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Phloroglucinol derivatives from *Mallotus pallidus*

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Abstract

From the leaves of *Mallotus pallidus* were isolated five phloroglucinol derivatives, namely pallidusol, dehydropallidusol, pallidol, mallopallidol and homomallopallidol. Their structures were determined by means of spectroscopic methods of analysis.

Keywords: *Mallotus pallidus*; Euphorbiaceae; Phloroglucinol

1. Introduction

Plants of the genus *Mallotus* (Euphorbiaceae) have been known to be a rich source of phenolic compounds such as phloroglucinols (Lounasmaa et al., 1975; Chan et al., 1989; Arisawa et al., 1985, 1986, 1990a,b,c,d; Fujita et al., 1988), tannins (Saijo et al., 1989), coumarins (Cheng and Chen, 2000), chalcones (Tanaka et al., 1998) and benzopyrans (An et al., 2001). *Mallotus pallidus* (Airy Shaw) Airy Shaw is a shrub endemic to Thailand, growing in the southwestern part of the country (Shaw, 1997); however, to date, neither a chemical nor a biological study has been reported for this plant. As a continuation of our studies on naturally occurring phenolics (Kaewamatawong et al., 2002), we examined the constituents of the leaves of *M. pallidus*. This has resulted in the isolation of several new compounds, including three monomeric (**1**–**3**) and two dimeric phloroglucinol derivatives (**4**–**5**). In the present paper, we report the isolation and structural elucidation of these compounds.

2. Results and discussion

Pallidusol (**1**) was obtained as colorless needles. The molecular formula was deduced to be $C_{14}H_{20}O_4$ from the $[M + Na]^+$ at *m*/*z* 275.1248 in the HR-ESI-MS. The UV absorptions at 294 and 235 nm suggested an aromatic structure and the IR spectrum indicated the presence of a hydroxyl (3435 cm^{-1}) and a conjugated carbonyl group (1627 cm^{-1}). Compound **1** appeared to be a pentasubstituted benzene, as evidenced by the ^{13}C NMR signals for aromatic carbons at δ 163.8 (C-1), 105.9 (C-2), 163.1 (C-3), 85.7 (C-4), 161.0 (C-5) and 105.9 (C-6) (Table 1). The ^1H NMR spectrum (Table 1) displayed signals for an aromatic proton at δ 5.93 (1H, *s*, H-4), a hydrogen-bonded phenolic proton at δ 14.04 (1H, *s*, OH-1), two *O*-methyls at δ 3.87 and δ 3.86 (3H each, *s*, CH_3O-3 and CH_3O-5) and an aromatic methyl at δ 1.99 (3H, *s*, CH_3-2).

Comparison of the ^{13}C NMR spectral data of **1** with those of the phloroglucinol, baeckeol (**6**) (Dastlik et al., 1989) revealed their structural resemblance. The only difference was the presence of a 3-methylbutanoyl group at C-6 in **1** instead of an isobutanoyl, as suggested by the carbon resonances at δ 205.8 (C-7), 53.3 (C-8), 25.4 (C-9), 22.8 (C-10) and 22.8 (C-11) in the ^{13}C NMR, DEPT and HMQC spectra (Chan et al., 1989; Lee et al., 2003).

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Table 1
^1H and ^{13}C NMR spectral data for pallidusol (**1**), dehydropallidusol (**2**)[a] and baeckeol (**6**)[b]

