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FLAVONOL GLYCOSIDES FROM *DRYAS OCTOPETALA*

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ABSTRACT.—Six flavonol glycosides and *ent*-epicatechin were isolated from *Dryas octopetala* and their structures elucidated by chemical and spectroscopic methods. Two new flavonoids, 3-O-α-L-arabinofuranosyl-8-methoxyquercetin (**2**) and 3-O-β-galactopyranosyl-8-methoxykaempferol (**6**), were identified along with 3-O-β-D-galactopyranosylquercetin (hyperin) (**3**), 3-O-α-L-arabinofuranosylquercetin (avicularin) (**5**), 3-O-β-L-arabinopyranosylquercetin (**4**), and 3-O-β-D-galactopyranosyl-8-methoxyquercetin (**1**).

Dryas octopetala L. (Rosaceae) is a creeping shrublet, widely distributed in the northern hemisphere from Alaska and Siberia southward. In Italy, it has a wide distribution on screes and rocky pastures in the pre-alpine and alpine regions (1). In France, Switzerland, and Austria, a powder, infusion, or extract of the leaves is used internally and externally as a digestive aid, astringent, and antidiarrhetic. In addition, various other healing properties have been attributed to this shrub (2-4), e.g., in Val Rendena (Trento) an infusion of the leaves is considered useful in curing heart ailments (5). The medicinal properties of this species are believed to depend on the amount of tannins present in the plant, which are reputed to be high (6). The only chemical study of *D. octopetala* reports that seven flavonol aglycones were isolated, but only after hydrolysis of the leaf extract (7). Because of these documented folk usages, an investigation of the biologically active substances of *D. octopetala* was undertaken.

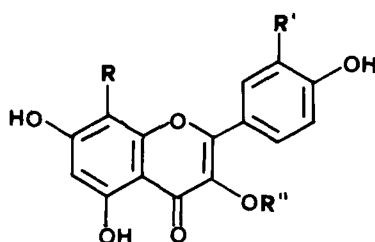
The leaves, collected on mountain valleys of the Dolomites, were extracted in two different ways: with hot H_2O, following the folk procedure of preparing a "tea" or infusion, and with a sequence of organic solvents. Both extracts showed similar flavonoid composition by tlc and hplc.

From the first procedure, a brown residue containing chlorophyll, flavonoids, free sugars, and tannins was obtained after evaporation of H_2O *in vacuo*. Partitioning of the extract between solvents of differing polarity was performed to remove chlorophyll and tannins, but this was time consuming and gave poor results. We found it best to extract the leaf material by percolating with solvents of increasing polarity (see Experimental section).

A preliminary tlc screening of the chlorophyll-free extract on Si gel plates ($CHCl_3$-EtOH-H_2O, 98:20:2) revealed the presence of flavonoid O-glycosides, but no flavonoid aglycones were detected.

The similar mobilities of the flavonoid glycosides made their separation with standard chromatographic procedures quite difficult (8). Fdms analysis revealed that most of the fractions obtained by separation on column chromatography, using various substrates, were still mixtures of two or more flavonoids. Eventually, we found that μ-Bondapak RP-18 liquid chromatography, using various ratios of *t*-BuOH-H_2O as a solvent, afforded the best separations on both an analytical and a preparative scale (9).

Compounds **1-5** were obtained from the second extract, while compounds **1** and **6** were isolated by cellulose and polyamide column chromatography of the first infusion extract.



	R	R'	R''
1	CH_3O	OH	β-D-galactopyranosyl
2	CH_3O	OH	α-L-arabinofuranosyl
3	H	OH	β-D-galactopyranosyl
4	H	OH	β-L-arabinopyranosyl
5	H	OH	α-L-arabinofuranosyl
6	CH_3O	H	β-D-galactopyranosyl

Ent-epicatechin, isolated via polyamide column chromatography, was identified by ir spectrum (OH and aromatic bands, no CO bands) and the pmr data of *ent*-epicatechin acetate. the coupling constants of the pyrane ring protons being indicative of a *syn*-relationship between H-2 and H-3. Mp and specific rotation of the isolated compound corresponded to those of 2S,3S-(+)-epicatechin (10) (*ent*-epicatechin).

