Synthesis of α-tocopherol (vitamin E), vitamin K_1-chromanol, and their analogs in the presence of aluminosilicate catalysts Tseokar-10 and Pentasil

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Dedicated to Professor Boris A. Trofimov on his 65th birthday

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Abstract

The highly effective heterogeneous catalysts, the aluminosilicates Tseokar-10 and Pentasil, were found to condense hydroquinones with tertiary isoprenoid allylic alcohols. Using these catalysts *d,l*-α-tocopherol, (2*RS*,4′*R*,8′*R*)-α-tocopherol, and vitamin K_1-chromanol with chiral homogeneous side chains were synthesized in high yields. The analogs of α-tocopherol – chromanols and chromenols with the terminal isopropylidene group in the side chain – were synthesized, whose selective ozonolysis resulted in the corresponding chromanes with ω-formyl- or ω-hydroxyl groups in the side chain.

Keywords: α-Tocopherol, vitamin K_1-chromanol, Δ^3-chromenes, condensation, aluminosilicate catalysts

Introduction

α-Tocopherol is the most significant representative of the tocopherol group (vitamin E); it is a natural inhibitor of the peroxidation of lipids *in vivo*, and helps to retain intact the structure and functional activity of cells' membranes.[1]

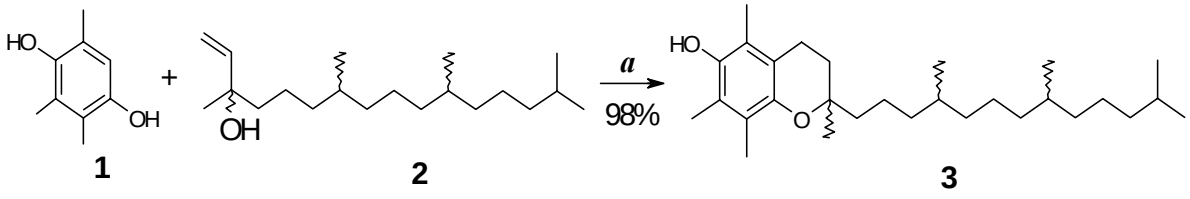
The chemistry of tocopherol has been extensively studied over sixty years, but now this compound is of interest as a treatment- and prophylactic agent, and as a nutritional additive. At present, intensive searches are being carried out for new methods of synthesis of racemic and optically active α-tocopherol using new catalysts, reagents and synthons.[2]

The method based on the acid-catalyzed condensation of 2,3,5-trimethylhydroquinone (TMHQ) with phytol and isophytol to obtain racemic α-tocopherol (a mixture of all possible stereoisomers), and (2*RS*, 4′*R*, 8′*R*)-α-tocopherol is of great importance. Brønsted and Lewis

acids *e.g.,* HCO_2H, $MeCO_2H$, $BF_3{\cdot}OEt_2$, $ZnCl_2$, are used as catalysts. Recently, data were published concerning the use of heterogeneous catalysts, whose main merits are the simple separation of a solid catalyst from the reaction mass, the absence of washing water containing the dead catalyst, and a higher purity (96–97%) of α-tocopherol.[3] The aluminosilicates are most preferred heterogeneous catalysts, owing to their accessibility and capacity. The AShNTs and Tseokar-2 aluminosilicates have been used for TMHQ condensation with isophytol and dihydrolinalool.[4]

Synthesis of all-*rac*.-α-tocopherol, 2-*ambo*-α-tocopherol and vitamin K_1–chromanol

We have studied the new aluminosilicate catalyst Tseokar-10 (which contains the high module zeolite Y as the active component (10 wt. %) and is used for cracking of petroleum fractions manufactured at the Salavatnefteorgsintez plant) to condense TMHQ **1** with isophytol **2**. It was found that reaction in boiling hydrocarbon solvents (*n*-heptane, *n*-nonane) gave all-*rac*.-α-tocopherol (**3**) in nearly quantitative yield (≥ 98%) (Scheme 1).[5]

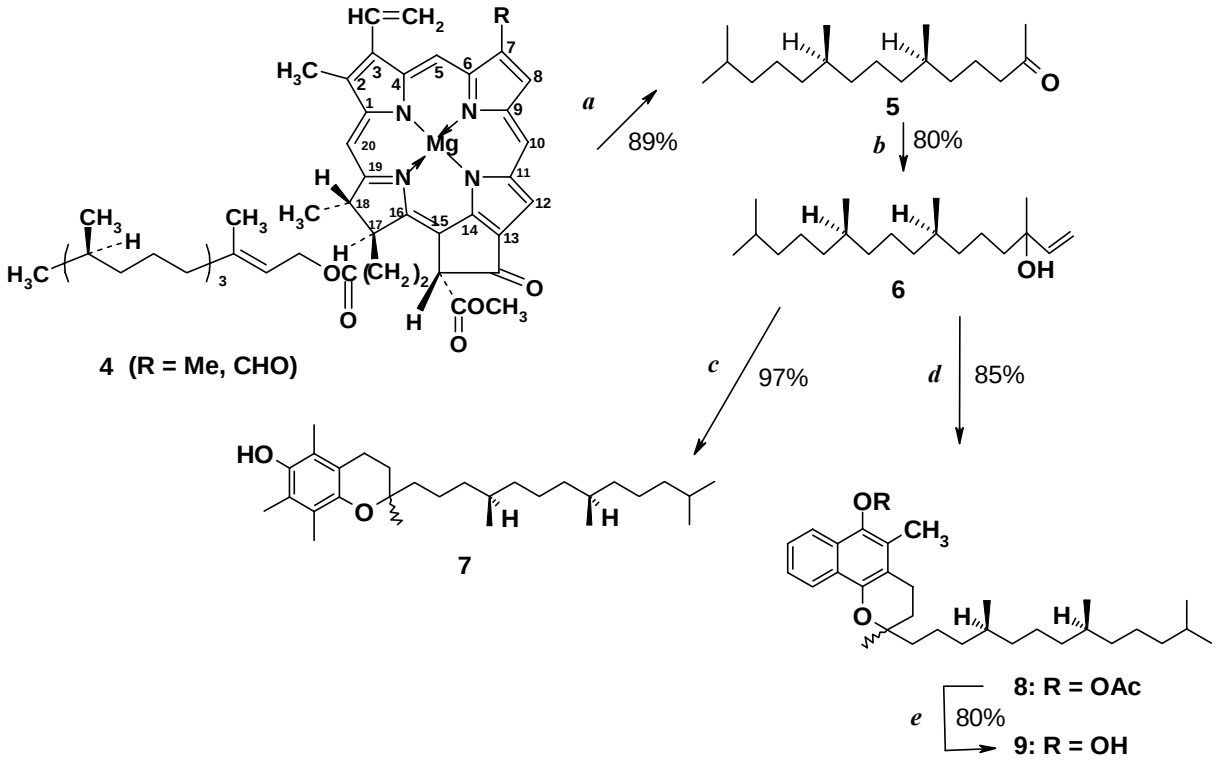


Scheme 1. TMHQ, Tseokar-10, *n*-C_9H_{20}.

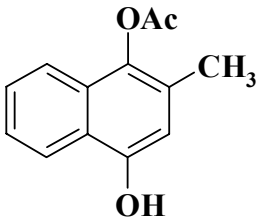
Tseokar-10 was also effective in the synthesis of (2*RS*, 4′*R*, 8′*R*)-α-tocopherol **7** (equimolar mixture of 2*R*- and 2*S*- epimers, called 2-*ambo*-α-tocopherol).[6] This compound was obtained by the condensation of TMHQ with (2*E*,7*R*,11*R*)-phytol, whose syntheses are complicated and have many steps.[7] The treatment of the acetone extract of chlorophyll of green plants with alkali also leads to this compound, but this pathway requires pre-purification of the chlorophyll from lipids.[8] In addition, the alkaline hydrolysis of chlorophyll in acetone solution gives the products of acetone self-condensation, and salts of fatty and chlorophyll-based acids hampers the isolation of pure phytol.

In the condensation reaction with TMHQ (3*RS*,7*R*,11*R*)-isophytol **6** was used, which was obtained by the vinylation of (6*R*,10*R*)-6,10,14-trimethylpentadecane-2-one (*R,R*-phytone) **5**. To synthesize the latter an effective method was developed of ozonolysis of the acetone extract of chlorophyll **4** (a mixture of chlorophyll *a* and *b*, R = Me or CHO, respectively) from the great nettle (*Urtica dioica L.*) without its pre-purification from accompanying lipids (Scheme 2). Ozonolysis in the presence of $Ba(OH)_2$ (the so-called "non-peroxide ozonolysis"[9]) led to phytone **5** in ~90% yield (with respect to chlorophyll **4** in the acetone extract, determined using electronic spectroscopy in the range λ 640–665 nm). The pure phytone **5** was isolated most easily, and in high yield, from the ozonization product when 9 mol. equiv. of ozone, with respect to the content of chlorophyll in the extract, was used, whereas decreasing the excess of ozone hinders the isolation of the pure target product. Apparently, ozone is needed not only to cleave the double

bonds in the vinyl group at C(3) and the phytyl propionate residue at C(17) in chlorophyll **4**, but also to ozonize the corresponding unsaturated compounds in the acetone extract (carotenoids and xanthophylls). The condensation of isophytol **6** with TMHQ in the presence of the Tseokar-10 catalyst (nonane, boiling, 5 h) led to the target 2-*ambo*-α-tocopherol **7** in high yield.



Scheme 2. (a) O_3, Me_2CO, $Ba(OH)_2$; (b) CH_2=CHMgBr, THF; (c) TMHQ, Tseokar–10, *n*-C_9H_{20}; (d) Tseokar –10, PhMe; (e) $LiAlH_4$, Et_2O.



