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Synthesis of 2-hydroxy-3-methylbut-3-enyl substituted coumarins and xanthones as natural products. Application of the Schenck ene reaction of singlet oxygen with *ortho*-prenylphenol precursors

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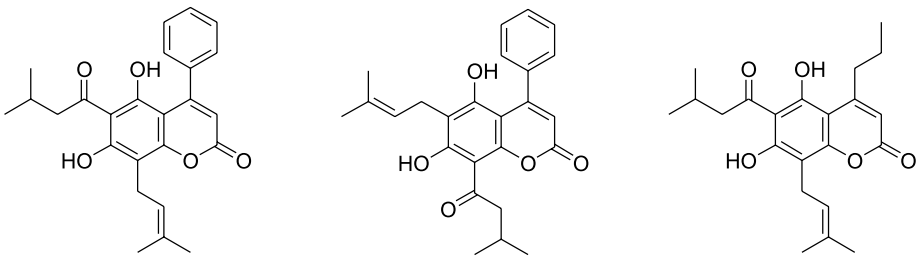
Abstract—Application of our original photooxidation–reduction methodology to prenylated dihydroxycoumarin and trihydroxyxanthone compounds led to the corresponding *ortho*-(2-hydroxy-3-methylbut-3-enyl)phenol derivatives with yields ranging from 8 to 65%. In most of the reported experiments, the oxidation products distribution, after the photooxygenation step, was controlled by the competition between the large group effect and the stabilising phenolic assistance effect. We also showed that *ortho*-(3-hydroxy-3-methylbut-1-enyl)phenol derivatives could be considered as biogenetic precursors of 2,2-dimethylbenzopyranic structures.

1. Introduction

Phytochemical studies of tropical plants, *Calophyllum dispar*, *Calophyllum caledonicum* and *Mesua racemosa*, led us to the isolation and the characterization of various original coumarin and xanthone compounds. Among them, *ortho*-(2-hydroxy-3-methylbut-3-enyl)phenol derivatives retained our attention because of their biological activity.[1–3] First attempts to synthesize this sort of products relied on the previously described rearrangement of epoxide starting from *ortho*-prenylphenol precursors.[4,5] This method required preliminary phenolic group protection to avoid further intramolecular cyclisation.[6,7] As the final deprotection step limited the overall yield in a 2–5% range,[3c] we aimed to develop an alternative access to *ortho*-(2-hydroxy-3-methylbut-3-enyl)phenol appendage. A second method, based on the Schenck ene reaction,[8] was also reported to oxidize prenyl side chain into 2-hydroxy-3-methylbut-3-enyl chain but only in the case of protected phenolic derivatives.[9,10] This methodology, based on the reactivity of singlet oxygen with olefin bearing allylic hydrogens, yielded intermediate hydroperoxides which were quantitatively reduced into the corresponding allylic alcohols. We recently developed a new and selective access to *ortho*-(2-hydroxy-3-methylbut-3-enyl)phenols derivatives by direct photooxygenation of *ortho*-prenylphenol precursors.[11] In the present paper, we reported the application of this original strategy to the synthesis of natural heterocyclic compounds in the coumarin and xanthone series.



1 (23%)
mammea A/AA

2 (40%)
mammea A/BA

3 (9%)
mammea B/AA

Figure 1. The mammea A/AA, A/BA, B/AA according to the nomenclature proposed by Crombie.[18]

Keywords: Schenck ene reaction; Photooxygenation; Regioselectivity; *ortho*-(2-Hydroxy-3-methylbut-3-enyl)phenols; Coumarin; Xanthone.
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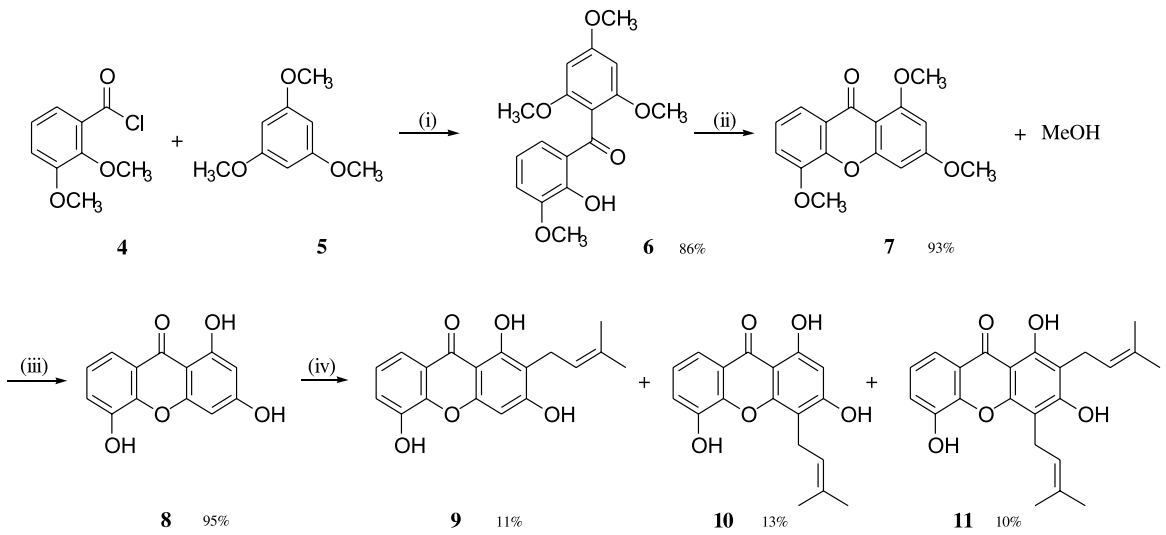


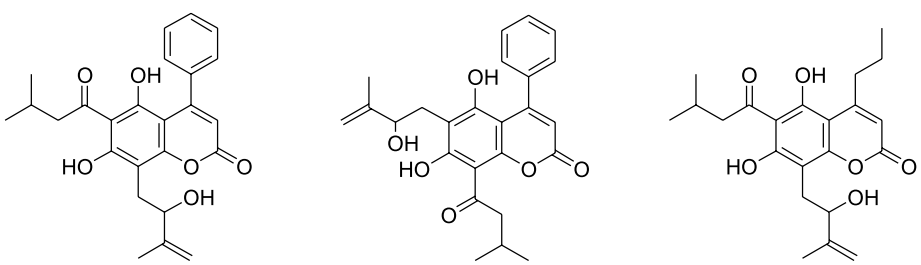
Scheme 1. (i) $AlCl_3$, CH_2Cl_2, rt, overnight; (ii) $Me_4NH^+OH^-$, pyridine, H_2O, reflux, 4 h; (iii) HI, phenol, reflux, 24 h; (iv) 3-methylbut-2-enyl bromide, aq. KOH 10%, rt, overnight.

