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Synthesis of chromenes with isoprenoid side chains and their selective ozonolysis

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The reactions of trimethylhydroquinone with isoprenoid allylic alcohols catalyzed by a Pentasil type zeolite in the H-form gave trimethyl-1,4-benzoquinones with the corresponding isoprenoid group, which were subsequently transformed into the target Δ^3-chromenes on treatment with pyridine. Partial ozonolysis of chromenes proceeded selectively at the Δ-bond of the side chain, resulting in the corresponding chromenes with an ω-carbonyl group.

Key words: 1,4-benzoquinones, Δ^3-chromenes, isoprenoids, allylic alcohols, hydroquinones, zeolites, ozonolysis, aldehydes.

Chromenes with isoprenoid side chains are frequently encountered in nature, being structural analogs of prenylated coumarins, chalcones, and cannabinoids;[1—3] this accounts for the enhanced interest in the synthesis of these compounds. Two approaches have been developed most thoroughly, namely, (1) an approach using the pyridine-catalyzed reaction of α,β-unsaturated aldehydes with phenols[4] and (2) a two-step route comprising the reaction of trimethylhydroquinone (TMHQ) with tertiary allylic alcohols to give prenylated 1,4-benzoquinones and subsequent cyclization of these compounds induced by pyridine.[5] Alkylation of TMHQ with allylic alcohols catalyzed by Lewis acids (usually $ZnCl_2$ or $BF_3 \cdot OEt_2$) is the key step in the latter method.

We synthesized prenylated 1,4-benzoquinones using a heterogeneous zeolite of the Pentasil type in the H-form. Unlike the zeolite-containing Tseokar-10 catalyst, which we used in the synthesis of α-tocopherol and its analogs,[6,7] the Pentasil catalyst is less active because the concentration of the acidic active sites on its surface is lower.[8]

The reactions of TMHQ with linalool (**1**) and a 1 : 1 mixture of (3*R*,4*S*)- and (3*S*,4*S*)-3,4,8-trimethylnona-1,7-dien-3-ols (**2**) (*ee* ~50%) in the presence of Pentasil were found to afford 1,4-benzoquinones **3** and **4**, respectively. Pyridine-induced cyclization of these products proceeded smoothly to give chromene **5** and a mixture of chromene **6** diasteromers, respectively.

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The configuration of the double bond in the isoprenoid side chain of quinones **3** and **4** was confirmed unambiguously by the ^1H and ^{13}C NMR spectra. Thus in ^1H NMR spectra, the presence of only three singlets for the CH_3-group protons corresponding to two terminal methyl groups and one internal CH_3 group at the double bonds point to a uniform configuration of the isoprenoid $\Delta^{2',3'}$-bond in compounds **3** and **4**. The *trans*-geometry of this bond can be derived[9] from the ^{13}C NMR spectra in which the CH_3 groups at the internal double bond are responsible for signals at δ 16.0—17.5, while the signals for the C(4′) allylic carbon atoms connected to tetrasubstituted carbon occur at about δ 39.6 (for **3**) and 42.3 (for **4**).

As in the case of allylic alcohols **1** and **2**, the use of racemic (*RS*)-isophytol (**9**) resulted in the successive synthesis of diastereomeric mixtures of quinones **10** and chromenes **11**. It should be noted that the attempts to prepare chromene **11** by the reaction of phytal with TMHQ failed.[3]