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The same approach was used to synthesize 2,5-dimethyl-2-(4,8,12-trimethyltridecan-1-yl)-6-hydroxybenzo[*h*]chroman, a cyclic form of vitamin K_1, also called vitamin K_1-chromanol, or naphthotocopherol, **9**. The effect of vitamin K_1 on a number of biochemical processes (blood coagulation, conjugate oxidation, phosphorylation) is known to be caused by naphthotocopherol[10] identified in the product of the enzymic reduction of vitamin K_1.[11]

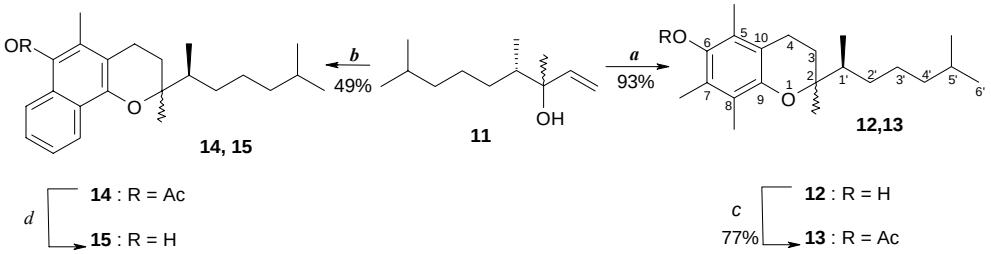
Spectrophotometric studies of antioxidants in the phenol series confirmed the highest activity of naphthotocopherol, whose antioxidant activity was 6.9 times as great as that of α-tocopherol.[12]

First, we have synthesized optically active naphthotocopherol with the chiral homogeneous side phytyl chain of (*R*,*R*)- configuration, **9**, based on the condensation of 1-*O*-acetyl-2-methyl-1,4-naphthohydroquinone (menadiol acetate) **10** with (3*RS,*7*R,*11*R*)-isophytol **6** in the presence of the Tseokar-10 catalyst. The condensation product **8** was further deacetylated with lithium aluminum hydride in diethyl ether. The yield of the target naphthotocopherol **9** was equal to 68% with respect to isophytol **6**.

Synthesis of analogs of *α*-tocopherol and naphthotocopherol with a shortened side chain

In recent years, considerable attention has been given to the synthesis of analogs of α-tocopherol with a shortened side chain. The resulting compounds, based on linalool and dihydrolinalool, were found to exhibit high biological activity. These analogs are named C_6- analogs of α-tocopherol, from the number of carbon atoms in the side chain.[4]

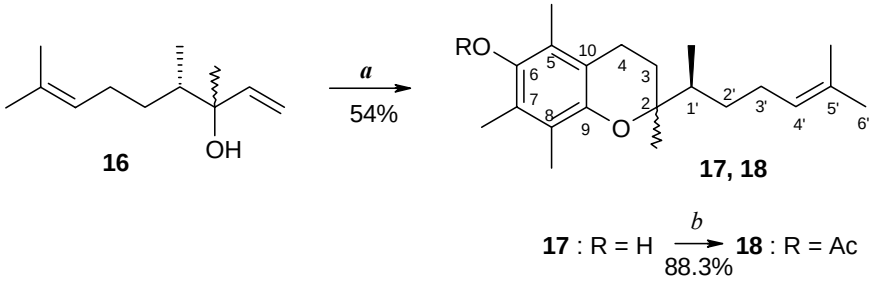
The condensation of (3*RS*,4*S*)-3,4,8-trimethyl-1-nonene-3-ol **11**, obtained from the accessible enantiomerically enriched (*ee*~50%) (*S*)-(+)-dihydromyrcene[13,14]) with TMHQ[14] and menadiol acetate, **10**, catalyzed by Tseokar-10, resulted in new optically active analogs of α-tocopherol **12** and naphthotocopherol **14**, and converted then into the acetate **13** and the alcohol **15**, respectively (Scheme 3). The C_8-chromans **12**, **13** and C_8-benzochromans **14**, **15** were synthesized in equimolar mixtures of (2*R*,1′*S*)-*erythro*- and (2*S*,1′*S*)-*threo*- diastereomers. Since the starting **11** is characterized by an *ee* of ~50%, it is evident that the *erythro*- and *threo*-diastereomers of the chromans **12** and **15** are enriched to the same extent with the epimers with the *S*- configuration at the C(1′)- atom.



Scheme 3. (a) TMHQ, Tseokar-10, *n*-C_9H_{20}; (b) **10**, Tseokar-10, PhMe; (c) Ac_2O; (d) $LiAlH_4$, Et_2O.

The usual catalysts are known to be unsuitable for reactions of tertiary vinyl carbinols with unsaturated isoprenoid radicals because the reaction is complicated by side cyclization resulting in tricyclic compounds.[15] At the same time, analogs of α-tocopherol with an unsaturated side chain are of interest as precursors of the corresponding chromanols with an ω-functionalized side chain, which are of interest in biological studies and as building blocks for the synthesis of other vitamin E analogs.

We report the capacity of the aluminosilicate catalyst Tseokar-10 in the synthesis of chromanols with the terminal isopropylidene group in the isoprenoid side chain.[16] In this, (3*RS*,4*S*)-3,4,8-trimethyl-1,7-nonadien-3-ol **16** (a 1:1 mixture of (3*R*,4*S*)-*erythro*- and (3*S*,4*S*)-*threo*- diastereomers, *ee*~50%, obtained according to refs 13 and14) and linalool **19** served as the allyl isoprenoid alcohols for the condensation with TMHQ.



It was found that the reaction of TMHQ with **16** in boiling heptane in the presence of the Tseokar-10 aluminosilicate gives a mixture of diastereomeric optically active chromanols **17** (*erythro*- /*threo*- ~ 1:1, GLC data, *ee* ~50%). Under the same conditions, the condensation of TMHQ with **19** is less selective, resulting in the formation of a considerable amount of the tricyclic isomer **22** besides the target chromanol **20**. Compounds **20** and **22** were separated and characterized as the corresponding acetates **21** and **23** (Scheme 4).

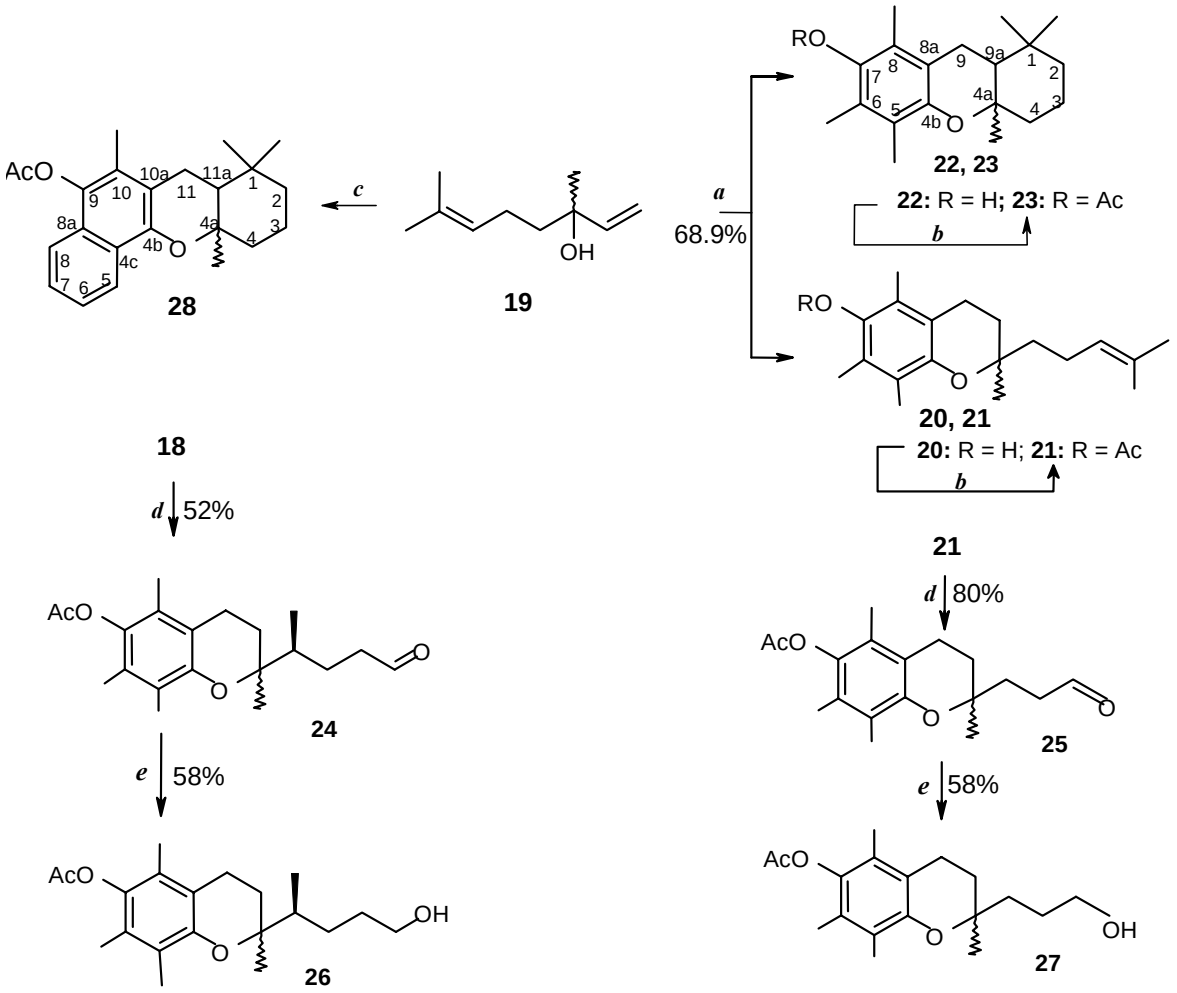
Oxidative cleavage of the chromanyl acetates **18** and **21** by ozonolysis in aqueous acetone in the presence of $Ba(OH)_2$, gave aldehydes **24** and **25** in 52% and 80%, respectively, in one step. The hydride reduction of **24** and **25** yielded the corresponding alcohols **26** and **27** (Scheme 4).

In contrast to TMHQ, the reaction of menadiol acetate **10** with linalool **19** in the presence of the Tseokar-10 leads mainly to the cyclic compound **28** (70%, GLC).

