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NOVEL CHROMONES FROM *SPATHELIA SORBIFOLIA*[1]

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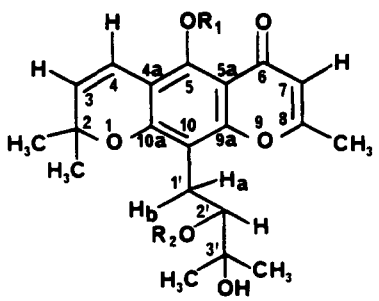
ABSTRACT.—Three new chromones, namely 10-(2′,3′-dihydroxy-3′-methylbutanyl)-spatheliachromen [**1**], 10-(1′,2′,3′-trihydroxy-3′-methylbutanyl)spatheliachromen [**2**], and 6-(3′-hydroxy-3′-methyl-*trans*-but-1′-enyl)-*O*-methylisospatheliachromen [**7**] were isolated from the 10% aqueous MeOH extract of the twigs and leaves of *Spathelia sorbifolia*, together with five known chromones. Compound **2**, the known spatheliabischromen, and 5-*O*-methylsorbifolin showed cytotoxicity against 9PS cells in culture.

Previous phytochemical investigations on constituents of the roots and stems of *Spathelia sorbifolia* L. (Rutaceae) yielded a seco-ring A tetranortriterpenoid (1), two 2-quinolones (2,3), and a number of chromones (4,5). As part of our continuing studies on the isolation of novel antineoplastic agents from higher plants, it was established that the 10% aqueous MeOH extract of the twigs and leaves of *S. sorbifolia* exhibited activity against 9PS cells in culture and the P-388 mouse leukemia systems (6). Using cytotoxicity as a guide to fractionation, eight chromones have been isolated. In this report, we present the structural elucidation of three new chromones based on extensive analysis of their spectral data and chemical correlations. The cytotoxic activity of these isolated chromones is also reported.

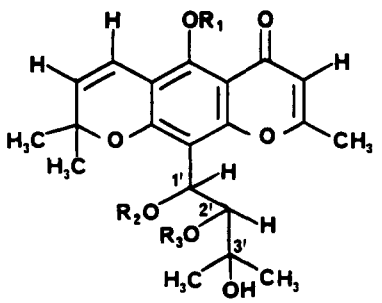
RESULTS AND DISCUSSION

The twigs and leaves of *S. sorbifolia* were extracted with 95% EtOH. The 95% EtOH extract was further partitioned, as described in the experimental section, to yield a 10% aqueous MeOH extract. This extract was then subjected to flash column chromatography on Si gel to yield 10 fractions. Chromatography of fraction D, which had the highest activity against 9PS cells in culture, afforded three new chromones [**1**, **2**, and **7**].

The molecular formula of **1** was determined to be $C_{20}H_{24}O_6$ (M^+, 360.157) by hrms. The ir spectrum showed the presence of hydroxyl (3410 cm^{-1}) and a carbonyl (1650 cm^{-1}) typical of that in chromones. The 200 MHz ^{1}H-nmr spectrum of **1** in $CDCl_3$ showed singlets for geminal methyls at δ 1.47 and 1.50, and it also exhibited a



1 $R_1=R_2=H$
3 $R_1=R_2=Ac$



2 $R_1=R_2=R_3=H$
4 $R_1=R_2=R_3=Ac$

[1]This article commemorates the 50th year of publication of the *Journal of Natural Products* (formerly *Lloydia*).

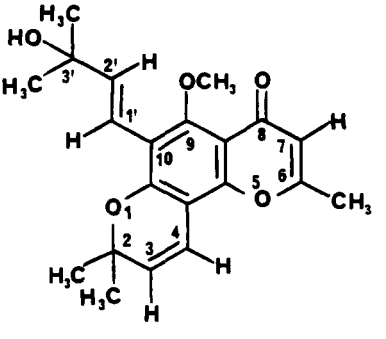
[2]Member of the Editorial Advisory Board of the *Journal of Natural Products* (*Lloydia*) since 1984.