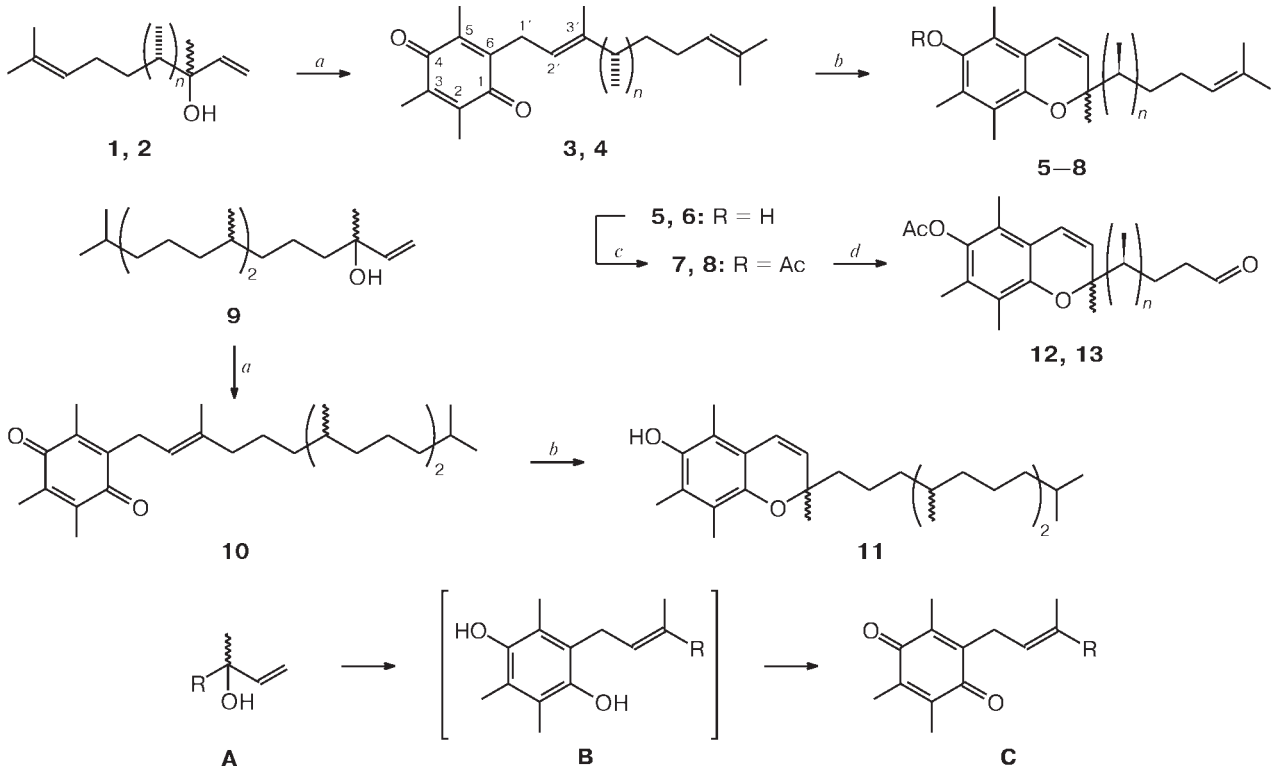
According to published data,[5] it can be conceived that the reaction of type **A** allylic alcohols with TMHQ under the given conditions gives rise to alkylated hydroquinones **B**. Evidently, due to the lower acidity of Pentasil (compared with the Tseokar-10 catalyst, which we used previously and which induced cyclization of the intermediate adduct to give the corresponding chromane[6,7]), the reaction stops at the step of type **B** hydroquinones, which are readily oxidized in air to give the corresponding quinones of type **C** (Scheme 1).

Ozonolysis of chromenes **5** and **6** at the side-chain double bond opens up the way to ω-functionalized chromenes, which can be further converted into more complex chromene derivatives. However, under ozonolysis conditions described previously, chromenes gave only benzaldehydes and benzoic acids with the corresponding substituents.[1] We found that in the ozonolysis of chromenyl acetates **7** and **8** with an equimolar amount of ozone (*cf.* Refs. 7, 10), it is possible to cleave selectively the double bond in the side chain and obtain the required aldehydes **12** and **13**. Thus, using a zeolite catalyst of the Pentasil type, chromenes with unsaturated isoprenoid chains were synthesized, whose partial ozonolysis yielded chromenes with the aldehyde group in the side chain.

Experimental

IR spectra of substances were obtained on a Specord 75-IR spectrometer (in thin film); UV spectra were measured on a

Scheme 1



n = 0 (**1**, **3**, **5**, **7**, **12**), 1 (**2**, **4**, **6**, **8**, **13**)

Reagents and conditions: *a*. (1) TMHQ/Pentasil ZSM-5/11, *n*-C_9H_{20}, refluxing, (2) O_2/SiO_2; *b*. Py, refluxing; *c*. Ac_2O/Py; *d*. $O_3/Me_2CO/Ba(OH)_2$.