Synthesis of chromenes with isoprenoid side chains

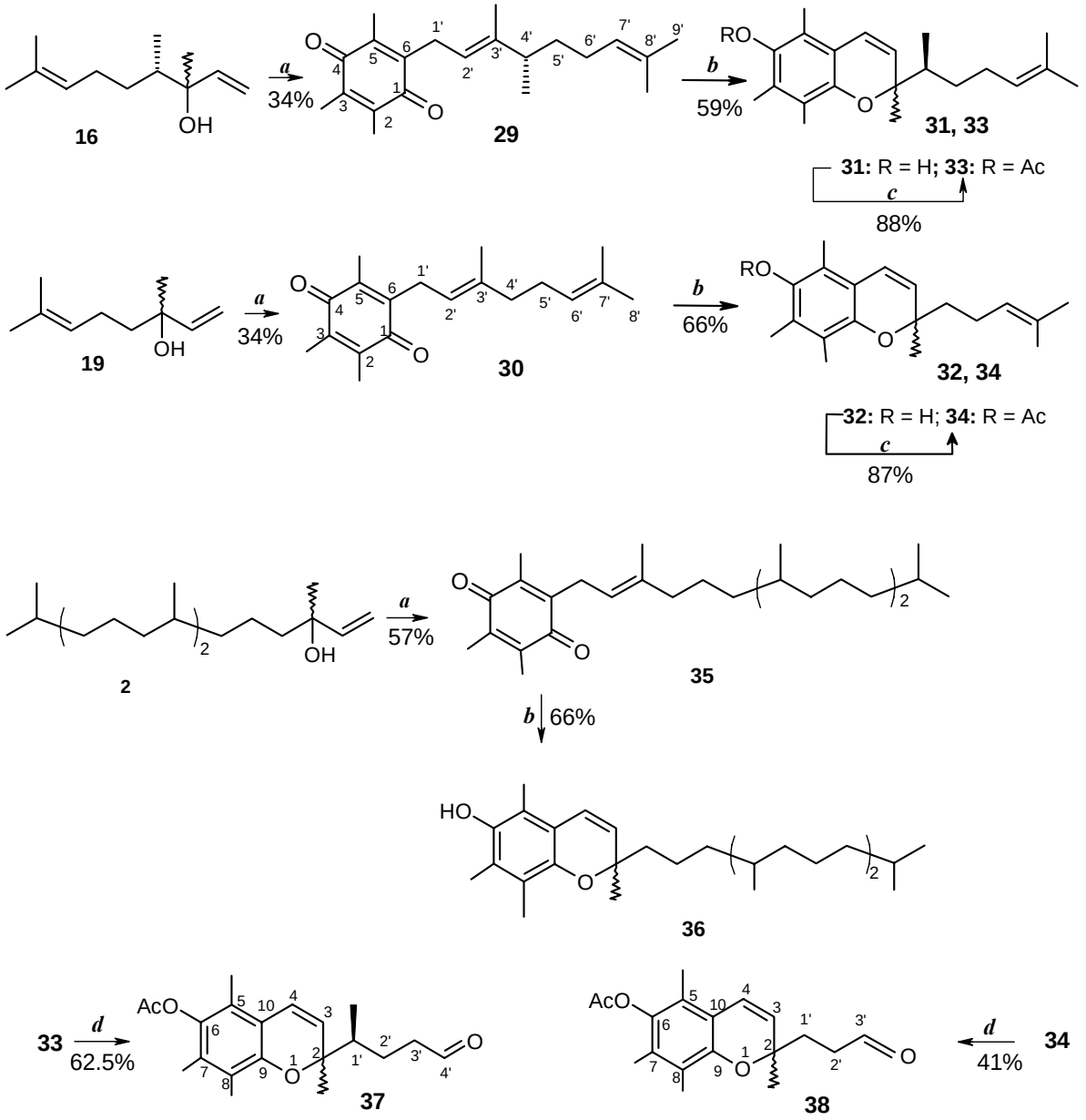
Chromenes with isoprenoid side chains are frequently encountered in nature, being structural analogs of prenylated coumarins, chalcones, and cannabinoids,[17–19] this accounts for the increased interest in their synthesis. Two approaches have been developed most thoroughly, (1) using the pyridine-catalyzed reaction of α,β-unsaturated aldehydes with phenols,[20] 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.[21] 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.[22]



Scheme 4. (a) TMHQ, Tseokar-10, *n*-C_7H_{16}; (b) Ac_2O, pyridine; (c) **10**, Tseokar-10, PhMe; (d) O_3, Me_2CO, $Ba(OH)_2$; (e) $NaBH_4$, MeOH.

The reactions of TMHQ with the vinyl carbinol **16** (a 1:1 mixture of (3*R*,4*S*)-*erythro*- and (3*S*,4*S*)-*threo*- diastereomers (*ee* ~50%)) and linalool **19** in the presence of Pentasil were found to afford the 1,4-benzoquinones **29** and **30**, respectively. Pyridine-induced cyclization of these products proceeded smoothly to give chromenes **31** and **32**, respectively (Scheme 5). As in the case of the vinyl carbinols **16** and **19**, the use of isophytol **2** resulted in the syntheses of the quinone **35** and chromene **36.**



Scheme 5. (a) TMHQ, ZSM-5/11, *n*-C_9H_{20}, then O_2, SiO_2; (b) Pyridine, reflux, 16 h; (c) Ac_2O, Pyridine; (d) O_3, Me_2CO, $Ba(OH)_2$.

Ozonolysis of chromenes **33** and **34** at the side-chain double bond opens the way to *ω*-functionalized chromenes, which can be further converted into more complex chromene derivatives. However, under the ozonolysis conditions described previously, the chromenes gave only benzaldehydes and benzoic acids with the corresponding substituents.[17] We found that in the ozonolysis of chromenyl acetates **33** and **34** with an equimolar amount of ozone it is possible to cleave selectively the double bond in the side chain and obtain the required aldehydes **37** and **38**. Thus, using a zeolite catalyst of the Pentasil type, chromenes were synthesized with the

isoprenoid side chain containing the double bond, and whose partial ozonolysis yielded chromenes with the aldehyde group in the side chain.

Conclusions

For the condensation of trimethylhydroquinone and 2-methyl-1,4-naphthohydroquinone with allylic isoprenoid alcohols, the new catalysts Tseokar-10 aluminosilicate and zeolite Pentasil were used. Using these catalysts, *d,l*-α-tocopherol, (2*RS*,4′*R*,8′*R*)-α-tocopherol, vitamin K_1-chromanol and their analogs with the shortened side chain were synthesized in high yields. The possibility of preparing the analogs of α-tocopherol-chromanols and chromenols with the double bond in the side chain is a particular quality of the new catalysts compared to those usually used in this type of reaction. The selective ozonolysis of these compounds resulted in analogs of α-tocopherol with an ω-functionalized side chain serving as synthons for α-tocopherol and its analogs.

Experimental Section

General Procedures. IR spectra were recorded on a Specord 75-IR spectrometer (in thin film); UV spectra using a Specord M-40 instrument. ^{1}H- and ^{13}C- NMR spectra were run on a Bruker AM-300 spectrometer (300.13 and 75 MHz for ^{1}H and ^{13}C, respectively) in $CDCl_3$. Chemical shifts are on the δ scale, relative to internal Me_4Si. GLC analysis used a Chrom-5 chromatograph with 2400 x 4 mm columns with the Chromaton N-AW-DMCS and SE-30 (5%) stationary phase at a temperature of50–300°C (8 K min^{-1}) using helium as carrier gas. The preparative separation of acetates **21** and **23** was carried out using a Carlo Erba chromatograph (6000 x 6 mm column) with SE-30 stationary phase, at 300 °C, with helium as carrier gas. HPLC used an LKB liquid chromatograph (Sweden) equipped with UV detector (λ=249 nm) and a column with Separon-C18 as adsorbent (125 x 4 mm, 5 μm); 87:13 MeOH–H_2O was used as eluent (0.3 mL·min^{-1}, 20°C). Optical rotation was measured using a Perkin–Elmer-141 polarimeter. Mass spectra at 70 eV, using the electron impact mode, were measured on a Finnigan MAT 8200 instrument.

(6*R*,10*R*)-6,10,14-Trimethylpentadecane-2-one (phytone) (5). Finely crushed air-dried leaves of great nettle (*Urtica dioica L.*) (100 g) were extracted with acetone (1 L) until the extract became slightly green. The latter was extracted to give the pasty dark-green residue containing chlorophyll **4** (0.38 g, 0.42 mmol) (determined from the solution's optical density according to Ref. 23). The residue was dissolved in 30 mL of acetone, then $Ba(OH)_2$ (8.6 g, 50 mmol) and H_2O (2 mL) were added, an ozone –oxygen mixture (ozonizer productivity 11 mmol·h^{-1}) was passed at 30 L·h^{-1} for 20 min (~9 mol O_3 /mol of chlorophyll **4**) at room temperature. The precipitate was filtered, washed with acetone (~30 mL), and the combined filtrates evaporated *in vacuo*. The residue (0.8 g) was separated on a column (SiO_2, 20 g), eluting with petroleum (bp 40–60 °C) to give the fraction of colorless non-polar substances (R_f = 0.71), then a fraction of R_f

= 0.49. The latter was evaporated to give **5** (0.1 g, 89%), n_D^{20} 1.4482, $[\alpha]_D^{20}$ +1.1° (c 1.78, $CHCl_3$); [lit.[24] n_D^{23} 1.4430, $[\alpha]_D^{24.6}$ +0.78°]; IR ν 1720 cm^{-1}; ^{1}H-NMR δ 0.85 (12 H, m, CH_3), 1.25 (16 H, m, CH_2), 1.43–1.62 (3H, m, CH), 2.10 (3 H, s, H_3CCO), 2.38 (2 H, t, H_2CCO, J = 7.4 Hz); ^{13}C-NMR δ 19.46 and 19.63 (6-CH_3, 10-CH_3), 22.50 and 22.50 (14-CH_3, 15-C), 24.34 and 24.72 (8-C, 12-C), 27.89 (14-C), 29.63 (4-C), 31.51 (1-C), 32.60 and 32.71 (6-C, 10-C), 37.17, 37.22, 37.34 and 37.57 (5-C, 7-C, 9-C, 11-C), 39.31 (13-C), 43.96 (3-C), 208.75 (2-C).

(3*RS*,7*R*,11*R*)-Isophytol (6). A solution of **5** (0.5 g, 1.87 mmol) in THF (0.6 mL) (Ar, ~25 °C) was added to a solution of Normant reagent prepared from Mg chips (0.2 g, 8.45 mmol) and vinyl bromide (0.9 g, 8.6 mmol) in THF (4 mL). The reaction mixture was stirred for 3 h, then treated with saturated NH_4Cl solution (5 mL). The organic layer was separated, and the aqueous one extracted with Et_2O. The combined organic layers were washed with NaCl, dried ($MgSO_4$), and evaporated *in vacuo* to give isophytol **6** (0.44 g, 80%) (the content of the basic compound is ≥ 97%, from GLC), n_D^{23} 1.4582; $[\alpha]_D^{20}$ +1.14° (c 2.8, $CHCl_3$) [lit.[25] n_D^{20} 1.4570]; ^{1}H-NMR δ 0.85 (12 H, m, CH_3), 1.0–1.6 (24 H, m, 3-CH_3, CH_2, CH), 5.0 (1 H, d, C=C$^1H_{cis}$, J = 10.7 Hz), 5.18 (1 H, d, C=C$^1H_{trans}$, J = 17.3 Hz), 5.89 (1 H, dd, HC^2=C, J = 10.7 Hz and 17.3 Hz); ^{13}C-NMR δ 19.68 and 19.63 (7-CH_3, 11-CH_3), 22.56 and 22.66 (3-CH_3, 15-CH_3, 16-C), 24.42 and 24.74 (9-C, 13-C), 27.90 (15-C), 29.66 (5-C), 32.73 (7-C, 11-C), 32.73 and 37.38 (6-C, 8-C, 10-C, 12-C), 42.66 (4-C), 73.95 (3-C), 111.42 (1-C), 145.18 (2-C).

