Reactions of Verbenol Epoxide with Aromatic Aldehydes Containing Hydroxy or Methoxy Groups in the Presence of Montmorillonite Clay

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The reactions of (−)-*cis*-verbenol epoxide with a number of aromatic aldehydes containing OH and/or MeO groups in the presence of montmorillonite *K10* clay have been studied. Several new O-containing heterocyclic compounds with different frameworks, including compounds with a previously unknown octahydro-2*H*-4,6-(epoxymethano)chromene framework, have been synthesized. Introduction of one donor substituent in the benzaldehyde molecule led to a decrease in the total yield of intermolecular by formed products, while the introduction of two and more substituents led to an increase in the yield of these products.

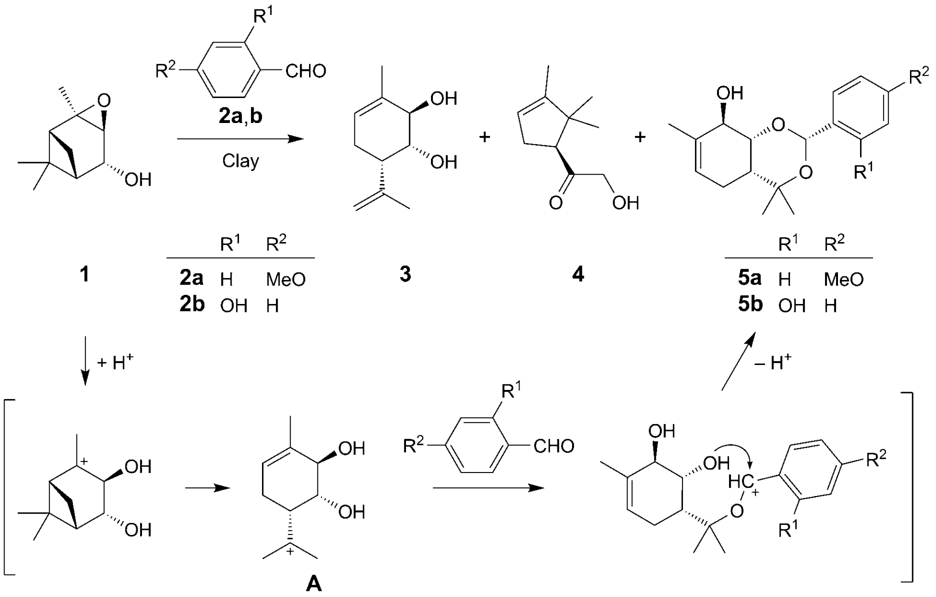
Introduction. – Pinene terpenoids are valuable recyclable raw materials. Due to their unique structure combined with high chemical lability and optical activity, they often serve as substrates for the synthesis of complex optically active compounds [1–5], including compounds with biological activity [6–9]. In acidic media, pinene terpenoids generally undergo numerous transformations leading to complex mixtures of products, which is one of the factors hindering the wide use of these compounds in fine organic chemistry. At the same time, the product ratio significantly depends on the type and characteristics of the acid catalysts used, and this occasionally allows one to select favorable conditions for the formation of a desired compound, stimulating the search for new catalytic systems and reaction conditions [10–14]. Clays play an especially important role among the acid catalysts in terpenoid transformations. On the one hand, these are inexpensive and accessible compounds, which allow ecologically clean synthesis; on the other hand, they often direct terpenoid transformations by new routes or lead to other product ratios compared with other acid catalysts [15–20].

Earlier, we studied the intermolecular reactions of several terpenoids from pinene, *p*-menthene, and carene series with aldehydes in the presence of montmorillonite clays (*K10* and the natural askanite-bentonite clay) [21–24]. As a result, we found unusual transformations, which occur during the reactions of terpene olefins and their derivatives with aldehydes, and form generally complex optically active heterocyclic compounds from simple reagents. The structure of the products depends strongly on small changes in the structure of both starting terpenoids and aldehydes.

For example, it was found [23] that the reaction of (−)-*cis*-verbenol epoxide (**1**), obtained from the widespread monoterpene *α*-pinene, with 4-methoxybenzaldehyde

(**2a**) and 2-hydroxybenzaldehyde (**2b**) in the presence of the natural montmorillonite clay askanite-bentonite gave not only the products of isomerization of epoxide **1** (*trans*-diol with a *p*-menthane framework **3** and hydroxy ketone **4**), but also the products of the intermolecular interaction with the aldehyde, *i.e.*, 1,3-benzodioxins **5a** and **5b** (with yields of 13 and 14%, resp.; *Scheme 1*). The hypothetical mechanism of the formation of **5a** and **5b** involves the protonation and cleavage of the epoxide ring, the skeletal rearrangement into the cation with a *p*-menthane framework **A**, and its subsequent interaction with the aldehyde molecule, which acts as a nucleophile.

Scheme 1. *Interaction of (−)-*cis*-Verbenol Epoxide* (**1**) *with 4-Methoxybenzaldehyde* (**2a**) *and 2-Hydroxybenzaldehyde* (**2b**) *on Askanite-Bentonite Clay* [23]

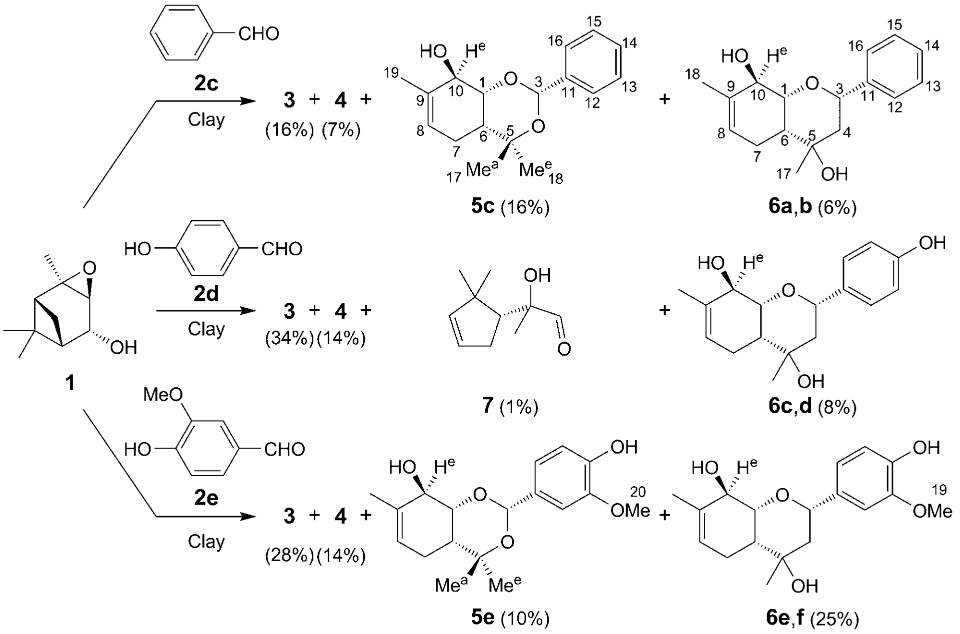


This work represents a continuation of our studies of this unusual reaction. The aim of this study was to investigate the influence of the structure of the aldehyde on the route of transformations. We examined the transformations of (−)-*cis*-verbenol epoxide (**1**) in the presence of the commercially accessible montmorillonite clay *K10* with benzaldehyde and a number of aromatic aldehydes containing a OH and/or MeO group. Due to the presence of these donor substituents in the aldehydes, the reactivity of the latter in nucleophilic reactions increases; moreover the products can exhibit high biological activity, because several bioactive compounds contain in their structures terpene moieties and an aromatic ring with O-containing substituents in their structure [25–28].

Results and Discussion. – We started our studies with the reaction of benzaldehyde (**2c**) in order to investigate how the introduction of substituents affects the route of transformations.

The reaction of (−)-*cis*-verbenol epoxide (**1**) with benzaldehyde (**2c**) on *K10* clay gave the known products of the epoxide isomerization, namely, *trans*-diol **3** and hydroxy ketone **4**, as well as the products of the intermolecular interaction of aldehyde and terpenoid, *i.e.*, compound **5c** with a 1,3-benzodioxin framework, which is an analog of **5a** and **5b**, and compounds **6a** and **6b** with a chromene framework as a mixture of diastereoisomers according to the position of substituents at C(5) (**6a**/**6b** 3 : 1; *Scheme 2*).