Specord M-40 spectrometer in $CHCl_3$. ^1H and ^{13}C NMR spectra were run on Bruker AM-300 instruments (operating at 300.13 MHz for ^1H and at 75 MHz, for ^{13}C) using $CDCl_3$ as the solvent. Chemical shifts are given in the δ scale relative to Me_4Si (internal standard). GLC analysis was carried out on a Chrom-5 chromatograph using a 2400×4 mm column, the Chromaton N-AW-DMCS stationary phase, and SE-30 (5%), at a working temperature of 50—300 °C (8 K min^{-1}), and using helium as the carrier gas. Specific rotation was measured on a Perkin—Elmer-141 polarimeter and expressed in (deg mL) $(g\ dm)^{-1}$, while the solution concentration is in g $(100\ mL)^{-1}$.

Allylic alcohol **1** (Fluka) was used as received and alcohol **2** ($[\alpha]_D^{13}$ −7.8 (*c* 6.9, $CHCl_3$)) was prepared by a previously described procedure.[6]

Preparation of the ZSM-5/11 catalyst. A Pentasil zeolite prepared by a previously described[11] procedure (except that monoethanolamine was used as the template) was converted into the H-form on treatment with a 1 *M* solution of NH_4NO_3 at 60 °C followed by heating at 540 °C for 4 h in an air flow.

2,3,5-Trimethyl-6-(3,7-dimethylocta-2*E*,6-dien-1-yl)-1,4-benzoquinone (geranyltrimethylbenzoquinone) (3). Allylic alcohol **1** (0.4 g, 2.6 mmol) was slowly added in a flow of Ar to a vigorously stirred suspension of TMHQ (0.2 g, 1.3 mmol) and finely crushed ZSM-5/11 catalyst (0.45 g) in 9 mL of anhydrous nonane. The reaction mixture was refluxed for 5 h and cooled to ~20 °C, the catalyst was filtered off, and the filtrate was concentrated *in vacuo*. The residue (0.5 g) was dissolved in ~2 mL of Et_2O, applied onto ~1 g of silica gel, and kept in a Petri dish at 50 °C for ~0.5 h. After complete evaporation of the solvent, silica gel with the substance was transferred onto the adsorbent bed in a chromatographic column, washed with hexane, and eluted with a 20 : 1 hexane—Et_2O mixture to give 0.13 g (34%) of quinone **3**, n_D^{24} 1.5247. IR, ν/cm^{-1}: 1630 (C=O). UV, λ_{max}/nm (ε): 257 (15883), 265 (15750) (*cf.* Ref. 12). ^1H NMR, δ: 1.48, 1.57 and 1.68 (all s, each 3 H, C(3′)CH_3, C(7′)CH_3, H(8′)); 1.95 (m, 13 H, C(3)CH_3, C(5)CH_3, C(6)CH_3, H(4′), H(5′)); 3.12 (d, 2 H, H(1′), *J* = 6.8 Hz); 4.85 (t, 1 H, H(2′), *J* = 6.8 Hz); 4.95 (t, 1 H, H(6′), *J* = 7.1 Hz). ^{13}C NMR, δ: 12.0, 12.2, 12.3 (C(2)$\underline{C}H_3$, C(3)$\underline{C}H_3$, C(5)$\underline{C}H_3$); 16.1 (C(3′)$\underline{C}H_3$); 17.5 (C(7′)$\underline{C}H_3$); 25.4 (C(5′)); 25.5 (C(8′)); 26.4 (C(1′)); 39.6 (C(4′)); 119.4 (C(2′)); 124.0 (C(6′)); 131.2 (C(7′)); 136.8 (C(3′)); 140.06, 140.1, 140.2 (C(2), C(3), C(5)); 143.0 (C(6)); 186.7, 187.7 (C(1), C(4)).