Position	(**1**)		(**2**)		(**6**)
	^1H	^{13}C	^1H	^{13}C	^{13}C
1	–	163.8 (*s*)	–	163.9 (*s*)	164.0
2	–	105.9 (*s*)	–	105.9 (*s*)	104.9
3	–	163.1 (*s*)	–	163.0 (*s*)	163.1
4	5.93 (1H, *s*)	85.7 (*d*)	5.93 (1H, s)	86.1 (*d*)	85.8
5	–	161.0 (*s*)	–	160.6 (*s*)	160.9
6	–	105.9 (*s*)	–	106.7 (*s*)	105.9
7	–	205.8 (*s*)	–	195.4 (*s*)	210.5
8	2.84 (2H, *d*, 6.7)	53.3 (*t*)	6.79 (1H, *s*)	127.1 (*d*)	39.6
9	2.17 (1H, *m*)	25.4 (*d*)	–	151.9 (*s*)	19.3
10	0.94 (3H, *d*, 6.8)	22.8 (*q*)	1.94 (3H, *s*)	27.9 (*q*)	19.3
11	0.94 (3H, *d*, 6.8)	22.8 (*q*)	2.12 (3H, *s*)	21.2(*q*)	–
OH-1	14.04 (1H, *s*)	–	13.96 (1H, *s*)	–	–
Me-2	1.99 (3H, *s*)	7.1 (*q*)	2.00 (3H, *s*)	7.3 (*q*)	7.2
MeO-3	3.87 (3H, *s*)[c]	55.4 (*q*)[c]	3.86 (3H, *s*)[c]	55.7(*q*)[c]	55.4
MeO-5	3.86 (3H, *s*)[c]	55.3 (*q*)[c]	3.85 (3H, *s*)[c]	55.4(*q*)[c]	55.4

[a] The data were obtained in $CDCl_3$ at 500 MHz for ^1H and 125 MHz for ^{13}C; *J* values are given in Hz; chemical shift values presented in ppm.
[b] Data from Dastlik et al. (1989).
[c] The assignments are interchangeable.

The ^1H–^1H COSY spectrum exhibited a spin system for the 3-methylbutanoyl moiety at δ 2.84 (2H, *d*, $J = 6.8$ Hz, H_2-8), 2.17 (1H, *m*, H-9) and 0.94 (6H, *d*, $J = 6.7$ Hz, H_3-10 and H_3-11). In addition, the presence of this alkanoyl group at C-6 was in accordance with the very low field position of OH-1 (δ 14.04) due to carbonyl-related H-bonding. The placement of the aromatic methyl at C-2 was supported by the HMBC connectivities of these methyl protons to C-1 and from C-1 to OH-1. Other significant HMBC correlations were found between the following proton/carbon pairs (H/C): OH-1/C-2, OH-1/C-6, CH_3-2/C-2, CH_3-2/C-3, CH_3O-3/C-3 and H_2-8/C-6. Finally, the structure of **1** was further confirmed by the NOESY correlations of H-4 with the two *O*-methyls (CH_3O-3 and CH_3O-5), H_2-8 with CH_3O-5, and CH_3-2 with CH_3O-3. On the basis of the above spectroscopic data, the structure of **1** is as shown.

Dehydropallidusol (**2**) showed an $[M + Na]^+$ peak at *m/z* 273.1092 in the HR-ESI-MS, corresponding to $CH_{14}H_{18}NaO_4$. The UV and IR spectral features of **2** resembled those of **1**, suggesting a structure for **2** related to a phloroglucinol derivative. The ^1H and ^{13}C NMR, DEPT, HMQC and HMBC spectroscopic data of **2** were also similar to those of **1**, except for the signals for the alkanoyl at C-6 (Table 1). In **2**, H-9 was absent while H-8 appeared as an olefinic proton at δ 6.79 (1H, *s*), and H_3-10 and H_3-11 as two methyl singlets at δ 1.94 (3H, *s*) and 2.12 (3H, *s*). Furthermore, the ^{13}C NMR spectroscopic signals for the methine C-8 and quaternary C-9 of **2** resonated at δ 127.1 and 151.9, respectively. The foregoing data, together with the molecular formula of **2** which was two mass units less than that of **1**, indicated that **2** was an 8,9-dehydro derivative of **1**. As expected, NOESY crosspeaks were observed between H-8 and CH_3O-5, and between CH_3-2 and CH_3O-3.