Scheme 2. *Interaction of Epoxide* **1** *with Aldehydes* **2c**–**2e** *on* K10 *Clay*



The formation of **6a**/**6b** was quite unexpected, because such products had not been observed before in the reaction of **1** with 4-methoxybenzaldehyde (**2a**) and 2-hydroxybenzaldehyde (**2b**) on clay [23].

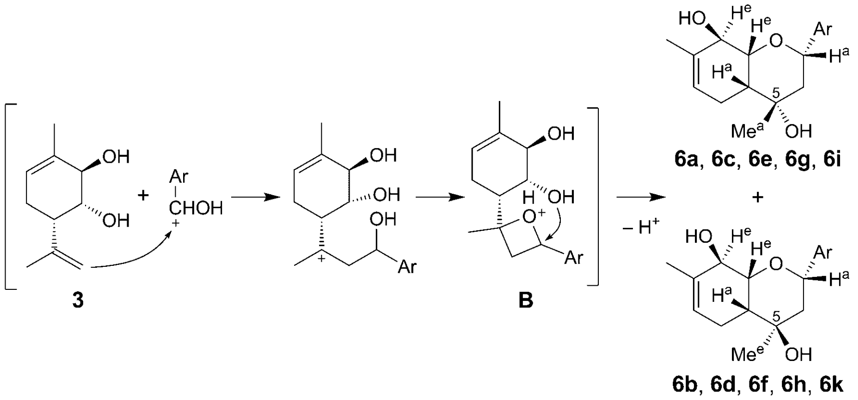
In the reaction of **1** with 4-hydroxybenzaldehyde (**2d**), an isomer of **2b**, the main transformation was the formation of **3** and **4**, as well as α-hydroxy aldehyde **7**, which was previously obtained in studies of the isomerization of epoxide **1** on clay [29]; the intermolecular products were compounds **6c** and **6d** (**6c**/**6d** 8 : 1), which are analogs of **6a** and **6b** (*Scheme 2*). Note that, in the reaction of **1** with **2d**, compounds with a 1,3-benzodioxin framework were not formed, in contrast to the reactions with 2-hydroxybenzaldehyde (**2b**) and benzaldehyde (**2c**).

Thus, the introduction of one donor group in the aldehyde molecule led to a decrease in the yields of intermolecular products compared with benzaldehyde (**2c**; *Schemes 1* and *2*).

The addition of an additional MeO group to the aldehyde on passing from 4-hydroxybenzaldehyde (**2d**) to 4-hydroxy-3-methoxybenzaldehyde (**2e**) led to a considerably increased total yield of intermolecular products **5e**, and **6e** and **6f** (**6e**/**6f** 2 : 1), and **6e** and **6f** were the major intermolecular products (*Scheme 2*).

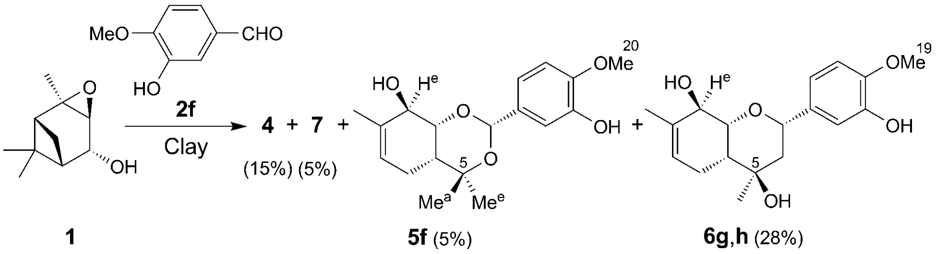
Analyzing the possible mechanism of the formation of compounds of type **6** (*Scheme 3*), it can be assumed that diol **3** is an intermediate neutral species, while the protonated aldehyde is an electrophile. The mechanism may include the formation of cation **B**. Indeed, when diol **3** was stored on clay in the presence of aldehyde **2e**, a mixture of diastereoisomers, (3 : 1), formed with a total yield of 50% based on changed diol **3**, whose conversion was 50%. This confirms our assumption that diol **3** can be an intermediate in the formation of **6** from epoxide **1**. Note that the use of diol **3** instead of verbenol epoxide **1** for the preparation of **6e**/**6f** facilitates the isolation of products and leads to high yields.

Scheme 3. *Possible Mechanism of the Formation of Compounds with Chromene Framework*



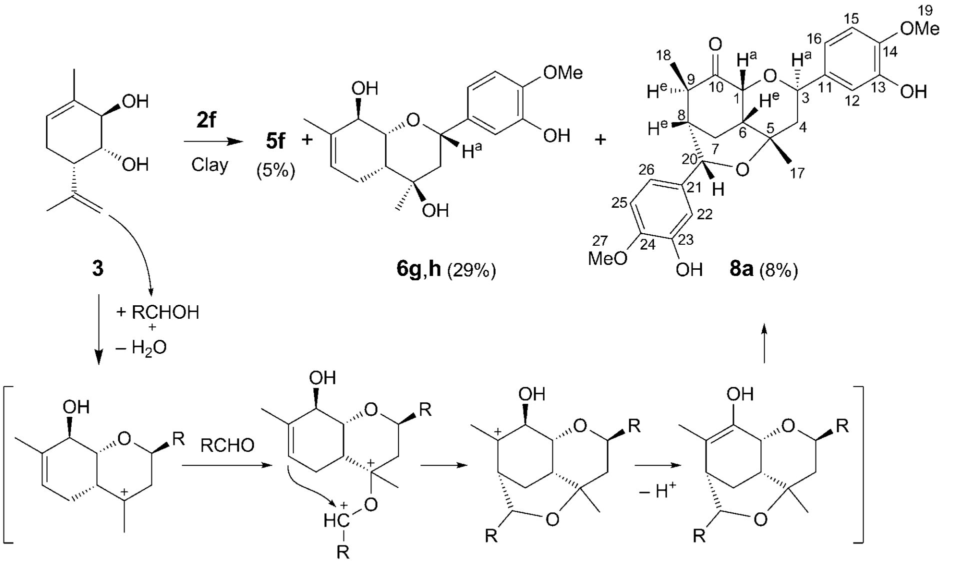
In the reaction of **1** with 3-hydroxy-4-methoxybenzaldehyde (**2f**), an isomer of aldehyde **2e**, the major products were the products of the intermolecular interaction of epoxide and aldehyde, compounds **6g**/**6h** (1 : 1) and compound **5f**. The reaction also led to hydroxy ketone **4** and α-hydroxy aldehyde **7** (*Scheme 4*). Note that, in this reaction, the reaction mixture did not contain *trans*-diol **3**, probably because in this case **3** completely reacted with the aldehyde under the reaction conditions.

Scheme 4. *Interaction of Epoxide* **1** *with Aldehyde* **2f** *on* K10 *Clay*



Unexpected results were obtained, when diol **3** was kept on *K10* clay in the presence of **2f** (*Scheme 5*). First, the reaction mixture contained compound **5f**; its formation from diol **3** might be rationalized by the fact that the protonation of **3** can form the same cation **A** as the protonation and further isomerization of verbenol epoxide **1** (*Scheme 1*). Interaction of cation **A** with the aldehyde molecule can lead to the formation of **5f**. Second, in addition to products **6g**/**6h** (5:1) and **5f**, the reaction yielded the tricyclic compound **8a**, which is the product of the addition of two aldehyde molecules to **3**. The hypothetical mechanism of its formation is presented in *Scheme 5*. It involves the addition of protonated aldehyde **2f** at the C=C bond of **3** and heterocyclization. Then, the formed cation interacts with a second aldehyde molecule. Subsequent loss of H^+ and tautomerization of the enol group lead to the formation of **8a**.