2,3,5-Trimethyl-6-(3,4*S*,8-trimethylnona-2*E*,7-dien-1-yl)-1,4-benzoquinone (4). TMHQ (0.2 g, 1.3 mmol), allylic alcohols **2** (0.48 g, 2.64 mmol), and the ZSM-5/11 catalyst (0.45 g) in 9 mL of anhydrous nonane were refluxed for 5 h and then worked-up as described in the previous experiment to give 0.14 g (34%) of quinone **4**, n_D^{24} 1.5218, $[\alpha]_D^{23}$ +0.39 (*c* 2.4, $CHCl_3$). Found (%): C, 80.00, H, 9.48. $C_{21}H_{30}O_2$. Calculated (%): C, 80.21, H, 9.62. IR, ν/cm^{-1}: 1630 (C=O). UV, λ_{max}/nm (ε): 257 (16117), 265 (16476). ^1H NMR, δ: 0.87 (d, 3 H, C(4′)CH_3, *J* = 6.8 Hz); 1.10—1.30 (m, 2 H, H(5′)); 1.42, 1.57, 1.59 (all s, each 3 H, C(3′)CH_3, C(8′)CH_3, H(9′)); 1.60—1.80 (m, 2 H, H(6′)); 1.90 (m, 9 H, C(3)CH_3, C(5)CH_3, C(6)CH_3); 3.12 (d, 2 H, H(1′), *J* = 6.8 Hz); 4.85 (t, 1 H, H(2′), *J* = 6.9 Hz); 4.95 (t, 1 H, H(7′), *J* = 7.1 Hz). ^{13}C NMR, δ: 11.9, 12.1 (C(2)$\underline{C}H_3$, C(3)$\underline{C}H_3$, C(5)$\underline{C}H_3$); 17.3 (C(3′)$\underline{C}H_3$ and C(8′)$\underline{C}H_3$); 19.5 (C(4′)$\underline{C}H_3$); 25.1 (C(6′)); 25.6 (C(9′)); 25.9 (C(1′)); 34.7 (C(5′)); 42.3 (C(4′)); 118.9 (C(2′)); 124.5 (C(7′)); 130.8 (C(8′)); 140.7 (C(3′)); 139.9, 140.0, 140.2 (C(2), C(3), C(5)); 143.0 (C(6)); 186.6, 187.5 (C(1), (C(4)).

2,3,5-Trimethyl-6-(3,7*RS*,11*RS*,15-tetramethylhexadec-2*E*-en-1-yl)-1,4-benzoquinones (phytyltrimethylbenzoquinones) (10). Refluxing of TMHQ (0.1 g, 0.66 mmol), isophytol **9** (0.39 g, 1.32 mmol), and ZSM-5/11 (0.1 g) in 4 mL of anhydrous nonane for 3 h gave, as described above, 0.16 g (57%) of quinones **10**, n_D^{20} 1.4942. IR, ν/cm^{-1}: 1630 (C=O). UV, λ_{max}/nm (ε): 257 (16120), 265 (16711) (*cf.* Ref. 12). ^1H NMR, δ: 0.85 (d, 12 H, C(7′)CH_3, C(11′)CH_3, C(15′)CH_3, H(16′), *J* = 6.1 Hz); 1.00—2.10 (m, 21 H, H(4′)—H(15′)); 2.00 (m, 9 H, C(3)CH_3, C(5)CH_3, C(6)CH_3); 3.10 (d, 2 H, H(1′), *J* = 6.9); 4.95 (t, 1 H, H(2′), *J* = 6.9 Hz). ^{13}C NMR, δ: 11.9, 12.2, 13.0 (C(2)$\underline{C}H_3$, C(3)$\underline{C}H_3$, C(5)$\underline{C}H_3$); 16.2 (C(3′)$\underline{C}H_3$); 19.7 (C(7′)$\underline{C}H_3$, C(11′)$\underline{C}H_3$); 22.7 (C(15′)$\underline{C}H_3$, C(16′)); 24.5 (C(3′)); 24.8 (C(9′)); 25.3 (C(5′)); 25.6 (C(1′)); 28.0 (C(15′)); 32.7 (C(11′)); 32.8 (C(7′)); 36.7 (C(6′)); 37.4 (C(8′), C(10′), C(12′)); 39.5 (C(14′)); 40.1 (C(4′)); 119.3 (C(2′)); 137.2 (C(3′)); 137.4, 140.3, 143.2 (C(2), C(3), C(5), C(6)); 186.8, 187.7 (C(1), (C(4)).