Pallidol (**3**) has the composition $C_{25}H_{30}O_8$ on the basis of its $[M + Na]^+$ ion at *m/z* 245.0788 ($C_{12}H_{14}NaO_4$) in the HR-ESI-MS. The UV absorptions at 296 and 334 nm and the IR bands at 1639 and 1585 cm^{-1} were typical of a phloroglucinol derivative. The ^1H and ^{13}C NMR spectra (Table 2) disclosed the absence of an *O*-methyl group. In addition, **3** appeared to possess a 2,3-dihydro-*4H*-1-benzopyran-4-one structure, as evidenced by the ^1H NMR signals for methylene protons at δ 2.66 (2H, *s*, H_2-8) and *gem*-dimethyl protons at δ 1.42 (6H, *s*, H_3-10 and H_3-11), and the ^{13}C NMR signals at δ 196.1 (C-7), 47.8 (C-8), 78.8(C-9), 26.7 (C-10 and C-11) (An et al., 2001). The ^1H and ^{13}C NMR spectral data also revealed the presence of an aromatic proton (δ 5.86, 1H, *s*, H-4), a hydrogen-bonded phenolic proton (δ 12.14, 1H, *s*, OH-1) and an aromatic methyl (δ_H 2.01, 3H, *s* δ_C 6.6; CH_3-2). The downfield shift of OH-1 indicated that the ketone functionality was *peri* to OH-1, and therefore the dihydropyranone ring should be fused to the aromatic ring at C-5 and C-6. This was confirmed by the HMBC connectivities from H_2-8 to C-6 and from C-6 to OH-1. The aromatic methyl functionality was situated at C-2, as illustrated by the $^3J_{CH}$ coupling of these protons with C-1 and the $^2J_{CH}$ coupling of C-1 with OH-1 observed in the HMBC spectrum. Other important CH long-range correlations were observed from C-10/C-11 to H_2-8, C-9 to H_2-8, and C-2 to H-4.

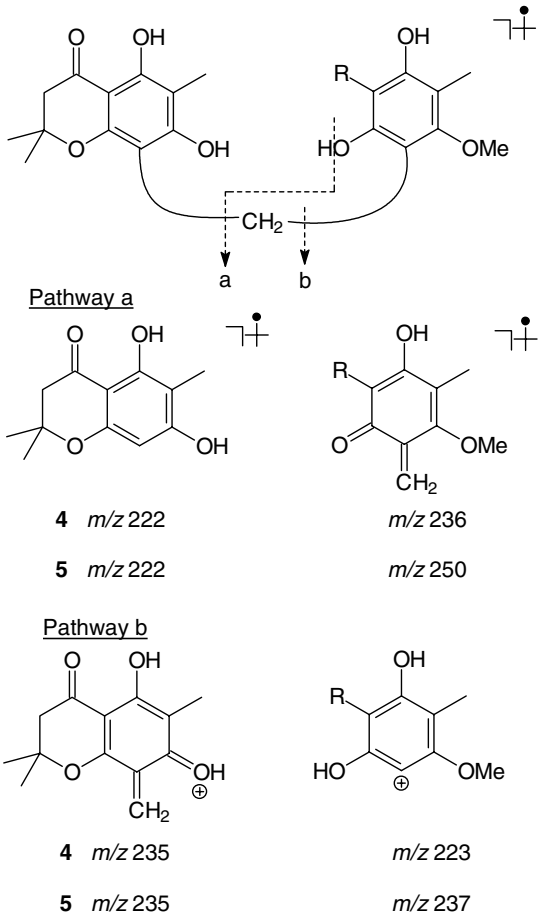
Compound **4** showed an $[M + Na]^+$ ion at *m/z* 481.1873 ($C_{25}H_{30}NaO_8$) in the HR-ESI-MS, suggesting the molecular formula $C_{25}H_{30}O_8$. The IR spectrum suggested the presence of a hydroxyl (3351 cm^{-1}) and a conjugated carbonyl (1623 cm^{-1}) group, and the UV

Table 2
^{1}H and ^{13}C NMR spectral data for pallidol (**3**), mallopallidol (**4**) and homomallopallidol (**5**)[a]