Scheme 5. *Interaction of Diol* **3** *with Aldehyde* **2f** *on* K10 *Clay*

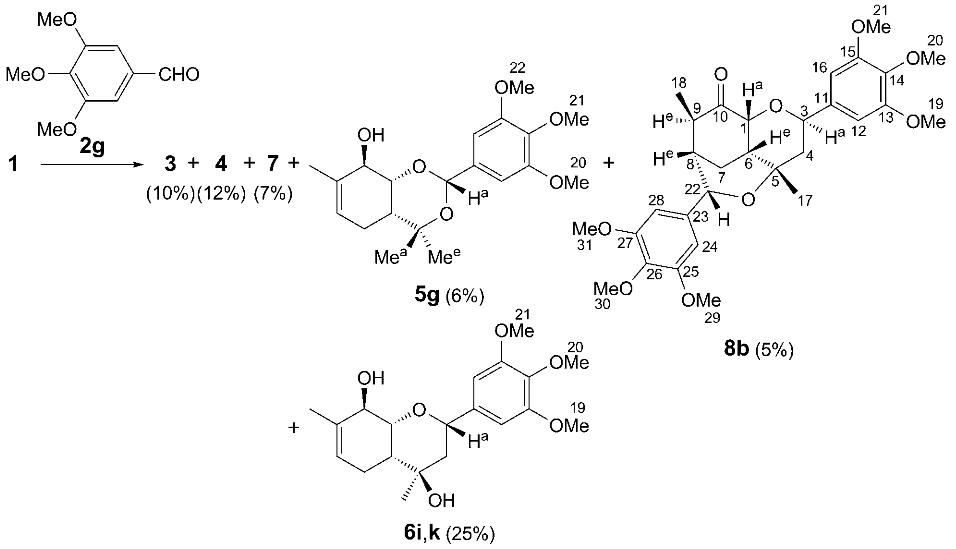


To the best of our knowledge, the octahydro-2*H*-4,6-(epoxymethano)chromene framework of **8a** is a novel structural motif.

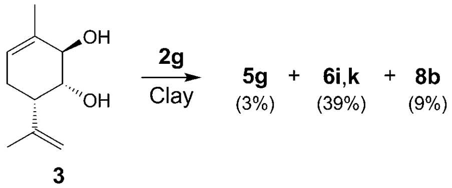
The reaction of (−)-*cis*-verbenol epoxide (**1**) with 3,4,5-trimethoxybenzaldehyde (**2g**) gave a mixture consisting of the products of epoxide isomerization **3**, **4**, and **7**, and a set of intermolecular products **5g**, **6i**/**6k** (1:1), and **8b** (*Scheme 6*).

When diol **3** was stored on *K10* clay in the presence of **2g**, a mixture of heterocyclic compounds **5g**, **6i**/**6k** (3:1), and **8b** formed, as in the case of aldehyde **2f** (*Scheme 7*).

Conclusions. – We have studied the reactions of (−)-*cis*-verbenol epoxide (**1**) with a number of aromatic aldehydes containing OH and/or MeO groups in the presence of montmorillonite *K10* clay. The introduction of one donor substituent in the benzaldehyde molecule led to a decrease in the total yield of intermolecular products, whereas the introduction of two and more substituents favors the formation of these products. Using the accessible monoterpenoid **1** as a starting compound, we obtained a set of new O-containing heterocyclic compounds with different types of framework, Scheme 6. *Interaction of Epoxide* **1** *with Aldehyde* **2g** *on* K10 *Clay*



Scheme 7. *Interaction of Diol* **3** *with Aldehyde* **2g** *on* K10 *Clay*



including compounds with a previously unknown octahydro-2*H*-4,6-(epoxymethano)-chromene framework. Mechanisms of formation were proposed for all new products and confirmed by the experimental model data.

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Experimental Part

1. *General.* All materials were of commercial reagent grade. As catalyst, we used *K10* clay (*Merck*). The clay was calcinated at 110° for 3 h immediately before use. CH_2Cl_2 was passed through calcined Al_2O_3. (−)-*cis*-Verbenol epoxide (**1**) ($[\alpha]^{20}_{580} = -60$ ($c = 0.41$, $CHCl_3$)) was prepared according to [23] from (−)-verbenone (*Aldrich*); the content of the main substance was not less than 98.0%. Column chromatography (CC): silica gel (SiO_2; 60–200 μ; *Macherey-Nagel*). GC (purity control and product analysis): *Agilent 7820A*; *HP-5* quartz column (30000 × 0.25 mm), He (1 atm) as carrier gas. GC/MS: *Hewlett-Packard 5890/II* gas chromatograph with a quadrupole mass spectrometer *(HP MSD 5971)* as a detector, *HP-5MS* quartz column, 30000 × 0.25 mm, He (1 atm) as carrier gas. Optical rotation: *polAAr 3005* spectrometer; $CHCl_3$ soln. ^1H- and ^{13}C-NMR: *Bruker DRX-500* apparatus at 500.13 (^1H) and 125.76 MHz (^{13}C), in $CDCl_3$ or $CDCl_3$/(D_6)acetone 1 : 1 (*v*/*v*) soln.; chemical shifts δ in ppm rel. to

residual $CHCl_3$ (δ(H) 7.24 and δ(C) 76.90 ppm), *J* in Hz; structure determinations by analyzing the ^{1}H-NMR spectra, ^{1}H,^{1}H double resonance spectra, *J*-modulated ^{13}C-NMR spectra (JMOD), ^{13}C-NMR spectra with H-atom off-resonance saturation and ^{13}C,^{1}H 2D-heteronuclear correlation with one-bond and long-rang spin-spin coupling constants (C,H COSY, ^1J(C,H) = 135 Hz, COLOC, $^{2,3}J$(C,H) = 10 Hz). HR-MS: *DFS-Thermo-Scientific* spectrometer in a full-scan mode (0 – 500 *m/z*, 70 eV electron-impact ionization (EI), direct sample introduction).

2. *Reaction of (−)-*cis*-Verbenol Epoxide* (**1**) *with Aldehydes on* K10 *Clay* (*General Procedure*). A soln. of aldehyde (0.5 g) in CH_2Cl_2 (5 ml) was added to a suspension of *K10* clay (2.5 g) in CH_2Cl_2 (10 ml). Then, a soln. of **1** (0.5 g) in CH_2Cl_2 (5 ml) was added dropwise. The mixture was stirred for 40 min at 20°. Then, Et_2O (10 ml) and acetone (10 ml) were added. The catalyst was filtered off, and the solvent was evaporated. The resulting mixture was separated by CC (SiO_2 (10 g); hexane/Et_2O 100 : 0 → 0 : 100, acetone).

2.1. *Reaction of* **1** *with Benzaldehyde* (**2c**) *on* K10 *Clay.* The products included **3** [23] (0.080 g, 16%), **4** [23] (0.035 g, 7%), **5c** (0.134 g, 16%), and a mixture of two isomers **6a**/**6b** (0.052 g, 6%; 3 : 1 (^{1}H-NMR)).

*(2*S*,4a*R*,8*R*,8a*R*)-4a,5,8,8a-Tetrahydro-4,4,7-trimethyl-2-phenyl-4*H*-1,3-benzodioxin-8-ol* (**5c**). $[\alpha]^{19}_D = -78$ (c = 1.64). ^{1}H-NMR ($CDCl_3$)[1]: 1.27 (*s*, Me(18)); 1.52 (*s*, Me(17)); 1.54 (*ddd*, *J*(6a,7a) = 10.8, *J*(6a,7e) = 6.0, *J*(6a,1e) = 2.0, H_a–C(6)); 1.80 (*m*, Me(19)); 2.08 (*dddq*, *J*(7e,7a) = 17.7, *J*(7e,6a) = 6.0, *J*(7e,8) = 5.2, *J*(7e,19) = 1.3, H_e–C(7)); 2.49 (*dddqd*, *J*(7a,7e) = 17.7, *J*(7a,6a) = 10.8, *J*(7a,8) = 2.5, *J*(7a,19) = 2.5, *J*(7a,10e) = 1.5, H_a–C(7)); 3.88 (*m*, H_e–C(10)); 4.34 (*dd*, *J*(1e,10e) = 2.4, *J*(1e,6a) = 2.0, H_e–C(1)); 5.66 (*dm*, *J*(8,7e) = 5.2, H–C(8)); 5.79 (*s*, H–C(3)); 7.27 – 7.36 (*m*, H–C(13), H–C(14), H–C(15)); 7.47 (*dd*, *J*(12,13) = 8.0, *J*(12,14) = 2.0, H–C(12), H–C(16)). ^{13}C-NMR ($CDCl_3$)[1]: 20.48 (*q*, C(19)); 22.59 (*q*, C(17)); 22.90 (*t*, C(7)); 27.12 (*q*, C(18)); 33.89 (*d*, C(6)); 70.27 (*d*, C(10)); 74.50 (*s*, C(5)); 75.03 (*d*, C(1)); 95.91 (*d*, C(3)); 125.25 (*d*, C(8)); 126.25 (*d*, C(12), C(16)); 128.11 (*d*, C(13), C(15)); 128.68 (*d*, C(14)); 130.59 (*s*, C(9)); 138.74 (*s*, C(11)). HR-MS: 274.1555 (M^+, $C_{17}H_{22}O_3^+$; calc. 274.1563).