Pmr spectra of compounds **1** and **2** showed a similar pattern for the aromatic protons and had significant differences only for the sugar moiety, which suggested they were different O-glycosides of the same aglycone. In fact, both of them gave corniculatusin (8-methoxy-quercetin) (ir pmr, ms) upon hydrolysis with trifluoroacetic acid. In addition, (+)-D-galactose and (+)-L-arabinose, identified by tlc and as trimethylsilyl ethers by gc, were obtained from **1** and **2**, respectively. The bathochromic shifts observed for the uv absorption maxima of **1** and **2** by addition of the standard shifts reagents (8) and the mass fragmentation patterns of the corresponding permethylated and acetylderivatives were clearly indicative of 3-O-glycosides. The structure of **1** was thus assigned as 3-O-β-D-galactopyranosylcorniculatusin (11), β-configuration being assigned to C-1″ on the basis of the coupling constant of the anomeric proton. Furthermore, co-chromatography with an authentic sample showed identical Rf values. In the case of **2**, the small coupling constant of H-1″ and H-2″, assigned by decoupling experiments, are typical of an α-furanoside (12). As expected, in the acetylderivative of **2** the H-2″, H-3″, and H-5″ signals were shifted downfield compared to **2**, while the chemical shift of H-4″ was not affected significantly. Thus, **2** is 3-O-α-L-arabinofuranosylcorniculatusin.

Compound **3** was identified as hyperin (3-O-β-D-galactopyranosyl quercetin) on the basis of mp, ir, uv, ms, and nmr data. Hydrolysis of **3** gave quercetin and D-(+)-galactose, and the structure of **3** was confirmed by co-chromatography with an authentic sample.

Compounds **4** and **5** had identical mw 434 and the aromatic feature of quercetin (pmr), and both gave by hydrolysis quercetin and L-(+)-arabinose. Furthermore, the uv spectra with the standard shift reagents showed very similar absorption maxima, and ms data of permethylated derivatives indicated that **4** and **5** are isomeric 3-O-arabinosyl derivatives of quercetin. Comparison of the analyzed pmr spectra of **4** and its eptaacetyl derivatives revealed that H-2″, H-3″, and H-4″ are shifted downfield by acetylation, while H-5″ was unaffected. The coupling constant of H-1″ (J=7.0 Hz) is typical of a β-pyranoside (13). Thus, the structure of 3-O-β-L-arabinopyranosylquercetin was assigned to **4**.

By contrast, in the case of **5**, the H-2″, H-3″, and H-5″ were shifted downfield by

acetylation, suggesting a furanoside sugar, where the unaffected H-4″ was on the acetylic carbon atom. The small coupling constant of H-1″ (J<1 Hz) indicated an α-furanosyl ring (12). On this basis, the structure of 3-O-α-L-arabinofuranosylquercetin (avicularin) (14) was assigned to **5**.

Compound **6** was isolated in a very small amount (2.0 mg). Its structure was determined mainly by ir, pmr, and ms data of its acetylderivative, taking advantage of the experience made on the previously described acetylated flavonoid glycosides **1-5**, especially that done on authentic samples (as for **1** and **3**). The acetylderivative of **6**, mw 772, showed in the pmr spectrum seven acetyl groups, in the aromatic region the signals of a 1,4-disubstituted phenyl (B ring), and a singlet at δ 6.80 (1H) for the H-6. The ms spectrum of acetylated **6** showed a low intensity peak (*m/z* 506) for the retro Diels-Alder fragmentation of the molecular ion, corresponding to the acetylated B_1 ion [$AcOC_6H_4$-C≡C-$OC_6H_7O_5(Ac)_4$ ion], indicating that the sugar cannot be on ring A.

Hydrolysis of acetylated **6** afforded sexangularetin (8-methoxykaempferol) as the aglycone, but the free sugar could not be identified unequivocally because of the small amount. However, since **6** did not correspond to 3-O-D-glucopyranosylsexangularetin by comparison with an authentic sample, and the pattern of the acetylated sugar moiety in the pmr spectrum was similar to that of the octaacetylderivative of **1**, we propose for **6** the structure of 3-O-β-galactopyranosylsexangularetin as most probable.