Position	(**3**)		(**4**)		(**5**)	
1	–	161.5 (*s*)	–	160.4 (*s*)	–	160.4 (*s*)
2	–	103.1 (*s*)	–	106.3 (*s*)	–	106.3 (*s*)
3	–	162.4 (*s*)	–	162.6 (*s*)	–	162.6 (*s*)
4	5.86 (1H, *s*)	95.0 (*d*)	–	104.2 (*s*)	–	104.2 (*s*)
5	–	159.2 (*s*)	–	153.2 (*s*)	–	153.3 (*s*)
6	–	102.3 (*s*)	–	101.2 (*s*)	–	101.3 (*s*)
7	–	196.1 (*s*)	–	195.1 (*s*)	–	195.1 (*s*)
8	2.66 (2H, *s*)	47.8 (*t*)	2.76 (2H, *s*)	47.7 (*t*)	2.75 (2H, *s*)	47.7 (*t*)
9	–	78.8 (*s*)	–	81.1 (*s*)	–	81.2 (*s*)
10	1.42 (3H, *s*)	26.7 (*q*)	1.59 (3H, *s*)	26.7 (*q*)	1.59 (3H, *s*)	26.6 (*q*)
11	1.42 (3H, *s*)	26.7 (*q*)	1.59 (3H, *s*)	26.7 (*q*)	1.59 (3H, *s*)	26.4 (*q*)
Me-2	2.01 (3H, *s*)	6.6 (*q*)	2.01 (3H, *s*)	7.2 (*q*)	2.01 (3H, *s*)	7.2 (*q*)
OH-1	12.14 (1H, *s*)		12.15 (1H, *s*)		12.15 (1H, *s*)	
OH-3	5.48 (1H, *br s*)		9.25 (1H, *s*)		9.27(1H, *s*)	
Ar–CH_2–*Ar*	–		3.69 (2H, *s*)	17.3 (*t*)	3.69 (2H, *s*)	17.4 (*t*)
1′	–		–	162.8 (*s*)	–	162.8 (*s*)
2′	–		–	110.4 (*s*)	–	110.4 (*s*)
3′	–		–	159.6 (*s*)	–	159.6 (*s*)
4′	–		–	108.4 (*s*)	–	108.4 (*s*)
5′	–		–	155.8 (*s*)	–	155.8 (*s*)
6′	–		–	107.9 (*s*)	–	108.4 (*s*)
7′	–		–	212.0 (*s*)	–	211.9 (*s*)
8′	–		3.90 (1H, *m*)	39.9 (*d*)	3.76 (1H, *m*)	46.7 (*d*)
9′	–		1.16 (1H, *d*, 6.7)	19.2 (*q*)	1.84 (1H, *m*), 1.38 (1H, *m*)	26.9 (*t*)
10′	–		1.16 (1H, *d*, 6.7)	19.2 (*q*)	0.90 (3H, *t*, 7.4)	12.1 (*q*)
11′	–		–	–	1.14 (3H, *d*, 6.7)	16.4 (*q*)
Me-2′	–		2.12 (3H, s)	8.9 (*q*)	2.12 (3H, s)	8.9 (*q*)
MeO-3′	–		3.96 (3H, s)	61.8 (*s*)	3.96 (3H, s)	61.8 (*s*)
OH-1′			13.46 (1H, s)		13.50 (1H, s)	
OH-5′			8.44 (1H, s)		8.42 (1H, s)	

[a] The data were obtained in $CDCl_3$ at 500 MHz for ^{1}H and 125 MHz for ^{13}C; *J* values are given in Hz; chemical shift values presented.

