was measured by Dr. Benjamin Rodríguez, Consejo Superior de Investigaciones Científicas Madrid, Spain.

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Phytochemistry, Vol. 22, No. 9, pp. 2090–2092, 1983.
Printed in Great Britain.

0031–9422/83 $3.00 + 0.00

5-METHOXY-2,2,8-TRIMETHYL-10-SENECIOYL-2*H*,6*H*-BENZO(1,2-b; 5,4-b′)DIPYRAN-6-ONE FROM *SPATHELIA WRIGHTII*

MARIA DIAZ, ALFRED PREISS*, HINRICH MEYER† and HELMUT RIPPERGER*

Institute of Botany, Academy of Sciences of Cuba, Havana, Cuba; *Institute of Plant Biochemistry, Academy of Sciences of the GDR, Halle (Saale), German Democratic Republic; †Department of Chemistry, Martin Luther University, Halle (Saale), German Democratic Republic

(*Received* 16 *December* 1982)

Key Word Index—*Spathelia wrightii*; Rutaceae; pyranochromone; 5-methoxy-2,2,8-trimethyl-10-senecioyl-2*H*,6*H*-benzo (1,2-b; 5,4-b′)dipyran-6-one.

Abstract—From leaflets of *Spathelia wrightii* a new pyranochromone has been isolated, the spectroscopic properties of which are in accordance with the structure 5-methoxy-2,2,8-trimethyl-10-senecioyl-2*H*,6*H*-benzo(1,2-b; 5,4-b′)dipyran-6-one (**1**).

From dried leaflets of *Spathelia wrightii* a pyranochromone was isolated in 2.9% yield. High resolution mass spectrometry revealed the elemental composition $C_{21}H_{22}O_5$. The structure was mainly deduced from NMR spectral information. The ^1H NMR signals (Table 1) were assigned and partial structures recognized by comparison with chemical shift data and coupling constants of compounds containing the 2,2-dimethylchromene [1–3] and 2-methylchromone ring systems [4] or the senecioyl side chain [5]. In deuterochloroform the signals of the C-14 and C-18 methyl groups coincide. Their membership to two spin systems was detected by decoupling experiments. The observed NOE values (Fig. 1) are only in agreement with one (**1**) of the 12 possible arrangements of the substituents at the benzene ring. In the NOE experiments, difficulties arose from the superimposition of the signals of H-14 and H-18 in deuterochloroform and the neighbourhood of the signals of H-14 and H-19 in deuterobenzene, respectively. Irradiation on the signal at $\delta 2.18$ in deuterobenzene showed that the C-18 methyl group does not produce a NOE. Therefore, the following measurements were carried out in deuterochloroform considering that signal enhancement by irradiation on the signal at $\delta 2.24$ has to be attributed exclusively to the C-14 methyl group. The ^{13}C NMR spectrum (Table 2), including the ^{13}C–^1H long-range coupling constants (Table 3), is in agreement with structure **1**. Signals were assigned by comparison with reported data for furochromones [6], mulberrochromene [7] and isobutenyl phenyl ketone [8] as well as by determination of the ^{13}C–^1H long-range coupling constants via selective decoupling experiments.

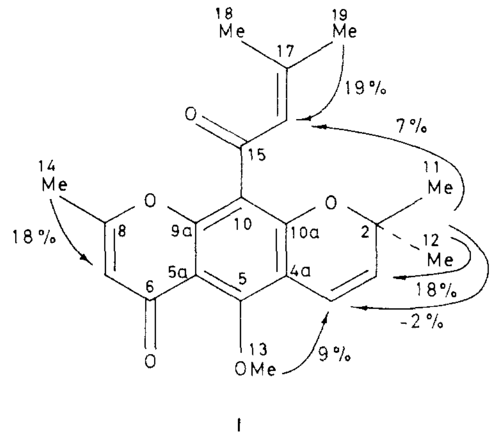

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Fig. 1. NOE values for 5-methoxy-2,2,8-trimethyl-10-senecioyl-2*H*,6*H*-benzo(1,2-b;5,4-b′)dipyran-6-one (**1**).