As a result of our study on the secondary chemistry of *D. octopetala,* we isolated five main flavonoid glycosides, **1-5**, and a sixth (**6**) present only in trace amounts; **2** and **6** are here newly reported. 3-O-β-D-Galactopyranosylcorniculatusin (**1**) was isolated previously from several sources: *Lotus corniculatus* (Leguminosae) (11), *Geraea canescens* (Compositae) (15), *Cowania* (Rosaceae) (15), and some species of *Ranunculus* (Ranunculaceae) (15). Two of the quercetin glycosides, hyperin (**3**) and avicularin (**5**), are widespread in nature. Although **4** does not correspond to any of the four known arabinosides of quercetin (16), from our data we cannot exclude the possibility that **4** is one of the not as yet well-characterized quercetin arabinosides reported in the literature.

Interesting is the finding of *ent*-epicatechin, which is the least widespread of the isomeric catechins. It was found previously in the Palmae (17,18) and recently in *Polygonum multiflorum* (19).

The presence of this latter compound in *D. octopetala* and that of procyanidin and propelargonidin as previously reported (7) may be related to the large amount of catechin-type tannins found in the leaves of this species.

In view of the above-cited folk usage of *Dryas* leaves "tea," it is also significant that the purified glycosides showed no effect whatsoever on in vitro guinea pig heart preparations. The results of different pharmacological tests will be reported elsewhere.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mps are uncorrected and were determined with a Fisher-Johns hot plate. Ir spectra were recorded in KBr disks on a Perkin-Elmer spectrophotometer, and pmr spectra on a Bruker 80 MHz or 300 MHz and on a Varian XL-100 spectrometer, using TMS as internal standard. Eims were obtained on a Du Pont 21-492 B instrument at 70 eV and fdms on a Varian 312 spectrometer. Specific rotations refer to MeOH solutions and were determined on an automatic Perkin-Elmer 141 polarimeter. Analytical and preparative hplc conditions are reported elsewhere (9). Gc analyses were carried out on a Perkin-Elmer Sigma 3B gas chromatograph equipped with an F.I.D. detector.

PLANT MATERIAL.—*D. octopetala* was collected in the Dolomites between 1500 and 2000 m (1.72 kg of fresh leaves); a voucher specimen of the plant is deposited in the herbarium of the Department of Biology, University of Milan.

EXTRACTION AND FRACTIONATION.—The leaves were extracted by successively percolating with hot C_6H_6, $CHCl_3$, EtOH, and *n*-BuOH. Most of the chlorophyll was removed from the alcoholic extracts by chromatography on a cellulose (Merck) column, using MeOH-H_2O (70:30) as the solvent. After in

vacuo evaporation of MeOH, the aqueous fraction was partitioned against hexane-MeOH (98:2) to remove any remaining chlorophyll.

A flavonoids-enriched residue (110.65 g) was chromatographed on a DCC silica gel (Woelm TSC, activity III) column (1.4 kg), using $CHCl_3$-MeOH-H_2O (68:28:4) as solvent. After elution of the first forty fractions of 300 ml each, a tannin-rich fraction (75 g) was recovered from the column by increasing the polarity of the solvent. Combining the fractions of similar composition, five main fractions (A-E) were obtained. Flavonoid glycosides were present in higher amounts in C (3.5 g) and in D (8.5 g). They were further separated by column chromatography using various substrates [Lichroprep RP-18, 25-40 μm (Merck); polyamide CC-6 (Macherey-Nagel); cellulose (Merck)]; however, only mixtures enriched in each flavonoid and no pure compound could be obtained by these methods. Eventually, reversed-phase preparative hplc (9) followed by crystallization from MeOH or by column chromatography over Sephadex LH-20 (Pharmacia) was the method of choice to obtain individual flavonoids in pure form. The total yields for the isolated compounds are not reported, since the hplc separations were performed on only a small amount of each fraction.

