New Synthetic Routes to Biologically Interesting Geranylated Flavanones and Geranylated Chalcones: First Total Synthesis of (±)-Prostratol F, Xanthoangelol, and (±)-Lespeol

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A new and efficient synthetic approach to biologically interesting geranylated flavanones and geranylated chalcones is described. Thus, the first total syntheses of the geranylated flavanones (±)-prostratol F (**1**), (±)-8-geranyl-3′,4′,7-trihydroxyflavanone (**2**), and (±)-6-geranyl-5,7-dihydroxy-3′,4′-dimethoxyflavanone (**3**) were carried out starting from 2,4-dihydroxyacetophenone (**10**) and 2,4,6-trihydroxyacethophenone (**17**) in five to six steps (*Schemes 2* and *3*). The geranylated chalcones xanthoangelol (**4**), 3-geranyl-2,3′,4,4′-tetrahydroxychalcone (**5**), (±)-lespeol (**6**), and lespeol derivatives (±)-**7**–**9** were synthesized starting from 2,4-dihydroxyacetophenone (**10**) in three to four steps (*Schemes 2* and *6*).

Introduction. – Geranylated flavanones and chalcones are an abundant subclass of flavonoids distributed widely in nature (*Fig.*) (flavanone = 2,3-dihydro-2-phenyl-4*H*-1-benzopyran-4-one; chalcone = (2*E*)-1,3-diphenylprop-2-en-1-one [1]. Interestingly, it was reported that the presence of the geranyl group leads to a remarkable increase in corresponding bioactivities [2], including antibacterial [3], antifungal [4], antitumor [5], antimetastatic [6], cancer chemopreventive [7], anti-HIV [8], and antidiabetic activities [9]. The plants containing these compounds have been used in traditional medicines [10]. This wide range of biological properties has stimulated interest in the synthesis of naturally occurring geranylated flavanones and chalcones. Among these, prostratol F (**1**), xanthoangelol (**4**), 3-geranyl-2,3′,4,4′-tetrahydroxychalcone (**5**), and lespeol (**6**) were isolated from the fruits of *Artocarpus nobilis*, which was distributed in Sri Lanka [11]. The 6-geranyl-5,7-dihydroxy-3′,4′-dimethoxyflavanone (**3**) has been isolated from *Paulownia tomentosa*, an ornamental tree widely distributed throughout China, Korea, and Japan [12]. In China, its stem bark has been used in herbal medicine as a component of remedies for infectious diseases such as gonorrhea and erysipelas [13]. Xanthoangelol (**4**) was isolated from *Angelica keiskei* KOIDZUMI (Japanese name 'Ashitaba'), a hardy perennial herb that grows mainly along the Pacific coast of Japan [14]. The roots of this plant have been used traditionally in Japan as a health food with diuretic, laxative, analeptic, and galactagogic effects [15]. Recent studies have shown that xanthoangelol (**4**) possesses various biological activities including antibacterial [3], antitumor [5], antimetastatic [6], antidiabetic [9], and antivasoconstriction activity [16], preventive effects upon hypertension [17], and gastric H^+,K^+-ATPase inhibition activity [18]. Importantly, **4** also shows antitumor-promoting activity in mouse-skin carcinogenesis induced by DMBA [19] and inhibits tumor growth and metastasis in

tumor-bearing mice without causing body-weight loss [5]. Compound **4** has also shown potent inhibitory effects upon induction *Epstein–Barr* virus early antigen (EBV-EA) by 12-*O*-tetradecanoylphorbol 1,3-acetate (TPA) [7] and on NF-κB activation [20]. The 3-geranyl-2,3′,4,4′-tetrahydroxychalcone (**5**) was isolated from *Artocarpus incisus* and shows interesting biological activities such as cytotoxicity against cancer cells, potent 5α-reductase inhibitory activity, and antibacterial and antiplatelet aggregation activities [21]. Lespeol (**6**) was separately isolated from *Lespedeza cyrtobotrya* [22] and *Artocarpus communis* [23] and has shown potent inhibition of melanin synthesis in normal human-epidermal melanocytes [22] and strong antioxidant activity against DPPH radicals [11].

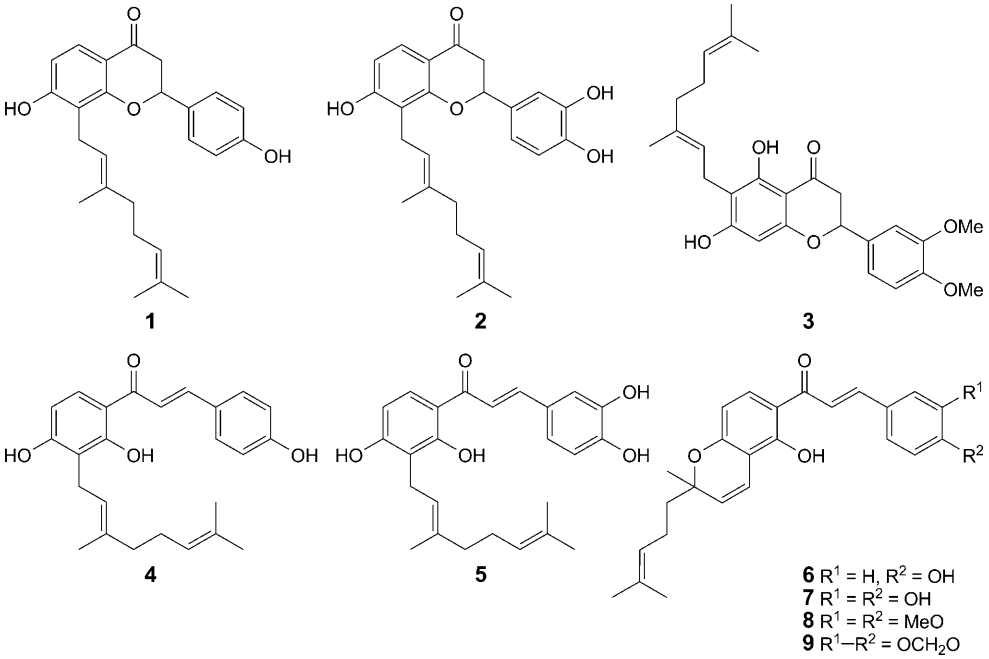


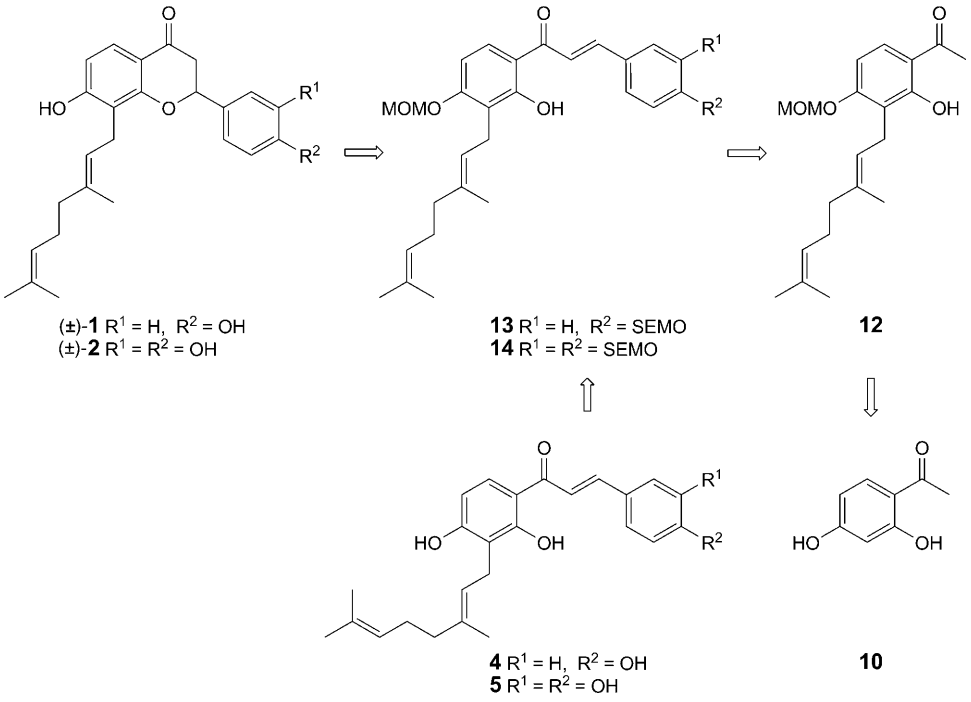
Figure. *Selected natural* (see **1** and **3**–**6**) *and unnatural* (see **2** and **7**–**9**) *geranylated flavanones and chalcones*

Recently, we reported on the synthesis of biologically interesting pyranochalcones [24] and pyranoflavones [25]. In our continuous efforts to synthesize biologically active molecules, we investigated a new and facile route for the synthesis of biologically interesting geranylated flavanones and geranylated chalcones. We report herein the first total synthesis of (±)-prostratol F (**1**), (±)-6-geranyl-5,7-dihydroxy-3′,4′-dimethoxyflavanone (**3**), xanthoangelol (**4**), 3-geranyl-2,3′,4,4′-tetrahydroxychalcone (**5**), and (±)-lespeol (**6**). We also report herein the synthesis of unnatural (±)-8-geranyl-3′,4′,7-trihydroxyflavanone (**2**) and lespeol derivatives (±)-**7**–**9**.