2. Results and discussion

Preparation of the three prenylated 5,7-dihydroxycoumarins (**1**–**3**, Fig. 1) was achieved starting from 1,3,5-trihydroxybenzene (phloroglucinol) in accordance with Crombie's method.[12] The 1,3,5-trihydroxyxanthone was previously synthesized in one step from phloroglucinol and 2,3-dihydroxybenzoic acid with 16% yield[13] according to the Grover, Shah and Shah reaction.[14] The same methodology was also applied to the synthesis of 1,3-dihydroxy-5-methoxyxanthone using 2,3-dimethoxybenzoic acid as starting material with yields ranging from 32 to 91%.[15,16] In our work, we decided to synthesize the 1,3,5-trihydroxyxanthone backbone via a polymethoxybenzophenone intermediate, easily obtained by Friedel–Crafts acylation. Thus, 2,3-dimethoxybenzoyl chloride **4**, prepared in situ from the corresponding acid in the presence of oxalyl chloride, reacted with 1,3,5-trimethoxybenzene **5** to give 2-hydroxy-2′,3,4′,6′-tetramethoxybenzophenone **6** with 86% yield (Scheme 1). As already described by Quillinan,[17] a monodemethylation occurred on the ring provided by the acid moiety in the position *ortho* to the carbonyl function. Then subsequent base-catalyzed cyclisation[17] of **6** led to 1,3,5-trimethoxyxanthone **7** with 93% yield along with methanol elimination (Scheme 1).

Finally, demethylation of 1,3,5-trimethoxyxanthone **7** was completed in the presence of iodhydric acid and phenol[19,20] leading to 1,3,5-trihydroxyxanthone **8** with 95% yield (Scheme 1). Thus, the three-steps synthesis of **8** was performed with a 76% overall yield.

The last step required the introduction of a prenyl side chain on the xanthone skeleton at the C-2 and C-4 positions, *ortho* to the C-1 and C-3 phenolic groups. Such nuclear prenylations have previously been achieved in an acidic medium (e.g., in the presence of boron trifluoride etherate).[21] In these conditions, the expected C-prenylated xanthones were obtained with particularly low yields. The prenylation step was also carried out in basic medium, such as methanolic sodium methoxide.[22,23] Starting from the 1,3-dihydroxy-5-methoxyxanthone, Jain et al. reported the formation of both the C-2 and C-4 monoprenylated xanthones and the 2,4-diprenylated xanthone.[22] The same basic conditions, applied to the 1,3,5-trihydroxyxanthone **8**, led to a complex mixture, allowing the isolation of the following pure compounds: the 1,3-dihydroxy-2,4-di-(3-methylbut-2-enyl)-5-(3-methylbut-2-enyloxy)xanthone, the 1,3,5-trihydroxy-2,4-di(3-methylbut-2-enyl)xanthone and the 1,3-dihydroxy-2-(3-methylbut-2-enyl)-5-(3-methylbut-2-enyloxy)xanthone.[23] Thus, this method never allowed to isolate the C-2 or C-4 monoprenylated xanthones. Based on these previous results, we decided to perform the prenylation of the 1,3,5-trihydroxyxanthone **8** in basic conditions similar to those already applied to the dihydroxycoumarin derivatives. In the presence of an aqueous



12 (60%)
Disparinol A

13 (63%)
Isodisparinol A

14 (65%)
Disprorinol A

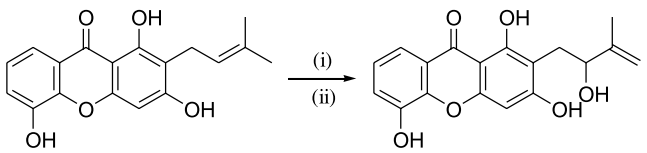
Figure 2.

potassium hydroxide solution, **8** reacted with 4-bromo-2-methyl-2-butene to lead to the prenylated derivatives **9**, **10** and **11**, already known as natural products,[24–26] with 11, 13 and 10% yield, respectively (Scheme 1).

Then, we studied the reactivity of these different prenylated heterocyclic compounds (e.g., **1**, **2**, **3**, **9**, **10**, **11**) towards the photooxidation–reduction sequence.

The Mammea A/AA, A/BA and B/AA (**1**, **2**, **3**, Fig. 1), treated in these conditions, led exclusively to the corresponding secondary allylic alcohols **12**, **13** and **14** with 60, 63 and 65% yield, respectively, (Fig. 2). These three coumarins have been characterized from the stem bark and the fruits of *Calophyllum dispar*.[1,27]

The yields, mentioned above in the coumarin series, underlined that the photooxygenation step followed the same regioselectivity rules than those observed in the acetophenone series.[11] Actually, in the first part of our study, we showed that the distribution of the prenyl side chain oxidation products resulted from a competition between the well known large group effect[28] and a new stabilising phenolic assistance effect.[29,30] Hence, this competition during the Schenck ene reaction led to the formation of the 2-hydroperoxy-3-methylbut-3-enyl derivative as the major oxidation product rather than the 3-hydroperoxy-3-methylbut-1-enyl derivative. Moreover, as already observed in the acetophenone series, the thermal instability of this tertiary hydroperoxide intermediate could explained that the secondary allylic alcohol is the sole oxidation product isolated after the two-steps sequence performed at 15 °C.



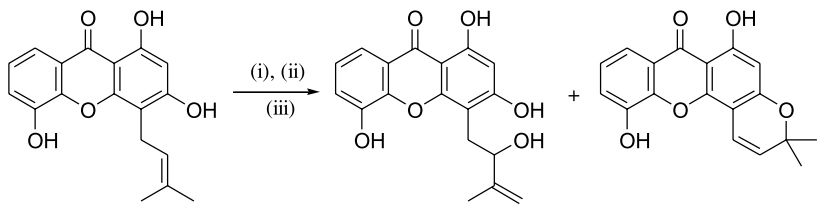
9 **15** (63%)

Scheme 2. (i) hν, O_2, tetraphenylporphine, CH_2Cl_2, 15 °C; (i) PPh_3, CH_2Cl_2, rt.

As an extent to our study on the synthesis of novel natural secondary allylic alcohol derivatives, the photooxygenation–reduction sequence was applied in the xanthone series. Thus, Caledol **15** was the sole oxidation product obtained from the 1,3,5-trihydroxy-2-(3-methylbut-2-enyl)xanthone **9** (Scheme 2).[3b] Therefore, regarding this result, we concluded that the oxidation of the prenyl chain located in the C-2 position on the xanthone skeleton followed the same regioselectivity rules as previously observed in both the acetophenone and coumarin series. In this experiment, the absence of the tertiary allylic alcohol was also observed. As a matter of fact, the ^{1}H NMR analysis of the crude mixture, formed via a photooxidation reaction, performed at −30 °C in $CDCl_3$, showed the presence of signals corresponding to the secondary and the tertiary allylic hydroperoxides in a 2:1 ratio. After leaving that sample at room temperature for a few hours, the disappearance of the signals, corresponding to the tertiary hydroperoxide protons in the ^{1}H NMR spectrum, confirmed the thermal instability of this intermediate.