ACETYLATION AND HYDROLYSIS.—Acetylation was performed with Ac_2O-pyridine at room temperature according to the usual procedure (8). Permethylation was performed with CH_3I and NaH following the standard procedures (20). Hydrolysis was carried out on a few milligrams of each glycoside with 1.5-2.0 ml of 40% CF_3COOH at 60° for 3-4 h. Yields were quantitative. The aglycone, partially precipitating in the reaction mixture, was identified by spectroscopic data and comparison with authentic samples. Aglycones arising from compounds **1, 2, 6** gave on tlc a brown spot under uv light [corniculatusin and sexangularetin (21)], those from **3-5** a yellow spot (quercetin). The sugar was identified by tlc (silica gel; $CHCl_3$-MeOH, 80:20) and by gc as the O-trimethylsilylderivative (8). Gc conditions: 2% OV-1 on G AW DMCS Chromosorb (80-100 mesh) glass column (2 m); flow of the carrier gas (N_2): 24 ml/min; after 3 min at 170° the temperature of the column was increased to 270° at 5° min; injector=250°; detector=300°.

IDENTIFICATIONS.—*Ent*-epicatechin: red spot by spraying the tlc plate with sulfovanillic reagent and heating; mp 234° [lit. (17) 236-238°], $[\alpha]^{21}D=+57.64°$ (c=0.25) [lit. (17) +65°, EtOH]; ir, ν max 3500, 3450 (OH), 1620 cm^{-1} (aromatic ring); pmr (100 MHz, $(CD_3)_2CO$), δ 2.82 (m, 2H, H-4), 4.22 (m, 1H, H-3), 4.88 (br s, 1H, H-2), 5.93 (d, J=3.0 Hz, 1H, H-6), 6.04 (d, J=3.0 Hz, 1H, H-8), 6.82 (m, 2H, H-5′ and H-6′), 7.07 (d, J=3.0 Hz, 1H, H-2′). Assignments of the signals were obtained by decoupling experiments for the aliphatic moiety and by nOe experiments on the aromatic protons, and are in agreement with the pmr literature data of catechins (22). Eims (70 eV) *m/z* 290 (M^+, 57%), 152 (retro Diels-Alder ion, HOCH-CH-$C_6H_3(OH_2$, 34), 139 ($C_7H_7O_3$, 100).

Ent-epicatechin-*pentacetate*: pmr (100 MHz, C_6D_6) δ 1.50, 1.68, 1.72, 1.79 (s, 15H, CH_3CO), 2.77 (dd, J_{gem}=17.0, J_{vic}=4.2 Hz, 1H, H-4), 2.91 (dd, J_{gem}=17.0, J_{vic}=2.2 Hz, 1H, H-4′), 4.48 (br s, 1H, H-2), 5.32 (ddd, $J_{3\text{-}4}$=4.2 Hz, $J_{3\text{-}4'}$=2.2 Hz, $J_{3\text{-}2}$=1.4 Hz, 1H, H-3), 6.75 (d, J=2.2 Hz, 1H, H-6), 6.91 (d, J=2.2 Hz, 1H, H-8), 6.97 (dd, J_{ortho}=8.4 Hz, J_{meta}=1.8 Hz, H-6′), 7.12 (d, J_{ortho}=8.4 Hz, 1H, H-5′), 7.55 (d, J_{meta}=1.8 Hz, 1H, H-2′).

Compound **1**: brown-red spot under uv light. Mp 212-214° [lit. (11) 216-217°]; $[\alpha]^{21}D=-43.3°$ (c=0.3); ir, ν max 3400 (OH), 1655 (flavonoid CO), 1605 (aromatic ring), 1075 and 1060 cm^{-1} (C-O); uv, λ max (MeOH) nm (log ε) 273 (4.15), 364 (4.02); NaOMe 281, 337, 420 without decomposition; NaOAc 282, 328 sh, 394; NaOAc+H_3BO_3 272, 385; $AlCl_3$ 282, 447; $AlCl_3$+HCl 275, 366, 417; fdms *m/z* 494 (M^+); pmr (80 MHz, CD_3OD) δ 3.43-3.80 (m, 6H, sugar protons), 3.93 (s, 3H, CH_3O), 5.20 (d, J=7.0 Hz, 1H, H-1″), 6.35 (s, 1H, H-6), 6.95 (d, J_{ortho}=9.0 Hz, 1H, H-5′), 7.75 (dd, J_{ortho}=9.0 Hz, J_{meta}=3.0, 1H, H-6′), 7.96 (d, J=3.0, 1H, H-2′).