absorptions at 332 and 292 nm were indicative of an aromatic skeleton. The ^{1}H and ^{13}C NMR, DEPT and HMQC data of **4** revealed in the aromatic region the presence of six oxygenated as well as six non-oxygenated carbons, suggesting a dimeric structure consisting of two phloroglucinol-type units. The two monomers should be connected through a methylene bridge, as was evident from the characteristic NMR signals at δ_H 3.69 (2H, *s*)/δ_C 17.3 (*t*) (Arisawa et al., 1985). The first monomeric moiety appeared to be derived from **3**, possessing a dihydrobenzopyranone structure since its ^{1}H and ^{13}C NMR resonances were similar to those of **3** except for the absence of H-4. The quaternary C-4 carbon of **4** appeared at a more downfiled position. This implied that C-4 was involved in the inter-phloroglucinol linkage, and in support of this, the C-3 and C-5 resonances of **4** were shifted upfield, as compared with their counterparts in **3**. Further analysis of the remaining ^{13}C NMR signals of **4** revealed that the other phloroglucinol monomer should be an *O*-demethyl analogue of **6**, with its C-4′ connected to the methylene bridge. This was supported by the prominent fragment ions in the EIMS at *m*/*z* 222 and 236 (pathway a) and *m*/*z* 235 and 223 (pathway b) which resulted from the cleavage of the methylene bridge with or without concomitant tranfer of a hydrogen atom to the other ring (Lounasmaa et al., 1975) (Scheme 1). Confirmation of the structure of the first phloroglucinol monomer was achieved by tracing key HMBC connectivities. The hydrogen bonded phenolic proton at δ 12.15 (OH-1) displayed HMBC correlations with the carbons at δ 160.4 (C-1), 106.3 (C-2) and δ 101.2 (C-6). The HMBC connectivities from H_2-8 (δ 2.76, 2H, *s* to C-6, C-9 (δ 81.1), C-10 (δ 26.7) and C-11 (δ 26.7) showed the existence of the *gem* dimethyldihydropyranone ring. A 2-bond coupling observed between C-2 and the methyl protons at δ 2.01 allowed the placement of this aromatic methyl at C-2. The CH_3-2 protons in turn displayed $^3J_{CH}$ coupling with C-1 and an oxygenated carbon at δ 162.6, assignable to C-3. The methylene bridge protons (δ 3.69) showed HMBC crosspeaks with C-3, as well as the carbons at δ 104.2 and 153.5, attributable to C-4 and C-5, respectively. Further analysis of the HMBC correlations of **4** allowed the assignments of all of the substituents in the second monomer. Thus, the OH-1′ proton (δ 13.46) showed HMBC connectivities to the aromatic carbons at δ 162.8, 110.4 and 107.9 which could be assigned to C-1′, C-2′ and C-6′, respectively. The HMBC



Scheme 1. Mass fragmentation of **4** and **5**.

connectivities of the aromatic methyl protons at δ 2.12 to C-1′ and C-2′ confimed the location of this substituent at C-2′. Support for the placement of the *O*-methyl at C-3′ came from the NOESY correlation of CH_3O-3′ with CH_3-2′ and the HMBC connectivities from C-3′ to the CH_3O-3′ and CH_3-2′ protons. Participation of C-4′ in the linkage was demonstrated by its $^2J_{CH}$ coupling with the $ArCH_2Ar$ protons at δ 3.69. Hence, the new phloroglucinol dimer (**4**) has the structure as shown, and was named mallopallidol.

Homomallopallidol (**5**) has the molecular formula $C_{26}H_{32}O_8$, as determined by the $[M + Na]^+$ ion at *m/z* 495.1970 in the HR-ESI-MS. Taking into consideration the molecular weight of **5** being fourteen units higher than that of **4** and the close resemblance of the ^1H and ^{13}C NMR data of the two compounds, **5** should also contain a dimeric structure, being comprised of similar phloroglucinol-type monomers with an additional methylene carbon. Close examination of the NMR data further revealed that the difference was in the side chain at C-6′ which appeared to be 3-methylbutanoyl in **5**, as reflected by the ^{13}C NMR signals for a carbonyl (δ 211.9, C-7′), a methine (δ 46.7, C-8′), a methylene (δ 26.9, C-9′) and two methyls (δ 12.1, C-10′ and δ 16.4, C-11′), and the ^1H NMR resonances of a terminal methyl at δ 0.90 (3H, *t*, $J = 7.4$ Hz, H_3-10′) and an internal methyl at δ 1.14 (3H, *d*, $J = 6.7$ Hz, H_3-11′) (Hu et al., 2000; Lee et al., 2003). Similar to **4**, compound **5** displayed, in the EIMS, the cleavage of the methylene bridge leading to the formation of fragment ions at *m/z* 222 and 250 in pathway a and at *m/z* 235 and 237 in pathway b. The NOESY and HMBC correlations observed for **5** were similar to those of **4**. The configuration at C-8′ was not determined. Thus, the structure of homomallopallidol (**5**) is as shown.

