Formation of the Compounds with an Epoxychromene Framework: Role of the Methoxy Groups

by **Oksana S. Mikhalchenko**[a]), **Dina V. Korchagina**[a]), **Konstantin P. Volcho***[a])[b]), and **Nariman F. Salakhutdinov**[a])[b])

[a]) N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences, Lavrentiev ave., 9, 630090 Novosibirsk, Russian Federation (fax: +73833309752; e-mail: volcho@nioch.nsc.ru)

[b]) Novosibirsk State University, Pirogov st., 2, 630090 Novosibirsk, Russian Federation

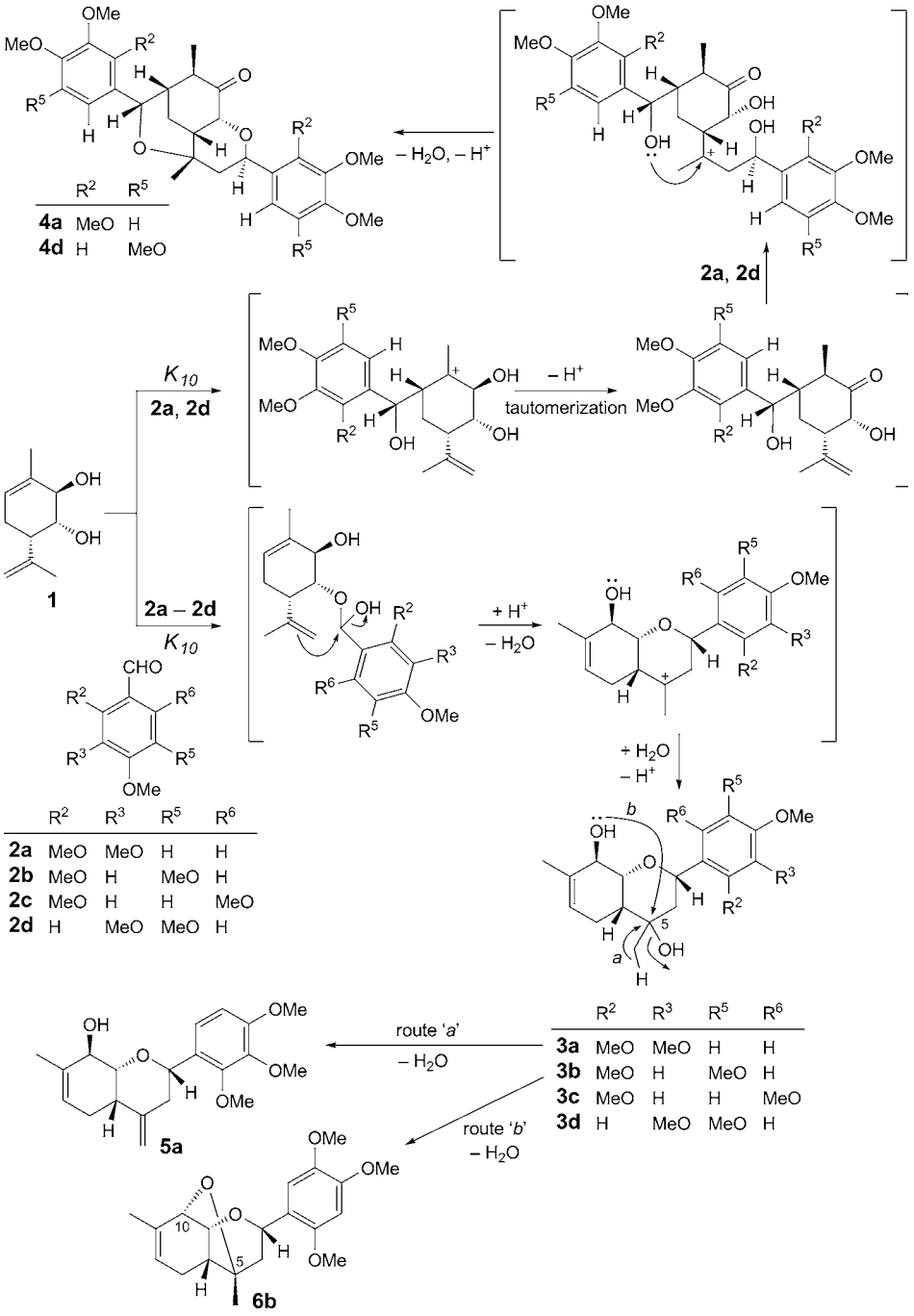
Earlier, it was found that the reaction of *para*-mentha-6,8-diene-2,3-diol with 2,4,5-trimethoxybenzaldehyde in the presence of *Montmorillonite K 10* clay led to the formation of a compound with an unusual epoxychromene framework among other products. In the current work, systematic studies of the effect of the number and position of MeO groups in the aromatic ring of the aldehyde on the reaction route were performed to reveal the structural parameters, which favor the formation of compounds with an epoxychromene framework. Compounds with an epoxychromene framework were shown to be formed if the benzaldehyde contained MeO substituents in *o*- and *p*-position. The highest yield was achieved in the case of 2,4,5-trimethoxybenzaldehyde.