pair of doublets (J=10 Hz) in the olefinic proton region of the spectrum (δ 5.61 and 6.72, 3-H, 4-H, respectively) consistent with the presence of the 2,2-dimethylpyran moiety. The three-proton doublet at δ 2.35 and one-proton quartet (J=0.7 Hz) at δ 6.02 were consistent with the presence of the 2-methyl-γ-pyrone unit of the chromone system. The one-proton singlet at δ 12.98, which disappeared after the addition of D_2O, was assigned to the chelated phenolic proton. The placement of this hydroxyl group at C-5 was further supported by a bathochromic shift in the uv spectrum of **1** upon adding $AlCl_3$ (7). Assignment of **1** to the spatheliachromen class of compounds was also based on the observed upfield shift of the 4-H signal (−0.25 ppm) and a smaller downfield shift of the 3-H signal (+0.14 ppm) in the ^{1}H-nmr spectrum of **3** (8). The remaining structural unit ($C_5H_{11}O_2$) which must reside at C-10 was determined to be the 2′,3′-dihydroxy-3′-methylbutanyl group by these ^{1}H-nmr signals: two three-proton singlets at δ 1.31 and 1.32 (3′-*gem*-methyls); two protons at δ 2.35-2.37 which disappeared after shaking with D_2O (2′-OH, 3′-OH); two one-proton doublet of doublets (AB system) at δ 2.80 and 2.96 (1′-Ha and 1′-Hb) with coupling constant of $J_{1'a,1'b}$=14 Hz, $J_{1'a,2'}$=9.7 Hz and $J_{1'b,1'a}$=14 Hz, $J_{1'b,2'}$= 2.7 Hz, respectively; a one-proton doublet of double doublets at δ 3.59 (2′-H) with coupling constants of $J_{2',1'a}$=9.7 Hz, $J_{2',1'b}$=2.7 Hz, $J_{2',2'OH}$=4.7 Hz which collapsed to a doublet of doublets with J=9.7, 2.7 Hz on addition of D_2O. In addition, the mass spectrum showed fragment ions at *m/z* 271 and 301 which were consistent with cleavage of this side chain at 1′,2′ and 2′,3′ bonds, respectively. Therefore, compound **1** was assigned as 10-(2′,3′-dihydroxy-3′-methylbutanyl)spatheliachromen which was further confirmed by its ^{13}C-nmr spectrum.

The chemical shifts in the ^{13}C-nmr spectrum of **1** were assigned based on the analysis of fully decoupled, gated decoupled, and selective decoupled spectra. The carbonyl carbon was readily identified at δ 182.33 based on comparison to a related chromone (10). The carbons bearing oxygen in the side chain (C-2′ and C-3′) were assigned at δ 77.80 and 72.52. The chemical shifts of C-9a (δ 155.11) and C-10a (δ 156.74) were unambiguously assigned by a selective decoupling experiment. When the 1′-methylene protons were irradiated, the C-10a quartet collapsed to a doublet and the C-9a triplet to a singlet, establishing their proximity based on three bond coupling. Using this approach C-4a (δ 104.91) and C-10 (δ 104.81) were simplified when the 3-*H* and 1′-methylene protons were irradiated, respectively. The long range coupling of C-4a, C-5, and C-5a with phenolic-OH was also observed in the gated decoupled spectrum. After treatment with D_2O, this coupling was lost.

The hrms of **2** showed M^+ at *m/z* 376.150, which corresponds to the formula $C_{20}H_{24}O_7$. The structure of **2** was closely related to **1** based on ^{1}H-nmr, ir, and uv spectral data and was shown to be a 10-substituted spatheliachromen. On acetylation of **2**, triacetate **4** was formed establishing that **2** contained an additional hydroxyl that must be located on the side chain ($C_5H_{11}O_3$). The 200 MHz ^{1}H-nmr spectrum of **2** confirmed the presence of the secondary hydroxyls showing the characteristic two one-proton doublets at δ 4.02 (J=9.2 Hz, which appeared downfield based on H-bonding to oxygen in the chromone ring) and 3.15 (J=5.5 Hz). The tertiary hydroxyl appeared as a one proton broad singlet at δ 2.86. Addition of D_2O resulted in the disappearance of these signals and in the collapse of the two one-proton double doublets at δ 5.41 (J=9.2, 3.7 Hz) and 3.55 (J=5.5, 3.7 Hz) into two simple doublets (J=3.7 Hz). The more deshielded methine signal at δ 5.41 was assigned to the benzylic 1′-H. The two singlets at δ 1.21 and 1.35 were assigned to the 3′-geminal methyls. The tertiary hydroxyl group that appeared at δ 2.86 must also be attached to C-3′. The side chain was, therefore, 1′,2′,3′-trihydroxy-3′-methylbutanyl leading to the proposal that **2** was 10-(1′,2′,3′-trihydroxy-3′- methylbutanyl) spatheliachromen.