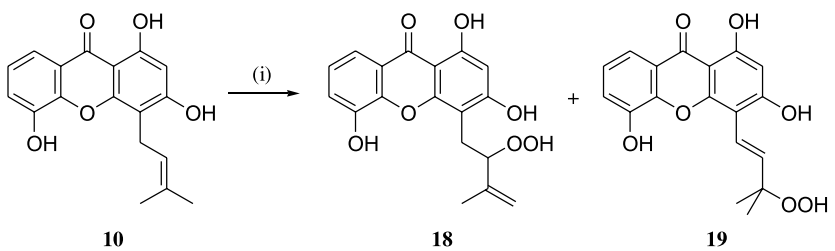
Prior to embark on the oxidation of the 2,4-bisprenylated xanthone **11**, we decided to apply the photooxygenation–reduction sequence conditions to the C-4 monoprenylated xanthone **10**. Surprisingly, after the reduction step, two products were isolated from the crude mixture: the secondary allylic alcohol **16** in 8% yield and as the major product with 17% yield the pyranoxanthone **17** (Scheme 3), already known as a natural compound named 6-deoxyisojacareubine.[25,31]

In order to analyse this unexpected result, starting from **10**, we performed a new photooxidation reaction in $CDCl_3$ at −30 °C. The ^{1}H NMR analysis of the crude mixture allowed us to observe proton signals corresponding to both the secondary and the tertiary allylic hydroperoxides **18** and **19** in a 1:2 ratio (Scheme 4).



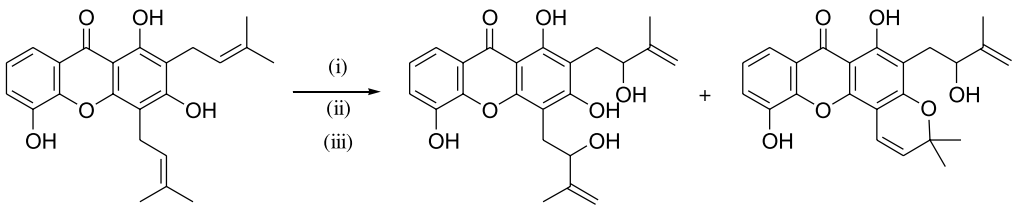
10 **16** (8%) **17** (17%)

Scheme 3. (i) hν, O_2, tetraphenylporphine, CH_2Cl_2, 15 °C; (ii) PPh_3, CH_2Cl_2, rt; (iii) SiO_2 (CH_2Cl_2/MeOH 99:1).



10 **18** **19**

Scheme 4. (i) hν, O_2, tetraphenylporphine, $CDCl_3$, −30 °C.



11 **21** (14%) **20** (21%)

Scheme 5. (i) hν, O_2, tetraphenylporphine, CH_2Cl_2, 15 °C; (ii) PPh_3, CH_2Cl_2, rt; (ii) SiO_2 (CH_2Cl_2/MeOH 95:5).

This ratio revealed a reverse regioselectivity pattern in the ene-reaction of the C-4 prenyl appendage with singlet oxygen. Hence, in that experiment, only the large group effect, which favoured the formation of the tertiary hydroperoxide, controlled the oxidation products distribution. Following that low-temperature experiment, we also showed that the tertiary allylic hydroperoxide was stable under higher temperature. The same 1:2 mixture of secondary and tertiary hydroperoxides **18** and **19** was allowed to reach room temperature, and after a few hours its ^{1}H NMR analysis provided the same spectrum profile than at low temperature, showing the thermal stability for these two products. Therefore, the tertiary hydroperoxide was sufficiently stable to be reduced in the presence of triphenylphosphine, leading to the corresponding alcohol. This latter compound, when exposed either to acidic medium (e.g., silica gel or $CDCl_3$) or to a slight increase of temperature (e.g., during the evaporation stage under reduced pressure) quantitatively led to the pyranoxanthone **17**.

In similar experimental conditions, **11** led to the xanthone **20** with 21% yield and to the Dicaledol **21** with 14% yield (Scheme 5). For this particular compound, we should notice that, despite the presence of two asymmetric carbons, we were unable to observe different chemical shifts in NMR analysis (^{1}H, ^{13}C) and to separate them using silica gel chromatography. The result obtained for the photooxygenation–reduction sequence starting from **11** confirmed that only the large group effect was implied in the products distribution during the oxidation of the C-4 prenyl side chain.

3. Conclusion

As a conclusion, the photooxygenation–reduction sequence permitted us to synthesize several natural secondary allylic alcohol derivatives (three in the coumarin series and two novel compounds in the xanthone series). Thus, according to this new two-steps synthetic route, the yield for the oxidation of the Mammea A/AA into the Disparinol A was increased from 2 to 60%. The regioselectivity rules, previously established in the acetophenone series,[11,31] were applicable to the coumarin series and also for the oxidation of 1,3,5-trihydroxy-2-(3-methylbut-2-enyl)-xanthone. Therefore, the phenolic assistance effect seemed to be still involved in the Schenck ene reaction of singlet oxygen with these different *ortho*-prenylphenol compounds.

During the photooxygenation step of the C-4 prenylated xanthone derivatives, we showed that the oxidation products distribution depended exclusively on the large group effect. This result could be due to a weaker acidic phenolic function, which would not participate to the stabilization of the intermediate state in the Shenk ene reaction. Moreover, during these same experiments, we also showed that, contrary to our previous results, the intermediate tertiary hydroperoxide was sufficiently stable at room temperature to be reduced into the tertiary allylic alcohol. So far, tertiary allylic hydroperoxides were stable at 15 °C when the *ortho*-phenolic group was protected. Once again, this unusual stability pointed out a different acidic character of the C-3 phenolic function.

Hence, the tertiary allylic alcohol could lead under smooth conditions to the corresponding pyranoxanthone. That result confirmed a biogenetic hypothesis already evoked in previous paper for the transformation of *ortho*-prenylphenol moiety into a 2,2-dimethylbenzopyranic structure.[32] Furthermore, the instability of both *ortho*-(3-hydroperoxy-3-methylbut-1-enyl)phenol and *ortho*-(3-hydroxy-3-methylbut-1-enyl)phenol derivatives could explain that such appendages were rarely isolated and characterized in natural products.

4. Experimental

4.1. General

Dichloromethane was distilled from calcium hydride. Si gel 60 (Macherey–Nagel, 230–400 mesh) was used for column chromatography and precoated Si gel plates (Macherey–Nagel, SIL G/UV254, 0.25 mm) were used for preparative TLC. NMR spectra were recorded in $CDCl_3$ or CD_3OD solutions on a Bruker Avance DRX 500 or a Jeol GSX 270 WB instruments. IR spectra were recorded on a Bruker Vector22 spectrometer. HREIMS (70 eV) were recorded on Varian MAT 311 spectrometer and HRFABMS were recorded on a Jeol JMS-700 spectrometer. Melting points were determined on an Electrothermal 8100 melting point apparatus and are uncorrected.