Permethylated **1**: ms *m/z* 606 (M^+, <1%) and 388 (A+H, 86).

Compound **1**-*octacetate*: pmr (270 MHz, C_6D_6) δ 1.54, 1.74, 1.77, 1.79, 1.81 (s, 3H, each, 5 CH_3CO), 1.96 (s, 6H, 2 CH_3CO), 2.30 (s, 3H, CH_3CO), 3.20 (br t, $J_{4''\text{-}5''}$<4 Hz, 1H, H-5″), 3.59 (s, 3H, CH_3O), 3.90 (d, J=6.5 Hz, 2H, H-6″), 5.22 (dd, $J_{2''\text{-}3''}$=10.5 Hz, $J_{3''\text{-}4''}$=2.5 Hz, 1H, H-3″), 5.36 (dd, $J_{4''\text{-}5''}$<4 Hz, $J_{3''\text{-}4''}$=2.5 Hz, 1H, H-4″), 5.77 (dd, $J_{1''\text{-}2''}$=8.0 Hz, $J_{2''\text{-}3''}$=10.5 Hz, 1H, H-2″), 5.91 (d, $J_{1''\text{-}2''}$=8.0 Hz, 1H, H-1″), 6.66 (s, 1H, H-6), 7.20 (d, J_{ortho}=8.5 Hz, 1H, H-5′), 7.92 (dd, J_{ortho}=8.5 Hz, J_{meta}=2.0 Hz, 1H, H-6′), 8.10 (d, J_{meta}=2.0, 1H, H-2′). Assignments of the sugar protons were made on the basis of decoupling experiments carried out starting by irradiation of the known low field doublet of the anomeric proton; thus, H-2″ could be determined. By irradiation of H-2″, H-3″ could be individuated, and so on.

Ms (70 eV) *m/z* 830 (M^+, 1%), 788 (M-42, 2), 746 (M-2×42, 2), 704 (M-3×42, 2), 564 (M-$C_{12}H_{10}O_7$, B_1 retro Diels-Alder, 2), 500 (tetraacetylated aglycone+H, 5), 458 (triacetylated aglycone+H, 7), 416 (diacetylated aglycone+H, 15), 374 (monoacetylated aglycone+H, 26), 332 (A+H, 38), 317 (A+H-CH_3, 29), 303 (A+H-CHO, 10).

Compound **2**: brown-red spot under the uv light. Mp 175-177°, $[\alpha]^{22}D=-73°$ (c=0.15); ir, ν max 3400 (OH), 1650 (flavonoid C=O), 1595 (aromatic ring), 1130, 1110 cm^{-1} (C-O); uv, λ max (MeOH) nm (log ϵ) 273 (4.23), 361 (4.12); NaOMe 280, 335, 413 without decomposition after 10 min, NaOAc 282, 330, 403; NaOAc+H_3BO_3 272, 378; $AlCl_3$, 281, 447; $AlCl_3$+HCl, 281, 361, 415; fdms *m/z* 464 (M^+); pmr (300 MHz, CD_3OD) δ 3.48 (dd, $J_{gem}=11.6$ Hz, $J_{vic}=4.5$ Hz, 1H, H-5A''), 3.52 (dd, $J_{gem}=11.6$ Hz, $J_{vic}=3.5$ Hz, 1H, H-5B''), 3.88 (m, $J_{4''-5A''}=4.5$ Hz, $J_{4''-5B''}=3.5$ Hz, $J_{4''-3''}=5.0$ Hz, 1H, H-4''), 3.90 (s, 3H, CH_3O), 3.91 (dd, $J_{3''-4''}=5.0$ Hz, $J_{3''-2''}=2.8$ Hz, 1H, H-3''), 4.34 (dd, $J_{3''-2''}=2.8$ Hz and $J_{2''-1''}=1.0$ Hz, 1H, H-2''), 5.50 (d, $J_{1''-2''}=1.0$ Hz, 1H, H-1''), 6.27 (s, 1H, H-6), 6.92 (d=8.2 Hz, 1H, H-5'), 7.58 (dd, $J_{ortho}=8.2$ Hz, $J_{meta}=2.5$ Hz, 1H, H-6'), 7.61 (d, $J_{meta}=2.5$, 1H, H-2').