Hrms of **5**,**6**, and **7** indicated that these three compounds were isomers with the molecular formula $C_{21}H_{24}O_5$. The ir and ^{1}H-nmr spectra confirmed the presence of hydroxyl, 2,2-dimethylpyran, and 2-methyl-γ-pyrone moieties. Each compound showed a three-proton singlet (δ 3.81 for **5**, 3.83 for **6**, and 3.73 for **7**) indicating the presence of a methoxyl group. The remaining isoprenoid unit, C_5H_9O, was assigned as 3′-hydroxy-3′-methyl-*trans*-but-1′-enyl based on analysis of the ^{1}H-nmr data. The *trans* olefinic bond was indicated by a large coupling constant (16.5 Hz). For compound **6** the chemical shifts of the 1′ and 2′ olefinic protons were coincident in $CDCl_3$; however, the *trans* coupling pattern could be observed in DMSO-d_6. Naturally occurring chromones generally carry oxygen functional groups at C-5 and C-7 (chromone numbering) (9). Thus, there are only three possible structures that can be attributed to these three isomeric chromones. The location of the methoxyl, isoprenoid, and 2,2-dimethylpyran groups was confirmed by homonuclear nOe experiments involving the irradiation of methoxyl protons and the enhancement of olefinic proton integral intensities.



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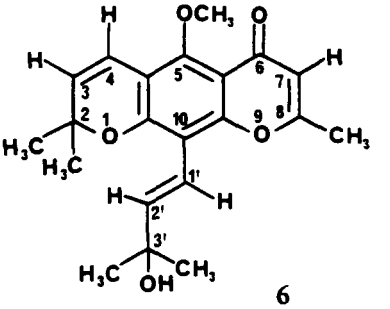

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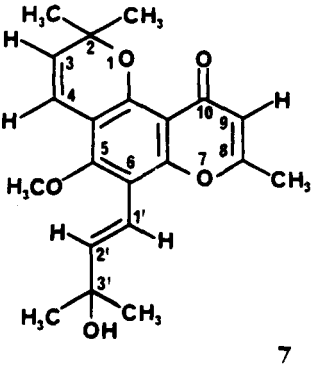

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The observed nOe values are shown in Table 1. A 7% enhancement of 1′-H and 2′-H in compound **5** indicated the proximity of the methoxyl group and the side chain and led to the conclusion that **5** was 5-*O*-methylsorbifolin that was previously isolated by Taylor and co-workers (5). Likewise, a 12% enhancement of 4-H in compound **6** indicated that the methoxyl and the 2,2-dimethylpyran groups were in proximity. Compound **6** was then assigned as 5-*O*-methylcneorumchromone K, which was previously isolated from *Cneorum tricoccon* (10). The enhancement of both 4-H and olefinic protons was interpreted as meaning that the methoxyl group was placed between the side chain and the 2,2-dimethylpyran group. Structure **7** was the only one consistent with this data. Compound **7** was, therefore, established to be a novel chromone, namely 6-(3′-hydroxy-3′-methyl-*trans*-but-1′-enyl)-*O*-methylisospatheliachromen.

Three additional compounds were isolated and identified as spatheliabischromen,

TABLE 1. The nOe for **5**, **6**, and **7** on Irradiation at -OCH_3

Compound	% nOe			
	3-H	4-H	1′-H	2′-H
5	—	—	7	7
6	—	12	—	—
7	—	15	6	6

O-methylalloptaeroxylin, and *O*-methylisospatheliachromen by comparison to literature data (5).

