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Constituents from *Miliusa balansae* (Annonaceae)

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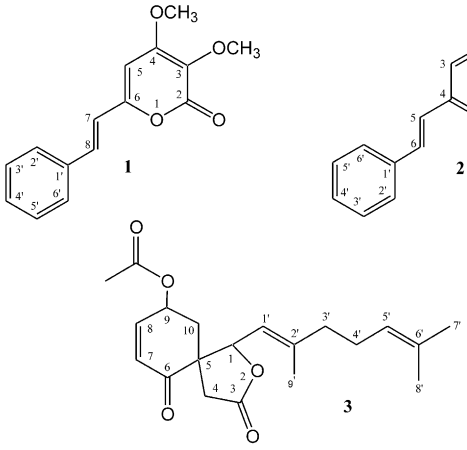
Abstract

The styryl derivatives 3,4-dimethoxy-6-styryl-pyran-2-one and (2*E*,5*E*)-2-methoxy-4-oxo-6-phenyl-hexa-2,5-dienoic acid methyl ester were isolated from leaves and branches of *Miliusa balansae* (Annonaceae). In addition, the geranylated homogentisic acid derivative miliusate, four flavanones and two dihydrochalcones were identified. Their structures were elucidated by spectroscopic means.

Keywords: *Miliusa balansae*; Annonaceae; 3,4-Dimethoxy-6-styryl-pyran-2-one; (2*E*, 5*E*)-2-Methoxy-4-oxo-6-phenyl-hexa-2,5-dienoic acid methyl ester; Miliusate; Flavanones; Dihydrochalcones

1. Introduction

The plant *Miliusa balansae* Fin. & Gagn. is a shrub of the family Annonaceae (Ho, 1999). In China, the plant is traditionally used for gastropathy and glomerulonephropathy (Wu et al., 2001). We now report the isolation and structural elucidation of two styryl derivatives (**1**–**2**) and seven known compounds (**3**–**9**) from this plant. In the genus *Miliusa* some oxoaporphine-alkaloids have already been found (Harrigan et al., 1994), and from *M. balansae* the spiro compound miliusate (**3**) was recently isolated (Wu et al., 2001).



1

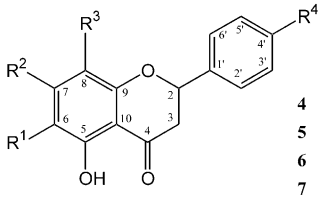
2

3

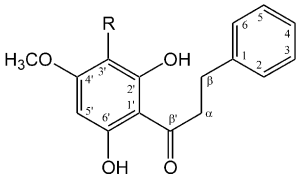
2. Results and discussion

From leaves and branches of *Miliusa balansae*, nine compounds (**1**–**9**) were isolated from the EtOAc-extract following silica gel column chromatography. Besides miliusate (**3**), four known flavanoids (**4**–**7**), two known dihydrochalcones (**8**–**9**) and new styryl derivatives **1** and **2** were obtained.

High- resolution ESI-TOF-MS of compound **1** gave a molecular ion $[M+H]^+$ of *m*/*z* 259.0925 that was consistent with the molecular formula $C_{15}H_{14}O_4$ and the presence of 9 double bond equivalents. The prominent



4 $R^1 = R^3 = R^4 = H$, $R^2 = OCH_3$
5 $R^1 = R^3 = H$, $R^2 = R^4 = OCH_3$
6 $R^1 = H$, $R^2 = R^3 = OCH_3$, $R^4 = H$
7 $R^1 = R^2 = OCH_3$, $R^3 = H$, $R^4 = H$