Results and Discussion. – The retrosynthetic strategy for geranylated flavanones **1** and **2** and geranylated chalcones **4** and **5** is shown in *Scheme 1*. The flavanones (±)-

prostratol F (**1**) and (±)-8-geranyl-3′,4′,7-trihydroxyflavanone (**2**) were prepared from chalcones **13** and **14** by cyclization and a deprotection reaction. The geranylated chalcones xanthoangelol (**4**) and 3-geranyl-2,3′,4,4′-tetrahydroxychalcone (**5**) were also generated from chalcones **13** and **14** by a deprotection reaction. Geranylated chalcones **13** and **14** could be prepared by base-catalyzed aldol reactions from compound **12** and corresponding benzaldehydes, and **12** was accessible from 2,4-dihydroxyacetophenone (**10**) by geranylation and MOM (methoxymethyl) ether protection.

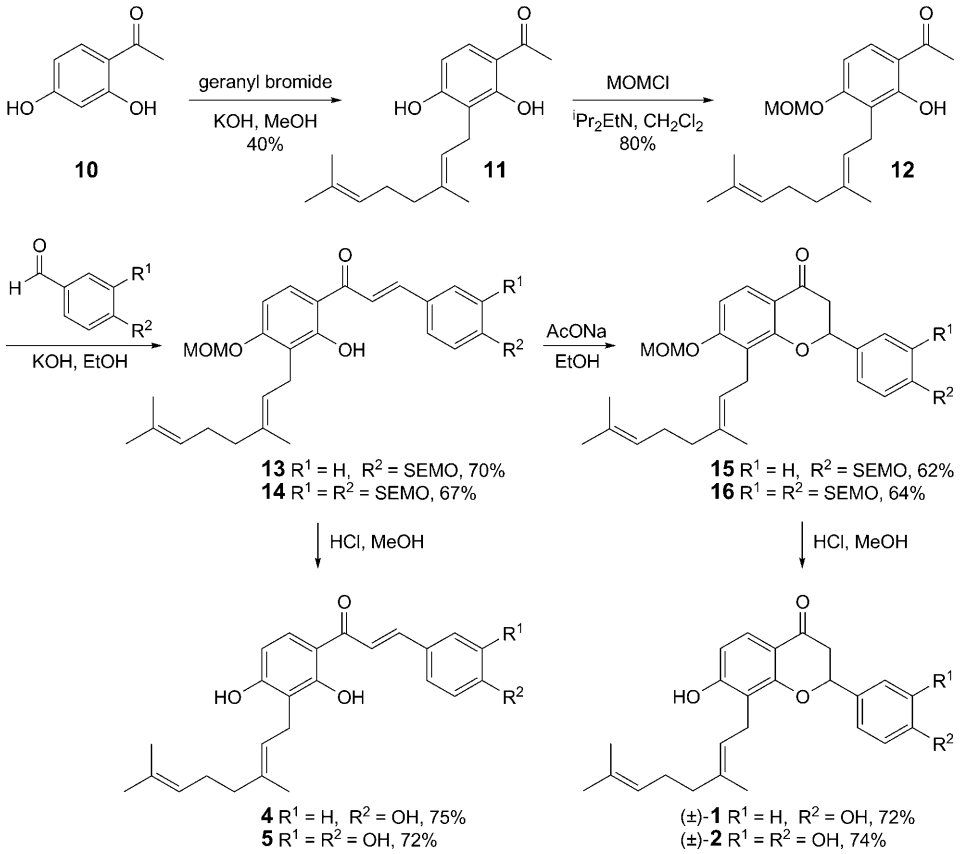
Scheme 1. *Retrosynthetic Analysis for the Synthesis of Geranylated Flavanones (±)-***1** *and (±)-***2** *and Geranylated Chalcones* **4** *and* **5**. MOMO = $MeOCH_2O$, SEMO = $Me_3SiCH_2CH_2OCH_2O$.



The total synthesis of geranylated flavanones (±)-**1** and (±)-**2** and geranylated chalcones **4** and **5** was carried out starting from 2,4-dihydroxyacetophenone (**10**) as shown in *Scheme 2*. Treatment of **10** and geranyl bromide with KOH in MeOH at room temperature for 24 h afforded the geranylated product **11** in 40% yield [26]. Then, **11** was protected by treatment with 1.0 equiv. of methoxymethyl chloride (MOMCl) to give **12** in 80% yield. Selective methoxymethylation was confirmed by ^{1}H-NMR analysis. The signal for the OH group at the benzene ring of **12** was observed as a *s* associated with a H-bond to the C=O group at δ 12.75. Furthermore, a MeO group of the MOM ether was observed as a *s* at δ 3.45. Condensation of **12** with the two corresponding benzaldehydes having [2-(trimethylsilyl)ethoxy]methyl(SEM)-protected OH groups was accomplished in KOH/EtOH at room temperature for 48 h to afford geranylated chalcones **13** and **14** in 70 and 67% yield, respectively. Treatment of **13** and **14** with AcONa in refluxing EtOH afforded cyclized products **15** and **16** in 62 and 64%

yield, respectively. Deprotection of the MOM and SEM ether groups of **15** and **16** with concentrated HCl solution in MeOH at room temperature for 10 h gave the expected products (±)-prostratol F (**1**) and unnatural (±)-8-geranyl-3′,4′,7-trihydroxyflavanone (**2**), in 72 and 74% yield, respectively. The spectroscopic data of the synthetic material **1** were in agreement with those reported for the natural product [27]. The removal of the protecting groups from **13** and **14** with concentrated HCl solution in MeOH afforded the natural geranylated chalcones **4** and **5** in 75 and 72% yield, respectively. The spectroscopic data of synthetic **4** and **5** were in agreement with those of the natural products [4][21].

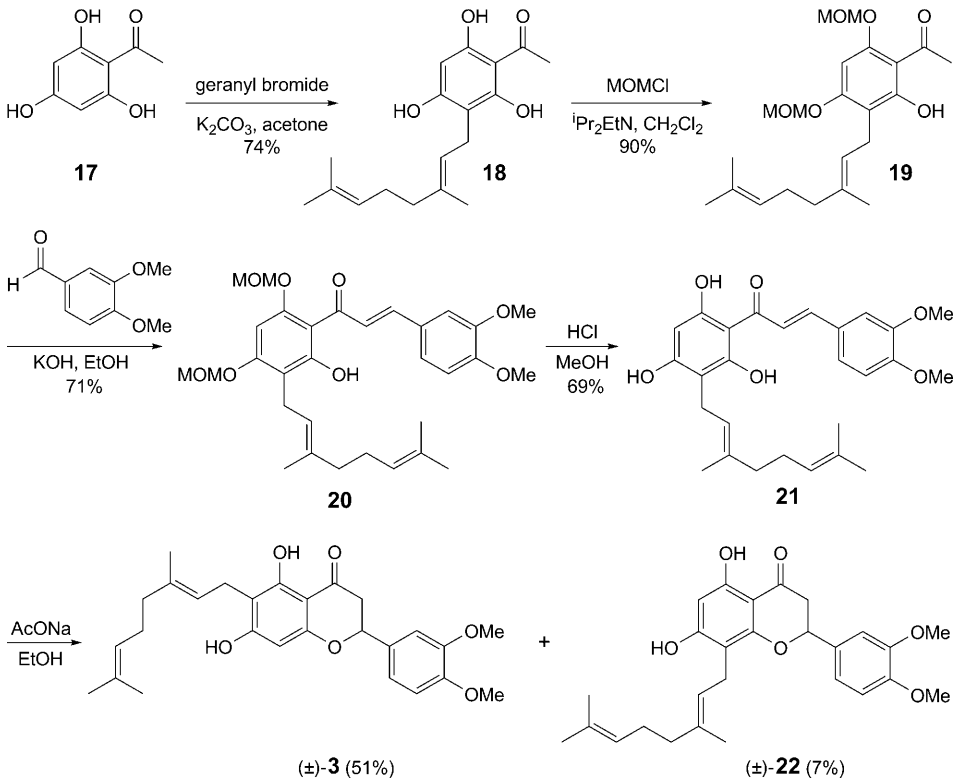
Scheme 2



As another application of this synthetic approach, the first total synthesis of the geranylated flavanone **3** was attempted. The synthesis was carried out as shown in *Scheme 3*. According to a previously described method, treatment of 2,4,6-trihydroxyacetophenone (**17**) and geranyl bromide with anhydrous K_2CO_3 in dry acetone under reflux for 24 h afforded **18** in 74% yield [24b]. Then, **18** was protected with 2.2 equiv. of methoxymethyl chloride (MOMCl) to give **19** in 90% yield. The selective bis-methoxymethylation was confirmed again by ^{1}H-NMR analysis. The signal for the less

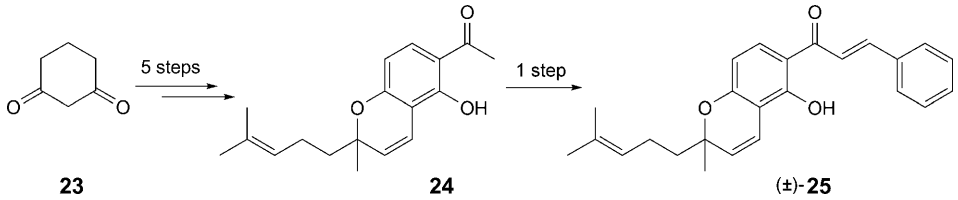
reactive OH group, due to steric hindrance in the benzene ring, was observed as a *s* at δ 13.79 indicating a H-bond to the C=O group. Two MeO signals of the MOM ethers were observed as two *s* at δ 3.49 and 3.45. Condensation of **19** with 3,4-dimethoxybenzaldehyde was next accomplished in KOH/EtOH at room temperature for 48 h to afford chalcone **20** in 71% yield. Deprotection of compound **20** by treatment with conc. HCl in MeOH at room temperature for 10 h gave the expected deprotected product **21** in 69% yield, and treatment of **21** with AcONa in refluxing EtOH afforded the expected product (±)-**3** (51%) and its regioisomer (±)-**22** (7%). These two compounds were readily separated by column chromatography, and their structures were assigned by comparison with spectroscopic data of the known natural product [12].