4.1.1. 2-Hydroxy-2′,3,4′,6′-tetramethoxybenzophenone 6. Under N_2, 2,3-dimethoxybenzoic acid (6 g, 33 mmol) in dry CH_2Cl_2 (45 mL) was treated with oxalyl chloride (12 mL, 132 mmol) and thoroughly stirred at room temperature. After 3 h, the solvent and the excess of oxalyl chloride were removed under reduced pressure. The residue was dissolved in dry CH_2Cl_2 (75 mL) and added to a CH_2Cl_2 solution (50 mL) of 1,3,5-trimethoxybenzene (5 g, 29.8 mmol). Then the reaction mixture was treated with aluminium III chloride (13.77 g, 103 mmol). After being stirred for 15 h at

room temperature, the mixture was poured into ice water containing concentrated HCl and extracted with CH_2Cl_2 (5×100 mL). The combined organic layers were dried over Na_2SO_4. After removal of the solvent under reduced pressure, purification of the crude product by column chromatography (1% MeOH/CH_2Cl_2) yielded **6** as a yellow solid (8.15 g, 86%), mp 156–157 °C; IR (cm^{-1}): 1629, 1607, 1255; ^1H NMR ($CDCl_3$, 270 MHz): δ 12.52 (s, 1H, OH), 7.04 (d, 1H arom., J=8 Hz), 6.95 (dd, 1H arom., J=8, 1.5 Hz), 6.73 (t, 1H arom., J=8 Hz), 6.17 (s, 2H arom.), 3.93 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 3.72 (s, 6H, 2×OCH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 201.4 (*C*O), 162.7, 158.3, 152.8, 148.4 (5×quat. arom. C), 124.3 (arom. CH), 121.4 (quat. arom. C), 117.9, 117.0 (2×arom. CH), 109.8 (quat. arom. C), 90.5 (2×arom. CH), 56.2, 55.8, 55.4 (4×O*C*H_3); EI-HRMS Calcd for $C_{17}H_{18}O_6$ (M^+) 311.1103, Found 311.1118.

4.1.2. 1,3,5-Trimethoxy-9*H*-xanthen-9-one 7. 2-Hydroxy-2′,3,4′,6′-tetramethoxybenzophenone **6** (3.9 g, 12.2 mmol) was treated with pyridine (72 mL), water (36 mL) and aqueous 10% tetramethylammonium hydroxide (24 mL). The mixture was refluxed for 4 h, poured into ice, acidified with HCl and extracted with AcOEt (5×150 mL). The combined organic layers were dried over Na_2SO_4 and removal of the solvent under reduced pressure yielded **7** as a white solid (3.29 g, 93%), mp 220–221 °C; IR (cm^{-1}): 1649, 1625, 1299; ^1H NMR ($CDCl_3$, 270 MHz): δ 7.88 (dd, 1H arom., J=8, 1.5 Hz), 7.26 (dd, 1H arom., J=8, 1.5 Hz), 7.18 (t, 1H arom., J=8 Hz), 6.64 (d, 1H arom., J=2 Hz), 6.36 (d, 1H arom., J=2 Hz), 4.03 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 175.2 (*C*O), 164.8, 161.8, 159.5, 147.8, 145.1, 124.0 (6×quat. arom. C), 123.2, 117.6, 114.3 (3×arom. CH), 107.1 (quat. arom. C), 95.4, 92.8 (2×arom. CH), 56.3, 56.3, 55.7 (3×O*C*H_3); EI-HRMS Calcd for $C_{16}H_{14}O_5$ (M^+) 286.0841, Found 286.0845.

4.1.3. 1,3,5-Trihydroxy-9*H*-xanthen-9-one 8. A mixture of **7** (1 g, 35 mmol), phenol (19.4 g, 0.2 mol) and an aqueous solution of HI (47%, 21 mL) was refluxed for 24 h. Then the reaction mixture was poured into aqueous 37% $NaHSO_3$ (70 mL). The resulting yellow precipitate was collected, washed several times with CH_2Cl_2 and dissolved in acetone. The solution was filtered and the solvent was removed under reduced pressure to yield **8** as a yellow solid (0.81 g, 95%), mp 274—276 °C; IR (cm^{-1}): 3567, 1653, 1577, 1169; ^1H NMR (CD_3OD, 270 MHz): δ 7.59 (dd, 1H arom., J=7.5, 2 Hz), 7.21 (dd, 1H arom., J=7.5, 2 Hz), 7.17 (dd, 1H arom., J=7.5, 7.5 Hz), 6.42 (d, 1H arom., J=2 Hz), 6.17 (d, 1H arom., J=2 Hz); ^{13}C NMR (CD_3OD, 67.5 MHz): δ 182.1 (*C*O), 167.3, 164.7, 159.1, 147.3, 146.6 (5×quat. arom. C), 124.9 (arom. CH), 122.5 (quat. arom. C), 121.4, 116.3 (2×arom. CH), 103.8 (quat. arom. C), 99.2, 95.2 (2×arom. CH); EI-HRMS Calcd for $C_{13}H_8O_5$ (M^+) 244.0312, Found 244.0373.

4.2. General procedure for the prenylation of 1,3,5-trihydroxyxanthone

To the 1,3,5-trihydroxyxanthone **8** (0.3 g, 1.23 mmol) in 10% aqueous potassium hydroxide (15 mL) was added 4-bromo-2-methyl-2-butene (0.21 mL, 1.85 mmol). The reaction mixture was stirred for 16 h at room temperature, acidified with diluted HCl (10%) and extracted with AcOEt (4×20 mL). Then the combined organic layers were dried over Na_2SO_4. After removal of the solvent under reduced pressure, purification of the crude product by column chromatography (5% MeOH/CH_2Cl_2) yielded successively **9**, **11**, and **10**.

4.2.1. 1,3,5-Trihydroxy-2-(3-methylbut-2-enyl)-9*H*-xanthen-9-one 9. The typical conditions described in Section 4.2 yielded **12** as a yellow solid (44 mg, 11%), mp 157–158 °C; IR (cm^{-1}): 3442, 1617, 1457, 1253; ^1H NMR ($CDCl_3$, 270 MHz): δ 13.27 (s, 1H, OH), 9.45 (s, 1H, OH), 7.68 (dd, 1H arom., J=7.5, 2 Hz), 7.33 (dd, 1H arom., J=7.5, 2 Hz), 7.27 (dd, 1H arom., J=7.5, 7.5 Hz), 6.58 (s, 1H arom.), 5.29 (t, 1H, CH_2CH, J=7.5 Hz), 3.37 (d, 2H, CH_2CH, J=7.5 Hz), 1.78 (s, 3H, CH_3), 1.65 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 181.0 (*C*O), 163.4, 161.5, 154.1, 147.0, 146.3 (5×quat. arom. C), 130.9 (CH=*C*$(CH_3)_2$), 123.7, 122.6 (2×arom. CH), 121.8 (quat. arom. C), 120.5 (CH_2CH), 115.4 (arom. CH), 106.9, 103.6 (2×quat. arom. C), 97.8 (arom. CH), 25.1 (*C*H_3), 21.3 (*C*H_2CH), 17.2 (*C*H_3); EI-HRMS Calcd for $C_{18}H_{16}O_5$ (M^+) 312.0998, Found 312.0975.