(2*RS*,4′*R*,8′*R*)-α-Tocopherol (2-*ambo*-α-tocopherol) (7). Compound **6** (0.78 g, 2.64 mmol) was added to a boiling suspension of TMHQ (0.2 g, 1.32 mmol) and finely crushed Tseokar-10 catalyst (0.45 g) in 6 mL of dried *n*-nonane at boiling (under Ar). The mixture was boiled for 5 h, cooled to room temperature, the catalyst was filtered off, and the filtrate was evaporated. The residue (0.85 g) was chromatographed on a SiO_2 column (20 g), eluting with *n*-hexane to isolate the fraction (R_f = 0.87) of non-polar substances, then with 10:1 *n*-hexane–Et_2O to give a fraction of R_f = 0.35, which was evaporated to give **7** (0.55 g, 97%). $[\alpha]_D^{20}$ +0.31° (*c* 0.26, $CHCl_3$) [lit.[21] $[\alpha]_D^{25}$ +0.38° (C_2H_5OH)]; UV (C_2H_5OH) λ_{max}/nm (ε) 295 (3800); ^{1}H-NMR δ 0.90 (12 H, m, CH_3), 1.0–1.9 (26 H, m, CH_3-2, CH_2, CH), 2.10 and 2.17 (9 H, both s CH_3-Ar), 2.61 (2 H, t, 4-H, J = 6.7 Hz), 4.3 (1 H, s OH); ^{13}C-NMR δ 11.26, 11.75 and 12.19 (CH_3-Ar), 19.67 and 19.75 (4′-CH_3, 8′-CH_3), 20.79 and 21.08 (4-C), 22.62 and 22.70 (12′-CH_3, 13′-C), 24.46 and 24.81 (2′-C, 6′-C, 10′-C), 27.99 (12′-C), 31.60 (3-C), 32.75 and 32.83 (4′-C, 8′-C), 37.32 and 37.48 (3′-C, 5′-C, 7′-C, 9′-C), 39.42 (11′-C), 39.91 and 39.97 (1′-C), 74.55 (2-C), 116.38 (5-C), 118.51 (10-C), 121.05 (8-C), 122.64 (7-C), 144.57 (9-C), 145.63 (6-C).

2,5-Dimethyl-2*RS*-(4*R*,8*R*,12-trimethyldecan-1-yl)-6-acetoxy-benzo[*h*]chroman (8). Compound **6** (0.4 g, 1.35 mmol) was slowly added to a boiling suspension of menadiol monoacetate **10** (0.56 g, 2.6 mmol) and finely crushed Tseokar-10 catalyst (1.1 g) in 8.4 mL of abs. toluene at boiling, under Ar. The mixture was boiled for 4 h, cooled to room temperature, the catalyst filtered off, and the filtrate evaporated. The residue was chromatographed on a SiO_2 column (20 g) using *n*-hexane to give the fraction (R_f = 0.7) of non-polar substances, then the fraction of R_f = 0.4 was eluted with a mixture (10:1) *n*-hexane–Et_2O, and evaporated to give **8** (0.56 g, 85%); the content of the basic compound was ≥97% (GLC data). $[\alpha]_D^{18}$ +1.1° (*c* 1.34, $CHCl_3$); IR ν 1760 (C=O), 1210, 1080 and 1060 (C-O) cm^{-1}; UV (C_2H_5OH) λ_{max}/nm (ε) 244 (39830), 305 (5330), 328 (3900); ^{1}H-NMR δ 0.95 (12 H, m, CH_3), 1.0–1.8 (21 H, m, CH_2,CH), 1.35 and 1.40 (3H, both s,

2-CH_3), 1.97 (2 H, m, 3-H), 2.28 (3 H, s, 5-CH_3), 2.51 (3 H, s, CH_3CO), 2.76 (2 H, t, 4-H, J = 6.4 Hz), 7.50 (2 H, m, 8-H, 9-H), 7.70, 8.30 (2 H, both d, 7-H, 10-H, J = 8.1 Hz); ^{13}C-NMR δ 12.56 (5-CH_3), 19.63, 19.69 (4′-CH_3, 8′-CH_3), 20.50 ($\underline{C}H_3CO$), 20.59 and 21.00 (4-C), 22.58, 22.68 (12'-CH_3, 13'-C), 23.65 (2-CH_3), 24.38, 24.75 (2′-C, 6′-C, 10′-C), 27.90 (12′-C), 30.95 (3-C), 32.61, 32.70 (4′-C, 8′-C), 37.23, 37.33, 37.50 (3′-C, 5′-C, 7′-C, 9′-C), 39.31 (11′-C), 39.99 and 40.06 (1′-C), 75.67 (2-C), 113.95 (5-C); 120.21, 121.90, 124,46, 126.0 (7-C, 8-C, 9-C, 10-C); 124.78, 125.72, 126.33 (4a-C, 6a-C, 10a-C); 136.79 (10b-C); 146.63 (6-C); 169.54 ($CH_3\underline{C}O$); Mass-spectra (70 eV), *m/z* (%): 494 $[M]^+$ (34), 452 $[M\text{-}COCH_2]^+$ (100), 229 (9), 187 (37), 186(49), 158 (3), 129 (2), 105 (6), 83 (2), 71 (6), 57 (14), 43 $[COCH_3]^+$ (31). Exact mass Calcd: 494.37597 for $C_{33}H_{50}O_3$. Found: *m/z* 494.37600 $[M]^+$.

2,5-Dimethyl-2*RS*-(4*R*,8*R*,12-trimethyltridecan-1-yl)-6-hydroxy-benzo[*h*]chroman (9). A solution of **8** (0.28 g, 0.56 mmol) and lithium aluminumhydride (0.02 g) in 22.7 mL of abs. diethyl ether was boiled for 1 h (Ar) with stirring. The mixture was cooled to 0 °C then 2 mL of moist ether and 0.5 mL of 3 *M* HCl were added. After shaking, the ether layer was separated, washed with water to neutral, dried $MgSO_4$, evaporated *in vacuo*, to give **9** (0.2 g, 80%) as a dark yellow viscous oil, $[\alpha]_D^{18} + 0.89°$ (*c* 6.0, $CHCl_3$). IR ν 1080, 1060, (C–O), 3400 (OH) cm^{-1}; UV ($CHCl_3$) λ_{max}/nm (ε) 253 (17310), 303 (1960), 322 (2360), 341 (2490); ^{1}H-NMR δ 0.95 (12 H, m, CH_3), 1.0–1.85 (21 H, m, CH_2, CH), 1.34 and 1.40 (3 H, both s, 2-CH_3), 1.98 (2 H, m, 3-H), 2.30 (3 H, s, 5-CH_3), 2.75 (2 H, t, 4-H, J = 6.5 Hz), 5.25 (1H, s, OH), 7.50 (2 H, m, 8-H, 9-H), 7.70 8.30 (2 H, both d, 7-H, 10-H, J = 8.1 Hz); ^{13}C-NMR δ 15.27 (5-CH_3), 19.78, 19.86 (4′-CH_3, 8′-CH_3), 21.01 and 21.18 (4-C), 22.75, 22.85 (12′-CH_3, 13′-C), 23.60 (2-CH_3), 24.56, 24.93 (2′-C, 6′-C, 10′-C), 28.07 (12′-C), 31.52 (3-C), 32.78, 32.87 (4′-C, 8′-C), 37.39, 37.49, 37.69 (3′-C, 5′-C, 7′-C, 9′-C), 39.47 (11′-C), 39.91 and 39.96 (1′-C), 75.12 (2-C), 114.48 (5-C), 117.50, 124.44, 124,57 (4a-C, 6a-C, 10a-C), 120.63, 121.66, 124.44, 125.08 (7-C, 8-C, 9-C, 10-C), 141.08 (10b-C), 142.88 (6-C).

2*RS*,5,7,8-Tetramethyl-2-(1*S*,5-dimethylhexyl)-6-hydroxychromans (12). A mixture of the alcohols **11** (0.7 g, 3.8 mmol) was added dropwise (Ar, 150 °C) to a suspension of TMHQ (0.24 g, 1.59 mmol) and the powdered catalyst Tseokar-10 (0.52 g) in anhydrous *n*-nonane (7 mL). The reaction mixture was heated at reflux for 4 h, cooled to ~20 °C, and filtered. The filtrate was concentrated and the residue was chromatographed on SiO_2. Elution first with *n*-hexane and then with an *n*-hexane–Et_2O mixture (10:1) gave 0.47 g (93%) of the chromans **12.** According to the HPLC data, these compounds existed as a mixture (1:1) of the *erythro*- and *threo*- diastereomers (t = 25.2 and 28.8 min respectively), $[\alpha]_D^{15}$ -1.67° (c 2.0, $CHCl_3$). Anal. Calcd. for $C_{21}H_{34}O_2$ (318.5): C, 79.19; H, 10.76. Found: C, 79.35; H, 10.88. UV ($CHCl_3$) λ_{max}/nm (ε) 295 (3900); ^{1}H-NMR δ 0.80–0.88 (6 H, m, 6′-H, 5′-CH_3), 0.90 (1.5 H, d, 1′-CH_3, J = 6.7 Hz), 0.95 (1.5 H, d, 1′-CH_3, J = 6.8 Hz), 1.11 (3 H, s, 2-CH_3), 1.2–1.9 (10 H, m, 3-H, 1′-H, 2′-H–4′H, 5′-H), 2.10 s (6 H, $ArCH_3$), 2.15 s (3 H, $ArCH_3$), 2.57 t (2 H, 4-H_2C, J = 6.7 Hz), 4.25 s (1 H, OH); ^{13}C-NMR δ 11.35 (5-CH_3), 11.86, 12.28 (8-CH_3), 13.47, 14.39 (7C-H_3), 19.45, 19.94 (1′-CH_3), 20.52, 20.60 (4-C), 22.62 (6′-C), 22.80, 22.86 (2-CH_3), 25.89, 25.97 (3′-C), 27.84, 27.97 (5′-C), 29.24, 29.67 (3-C), 30.69, 31.66 (2′-C), 39.29 (4′-C), 39.90 (1′-C), 77.15, 77.21 (2-C), 117.63 (5-C), 118.45, 118.55 (10-C), 121.04, 121.05 (8-C), 122.65 (7-C), 144.49 (9-C), 145.35 (6-C).