8 $R = OCH_3$
9 $R = H$

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fragments at m/z 103 $[C_6H_5–CH=CH]^+$ and 131 $[C_6H_5–CH=CH–C=O]^+$ suggested a cinnamoyl moiety. The ^1H and ^{13}C NMR spectra (Table 1) exhibited two methoxyl groups (δ_C 60.3 and 54.2, δ_H 4.00 and 3.88), one olefinic CH group (δ_H 6.11 *s*, δ_C 98.1), and signals for a *trans*-styryl moiety (δ_H 6.59, 7.43, both *d*, $J = 15.9$ Hz for the double bond, δ_H 7.49, 7.38, 7.34, δ_C 135.4, 129.3, 128.9, 127.3 for the phenyl moiety). From the number of double bond equivalents, the presence of two rings was deduced. The IR spectrum with bands at 1689 cm^{-1} ($\nu_{C=O}$) and 1643 ($\nu_{C=C}$) revealed a conjugated carbonyl group, which, due to the lack of a carbon signal for a ketone, had to be assigned to a conjugated ester function. These data suggested a 6-styryl-pyran-2-one structure with two methoxyl groups on the pyrone moiety. The C-H long-range correlations from the ^1H-^{13}C HMBC experiment confirmed this structure and located the methoxyl groups at postions 3 and 4 by the correlations C-3/H-5, C-4/H-5, C-5/H-7, C-6/H-5/H-7/H-8 and C-7/H-5. Moreover, irradiation of H-5 (δ_H 6.11) afforded a NOE at the 4-OCH_3 (δ_H 4.00) and no effect at the 3-OCH_3 (δ_H 3.88). The NOE interactions from H-5 to H-7 and the missing interaction from H-5 to H-8 revealed the *s-trans* conformation of the C-7/C-6 single bond. A NOE effect between the two methoxyl groups could not be observed, as their signals were too close together. Although similar structures like dimethoxy-6-styryl-pyran-2-one (yangonin) and 4′-desmethoxyyangonin from *Piper methysticum* (Boonen and Haeberlein, 1988) were known, this structure of 3,4-dimethoxy-6-styryl-pyran-2-one (**1**) is new.

The EI-MS of compound **2** gave only the $[M–H]^+$ peak at m/z 245. The molecular weight of 246 was obtained from the $[M+H]^+$ peak at m/z 247.0972 in the HR-ESI-TOF–MS, which also gave the formula $C_{14}H_{14}O_4$. As with compound **1**, the NMR spectra of **2** (Table 2) also showed a *trans*-styryl derivative with two methoxyl groups at δ_H 3.84 and 3.91, with the latter coming from an ester methoxyl group because of the smaller chemical shift of the connected carbon (δ_C 53.0). The corresponding carboxyl group was recognized as the signal at δ 164.3 by its strong C–H long-range correlation in the ^1H–^{13}C HMBC experiment to these methoxyl protons. This carboxyl carbon was adjacent to a tri-substituted double bond with a methoxyl and a keto substituent, revealed by the correlations δ_C 164.3/δ_H 5.84, δ_C161.5/δ_H 5.84 and 3.84 and δ_C 187.1/δ_H 5.84. This keto group was next to the double bond of the styryl moiety, because of the correlations to the protons at δ 6.80 and 7.60, indicating the structure 4-oxo-6-phenyl-hexa-2,5-dienoic acid methyl ester for **2**. The olefinic proton at δ 5.84 was positioned at C-3 from $^3J_{CH}$ correlations to C-5 and NOE interactions with both protons of the styryl double bond. Finally, the strong NOE effect between H-3 and the ether methoxyl group at δ 3.84 indicated an (*E*) configuration for this double bond. Structure **2** was supported by the IR bands at 1746 ($\nu_{C=O}$ ester) and 1652 cm^{-1} ($\nu_{C=O}$ α,β, α′,β′diunsaturated ketone) and by the mass fragmentation pattern (Fig. 1).

The ESI-MS of compound **3** gave the molecular formula as $C_{20}H_{26}O_5$ by high resolution of the $[M+Na]^+$

Table 1
NMR spectroscopic data for compound **1** in $CDCl_3$, 125/500 MHz (*J* in Hz)

	δ_C	δ_H	C–H long-range correlations[a]	NOE[b]
2	160.9	–	H-7 (w)	
3	128.4	–	H-5, 3-OCH_3	
4	158.7	–	H-5, 4-OCH_3	
5	98.1	6.11 *s*	H-7, H-8 (w)	4-OCH_3 (s), H-7 (m)
6	154.7	–	H-8, H-7, H-5	
7	118.4	6.59 *d* (15.9)	H-8, H-5	H-5 (s), H-2′/6′ (m)
8	135.2	7.43 *d* (15.9)	H-2′/6′, H-7	
1′	135.4	–	H-3′/5′, H-7, H-8, H-4′ (w)	
2′/6′	127.3	7.49 *dt* (7.0/1.6)	H-6′/2′, H-8, H-4′, H-7 (w)	
3′/5′	128.9	7.38 *tt* (7.3/1.5)	H-5′/3′, H-4′ (w)	
4′	129.3	7.34 *tt* (7.2/1.3)	H-2′/6′	
3-OCH_3	60.3	3.88 *s*		
4-OCH_3	57.4	4.00 *s*		H-5 (s)

(s) = Strong, (m) = medium, (w) = weak.
[a] From HMBC experiment, correlation signals of C-8 and C-1′ were not resolved.
[b] Obtained from the NOE difference spectra.