4.2.2. 1,3,5-Trihydroxy-4-(3-methylbut-2-enyl)-9*H*-xanthen-9-one 10. The typical conditions described in Section 4.2 yielded **13** as a yellow solid (50 mg, 13%), mp 188–190 °C; IR (cm^{-1}): 3446, 1651, 1566, 1293; ^1H NMR ($CDCl_3$, 270 MHz): δ 12.97 (s, 1H, OH), 9.52 (s, 1H, OH), 7.65 (dd, 1H arom., J=8, 1.5 Hz), 7.36 (dd, 1H arom., J=8, 1.5 Hz), 7.23 (t, 1H arom., J=8 Hz), 6.35 (s, 1H arom.), 5.36 (t, 1H, CH_2CH, J=7.5 Hz), 3.58 (d, 2H, CH_2CH, J=7.5 Hz), 1.84 (s, 3H, CH_3), 1.64 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 181.8 (*C*O), 164.0, 162.3, 155.4, 147.1, 146.4 (5×quat. arom. C), 131.7 (CH=*C*$(CH_3)_2$), 124.5, 123.4 (2×arom. CH), 122.1 (quat. arom. C), 121.2 (CH_2CH), 116.2 (arom. CH), 107.6, 103.7 (2×quat. arom. C), 98.5 (arom. CH), 25.9 (*C*H_3), 22.1 (*C*H_2CH), 18.0 (*C*H_3); EI-HRMS Calcd for $C_{18}H_{16}O_5$ (M^+) 312.0998, Found 312.0988.

4.2.3. 1,3,5-Trihydroxy-2,4-bis(3-methylbut-2-enyl)-9*H*-xanthen-9-one 11. The typical conditions described in Section 4.2 yielded **14** as a yellow solid (40 mg, 10%), mp 161–162 °C; IR (cm^{-1}): 3364, 1642, 1580, 1223; ^1H NMR ($CDCl_3$, 270 MHz): δ 13.19 (s, 1H, OH), 7.76 (dd, 1H arom., J=7.5, 1.5 Hz), 7.30 (dd, 1H arom., J=7.5, 1.5 Hz), 7.22 (dd, 1H arom., J=7.5, 7.5 Hz), 6.56 (s, 1H, OH), 5.87 (s, 1H, OH), 5.30–5.26 (m, 2H, CH_2CH), 3.55 (d, 2H, CH_2CH, J=7 Hz), 3.48 (d, 2H, CH_2CH, J=7 Hz), 1.87 (s, 6H, 2×CH_3), 1.80 (s, 3H, CH_3), 1.76 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 181.8 (*C*O), 160.9, 158.6, 152.3, 144.4, 144.3 (5×quat. arom. C), 136.1, 133.3 (2×CH=*C*$(CH_3)_2$), 123.8 (arom. CH), 122.2, 121.2 (2×CH_2CH), 120.8 (quat. arom. C), 119.8, 116.8 (arom. CH), 109.1, 105.4, 103.3 (3×quat. arom. C), 25.9, 25.6 (2×*C*H_3), 22.0, 21.6 (2×*C*H_2CH), 17.9 (2×*C*H_3); EI-HRMS Calcd for $C_{23}H_{24}O_5$ (M^+) 380.1624, Found 380.1614.

4.3. General procedure for the photooxygenation–reduction sequence at 15 °C

Dried air was bubbled through a CH_2Cl_2 solution (30 mL) of

prenylated heterocyclic derivative (30 mg) and tetraphenylporphine (3 mg, 0.005 mmol) as the photosensitizer. The reaction mixture was water-cooled at 15 °C and irradiated with a halogen lamp (500 W) for 1.5 h. Then 1.1 equiv. of triphenylphosphine was added and the solution was stirred overnight at room temperature.

Purification

Procedure A. The reaction mixture was washed four times with 30 mL of an aqueous solution of potassium hydroxide (5%). The combined aqueous layers were acidified down to pH=3 by addition of water-diluted chlorhydric acid (10%). Then this solution was extracted four times with 30 mL of dichloromethane. The combined organic layers were concentrated under reduced pressure and were subjected to a second cycle of basic extraction. The final organic layers were evaporated under reduced pressure and yielded the purified secondary allylic alcohol derivative.

Procedure B. The work-up, the same than that in procedure A, was achieved at low temperature (between 0 and 5 °C) by using cooled aqueous and organic solutions to avoid lactone ring opening in basic medium.

4.3.1. Disparinol A=5,7-dihydroxy-8-(2-hydroxy-3-methylbut-3-enyl)-6-(3-methyl-1-oxobutyl)-2*H*-4-phenyl-benzopyran-2-one 12. The typical conditions described in Section 4.3 were applied to **1** (30 mg, 0.07 mmol). The purification of the crude product according to procedure B followed by a recrystallization in AcOEt/hexane, yielded **12** as a yellow solid (19 mg, 60%), mp 115–116 °C; IR (cm^{-1}): 1700, 1622, 1580, 756, 697; ^1H NMR ($CDCl_3$, 270 MHz): δ 14.33 (s, 1H, OH), 10.18 (s, 1H, OH), 7.42 (m, 3H arom.), 7.33 (m, 2H arom.), 5.96 (s, 1H arom.), 5.03 (br s, 1H, $C(CH_3)$=CH_2), 4.94 (br s, 1H, $C(CH_3)$=CH_2), 4.50 (dd, 1H, CH_2CHOH, J=8, 2 Hz), 3.30 (dd, 1H, CH_2CHOH, J=15, 2 Hz), 3.04 (dd, 1H, CH_2CHOH, J=15, 8 Hz), 3.02 (d, 2H, COCH_2CH, J=6.5 Hz), 2.23 (m, 1H, $CH_2CH(CH_3)_2$), 1.93 (s, 3H, CH_3), 0.94 (d, 6H, J=6.5 Hz, $CH_2CH(CH_3)_2$); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 212.3 (*C*OCH_2CH), 163.4, 162.1 (2×quat. arom. C), 159.9 (O*C*OCH), 157.7, 156.7 (2×quat. arom. C), 146.0 (CH_2=*C*(CH_3)), 139.4 (quat. arom. C), 128.3, 127.7, 127.2, 112.2 (6×arom. CH), 111.2 (*C*H_2=C(CH_3)), 107.4, 104.7, 102.2 (3×quat. arom. C), 77.7 (CH_2*C*HOH), 46.6 (CO*C*H_2CH), 28.8 (*C*H_2CHOH), 26.8 (CH_2CH(*C*H_3)$_2$), 18.8 (*C*H_3), 16.4 (CH_2*C*H(CH_3)$_2$), 11.9 (CH_2CH(*C*H_3)$_2$); EI-HRMS Calcd for $C_{25}H_{26}O_6$ (M^+) 422.1729, Found 422.1726.