The NMR spectra of isomers **6a** and **6b** were recorded for **6a**/**6b** 3 : 1.

*(2*S*,4*S*,4a*R*,8*R*,8a*R*)-3,4,4a,5,8,8a-Hexahydro-4,7-dimethyl-2-phenyl-2*H*-chromene-4,8-diol* (**6a**). ^{1}H-NMR ($CDCl_3$ + (D_6)acetone)[1]: 1.47 (*d*, *J*(17,4a) = 0.7, Me(17)); 1.62 (*ddd*, *J*(4e,4a) = 13.4, *J*(4e,3a) = 2.7, *J*(4e,6) = 1.2, H_e–C(4)); 1.75 (*td*, *J*(18,7) = 2.0, *J*(18,8) = 1.6, Me(18)); 1.85 (br. *t*, *J*(6a,7) = 8.5, H_a–C(6)); 1.86 (*dd*, *J*(4a,4e) = 13.4, *J*(4a,3a) = 12.0, H_a–C(4)); 2.14 (*dm*, *J*(7,6) = 8.5, CH_2(7)); 3.26 (br. *s*, HO–C(5)); 3.60 (*d*, *J*(OH,10) = 6.5, HO–C(10)); 3.79 (*dd*, *J*(1e,10e) = 2.4, *J*(1e,6a) = 2.0, H_e–C(1)); 3.81 (br. *d*, *J*(10e,OH) = 6.5, H_e–C(10)); 4.40 (*dd*, *J*(3a,4a) = 12.0, *J*(3a,4e) = 2.7, H_a–C(3)); 5.55 (*tq*, *J*(8,7) = 3.8, *J*(8,18) = 1.6, H–C(8)); 7.13 – 7.27 (*m*, H–C(12) – H–C(16)). ^{13}C-NMR ($CDCl_3$ + (D_6)acetone)[1]: 20.86 (*q*, C(18)); 23.03 (*t*, C(7)); 27.03 (*q*, C(17)); 38.66 (*d*, C(6)); 43.53 (*t*, C(4)); 70.45 (*s*, C(5)); 70.52 (*d*, C(10)); 77.61 (*d*, C(3)); 78.36 (*d*, C(1)); 124.25 (*d*, C(8)); 125.97 (*d*, C(12), C(16)); 127.35 (*d*, C(14)); 128.27 (*d*, C(13), C(15)); 131.84 (*s*, C(9)); 142.87 (*s*, C(11)). HR-MS: 274.1543 (M^+, $C_{17}H_{22}O_3^+$; calc. 274.1563).

*(2*S*,4*R*,4a*R*,8*R*,8a*R*)-3,4,4a,5,8,8a-Hexahydro-4,7-dimethyl-2-phenyl-2*H*-chromene-4,8-diol* (**6b**). ^{1}H-NMR ($CDCl_3$ + (D_6)acetone)[1]: 1.18 (*s*, Me(17)); 1.60 (*ddd*, *J*(4e,4a) = 14.0, *J*(4e,3a) = 3.3, *J*(4e,6a) = 1.2, H_e–C(4)); 1.73 (*m*, Me(18)); 1.71 – 1.77 (*m*, H_a–C(6)); 1.67 (*dd*, *J*(4a,4e) = 14.0, *J*(4a,3a) = 11.3, H_a–C(4)); 1.95 (*dm*, *J*(7,6a) = 8.5, CH_2(7)); 3.30 (br. *s*, HO–C(5)); 3.49 (*d*, *J*(OH,10) = 6.5, HO–C(10)); 3.81 (br. *d*, *J*(10e,OH) = 6.5, H_e–C(10)); 4.24 (*dd*, *J*(1e,10e) = 2.5, *J*(1e,6a) = 2.0, H_e–C(1)); 4.75 (*dd*, *J*(3a,4a) = 11.3, *J*(3a,4e) = 3.3, H_a–C(3)); 5.50 (*tq*, *J*(8,7) = 3.8, *J*(8,18) = 1.6, H–C(8)); 7.11 – 7.27 (*m*, H–C(12) – H–C(16)). ^{13}C-NMR ($CDCl_3$ + (D_6)acetone)[1]: 20.95 (*q*, C(18)); 24.79 (*t*, C(7)); 28.18 (*q*, C(17)); 37.96 (*d*, C(6)); 42.64 (*t*, C(4)); 70.16 (*s*, C(5)); 70.50 (*d*, C(10)); 75.70 (*d*, C(1)); 75.82 (*d*, C(3)); 123.48 (*d*, C(8)); 125.91 (*d*, C(12), C(16)); 127.11 (*d*, C(14)); 128.21 (*d*, C(13), C(15)); 132.50 (*s*, C(9)); 143.54 (*s*, C(11)). HR-MS: 274.1543 (M^+, $C_{17}H_{22}O_3^+$; calc. 274.1563).

2.2. *Reaction of* **1** *with 4-Hydroxybenzaldehyde* (**2d**) *on* K10 *Clay.* The products included **3** (0.168 g, 34%), **4** (0.070 g, 14%), **7** (0.005 g, 1%), and a mixture of two isomers **6c**/**6d** (0.070 g, 8%; (8 : 1 (^{1}H-NMR).

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[1] Numbering as indicated in the *Formulae.*

The NMR spectra of isomers **6c** and **6d** were recorded for **6c**/**6d** 8 : 1. *(2S,4S,4aR,8R,8aR)-3,4,4a,5,8,8a-Hexahydro-2-(4-hydroxyphenyl)-4,7-dimethyl-2H-chromene-4,8-diol* (**6c**).

^{1}H-NMR ($CDCl_3$ + (D_6)acetone)^1)): 1.46 (*d*, *J*(17,4a) = 0.7, Me(17)); 1.58 (*ddd*, *J*(4e,4a) = 13.4, *J*(4e,3a) = 2.7, *J*(4e,6) = 1.2, H_e–C(4)); 1.75 (*td*, *J*(18,7) = 2.0, *J*(18,8) = 1.7, Me(18)); 1.84 (br. *t*, *J*(6a,7) = 8.5, H_a–C(6)); 1.88 (*dd*, *J*(4a,4e) = 13.4, *J*(4a,3a) = 12.0, H_a–C(4)); 2.15 (*dm*, *J*(7,6a) = 8.5, CH_2(7)); 3.76 (br. *dd*, *J*(10e,OH) = 6.6, *J*(10e,1e) = 2.4, H_e–C(10)); 3.78 (*dd*, *J*(1e,10e) = 2.4, *J*(1e,6) = 2.0, H_e–C(1)); 3.80 (*d*, *J*(OH,10e) = 6.6, HO–C(10)); 4.37 (*dd*, *J*(3a,4a) = 12.0, *J*(3a,4e) = 2.7, H_a–C(3)); 5.54 (*tq*, *J*(8,7) = 3.8, *J*(8,18) = 1.7, H–C(8)); 6.75 (*d*, *J* = 8.6, H–C(13), H–C(15)); 7.13 (*d*, *J* = 8.6, H–C(12), H–C(16)); 8.09 (*s*, HO–C(14)). ^{13}C-NMR ($CDCl_3$ + (D_6)acetone)^1)): 21.19 (*q*, C(18)); 23.67 (*t*, C(7)); 27.52 (*q*, C(17)); 39.48 (*d*, C(6)); 44.31 (*t*, C(4)); 70.62 (*s*, C(5)); 71.18 (*d*, C(10)); 77.93 (*d*, C(3)); 79.15 (*d*, C(1)); 115.58 (*d*, C(13), C(15)); 124.48 (*d*, C(8)); 127.93 (*d*, C(12), C(16)); 132.78 (*s*, C(9)); 134.90 (*s*, C(11)); 157.33 (*s*, C(14)). HR-MS: 290.1505 (M^+, $C_{17}H_{22}O_4^+$; calc. 290.1513).