2*RS*,5,7,8-Tetramethyl-2-(1*S*,5-dimethylhexyl)-6-acetoxychromans (13). A solution of a mixture of chromans **12** (0.15 g, 10.47 mmol) in Ac_2O (0.15 mL) was heated at reflux for 3 h, cooled, poured into iced water (10 mL), and extracted with Et_2O. The extract was successively washed with saturated solutions of $NaHCO_3$ and NaCl, dried with $MgSO_4$, concentrated, and chromatographed (SiO_2, hexane). A 1:1 mixture of the *erythro*- and *threo*- diastereomers of **13** (GLC data) was obtained in a yield of 0.13 g (77%), $[\alpha]_D^{14}$ –4.75° (c 1.8, $CHCl_3$). Anal. Calcd. for $C_{23}H_{36}O_3$ (360.5): C, 76.62; H, 10.07. Found: C, 76.91; H, 10.20%. IR ν 1740 (C=O) cm^{-1}; UV ($CHCl_3$) λ_{max}/nm (ε) 277 (1760), 286 (3100). ^{1}H-NMR δ 0.83–0.92 (6 H, t, 6′-H, 5′-CH_3), 0.95 (1.5 H, d, 1′-CH_3, *J* = 6.8 Hz), 1.05 (1.5 H, d, 1′-CH_3, *J* = 6.7 Hz), 1.18 (3 H, s, 2-CH_3), 1.30–1.90 (10 H, m, 3-H, 1′-H, 2′-H–4′-H, 5′-H), 2.02, 2.09, 2.18 (9 H, all s, ArCH_3), 2.39 (3 H, s, O=CCH_3), 2.60 (2 H, t, 4-H, *J* = 6.6 Hz); ^{13}C-NMR δ 11.85, 12.09 (8-CH_3), 12.94 (5-CH_3), 13.55, 14.15 (7-CH_3), 20.33, 20.41 (4-C), 20.56 (1′-CH_3, O=CCH_3), 22.55 (6′-C), 22.78 (2-CH_3), 25.85, 25.90 (3′-C′), 27.83, 27.92 (5′-C), 30.73, 31.55 (2′-C), 31.91 (3-C), 39.25 (1′-C, 4′-C), 77.67 (2-C), 117.60 (10-C), 124.80, 124.86 (8-C), 123.06 (5-C), 126.63 (7-C), 140.48 (9-C), 149.20 (6-C), 169.75 (C=O).

2,5-Dimethyl-2*RS*-(1*S*,5-dimethylhexyl)-6-acetoxybenzo[*h*]chroman (14). The alcohols **11** (0.21 g, 1.2 mmol) were slowly added to a boiling suspension of **10** (0.50 g, 2.3 mmol) and finely crushed Tseokar-10 catalyst (1.0 g) in 7.0 mL of abs. toluene at boiling (Ar). The reaction mixture was boiled for 10 h, cooled to room temperature, the catalyst filtered off, and the filtrate evaporated. The residue was chromatographed on a SiO_2 column (20 g) eluted with *n*-hexane to give the fraction (R_f = 0.7) of non-polar substances, then the fraction (R_f = 0.4) was eluted using a mixture (10:1) of *n*-hexane–Et_2O, evaporated to give a 1:1 mixture of *erythro*- and *threo*-diastereomers of **14** (0.21 g, 49%), the content of the basic compound was ≥97% (GLC data). $[\alpha]_D^{18}$ −1.0° (*c* 2.0, $CHCl_3$). Anal. Calcd. for $C_{25}H_{34}O_3$ (382.5): C, 78.43; H, 8.89. Found: C, 78.71; H, 8.91%. IR ν 1760 (C=O), 1210, 1080 and 1060 (C-O) cm^{-1}. UV ($CHCl_3$) λ_{max}/nm (ε) 245 (80200), 309 (4080), 330 (3560); ^{1}H-NMR δ 0.92 (6 H, m, 6′-H, 5′-CH_3), 1.04 (1.5 H, d, 1′-CH_3, *J* = 6.7 Hz), 1.15 (1.5 H, d, 1′-CH_3, *J* = 6.8 Hz), 1.32 (3 H, s, 2-CH_3), 1.20–2.10 (10 H, m, 3-H, 1′-H, 2′-H–4′-H, 5′-H), 2.25 (3 H, s, ArCH_3), 2.54 (3 H, s, CH_3C=O), 2.75 (2 H, t, 4-H, *J* = 6.7 Hz), 7.48 (2 H, m, 8-H, 9-H), 7.70, 8.28 (2 H, both d, 7-H, 10-H, *J* = 8.7 Hz); ^{13}C-NMR δ 12.56 (5-CH_3), 20.30, 20.38 (4-C), 20.56 ($\underline{C}H_3$C=O, 1′-CH_3), 22.43 (6′-C), 22.64 (2-CH_3), 25.76, 25.81 (3′-C), 27.75, 27.84 (5′-C, 1′-C), 30.77 (2′-C), 31.48 (3-C), 39.13 (4′-C), 78.33 (2-C), 114.28 (5-C), 120.19, 121.86, 124,47, 126.02 (7-C, 8-C, 9-C, 10-C), 124.79, 125.72 (4a-C, 6a-C, 10a-C), 136.67 (10b-C), 146.48 (6-C), 169.64 ($CH_3\underline{C}$=O).

2,5-Dimethyl-2*RS*-(1*S*,5-dimethylhexyl)-6-hydroxybenzo[*h*]chroman (15). A solution of **14** (0.12 g, 0.32 mmol) and lithium aluminumhydride (0.01 g) in 10.0 mL of abs. diethyl ether was boiled for 1 h with stirring (Ar). The reaction mixture was cooled to 0 °C then 2 ml of moist ether and 0.5 mL of 3 *M* HCl added. The ether layer was separated, washed with water to neutral, dried over $MgSO_4$, and evaporated *in vacuo*, to give **15** (0.085 g, 78%) as dark yellow viscous oil, $[\alpha]_D^{18}$ −0.70° (*c* 5.8, $CHCl_3$). Anal. Calcd. for $C_{23}H_{32}O_2$ (340.5): C, 81.06; H, 9.40. Found: C, 81.21; H, 9.37%. IR ν 1080, 1060, (C–O), 3400 (OH) cm^{-1}; UV ($CHCl_3$) λ_{max}/nm (ε) 251 (15400), 325 (3070), 340 (3050); ^{1}H-NMR δ 0.95 (6 H, m, 6′-H, 5′-CH_3), 1.10 (1.5 H, d, 1′-CH_3,

J = 6.5 Hz), 1.18 (1.5 H, d, 1′-CH_3, *J* = 6.5 Hz), 1.25 (1.5 H, s, 2-CH_3), 1.32 (1.5 H, s, 2-CH_3), 1.40–2.10 (10 H, m, 3-H, 1′-H, 2′-H, 4′-H, 5′-H), 2.30 (3 H, br. s, ArCH_3), 2.70 (2 H, m, 4-H), 7.45 (2 H, m, 8-H, 9-H), 8.00, 8.20 (2 H, m, 7-H, 10-H).

2*RS*,5,7,8-Tetramethyl-2-(1*S*,5-dimethyl-4-hexen-1-yl)-6-hydroxychromans (17). A mixture of alcohols **16** (2.5 g, 13.74 mmol) (prepared by a known procedure[14]) was added dropwise (Ar, 98 °C) to a suspension of TMHQ (1.04 g, 6.87 mmol) and the powdered Tseokar-10 catalyst (2.4 g) in 30 ml of dry *n*-heptane. The reaction mixture was refluxed for 5 h, cooled to ~20 °C, and filtered. The filtrate was concentrated and the residue chromatographed on SiO_2. Elution, first with *n*-hexane and then with an *n*-hexane–Et_2O mixture (10:1) gave 1.16 g (54%) of chromans **17**; according to GLC, this was a 1:1 mixture of *erythro*- and *threo*- diastereomers; $[\alpha]_D^{14}$ -2.0° (c 3.0, $CHC1_3$). Anal. Calcd. for $C_{21}H_{32}O_2$ (316.5): C, 79.70; H, 10.19. Found: C, 79.52, H, 10.02%. UV ($CHCl_3$) λ_{max}/nm (ε) 296 (3780); ^{1}H-NMR δ 1.02 (1.5 H, d, 1′-CH_3, *J* = 6.7 Hz), 1.08 (1.5 H, d, 1′-CH_3, *J*= 6.8 Hz), 1.22 (3 H, s, 2-CH_3), 1.6–2.1 (7 H, m, 3-H, 1′-H, 2′-H, 1′-H), 1.66, 1.70, 1.72, 1.80 (6 H, all s, 5′-CH_3, 6′-H), 2.18, 2.22, 2.24 (9 H, all s, ArCH_3), 2.68 (2 H, t, 4-H, *J* = 6.6 Hz), 4.50 (1 H, s, OH), 5.13 (0.5 H, t, 4′-H, *J* = 7.5 Hz), 5.26 (0.5 H, t, 4′-H, *J* = 7.5 Hz).