4.3.2. Isodisparinol A=5,7-dihydroxy-6-(2-hydroxy-3-methylbut-3-enyl)-8-(3-methyl-1-oxobutyl)-2*H*-4-phenyl-benzopyran-2-one 13. The typical conditions described in Section 4.3 were applied to **2** (30 mg, 0.07 mmol). The purification of the crude product according to procedure B yielded **13** as a colorless oil (20 mg, 63%), IR (cm^{-1}): 3407, 1717, 1620, 1597, 758, 702; ^1H NMR ($CDCl_3$, 270 MHz): δ 14.80 (s, 1H, OH), 9.29 (s, 1H, OH), 7.41 (m, 3H arom.), 7.32 (m, 2H arom.), 6.03 (s, 1H arom.), 4.93 (br s, 1H, $C(CH_3)$=CH_2), 4.86 (br s, 1H, $C(CH_3)$=CH_2), 4.49 (dd, 1H, CH_2CHOH, J=8.5, 2 Hz), 3.20 (dd, 2H, COCH_2CH, J=6.5, 1.5 Hz), 3.13 (dd, 1H, CH_2CHOH, J=15, 2 Hz), 2.77 (dd, 1H, CH_2CHOH, J=15, 8 Hz), 2.32 (m, 1H, $CH_2CH(CH_3)_2$), 1.81 (s, 3H, CH_3), 1.06 (d, 6H, J=7 Hz, $CH_2CH(CH_3)_2$); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 210.6 (*C*OCH_2CH), 167.0, 160.2 (2×quat. arom. C), 159.2 (O*C*OCH), 156.4, 156.3 (2×quat. arom. C), 146.5 (CH_2=*C*(CH_3)), 139.8 (quat. arom. C), 128.2, 127.8, 127.1, 112.3 (6×arom. CH), 110.7 (*C*H_2=C(CH_3)), 109.9, 103.8, 102.3 (3×quat. arom. C), 76.8 (CH_2*C*HOH), 46.8 (CO*C*H_2CH), 28.7 (*C*H_2CHOH), 27.2 (CH_2CH(*C*H_3)$_2$), 18.4 (*C*H_3), 16.6 (CH_2*C*H(CH_3)$_2$), 11.9 (CH_2CH(*C*H_3)$_2$); EI-HRMS Calcd for $C_{25}H_{26}O_6$ (M^+) 422.1729, Found 422.1726.

4.3.3. Disprorinol A=5,7-dihydroxy-8-(2-hydroxy-3-methylbut-3-enyl)-6-(3-methyl-1-oxobutyl)-2*H*-4-phenyl-benzopyran-2-one 14. The typical conditions described in Section 4.3 were applied to **3** (30 mg, 0.08 mmol). The purification of the crude product according to procedure B followed by a recrystallization in AcOEt/hexane afforded **14** as a yellow solid (20 mg, 65%), mp 111–112 °C; acetate IR (cm^{-1}): 3306, 1703, 1617, 1579, 1186; ^1H NMR ($CDCl_3$, 270 MHz): δ 15.32 (s, 1H, OH), 10.18 (s, 1H, OH), 5.91 (s, 1H arom.), 4.99 (br s, 1H, $C(CH_3)$=CH_2), 4.88 (br s, 1H, $C(CH_3)$=CH_2), 4.44 (dd, 1H, CH_2CHOH, J=7.5, 1.5 Hz), 3.24 (dd, 1H, CH_2CHOH, J=15, 1.5 Hz), 2.95 (m, 1H, CH_2CHOH), 2.95 (m, 2H, C$H_2CH_2CH_3$), 3.07 (dd, 2H, COCH_2CH, J=6.5, 1.5 Hz), 2.27 (m, 1H, $CH_2CH(CH_3)_2$), 1.65 (m, 2H, $CH_2CH_2CH_3$), 1.91 (s, 3H, CH_3), 1.01 (t, 3H, J=7.5 Hz, $CH_2CH_2CH_3$), 0.94 (d, 6H, J=6.5 Hz, $CH_2CH(CH_3)_2$); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 212.3 (*C*OCH_2CH), 164.3, 161.9 (2×quat. arom. C), 160.6* (O*C*OCH), 160.2*, 157.9 (2×quat. arom. C), 145.9 (CH_2=*C*(CH_3)), 111.2 (*C*H_2=C(CH_3)), 109.5 (arom. CH), 107.8, 104.6, 103.1 (3×quat. arom. C), 77.6 (CH_2*C*HOH), 53.6 (CO*C*H_2CH), 38.6 (*C*$H_2CH_2CH_3$), 28.8 (*C*H_2CHOH), 25.2 (CH_2*C*H(CH_3)$_2$), 22.8 (CH_2CH(*C*H_3)$_2$), 22.6 (CH_2*C*H_2CH_3), 18.7 (*C*H_3), 14.0 (CH_2CH_2*C*H_3); EI-HRMS Calcd for $C_{22}H_{28}O_6$ (M^+) 388.1886, Found 388.1881.

4.3.4. Caledol=1,3,5-trihydroxy-2-(2-hydroxy-3-methylbut-3-enyl)-9*H*-xanthen-9-one 15. The typical conditions described in Section 4.3 were applied to **9** (15 mg, 0.05 mmol). The purification of the crude product according to procedure A yielded **15** as an orange oil (10 mg, 63%), IR (cm^{-1}): 3233, 1645, 1619, 1455, 1223; ^1H NMR ($CDCl_3$, 270 MHz): δ 13.46 (s, 1H, OH), 7.67 (dd, 1H arom., J=7.5, 1.5 Hz), 7.34 (dd, 1H arom., J=8, 1.5 Hz), 7.27 (dd, 1H arom., J=8, 7.5 Hz), 6.50 (s, 1H arom.), 4.93 (br s, 1H, $C(CH_3)$=CH_2), 4.76 (br s, 1H, $C(CH_3)$=CH_2), 4.44 (dd, 1H, CH_2CHOH, J=7.5, 4 Hz), 3.09 (dd, 1H, CH_2CHOH, J=14, 4 Hz), 2.93 (dd, 1H, CH_2CHOH, J=14, 7.5 Hz), 1.84 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 181.2 (*C*O), 166.0, 161.8, 156.6 (3×quat. arom. C), 148.1 (CH_2=*C*(CH_3)), 146.8, 145.8 (2×quat. arom. C), 124.5 (arom. CH), 122.0 (quat. arom. C), 121.0, 116.0 (2×arom. CH), 110.2 (*C*H_2=C(CH_3)), 109.3, 103.3 (2×quat. arom. C), 95.1 (arom. CH), 76.2 (CH_2*C*HOH), 29.3 (*C*H_2CHOH), 18.1 (*C*H_3); EI-HRMS Calcd for $C_{18}H_{16}O_6$ (M^+) 328.0947, Found 328.0940.