(2S,4R,4aR,8R,8aR)-3,4,4a,5,8,8a-Hexahydro-2-(4-hydroxyphenyl)-4,7-dimethyl-2H-chromene-4,8-diol (**6d**). ^{1}H-NMR ($CDCl_3$ + (D_6)acetone)^1)): 1.19 (*s*, Me(17)); 1.55 (*ddd*, *J*(4e,4a) = 14.1, *J*(4e,3a) = 2.9, *J*(4e,6a) = 1.4, H_e–C(4)); 1.72 – 1.74 (*m*, Me(18)); 1.94 – 2.00 (*m*, CH_2(7)); 4.24 (*dd*, *J*(1e,10e) = 2.4, *J*(1e,6a) = 2.1, H_e–C(1)); 4.68 (*dd*, *J*(3a,4a) = 11.6, *J*(3a,4e) = 2.8, H_a–C(3)); 5.47 – 5.51 (*m*, H–C(8)); 6.73 (*d*, *J* = 8.5, H–C(13), H–C(15)); 7.11 (*d*, *J* = 8.5, H–C(12), H–C(16)); 8.05 (*s*, HO–C(14)). Signals from the other H-atoms were overlapped by those of the major isomer **6c**.

2.3. *Reaction of* **1** *with 4-Hydroxy-3-methoxybenzaldehyde* (**2e**) *on* K10 *Clay.* The products included **3** (0.140 g, 28%), **4** (0.070 g, 14%), **5e** (0.095 g, 10%), and a mixture of two isomers **6e**/**6f** (0.239 g, 25%; 2 : 1 (^{1}H-NMR).

(2S,4aR,8R,8aR)-4a,5,8,8a-Tetrahydro-2-(4-hydroxy-3-methoxyphenyl)-4,4,7-trimethyl-4H-1,3-benzodioxin-8-ol (**5e**). $[\alpha]_D^{19} = -71$ ($c = 0.60$). ^{1}H-NMR ($CDCl_3$)^1)): 1.24 (*s*, Me(18)); 1.48 (*ddd*, *J*(6a,7a) = 10.8, *J*(6a,7e) = 6.0, *J*(6a,1e) = 2.0, H_a–C(6)); 1.50 (*s*, Me(17)); 1.79 (br. *s*, Me(19)); 2.04 (*dddq*, *J*(,7a) = 17.8, *J*(7e,6a) = 6.0, *J*(7e,8) = 5.2, *J*(7e,19) = 1.2, H_e–C(7)); 2.43 (*ddm*, *J*(7a,7e) = 17.8, *J*(7a,6a) = 10.8, H_a–C(7)); 3.82 (br. *s*, H_e–C(10)); 3.88 (*s*, MeO); 4.28 (*dd*, *J*(1e,10e) = 2.5, *J*(1e,6a) = 2.0, H_e–C(1)); 5.61 (br. *s*, HO–C(10)); 5.62 (*m*, H–C(8)); 5.67 (*s*, H–C(3)); 6.82 (*d*, *J*(15,16) = 8.0, H–C(15)); 6.91 (br. *s*, H–C(12)); 6.92 (*dd*, *J*(16,15) = 8.0, *J*(16,12) = 2.0, H–C(16)). ^{13}C-NMR ($CDCl_3$)^1)): 20.62 (*q*, C(19)); 22.81 (*q*, C(17)); 23.09 (*t*, C(7)); 27.33 (*q*, C(18)); 34.07 (*d*, C(6)); 55.73 (*q*, C(20)); 70.45 (*d*, C(10)); 74.50 (*s*, C(5)); 75.13 (*d*, C(1)); 95.95 (*d*, C(3)); 108.76 (*d*, C(12)); 114.00 (*d*, C(15)); 119.79 (*d*, C(16)); 125.25 (*d*, C(8)); 130.95, 131.01 (2*s*, C(9), C(11)); 146.12, 146.16 (2*s*, C(13), C(14)). HR-MS: 320.1610 (M^+, $C_{18}H_{24}O_5^+$; calc. 320.1618).

The NMR spectra of isomers **6e** and **6f** were recorded for **6e**/**6f** 4 : 1 and 1 : 2, resp. *(2S,4S,4aR,8R,8aR)-3,4,4a,5,8,8a-Hexahydro-2-(4-hydroxy-3-methoxyphenyl)-4,7-dimethyl-2H-chromene-4,8-diol* (**6e**).

^{1}H-NMR ($CDCl_3$ + (D_6)acetone)^1)): 1.46 (*d*, *J*(17,4a) = 0.7, Me(17)); 1.59 (*ddd*, *J*(4e,4a) = 13.3, *J*(4e,3a) = 2.7, *J*(4e,6) = 1.2, H_e–C(4)); 1.74 (*td*, *J*(18,7) = 2.0, *J*(18,8) = 1.7, Me(18)); 1.83 (br. *t*, *J*(6,7) = 8.5, H_a–C(6)); 1.89 (*dd*, *J*(4a,4e) = 13.3, *J*(4a,3a) = 12.0, H_a–C(4)); 2.14 (*dm*, *J*(7,6) = 8.5, CH_2(7)); 3.76 (*m*, H–C(1), H–C(10)); 3.79 (*s*, MeO); 4.34 (*dd*, *J*(3a,4a) = 12.0, *J*(3a,4e) = 2.7, H_a–C(3)); 5.53 (*tq*, *J*(8,7) = 3.8, *J*(8,18) = 1.7, H–C(8)); 6.73 (*d*, *J*(15,16) = 8.1, H–C(15)); 6.75 (*dd*, *J*(16,15) = 8.1, *J*(16,12) = 1.8, H–C(16)); 6.85 (*d*, *J*(12,16) = 1.8, H–C(12)). ^{13}C-NMR ($CDCl_3$ + (D_6)acetone)^1)): 21.11 (*q*, C(18)); 23.43 (*t*, C(7)); 27.36 (*q*, C(17)); 39.19 (*d*, C(6)); 43.83 (*t*, C(4)); 56.10 (*q*, C(19)); 70.57 (*s*, C(5)); 70.89 (*d*, C(10)); 77.94 (*d*, C(3)); 78.93 (*d*, C(1)); 110.43 (*d*, C(12)); 115.12 (*d*, C(15)); 119.29 (*d*, C(16)); 124.40 (*d*, C(8)); 132.42 (*s*, C(9)); 135.03 (*s*, C(11)); 146.31 (*s*, C(14)); 147.59 (*s*, C(13)). HR-MS: 320.1608 (M^+, $C_{18}H_{24}O_5^+$; calc. 320.1618).

(2S,4R,4aR,8R,8aR)-3,4,4a,5,8,8a-Hexahydro-2-(4-hydroxy-3-methoxyphenyl)-4,7-dimethyl-2H-chromene-4,8-diol (**6f**). The NMR spectra of isomer **6f** were recorded for **6e**/**6f** 1 : 2. ^{1}H-NMR ($CDCl_3$ + (D_6)acetone)^1)): 1.16 (*s*, Me(17)); 1.55 (*ddd*, *J*(4e,4a) = 14.0, *J*(4e,3a) = 3.0, *J*(4e,6) = 1.3, H_e–C(4)); 1.66 (*dd*, *J*(4a,4e) = 14.0, *J*(4a,3a) = 11.5, H_a–C(4)); 1.68 (br. *t*, *J*(6a,7) = 8.5, H_a–C(6)); 1.74 (*td*, *J*(18,7) = 2.0, *J*(18,8) = 1.7, Me(18)); 1.93 (*dm*, *J*(7,6) = 8.5, CH_2(7)); 3.77 (br. *s*, H_e–C(10)); 3.78 (*s*, MeO); 4.18 (*dd*, *J*(1e,10e) = 2.5, *J*(1e,6a) = 2.0, H_e–C(1)); 4.64 (*dd*, *J*(3a,4a) = 11.5, *J*(3a,4e) = 3.0, H_a–C(3)); 5.47 (*tq*, *J*(8,7) = 3.8, *J*(8,18) = 1.7, H–C(8)); 6.59 (br. *s*, HO–C(14)); 6.69 – 6.72 (*m*, H–C(15), H–C(16)); 6.76 (br. *s*, H–C(12)). ^{13}C-NMR ($CDCl_3$ + (D_6)acetone)^1)): 20.97 (*q*, C(18)); 24.76 (*t*, C(7)); 28.24 (*q*, C(17));

37.99 (*d*, C(6)); 42.42 (*t*, C(4)); 55.81 (*q*, C(19)); 70.27 (*s*, C(5)); 70.47 (*d*, C(10)); 75.71 (*d*, C(1)); 75.80 (*d*, C(3)); 114.50 (*d*, C(15)); 118.81 (*d*, C(16)); 123.44 (*d*, C(8)); 132.48 (*s*, C(9)); 134.98 (*s*, C(11)); 109.50 (*d*, C(12)); 145.36 (*s*, C(14)); 146.81 (*s*, C(13)). HR-MS: 320.1608 (M^+, $C_{18}H_{24}O_5^+$; calc. 320.1618).