Table 2
NMR spectroscopic data for compound **2** in $CDCl_3$ (75/300 MHz)

	δ_C	δ_H	C–H long-range correlations[a]	NOE[b]
1	164.3	–	H-3 (m), 1-OCH_3 (s)	
2	161.5	–	H-3 (m), 2-OCH_3 (s)	
3	100.9	5.84 *s*	H-5 (w)	H-6 (m), H-5 (m-s), 2-OCH_3 (s)
4	187.1	–	H-6 (m), H-5 (m), H-3 (w)	
5	126.6	6.80 *d* (15.9)	–	H-2′/6′ (m), H-3 (s)
6	142.9	7.60 *d* (15.9)	H-2′/5′ (w)	
1′	134.4	–	H-3′/5′ (m), H-5 (m)	
2′/6′	128.2	5.57–5.53		
3′/5′	128.8	7.42–7.37		
4′	130.4	7.42–7.37		
1-OCH_3	53.0	3.91 *s*	–	–
2-OCH_3	57.1	3.84 *s*	–	H-3 (s)

[a] From HMBC experiment at 125/500 MHz.
[b] Obtained from difference pulsed field gradient NOE spectra (DPFG-NOE) at 500 MHz.

peak at m/z 369.0973. Analysis of the 1D and 2D NMR spectra (HH-COSY, HMQC, HMBC) showed, in addition to one acetyl group, the partial structure $(CH_3)_2C{=}CH{-}CH_2{-}CH_2{-}CH(CH_3){=}CH{-}CHR'{-}OR$, which represented a geranyl moiety with an additional substituent R′, thus leaving for the central moiety of the molecule $C_8H_7O_3$ a *cis* double bond (δ_C 143.9/δ_H 6.82 and δ_C 130.9/δ_H 6.08 with a mutual $^3J_{HH}$ of 10.2 Hz), one α,β-unsaturated ketone (δ_C 194.9), one ester or lactone (δ_C 174.5) and two double bond equivalents for the presence of two rings. Only one carbon at δ_C 52.3 was able to function as a bridge-head. The $^1H{-}^{13}C$ HMBC spectrum displayed CH long-range correlations to H-1′ of the side chain and all protons of the central moiety except H-9 indicating a spiro structure. Full analysis of all spectra led to the structure of the homogentisic acid derivative 9-acetoxy-1-[(1*E*)-2,6-dimethyl-hepta-1,5-dienyl]-3,6-dioxo-2-oxa-spiro[4.5]dec-7-ene for **3**, which was very recently isolated from the same species and named 'miliusate' (Wu et al., 2001). This was the first time that this skeletal structure was discovered.

The two common flavanoids, pinostrobin (**4**, 5-hydroxy-7-methoxyflavanone $[M]^+$ m/z 270, $C_{16}H_{14}O_4$) and its 4′-methoxy derivative (**5** ($[M]^+$ m/z 300, $C_{17}H_{16}O_5$), were identified by comparison of the proton and carbon shifts with reference data (Cuong et al., 1996) and with the NMR spectra of **4**, respectively. The two isomeric and rare flavanoids 5-hydroxy-7,8-dimethoxyflavanone (**6**, $[M]^+$ m/z 300, $C_{17}H_{16}O_5$) and 5-hydroxy-6,7-dimethoxyflavanone (**7**, $[M]^+$ m/z 300, $C_{17}H_{16}O_5$) were identified by analysis of their NMR spectra and comparison of their melting points. As no complete NMR data of **6** and **7** were available, the signals of **6** were assigned by the CH long-range correlations from the HMBC experiment, and those of **7** by comparison with **6**.