Scheme 3



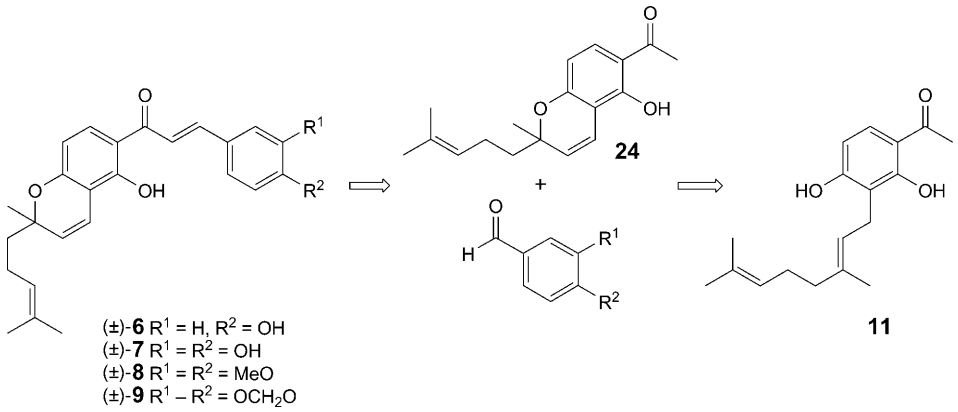
Recently, we reported on the synthesis of the biologically interesting (±)-spinochalcone B (**25**), starting from cyclohexane-1,3-dione (**23**), in six steps (overall yield, 14%) *via* a key intermediate **24** (*Scheme 4*) [28]. This synthetic approach to natural chalcones suffered somewhat from a low overall yield due to numerous reaction steps. The necessity for overcoming these problems has promoted research for the development of a concise and efficient synthetic route to (±)-lespeol (**6**) and its unnatural chalcones (±)-**7**–**9**.

Scheme 4



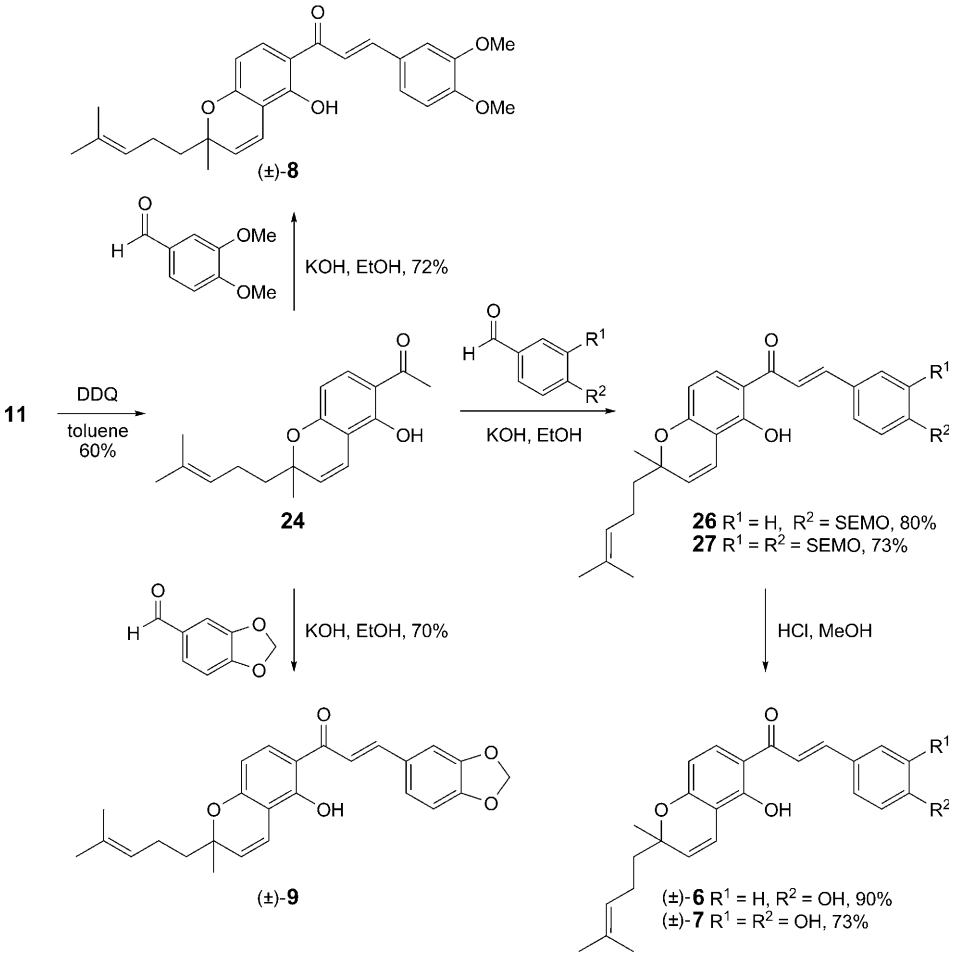
The retrosynthetic strategy for the preparation of (±)-lespeol (**6**) and its unnatural derivatives (±)-**7**–**9** through the key intermediate **24** is depicted in *Scheme 5 via* base-catalyzed aldol condensation of **24** with a corresponding arenecarboxaldehydes. Compound **24** could be generated from 3-geranyl-2,4-dihydroxyacetophenone (**11**) in a benzopyran-formation reaction.

Scheme 5. *Retrosynthetic Analysis for the Synthesis of (±)-Lespeol* (**6**) *and Its Unnatural Derivatives (±)-***7**–**9**



The first total synthesis of (±)-lespeol (**6**) and derivatives (±)-**7**–**9** was achieved from **11** as shown in *Scheme 6*. Treatment of **11** with 4,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile (DDQ) in refluxing toluene for 4 h gave the cyclized product **24** in 60% yield. The structure of **24** was identified by the observation of the expected chemical shifts of two olefinic H-atoms at δ 6.73 ($J = 9.9$ Hz) and 5.50 ($J = 9.9$ Hz), associated with the benzopyran ring. Condensation of **24** with the corresponding benzaldehydes in KOH/EtOH at room temperature for 48 h afforded products **26** and **27** in 80 and 73% yield, respectively. Treatment of **26** and **27** with conc. HCl solution in MeOH at room temperature for 10 h afforded (±)-lespeol (**6**) and its unnatural derivative (±)-**7** in 90 and 73% yield, respectively. The spectroscopic data of synthetic **6** were in agreement with those reported in the literature [23][29]. Similarly, reactions of **24** with 3,4-dimethoxybenzaldehyde and piperonal (=1,3-benzodioxole-5-carboxaldehyde) afforded the desired products **8** and **9** in 72 and 70% yield, respectively.

Scheme 6



In conclusion, a concise and efficient synthetic route for biologically interesting geranylated flavanones and geranylated chalcones is described. The total synthesis of the geranylated flavanones prostratol F (**1**), 8-geranyl-3′,4′,7-trihydroxyflavanone (**2**), and 6-geranyl-5,7-dihydroxy-3′,4′-dimethoxyflavanone (**3**) were accomplished starting from commercially available 2,4-dihydroxyacetophenone (**10**) and 2,4,6-trihydroxyacetophenone (**17**), respectively, *via* geranylation, aldol condensation, and cyclization reactions. The geranylated chalcones xanthoangelol (**4**), 3-geranyl-2,3′,4,4′-tetrahydroxychalcone (**5**), lespeol (**6**), and lespeol derivatives **7**–**9** were also synthesized from 2,4-dihydroxyacetophenone (**10**) *via* geranylation, pyranylation, and aldol condensation.

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Experimental Part

General. All experiments were carried out under N_2. Anal. TLC: precoated silica gel plates (Art. *5554*, *Merck*) with a fluorescent indicator. Flash column chromatography (FC): silica gel *9385* (*Merck*). IR Spectra: *Jasco-FTIR-5300* spectrophotometer; $\tilde{\nu}$ in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker-ARX* spectrometer; at 300 and 75 MHz, resp., in $CDCl_3$ and (D_6)acetone; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. HR-EI- and HR-FAB-MS: *Jeol-JMS-700* spectrometer; performed at the Korea Basic Science Institute; in *m*/*z* (rel. %).