Compound **2**, 5-*O*-methylsorbifolin and spatheliabischromen were cytotoxic against 9PS cells in culture at $ED_{50}=5\times10^{-1}$, 3×10^{-1}, and 3×10^{0} μg/ml, respectively.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—All melting points are uncorrected. The uv spectra were obtained in MeOH. Ir spectra were taken as KBr pellets. High resolution (200 MHz) ^{1}H-nmr spectra were recorded in $CDCl_3$ (δ in ppm, *J* in Hz), using TMS as internal standard on a Varian XL-200 NMR spectrometer. 50 MHz ^{13}C-nmr spectra were recorded on a Chemagnetics A-200 NMR spectrometer. Low and high resolution mass spectra were measured on a Finnegan 4023 gc/ms with Incos 2000 data system and a Kratos MS50S, respectively, and recorded at 70 eV. Si gel (230-400 mesh size) was used for flash column chromatography. Fractions were combined on the basis of their tlc patterns detected by uv light (250 and 360 nm).

PLANT MATERIALS.—The twig and leaf of *S. sorbifolia* were collected from Jamaica in 1982. Its identity was confirmed, and a voucher specimen has been deposited by Dr. Sandra Saufferer, Economic Botany Laboratory, Plant Genetics and Germplasm Institute, Beltsville, Maryland.

EXTRACTION AND ISOLATION.—The coarsely milled, dried plant material (12 kg) was exhaustively percolated with 95% EtOH. This extract was concentrated to dryness in vacuo at 40° and yielded EtOH extract (1420 g), which was then partitioned between $CHCl_3$ and H_2O. The dried $CHCl_3$ extract (850 g) showed activity against PS cells in culture at $ED_{50}=20$ μg/ml and was further partitioned between hexane and 10% aqueous MeOH. The biological activity was now concentrated in 320 g of dried 10% aqueous MeOH extract (9PS, $ED_{50}=6$ μg/mg; 3PS, TX/400, 100/200).

A 50-g portion of the 10% aqueous MeOH extract was subjected to chromatography on a silica gel flash column eluted with hexane-Me_2CO (1:1) and MeOH. This fractionation yielded 10 fractions (A-J) that exhibited decreasing Rf values and were combined based on tlc.

Fraction D (7 g; Rf=0.25-0.35; 9PS, ED_{50} 1.2 μg/ml) was chromatographed on a Si gel flash column eluted with 5% MeOH in $CHCl_3$ and gave 5 fractions (I-V) which showed decreasing Rf value. Fraction IV (2.2 g; Rf=0.15-0.25; 9PS, $ED_{50}=0.36$ μg/ml) was further purified by crystallization with Et_2O and afforded compound **1** as yellow crystals (1 g). The mother liquor was further chromatographed by preparative tlc on Si gel plates with a solvent mixture of MeOH, Me_2CO, and Et_2O (3.5:5:91.5) and yielded three major bands. The highest-Rf band contains **1** as a main compound. A band with Rf about 0.5 was purified by preparative tlc on Si gel plates with a mixture solvent of MeOH, MeCN, and $CHCl_3$ (5:10:85) to yield 5-*O*-methylsorbifolin [**5**] (15 mg) which was crystallized from Et_2O/CH_2Cl_2. Compound **2** was isolated as an amorphous solid (10 mg) from the lowest Rf band by preparative tlc on Si gel plates with 10% Me_2CO in Et_2O.

Fraction III (1.5 g; Rf=0.25-0.40; 9PS, $ED_{50}=0.17$ μg/ml) also yielded **1** (0.8 g) by crystallization from Et_2O. The mother liquor was then rechromatographed on preparative tlc with MeOH-MeCN-Et_2O (3:10:87). The higher Rf band yielded **1** while the lower-Rf band was further separated by preparative tlc by double developing with Me_2CO-hexane (1:2) and then with 1% MeOH in $CHCl_3$. This method yielded 5-*O*-methylcneorumchromone K [**6**] (2 mg) and **7** (1 mg) which were crystallized from Et_2O/CH_2Cl_2.

Fraction C (7.1 g; Rf=0.35-0.45; 9PS, $ED_{50}=3.4$ μg/ml) was chromatographed on a Si gel flash column by using 10% Me_2CO in Et_2O as eluent. Spatheliabischromen (5) was crystallized from the higher-Rf fraction with Et_2O as pale yellow crystals (100 mg), and *O*-methylisospatheliachromen (5) was crystallized from the lower-Rf fraction with Et_2O as white crystals (60 mg).

O-Methylalloptaeroxylin (5) (300 mg) was isolated from Fraction F (3.7 g; Rf=0.22-0.10; 9PS, $ED_{50}=8$ μg/ml) as white crystals by crystallization with Me_2CO.