The two dihydro chalcones **8** and **9** were identified as dihydropashanone (2′,6′-dihydroxy-3′,4′-dimethoxydihydrochalcone) and 2′,6′-dihydroxy-4′-methoxydihydrochalcone by comparison with reference data (Ichino et al., 1988; Agrawal, 1989) assuming one misprint for C-3′ of **8**, which resonated in our spectra at δ_C 127.8.

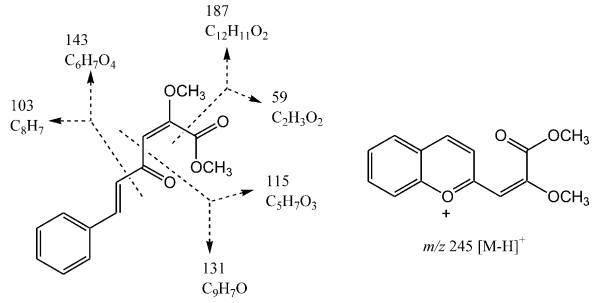

Fig. 1. Proposed mass spectral fragmentation of compound **2**.

3. Experimental

3.1. General

Mps are uncorrected. EIMS: AMD 402, 70 eV. ESI MS: Finnigan TSQ 700. TOF-HR-ESI–MS: QStar Pulsar (Applied Biosystems). NMR: Varian Gemini 300, Unity 500, Bruker Avance 500. FT-IR: Nicolet IMPACT 410, Bruker IFS28 (s = strong, m = medium, w = weak, v = very). CC: silica gel 60, 40–63 μm (Merck).

3.2. Plant material

Leaves and branches of *Miliusa balansae* Fin. & Gagn. were collected in Hoa Binh province, North Viet Nam, in June 1999 and identified by Professor Dr. Nguyen Tien Bau, Institute of Biological Resources and Ecology, National Center for Natural Science and Technology, Hanoi, Viet Nam. A voucher specimen (Nr. 2142) is deposited at this Institute.

3.3. Extraction and isolation

The dried and ground leaves and branches (750 g) were extracted several times with MeOH–H_2O (95:5). The organic solvent was evaporated under red. pres. and the aq. residue extracted with *n*-hexane, EtOAc and *n*-BuOH, successively (each 3×), giving *n*-hexane (15 g), EtOAc (19 g) and *n*-BuOH (11 g) extracts. The EtOAc extract was separated on silica gel (350 g, 230–400 mesh) with solvents of increasing polarity (0–100% EtOAc in *n*-hexane). Frs. 6 and 7 after fractionation on silica gel with *n*-hexane–EtOAc (98:2) yielded compound **4** (78 mg). Frs. 13–14, which eluted with *n*-hexane–EtOAc (9:1), gave compound **5** (23 mg) after crystallization from *n*-hexane–EtOAc. Compounds **6** (52 mg) and **7** (210 mg) were obtained from frs. 25–27 and frs. 35–36, (eluting with *n*-hexane–EtOAc 85:15 and 8:2), respectively, after crystallisation from *n*-hexane–EtOAc. Frs. 39–46 (eluting with *n*-hexane–EtOAc 8:2) yielded compound **8** (41 mg) after crystallisation from *n*-hexane–EtOAc. Frs. 58–59 (8.1 g) were subjected to CC on silica gel using mixtures of $CHCl_3$ and MeOH of increasing polarity (98:2, 95:5, 9:1, 8:2, 1:1). Frs. 6–7 gave compound **1** (50 mg) after crystallisation from *n*-hexane–EtOAc (7:3). Frs. 15–23 (5.1 g) were further fractionated (silica gel, *n*-hexane–EtOAc–MeOH 4:1:0.1) into frs. 21–25 (467 mg), which yielded compound **3** (24 mg) after purification by CC (*n*-hexane–EtOAc 7:3), and frs. 26–32 (920 mg), which gave compound **2** (18.5 mg) after CC on silica gel with *n*-hexane–EtOAc (7:3).