Introduction. – As is well known, the reactions of monoterpenoids of the *para*-menthane series with aldehydes, catalyzed by various *Brønsted* and *Lewis* acids, lead to the formation of chiral O-containing heterocyclic compounds of different structural types [1–11]. Interest in these compounds is primarily based on the pronounced biological activity exhibited by some of them [12–14].

Recently, we studied the reactions of mentha-6,8-diene-2,3-diol **1** with aromatic aldehydes containing three MeO groups in different positions of the aromatic ring and showed that these transformations led to the formation of sets of compounds with frameworks of different types (*Scheme 1*).

The main products were compounds with a hexahydro-2*H*-chromene framework, **3a**–**3d**, in all cases, while the structure of minor heterocyclic products depended on the arrangement of substituents in the benzaldehyde used [9][13]. Products of type **3** are evidently formed as a result of the interaction of the acid-activated aldehyde with the OH group of diol **1** to give a pair of diastereoisomers with respect to the substituents at C(5). Further dehydration of products of type **3** can lead to the products of type **5** with an exocyclic C=C bond (*Scheme 1*, route *a*) or be accompanied by intramolecular heterocyclization, leading to an unusual products of type **6** with a hexahydro-2*H*-4,8-epoxychromene type of framework (*Scheme 1*, route *b*). We have not found any compounds with an epoxychromene type of framework in the literature, but a similar epoxydecalin fragment is encountered in the molecule of nodusmicin, a macrolide antibiotic isolated from cultures of *Saccharopolyspora hirsute* (*Fig. 1*) [15][16].