(*RS*)-2,5,7,8-Tetramethyl-2-(4-methylpent-3-en-1-yl)-6-hydroxy-3-chromene (5). A solution of quinone **3** (0.59 g, 1.22 mmol) in 9 mL of anhydrous Py was refluxed for 16 h, cooled to ~20 °C, diluted with brine, and extracted with hexane. The extract was washed with H_2O and dried with $MgSO_4$. The residue after solvent evaporation *in vacuo* was chromatographed on SiO_2, the product being eluted with a 10 : 1 *n*-hexane—Et_2O mixture to give 0.39 g (66%) of chromene **5**, n_D^{24} 1.5448. UV, λ_{max}/nm (ε): 276 (8528), 286 (8210), 334 (3113) (*cf.* Ref. 12). ^1H NMR, δ: 1.45 (s, 3 H, C(2)CH_3); 1.68 and 1.75 (both s, 6 H, H(5′), C(4′)CH_3); 1.75 (m, 2 H, H(1′)); 2.20 (m, 11 H, H(2′), ArCH_3); 4.65 (s, 1 H, OH); 5.18 (t, 1 H, H(3′), *J* = 7.1 Hz); 5.68 (d, 1 H, H(3), *J* = 10.0 Hz); 6.60 (d, 1 H, H(4), *J* = 10.0 Hz). ^{13}C NMR, δ: 10.8, 11.5, 12.3 (C(5)$\underline{C}H_3$, C(7)$\underline{C}H_3$, C(8)$\underline{C}H_3$); 17.4 (C(4′)$\underline{C}H_3$); 22.6 (C(2′)); 25.2 (C(2)$\underline{C}H_3$); 25.6 (C(5′)); 40.2 (C(1′)); 76.4 (C(2)); 120.1 (C(3′)); 116.5 (C(10)); 117.6 (C(5)); 122.1 (C(8)); 123.2 (C(7)); 124.3 (C(3)); 129.6 (C(4)); 131.3 (C(4′)); 144.5 (C(9)); 145.2 (C(6)).

2*RS*,5,7,8-Tetramethyl-2-(1*S*,5-dimethylhex-4-en-1-yl)-6-hydroxy-3-chromenes (6). Refluxing of quinone **4** (0.21 g, 0.69 mmol) in 3 mL of anhydrous Py gave, as described above, 0.13 g (59%) of a mixture of (2*R*,1′*S*)-*erythro*- and (2*S*,1′*S*)-*threo*-chromenes **6**, $[\alpha]_D^{20}$ −7.0 (*c* 0.47, $CHCl_3$). Found (%): C, 80.13, H, 9.50. $C_{21}H_{30}O_2$. Calculated (%): C, 80.21, H, 9.62. UV, λ_{max}/nm (ε): 273 (7828), 284 (7617), 334 (3513). ^1H NMR, δ: 1.00 (m, 3 H, C(1′)CH_3); 1.30 (s, 3 H, C(2)CH_3); 1.59, 1.61, 1.67, 1.70 (all s, 6 H, C(5′)CH_3, H(6′)); 1.50—1.90 (m, 5 H, H(1′), H(2′), H(3′)); 2.15 (m, 9 H, ArCH_3); 4.48 (br.s, 1 H, OH); 5.10 (m, 1 H, H(4′)); 5.68 (m, 1 H, H(3)); 6.53 (d, 1 H, H(4), *J* = 10.0 Hz). ^{13}C NMR, δ: 10.9, 11.6, 12.5 (C(5)$\underline{C}H_3$, C(7)$\underline{C}H_3$, C(8)$\underline{C}H_3$); 14.0, 13.9 ((C(1′)$\underline{C}H_3$); 17.7 (C(5′)$\underline{C}H_3$); 21.9, 22.7 (C(2)$\underline{C}H_3$); 25.7 (C(6′)); 26.2, 26.5 (C(3′)); 31.3, 31.6 (C(2′)); 40.5, 40.7 (C(1′)); 79.2, 79.3 (C(2)); 120.1 (C(4′)); 116.2 (C(10)); 118.0 (C(5)); 122.2 (C(8)); 123.2 (C(7)); 124.8 (C(3)); 129.2, 129.6 (C(4)); 131.4 (C(5′)); 144.5 (C(9)); 145.3 (C(6)).