Table 1. ^1H NMR chemical shifts of compound **1***

Proton No.	$CDCl_3$	C_6D_6	Proton No.	$CDCl_3$	C_6D_6
3	5.69 (*d*)†	5.21	14	2.24 (*d*)	1.43
4	6.60 (*d*)	6.69	16	6.28 (*qq*)	6.25
7	5.96 (*q*)	5.74	18	2.24 (*d*)	2.18
11,12	1.46 (*s*)	1.18	19	1.97 (*d*)	1.53
13	3.89 (*s*)	3.90			

*δ-Values (ppm) measured from the solvent line and calculated relative to TMS ($\delta_{TMS} = \delta_{CDCl_3} + 7.24$ ppm, $\delta_{TMS} = \delta_{C_6D_6} + 7.15$ ppm).

†Multiplicities; $J_{3,4} = 10.2$ Hz, $J_{7,14} = 0.8$ Hz, $J_{16,18} = 1.3$ Hz, $J_{16,19} = 1.3$ Hz.

Table 2. ^{13}C NMR chemical shifts of compound **1***

Carbon No.	δ	Carbon No.	δ	Carbon No.	δ
2	78.0 (*s*)†	7	111.9 (*d*)	14	19.0 (*q*)
3	130.5 (*d*)	8	162.9 (*s*)	15	189.2 (*s*)
4	116.6 (*d*)	9a	155.9 (*s*)	16	127.0 (*d*)
4a	113.1 (*s*)	10	117.3 (*s*)	17	154.1 (*s*)
5	156.2 (*s*)	10a	154.6 (*s*)	18	20.8 (*q*)
5a	112.9 (*s*)	11,12	28.0 (*q*)	19	27.3 (*q*)
6	175.5 (*s*)	13	62.8 (*q*)		

*δ-Values (ppm) measured from the central solvent line (C_6D_6) and calculated relative to TMS ($\delta_{TMS} = \delta_{C_6D_6} + 128.0$ ppm).

†Multiplicities from the SFORD spectrum; under these conditions long-range couplings were not observed.

Table 3. ^{13}C–^1H long-range coupling constants (Hz) for quaternary sp^2-carbon atoms in compound **1**

	Proton No.					
Carbon No.	3	4	7	13	14	16
4a (*dd*)*	8.5	1.8	—	—	—	—
5 (*dq*)	—	2.4	—	2.4	—	—
5a (*d*)	—	—	3.0	—	—	—
6 (*d*)	—	—	1.2	—	—	—
8 (*dq*)	—	—	6.7	—	6.7	—
9a (*s*)	—	—	—	—	—	—
10 (*s*)	—	—	—	—	—	not observed
10a (*d*)	—	4.3	—	—	—	—
15 (*d*)	—	—	—	—	—	3.6

*Multiplicities due to long-range couplings.

The 5-hydroxy compound corresponding to chromone (**1**), 10-senecioylspatheliachromene, has been isolated from *Spathelia sorbifolia* and has a similar ^1H NMR spectrum [9].

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded at 200.13 and 50.327 MHz, respectively. The NOE studies were performed on degassed samples of less than 5% concn (w/v) in $CDCl_3$ and C_6D_6, respectively. Each resonance was integrated × 7 in a homo inverse-gated decoupled and in a decoupled spectrum and the NOEs were calculated from the average areas. Accuracies of NOE values are *ca* ±1.5%.

Spathelia wrightii M. Vict. was collected in November at Yagrumajes River, Moa, Oriente, Cuba, and identified by Lic. Pedro Herrera. A voucher specimen is retained in the Herbarium of the Institute of Botany, Academy of Sciences of Cuba, Havana.

5-Methoxy-2,2,8-trimethyl-10-senecioyl-2H,6H-benzo (1,2-b; 5,4-b')dipyran-6-one (**1**). Dried and ground leaflets of *S. wrightii* were extracted with EtOH at room temp. Evaporation of the solvent *in vacuo* gave a residue which was partitioned between 0.5 N HCl and C_6H_6–Et_2O (1:1). The residue of the organic phase was chromatographed over Si gel with Et_2O. From MeOH crystals with mp 126–127°. IR ν_{max}^{nujol} cm^{-1}: 1660, 1634, 1611,

1582. UV λ_{max}^{MeOH} nm (log ε): 335 (3.87), 262 (4.71). EIMS, 70 eV m/z (rel. int.): 354.1455 (calc. for $C_{21}H_{22}O_5$: 354.1467; 55), 339.1189 (calc. for $C_{20}H_{19}O_5$: 339.1232; 100), 321.1164 (calc. for $C_{20}H_{17}O_4$: 321.1127; 6).