3. Experimental

3.1. General experimental procedures

Melting points were measured on a Fisher–Johns melting point apparatus. Optical rotations were obtained on a Perkin–Elmer Polarimeter 341. IR spectra were recorded as KBr disc on a JASCO FT/IR-300E spectrophotometer, and UV spectra were measured on a Thermospectronic UV-1 spectrophotometer. ^1H (500 MHz) and ^{13}C (125 MHz) NMR spectra in $CDCl_3$ were recorded on a Bruker DPX 500 spectrometer. Mass spectra including EI-MS, ESI-MS and HR-ESI-MS were taken on a JEOL IMS-AX505W mass spectrometer.

3.2. Plant material

The leaves of *M. pallidus* were collected from Prachuap Khiri Khan province, Thailand, in August 2001. The plant was identified by comparison with herbarium specimens (BKF 110693) at the Royal Forest Department, Ministry of Agriculture and Cooperatives, Bangkok, Thailand. A voucher specimen has been kept at the Department of Pharmacognosy, Faculty of Pharmaceutical Sciences, Chulalongkorn University, Bangkok, Thailand.

3.3. Extraction and isolation

The dried leaves of *M. pallidus* (1.2 kg) were extracted with hexane (3×6 l) at room temperature. Removal of the solvent under reduced pressure left an oily extract (40 g). The extract (40 g) was then subjected to vacuum liquid column chromatography over silica gel eluted with *n*-hexane containing increasing amounts of EtOAc to yield fractions I–VI. Fraction II (16.0 g) was further separated on silica gel by silica gel flash column chromatography using *n*-hexane–EtOAc step gradient to give fractions IIa–IIc. Separation of fraction IIb (92 mg) on a siliga gel column using mixtures of *n*-hexane and EtOAc of increasing polarity as eluant afforded **2** (26 mg). Fraction III (2.4 g) was chromatographed on silica gel by stepwise elution with *n*-hexane–EtOAc to yield

fractions IIIa–IIId. Fraction IIIb (707 mg) was subsequently refractionated by silica gel flash CC, eluted with a *n*-hexane–EtOAc step gradient to give 2 fractions. Fraction IIIb1 (385 mg) was further purified on a Sephadex LH-20 column (40 × 3.8 cm) eluted with CHCl3:MeOH (1:1) to furnish **1** (5 mg). Fraction IIId (291 mg) was passed through a column of Sephadex LH-20 (40 × 3.8 cm), eluted with $CHCl_3$:MeOH (1:1) to give three fractions, IIId1–3. A final purification step of **4** and **5** was carried out by preparative TLC of fraction IIId2 (63 mg) on silica gel plates of 1-mm thickness. Double development with *n*-hexane–$CHCl_3$ (16:4) furnished **4** (5 mg) and **5** (10 mg). Fraction V (5 g) was further subjected to silica gel CC (*n*-hexane–EtOAc step gradient) to give three fractions Va–Vc. Fraction Vb (1 g) was separated on a Sephadex LH-20 column (40 × 3.8 cm) with $CHCl_3$–MeOH (1:1) as eluant to give three fractions, Vb1–Vb3. Fraction Vb2 (34 mg) was reapplied on a Sephadex LH-20 column (40 × 3.8 cm) and eluted with a similar solvent system to afford **3** (4 mg).

*3.3.1. 1-(2-Hydroxy-4,6-dimethoxy-3-methyl-phenyl)-3-methyl-butan-1-one (pallidusol) (**1**)*

Mp 101–102 °C; UV (EtOH) λ_{max} (log ε): 339 (3.51), 293 (4.33), 235 (4.05), 214 (4.35) nm; IR (KBr) ν_{max} 3435, 2953, 1627, 1593, 1467, 1411, 1233, 1139 cm^{-1}; EI-MS *m/z* 252 (M^+, 20), 237 (9), 196 (12), 195 (100), 180 (8), 167 (7); HR-ESI-MS $[M + Na]^+$ *m/z* 275.1248 ($CH_{14}H_{20}NaO_4$, calcd 275.1254); for ^1H and ^{13}C NMR spectral data, see Table 1.