3-Geranyl-2,4-dihydroxyacetophenone (=*1-{3-[(2*E*)-3,7-Dimethylocta-2,6-dien-1-yl]-2,4-dihydroxyphenyl}ethanone*; **11**). To a soln. of 2,4-dihydroxyacetophenone (**10**; 2.450 g, 16.1 mmol) in MeOH (50 ml) was added geranyl bromide (3.846 g, 17.7 mmol) and anh. KOH (9.034 g, 161.0 mmol). The mixture was stirred at r.t. for 24 h. Evaporation of MeOH, addition of 2N HCl (50 ml), and extraction with AcOEt (3 × 100 ml), washing with brine (100 ml), drying ($MgSO_4$), and removal of the solvent followed by FC (hexane/AcOEt 7:1) gave **11** (1.875 g, 40%). Solid. M.p. 101–102°. IR (KBr): 3167, 2969, 1624, 1449, 1374, 1274, 1163, 1055, 915, 792, 712, 609. ^1H-NMR ($CDCl_3$, 300 MHz): 13.09 (*s*, 1 H); 7.52 (*d*, *J* = 9.0, 1 H); 6.36 (*d*, *J* = 9.0, 1 H); 5.25 (*t*, *J* = 6.6, 1 H); 5.03 (*t*, *J* = 6.3, 1 H); 3.43 (*d*, *J* = 6.3, 2 H); 2.54 (*s*, 3 H); 2.15–2.01 (*m*, 4 H); 1.80 (*s*, 3 H); 1.65 (*s*, 3 H); 1.57 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 202.8; 162.7; 161.8; 137.3; 131.4; 130.0; 124.0; 121.3; 114.7; 113.4; 107.6; 39.6; 26.4; 25.9; 25.5; 21.4; 17.5; 16.0. HR-EI-MS: 288.1722 (M^+, $C_{18}H_{24}O_3^+$; calc. 288.1725).

1-[3-Geranyl-2-hydroxy-4-(methoxymethoxy)phenyl]ethanone (=*1-{3-[(2*E*)-3,7-Dimethylocta-2,6-dien-1-yl]-2-hydroxy-4-(methoxymethoxy)phenyl}ethanone*; **12**). MOMCl (0.335 g, 4.2 mmol) was added to a soln. of **11** (1.20 g, 4.2 mmol) and $^iPr_2EtN$ (3.361 g, 26.0 mmol) in dry CH_2Cl_2 (20 ml). The mixture was stirred at r.t. for 4 h, and then H_2O (30 ml) was added. The mixture was extracted with CH_2Cl_2 (3 × 30 ml), the combined org. extract washed with sat. NH_4Cl soln. (30 ml) and concentrated, and the residue subjected to FC (hexane/AcOEt 6:1): **12** (1.106 g, 80%). Oil. IR (neat): 2919, 1629, 1496, 1419, 1370, 1260, 1157, 1054, 988, 797, 688. ^1H-NMR ($CDCl_3$, 300 MHz): 12.75 (*s*, 1 H); 7.55 (*d*, *J* = 9.0, 1 H); 6.62 (*d*, *J* = 9.0, 1 H); 5.24 (*s*, 2 H); 5.20 (*t*, *J* = 6.3, 1 H); 5.04 (*t*, *J* = 6.3, 1 H); 3.45 (*s*, 3 H); 3.37 (*d*, *J* = 6.3, 2 H); 2.54 (*s*, 3 H); 2.06–1.91 (*m*, 4 H); 1.77 (*s*, 3 H); 1.61 (*s*, 3 H); 1.54 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 202.7; 161.7; 160.5; 134.8; 130.8; 129.6; 124.2; 121.7; 117.9; 114.5; 104.6; 93.5; 55.8; 39.6; 26.5; 25.9; 25.4; 21.5; 17.3; 15.8. HR-EI-MS: 332.1986 (M^+, $C_{20}H_{28}O_4^+$; calc. 332.1988).

*(2*E*)-1-[3-Geranyl-2-hydroxy-4-(methoxymethoxy)phenyl]-3-{4-{[2-(trimethylsilyl)ethoxy]methoxy}-phenyl}prop-2-en-1-one* (=*(2*E*)-1-{3-[(2*E*)-3,7-Dimethylocta-2,6-dien-1-yl]-2-hydroxy-4-(methoxymethoxy)phenyl}-3-{4-{[2-(trimethylsilyl)ethoxy]methoxy}phenyl}prop-2-en-1-one*; **13**). To a soln. of **12** (0.60 g, 1.8 mmol) in EtOH (20 ml) was added KOH (1.014 g, 18.0 mmol) and 4-{[2-(trimethylsilyl)-ethoxy]methoxy}benzaldehyde (0.456 g, 1.8 mmol). The mixture was stirred at r.t. for 48 h. Evaporation of EtOH, addition of NH_4Cl soln. (50 ml), extraction with AcOEt (3 × 50 ml), washing with brine (30 ml), and removal of the solvent followed by FC (hexane/AcOEt 30:1) gave **13** (0.719 g, 70%). Oil. IR (neat): 2918, 1634, 1573, 1509, 1419, 1370, 1309, 1235, 1170, 1088, 991, 853. ^1H-NMR ($CDCl_3$, 300 MHz): 7.84 (*d*, *J* = 15.6, 1 H); 7.74 (*d*, *J* = 9.0, 1 H); 7.58 (*d*, *J* = 8.6, 2 H); 7.46 (*d*, *J* = 15.6, 1 H); 7.06 (*d*, *J* = 8.6, 2 H); 6.66 (*d*, *J* = 9.0, 1 H); 5.26 (*s*, 2 H); 5.25 (*s*, 2 H); 5.21 (*t*, *J* = 6.9, 1 H); 5.05 (*t*, *J* = 6.6, 1 H); 3.75 (*t*, *J* = 8.4, 2 H); 3.45 (*s*, 3 H); 3.41 (*d*, *J* = 6.9, 2 H); 2.02–1.94 (*m*, 4 H); 1.79 (*s*, 3 H); 1.62 (*s*, 3 H); 1.54 (*s*, 3 H); 0.94 (*t*, *J* = 8.4, 2 H); −0.01 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 192.3; 163.2; 160.6; 159.5; 144.0; 135.2; 131.1; 130.2; 128.6; 128.3; 124.3; 121.8; 118.4; 118.3; 116.4; 115.0; 104.7; 93.7; 92.6; 66.4; 56.1; 39.7; 26.6; 25.6; 21.8; 18.0; 17.5; 16.1; −1.4. HR-FAB-MS: 567.3140 ($[M+H]^+$, $C_{33}H_{47}O_6Si^+$; calc. 567.3142).

*(2*E*)-3-{3,4-Bis{[2-(trimethylsilyl)ethoxy]methoxy}phenyl}-1-[3-geranyl-2-hydroxy-4-(methoxymethoxy)phenyl]prop-2-en-1-one* (=*(2*E*)-3-{3,4-Bis{[2-(trimethylsilyl)ethoxy]methoxy}phenyl-1-{3-[(2*E*)-3,7-dimethylocta-2,6-dien-1-yl]-2-hydroxy-4-(methoxymethoxy)phenyl}prop-2-en-1-one*; **14**). As described for **13**, with **12** (0.40 g, 1.2 mmol), EtOH (20 ml), KOH (0.676 g, 12.0 mmol), and 3,4-bis{[2-(trimethylsilyl)ethoxy]methoxy}benzaldehyde (0.480 g, 1.2 mmol): **14** (0.575 g, 67%). Oil. IR (neat): 2955, 1635, 1574, 1509, 1417, 1372, 1309, 1253, 1153, 1086, 990, 856, 684. ^1H-NMR ($CDCl_3$, 300 MHz): 7.83 (*d*, *J* = 15.3, 1 H); 7.77 (*d*, *J* = 9.0, 1 H); 7.51 (*s*, 1 H); 7.47 (*d*, *J* = 15.3, 1 H); 7.30–7.21 (*m*, 2 H); 6.69 (*d*, *J* = 9.0, 1 H); 5.34 (*s*, 4 H); 5.29 (*s*, 2 H); 5.26 (*t*, *J* = 6.9, 1 H); 5.05 (*t*, *J* = 6.6, 1 H); 3.88–3.79 (*m*, 4 H);

3.49 (*s*, 3 H); 3.44 (*d*, *J* = 6.9, 2 H) 2.10–1.96 (*m*, 4 H); 1.82 (*s*, 3 H); 1.64 (*s*, 3 H); 1.57 (*s*, 3 H); 1.02–0.95 (*m*, 4 H); 0.02 (*s*, 9 H); 0.01 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 192.1; 163.1; 160.6; 149.6; 147.4; 144.0; 134.9; 130.9; 128.8; 128.6; 124.2; 123.8; 121.8; 118.7; 118.3; 115.9; 115.7; 114.9; 104.6; 93.8; 93.7; 93.4; 66.4; 56.0; 39.6; 26.5; 25.4; 21.7; 17.9; 17.4; 16.0; −1.5. HR-FAB-MS: 713.3903 ($[M+H]^+$, $C_{39}H_{61}O_8Si_2^+$; calc. 713.3905).

8-Geranyl-7-(methoxymethoxy)-2-{4-{[2-(trimethylsilyl)ethoxy]methoxy}phenyl}chroman-4-one (= *8-[(2*E*)-3,7-Dimethylocta-2,6-dien-1-yl]-2,3-dihydro-7-(methoxymethoxy)-2-{4-{[2-(trimethylsilyl)-ethoxy]methoxy}phenyl}-4*H*-1-benzopyran-4-one*; **15**). To a soln. of AcONa (0.578 g, 7.1 mmol) in EtOH (30 ml) was added **13** (0.4 g, 0.7 mmol). The mixture was refluxed for 48 h. The solvent was distilled off and the residue dissolved in H_2O (30 ml). After acidification with 2N HCl (30 ml), the mixture was extracted with AcOEt (3 × 30 ml), the extract washed with H_2O, dried (anh. Na_2SO_4), and concentrated, and the oily residue purified by FC: **15** (0.248 g, 62%). Oil. IR (neat): 2955, 1687, 1599, 1513, 1436, 1256, 1155, 1086, 998, 857, 762, 691. ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.78 (*d*, *J* = 9.3, 1 H); 7.37 (*d*, *J* = 8.7, 2 H); 7.06 (*d*, *J* = 8.7, 2 H); 6.79 (*d*, *J* = 9.0, 1 H); 5.39 (*dd*, *J* = 13.0, 3.3, 1 H); 5.24 (*s*, 2 H); 5.23 (*s*, 2 H); 5.18 (*t*, *J* = 6.9, 1 H); 5.04 (*t*, *J* = 6.6, 1 H); 3.75 (*t*, *J* = 8.4, 2 H); 3.46 (*s*, 3 H); 3.36 (*d*, *J* = 6.9, 2 H); 2.99 (*dd*, *J* = 17.1, 13.0, 1 H); 2.81 (*dd*, *J* = 17.1, 3.3, 1 H); 2.01–1.92 (*m*, 4 H); 1.64 (*s*, 3 H); 1.61 (*s*, 3 H); 1.54 (*s*, 3 H); 0.95 (*t*, *J* = 8.4, 2 H); −0.01 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 191.2; 160.6; 160.2; 157.4; 135.0; 132.1; 130.9; 127.2; 125.8; 124.1; 121.6; 118.5; 116.1; 115.7; 107.5; 93.8; 92.6; 79.0; 66.0; 56.0; 44.1; 39.6; 26.4; 25.5; 22.1; 17.8; 17.4; 15.9; −1.5. HR-FAB-MS: 567.3146 ($[M+H]^+$, $C_{33}H_{47}O_6Si^+$; calc. 567.3142).