The fractions and purified compounds were tested against 9PS cells in culture in accordance with established protocols (6).

PHYSICAL CONSTANTS OF 10-(2',3'-DIHYDROXY-3'-METHYLBUTANYL)SPATHELIACHROMEN [**1**].—Mp 150-152°; uv λ max nm (log ε) 279 (4.58), 249 (4.20), 225 (4.28), shifted to 300 (4.59), 226 (4.45) on addition of $AlCl_3$ or $AlCl_3$ and HCl; ir ν max cm^{-1} 3410 (br), 1650, 1610, 1570, 1110; ^1H nmr see text; ms *m/z* M^+ 360.157 (47, calcd. $C_{20}H_{24}O_6$ 360.157), 345 (48), 301 (22), 271 (100); ^{13}C nmr $CDCl_3$ δ 20.16, dq, *J*=129.0, 2.5 (H-7), 8-CH_3; 23.32, q, *J*=126.0, 3'-CH_3; 25.17, t, *J*=128.0, C-1'; 26.05, q, *J*=127.0, 3'-CH_3; 28.12, 28.21, q, *J*=128.0, 2-*gem*-methyl carbons; 72.52, br s, C-3'; 77.80, br d, *J*=144.0, C-2'; 78.05, nonet, *J*=3.6 (2-*gem*-methyl protons, H-3, H-4) C-2; 104.42, dd, *J*=5.6 (H-7), 3.9 (5-OH), C-5a; 104.81, dt, *J*=5.0 (H-1'), 3.0 (H-2'), C-10; 104.91, ddd, *J*=10.0 (H-3), 5.0 (H-4), 2.0 (5-OH), C-4a; 107.83, qd, *J*=168.5, 3.9 (8-methyl protons), C-7; 115.37, d, *J*=167.3, C-4; 127.44, md, *J*=163.5, C-3; 154.43, dd, *J*=4.7 (5-OH), 2.5 (H-4), C-5; 155.11, t, *J*=3.8 (H-1'), C-9a; 156.74, q, *J*=4.1 (H-1', H-4), C-10a; 166.45, pentet, *J*=6.3 (H-7, 8-methyl protons), C-8; 182.33, s, C-6.

PHYSICAL CONSTANTS OF 10-(1',2',3'-TRIHYDROXY-3'-METHYLBUTANYL)SPATHELIACHROMEN [**2**].—Mp 120-122°; uv λmax nm (log ε) 275 (4.50), 250 (4.22), 232 (4.25), shifted to 298 (4.42), 238 (4.39) on addition of $AlCl_3$ or $AlCl_3$ and HCl; ir ν max cm^{-1} 3420 (br), 1650, 1610, 1570, 1110; ms *m/z* M^+ 376.150 (1.4, calcd. $C_{20}H_{24}O_7$ 376.152), 317 (2), 287 (100); ^1H nmr δ 1.21, 1.35 (3H each, s, 3'-*gem*-methyls), 1.52, 1.53 (3H, each, s, 2-*gem* methyls), 2.36 (3H, d, *J*=0.6, 8-CH_3), 2.86 (1H, br s, 3'-OH), 3.15 (1H, d, *J*=5.5, 2'OH), 3.58 (1H, dd, *J*=5.5, 3.7, H-2'), 4.02 (1H, d, *J*=9.2, 1'OH), 5.41 (1H, dd, *J*=9.2, 3.7, H-1'), 5.63 (1H, d, *J*=10.0, H-3), 6.05 (1H, q, *J*=0.6, H-7), 6.71 (1H, d, *J*=10.0, H-4), 13.10 (1H, s, 5-OH).

PHYSICAL CONSTANTS OF 5-*O*-METHYLSORBIFOLIN [**5**].—Mp 120-121° [lit. (5): no mp reported]. This compound was identified as 5-*O*-methylsorbifolin by comparison of uv, ir, ^1H-nmr, and ms data to literature values (5). Ci hrms *m/z* $(M+H)^+$ 357.169 (calcd. protonated $C_{21}H_{24}O_5$ 357.170).

PHYSICAL CONSTANTS OF 5-*O*-METHYLCNEORUMCHROMONE K [**6**].—Mp 161-162° [lit. (10): 166°]. This compound was identified as 5-*O*-methylcneorumchromone K by comparison of uv, ir, ^1H-nmr, and ms data to literature values (10). Ci hrms *m/z* $(M+H)^+$ 357.170 (calcd. protonated $C_{21}H_{24}O_5$ 357.170.)