Compound **2**-*heptaacetate*: pmr (80 MHz, C_6D_6) δ 1.58, 1.67, 1.72, 1.77, 1.81, 2.21 (s, 21H, 7 CH_3CO), 3.53 (s, 3H, CH_3O), 4.28 (m, 3H, H-4'', 2 H-5''), 5.27 (dd, $J_{3''-4''}=5.0$ Hz, $J_{3''-2''}=2.5$ Hz, 1H, H-3''), 5.88 (br d, $J=2.5$ Hz, 1H, H-2''), 6.25 (br s, 1H, H-1''), 6.6 (s, 1H, H-6), 7.09 (d, $J_{ortho}=8.5$ Hz, 1H, H-5'), 7.63 (dd, $J_{ortho}=8.5$ Hz, $J_{meta}=2.5$ Hz, 1H, H-6'), 7.85 (d, $J_{meta}=2.5$ Hz, 1H, H-2'). Assignments of the sugar protons were made by decoupling experiments as reported for **1**.

Permethylated **2**: ms *m/z* 562 (M^+, <1%), 388 (A+H, 100).

Compound **3**: brown-red spot under uv light; fdms, 464 (M^+); tlc Rf and uv, pmr spectra of **3** identical to an authentic sample of hyperin. Hydrolysis gave quercetin and D-galactose.

Compound **4**: brown-red spot under uv light. Mp 181-183°, $[\alpha]^{21}D=-45.6°$ (c=1); ir, ν max 3400 (OH), 1655 (flavonoid C=O), 1605 (aromatic ring), 1080, 1023 cm^{-1} (C-O); uv, λ max (MeOH) nm (log ϵ) 271 (3.88), 357 (3.88); NaOMe 273, 335, 406 without decomposition after 10 min; NaOAc 275, 325, 380; NaOAc+H_3BO_3 273, 375; $AlCl_3$ 275, 445; $AlCl_3$+HCl 273, 412; pmr (300 MHz, CD_3OD) δ 3.40-4.1 (m, 5H, H-2'', H-3'', H-4'', 2 H-5''), 5.15 (d, $J_{1''-2''}=6.6$ Hz, 1H, H-1''), 6.19 (d, $J_{meta}=2.0$ Hz, 1H, H-6), 6.39 (d, $J_{meta}=2.0$ Hz, 1H, H-8), 6.87 (d, $J_{ortho}=8.5$ Hz, 1H, H-5'), 7.57 (dd, $J_{ortho}=8.5$ Hz, $J_{meta}=2.0$ Hz, 1H, H-6'), 7.74 (d, $J_{meta}=2.0$ Hz, 1H, H-2').

Compound **4**-*heptaacetate*: pmr (300 MHz, $CDCl_3$) δ 2.05, 2.09, 2.12 (s, 3H each, 3 sugar CH_3CO), 2.32, 2.34, 2.35, 2.45 (s, 3H each, 4 aglycone CH_3CO), 3.51 (dd, $J_{gem}=13.0$ Hz and $J_{vic}=2.0$ Hz, 1H, H-5''), 3.79 (dd, $J_{gem}=13.0$ Hz, $J_{vic}=3.4$ Hz, 1H, H-5''), 5.13 (dd, $J_{3''-2''}=9.2$ Hz, $J_{3''-4''}=3.6$ Hz, 1H, H-3''), 5.20 (m, 1H, H-4''), 5.39 (dd, $J_{3''-2''}=9.2$ Hz, $J_{2''-1''}=6.9$ Hz, 1H, H-2''), 5.56 (d, $J_{2''-1''}=6.9$ Hz, 1H, H-1''), 6.83 (d, $J_{meta}=2.2$ Hz, 1H, H-6), 7.31 (d, $J_{meta}=2.2$ Hz, 1H, H-8), 7.35 (d, $J_{ortho}=8.5$ Hz, 1H, H-5'), 7.96 (d, $J_{meta}=2.0$ Hz, 1H, H-2'), 8.05 (dd, $J_{ortho}=8.5$ Hz, $J_{meta}=2.0$ Hz, 1H, H-6'). Assignments were made by decoupling experiments.