4.3.5. 1,3,5-Trihydroxy-4-(2-hydroxy-3-methylbut-3-enyl)-9*H*-xanthen-9-one 16. The typical conditions

described in Section 4.3 were applied to **13** (30 mg, 0.1 mmol). The purification of the crude product by preparative TLC (1% MeOH/CH_2Cl_2) yielded **19** as an orange oil (3 mg, 8%), IR (cm^{-1}): 3274, 1648, 1562, 1274; ^1H NMR ($(CD_3)_2CO$, 270 MHz): δ 12.96 (s, 1H, OH), 7.67 (d, 1H arom., J=8 Hz), 7.37 (d, 1H arom., J=8 Hz), 7.26 (t, 1H arom., J=8 Hz), 6.30 (s, 1H arom.), 4.92 (br s, 1H, $C(CH_3)$=CH_2), 4.73 (br s, 1H, $C(CH_3)$=CH_2), 4.51 (dd, 1H, CH_2CHOH, J=7.5, 4 Hz), 3.33 (dd, 1H, CH_2CHOH, J=14.5, 4 Hz), 3.13 (dd, 1H, CH_2CHOH, J=14.5, 7.5 Hz), 1.88 (s, 3H, CH_3); ^{13}C NMR ($(CD_3)_2CO$, 270 MHz): δ 181.9 (*C*O), 165.5, 162.8, 156.0 (3×quat. arom. C), 148.3 (CH_2=*C*(CH_3)), 147.1, 146.2 (2×quat. arom. C), 124.7 (arom. CH), 122.1 (quat. arom. C), 121.2, 116.2 (2×arom. CH), 110.3 (*C*H_2=C(CH_3)), 105.5, 103.7 (2×quat. arom. C), 99.4 (arom. CH), 76.4 (CH_2*C*HOH), 29.9 (*C*H_2CHOH), 18.6 (*C*H_3); EI-HRMS Calcd for $C_{18}H_{16}O_6$ (M^+) 328.0947, Found 328.0936.

4.3.6. 6-Deoxyisojacareubin=6,11-dihydroxy-3,3-dimethyl-3*H*,7*H*-pyrano[2,3-*c*]-xanthen-7-one 17. The typical conditions described in Section 4.3 were applied to **10** (30 mg, 0.1 mmol). The purification of the crude product by preparative TLC (1% MeOH/CH_2Cl_2) yielded **17** as a yellow solid (5 mg, 17%), mp 235–236 °C; IR (cm^{-1}): 3223, 1646, 1579, 1289; ^1H NMR ($(CD_3)_2CO$, 270 MHz): δ 13.10 (s, 1H, OH), 9.22 (s, 1H, OH), 7.68 (dd, 1H arom., J=8, 1.5 Hz), 7.39 (dd, 1H arom., J=8, 1.5 Hz), 7.30 (dd, 1H arom., J=8, 7.5 Hz), 7.05 (d, 1H arom., J=10 Hz), 6.20 (s, 1H arom.), 5.77 (d, 1H arom., J=10 Hz), 1.48 (s, 6H, 2×CH_3); ^{13}C NMR ($(CD_3)_2CO$, 270 MHz): δ 181.8 (*C*O), 164.1, 161.7, 156.1, 146.9, 146.0 (5×quat. arom. C), 128.1, 125.1 (2×arom. CH), 122.2 (quat. arom. C), 122.0, 116.5, 115.7 (3×arom. CH), 104.1, 102.1 (2×quat. arom. C), 99.6 (arom. CH), 79.1 (CH*C*(CH_3)$_2$), 28.4 (2×*C*H_3); EI-HRMS Calcd for $C_{18}H_{14}O_5$ (M^+) 310.0841, Found 310.0836.

4.3.7. Dicaledol=1,3,5-trihydroxy-2,4-bis(2-hydroxy-3-methylbut-3-enyl)-9*H*-xanthen-9-one 21. The typical conditions described in Section 4.3 were applied to **11** (20 mg, 0.05 mmol). The purification of the crude product by preparative TLC (5% MeOH/CH_2Cl_2) yielded **21** as a yellow solid (3 mg, 14%), mp 159–161 °C; IR (cm^{-1}): 3219, 1641, 1580, 1222; ^1H NMR ($(CD_3)_2CO$, 270 MHz): δ 13.47 (s, 1H, OH), 7.67 (dd, 1H arom., J=8, 1.5 Hz), 7.36 (dd, 1H arom., J=8, 1.5 Hz), 7.26 (t, 1H arom., J=8 Hz), 4.92 (br s, 1H, $C(CH_3)$=CH_2), 4.86 (br s, 1H, $C(CH_3)$=CH_2), 4.75 (br s, 1H, $C(CH_3)$=CH_2), 4.68 (br s, 1H, $C(CH_3)$=CH_2), 4.50 (dd, 1H, CH_2CHOH, J=7.5, 4 Hz), 4.42 (dd, 1H, CH_2CHOH, J=8, 4 Hz), 3.29 (dd, 1H, CH_2CHOH, J=14.5, 4 Hz), 3.14 (dd, 1H, CH_2CHOH, J=14.5, 7.5 Hz), 3.10 (dd, 1H, CH_2CHOH, J=14, 4 Hz), 2.93 (dd, 1H, CH_2CHOH, J=14, 8 Hz), 1.89 (s, 3H, CH_3), 1.85 (s, 3H, CH_3); ^{13}C NMR ($(CD_3)_2CO$, 270 MHz): δ 182.0 (*C*O), 164.3, 160.3, 154.5 (3×quat. arom. C), 148.6, 148.4 (2×CH_2=*C*(CH_3)), 147.0, 146.2 (2×quat. arom. C), 124.5 (arom. CH), 122.0 (quat. arom. C), 121.1, 116.3 (2×arom. CH), 110.4, 110.1 (2×*C*H_2=C(CH_3)), 109.5, 105.8, 103.4 (3×quat. arom. C), 76.5, 76.3 (2×CH_2*C*HOH), 30.3, 29.9 (2×*C*H_2CHOH), 18.4, 18.2 (2×*C*H_3); CI-HRMS Calcd for $C_{23}H_{25}O_7$ ([M+H]$^+$) 413.1600, Found 413.1585.