2-{3,4-Bis{[2-(trimethylsilyl)ethoxy]methoxy}phenyl}-8-geranyl-7-(methoxymethoxy)chroman-4-one (= *2-{3,4-Bis{[2-(trimethylsilyl)ethoxy]methoxy}phenyl-8-[(2*E*)-3,7-dimethylocta-2,6-dien-1-yl]-2,3-dihydro-7-(methoxymethoxy)-4*H*-1-benzopyran-4-one*; **16**). As described for **15**, with AcONa (0.341 g, 4.2 mmol), EtOH (30 ml), and **14** (0.30 g, 0.4 mmol): **16** (0.192 g, 64%). Oil. IR (neat): 2955, 1687, 1599, 1513, 1436, 1256, 1155, 1086, 998, 857, 762, 691. ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.77 (*d*, *J* = 9.0, 1 H); 7.29 (*s*, 1 H); 7.20 (*d*, *J* = 8.7, 1 H); 7.04 (*d*, *J* = 8.7, 1 H); 6.79 (*d*, *J* = 9.0, 1 H); 5.36 (*dd*, *J* = 13.5, 3.0, 1 H); 5.28 (*s*, 4 H); 5.24 (*s*, 2 H); 5.20 (*t*, *J* = 6.9, 1 H); 5.02 (*t*, *J* = 6.3, 1 H); 3.81–3.76 (*m*, 4 H); 3.46 (*s*, 3 H); 3.32 (*d*, *J* = 6.9, 2 H); 2.98 (*dd*, *J* = 16.8, 13.5, 1 H); 2.81 (*dd*, *J* = 16.8, 3.3, 1 H); 2.01–1.92 (*m*, 4 H); 1.65 (*s*, 3 H); 1.60 (*s*, 3 H); 1.53 (*s*, 3 H); 0.98–0.91 (*m*, 4 H); −0.02 (*s*, 9 H); −0.03 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 191.2; 160.6; 160.2; 147.4; 147.3; 135.1; 133.1; 131.0; 125.8; 124.1; 121.6; 119.7; 118.6; 116.2; 115.7; 114.3; 107.5; 93.8; 93.6; 79.1; 66.3; 66.2; 56.0; 44.3; 39.6; 26.5; 25.5; 22.2; 17.9; 17.5; 15.9; −1.5. HR-FAB-MS: 713.3903 ($[M+H]^+$, $C_{39}H_{61}O_8Si_2^+$; calc. 713.3905).

(±)-Prostratol F (= *8-[(2*E*)-3,7-Dimethylocta-2,6-dien-1-yl]-2,3-dihydro-7-hydroxy-2-(4-hydroxy-phenyl)-4*H*-1-benzopyran-4-one*; **1**). To a soln. of **15** (0.14 g, 0.3 mmol) in MeOH (5 ml) was added conc. HCl soln. (0.2 ml), and the mixture was stirred at r.t. for 10 h. The mixture was diluted with sat. $NaHCO_3$ soln. (30 ml) and extracted with AcOEt (3 × 30 ml). After removal of the solvent, the oily residue was purified by FC (hexane/AcOEt 3 : 1): **1** (0.070 g, 72%). Oil. IR (neat): 3336, 2921, 1656, 1593, 1516, 1442, 1336, 1284, 1106, 1068, 905, 821, 740. ^{1}H-NMR ((D$_6$)acetone, 300 MHz): 9.25 (*s*, 1 H); 8.60 (*s*, 1 H); 7.69 (*d*, *J* = 8.7, 1 H); 7.51 (*d*, *J* = 8.4, 2 H); 7.01 (*d*, *J* = 8.4, 2 H); 6.72 (*d*, *J* = 8.7, 1 H); 5.53 (*dd*, *J* = 13.0, 3.3, 1 H); 5.35 (*t*, *J* = 6.9, 1 H); 5.15 (*t*, *J* = 6.6, 1 H); 3.45 (*d*, *J* = 6.9, 2 H); 3.10 (*J* = 16,6, 13.0, 1 H); 2.81 (*dd*, *J* = 16.6, 3.3, 1 H); 2.14–2.02 (*m*, 4 H); 1.73 (*s*, 3 H); 1.69 (*s*, 3 H); 1.64 (*s*, 3 H). ^{13}C-NMR ((D$_6$)acetone, 75 MHz): 191.5; 162.4; 162.1; 158.4; 135.4; 131.6; 131.5; 128.8; 126.4; 125.2; 123.1; 116.6; 116.1; 115.3; 110.5; 80.3; 44.6; 40.5; 27.4; 25.9; 22.7; 17.8; 16.4. HR-EI-MS: 392.1990 (M^+, $C_{25}H_{28}O_4^+$; calc. 392.1988).

(±)-8-Geranyl-3′,4′,7-trihydroxyflavanone (= *2-(3,4-Dihydroxyphenyl)-8-[(2*E*)-3,7-dimethylocta-2,6-dien-1-yl]-2,3-dihydro-7-hydroxy-4*H*-1-benzopyran-4-one*; **2**). As described for **1**, with **16** (0.16 g, 0.2 mmol), MeOH (5 ml), and conc. HCl soln. (0.2 ml). FC (hexane/AcOEt 4 : 1) gave **2** (0.067 g, 74%). Oil. IR (neat): 3391, 2923, 1655, 1591, 1521, 1440, 1333, 1283, 1203, 1107, 810, 738, 584. ^{1}H-NMR ((D$_6$)acetone, 300 MHz): 7.58 (*d*, *J* = 8.7, 1 H); 7.06 (*s*, 1 H); 6.91–6.85 (*m*, 2 H); 6.62 (*d*, *J* = 8.7, 1 H); 5.38 (*dd*, *J* = 12.6, 3.0, 1 H); 5.26 (*t*, *J* = 7.2, 1 H); 5.06 (*t*, *J* = 6.6, 1 H); 3.35 (*d*, *J* = 7.2, 2 H); 2.96 (*dd*, *J* = 16.8, 12.6, 1 H); 2.69 (*dd*, *J* = 16.8, 3.0, 1 H); 2.04–1.91 (*m*, 4 H); 1.65 (*s*, 3 H); 1.59 (*s*, 3 H); 1.54 (*s*, 3 H). ^{13}C-NMR ((D$_6$)acetone, 75 MHz): 191.2; 162.5; 162.0; 146.2; 146.1; 135.4; 132.3; 131.6; 126.3; 125.2; 123.1; 119.0; 116.6; 116.0; 115.4; 114.6; 110.5; 80.4; 44.7; 40.5; 27.4; 25.8; 22.7; 17.8; 16.3. HR-EI-MS: 408.1938 (M^+, $C_{25}H_{28}O_5^+$; calc. 408.1937).

Xanthoangelol (=*(2*E*)-1-{3-[(2*E*)-3,7-Dimethylocta-2,6-dien-1-yl]-2,4-dihydroxyphenyl}-3-(4-hydroxyphenyl)prop-2-en-1-one*; **4**). As described for **1**, with **13** (0.20 g, 0.4 mmol), MeOH (5 ml), and conc. HCl soln. (0.2 ml). FC (hexane/AcOEt 4:1) gave **4** (0.104 g, 75%). Solid. M.p. 142–143°. IR (KBr): 3386, 2921, 1607, 1512, 1444, 1371, 1318, 1237, 1169, 1107, 831, 627. ^{1}H-NMR ($CDCl_3$, 300 MHz): 13.86 (*s*, 1 H); 7.79 (*d*, *J* = 15.3, 1 H); 7.69 (*d*, *J* = 9.0, 1 H); 7.48 (*d*, *J* = 8.6, 2 H); 7.43 (*d*, *J* = 15.3, 1 H); 6.87 (*d*, *J* = 8.6, 2 H); 6.44 (*d*, *J* = 9.0, 1 H); 5.31 (*t*, *J* = 7.2, 1 H); 5.06 (*t*, *J* = 6.6, 1 H); 3.48 (*d*, *J* = 7.2, 2 H); 2.20–1.98 (*m*, 4 H); 1.83 (*s*, 3 H); 1.67 (*s*, 3 H); 1.59 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 192.5; 163.9; 161.9; 158.5; 144.5; 139.0; 132.0; 130.7; 129.4; 127.3; 123.8; 121.1; 117.8; 116.1; 114.5; 114.0; 108.0; 39.7; 26.4; 25.7; 21.7; 17.7; 16.3. HR-EI-MS: 392.1989 (M^+, $C_{25}H_{28}O_4^+$; calc. 392.1988).