3.3.1. 3,4-Dimethoxy-6-styryl-pyran-2-one (*1*)

Yellow needles from *n*-hexane–EtOAc, mp. 92–93 °C. The compound gave a positive reaction with Dragendorff reagent. IR ν_{max}^{KBr} (cm^{-1}): 3085 (w), 2939 (w), 1689 (vs, $\nu_{C=O}$ conjugated ester), 1643 (m, $\nu_{C=C}$ conjugated with

C=O), 1612 (w), 1548 (m), 1359 (m), 1205 (m), 1151 (m), 1017 (m), 961 (m), 688 (m). EI-MS (70 eV) *m/z* (rel. int.): 258 $[M]^+$ (94), 243 $[M–CH_3]^+$ (7), 215 $[243\text{-}CO]^+$ (100), 197 (4), 187 (16), 183 (13), 173 (33), 155 (20), 131 $[C_6H_5–CH=CH–C=O]^+$ (93), 115 (6), 103 $[C_6H_5–CH=CH]^+$, 77 (30), 69 (49). HR-ESI MS: 259.0925 $[M+H]^+$ ($C_{15}H_{15}O_4$ requires 259.0970), 244.0696 $[M+H–CH_3]^+$ ($C_{14}H_{12}O_4$ requires 244.0736).

3.3.2. 2-Methoxy-4-oxo-6-phenyl-hexa-2,5-dienoic acid methyl ester (2)

Oil. IR $\nu_{max}^{CHCl_3}$ (cm^{-1}): 2951 (w), 2936 (w), 1746 (s, $\nu_{C=O}$, ester), 1652 (m, $\nu_{C=O}$, α,β,α′,β′-diunsaturated ketone), 1612 (*s*, $\nu_{C=C}$, conjugated with C=O), 1580 (*s*), 1434 (m), 1380 (m), 1172 (m), 1094 (m). EI-MS (70 eV) *m/z* (rel. int.): 245 $[M–H]^+$ (51), 231 $[M–CH_3]^+$ (17), 215 $[M–OCH_3]^+$ (20), 214 $[M–H–OCH_3]^+$ (33), 199 (13), 187 $[M–COOCH_3]^+$ (100), 171 $[M\text{-}COCH_3–CH_3OH]^+$ (81), 155 $[M–COOCH_3–CH_3OH]^+$ (31), 143 $[171\text{-}CO]^+$ (88), 131 [cinnamoyl]$^+$ (78), 115 [M-cinnamoyl]$^+$ (94), 103 [styryl]$^+$ (62), 77 $[C_6H_5]^+$ (33), 69 (30). HR-ESI-TOF–MS (*m/z*): 269.0793 $[M+Na]^+$ ($C_{14}H_{14}O_4Na$ requires 269.0790), 247.0972 $[M+H]^+$ ($C_{14}H_{15}O_4$ requires 247.0970).

3.3.3. Miliusate (3, 9-acetoxy-1-(2,6-dimethyl-hepta-1,5-dienyl)-3,6-dioxo-2-oxa-spiro[4.5]dec-7-ene)

Colourless oil. IR ν_{max}^{film} (cm^{-1}): 2966 (s), 2925 (vs), 2857 (s), 1790 (vs, $\nu_{C=O}$, γ-lactone), 1746 (*s*, $\nu_{C=O}$, acetoxy), 1683 (*s*, $\nu_{C=O}$, α,β-unsaturated ketone), 1436 (*m*, *br*), 1374 (m), 1324 (m), 1219 (s), 991 (m). EI-MS *m/z* (rel. int.): 287 $[M–OAc]^+$ (14), 218 $[287\text{-}C_5H_9]^+$ (15), 190 [218- CO]$^+$ (46), 153 (28), 151 (26), 145 (18), 135 (86), 134 (100), 126 [RDA product $C_6H_6O_3]^+$ (47), 107 (55), 93 (27), 85 (43), 69 $[C_5H_9]^+$ (62), 59 $[OAc]^+$ (13), 55 $[C_4H_7]^+$ (30). HR-ESI-TOF–MS, *m/z*: 369.16764 $[M+Na]^+$ ($C_{20}H_{26}O_5Na$ requires 369.16725). ^{13}C NMR ($CDCl_3$, 125 MHz): 81.0 (C-1), 174.5 (C-3), 37.1 (C-4), 52.3 (C-5), 194.9 (C-6), 130.9 (C-7), 143.9 (C-8), 65.1 (C-9), 36.6 (C-10), 118.6 (C-1′), 144.6 (C-2′), 39.7 (C-3′), 26.1 (C-4′), 123.3 (C-5′), 132.2 (C-6′), 25.8 (C-7′), 17.80 (C-8′), 16.9 (C-9′), 169.8 (O<u>C</u>O-CH$_3$), 21.1 (OCO-<u>CH$_3$</u>). ^1H NMR ($CDCl_3$, 500 MHz): 5.49 (1H, *d*, *J*=10.1 Hz, H-1), 2.27 (1H, *d*, *J*=17.6 Hz, H-4^A), 3.37 (1H, *d*, *J*=17.6 Hz, H-4^B), 6.08 (1H, *dd*, *J*=10.2 and 1.2 Hz, H-7), 6.82 (1H, *ddd*, *J*=10.2, 4.0 and 1.0 Hz, H-8), 5.57 (1H, *m*, H-9), 2.26 (1H, *dd*, *J*=14.8 and 5.5 Hz, H-10^A), 2.41 (1H, *ddd*, *J*=14.8, 4.2 and 1.0 Hz, H-10^B), 5.14 (1H, *dq*, *J*=10.1 and 1.2 Hz, H-1′), 2.03 (2H, *m*, H$_2$-3′), 2.01 (2H, *m*, H$_2$-4′), 5.00 (1H, *m*, H-5′), 1.68 (3H, *s*, H$_3$-7′), 1.59 (3H, *s*, H$_3$-8′), 1.70 (3H, *d*, *J*=1.4 Hz, H$_3$-9′), 2.16 (3H, *s*, OCO-<u>CH$_3$</u>).