2*RS*,5,7,8-Tetramethyl-2-(1*S*,5-dimethyl-4-hexen-1-yl)-6-acetoxychromans (18). A solution of the mixture of chromans **17** (0.5 g, 1.58 mmol) in 4 mL of Ac_2O and 5 mL of anhydrous pyridine was kept for 0.5 h at ~20 °C, then poured into 20 mL of ice water and extracted with EtOAc. The extract was washed with 3 *M* HCl, saturated aq. $NaHCO_3$, then H_2O, dried with $MgSO_4$, and concentrated to give 0.5 g (88.3%) of a mixture of *erythro*- and *threo*-diastereomers of **18**; $[\alpha]_D^{20}$ –5.7° (c 0.34, $CHCl_3$). Anal. Calcd. for $C_{23}H_{34}O_3$ (358.5): C, 77.10; H, 9.50. Found: C, 77.27; H, 9.63%. IR ν 1740 (C=O) cm^{-1}; UV (EtOH) λ_{max}/nm (ε) 285 (2400). ^{1}H-NMR δ 0.97, 1.03 (3H, d of d, 1′-CH_3, *J* = 7.0 Hz), 1.99 (3 H, s, 2-CH_3), 1.6–2.0 (7 H, m, 3-H, 1′-H – 3′-H), 1.62, 1.75 (6 H, both s, 5′-CH_3, 6′-H), 2.02, 2.06, 2.18 (9 H, all s, ArCH_3), 2.38 (3 H, s, CH_3C=O), 2.60 (2 H, t, 4-H), 5.17 t (1 H, 4′-H, *J* = 6.7 Hz).

2*RS*,5,7,8-Tetramethyl-2-(4-methylpent-3-en-1-yl)-6-acetoxychroman (21) and 7-acetoxy-1,1,4a,5,6,8-hexamethyl-1,2,3,4,4a,9a-hexahydroxanthene (23). Alcohol **19** (1.63 g, 10.56 mmol) was added dropwise to a suspension of TMHQ (0.8 g, 5.28 mmol) and powdered Tseokar-10 catalyst (1.8 g) in 24 mL of boiling anhydrous *n*-heptane (under Ar). The mixture was heated at reflux for 6 h, cooled to ~20 °C, and filtered. The filtrate was concentrated and the residue (1.9 g) chromatographed on SiO_2 as described above for **17,** to give a mixture of chromanols **20** and **22** (1.12 g) (2:1, GLC retention times 20.89 and 22.02 min, respectively). The mixture of **20** and **22** was dissolved in 11 mL of anhydrous pyridine and 8.5 mL of Ac_2O added with stirring. The mixture was kept for 0.5 h at ~20 °C and poured into 25 mL of ice water, the products extracted with EtOAc, then washed with 3 *M* HCl, aq. $NaHCO_3$, and H_2O, and dried with $MgSO_4$ to give 1.20 g (68.9%) of a mixture of acetates **21** and **23** (2:1, GLC retention times 21.45 and 22.76 min, respectively). The mixture was separated by preparative GLC.

Acetate 21. IR ν 1740 (C=O) cm^{-1}; UV (EtOH) λ_{max}/nm (ε) 285 (1900). ^{1}H-NMR δ 1.30 (3 H, s, 2-CH_3), 1.65, 1.73 (6 H, both s, 4′-CH_3, 5′-H), 1.70–1.95 (6 H, m, 3-H, 1′-H, 2′-H), 2.02, 2.08,

2.15 (9 H, all s, $ArCH_3$), 2.38 (3 H, s, CH_3CO), 2.68 t (2 H, 4-H, J = 6.7 Hz), 5.19 t (1 H, 3′-H, J = 7.0 Hz).

Acetate 23. mp 138–9 °C; IR ν 1740 (C=O) cm^{-1}; UV (EtOH) λ_{max}/nm (ε) 285 (1700). ^{1}H-NMR δ 0.95, 1.03 (6 H, both s, 1-CH_3), 1.19 (3 H, s, 4a-CH_3), 1.30–1.80 (6 H, m, 2-H–4-H), 2.10 (1 H, m, 9a-H), 2.01, 2.03, 2.10 (9 H, all s, $ArCH_3$), 2.38 (3 H, s, CH_3C=O), 2.61 (2 H, dd, 9-H, J = 5.1 and J = 16.0 Hz).

2*RS*,5,7,8-tetramethyl-2-(1*S*-methyl-4-oxobut-1-yl)-6-acetoxychroman (24). An ozone–oxygen mixture was passed for 8 min through a mixture of acetates **18** (0.5 g, 1.4 mmol), $Ba(OH)_2$ (0.48 g, 2.8 mmol), H_2O (0.12 mL), and acetone (5 mL) at ~20 °C, at a flow of 30 $L{\cdot}h^{-1}$ (1.45 mmol of O_3). After the reaction was completed, the precipitate was filtered off and the filtrate concentrated *in vacuo*. The residue was dissolved in 10 mL of Et_2O, dried with $MgSO_4$, and concentrated. The residue was chromatographed on SiO_2 using an *n*-hexane–Et_2O mixture (10:1) as eluent to give 0.24 g (52%) of aldehyde **24**, $[\alpha]_D^{20}$ –5.9° (c 0.54, $CHCl_3$). Anal. Calcd. for $C_{20}H_{28}O_4$ (332.4): C, 72.26; H, 8.49. Found: C, 72.47; H, 8.50%. IR ν 1710 and 1740 (C=O) cm^{-1}; UV ($CHCl_3$) λ_{max}/nm (ε) 280 (1400), 288 (1600); ^{1}H-NMR δ 0.92, 0.98 (3 H, both d, 1′-CH_3, J = 6.9 Hz, J = 6.7 Hz), 1.15 (3 H, s, 2-CH_3), 1.6–2.0 (5 H, m, 3-H, 1′-H, 2′-H), 1.98, 2.00, 2.10 (9 H, all s, $ArCH_3$), 2.30 (3 H, s, CH_3CO), 2.58 (4 H, m, 4-H, 3′-H), 9.80 (1 H, s, 4′-H).

2*RS*,5,7,8-Tetramethyl-2-(3-oxoprop-1-yl)-6-acetoxychroman (25). An ozone–oxygen mixture was passed for 15 min through a mixture of acetates **21** and **23** (0.8 g) (containing 0.48 g [1.45 mmol] of **21**), $Ba(OH)_2$ (0.87 g, 5.04 mmol), H_2O (0.2 mL), and acetone (8 mL) at ~20 °C at a velocity of 30 $L{\cdot}h^{-1}$ (2.05 mmol of O_3). The mixture was worked-up as described in the previous experiment to give 0.35 g (80%) of aldehyde **25** and 0.25 g of compound **23**.

Aldehyde 25. IR ν 1710 and 1740 (C=O) cm^{-1}; UV ($CHCl_3$) λ_{max}/nm (ε) 278 (1600), 287 (1800). ^{1}H-NMR δ 1.20 (3 H, s, 2-CH_3), 1.75 (4 H, m, 3-H, 1′-H), 1.95, 2.00, 2.03 (9 H, all s, $ArCH_3$), 2.10 (3 H, s, CH_3CO), 2.58 (4 H, m, 4-H, 2′-H), 9.75 (1 H, s, 3′-H).

2*RS*,5,7,8-Tetramethyl-2-(1*S*-methyl-4-hydroxybut-1-yl)-6-acetoxychroman (26). $NaBH_4$ (0.017 g, 0.42 mmol) was added in one portion to a solution of aldehyde **24** (0.14 g, 0.4 mmol) in 2 mL of MeOH. The mixture was stirred for 12 h, then the solvent was removed *in vacuo*. The residue was dissolved in EtOAc, washed with 3 *M* HCl, saturated aq. $NaHCO_3$, then brine, and dried with $MgSO_4$. The solution was concentrated and the residue was chromatographed on SiO_2 using a 10:1 hexane–EtOAc mixture as eluent to give 0.08 g (58%) of alcohol **26**, $[\alpha]_D^{20}$ –5.8° (c 0.37, $CHCl_3$). Anal. Calcd. for $C_{20}H_{30}O_4$ (334.5): C, 71.82; H, 9.04. Found: C, 71.97; H, 8.90. IR ν 3400 (OH), 1740 (C=O) cm^{-1}; UV ($CHCl_3$) λ_{max}/nm (ε) 280 (2100), 288 (2500); ^{1}H-NMR δ 0.94, 1.00 (3 H, both d, 1′-CH_3, J = 6.5 Hz), 1.15 (3 H, s, 2-CH_3), 1.61–2.02 (7 H, m, 3-H, 1′-H – 3′-H), 2.00, 2.07, 2.13 (9 H, all s, $ArCH_3$), 2.34 (3 H, s, CH_3CO), 2.58 (2 H, t, 4-H, J = 6.6 Hz), 3.60, 3.65 (2 H, both t, 4′-H, J = 6.1 Hz).

2*RS*,5,7,8-Tetramethyl-2-(3-hydroxyprop-1-yl)-6-acetoxychroman (27). The reaction of aldehyde **25** (0.32 g, 1.04 mmol) and $NaBH_4$ (0.04 g, 1.04 mmol) in 3 mL of MeOH, carried out as above gave 0.18 g (58%) of alcohol **27.** IR ν 3400 (OH), 1740 (CH_3CO) cm^{-1}; UV ($CHCl_3$) λ_{max}/nm (ε) 280 (1500), 287 (1700); ^{1}H-NMR δ 1.25 (3 H, s, CH_3-2), 1.65 (4 H, m, 1′-H, 2′-H),

1.78 (2 H, m, 3-H), 1.98, 2.02, 2.10 (9 H, all s, $ArCH_3$), 2.32 (3 H, s, CH_3CO), 2.59 (2 H, t, 4-H, J = 6.6 Hz), 3.60 (3 H, m, 3′-H, OH).

9-Acetoxy-1,1,4a,10-tetramethyl-1,2,3,4,4a,11a-hexahydro-benzo[*f*]xanthene (28). Alcohol **19** (0.21 g, 1.4 mmol) was added slowly to a boiling suspension of **10** (0.60 g, 2.8 mmol) and finely crushed Tseokar-10 catalyst (1.0 g) in 9.0 mL of boiling abs. toluene at (Ar). The mixture was boiled for 5 h, cooled to room temperature, the catalyst filtered off, and the filtrate evaporated. The residue was chromatographed on a SiO_2 column (20 g) eluting with *n*-hexane to give the fraction (R_f = 0.7) of non-polar substances, then the fraction (R_f = 0.5) was eluted using *n*-hexane–Et_2O (10:1), and evaporated to give **28** (0.307 g, 62%), mp 191–3°C. Anal. Calcd. for $C_{23}H_{28}O_3$ (352.5): C, 78.30; H, 7.94. Found: C, 78.16; H, 7.81%. IR ν 1760 (C=O), 1210, 1080 and 1060 (C-O) cm^{-1}; UV ($CHCl_3$) λ_{max}/nm (ε) 245 (34650), 308 (6410), 343 (5410); ^{1}H-NMR δ 1.00, 1.10 (6 H, both s, 1-CH_3), 1.30 (3 H, s, 4a-CH_3), 1.40–1.90 (6 H, m, 2-H–4-H), 2.15 (1 H, m, 11a-H), 2.28 (3 H, s, 10-CH_3), 2.50 (3 H, s, CH_3C=O), 2.80 (2 H, dd, 11-H, J = 5.2 Hz and J = 16.1 Hz), 7.48 (2 H, m, 6-H, 7-H), 7.70, 8.28 (2 H, both d, 8-H, 5-H, J = 8.0 Hz); ^{13}C-NMR δ 12.60 (10-CH_3), 20.55 (1-CH_3, $\underline{C}H_3C$=O), 21.69 (1-C), 32.03 (4a-CH_3), 33.33 (3-C, 11-C), 39.71 (2-C), 41.50 (4-C), 47.92 (11a-C), 75.41 (4a-C), 114.00 (10a-C), 120.04, 120.15, 121.97, 124,43, 124.62, 125.91, 125.99 (10-C, 8a-C, 8-C, 7-C, 6-C, 5-C, 4c-C), 136.86 (4b-C), 146.01 (9-C), 169.66 ($CH_3\underline{C}$=O).