*3.3.2. 1-(2-Hydroxy-4,6-dimethoxy-3-methyl-phenyl)-3-methyl-but-2-en-1-one (dehydropallidusol) (**2**)*

Mp 75–75 °C; UV (EtOH) λ_{max} (log ε): 312 (3.77), 272 (3.42) nm; IR (KBr) ν_{max} 3433, 2928, 1627, 1593, 1430, 1351, 1284, 1145, 1129, 1054 cm^{-1}; EI-MS *m/z* 250 (M^+, 15), 235 (100), 220 (19), 195 (21), 180 (12), 155 (10); HR-ESI-MS $[M + Na]^+$ *m/z* 273.1092 ($CH_{14}H_{18}NaO_4$, calcd 273.1097); for ^1H and ^{13}C NMR spectral data, see Table 1.

*3.3.3. 5,7-Dihydroxy-2,2,6-trimethyl-chroman-4-one (pallidol) (**3**)*

Mp 199–200 °C; UV (EtOH) λ_{max} (log ε): 334 (3.48), 296 (4.06), 211 (4.19) nm; IR (KBr) ν_{max} 3433, 2926, 1639, 1585, 1462, 1328, 1168, 1110, 1080 cm^{-1}; EI-MS *m/z* 222 (M^+, 45), 208 (13), 207 (100), 167 (46), 166 (18), 138 (17), 110 (6), 69 (7); HR-ESI-MS: $[M + Na]^+$ *m/z* 245.0788 ($CH_{12}H_{14}NaO_4$, calcd 245.0784); for ^1H and ^{13}C NMR spectral data, see Table 2.

*3.3.4. 8-(2-4-Dihydroxy-3-isobutyryl-6-methoxy-5-methyl-benzyl)-5,7-dihydroxy-2,2,6-trimethyl-chroman-4-one (mallopallidol) (**4**)*

Mp 185–186 °C; UV (EtOH) λ_{max} (log ε): 332 (4.23), 292 (4.10) nm; IR (KBr) ν_{max} 3351, 2972, 2929, 1623, 1460, 1412, 1358, 1327, 1283, 1195, 1130, 1099 cm^{-1}; EI-MS *m/z* 458 (M^+, 13), 457 (33), 256 (8), 236 (18), 235 (59), 223 (29), 222 (100), 207 (42), 179 (14), 43 (7); HRESI- MS: $[M + Na]^+$ *m/z* 481.1873 ($C_{25}H_{30}NaO_8$, calcd 481.1833); for ^1H and ^{13}C NMR spectral data, Table 2.

*3.3.5. 8-[2-4-Dihydroxy-6-methoxy-5-methyl-3-(2-methyl-butyryl)-benzyl]-5,7-dihydroxy-2,2,6-trimethyl-chroman-4-one (homomallopallidol) (**5**)*

Mp 178–179 °C; $[\alpha]_D^{20} + 2.83$ (*c* 0.1, MeOH); UV (EtOH) λ_{max} (log ε): 332 (4.31), 293 (4.17); IR (KBr) ν_{max} 3354, 2962, 2931, 1639, 1617, 1450, 1420, 1368, 1324, 1286, 1195, 1130, 1103 cm^{-1}; EI-MS *m/z* 472 (M^+, 12), 471 (33), 439 (4), 256 (9), 250 (9), 237 (6), 235 (64), 223 (27), 222 (100), 219 (10), 207 (39), 179 (14), 57 (24); HR-ESI-MS: $[M + Na]^+$ *m/z* 495.1971 ($CH_{26}H_{32}NaO_8$, calcd 495.1989); for ^1H and ^{13}C NMR, spectral data Table 2.

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