2*RS*,5,7,8-Tetramethyl-2-(4*RS*,8*RS*,12-trimethyltridec-1-yl)-6-hydroxy-3-chromenes (11). Refluxing of quinones **10** (0.44 g, 1.02 mmol) in 4.4 mL of anhydrous Py gave, as de-

scribed above, 0.29 g (66%) of a mixture of chromenes **11**, n_D^{24} 1.5096, UV, λ_{max}/nm (ε): 272 (9200), 283 (8200), 333 (4100) (*cf*. Ref. 12). ^{1}H NMR, δ: 0.92 (m, 12 H, C(4′)CH$_3$, C(8′)CH$_3$, C(12′)CH$_3$, H(13′)); 1.05—1.72 (m, 21 H, H(1′)—H(12′)); 1.38 (s, 3 H, C(2)CH$_3$); 2.20 (m, 9 H, ArCH$_3$); 4.48 (br.s, 1 H, OH); 5.65 (d, 1 H, H(3), J = 10.0 Hz); 6.57 (d, 1 H, H(4), J = 10.0 Hz). ^{13}C NMR, δ: 10.8, 11.5, 12.4 (C(5)CH$_3$, C(7)CH$_3$, C(8)CH$_3$); 19.6, 19.6, 19.7, 19.7 (C(4′)CH$_3$, C(8′)CH$_3$); 22.6, 22.7 (C(12′)CH$_3$, C(13′)); 24.4 (C(6′)); 24.8 (C(2′) C(10′)); 28.0 (C(12′)); 32.8, 32.9 (C(4′), C(8′)); 37.2, 37.3, 37.4, 37.4 (C(3′), C(5′), C(7′), C(9′)); 39.4 (C(11′)); 40.0 (C(1′)); 76.6 (C(2)); 116.2 (C(5)); 118.5 (C(10)); 120.1 (C(3)); 122.2 (C(8)); 123.1 (C(7)); 129.9 (C(4)); 144.9 (C(9)); 145.3 (C(6)).

(*RS*)-2,5,7,8-Tetramethyl-2-(4-methylpent-3-en-1-yl)-6-acetoxy-3-chromene (7). A solution of chromene **5** (0.42 g, 1.48 mmol) in 4 mL of Ac$_2$O and 5.3 mL of anhydrous Py was kept at ~20 °C for 3 h, poured on ice, extracted with Et$_2$O, washed with 3 *M* HCl, a saturated solution of NaHCO$_3$, and H$_2$O, and dried with MgSO$_4$ to give 0.42 g (87%) of a mixture of chromenes **7**. Found (%): C, 76.53; H, 8.45. C$_{21}$H$_{28}$O$_3$. Calculated (%): C, 76.79; H, 8.59. IR, ν/cm^{-1}: 1740 (C=O). UV, λ_{max}/nm (ε): 272 (8600); 283 (6900); 320 (2600). ^{1}H NMR, δ: 1.38 (s, 3 H, C(2)CH$_3$); 1.60, 1.70 (both s, 6 H, H(5′), C(4′)CH$_3$); 1.70 (m, 2 H, H(1′)); 2.04, 2.08, 2.15 (all s, 9 H, ArCH$_3$); 2.15 (m, 2 H, H(2′)); 2.33 (s, 3 H, CH$_3$C=O); 5.12 (t, 1 H, H(3′), J = 6.9 Hz); 5.60 (d, 1 H, H(3), J = 10.0 Hz); 6.52 (d, 1 H, H(4), J = 10.0 Hz). ^{13}C NMR, δ: 11.4, 11.8, 13.0 (C(5)CH$_3$, C(7)CH$_3$, C(8)CH$_3$); 17.5 (C(4′)CH$_3$); 20.2 (CH$_3$CO); 22.6 (C(2′)); 25.5 (C(2)CH$_3$); 25.7 (C(5′)); 40.6 (C(1′)); 77.1 (C(2)); 117.4 (C(10)); 119.8 (C(3′)); 122.2 (C(8)); 122.4 (C(5)); 124.1 (C(3)); 129.2 (C(7)); 129.3 (C(4)); 131.3 (C(4′)); 145.0 (C(9)); 148.3 (C(6)); 169.3 (C=O).