2.4. *Reaction of* **1** *with 3-Hydroxy-4-methoxybenzaldehyde* (**2f**) *on* K10 *Clay.* The products included **4** (0.075 g, 15%), **7** (0.025 g, 5%), **5f** (0.048 g, 5%), and a mixture of two isomers **6g**/**6h** (0.266 g, 28%; 1:1 (^{1}H-NMR).

*(2*S*,4a*R*,8*R*,8a*R*)-4a,5,8,8a-Tetrahydro-2-(3-hydroxy-4-methoxyphenyl)-4,4,7-trimethyl-4*H*-1,3-benzodioxin-8-ol* (**5f**). $[\alpha]_D^{19} = -46$ ($c = 0.73$). ^{1}H-NMR (CDCl$_3$)1): 1.23 (*s*, Me(18)); 1.49 (*s*, Me(17)); 1.50 (*ddd*, *J*(6a,7a) = 10.8, *J*(6a,7e) = 6.1, *J*(6a,1e) = 2.0, H$_a$–C(6)); 1.78 (br. *s*, Me(19)); 2.04 (*dddq*, *J*(7e,6a) = 17.7, *J*(7e,6a) = 6.1, *J*(7e,8) = 5.2, *J*(7e,19) = 1.2, H$_e$–C(7)); 2.45 (*ddm*, *J*(7a,7e) = 17.7, *J*(7a,6a) = 10.8, H$_a$–C(7)); 3.83 (*s*, MeO); 3.86 (*m*, H$_e$–C(10)); 4.31 (*dd*, *J*(1e,10e) = 2.5, *J*(1e,6a) = 2.0, H$_e$–C(1)); 5.63 (*dm*, *J*(8,7e) = 5.2, H–C(8)); 5.69 (*s*, H–C(3)), 6.78 (*d*, *J*(15,16) = 8.2, H–C(15); 6.92 (*dd*, *J*(16,15) = 8.2, *J*(16,12) = 2.0, H–C(16)); 7.04 (*d*, *J*(12,16) = 2.0, H–C(12)). ^{13}C-NMR (CDCl$_3$)1): 20.48 (*q*, C(19)); 22.67 (*q*, C(17)); 22.99 (*t*, C(7)); 27.20 (*q*, C(18)); 33.97 (*d*, C(6)); 55.93 (*q*, C(20)); 70.48 (*d*, C(10)); 74.50 (*s*, C(5)); 74.96 (*d*, C(1)); 95.71 (*d*, C(3)); 110.24 (*d*, C(15)); 112.73 (*d*, C(12)); 118.21 (*d*, C(16)); 125.41 (*d*, C(8)); 130.69 (*s*, C(9)); 132.48 (*s*, C(11)); 145.46 (*s*, C(13)); 146.97 (*s*, C(14)). HR-MS: 320.1616 (M^+, $C_{18}H_{24}O_5^+$; calc. 320.1618).

The NMR spectra of isomers **6g** and **6h** were recorded for **6g**/**6h** 2:1. *(2*S*,4*S*,4a*R*,8*R*,8a*R*)-3,4,4a,5,8,8a-Hexahydro-2-(3-hydroxy-4-methoxyphenyl)-4,7-dimethyl-2*H*-chromene-4,8-diol* (**6g**).

^{1}H-NMR (CDCl$_3$)1): 1.49 (*d*, *J*(17,4a) = 0.8, Me(17)); 1.63 (*ddd*, *J*(4e,4a) = 13.4, *J*(4e,3a) = 2.7, *J*(4e,6) = 1.2, H$_e$–C(4)); 1.79 (*m*, Me(18)); 1.77 – 1.82 (*m*, H$_a$–C(6)); 1.88 (*dd*, *J*(4a,4e) = 13.4, *J*(4a,3a) = 12.0, H$_a$–C(4)); 2.15 (*dm*, *J*(7,6) = 8.5, CH$_2$(7)); 3.77 (*dd*, *J*(1e,10e) = 2.4, *J*(1e,6a) = 2.0, H$_e$–C(1)); 3.83 (*s*, MeO); 3.89 (br. *d*, *J*(10e,1e) = 2.4, H$_e$–C(10)); 4.32 (*dd*, *J*(3a,4a) = 12.0, *J*(3a,4e) = 2.7, H$_a$–C(3)); 5.62 (*tq*, *J*(8,7) = 3.8, *J*(8,18) = 1.5, H–C(8)); 6.73 – 6.79 (*m*, H–C(15), H–C(16)); 6.88 – 6.91 (*m*, H–C(12)). ^{13}C-NMR (CDCl$_3$)1): 20.64 (*q*, C(18)); 22.66 (*t*, C(7)); 26.99 (*q*, C(17)); 38.37 (*d*, C(6)); 43.13 (*t*, C(4)); 55.93 (*q*, C(19)); 70.59 (*d*, C(10)); 71.12 (*s*, C(5)); 77.20 (*d*, C(3)); 77.60 (*d*, C(1)); 110.45 (*d*, C(15)); 112.45 (*d*, C(12)); 117.52 (*d*, C(16)); 124.61 (*d*, C(8)); 131.37 (*s*, C(9)); 135.34 (*s*, C(11)); 145.51 (*s*, C(13)); 146.03 (*s*, C(14)). HR-MS: 320.1615 (M^+, $C_{18}H_{24}O_5^+$; calc. 320.1618).

*(2*S*,4*R*,4a*R*,8*R*,8a*R*)-3,4,4a,5,8,8a-Hexahydro-2-(3-hydroxy-4-methoxyphenyl)-4,7-dimethyl-2*H*-chromene-4,8-diol* (**6h**). ^{1}H-NMR (CDCl$_3$)1): 1.21 (*s*, Me(17)); 1.59 (*ddd*, *J*(4e,4a) = 14.2, *J*(4e,3a) = 2.9, *J*(4e,6a) = 1.4, H$_e$–C(4)); 1.67 (br. *t*, *J*(6a,7) = 8.7, H$_a$–C(6)); 1.74 (*dd*, *J*(4a,4e) = 14.2, *J*(4a,3a) = 11.7, H$_a$–C(4)); 1.79 (*m*, Me(18)); 1.97 – 2.02 (*m*, CH$_2$(7)); 3.82 (*s*, MeO); 3.91 (br. *s*, H$_e$–C(10)); 4.21 (*dd*, *J*(1e,10e) = 2.5, *J*(1e,6a) = 2.0, H$_e$–C(1)); 4.68 (*dd*, *J*(3a,4a) = 11.7, *J*(3a,4e) = 2.9, H$_a$–C(3)); 5.56 (*m*, H–C(8)), 5.67 (br. *s*, HO–C(13)); 6.73 – 6.79 (*m*, H–C(15), H–C(16)); 6.88 – 6.91 (*m*, H–C(12)). ^{13}C-NMR (CDCl$_3$)1): 20.74 (*q*, C(18)); 24.58 (*t*, C(7)); 28.33 (*q*, C(17)); 38.10 (*d*, C(6)); 42.08 (*t*, C(4)); 55.93 (*q*, C(19)); 70.57 (*d*, C(10)); 70.85 (*s*, C(5)); 75.11 (*d*, C(1)); 75.41 (*d*, C(3)); 110.45 (*d*, C(15)); 112.40 (*d*, C(12)); 117.57 (*d*, C(16)); 123.97 (*d*, C(8)); 131.87 (*s*, C(9)); 136.03 (*s*, C(11)); 145.48 (*s*, C(13)); 145.87 (*s*, C(14)). HR-MS: 320.1615 (M^+, $C_{18}H_{24}O_5^+$; calc. 320.1618).