3.3.4. 5-Hydroxy-7,8-dimethoxyflavanone (6)

Colourless needles from *n*-hexane-EtOAc, mp 97 °C. EIMS *m/z* (rel. int.) 300 $[M]^+$ (100). ^{13}C NMR ($CDCl_3$, 125 MHz): 79.1 (C-2), 43.3 (C-3), 196.0 (C-4), 159.9 (C-5), 93.0 (C-6), 161.5 (C-7), 129.8 (C-8), 153.5 (C-9), 102.9 (C-10), 138.5 (C-1′), 126.0 (C-2′/6′), 128.8 (C-3′/5′), 128.7 (C-4′), 56.2 (7-OCH$_3$), 61.3 (8-OCH$_3$). ^1H NMR ($CDCl_3$, 300 MHz): 5.48 (1H, *dd*, *J*=12.1 and 3.3 Hz, H-2), 2.89 (1H, *dd*, *J*=17.2 and 3.4 Hz, H^A-3), 3.09 (1H, *dd*, *J*=17.3 and 12.1 Hz, H^B-3), 6.12 (1H, *s*, H-6), 7.38–7.49 (5H, m, H-2′/3′/4′/5′/6′), 3.90 (3H, *s*, 7-OCH$_3$), 3.79 (3H, *s*, 8-OCH$_3$), 12.0 (1H, *s*, 5-OH).

3.3.5. 5-Hydroxy-6,7-dimethoxyflavanone (7, onysilin)

Thick, yellow plates from *n*-hexane–EtOAc, mp 149–150° C. EIMS *m/z* (rel. int.) 300 $[M]^+$ (100). ^{13}C NMR ($CDCl_3$, 125 MHz): 79.4 (C-2), 43.2 (C-3), 196.3 (C-4), 154.9 (C-5), 130.5 (C-6), 160.9 (C-7), 91.6 (C-8), 158.6 (C-9), 103.1 (C-10), 138.2 (C-1′), 126.1 (C-2′/6′), 128.82 (C-3′/5′), 128.86 (C-4′), 60.8 (6-OCH$_3$), 56.1 (7-OCH$_3$). ^1H NMR ($CDCl_3$, 300 MHz): 5.42 (1H, *dd*, *J*=13.2 and 3.0 Hz, H-2), 2.83 (1H, *dd*, *J*=17.2 and 3.2 Hz, H^A-3), 3.10 (1H, *dd*, *J*=17.3 and 13.2 Hz, H^B-3), 6.13 (1H *s*, H-8), 7.38–7.47 (5H, *m*, H-2′/3′/4′/5′/6′), 3.85 (3H, *s*, 6-OCH$_3$), 3.88 (3H, *s*, 7-OCH$_3$), 11.9 (1H, *s*, 5-OH).

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