2*RS*,5,7,8-Tetramethyl-2-(1*S*,5-dimethylhex-4-en-1-yl)-6-acetoxy-3-chromenes (8). A solution of a mixture of chromenes **6** (0.63 g, 2.01 mmol) in 5.5 mL of Ac$_2$O and 7 mL of anhydrous Py was kept at ~20 °C for 3 h, poured on ice, extracted with Et$_2$O, washed with 3 *M* HCl, a saturated solution of NaHCO$_3$, and H$_2$O, and dried with MgSO$_4$ to give 0.63 g (88%) of a mixture of (2*R*,1′*S*)-*erythro*- and (2*S*,1′*S*)-*threo*-diastereomers **8**, $[\alpha]_D^{20}$ −5.5 (*c* 0.74, CHCl$_3$). Found (%): C, 77.31; H, 8.96. C$_{23}$H$_{32}$O$_3$. Calculated (%): C, 77.49; H, 9.05. IR, ν/cm^{-1}: 1740 (C=O). UV, λ_{max}/nm (ε): 273 (5700); 283 (5000); 321 (1950). ^{1}H NMR, δ: 0.98 (d, 3 H, C(1′)CH$_3$, J = 6.8 Hz); 1.32 (s, 3 H, C(2)CH$_3$); 1.58, 1.60, 1.68, 1.70 (all s, 6 H, C(5′)CH$_3$, H(6′)); 1.50—2.00 (m, 5 H, H(1′), H(2′), H(3′)); 2.00, 2.05, 2.08, 2.10 (all s, 9 H, ArCH$_3$); 2.33 (s, 3 H, CH$_3$C=O); 5.10 (m, 1 H, H(4′)); 5.15 (m, 1 H, H(3)); 6.50 (d, 1 H, H(4), J = 10.2 Hz). ^{13}C NMR, δ: 11.3, 11.4, 13.0 (C(5)CH$_3$, C(7)CH$_3$, C(8)CH$_3$); 13.7, 13.8 (C(1′)CH$_3$); 17.8 (C(5′)CH$_3$); 20.3 (CH$_3$CO); 22.4 (C(2)CH$_3$); 25.5 (C(6′)); 26.0, 26.2 (C(3′)); 31.2, 31.3 (C(2′)); 40.9, 41.0 (C(1′)); 79.8 (C(2)); 117.5 (C(10)); 119.6 (C(4′)); 122.2 (C(8)); 122.3 (C(5)); 124.6 (C(3)); 128.6 (C(7)); 128.8, 129.0 (C(4)); 131.2 (C(5′)); 141.1 (C(9)); 148.2 (C(6)); 169.4 (C=O).