3-Geranyl-2,3′,4,4′-tetrahydroxychalcone (=*(2*E*)-3-(3,4-Dihydroxyphenyl)-1-{3-[(2*E*)-3,7-dimethylocta-2,6-dien-1-yl]-2,4-dihydroxyphenyl}prop-2-en-1-one*; **5**). As described for **1**, with **14** (0.15 g, 0.2 mmol), MeOH (5 ml), and conc. HCl soln. (0.2 ml). FC (hexane/AcOEt 2:1) gave **5** (0.061 g, 72%). Solid. M.p. 131–133°. IR (KBr): 3424, 2963, 1608, 1554, 1449, 1376, 1276, 1106, 976, 800, 743, 636. ^{1}H-NMR ((D$_6$)acetone, 300 MHz): 7.97 (*d*, *J* = 8.7, 1 H); 7.77 (*d*, *J* = 15.3, 1 H); 7.68 (*d*, *J* = 15.3, 1 H); 7.33 (*d*, *J* = 2.0, 1 H); 7.21 (*dd*, *J* = 8.4, 2.0, 1 H); 6.90 (*d*, *J* = 8.4, 1 H); 6.52 (*d*, *J* = 8.7, 1 H); 5.30 (*t*, *J* = 7.2, 1 H); 5.06 (*t*, *J* = 6.6, 1 H); 3.38 (*d*, *J* = 7.2, 2 H); 2.07–1.91 (*m*, 4 H); 1.79 (*s*, 3 H); 1.59 (*s*, 3 H); 1.54 (*s*, 3 H). ^{13}C-NMR ((D$_6$)acetone, 75 MHz): 193.0; 165.2; 162.7; 149.1; 146.4; 145.3; 135.2; 131.6; 130.2; 128.3; 125.1; 123.4; 123.2; 118.5; 116.4; 116.2; 116.0; 114.4; 108.0; 40.5; 27.4; 25.8; 22.2; 17.7; 16.3. HR-EI-MS: 408.1934 (M^+, $C_{25}H_{28}O_5^+$; calc. 408.1937).

3-Geranyl-2,4,6-trihydroxyacetophenone (=*1-{3-[(2*E*)-3,7-Dimethylocta-2,6-dien-1-yl]-2,4,6-trihydroxyphenyl}ethanone*; **18**) [24b]. To a soln. of 2,4,6-trihydroxyacetophenone (**17**; 0.505 g, 3.0 mmol) and geranyl bromide (0.652 g, 3.0 mmol) in dry acetone (50 ml) was added anh. K_2CO_3 (0.830 g, 6.0 mmol). The mixture was refluxed for 24 h. Evaporation of the acetone, addition of 2N HCl (30 ml), and extraction with AcOEt (3 × 30 ml), washing with brine (30 ml), drying ($MgSO_4$), and removal of the solvent followed by FC (hexane/AcOEt 7:1) gave **18** (0.676 g, 74%) as solid material.

1-[3-Geranyl-2-hydroxy-4,6-bis(methoxymethoxy)phenyl]ethanone (=*1-{3-[(2*E*)-3,7-Dimethylocta-2,6-dien-1-yl]-2-hydroxy-4,6-bis(methoxymethoxy)phenyl}ethanone*; **19**). As described for **12**, with MOMCl (0.177 g, 2.2 mmol), **18** (0.304 g, 1.0 mmol), ^{i}Pr$_2$EtN (0.646 g, 5.0 mmol), and dry CH_2Cl_2 (20 ml). FC (hexane/AcOEt 10:1) afforded **19** (0.353 g, 90%). Oil. IR (neat): 2916, 1615, 1426, 1372, 1272, 1230, 1153, 1106, 1069, 962, 924, 872, 722. ^{1}H-NMR ($CDCl_3$, 300 MHz): 13.79 (*s*, 1 H); 6.37 (*s*, 1 H); 5.23 (*s*, 2 H); 5.21 (*s*, 2 H); 5.17 (*t*, *J* = 6.9, 1 H); 5.04 (*t*, *J* = 6.6, 1 H); 3.49 (*s*, 3 H); 3.45 (*s*, 3 H); 3.29 (*d*, *J* = 6.9, 2 H); 2.64 (*s*, 3 H); 2.06–1.90 (*m*, 4 H); 1.75 (*s*, 3 H); 1.62 (*s*, 3 H); 1.54 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 203.3; 163.3; 160.6; 158.6; 134.6; 130.9; 124.3; 122.3; 110.4; 106.7; 94.4; 93.7; 91.1; 56.4; 56.1; 39.6; 32.9; 26.6; 25.4; 21.3; 17.4; 15.9. HR-EI-MS: 392.2198 (M^+, $C_{22}H_{32}O_6^+$; calc. 392.12199).

*(2*E*)-3-(3,4-Dimethoxyphenyl)-1-[3-geranyl-2-hydroxy-4,6-bis(methoxymethoxy)phenyl]prop-2-en-1-one* (=*(2*E*)-3-(3,4-Dimethoxyphenyl)-1-{3-[(2*E*)-3,7-dimethylocta-2,6-dien-1-yl]-2-hydroxy-4,6-(bis-(methoxymethoxy)phenyl}prop-2-en-1-one*; **20**). As described for **13**, with **19** (0.30 g, 0.8 mmol), EtOH (20 ml), KOH (0.429 g, 7.6 mmol), and 3,4-dimethoxybenzaldehyde (0.165 g, 1.0 mmol). Workup with sat. NH_4Cl soln. (80 ml), AcOEt (3 × 80 ml), and brine (30 ml), followed by FC (hexane/AcOEt 10:1): **20** (0.294 g, 71%). Oil. IR (neat): 2918, 1616, 1512, 1416, 1308, 1261, 1135, 1072, 959, 808, 721. ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.81 (*d*, *J* = 15.6, 1 H); 7.72 (*d*, *J* = 15.6, 1 H); 7.16 (*d*, *J* = 8.1, 1 H); 7.11 (*s*, 1 H); 6.85 (*d*, *J* = 8.1, 1 H); 6.34 (*s*, 1 H); 5.25–5.24 (*m*, 3 H); 5.21 (*s*, 2 H); 5.04 (*t*, *J* = 6.6, 1 H); 3.89 (*s*, 6 H); 3.50 (*s*, 3 H); 3.45 (*s*, 3 H); 3.31 (*d*, *J* = 6.9, 2 H); 2.08–1.90 (*m*, 4 H); 1.76 (*s*, 3 H); 1.61 (*s*, 3 H); 1.54 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 192.9; 163.7; 160.5; 157.9; 151.0; 149.1; 142.3; 134.7; 131.0; 128.4; 125.5; 124.3; 122.7; 122.3; 112.0; 111.0; 109.9; 107.6; 95.5; 93.8; 92.1; 56.8; 56.1; 55.8; 55.6; 39.7; 26.6; 25.5; 21.5; 17.5; 16.0. HR-FAB-MS: 541.2803 ($[M+H]^+$, $C_{31}H_{41}O_8^+$; calc. 541.2801).

*(2*E*)-3-(3,4-Dimethoxyphenyl)-1-[3-geranyl-2,4,6-trihydroxyphenyl]prop-2-en-1-one* (=*(2*E*)-3-(3,4-Dimethoxyphenyl)-1-{3-[(2*E*)-3,7-dimethylocta-2,6-dien-1-yl]-2,4,6-trihydroxyphenyl}prop-2-en-1-one*; **21**). As described for **1**, with **20** (0.20 g, 0.4 mmol), MeOH (5 ml), and conc. HCl soln. (0.2 ml): **21** (0.115 g, 69%). Oil. IR (neat): 3413, 2931, 1711, 1623, 1514, 1443, 1336, 1261, 1138, 1080, 1024, 980, 848, 813. ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.87(*d*, *J* = 15.6, 1 H); 7.73 (*d*, *J* = 15.6, 1 H); 7.15 (*d*, *J* = 8.1, 1 H); 7.06 (*s*, 1 H); 6.81 (*d*, *J* = 8.1, 1 H); 5.92 (*s*, 1 H); 5.25 (*t*, *J* = 6.9, 1 H); 5.03 (*t*, *J* = 6.6, 1 H); 3.87 (*s*, 3 H); 3.86 (*s*, 3 H); 3.37 (*d*, *J* = 6.9, 2 H); 2.12–2.04 (*m*, 4 H); 1.79 (*s*, 3 H); 1.64 (*s*, 3 H); 1.56 (*s*, 3 H). ^{13}C-NMR

($CDCl_3$, 75 MHz): 192.8; 163.0; 161.6; 160.0; 150.8; 148.8; 143.0; 138.6; 131.8; 128.3; 125.1; 123.7; 122.8; 121.6; 110.9; 110.4; 106.3; 105.4; 95.5; 55.7; 55.6; 39.6; 26.3; 25.5; 21.4; 17.5; 16.0. HR-EI-MS: 452.2196 (M^+, $C_{27}H_{32}O_6^+$; calc. 452.2199).