4.3.8. 6,11-Dihydroxy-5-(2-hydroxy-3-methylbut-3-enyl)-3,3-dimethyl-3*H*,7*H*-pyrano[2,3-*c*]-xanthen-7-one 20. The typical conditions described in Section 4.3 were applied to **11** (20 mg, 0.05 mmol). The purification of the crude product by preparative TLC (5% MeOH/CH_2Cl_2) yielded **20** as a green solid (5 mg, 21%), mp 180–182 °C; IR (cm^{-1}): 3397, 1647, 1616, 1118; ^1H NMR ($(CD_3)_2CO$, 270 MHz): δ 13.49 (s, 1H, OH), 9.18 (s, 1H, OH), 7.69 (dd, 1H arom., J=8, 1.5 Hz), 7.39 (dd, 1H arom., J=8, 1.5 Hz), 7.29 (t, 1H arom., J=8 Hz), 7.07 (d, 1H arom., J=10 Hz), 5.77 (d, 1H arom., J=10 Hz), 4.75 (br s, 1H, $C(CH_3)$=CH_2), 4.67 (br s, 1H, $C(CH_3)$=CH_2), 4.42 (m, 1H, CH_2CHOH), 2.96 (dd, 1H, CH_2CHOH, J=13.5, 6.5 Hz), 2.83–2.90 (m, 1H, CH_2CHOH), 1.85 (s, 3H, CH_3), 1.52 (s, 6H, 2×CH_3); ^{13}C NMR ($(CD_3)_2CO$, 270 MHz): δ 181.9 (*C*O), 162.0, 159.8, 150.9 (3×quat. arom. C), 149.1 (CH_2=*C*(CH_3)), 146.9, 146.0 (2×quat. arom. C), 127.7, 125.0 (2×arom. CH), 122.2 (quat. arom. C), 121.8, 116.5, 116.0 (3×arom. CH), 110.3 (*C*H_2=C(CH_3)), 109.9, 103.6, 101.6 (3×quat. arom. C), 79.2 (CH*C*(CH_3)$_2$), 75.2 (CH_2*C*HOH), 29.7 (*C*H_2CHOH), 28.5, 28.4, 17.1 (3×*C*H_3); EI-HRMS Calcd for $C_{23}H_{22}O_6$ (M^+) 394.1416, Found 394.1412.

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References and notes

1. Guilet, D.; Morel, C.; Noyer, N.; Cornec, M.; Séraphin, D.; Wiart, C.; Hamid, A.; Hadi, A.; Sévenet, T.; Richomme, P.; Bruneton, J. *Heterocycles* **1999**, *51*, 67–76.
2. Morel, C.; Dartiguelongue, C.; Youhanna, T.; Oger, J.-M.; Séraphin, D.; Duval, O.; Richomme, P.; Bruneton, J. *Heterocycles* **1999**, *17*(3), 195–199.
3. (a) Guilet, D.; Rondeau, D.; Séraphin, D.; Richomme, P.; Bruneton, J. *Phytochemistry* **2001**, *58*, 571–575. (b) Oger, J.-M.; Morel, C.; Hélesbeux, J. J.; Litaudon, M.; Séraphin, D.; Dartiguelongue, C.; Larcher, G.; Richomme, P.; Duval, O. *Nat. Prod. Res.* **2003**, *17*(3), 195–199. (c) Guilet, D. PhD Dissertation, Université d' Angers, 2000.
4. Terao, L. S.; Shiraishi, M.; Kato, K. *Synthesis* **1979**, 467–468.
5. Sharma, P. D.; Shoeb, A.; Kapil, R. S.; Popli, S. P. *Ind. J. Chem. B* **1980**, *19*, 938–939.
6. Gupta, G. K.; Suri, J. L.; Gupta, B. K.; Dhar, K. L. *Phytochemistry* **1982**, *21*, 2149–2151.
7. Crombie, L.; Games, D. E.; Haskins, N. J.; Reed, G. F. *J. Chem. Soc. Perkin Trans. 1* **1972**, 2255–2260.
8. Schenck, G. O. *Angew. Chem.* **1957**, *69*, 579–599.
9. Ito, C.; Furukawa, H. *Chem. Pharm. Bull.* **1989**, *37*, 819–820.
10. Ito, C.; Fujiwara, K.; Kajita, M.; Ju-Ichi, M.; Takemura, Y.; Suzuki, Y.; Tanaka, K.; Omura, M.; Furukawa, H. *Chem. Pharm. Bull.* **1991**, *39*, 2509–2513.
11. Hélesbeux, J.-J.; Guilet, D.; Séraphin, D.; Duval, O.;

Richomme, P.; Bruneton, J. *Tetrahedron Lett.* **2000**, *41*, 4559–4562.
12. Crombie, L.; Jones, R. C. F.; Palmer, C. J. *J. Chem. Soc. Perkin Trans. 1* **1987**, 317–331.
13. Govindachari, T. R.; Pai, B. R.; Subramaniam, P. S.; Rao, U. R.; Muthukumaraswamy, N. *Tetrahedron Lett.* **1967**, *23*, 243–248.
14. Grover, P. K.; Shah, G. D.; Shah, R. C. *J. Chem. Soc.* **1955**, 3982–3985.
15. Scannell, R. T.; Stevenson, R. *J. Heterocycl. Chem.* **1986**, *23*, 857–859.
16. Ho, D. K.; McKenzie, A. T.; Byrn, S. R.; Cassady, J. M. *J. Org. Chem.* **1987**, *52*, 342–347.
17. Quillinan, A. J.; Scheinmann, F. *J. Chem. Soc. Perkin Trans. 1* **1973**, 1329–1337.
18. Crombie, L.; Games, D. E.; McCormick, A. *Tetrahedron Lett.* **1966**, 151–156.
19. Lin, C. N.; Liou, S. S.; Ko, F. N.; Teng, C. M. *J. Pharm. Sci.* **1992**, *81*, 1109–1112.
20. Liou, S.-S.; Shieh, W.-L.; Cheng, T.-H.; Won, S.-J.; Lin, C.-N. *J. Pharm. Pharmacol.* **1993**, *45*, 791–794.
21. Gujral, V.; Gupta, S. R. *Bull. Chem. Soc. Jpn* **1979**, *52*, 3679–3681.
22. Anand, S. M.; Jain, A. C. *Tetrahedron* **1972**, *28*, 987–990.
23. Anand, S. M.; Jain, A. C. *Aust. J. Chem.* **1974**, *27*, 1515–1520.
24. Jackson, B.; Locksley, H. D.; Scheinmann, F. *J. Chem. Soc. (C)* **1967**, 2500–2507.
25. Scheinmann, F.; Owen, P. J. *J. Chem. Soc. Perkin Trans. 1* **1974**, 1018–1021.
26. Govindachari, T. R.; Kalyanaraman, P. S.; Muthukumaraswamy, N.; Pai, B. R. *Tetrahedron* **1971**, *23*, 3919–3926.
27. Guilet, D.; Séraphin, D.; Rondeau, D.; Richomme, P.; Bruneton, J. *Phytochemistry* **2001**, *58*, 571–575.
28. Stratakis, M.; Orfanopoulos, M. *Tetrahedron* **2000**, *56*, 1595–1615.
29. Hélesbeux, J.-J. PhD Dissertation, University of Angers, 2002.
30. Hélesbeux, J.-J.; Duval, O.; Guilet, D.; Séraphin, D.; Rondeau, D.; Richomme, P. *Tetrahedron* **2003**, *59*, 5091–5104.
31. Wu, Q.-L.; Wang, S.-P.; Du, L.-J.; Yang, J.-S.; Xiao, P.-G. *Phytochemistry* **1998**, *49*, 1395–1402.
32. Fourrey, J. L.; Rondest, J.; Polonsky, J. *Tetrahedron* **1970**, *26*, 3839–3847.