Scheme 1. *Reactions of Compound* **1** *with Benzaldehydes* **2a**–**2d**



	R^2	R^5
4a	MeO	H
4d	H	MeO

	R^2	R^3	R^5	R^6
2a	MeO	MeO	H	H
2b	MeO	H	MeO	H
2c	MeO	H	H	MeO
2d	H	MeO	MeO	H

	R^2	R^3	R^5	R^6
3a	MeO	MeO	H	H
3b	MeO	H	MeO	H
3c	MeO	H	H	MeO
3d	H	MeO	MeO	H

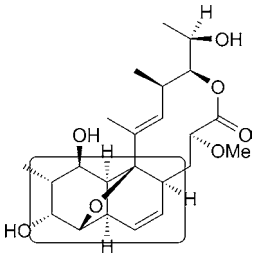


Fig. 1. *Structure of nodusmicin*

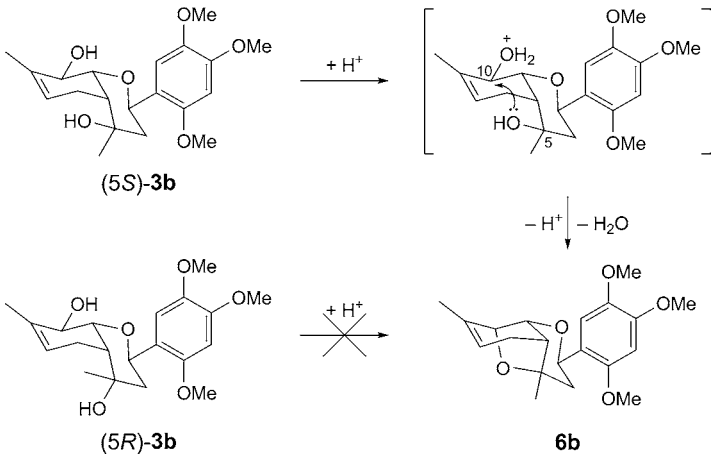
Products **4a** and **4d** are formed, when two aldehyde molecules are added to monoterpenoid **1**. At the first stage, the aldehyde can react with the endocyclic C=C bond of diol **1**, followed by deprotonation and tautomerization. Further addition of the aldehyde molecule at the exocyclic C=C bond and heterocyclization furnish compounds **4a** and **4d** with a hexahydro-2*H*-4,6-(epoxymethano)chromene framework (*Scheme 1*).

We found [13] that the transformations of compounds of type **3** occurred by route *b*, forming product **6** with a hexahydro-2*H*-4,8-epoxychromene type of framework only when the MeO groups were in the 2, 4, and 5 position of the benzaldehyde (compound **2b**). With all other variants of the arrangement of three MeO groups (*Scheme 1*), compounds of type **6** were not observed.

Product **6b** is presumably formed in the reaction of the OH group at C(10) in compound **3b** with the acid center of clay *Montmorillonite K10*. This results in C–O bond loosening, followed by the nucleophilic attack of OH groups at C(5) and the formation of a heterocycle. For steric reasons, intramolecular heterocyclization can occur only in isomer (5*S*)-**3b**, but not in (5*R*)-**3b** (*Scheme 2*).

Studies of the physiological activity of the resulting compounds **3a**–**3d**, **4a** and **4d**, and **6b** revealed [13] that **6b** exhibited high analgesic activity combined with low acute

Scheme 2. *Proposed Mechanism of Formation of Compound* **6b**



toxicity. This necessitates more detailed studies of the synthesis of compounds with an epoxychromene framework.

Results and Discussion. – We started by investigating the effect of the reaction time on the product ratio. The reactions of diol **1** with aldehyde **2b** were performed using *Montmorillonite* clay *K10* as a heterogeneous acid catalyst. To a solution of aldehyde in CH_2Cl_2, a solution of diol **1** in CH_2Cl_2 was added, followed by a suspension of clay in CH_2Cl_2. Then, the solvent was distilled off, and the reaction mixture was stored for 7 d at room temperature. The solvent was used in this case for a uniform deposition of the reactants on the catalyst. According to our previous observations [17], subsequent removal of the solvent allows a substantial increase in the reaction rate relative to the rate of transformations in the presence of a solvent. It appeared that the formation of the product of intramolecular heterocyclization of type **6** required prolonged reaction time. Thus, when diol **1** was kept with aldehyde **2b** on clay *K10*, the products ratio **3b**/**6b** changed (according to GC/MS data) from 20 : 1 after 1 d of reaction to 1 : 2 after 7 d (*Table 1*); the ratio of diastereoisomers (5*S*)-**3b**/(5*R*)-**3b** changed in this time interval from 3 : 1 to 1 : 2. The fraction of the (*R*)-isomer increased, while the content of isomer (5*S*)-**3b** in the reaction mixture was only 6% according to GC/MS data. This is consistent with the suggested mechanism proposed in *Scheme 2*, according to which product **6b** is formed from diastereoisomer (5*S*)-**3b**, but not from (5*R*)-**3b** (*Scheme 2*). Further prolongation of the reaction time did not lead to any pronounced increase in the amount of compound **6b** in the reaction mixture, obviously, because of the decrease of the content of isomer (5*S*)-**3b** and side-processes that led to tar-like products. When the reaction of diol **1** with aldehyde **2b** was repeated in this study, we succeeded in increasing the yield of the product with a chromene framework **3b** to 55% and the yield of tricyclic epoxychromene compound **6b** to 25% (*Scheme 3* and *Table 2*) compared with previously obtained yields (39 and 15% [13], resp.).