(±)-6-Geranyl-5,7-dihydroxy-3′,4′-dimethoxyflavanone (*=2-(3,4-Dimethoxyphenyl)-6-[(2*E*)-3,7-dimethylocta-2,6-dien-1-yl]-2,3-dihydro-5,7-dihydroxy-4*H*-1-benzopyran-4-one*; **3**) *and 8-Geranyl-5,7-dihydroxy-3′,4′-dimethoxyflavanone* (*=2-(3,4-Dimethoxyphenyl)-8-[(2*E*)-3,7-dimethylocta-2,6-dien-1-yl]-2,3-dihydro-5,7-dihydroxy-4*H*-1-benzopyran-4-one*; **22**). As described for **15**, with AcONa (0.181 g, 2.2 mmol), EtOH (20 ml), and **21** (0.10 g, 0.2 mmol): **3** (0.051 g, 51%) and **22** (0.07 g, 7%). Oils.

Data of **3**: IR (neat): 3413, 2931, 1711, 1623, 1514, 1443, 1336, 1261, 1138, 1080, 1024, 980, 848, 813. ^{1}H-NMR ($CDCl_3$, 300 MHz): 12.40 (*s*, 1 H); 6.98 (*s*, 1 H); 6.97 (*d*, *J* = 8.5, 1 H); 6.89 (*d*, *J* = 8.5, 1 H); 6.29 (*s*, 1 H); 6.01 (*s*, 1 H); 5.33 (*dd*, *J* = 13.2, 3.0, 1 H); 5.26 (*t*, *J* = 7.2, 1 H); 5.05 (*t*, *J* = 6.6, 1 H); 3.91 (*s*, 3 H); 3.89 (*s*, 3 H); 3.37 (*d*, *J* = 7.2, 2 H); 3.09 (*dd*, *J* = 16.7, 13.2, 1 H); 2.79 (*dd*, *J* = 16.7, 3.0, 1 H); 2.14 – 2.04 (*m*, 4 H); 1.81 (*s*, 3 H); 1.67 (*s*, 3 H); 1.59 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 196.0; 164.0; 161.2; 161.0; 149.4; 149.2; 138.7; 131.8; 130.9; 123.7; 121.3; 118.8; 111.1; 109.4; 107.2; 102.7; 95.5; 78.9; 55.9; 43.3; 39.6; 26.3; 25.6; 21.0; 17.6; 16.1. HR-EI-MS: 452.2197 (M^+, $C_{27}H_{32}O_6^+$; calc. 452.2199).

Data of **22**: IR (neat): 3432, 2924, 1640, 1514, 1382, 1262, 1144, 1089, 810. ^{1}H-NMR (300 MHz, $CDCl_3$): 11.98 (*s*, 1 H); 6.97 (*d*, *J* = 8.4, 1 H); 6.96 (*s*, 1 H); 6.87 (*d*, *J* = 8.4, 1 H); 6.15 (*s*, 1 H); 6.01 (*s*, 1 H); 5.34 (*dd*, *J* = 12.6, 2.9, 1 H); 5.21 (*t*, *J* = 7.2, 1 H); 5.02 (*t*, *J* = 6.6, 1 H); 3.89 (*s*, 6 H); 3.31 (*d*, *J* = 7.2, 2 H); 3.05 (*dd*, *J* = 16.5, 12.6, 1 H); 2.80 (*dd*, *J* = 16.5, 2.9, 1 H); 2.14 – 1.98 (*m*, 4 H); 1.70 (*s*, 3 H); 1.64 (*s*, 3 H); 1.56 (*s*, 3 H). HR-EI-MS: 452.2196 (M^+, $C_{27}H_{32}O_6^+$; calc. 452.2199).

*1-[5-Hydroxy-2-methyl-2-(4-methylpent-3-en-1-yl)-2*H*-chromen-6-yl]ethanone* (*=1-[5-Hydroxy-2-methyl-2-(4-methylpent-3-en-1-yl)-2*H*-1-benzopyran-6-yl]ethanone*; **24**). To a soln. of **11** (1.0 g, 3.5 mmol) in toluene (20 ml) was added DDQ (1.180 g, 5.2 mmol), and the mixture was refluxed for 4 h. The mixture was diluted with sat. $NaHCO_3$ soln. (30 ml) and extracted with AcOEt (3 × 30 ml). The extract was concentrated and the oily residue purified by FC (hexane/AcOEt 10 : 1): **24** (0.596 g, 60%). Oil. IR (neat): 2970, 2926, 1622, 1487, 1427, 1389, 1368, 1273, 1188, 1123, 1088, 976, 804. ^{1}H-NMR (300 MHz, $CDCl_3$): 12.95 (*s*, 1 H); 7.48 (*d*, *J* = 8.7, 1 H); 6.73 (*d*, *J* = 9.9, 1 H); 6.30 (*d*, *J* = 8.7, 1 H); 5.50 (*d*, *J* = 9.9, 1 H); 5.09 – 5.04 (*m*, 1 H); 2.54 (*s*, 3 H); 2.11 – 2.04 (*m*, 2 H); 1.80 – 1.65 (*m*, 2 H); 1.64 (*s*, 3 H); 1.54 (*s*, 3 H); 1.40 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 202.7; 160.1; 159.9; 131.9; 131.6; 127.0; 123.8; 116.2; 113.7; 109.0; 108.0; 80.2; 41.6; 27.1; 26.1; 25.6; 22.6; 17.6. HR-EI-MS: 286.1567 (M^+, $C_{18}H_{22}O_3^+$; calc. 286.1569).

*(2*E*)-1-[5-Hydroxy-2-methyl-2-(4-methylpent-3-en-1-yl)-2*H*-chromen-6-yl]-3-{4-{[2-(trimethylsilyl)-ethoxy]methoxy}phenyl}prop-2-en-1-one* (*=(2*E*)-1-[5-Hydroxy-2-methyl-2-(4-methylpent-3-en-1-yl)-2*H*-1-benzopyran-6-yl]-3-{4-{[2-(trimethylsilyl)ethoxy]methoxy}phenyl}prop-2-en-1-one*; **26**). As described for **13**, with **24** (0.15 g, 0.5 mmol), EtOH (20 ml), KOH (0.292 g, 5.2 mmol), and 4-{[2-(trimethylsilyl)ethoxy]methoxy}benzaldehyde (0.158 g, 0.6 mmol). Workup with NH_4Cl soln. (30 ml), AcOEt (3 × 30 ml), and brine (30 ml), followed by FC (hexane/AcOEt 20 : 1): **26** (0.218 g, 80%). Oil. IR (neat): 2954, 1633, 1583, 1509, 1483, 1423, 1350, 1285, 1232, 1174, 1111, 1048, 990, 916, 835, 801, 701. ^{1}H-NMR ($CDCl_3$, 300 MHz): 13.78 (*s*, 1 H); 7.82 (*d*, *J* = 15.3, 1 H); 7.68 (*d*, *J* = 9.0, 1 H); 7.56 (*d*, *J* = 8.4, 2 H); 7.42 (*d*, *J* = 15.3, 1 H); 7.05 (*d*, *J* = 8.4, 2 H); 6.78 (*d*, *J* = 10.0, 1 H); 6.35 (*d*, *J* = 9.0, 1 H); 5.51 (*d*, *J* = 10.0, 1 H); 5.24 (*s*, 2 H); 5.08 (*t*, *J* = 6.6, 1 H); 3.75 (*t*, *J* = 8.4, 2 H); 2.13 – 2.01 (*m*, 2 H); 1.81 – 1.64 (*m*, 2 H); 1.64 (*s*, 3 H); 1.55 (*s*, 3 H); 1.41 (*s*, 3 H); 0.95 (*t*, *J* = 8.4, 2 H); −0.01 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 191.6; 160.8; 159.8; 159.4; 143.7; 131.5; 130.4; 130.0; 128.2; 126.6; 123.7; 117.9; 116.3; 113.8; 109.0; 107.8; 92.4; 80.0; 66.3; 41.5; 26.9; 25.5; 22.5; 17.8; 17.4; −1.5. HR-FAB-MS: 521.2726 ($[M+H]^+$, $C_{31}H_{41}O_5Si^+$; calc. 521.2723).

*(2*E*)-3-{3,4-Bis{[2-(trimethylsilyl)ethoxy]methoxy}phenyl}-1-[5-hydroxy-2-methyl-2-(4-methylpent-3-en-1-yl)-2*H*-chromen-6-yl]prop-2-en-1-one* (*=(2*E*)-3-{3,4-Bis{[2-(trimethylsilyl)ethoxy]methoxy}-phenyl}-1-[5-hydroxy-2-methyl-2-(4-methylpent-3-en-1-yl)-2*H*-1-benzopyran-6-yl]prop-2-en-1-one*; **27**). As described for **13**, with **24** (0.15 g, 0.5 mmol), EtOH (20 ml), KOH (0.292 g, 5.2 mmol), and 3,4-bis{[2-(trimethylsilyl)ethoxy]methoxy}benzaldehyde (0.249 g, 0.6 mmol). Workup with sat. NH_4Cl soln. (30 ml), AcOEt (3 × 30 ml), and brine (30 ml), followed by FC (hexane/AcOEt 20 : 1): **27** (0.256 g, 73%). Oil. IR (neat): 3560, 2953, 1635, 1584, 1509, 1427, 1361, 1252, 1110, 989, 858, 836. ^{1}H-NMR ($CDCl_3$, 300 MHz): 13.80 (*s*, 1 H); 7.86 (*d*, *J* = 15.6, 1 H); 7.75 (*d*, *J* = 9.0, 1 H); 7.55 (*s*, 1 H); 7.51 (*d*, *J* = 15.6, 1 H);

7.30–7.24 (*m*, 2 H); 6.84 (*d*, *J* = 10.0, 1 H); 6.41 (*d*, *J* = 9.0, 1 H); 5.58 (*d*, *J* = 10.0, 1 H); 5.37 (*s*, 4 H); 5.13 (*t*, *J* = 6.6, 1 H); 3.91–3.82 (*m*, 4 H); 2.19–2.08 (*m*, 2 H); 1.89–1.65 (*m*, 2 H); 1.70 (*s*, 3 H); 1.61 (*s*, 3 H); 1.47 (*s*, 3 H); 1.05–0.98 (*m*, 4 H); 0.06 (*s*, 9 H); 0.04 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 191.7; 160.8; 160.0; 147.5; 144.1; 131.7; 130.6; 128.9; 126.8; 124.0; 123.8; 118.4; 116.4; 116.2; 115.9; 115.5; 113.9; 109.1; 107.9; 93.9; 93.5; 80.2; 66.5; 41.6; 27.1; 25.6; 22.6; 18.0; 17.5; −1.4. HR-FAB-MS: 667.3488 ($[M+H]^+$, $C_{37}H_{55}O_7Si_2^+$; calc. 667.3486).