Permethylated **4**: ms *m/z* 532 (M^+, 2%), 358 (A+H, 100), 175 (T, 8), 174 (T, 8).

Compound **5**: brown-red spot under uv light. Mp 213-215° [lit. (14) 217°]; $[\alpha]^{22}D=-147.2°$ (c=0.5); ir, ν max 3350 (OH), 1650 (flavonoid C=O), 1603 (aromatic ring), 1200, 1110 cm^{-1} (C-O); uv, λ max (MeOH) nm (log ϵ) 270 (4.17), 358 (4.20); NaOMe 273, 330, 404 without decomposition after 10 min; NaOAc 276, 325, 390; NaOAc+H_3BO_3 270, 375; $AlCl_3$ 276, 436; $AlCl_3$+HCl 272, 363, 402; pmr (80 MHz, CD_3OD) δ 3.55 (m, 2H, 2H-5''), 3.93 (m, 2H, H-3'', H-4''), 4.35 (d, $J=2.0$ Hz, 1H, H-2''), 5.42 (s, 1H, H-1''), 6.25 (d, $J_{meta}=2.5$ Hz, 1H, H-6), 6.43 (d, $J_{meta}=2.5$ Hz, 1H, H-8), 6.91 (d, $J_{ortho}=8.5$ Hz, 1H, H-5'), 7.43-7.65 (m, 2H, H-2'', H-6'').

Compound **5**-*heptaacetate*: pmr (80 MHz, $CDCl_3$) δ 2.00, 2.08, 2.11 (s, 3H each, sugar CH_3CO), 2.33 (s, 9H, 3 aglycone CH_3CO), 2.43 (s, 3H, aglycone CH_3CO), 3.80 (m, 1H, H-4''), 4.10 (m, 2H, 2 H-5''), 4.98 (dd, $J_{3''-4''}=5.5$ Hz, $J_{3''-2''}=2.0$ Hz, 1H, H-3''), 5.48 (d, $J_{2''-3''}=2.0$ Hz, 1H, H-2''), 5.78 (s, 1H, H-1''), 6.81 (d, $J_{meta}=2.5$ Hz, 1H, H-6), 7.16-7.31 (m, 2H, H-8, H-5'), 7.65-7.93 (m, 2H, H-2', H-6').

Permethylated **5**: ms *m/z* 532 (M^+, 1.4%), 358 (A+H, 100%), 175 (T, 7), 174 (T, 5).

Compound **6**-*heptaaceate*: ir, ν max 1770, 1740 (ester C=O), 1640 (flavonoid C=O), 1600 (aromatic ring), 1210 (ester C-O); pmr (100 MHz, $CDCl_3$) δ 1.91, 1.99, 2.12, 2.13 (s, 3H each, sugar CH_3CO), 2.34, 2.38, 2.43 (s, 3H each, aglycone CH_3CO), 3.99 (s, 3H, CH_3O), 4.20 (m, 2H, 2 H-6''), 5.0-5.5 (m, 4H, H-2'', H-3'', H-4'', H-5''), 5.70 (d, $J=7.0$ Hz, 1H, H-1''), 6.80 (s, 1H, H-6), 7.24 (d, $J_{ortho}=8.5$ Hz, 2H, H-3', H-5'), 8.15 (d, $J_{ortho}=8.5$ Hz, 2H, H-2', H-6'); eims (70 eV) *m/z* 772 (M^+, <1%), 506 ($M-C_{12}H_{10}O_7$, retro Diels-Alder B_1, 1), 442 (aglycone+H triacetate, 2), 400 (A+H diacetate, 2), 316 (A+H), 301 (A+H-CH_3, 3), 69 (100).

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