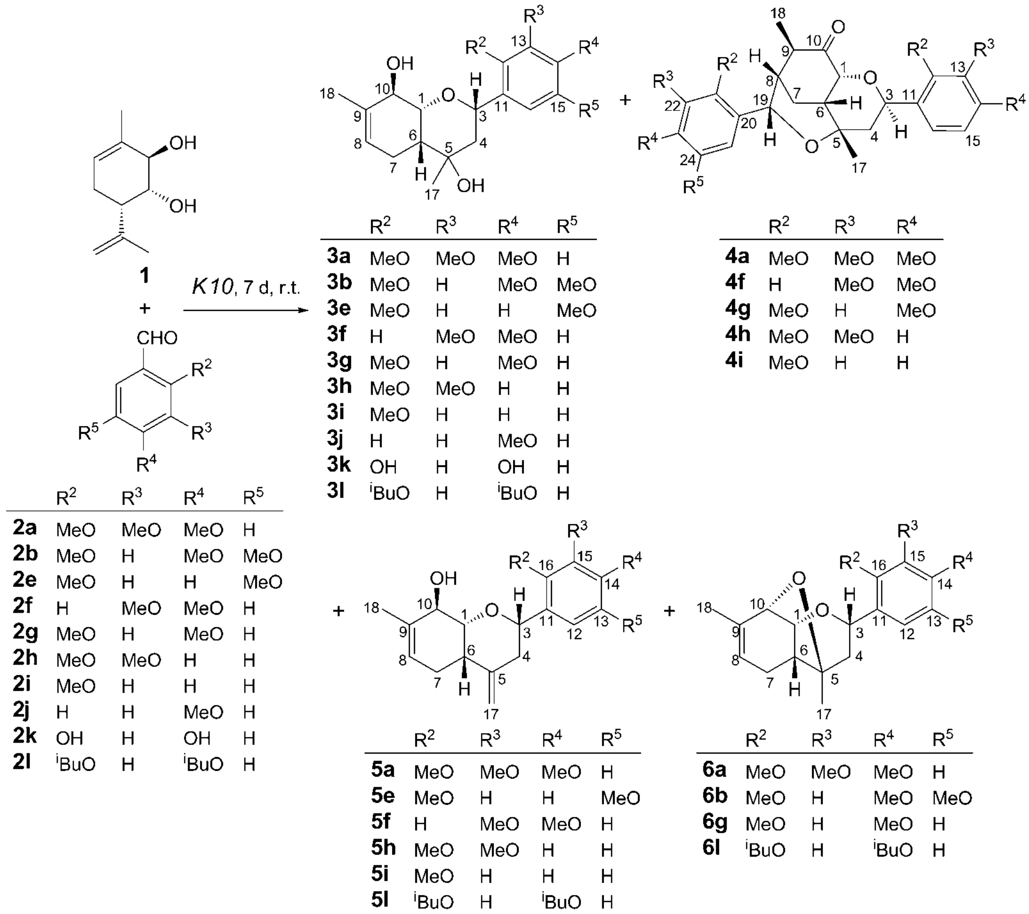
In former experiments [13], it was found that the reaction of diol **1** with 2,4,6-trimethoxybenzaldehyde **2c** in the presence of clay *K10* for 7 d afforded a single product **3c** (*Scheme 1*).

