the empirical assignment published some 35 years ago by Gaffield [16]. It seems reasonable to conclude that the uncertainty that has arisen may be partly attributed to the fact that assignment of the absolute configuration at C(2) of flavanones sometimes changes from *S* to *R*, based on a change in the priorities of the C(2) ligands, without a change in the true absolute configuration of the C(2) center.

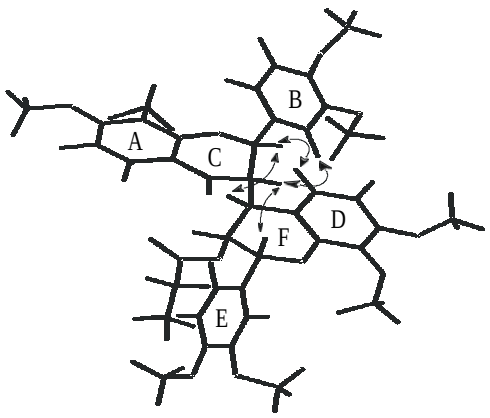


Fig. 1. Computer model of 3′,4′,7,8-tetra-*O*-methylflavanone-(3,4)-tetra-*O*-methyl-ent-epimesquitol acetate (**4**).

It is the opinion of the authors that a convention based on a system utilized to denote the absolute stereochemistry of the monosaccharides may also be applied successfully in the case of flavanones.

In the case of monosaccharides, a generally accepted drawing of D-glucopyranose is made, followed by the placement of the equatorial/axial substituents as either α or β.

In harmony with this convention and hopefully to the exclusion of uncertainty, we recommend that the structures of flavanones and derivatives thereof are drawn as depicted in **5**, i.e., with the basic $C_6.C_3.C_6$ skeleton horizontal, A-ring on the left, B-ring on the right, and heterocyclic oxygen at the top. For those flavanones with negative Cotton effect at λ 290 nm, the B-ring at C(2) is drawn with a dotted wedge, indicating an equatorial bond pointing downwards (α-orientation), while a positive Cotton effect at 290 nm would give a clear indication of the B-ring in the axial position (β-orientation) and hence drawn with a bold wedge. To extend the proposed convention to the elegant results of Rosini *et al*. [15] (*vide supra*) would thus imply that their non-empirical correlation of the 2*S*-configuration of the natural flavanone (naringenin) with a negative CE at *ca*. λ 290 nm, would mean that the B-ring in naringenin has the α-orientation and can therefore be referred to as having the 2α stereochemistry.

To unravel the absolute stereochemistry of the flavanone **4**, focus is thus placed on those crucial absorption bands at 330 and 285 nm (due to the $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions of the benzoyl chromophore) in the CD-spectrum of the flavanone derivative **4** aimed at assessment of the absolute configuration of C(2) of the 'upper' flavanone monomeric unit. In addition, the magnitude of the relevant coupling constants will be interpreted to establish the relative stereochemistry of the stereogenic centers. Finally, the proposed structure will be corroborated by n.O.e associations and molecular modelling to unambiguously assign the absolute configuration of all five centres.

The striking observation in the CD-spectrum of the dimer **4** is a high-amplitude positive Cotton effect, $[\theta]$ $+1.114 \times 10^4$ at λ 294.10 nm. In addition, there are two relative prominent negative absorption bands at λ 327.1 nm (-7.676×10^3) and at λ 245.20 nm (-1.024×10^4). These observations, in conjunction with the conclusion of previous authors (*vide supra*), are rationalized confidently to imply that the absolute configuration of C(2) of the flavanone unit of dimer **4** is indeed 2β (2*R)*.

The C(2)–C(3)-relative stereochemistry of the C-ring merits some special comment: While the overwhelming number of C(3)-substituted flavanones are characterized by the expected 2,3-*trans* relative stereochemistry and a 2-H, 3-H coupling constant of J ~ 12 Hz, a notable smaller coupling constant (J = 3.5 Hz) is displayed in the spectrum of **4**. This either points towards a highly unlikely 2,3-*cis* relative configuration for the bulky flavanyl- and phenyl substituents or 2,3-*trans* relative stereochemistry with a C-ring conformation in which these units occupy axial/*quasi*-axial positions. The presence of a positive n.O.e. association between H-2′(B) and H-3(C) in the NOESY spectum, however, eliminates the possibility of a 2,3-*cis* configuration for this flavanone-flavanol dimer. The proposed structure for **4** (fig. 1) therefore encompasses a structural assembly in which the C(2)-B-ring occupies the axial position, whereas the C(3)-flavanyl moiety is *quasi*-axial oriented. Furthermore, the model (Dreiding) of this compound with the suggested orientation of the two bulky constituents at C(2) and C(3) revealed that free rotation of the C(3)-flavanyl moiety about the C-3(C)–C-4(F)-axis is indeed possible. This degree of rotational freedom

is clearly supported by an NMR spectrum at ambient temperatures which is devoid of any effect related to rotational isomerism. Subsequent scrutiny of the data obtained from computer modeling (Fig. 1) is in total harmony with this unique relative stereochemistry at C(2) and C(3) of the flavanone heterocyclic ring, thus defining the absolute stereochemistry as 2*R*,3*S*.