(*RS*)-2,5,7,8-Tetramethyl-2-(3-oxoprop-1-yl)-6-acetoxy-3-chromene (12). An ozone—oxygen mixture (ozonizer productivity 15 mmol h^{-1}) at a flow rate of 30 L h^{-1} was passed for 5 min (1.28 mmol O$_3$) at ~20 °C through a mixture of acetate **7** (0.42 g, 1.28 mmol), Ba(OH)$_2$ (0.44 g, 2.57 mmol), 0.1 mL of H$_2$O, and 4 mL of acetone at ~20 °C. After completion of the reaction, the precipitate was filtered off and the filtrate was concentrated *in vacuo*. The residue was dissolved in 10 mL of EtOAc and dried with MgSO$_4$ and the solvent was evaporated. The residue was chromatographed on SiO$_2$ using a 10 : 1 *n*-hexane—Et$_2$O mixture as the eluent to give 0.123 g (41%) of aldehyde **12**. Found (%): C, 71.29; H, 7.20. C$_{18}$H$_{22}$O$_4$. Calculated (%): C, 71.50; H, 7.33. IR, ν/cm^{-1}: 1710 and 1740 (C=O). UV, λ_{max}/nm (ε): 272 (9300); 282.5 (7500); 318 (2900). ^{1}H NMR, δ: 1.35 (s, 3 H, C(2)CH$_3$); 2.02, 2.05, 2.08 (all s, 9 H, ArCH$_3$); 2.15 (m, 2 H, H(1′)); 2.32 (s, 3 H, CH$_3$C=O); 2.60 (m, 2 H, H(2′)); 5.53 (d, 1 H, H(3), J = 10.1 Hz); 6.55 (d, 1 H, H(4), J = 10.1 Hz); 9.78 (t, 1 H, H(3′), J = 1.1 Hz). ^{13}C NMR, δ: 11.5, 11.5, 13.1 (C(5)CH$_3$, C(7)CH$_3$, C(8)CH$_3$); 20.4 (CH$_3$CO); 26.1 (C(2)CH$_3$); 39.1 (C(1′)); 65.8 (C(2′)); 76.8 (C(2)); 117.2 (C(10)); 120.9 (C(3)); 122.6 (C(8)); 122.7 (C(5)); 128.1 (C(4)); 129.4 (C(7)); 141.6 (C(9)); 148.0 (C(6)); 169.4 (CH$_3$CO); 202.1 (CO).

2*RS*,5,7,8-Tetramethyl-2-(1*S*-methyl-4-oxobut-1-yl)-6-acetoxy-3-chromenes (13). An ozone—oxygen mixture at a flow rate of 30 L h^{-1} was passed for 4 min (0.98 mmol O$_3$) at ~20 °C through a mixture of acetates **8** (0.35 g, 0.95 mmol), Ba(OH)$_2$ (0.34 g, 1.99 mmol), 0.08 mL of H$_2$O, and 3 mL of acetone. The mixture was worked-up as described in the previous experiment to give 0.2 g (62.5%) of a mixture of (2*R*,1′*S*)-*erythro*- and (2*S*,1′*S*)-*threo*-aldehydes **13**, $[\alpha]_D^{20}$ −4.5 (*c* 0.3, CHCl$_3$). Found (%): C, 72.56; H, 7.81. C$_{20}$H$_{26}$O$_4$. Calculated (%): C, 72.70; H, 7.93. IR, ν/cm^{-1}: 1710 and 1740 (C=O). UV, λ_{max}/nm (ε): 273 (7500); 283 (6600), 319 (2400). ^{1}H NMR, δ: 0.87, 0.98 (both d, 3 H, C(1′)CH$_3$, J = 5.9 Hz); 1.32 (s, 3 H, C(2)CH$_3$); 2.02, 2.05, 2.10 (all s, 9 H, ArCH$_3$); 2.33 (s, 3 H, CH$_3$C=O); 1.40—2.00 (m, 3 H, H(2′), H(1′)); 2.53 (m, 2 H, H(3′)); 5.65 (m, 1 H, H(3)); 6.50 (m, 1 H, H(4)); 9.80 (t, 1 H, H(4′), J = 1.1 Hz). ^{13}C NMR, δ: 11.4, 13.0 (C(5)CH$_3$), C(7)CH$_3$), C(8)CH$_3$); 17.3, 17.4 (C(1′)CH$_3$); 20.3 (CH$_3$CO); 20.6 (C(2)CH$_3$); 31.3, 31.5 (C(2′)); 40.9, 41.1 (C(1′)); 65.7 (C(3′)); 79.7 (C(2)); 117.6 (C(10)); 120.2 (C(3)); 122.2 (C(8)); 122.4 (C(5)); 128.8 (C(4)); 128.9, 129.0 (C(7)); 141.1, 141.2 (C(9)); 148.1 (C(6)); 169.4 (CH$_3$CO); 202.7 (C=O).

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