2.5. *Reaction of* **1** *with 3,4,5-Trimethoxybenzaldehyde* (**2g**) *on* K10 *Clay.* The products included **3** (0. 050 g, 10%), **5** (0.060 g, 12%), **7** (0.036 g, 7%), **5g** (0.063 g, 6%), a mixture of two diasteroisomers **6i**/**6k** (0.267 g, 25%; 3:1 (^{1}H-NMR), and compound **8b** (0.077 g, 5%).

*(2*S*,4a*R*,8*R*,8a*R*)-4a,5,8,8a-Tetrahydro-4,4,7-trimethyl-2-(3,4,5-trimethoxyphenyl)-4*H*-1,3-benzodioxin-8-ol* (**5g**). $[\alpha]_D^{19} = -69$ ($c = 0.88$). ^{1}H-NMR (CDCl$_3$)1): 1.26 (*s*, Me(18)); 1.50 (*s*, Me(17)); 1.51 (*ddd*, *J*(6a,7a) = 10.8, *J*(6a,7e) = 6.0, *J*(6a,1e) = 1.9, H$_a$–C(6)); 1.78 (*m*, Me(19)); 2.07 (*dddq*, *J*(7e,7a) = 17.7, *J*(7e,6a) = 6.0, *J*(7e,8) = 5.4, *J*(7e,19) = 1.3, H$_e$–C(7)); 2.44 (*ddm*, *J*(7a,7e) = 17.7, *J*(7a,6a) = 10.8, H$_a$–C(7)); 3.76 (*s*, MeO(21)); 3.84 (*s*, MeO(20), MeO(22)); 3.88 (br. *s*, H$_e$–C(10)); 4.33 (*dd*, *J*(1e,10e) = 2.5, *J*(1e,6a) = 1.9, H$_e$–C(1)); 5.63 (*dm*, *J*(8,7e) = 5.4, H–C(8)); 5.70 (*s*, H$_a$–C(3)); 6.68 (*s*, H–C(12), H–C(16)). ^{13}C-NMR (CDCl$_3$)1): 20.43 (*q*, C(19)); 22.66 (*q*, C(17)); 22.95 (*t*, C(7)); 27.15 (*q*, C(18)); 34.01 (*d*, C(6)); 55.93 (*q*, C(20), C(22)); 60.48 (*q*, C(21)); 70.36 (*d*, C(10)); 74.71 (*s*, C(5)); 75.25 (*d*, C(1)); 95.99 (*d*, C(3)); 103.52 (*d*, C(12); C(16)); 125.21 (*d*, C(8)); 130.75 (*s*, C(9)); 134.32 (*s*, C(11), C(14)); 153.10 (*s*, C(13), C(15)). HR-MS: 364.1883 (M^+, $C_{20}H_{28}O_6^+$; calc. 364.1880).

The NMR spectra of isomers **6i** and **6k** were recorded for **6i**/**6k** 1:1.4. *(2*S*,4*S*,4a*R*,8*R*,8a*R*)-3,4,4a,5,8,8a-Hexahydro-4,7-dimethyl-2-(3,4,5-trimethoxyphenyl)-2*H*-chromene-4,8-diol* (**6i**).

^{1}H-NMR ($CDCl_3$)1)): 1.51 (*d*, *J*(17,4a) = 0.7, Me(17)); 1.67 (*dm*, *J*(4e,4a) = 13.3, H_e–C(4)); 1.80 (*m*, Me(18)); 1.82 (br. *t*, *J*(6a,7) = 8.5, H_a–C(6)); 1.95 (*dd*, *J*(4a,4e) = 13.3, *J*(4a,3a) = 12.0, H_a–C(4)); 2.14–2.20 (*m*, 2 H(7)); 3.78 (*s*, Me(20)O); 3.81 (*m*, H_e–C(1)); 3.83 (*s*, Me(19)O, Me(21)O); 3.92 (br. *s*, H_e–C(10)); 4.35 (*dd*, *J*(3a,4a) = 12.0, *J*(3a,4e) = 2.7, H_a–C(3)); 5.64 (*tm*, *J*(8,7) = 3.9, H–C(8)); 6.52 (*s*, H–C(12), H–C(16)). ^{13}C-NMR ($CDCl_3$)1)): 20.62 (*q*, C(18)); 22.65 (*t*, C(7)); 27.08 (*q*, C(17)); 38.41 (*d*, C(6)); 42.63 (*t*, C(4)); 60.60 (*q*, C(20)); 70.52 (*d*, C(10)); 71.05 (*s*, C(5)); 77.76 (*d*, C(3)); 77.83 (*d*, C(1)); 103.31 (*d*, C(12), C(16)); 124.55 (*d*, C(8)); 131.37 (*s*, C(9)); 137.24 (*s*, C(11)); 137.54 (*s*, C(14)); 153.13 (*s*, C(13), C(15)); 56.03 (*q*, C(19), C(21)). HR-MS: 364.1881 (M^+, $C_{20}H_{28}O_6^+$; calc. 364.1880).

*(2*S*,4*R*,4a*R*,8*R*,8a*R*)-3,4,4a,5,8,8a-Hexahydro-4,7-dimethyl-2-(3,4,5-trimethoxyphenyl)-2*H*-chromene-4,8-diol* (**6k**). ^{1}H-NMR ($CDCl_3$)1)): 1.24 (*s*, Me(17)); 1.64 (*ddd*, *J*(4e,4a) = 14.2, *J*(4e,3a) = 2.8, *J*(4e,6a) = 1.3, H_e–C(4)); 1.68 (br. *t*, *J*(6a,7) = 8.5, H_a–C(6)); 1.77 (*dd*, *J*(4a,4e) = 14.2, *J*(4a,3a) = 11.6, H_a–C(4)); 1.80 (*m*, Me(18)); 1.98–2.04 (*m*, CH_2(7)); 3.77 (*s*, Me(20)O); 3.82 (*s*, Me(19)O, Me(21)O); 3.94 (br. *s*, H_e–C(10)); 4.25 (*dd*, *J*(1e,10e) = 2.5, *J*(1e,6a) = 2.0, H_e–C(1)); 4.71 (*dd*, *J*(3a,4a) = 11.6, *J*(3a,4e) = 2.8, H_a–C(3)); 5.58 (*m*, H–C(8)); 6.52 (*s*, H–C(12), H(16)). ^{13}C-NMR ($CDCl_3$)1)): 20.72 (*q*, C(18)); 24.56 (*t*, C(7)); 28.34 (*q*, C(17)); 38.17 (*d*, C(6)); 41.88 (*t*, C(4)); 60.60 (*q*, C(20)); 70.51 (*d*, C(10)); 70.81 (*s*, C(5)); 75.35 (*d*, C(1)); 76.06 (*d*, C(3)); 103.15 (*d*, C(12), C(16)); 123.88 (*d*, C(8)); 131.87 (*s*, C(9)); 137.30 (*s*, C(14)); 138.07 (*s*, C(11)); 153.10 (*s*, C(13), C(15)); 56.02 (*q*, C(19), C(21)). HR-MS: 364.1881 (M^+, $C_{20}H_{28}O_6^+$; calc. 364.1880).