In view of the higher reactivity of aldehydes **2a** and **2d**, their transformations were performed earlier [13] for 1 d. This reaction time, however, may prove insufficient for the formation of products **6**, as shown in the case of the reaction with aldehyde **2b**. Therefore, in this work, we studied again the reactions of diol **1** with aldehydes **2a** and **2d**, but now for 7 d. In the case of aldehyde **2d**, only compound **3d** was identified in the mixture, while product type **6** was not found according to GC/MS and ^{1}H-NMR data. In the case of 2,3,4-trimethoxybenzaldehyde **2a**, with the reaction time increased to 7 d, epoxychromene product **6a** was formed in an insignificant amount (characteristic

Table 1. *Ratio of Products* **3b**/**6b** *and Isomers* (5S)-**3b**/(5R)-**3b** *Depending on the Reaction Time* (GC/MS data)

Reaction time [d]	**3b**/**6b**	(5*S*)-**3b**/(5*R*)-**3b**
1	20 : 1	3 : 1
3	1 : 1	2 : 1
7	1 : 2	1 : 2

Scheme 3. *Reactions of Compound* **1** *with Aldehydes* **2a**, **2b**, *and* **2e**–**2l**



signals appeared at δ(H) 4.25 (br. *s*, H–C(10)) and 4.42 (*d*, $J(1,6) = 1.2$, H–C(1))) (GC/MS and ^{1}H-NMR data) and was not isolated in pure form.

Thus, in the reaction of diol **1** with various trimethoxybenzaldehydes **2a**–**2d**, a compound of type **6** with an epoxychromene framework was formed in significant amounts only when 2,4,5-trimethoxybenzaldehyde **2b** was used.

To clarify whether the presence of all of the three 2,4,5-MeO groups is necessary for the formation of compounds with an epoxychromene framework, we used the analogs of aldehyde **2b**, *i.e.*, aldehydes **2e**–**2g** (*Fig. 2*), each having two MeO groups.

When 2,5-dimethoxybenzaldehyde (**2e**), which differs from aldehyde **2b** in the absence of the MeO group at C(4), was maintained with diol **1** on clay *K10*, only compound **3e** was isolated from the mixture in individual form with a yield of 43%; the desired product with an epoxychromene framework was not found (*Scheme 3*). Moreover, a fraction was obtained, which was a complex mixture of products with a molecular mass of 316. According to ^{1}H-NMR and GC/MS data of this fraction, its

Table 2. *Yields of Products of the Reactions of Diol* **1** *with Benzaldehydes* **2a**, **2b**, *and* **2e**–**2l**[a])

Aldehyde	R^2	R^3	R^4	R^5	R^6	Yields [%]			
						3 (5*S*/5*R*)	**4**	**5**	**6**
2a	MeO	MeO	MeO	H	H	40 (67:33)	20	13	(*ca.* 3)[b])
2b	MeO	H	MeO	MeO	H	55 (67:33)	–	–	25
2e	MeO	H	H	MeO	H	43 (50:50)	–	(*ca.* 7)[b])	–
2f	H	MeO	MeO	H	H	57 (75:25)	13	5	–
2g	MeO	H	MeO	H	H	22 (67:33)	7	–	5
2h	MeO	MeO	H	H	H	42 (67:33)	12	8	–
2i	MeO	H	H	H	H	52 (60:40)	14	5	–
2j	H	H	MeO	H	H	84 (75:25)	–	–	–
2k	OH	H	OH	H	H	82 (70:30)	–	–	–
2l	^{i}BuO	H	^{i}BuO	H	H	35 (67:33)	–	14	4

[a]) Reactions were carried out in the presence of clay *K10* at room temperature during 7 d. [b]) The products were not isolated individually; their contents in the reaction mixtures are given based on GC/MS and ^{1}H-NMR data.