2,3,5-Trimethyl-6-(3,7-dimethylocta-2*E*,6-dien-1-yl)-1,4-benzoquinone(geranyltrimethylbenzo-quinone) (30). The allylic alcohol **19** (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 mixture was heated at reflux for 5 h and cooled to ~20 °C, the catalyst filtered off, and the filtrate 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, the silica gel with the substance was transferred onto the adsorbent bed in a chromatographic column, washed in with hexane, and eluted with 20:1 hexane–Et_2O mixture to give 0.13 g (34%) of quinone **30**, n_D^{24} 1.5247. IR ν 1630 (C=O) cm^{-1}; UV ($CHCl_3$) λ_{max}/nm (ε) 257 (15883), 265 (15750); ^{1}H-NMR δ 1.48, 1.57 and 1.68 (each 3 H, all s, 3′-CH_3, 7′-CH_3, 8′-H), 1.95 (13 H, m, 2-CH_3, 3-CH_3, 5-CH_3, 4′-H, 5′-H), 3.12 (2 H, d, 1′-H, J = 6.8 Hz), 4.85 (1 H, t, 2′-H, J = 6.8 Hz), 4.95 (1 H, t, 6′-H, J = 7.1 Hz); ^{13}C-NMR δ 12.0. 12.2, 12.3 (2-CH_3, 3-CH_3, 5-CH_3), 16.1 (3-CH_3), 17.5 (7′-CH_3), 25.4 (5′-C), 25.5 (8′-C), 26.4 (1′-C), 39.6 (4′-C), 119.4 (2′-C), 124.0 (6′-C), 131.2 (7′-C), 136.8 (3′-C), 140.06, 140.1, 140.2 (2-C, 3-C, 5-C), 143.0 (6-C), 186.7, 187.7 (1-C, 4-C).

2,3,5-Trimethyl-6-(3,4*S*,8-trimethylnona-2*E*,7-dien-1-yl)-1,4-benzoquinone (29). TMHQ (0.2 g, 1.3 mmol), the allylic alcohols **16** (0.48 g, 2.64 mmol), and the ZSM-5/11 catalyst [*] (0.45 g) in 9 mL of anhydrous nonane were heated under reflux for 5 h and then worked-up as described in the previous experiment to give 0.14 g (34%) of quinone **29,** n_D^{24} 1.5218, $[\alpha]_D^{23}$ + 0.39 (c 2.4, $CHCl_3$). Anal. Calcd. for $C_{21}H_{30}O_2$ (314.5): C, 80.21, H, 9.62. Found: C, 80.00, H,

[*] **Preparation of the ZSM-5/11 catalyst.** A Pentasil zeolite prepared by a previously described procedure[26] (except that *mono*-ethanolamine 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.

9.48%. IR ν 1630 (C=O) cm^{-1}; UV ($CHCl_3$) λ_{max}/nm (ε) 257 (16117), 265 (16476). ^{1}H-NMR δ 0.87 (3 H, d, 4′-CH_3, *J* = 6.8 Hz), 1.10–1.30 (2 H, m, 5′-H), 1.42, 1.57, 1.59 (each 3 H, all s, 3′-CH_3, 8′-CH_3, 9′-CH_3), 1.60–1.80 m (2 H, 6′-H_2C), 1.90 m (9 H, 2-CH_3, 3-CH_3, 5-CH_3), 3.12 d (2 H, 1-H_2C, *J* = 6.8 Hz), 4.85 t (1 H, 2′-HC, *J* = 6.9 Hz), 4.95 t (1 H, 7′-HC, *J* = 7.1 Hz); ^{13}C-NMR δ 11.9, 12.1 (2-CH_3, 3-CH_3, 5-CH_3), 17.3 (3′-CH_3, 8′-CH_3), 19.5(4′-CH_3), 25.1 (6′-C), 25.6 (9′-C), 25.9 (1′-C), 34.7 (5′-C), 42.3 (4′-C), 118.9 (2′-C), 124.5 (7′-C), 130.8 (8′-C), 140.7 (3′-C), 139.9, 140.0, 140.2 (2-C, 3-C, 5-C), 143.0 (6-C), 186.6, 187.5 (1-C, 4-C).

2,3,5-Trimethyl-6-(3,7*RS*,11*RS*,15-tetramethylhexadec-2*E*-en-1-yl)-1,4-benzoquinones (phytyl-trimethylbenzoquinones) (35). Heating under reflux of TMHQ (0.1 g, 0.66 mmol), isophytol **2** (0.39 g, 1.32 mmol), and ZSM-5/11 (0.1 g) in 4 mL of anhydrous nonane for 3 h, as described above, gave 0.16 g (57%) of quinones **35**, n_D^{20} 1.4942; IR ν 1630 (C=O) cm^{-1}; UV ($CHCl_3$) λ_{max}/nm (ε) 257 (16120), 265 (16711); ^{1}H-NMR δ 0.85 (12 H, d, 7′-CH_3, 11′-CH_3, 15′-CH_3, 16′-H, *J* = 6.1 Hz), 1.00–2.10 (21 H, m, 4′-H–15′H), 2.00 (9 H, m, 2-CH_3, 3-CH_3, 5-CH_3), 3.10 (2 H, d, 1′-H, *J* = 6.9 Hz), 4.95 (1 H, t, 2′-H, *J* = 6.9 Hz); ^{13}C-NMR δ 11.9, 12.2, 13.0 (2-CH_3, 3-CH_3, 5-CH_3), 16.2 (3′-CH_3), 19.7 (7′-CH_3, 11′-CH_3), 22.7 (15′-CH_3, 16′-C), 24.8 (9′-C), 25.3 (5′-C), 25.6 (1′-C), 28.0 (15′-C), 32.7 (11′-C), 32.8 (7′-C), 36.7 (6′-C), 37.4 (8′-C, 10′-C, 12′-C), 39.5 (14′-C), 40.1 (4′-C), 119.3 (2′-C), 137.2 (3′-C), 137.4, 140.3, 143.2 (2-C, 3-C, 5-C, 6-C), 186.8, 187.7 (1-C, 4-C).

2*RS*,5,7,8-Tetramethyl-2-(4-methylpent-3-en-1-yl)-6-hydroxy-3-chromene (32). A solution of the quinone **30** (0.59 g, 1.22 mmol) in 9 mL of anhydrous pyridine was heated at reflux 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 **32**, n_D^{24} 1.5448; UV ($CHCl_3$) λ_{max}/nm (ε) 276 (8528), 286 (8210), 334 (3113). ^{1}H-NMR δ 1.45 (3 H, s, 2-CH_3), 1.68 and 1.75 (6 H, both s, 4′-CH_3, 5′-H), 1.75 (2 H, m, 1′-H), 2.20 (11 H, m, 2′-H, ArCH_3), 4.65 (1 H, s, OH), 5.18 (1 H, t, 3′-H, *J* = 7.1 Hz), 5.68 (1 H, d, 3-H, *J* = 10.0 Hz), 6.60 (1 H, d, 4-H, *J* = 10.0 Hz); ^{13}C-NMR δ 10.8, 11.5, 12.3 (5-CH_3, 7-CH_3, 8-CH_3), 17.4 (4′-CH_3), 22.6 (2′-C), 25.2 (2-CH_3), 25.6 (5′-C), 40.2 (1′-C), 76.4 (2-C), 120.1 (3′-C), 116.5 (10-C), 117.6 (5-C), 122.1 (8-C), 123.2 (7-C), 124.3 (3-C), 129.6 (4-C), 131.3 (4′-C), 144.5 (9-C), 145.2 (6-C).

2*RS*,5,7,8-Tetramethyl-2-(1*S*,5-dimethylhex-4-en-1-yl)-6-hydroxy-3-chromenes (31). Heating of quinone **29** (0.21 g, 0.69 mmol) at reflux in 3 mL of anhydrous pyridine, as described above, gave 0.13 g (59%) of a mixture of (2*R*,1′*S*)-*erythro*- and (2*S*,l′*S*)-*threo*- chromenes **31,** $[\alpha]_D^{20}$ –7.0° (c 0.47, $CHCl_3$). Anal. Calcd. for $C_{21}H_{30}O_2$ (314.5): C, 80.21, H, 9.62. Found: C, 80.13, H, 9.50%. UV ($CHCl_3$) λ_{max}/nm (ε) 273 (7828), 284 (7617), 334 (3513); ^{1}H-NMR δ 1.00 (3 H, m, 1′-CH_3), 1.30 (3 H, s, 2-CH_3), 1.59, 1.61, 1.67, 1.70 (6 H, all s, 5′-CH_3, 6′-H), 1.50–1.90 (5 H, m, 1′-H – 3′-H), 2.15 (9 H, m, ArCH_3), 4.48 (1 H, br. s, OH), 5.10 (1 H, m, 4′-H), 5.68 (1 H, m, 3-H), 6.53 (1 H, d, 4-H, *J* = 10.0 Hz); ^{13}C-NMR δ 10.9, 11.6, 12.5 (5- CH_3, 7-CH_3, 8-CH_3), 13.9, 14.0 (1′-CH_3), 17.7 (5′-CH_3), 21.9, 22.7 (2-CH_3), 25.7 (6′-C), 26.2, 26.5 (3′-C), 31.3, 31.6 (2′-C), 40.5, 40.7 (1′-C), 79.2, 79.3 (2-C), 120.1 (4′-C), 116.2 (10-C), 118.0 (5-C), 122.2 (8-C), 123.2 (7-C), 124.8 (3-C), 129.2, 129.6 (4-C), 131.4 (5′-C), 144.5 (9-C), 145.3 (6-C).