*(2*R*,4*S*,4a*R*,6*S*,7*R*,8a*R*,9*S*)-Hexahydro-4,7-dimethyl-2,9-bis(3,4,5-trimethoxyphenyl)-2*H*-4,6-(epoxymethano)chromen-8(5*H*)-one* (**8b**). $[\alpha]_{\rm D}^{19} = -60$ ($c = 0.67$). ^{1}H-NMR ($CDCl_3$)1)): 1.12 (*d*, *J*(18,9) = 7.5, Me(18)); 1.43 (*s*, Me(17)); 1.70 (*dd*, *J*(4a,4e) = 13.8, *J*(4a,3a) = 12.0, H_a–C(4)); 1.86 (*m*, all $J \leq 3.3$, H_e–C(8)); 2.04 (*dd*, *J*(4e,4a) = 13.8, *J*(4e,3a) = 2.5, H_e–C(4)); 2.28 (*ddd*, *J*(7a,7e) = 14.2, *J*(7a,6e) = 3.3, *J*(7a,8e) = 3.1, H–C(7)); 2.34 (*dddd*, *J*(6e,1a) = 5.8, *J*(6e,7a) = 3.3, *J*(6e,7e) = 3.1, *J*(6e,8e) = 0.6, H_e–C(6)); 2.43 (*dddd*, *J*(7e,7a) = 14.2, *J*(7e,8e) = 3.3, *J*(7e,6e) = 3.1, *J*(7e,9e) = 1.7, H_e–C(7)); 2.57 (*qdd*, *J*(9e,18) = 7.5, *J*(9e,8e) = 2.0, *J*(9e,7e) = 1.7, H_e–C(9)); 3.79, 3.80 (2*s*, Me(20)O, Me(30)O); 3.85, 3.86 (2*s*, Me(19)O, Me(21)O, Me(29)O, Me(31)O); 4.45 (*d*, *J*(1a,6e) = 5.8, H_a–C(1)); 5.02 (*d*, *J*(22,8e) = 2.0, H–C(22)); 5.07 (*dd*, *J*(3a,4a) = 12.0, *J*(3a,4e) = 2.5, H_a–C(3)); 6.48 (*s*, H–C(24), H–C(28)), 6.63 (*s*, H–C(12), H–C(16)). ^{13}C-NMR ($CDCl_3$)1)): 17.48 (*q*, C(18)); 21.97 (*q*, C(17)); 22.34 (*t*, C(7)); 41.18 (*d*, C(6)); 42.34 (*d*, C(8)); 43.47 (*d*, C(9)); 46.20 (*t*, C(4)); 55.99, 56.01 (2*q*, C(19), C(21), C(29), C(31)); 60.65 (*q*, C(20), C(30)); 69.32 (*d*, C(3)); 73.04 (*s*, C(5)); 76.00 (*d*, C(22)); 76.16 (*d*, C(1)); 102.88 (*d*, C(12), C(16)); 137.05 (*s*, C(26)); 137.19 (*s*, C(14)); 137.70 (*s*, C(11)); 153.06 (*s*, C(13), C(15)); 135.58 (*s*, C(23)); 103.21 (*d*, C(24), C(28)); 153.01 (*s*, C(25), C(27)); 209.55 (*s*, C(10)). HR-MS: 542.2508 (M^+, $C_{30}H_{38}O_9^+$; calc. 542.2510).

3. *Reaction of Diol* **3** *with Aldehydes on* K10 *Clay*. 3.1. *Reaction of Diol* **3** *with 4-Hydroxy-3-methoxybenzaldehyde* (**2e**) *on* K10 *Clay*. A soln. of **3** (0.20 g) and **2e** (0.20 g) in CH_2Cl_2 (5 ml) was added to a suspension of *K10* clay (0.80 g) in CH_2Cl_2 (10 ml). The solvent was evaporated, and the mixture was maintained at r.t. for 7 d. Then, Et_2O (5 ml) was added. The catalyst was filtered off, and the solvent was evaporated. The resulting mixture was separated by CC (SiO_2 (10 g); hexane/Et_2O 100 : 0 → 0 : 100, acetone) to afford **3** (0.100 g, conversion 50%), and mixture of isomers **6e**/**6f** (3 : 1 (^{1}H-NMR); 0.094 g, 50%); yield based on converted **3**.

3.2. *Reaction of Diol* **3** *with 3-Hydroxy-4-methoxybenzaldehyde* (**2f**) *on* K10 *Clay*. A soln. of **3** (0.60 g) and **2f** (0.70 g) in CH_2Cl_2 (15 ml) was added to a suspension of *K10* clay (3.0 g) in CH_2Cl_2 (10 ml). The solvent was evaporated, and the mixture was maintained at r.t. for 4 d. Then, Et_2O (20 ml) and AcOEt (20 ml) were added. The catalyst was filtered off, and the solvent evaporated. The resulting mixture was separated by CC (SiO_2 (10 g); hexane/AcOEt 100 : 0 → 0 : 100, acetone) to afford **5f** (0.058 g, 5%), mixture of isomers **6g**/**6h** (5 : 1 (^{1}H-NMR); 0.336 g, 29%) and **8a** (0.126 g, 8%).

*(2*R*,4*S*,4aR,6*S*,7*R*,8a*R*,9*S*)-Hexahydro-2,9-bis(3-hydroxy-4-methoxyphenyl)-4,7-dimethyl-2*H*-4,6-(epoxymethano)chromen-8(5*H*)-one* (**8a**). $[\alpha]_{\rm D}^{19} = -74$ ($c = 0.76$). ^{1}H-NMR ($CDCl_3$)1)): 1.10 (*d*, *J*(18,9) = 7.5, Me(18)); 1.46 (*s*, Me(17)); 1.88 (*m*, all $J \leq 3.1$, H_e–C(8)); 1.91 (*dd*, *J*(4e,4a) = 15.0, *J*(4e,3a) = 2.6, H_e–C(4)); 2.21 (*dd*, *J*(4a,4e) = 15.0, *J*(4a,3a) = 13.2, H_a–C(4)); 2.38 (*dd*, *J*(7,6e) = 3.1, *J*(7,8e) = 3.1, CH_2(7)); 2.52 (br. *q*, *J*(9e,18) = 7.5, H_e–C(9)); 2.57 (*dtd*, *J*(6e,1a) = 5.3, *J*(6e,7) = 3.1, *J*(6e,8e) = 1.0, H_e–C(6)); 3.85, 3.87 (2*s*, 2 MeO); 4.52 (*dd*, *J*(1a, 6e) = 5.3, *J*(1a,9e) = 0.6, H_a–C(1)); 4.68 (*dd*, *J*(3a,4a) = 13.2, *J*(3a,4e) = 2.6, H_a–C(3)); 4.74 (*d*, *J*(20,8e) = 1.6, H–C(20)); 5.57, 5.59 (2*s*, 2 OH); 6.74–6.82 (*m*,

H–C(22), H–C(25), H–C(26)); 6.84 (*d*, *J*(15,16) = 8.2, H–C(15)); 7.11 (*d*, *J*(12,16) = 2.1, H–C(12)); 7.15 (*dd*, *J*(16,15) = 8.2, *J*(16,12) = 2.1, H–C(16)). ^{13}C-NMR (CDCl$_3$)1): 17.71 (*q*, C(18)); 23.16 (*q*, C(17)); 24.35 (*t*, C(7)); 39.02 (*d*, C(6)); 42.50 (*d*, C(9)); 43.51 (*d*, C(8)); 48.27 (*t*, C(4)); 55.89 (*q*, C(19), C(27)); 71.82 (*d*, C(3)); 72.93 (*s*, C(5)); 75.02 (*d*, C(20)); 76.39 (*d*, C(1)); 110.48 (*d*, C(25)); 110.61 (*d*, C(15)); 112.05 (*d*, C(22)); 113.07 (*d*, C(12)); 117.40 (*d*, C(26)); 118.22 (*d*, C(16)); 133.58 (*s*, C(21)); 135.36 (*s*, C(11)); 145.25 (*s*, C(23)); 145.33 (*s*, C(13)); 145.55 (*s*, C(24)); 146.11 (*s*, C(14)); 212.06 (*s*, C(10)). HR-MS: 454.1982 (M^+, $C_{26}H_{30}O_7^+$; calc. 454.1986).

3.3. *Reaction of Diol* **3** *with 3,4,5-Trimethoxybenzaldehyde* (**2g**) *on* K10 *Clay.* A soln. of **3** (0.50 g) in CH_2Cl_2 (15 ml) and aldehyde **2g** (0.60 g) was added to a suspension of *K10* clay (2.5 g) in CH_2Cl_2 (10 ml). The solvent was evaporated, and the mixture was maintained at r.t. for 7 d. Then, acetone (20 ml) and AcOEt (20 ml) were added. The catalyst was filtered off, and the solvent was evaporated. The resulting mixture was separated by CC (SiO_2 (17 g); hexane/Et_2O 100 : 0 → 0 : 100, acetone) to afford **5g** (0.034 g, 3%), mixture of isomers **6i**/**6k** (3 : 1 (^{1}H-NMR); 0.421 g, 39%) and **8b** (0.149 g, 9%).

Axial or equatorial positions of H-atoms in all compounds were determined from vicinal coupling and long-range coupling constants of observable atoms. Axial position of Me(17) in compounds **6a**, **6c**, **6e**, **6g**, and **6k** was assigned due to observation of long-rang spin-spin coupling constant of this group with H_a–C(4) (*J* 0.7 – 0.8 Hz).

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