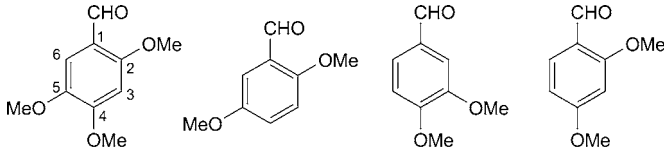


Fig. 2. *Structures of aldehydes* **2b** *and* **2e**–**2g**

main component was assumed to be product **5e** with an exocyclic methylidene group; however, it was not isolated.

The reaction of diol **1** with 3,4-dimethoxybenzaldehyde (**2f**), lacking MeO group at C(2) compared to **2b**, also did not lead to the formation of product of type **6** with an epoxychromene framework. Under these conditions, we isolated compounds **3f** and **5f** with a chromene framework and tricyclic product **4f**, which formed after the addition of two aldehyde molecules to the monoterpenoid (*Scheme 3* and *Table 2*).

From the reaction of diol **1** with 2,4-dimethoxybenzaldehyde **2g**, missing MeO group at C(5) in comparison with **2b**, we ultimately obtained the desired epoxychromene product **6g** in 5% yield, along with products **3g** and **4g** (*Scheme 3* and *Table 2*). The yield of compound **6g** proved to be much lower as compared with that of its analog **6b**, and the total yield of heterocyclic products in this reaction was rather low.

In the case of 2,3-dimethoxybenzaldehyde (**2h**), a product of type **6** was not formed. Its reaction with diol **1** led to compounds **3h** and **5h** with a chromene framework and to tricyclic compound **4h**.

Note that on passing to dimethoxybenzaldehydes **2e, 2g,** and **2h**, the total yield of products slightly decreased, as compared with the yield of 2,4,5-trimethoxybenzaldehyde (**2b**).

To clarify whether the presence of both MeO–C(2) and MeO–C(4) was essential for product formation, we studied the reaction of diol **1** with 2- and 4-methoxybenzaldehyde (**2i** and **2j**, resp.). Storage of **2i** with diol **1** on clay *K10* led to the formation of products **3i** and **5i** with a chromene framework, and to the product of addition of two aldehyde molecules to compound **4i**; a product of type **6** was not found. The reaction of **2j** with diol **1** under similar conditions gave only diastereoisomers **3j** in a very good yield of 84%.

Thus, it appeared that the presence of MeO–C(2) and MeO–C(4) in benzaldehydes is a crucial and sufficient condition for the intramolecular heterocyclization (*Scheme 2*) and formation of compounds with an epoxychromene framework.

To study if RO groups other than MeO at C(2) and C(4) can be used, we performed the reactions of diol **1** with 2,4-dihydroxybenzaldehyde (**2k**) and 2,4-diisobutoxybenzaldehyde (**2l**).

When the MeO substituents were replaced by HO, the reaction led only to compound **3k** in a high yield (82%) (*Scheme 3* and *Table 2*).

When MeO groups at C(2) and C(4) were replaced by slightly bulkier ^{i}BuO groups, we observed the formation of compounds **6l** with an epoxychromene framework, along with products **3l** and **5l** (*Scheme 3*). The total yield of reaction products slightly increased as compared with **2g**, but the desired compound with an epoxychromene framework was formed in a rather low yield.

Thus, the formation of a product of type **6** with an epoxychromene framework requires the presence of alkoxy groups at C(2) and C(4) of the starting benzaldehyde. An additional MeO group at C(5) (see **2b**) substantially increased the yield of the product with an epoxychromene framework.

According to *Scheme 1*, when stored on clay, compounds of type **3** can be transformed either to products **6** with an epoxychromene framework or to compounds **5** with a exocyclic C=C bond; the reactions generally proceed by only one of these routes, except the reactions with aldehydes **2a** and **2l** (*Scheme 3* and *Table 2*).