(±)-Lespeol (=*(2*E*)-1-[5-Hydroxy-2-methyl-2-(4-methylpent-3-en-1-yl)-2*H*-1-benzopyran-6-yl]-3-(4-hydroxyphenyl)prop-2-en-1-one*; **6**). As described for **1**, with **26** (0.20 g, 0.4 mmol), MeOH (10 ml), and conc. HCl soln. (0.2 ml): **6** (0.134 g, 90%). Oil. IR (neat): 3370, 2969, 1607, 1578, 1512, 1482, 1442, 1364, 1285 ,1229, 1173, 1112, 1048, 979, 912, 833, 803, 743, 710. ^{1}H-NMR ($CDCl_3$, 300 MHz): 13.83 (*s*, 1 H); 7.81 (*d*, *J* = 15.3, 1 H); 7.69 (*d*, *J* = 8.8, 1 H); 7.48 (*d*, *J* = 8.4, 2 H); 7.40 (*d*, *J* = 15.3, 1 H); 6.88 (*d*, *J* = 8.4, 2 H); 679 (*d*, *J* = 10.0, 1 H); 6.38 (*d*, *J* = 8.8, 1 H); 5.53 (*d*, *J* = 10.0, 1 H); 5.09 (*t*, *J* = 6.6, 1 H); 2.15–2.07 (*m*, 2 H); 1.83–1.61 (*m*, 2 H); 1.65 (*s*, 3 H); 1.56 (*s*, 3 H); 1.43 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 192.2; 160.7; 160.2; 158.6; 144.6; 131.8; 130.8; 130.6; 127.1; 127.0; 123.8; 117.3; 116.2; 116.0; 113.8; 109.1; 108.2; 80.4; 41.5; 27.0; 25.6; 22.5; 17.6. HR-EI-MS: 390.1834 (M^+, $C_{25}H_{26}O_4^+$; calc. 390.1831).

*(±)-(2*E*)-3-(3,4-Dihydroxyphenyl)-1-[5-hydroxy-2-methyl-2-(4-methylpent-3-en-1-yl)-2*H*-chromen-6-yl]prop-2-en-1-one* (=*(2*E*)-3-(3,4-Dihydroxyphenyl)-1-[5-hydroxy-2-methyl-2-(4-methylpent-3-en-1-yl)-2*H*-1-benzopyran-6-yl)-prop-2-en-1-one*; **7**). As described for **1**, with **27** (0.20 g, 0.3 mmol), MeOH (10 ml), and conc. HCl soln. (0.2 ml). FC (hexane/AcOEt 2:1) gave **7** (0.088 g, 73%). Oil. IR (neat): 3412, 2970, 1605, 1516, 1482, 1447, 1370, 1274, 1111, 976, 802, 740. ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.70 (*d*, *J* = 15.3, 1 H); 7.65 (*d*, *J* = 8.8, 1 H); 7.33 (*d*, *J* = 15.3, 1 H); 7.14 (*s*, 1 H); 7.06 (*d*, *J* = 8.0, 1 H); 6.86 (*d*, *J* = 8.0, 1 H); 6.75 (*d*, *J* = 10.0, 1 H); 6.34 (*d*, *J* = 8.8, 1 H); 5.52 (*d*, *J* = 10.0, 1 H); 5.06 (*t*, *J* = 6.6, 1 H); 2.09–2.05 (*m*, 2 H); 1.80–1.68 (*m*, 2 H); 1.63 (*s*, 3 H); 1.54 (*s*, 3 H); 1.41 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 192.1; 160.7; 160.2; 146.7; 144.4; 143.9; 131.9; 130.7; 128.0; 127.0; 123.7; 123.1; 118.0; 116.2; 115.6; 114.7; 113.9; 109.1; 108.2; 80.4; 41.6; 27.1; 25.6; 22.6; 17.6. HR-EI-MS: 406.1777 (M^+, $C_{25}H_{26}O_5^+$; calc. 406.1780).

*(±)-(2*E*)-3-(3,4-Dimethoxyphenyl)-1-[5-hydroxy-2-methyl-2-(4-methylpent-3-en-1-yl)-2*H*-chromen-6-yl]prop-2-en-1-one* (=*(2*E*)-3-(3,4-Dimethoxyphenyl)-1-[5-hydroxy-2-methyl-2-(4-methylpent-3-en-1-yl)-2*H*-1-benzopyran-6-yl)prop-2-en-1-one*; **8**). As described for **13**, with **24** (0.06 g, 0.2 mmol), EtOH (20 ml), KOH (0.117 g, 2.1 mmol), and 3,4-dimethoxybenzaldehyde (0.038 g, 0.2 mmol). Workup with sat. NH_4Cl soln. (30 ml), AcOEt (3 × 30 ml), and brine (30 ml), followed by FC (hexane/AcOEt 30:1): **8** (0.066 g, 72%). Oil. IR (neat): 3520, 2966, 1631, 1583, 1512, 1483, 1452, 1422, 1368 , 1262, 1140, 1111, 1024, 979, 908, 848, 800, 737, 700. ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.79 (*d*, *J* = 15.3, 1 H); 7.68 (*d*, *J* = 8.7, 1 H); 7.38 (*d*, *J* = 15.3, 1 H); 7.20 (*d*, *J* = 8.1, 1 H); 7.11 (*s*, 1 H); 6.86 (*d*, *J* = 8.1, 1 H); 6.76 (*d*, *J* = 10.0, 1 H); 6.34 (*d*, *J* = 8.7, 1 H); 5.50 (*d*, *J* = 10.0, 1 H); 5.06 (*t*, *J* = 6.6, 1 H); 3.92 (*s*, 3 H); 3.90 (*s*, 3 H); 2.12–2.01 (*m*, 2 H); 1.80–1.64 (*m*, 2 H); 1.63 (*s*, 3 H); 1.54 (*s*, 3 H); 1.40 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 191.7; 160.8; 160.0; 151.4; 149.2; 144.3; 131.8; 130.5; 127.7; 126.8; 123.7; 123.2; 117.9; 116.3; 113.9; 111.0; 110.1; 109.1; 107.9; 80.2; 55.9; 41.6; 27.1; 25.5; 22.6; 17.5. HR-EI-MS: 434.2095 (M^+, $C_{27}H_{30}O_5^+$; calc. 434.2093).

*(±)-(2*E*)-3-(1,3-Benzodioxol-5-yl)-1-[5-hydroxy-2-methyl-2-(4-methylpent-3-en-1-yl)-2*H*-chromen-6-yl]prop-2-en-1-one* (=*(2*E*)-3-(1,3-Benzodioxol-5-yl)-1-[5-hydroxy-2-methyl-2-(4-methylpent-3-en-1-yl)-2*H*-1-benzopyran-6-yl]prop-2-en-1-one*; **9**). As described for **13**, with **24** (0.06 g, 0.2 mmol), EtOH (20 ml), KOH (0.117 g, 2.1 mmol), and piperonal (0.038 g, 0.3 mmol). Workup with sat. NH_4Cl soln. (30 ml), AcOEt (3 × 30 ml), and brine (30 ml), followed by FC (hexane/AcOEt 30:1): **9** (0.061 g, 70%). Oil. IR (neat): 2968, 1632, 1582, 1486, 1448, 1373, 1250, 1181, 1109, 1040, 978, 933, 850, 800, 741. ^{1}H-NMR ($CDCl_3$, 300 MHz): 13.81 (*s*, 1 H); 7.87 (*d*, *J* = 15.3, 1 H); 7.77 (*d*, *J* = 8.8, 1 H); 7.47 (*d*, *J* = 15.3, 1 H); 7.34 (*s*, 1 H); 7.21 (*d*, *J* = 8.1, 1 H); 6.93 (*d*, *J* = 8.1, 1 H); 6.87 (*d*, *J* = 10.2, 1 H); 6.44 (*d*, *J* = 8.8, 1 H); 6.11 (*s*, 2 H); 5.61 (*d*, *J* = 10.2, 1 H); 5.17 (*t*, *J* = 6.6, 1 H); 2.25–2.15 (*m*, 2 H); 1.91–1.65 (*m*, 2 H); 1.74 (*s*, 3 H); 1.65 (*s*, 3 H); 1.51 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 191.7; 160.9; 160.1; 149.9; 148.4; 144.0; 131.8; 130.5; 129.3; 126.9; 125.3; 123.7; 118.2; 116.3; 113.9; 109.2; 108.6; 108.0; 106.6; 101.6; 80.2; 41.6; 27.1; 25.6; 22.6; 17.6. HR-EI-MS: 418.1784 (M^+, $C_{26}H_{26}O_5^+$; calc. 418.1780).

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