2*RS*,5,7,8-Tetramethyl-2-(4*RS*,8*RS*,12-trimethyltridec-1-yl)-6-hydroxy-3-chromenes (36). The quinones **35** (0.44 g, 1.02 mmol) were heated at reflux in 4.4 mL of anhydrous pyridine, as described above, gave 0.29 g (66%) of a mixture of chromenes **36,** n_D^{24} 1.5096; UV ($CHCl_3$) λ_{max}/nm (ε) 272 (9200), 283 (8200), 333 (4100); ^{1}H-NMR δ 0.92 (12 H, m, 4′-CH_3, 8′-CH_3, 12′-CH_3, 13′-H), 1.05–1.72 (21 H, m, 1′-H – 12′-H), 1.38 (3 H, s, 2-CH_3), 2.20 (9 H, m, ArCH_3), 4.48 (1 H, br. s, OH), 5.65 (1 H, d, 3-H, *J* = 10.0 Hz), 6.57 (1 H, d, 4-H, *J* = 10.0 Hz); ^{13}C-NMR δ 10.8, 11.5, 12.4 (5-CH_3, 7-CH_3, 8-CH_3), 19.6, 19.7 (4′-CH_3, 8′-CH_3), 22.6, 22.7 (12′-CH_3, 13′-C), 24.4 (6′-C), 24.8 (2′-C, 10′-C), 28.0 (12′-C), 32.8, 32.9 (4′-C, 8′-C), 37.2, 37.3, 37.4 (3′-C, 5′-C, 7′-C, 9′-C), 39.4 (11′-C), 40.0 (1′-C′), 76.6 (2-C), 116.2 (5-C), 118.5 (10-C), 120.1 (3-C), 122.2 (8-C), 123.1 (7-C), 129.9 (4-C), 144.9 (9-C), 145.3 (6-C).

2*RS*,5,7,8-Tetramethyl-2-(4-methylpent-3-en-1-yl)-6-acetoxy-3-chromene (**34).** A solution of the chromene **32** (0.42 g, 1.48 mmol) in 4 mL of Ac_2O and 5.3 mL of anhydrous pyridine was kept at ~20 °C for 3 h, poured on ice, extracted with Et_2O, washed with 3 *M* HCl, then a saturated solution of $NaHCO_3$, and H_2O, and dried with $MgSO_4$ to give 0.42 g (87%) of a mixture of the chromenes **34**. Anal. Calcd. for $C_{21}H_{28}O_3$ (328.5): C, 76.79; H, 8.59. Found: C, 76.53; H, 8.45%. IR ν 1740 (C=O) cm^{-1}; UV ($CHCl_3$) λ_{max}/nm (ε) 272 (8600), 283 (6900), 320 (2600); ^{1}H-NMR δ 1.38 (3 H, s, 2-CH_3), 1.60, 1.70 (6 H, both s, 5′-H, 4′-CH_3), 1.70 (2 H, m, 1′-H); 2.04, 2.08, 2.15 (9 H, all s, ArCH_3), 2.15 (2 H, m, 2′-H), 2.33 (3 H, s, CH_3C=O), 5.12 (1 H, t, 3′-H, *J* = 6.9 Hz), 5.60 (1 H, d, 3-H, *J* = 10.0 Hz), 6.52 (1 H, d, 4-H, *J* = 10.0 Hz); ^{13}C-NMR δ 11.4, 11.8, 13.0 (5-CH_3, 7-CH_3, 8-CH_3), 17.5 (4′-CH_3), 20.2 ($\underline{C}H_3CO$), 22.6 (2′-C), 25.5 (2-CH_3), 25.7 (5′-C), 40.6 (1′-C), 77.1 (2-C), 117.4 (10-C), 119.8 (3′-C), 122.2 (8-C), 122.4 (5-C), 124.1 (3-C), 129.2 (7-C), 129.3 (4-C), 131.3 (4′-C), 145.0 (9-C), 148.3 (6-C), 169.3 (C=O).

2*RS*,5,7,8-Tetramethyl-2-(1*S*,5-dimethylhex-4-en-1-yl)-6-acetoxy-3-chromenes (33). A solution of a mixture of chromenes **31** (0.63 g, 2.01 mmol) in 5.5 mL of Ac_2O and 7 mL of anhydrous pyridine was kept at ~20 °C for 3 h, poured on ice, extracted with Et_2O, washed with 3 *M* HCl, then a saturated $NaHCO_3$ solution, then H_2O, 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 **33**, $[\alpha]_D^{20}$ −5.5° (c 0.74, $CHCl_3$). Anal. Calcd. for $C_{23}H_{32}O_3$ (356.5): C, 77.49; H, 9.05. Found: C, 77.31; H, 8.96%. IR ν 1740 (C=O) cm^{-1}; UV ($CHCl_3$) λ_{max}/nm (ε) 273 (5700), 283 (5000), 321 (1950). ^{1}H-NMR δ 0.98 (3 H, d, 1′-CH_3, *J*=6.8 Hz), 1.32 (3 H, s, 2-CH_3), 1.58, 1.60, 1.68, 1.70 (6 H, all s, 5′-CH_3, 6′-H), 1.50–2.00 (5 H, m, 1′-H – 3′-H), 2.00, 2.08, 2.10 (9 H, all s, ArCH_3), 2.33 (3 H, s, CH_3C=O), 5.10 (1 H, m, 4′-H), 5.15 (1 H, m, 3-H), 6.50 (1 H, d, 4-H, *J*=10.2 Hz); ^{13}C-NMR δ 11.3, 11.4, 13.0 (5-CH_3, 7-CH_3, 8-CH_3), 13.7, 13.8 (1′-CH_3), 17.8 (5′-CH_3), 20.3 ($\underline{C}H_3CO$), 22.4 (2′-CH_3), 25.5 (6′-C), 26.0, 26.2 (3′-C), 31.2, 31.3 (2′-C), 40.9, 41.0 (1′-C), 79.8 (2-C), 117.5 (10-C), 119.6 (4′-C), 122.2 (8-C), 122.3 (5-C), 124.6 (3-C), 128.6 (7-C), 128.8, 129.0 (4-C), 131.2 (5′-C), 141.1 (9-C), 148.2 (6-C), 169.4 (C=O).

2*RS*,5,7,8-Tetramethyl-2-(3-oxoprop-1-yl)-6-acetoxy-3-chromene (38). 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 the acetate **34** (0.42 g, 1.28 mmol), $Ba(OH)_2$ (0.44 g, 2.57 mmol), 0.1 mL of H_2O, 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, dried with $MgSO_4$, and the solvent evaporated. The residue

was chromatographed on SiO_2 using a 10:1 *n*-hexane–Et_2O mixture as eluent to give 0.123 g (41%) of aldehyde **38**. Anal. Calcd. for $C_{18}H_{22}O_4$ (302.4): C, 71.50; H, 7.33. Found: C, 71.29; H, 7.20%. IR ν 1710 and 1740 (C=O) cm^{-1}; UV ($CHCl_3$) λ_{max}/nm (ε) 272 (9300), 282.5 (7500), 318 (2900); ^{1}H-NMR δ 1.35 (3 H**,** s, 2-CH_3), 2.02, 2.05, 2.08 (9 H, all s, ArCH_3), 2.15 (2 H, m, 1′-H), 2.32 (3 H, s, CH_3C=O), 2.60 (2 H, m, 2′-H), 5.53 (1 H, d, 3-H, *J* = 10.1 Hz), 6.55 (1 H, d, 4-H, *J* = 10.1 Hz), 9.78 (1 H, t, 3′-H, *J* = 1.1 Hz); ^{13}C-NMR δ 11.5, 13.1 (5-CH_3, 7-CH_3, 8-CH_3), 20.4 ($\underline{C}H_3CO$), 26.1 (2-CH_3), 39.1 (1′-C), 65.8 (2′-C), 76.8 (2-C), 117.2 (10-C), 120.9 (3-C), 122.6 (8-C), 122.7 (5-C), 128.1 (4-C), 129.4 (7-C), 141.6 (9-C), 148.0 (6-C), 169.4 ($CH_3\underline{C}O$), 202.1 (C=O).

2*RS*,5,7,8-Tetramethyl-2-(1*S*-methyl-4-oxobut-1-yl)-6-acetoxy-3-chromenes (37). An ozone–oxygen mixture was passed for 4 min (0.98 mmol O_3) at a flow rate of 30 $L\cdot h^{-1}$ at ~20 °C through a mixture of acetates **33** (0.35 g, 0.95 mmol), $Ba(OH)_2$ (0.34 g, 1.99 mmol), 0.08 mL of H_2O, 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*,l′*S*)-*threo*-aldehydes **37,** $[\alpha]_D^{20}$ -4.5 (c 0.3, $CHCl_3$). Anal. Calcd. for $C_{20}H_{26}O_4$. (330.4): C, 72.70; H, 7.93. Found: C, 72.56; H, 7.81%. IR ν 1710 and 1740 (C=O) cm^{-1}; UV ($CHCl_3$) λ_{max}/nm (ε) 273 (7500), 283 (6600), 319 (2400); ^{1}H-NMR δ 0.87, 0.98 (3 H, both d, 1′-CH_3, *J* = 5.9 Hz), 1.32 (3 H, s, 2-CH_3), 2.02, 2.05, 2.10 (9 H, all s, ArCH_3), 2.33 (3 H, s, CH_3C=O), 1.40–2.00 (3 H, m, 2′-H, 1′-H), 2.53 (2 H, m, 3′-H), 5.65 (1 H, m, 3-H), 6.50 (1 H, m, 4-H), 9.80 (1 H, t, 4′-H, *J* = 1.1 Hz); ^{13}C-NMR δ 11.4, 13.0 (5-CH_3, 7-CH_3, 8-CH_3), 17.3, 17.4 (1′-CH_3), 20.3 ($\underline{C}H_3CO$), 20.6 (2-CH_3), 31.3, 31.5 (2′-C), 40.9, 41.1 (1′-C), 65.7 (3′-C), 79.7 (2-C), 117.6 (10-C), 120.2 (3-C), 122.2 (8-C), 122.4 (5-C), 128.8 (4-C), 128.9, 129.0 (7-C), 141.1, 141.2 (9-C), 148.1 (6-C), 169.4 ($CH_3\underline{C}O$), 202.7 (C=O).

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