PHYSICAL CONSTANTS OF 6-(3'-HYDROXY-3'-METHYL-*TRANS*-BUT-1'-ENYL)-*O*-METHYLISOSPATHELIACHROMEN [**7**].—Mp 135-136°; uv λ max nm (log ε) 244 (4.64), 271 (sh, 4.40), 351 (3.71); ir ν max cm^{-1} 3400 (br), 1650, 1623, 1615, 1560; cims *m/z* $(M+H)^+$ 357.170 (calcd. protonated $C_{21}H_{24}O_5$ 375.170), 339; ^1H nmr δ 1.43 (6H, s, 2-*gem* methyls), 1.50 (6H, s, 3'-*gem*-methyls), 2.28 (3H, d, *J*=0.6, 8-CH_3), 3.73 (3H, s, OCH_3), 5.65 (1H, d, *J*=10, H-3), 5.96 (1H, q, *J*=0.6, H-9), 6.55 (1H, d, *J*=10, H-4), 6.66 (1H, d, *J*=16.5, H-2'), 6.72 (1H, d, *J*=16.5, H-1').

PHYSICAL CONSTANTS OF SPATHELIABISCHROMEN.—Mp 147-149° [lit (5): 146-148.5°]. This compound was identified as spatheliabischromen by comparison of uv, ir, ^1H-nmr, and ms data to literature values (5).

PHYSICAL CONSTANTS OF *O*-METHYLISOSPATHELIACHROMEN.—Mp 130-131° [lit. (5): 143-145°]. This compound was identified as *O*-methylisospatheliachromen by uv, ir, ^1H-nmr and ms data comparison to literature values (5).

PHYSICAL CONSTANTS OF *O*-METHYLALLOPTAEROXYLIN.—Mp 154-155° [lit. (5): 152-154°]. This compound was identified as *O*-methylalloptaeroxylin by comparison of uv, ir, ^1H-nmr, and ms data to literature values (5).

ACETYLATION OF **1**.—Compound **1** was acetylated with Ac_2O and anhydrous pyridine at room temperature for 2 days and yielded diacetyl derivative **3**. Mp 156-157°, ir ν max cm^{-1} 3450, 1770, 1735, 1650, 1600; ms *m/z* $(M+H)^+$ 445 (30, protonated $C_{24}H_{28}O_8$), 402 (76), 387 (100), 271 (82); ^1H nmr δ 1.30, 1.34 (3H each, s, 3'-*gem*-methyls), 1.50 (6H, s, 2-*gem*-methyls), 1.83 (3H, s, 2'-OAc) 2.33 (3H, d, *J*=0.7, 8-CH_3), 2.43 (3H, s, 5-OAc), 3.00 (1H, dd, *J*=14, 3.9, H-1'b), 3.20 (1H, dd, *J*=14, 9.7, H-1'a), 5.11 (1H, dd, *J*=9.7, 3.9, H-2'), 5.74 (1H, d, *J*=10, H-3), 5.96 (H, q, *J*=0.7, H-7), 6.47 (1H, d, *J*=10, H-4).

ACETYLATION OF **2**.—Compound **2** was acetylated with Ac_2O and anhydrous pyridine at room temperature for 2 days and yielded triacetyl derivative **4**. Ir ν max cm^{-1} 3400, 1770, 1730, 1648, 1590; ms *m/z* $(M+H)^+$ 503 (32, protonated $C_{26}H_{30}O_{10}$), 460 (63), 445 (90), 287 (100); ^1H nmr δ 1.12, 1.16 (3H each, s, 3'-*gem*-methyls), 1.56 (6H, br s, 2-*gem*-methyls), 1.99 (3H, 5, 2'-OAc), 2.13 (3H, s, 1'-OAc),

2.39 (3H, d, J=0.6, 8-CH_3), 2.43 (3H, s, 5-OAc), 5.79 (1H, d, J=10, H-3), 5.89 (1H, d, J=9.7, H-2′), 5.96 (1H, q, J=0.6, H-7), 6.47 (1H, d, J=10, H-4), 6.69 (1H, d, J= 9.7, H-1′).

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