The established relative stereochemistry of the flavan-3-ol "lower" unit as 2,3-*cis*-3,4-*trans* implies an absolute stereochemistry for the F-ring as either 2*R*,3*R*,4*R* or 2*S*,3*S*,4*S*. NOESY experiments illuminated not only crucial associations within each monomeric unit, but also assisted to conclusively assign the absolute stereochemistry of the flavan-2-ol unit as 2*R*,3*R*,4*R* *via* scrutiny of those pivotal n.O.e associations between the flavanone unit, with known absolute stereochemistry, and the flavanol moiety.

EXPERIMENTAL

General Experimental Procedures. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE DPX 300 spectrometer with TMS as internal standard. Electron Impact Mass Spectroscopy (EIMS) data were recorded on a VG-70E instrument. CD data was obtained in MeOH as solvent on a Jasco J-710 spectropolarimeter. TLC was performed on precoated Merck plastic sheets (silica gel 60 PF_{254}, 0.25 mm), and the plates were sprayed with H_2SO_4–HCHO (40:1, v/v) after development. Preparative plates (PLC) [20×22 cm, Kieselgel PF_{254} (1.0 mm)] were air dried and used without prior activation. Column chromatography was done on Sephadex LH-20 in 120×4 cm columns, at a flow rate of 30 mL/hr using EtOH as eluent. Flash column chromatography (FCC) was carried out in a glass column (54×6.5 cm) charged with Merck Kieselgel 60 (230–400 mesh) using C_6H_6–Me_2CO as eluent at a flow rate of 60 mL/min. Acetylations were conducted in Ac_2O-py at 50°C for 24 hrs. Phenolic specific methylations were carried out with diazomethane at –15°C. Evaporations were done under reduced pressure at ambient temperature in a rotary evaporator, and freeze drying of aqueous solutions on a Virtis 12 SL freezemobile. The PC Spartan Pro Mechanics Program (PC/X86) 6.0.6 was used to do the calculations and construct the low energy conformer calculated by the semi-empirical (PM3) method, as depicted in Fig. 1.

Plant Material. The trunk of *A. nigrescens* was collected near Ellisras, Northern Province, South Africa and identified by Pricilla Swartz from the National Botanical Research Institute in Pretoria. Voucher reference National Herbarium Pretoria 3446000/113.

Extraction and Isolation. Drillings (11.3 kg) from the heartwood of *A. nigrescens* were first extracted with $(CH_3)_2CO$ (3 × 3.0 L) for 24 h periods at room temperature (25°C). the dried drillings were extracted with MeOH (3 × 3.0 L) under the same conditions. Subsequently, the solid residue was obtained by evaporating the MeOH under vacuum at 40°C (315 g). An enriched extract was obtained by repeated FCC of 7 × 6 g of the MeOH extract, using Merck Kieselgel 60 as stationary phase and C_6H_6-Me_2CO (8:2, v/v) as eluent. The following combinations were obtained: A (tubes 21–25, 9.09 g), B (53–143, 14.82 g) and C (144–360, 6.72 g). The enriched combination C (6.72 g) was separated on Sephadex LH-20 using EtOH as eluent resulting in the following combinations: A1 up to A17 (3.582 g) comprised the monomeric flavonoids as reported previously [7]; A18 to A22 (named A20) were combined (1.153 g). Prior to methylation, 20 mg of the combined fraction was dissolved in acetone-d_6 and subjected to ^{1}H NMR screening for possible naturally occurring methoxyl groups, but none were present. After methylation, fraction A20 was subjected to FCC separation using C_6H_6–Me_2CO (9:1, v/v) as eluent at a flow rate of 60 mL/min. The following 22 fractions were collected and combined with the use of TLC to monitor the fractions A20/1 to A20/22, from which most of the fractions comprised polymeric material except fractions A20/6 (68 mg, R_f 0.43–0.58), A20/10 (41 mg, R_f 0.31–0.43), and A20/16 (35 mg, R_f 0.20–0.35), all three of which were run in C_6H_6–Me_2CO (8:2×2, v/v), and fraction A20/21 (104 mg, R_f 0.1–0.26, C_6H_6–Me_2CO 8:2×3, v/v). All four fractions were acetylated and subsequently purified by TLC as reported with the specific compounds isolated.