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Phytochemistry, Vol. 22, No. 9, pp. 2092–2093, 1983.
Printed in Great Britain.

0031-9422/83 $3.00 + 0.00

5,7,3′-TRIHYDROXY-6,8-DI-*C*-METHYL-4′,5′-DIMETHOXYFLAVANONE FROM *ALLUAUDIOPSIS MARNIERIANA*

ZAFERA RABESA and BERNARD VOIRIN*

Départment d'Ethnobotanique, Centre National de Recherches Pharmaceutiques, B.P. 702, Antananarivo, Madagascar; *†Laboratoire de Phytochimie, Département de Biologie Végétale, 43 Boulevard du 11 novembre 1918, 69622 Villeurbanne, France

(*Revised received* 28 *January* 1983)

Key Word Index—*Alluaudiopsis marnieriana*; Didiereaceae; 5,7,3′-trihydroxy-6,8-di-*C*-methyl-4′,5′-dimethoxyflavanone; new natural compound.

Abstract—From bark and spines of *Alluaudiopsis marnieriana*, a novel flavanone has been isolated and identified as 5,7,3′-trihydroxy-6,8-di-*C*-methyl-4′,5′-dimethoxyflavanone by UV, ^1H NMR and mass spectroscopy.

Previous studies of flavonoids of Didiereaceae have revealed different *C*- and *O*-methylated flavonols [1–7]. Of the four genera of this family, *Didierea*, *Decaryia*, *Alluaudia* and *Alluaudiopsis*, only the latter lacks flavonols; instead it produces flavanones. We now report the structural elucidation of a new natural compound of this class, 5,7,3′-trihydroxy-6,8-di-*C*-methyl-4′,5′-dimethoxyflavanone from *Alluaudiopsis marnieriana* Rauh, which was originally thought to be the 4′-hydroxy-3′-methoxy isomer [8].

The grey-violet fluorescence in UV light and the UV spectrum in methanol, band II main peak at 297 nm and band I at 348 nm, appeared typical of a flavanone [9]. This was confirmed by the presence of characteristic signals at δ5.34 (1H, *dd*) and at 3.04 and 2.75 (1H, *dd*) corresponding to H-2 and H-3, respectively, in the ^1H NMR spectrum. Moreover, this spectrum exhibited signals at δ1.97 (3H, *s*) and 1.99 (3H, *s*) and δ3.71 (3H, *s*) and 3.80 (3H, *s*) typical for two C–Me and two methoxyls, respectively, and only two aromatic proton signals at δ6.67 (1H, *d*, $J = 2$ Hz) and 6.69 (1H, *d*, $J = 2$ Hz) corresponding to two protons in the *m*-position. The positive results obtained after irradiation of each aromatic signal indicated that these protons were located in the B ring at C-2′ and C-6′. The mass spectrum exhibited a molecular ion peak at m/z 360 (85 %) in accord with a flavanone containing three hydroxyl, two methoxyl and two *C*-methyl substituents ($C_{19}H_{20}O_7$, calc. 360.1209, found 360.1213). After fragmentation, a peak at m/z 207 ($[M]^+$ B ring according to ref. [10]) and high resolution measurement of peak B at m/z 180 ($C_{10}H_{12}O_3$ calc. 180.0786, found 180.0781) indicated that the B ring was substituted by one hydroxyl and two methoxyl groups. Of the two structural possibilities, 4′-hydroxy-3′,5′-dimethoxy or 3′-hydroxy-4′5′-dimethoxy, the latter seemed more likely since in ^1H NMR spectrum the proton signals as well as those of methoxyl groups were separated. Nevertheless, this conclusion was confirmed by an NOE experiment; after irradiation of each methoxyl, only the irradiation on the methoxyl at δ3.80 (C-5′) gave rise to a significant result in the singlet at 6.69 (C-6′). In the A ring, two hydroxyls were located at C-5 and C-7, band II showing a bathochromic shift (43 nm) after addition of sodium methoxide in the UV spectrum [9]. The two remaining *C*-methyl groups were, thus, located at C-6 and C-8. High resolution measurements of ion fragments obtained after RDA reaction of peak D at m/z 181 ($C_9H_9O_4$ calc. 181.0501, found 181.0503) and

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†To whom correspondence should be addressed.