Chemical methods for derivatization:

a) Methylation with Diazomethane. Methylations were performed with an excess of diazomethane prepared by the reaction of KOH [(5 g) in a 95% (v/v) EtOH solution] with *N*-methyl-*N*-nitroso-*p*-toluene sulfonamide (15 g) in ether and distilled directly into the previously prepared reaction mixture [200 mg dry phenolic material dissolved in MeOH (50 mL) and cooled to –10°C]. After about 48 hours at –15°C the excess diazomethane and solvent were evaporated at room temperature.

b) Acetylation. Dry phenolic material was dissolved in the minimum volume of pyridine, and twice the amount of acetic anhydride was added. After 8 hours at ambient temperature the reaction was terminated by addition of ice, and the excess pyridine was removed by washing out with cold water.

Mesquitol-(4$\alpha\rightarrow$5)-epimesquitol-4β-ol octa-*O*-methylether Triacetate (2). Purified as a white amorphous solid (R_f 0.40, 14.1 mg). (Found: M^+, 832.2940. $C_{44}H_{48}O_{16}$ requires 832.2942. δ_H (Table 1); ^{13}C NMR [$(CD_3)_2CO$, 21°C]: δ 80.9 [C-2(C)], 71.9 [c-3(C)], 43.7 [C-4(C)], 123.2 [C-5 (A)], 106.1 [C-6(A)], 152.9 [C-7(A)], 137.7 [C-8(A)], 148.3 [C-9(A)], 118.8 [C-10(A)], 130.1 [C-1′(B)], 111.8 [C-2′(B)], 149.6 [C-3′(B)], 150.1 [C-4′(B)], 111.5 [C-5′(B)], 121.0 [C-6′(B)], 73.7 [C-2(F)], 68.2 [C-3(F)], 63.6 [C-4(F)], 112.1 [C-5(D)], 105.9 [C-6(D)], 154.6 [C-7(D)], 136.4 [C-8(D)], 149.8 [C-9(D)], 136.8 [C-10(D)], 129.9 [C-1′(E)], 111.1 [C-2′(E)], 149.6 [C-3′(E)], 150.1 [C-4′(E)], 111.8 [C-5′(E)], 119.5 [C-6′(E)], 55.2 (′2), 55.6, 55.7, 55.8, 55.9, 60.1, 60.3 [–OCH_3], 20.1 (′2), 20.9 [CH_3COO-], 168.4, 168.7, 169.5 (CH_3COO-]; CD $[\theta]_{234.7}$ 1607, $[\theta]_{246.4}$ –15580, $[\theta]_{271.7}$ –1989, $[\theta]_{286.5}$ 1143.

3′,4′,7,8-Tetra-*O*-methylflavanone-(3$\rightarrow$4)-tetra-*O*-methyl-ent-epimesquitol Acetate (4). The acetylated fraction A20/6 was purified on TLC utilizing C_6H_6–Me_2CO as solvent (8:2, v/v) and the band with R_f 0.50 yielded the title compound (6.2 mg) as a white amorphous solid. (Found: M^+, 730. $C_{40}H_{42}O_{13}$ requires 730. δ_H (Table 1); IR ($CHCl_3$ ν_{max}, cm^{-1}): 3504, 1740, 1674, 1600, 1514; UV (EtOH, λ_{max}, nm): 288.0, 230, 204 (log ε 3.85, 3.92, 4.44); ^{13}C NMR [$(CD_3)_2CO$, 21°C]: δ 74.0 [C-2(F)], 69.6 [C-3(F)], 38.7 [C-4(F)], 125.7 [C-5(D)], 105.2 [C-6(D)], 153.4 [C-7(D)], 137.8 [C-8(D)], 149.9 [C-9(D)], 112.9 [C-10(D)], 131.0 [C-1′- (E)], 111.1 [C-2′ (E)], 149.7 [C-3′(E)], 149.5 [C-4′(E)], 111.8 [C-5′(E)], 119.3 [C-6′(E)], 79.4 [C-2(C)], 53.9 [C-3(C)], 191.7 [C-4(C)], 123.2 [C-5(A)], 106.6 [C-6(A)], 159.8 [C-7(A)], 137.5 [C-8(A)], 153.5 [C-9(A)], 116.3 [C-10(A)], 130.2 [C-1′(B)], 110.8 [C-2′(B)], 149.8 [3′-C(B)], 149.4 [4′-C(B)], 111.7 [5′-C(B)], 119.6 [6′-C(B)], 55.4, 55.5 (′2), 55.8, 56.1, 56.6, 60.2, 60.6 [–OCH_3], 20.1 [CH_3COO-], 169.1 [CH_3*C*OO-]; CD $[\theta]_{236.9}$ 579, $[\theta]_{245.2}$ –10240, $[\theta]_{294.1}$ 11140, $[\theta]_{327.1}$ –7676.

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