Quantum-chemical calculations of the thermodynamic stability of products **5** and **6**, performed by the DFT method using the PBE functional and the 6-31G(d) basis, revealed that the formation of compounds of type **6** with an epoxychromene framework is thermodynamically more favorable than the formation of compounds **5** in the case of the reaction of diol **1** with all aldehydes **2a**–**2l**. Consequently, the possibility that a defined type of compound will form depends on factors other than the thermodynamic stability of products, for example, on the specific adsorption of compounds **3** on clay, which makes cyclization possible for steric reasons.

Conclusions. – To summarize, the effect of the number and position of MeO groups in benzaldehydes on the route of the reactions with diol **1** catalyzed by clay *K10* was studied systematically to find out the conditions that favor the formation of compounds with an unusual epoxychromene framework. It was concluded that compounds with an epoxychromene framework are formed if the benzaldehydes contains MeO (^{i}BuO) substituents at C(2) and C(4), but the highest yield is achieved in the case of 2,4,5-trimethoxybenzaldehyde. In the presence of these groups, compounds of type **3** are probably adsorbed on clay in such a way that the intramolecular heterocyclization becomes sterically possible and favarable.

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Experimental Part

1. *General.* All chemicals were of commercial-reagent grade. As catalyst, we used *Montmorillonite K10* clay (*Fluka*). The clay was calcinated at 105° for 3 h immediately before use. CH_2Cl_2 was passed through calcined Al_2O_3. *(1*R,2R,*6*S*)-3-Methyl-6-(prop-1-en-2-yl)cyclohex-3-ene-1,2-diol* (**1**; $[\alpha]_D^{31} = -49.1$ ($c = 2.6$, $CHCl_3$)) was synthesized as described in [10] 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*); hexane/AcOEt 100:0 → 0:100, acetone. Yields were calculated based on converted aldehydes **2**. GC/MS (purity control and products analysis): *Agilent 7890A* with a quadrupole mass spectrometer *Agilent 5975C* as a detector, *HP-5 MS* quartz column, 30000 × 0.25 mm, He (1 atm) as carrier gas. Optical rotation: *polAAr 3005* spectrometer, $CHCl_3$ soln. ^{1}H- and ^{13}C-NMR: *Bruker DRX-500* apparatus at 500.13 (^{1}H) and 125.76 MHz (^{13}C); in $CDCl_3$ or $CDCl_3/CD_3OD$ 10:1 (*v*/*v*); chemical shifts, δ, in ppm rel. to residual $CHCl_3$ (δ(H) 7.24, δ(C) 76.90 ppm), *J* in Hz; structure determinations by analyzing the ^{1}H-NMR spectra, including ^{1}H,^{1}H double resonance spectra and ^{1}H,^{1}H-2D homonuclear correlation, *J*-modulated; ^{13}C-NMR spectra (JMOD) and ^{13}C,^{1}H-2D heteronuclear correlation with one-bond and long-range spin-spin coupling constants (C,H-COSY, ^1J(C,H) = 160 Hz, COLOC, $^{2,3}J$(C,H) = 10 Hz). The NMR spectra of (*S*)-**3** and (*R*)-**3** were recorded for the mixture of isomers. The ratio of diastereoisomers (*S*)/(*R*) for products of type **3** were determined from the NMR spectrum by the ratio of the signal areas of H_a–C(3). Me Group at C(5) (*Scheme 2*) is axial in (*S*)-**3**, as indicated by the ^4J(Me(17), H_a–C(4)) of 0.8 Hz, but equatorial in (*R*)-**3**. In the latter case, as would be expected, the axial OH group causes a paramagnetic shift $\Delta\delta$ of 0.34 of the H_a–C(3) signal, due to the 1,3-diaxial interaction. For the assignments, the numbering of the atoms of compounds is performed as indicating in *Scheme 3* is used; a, axial; e, equatbrial. HR-MS: *DFS-Thermo-Scientific* spectrometer in a full scan mode (15–500 *m*/*z*, 70 eV electron-impact (EI) ionization, direct sample introduction).

2. *Reactions of Diol* **1** *with Benzaldehydes* **2a** *and* **2e**–**2l** *on Clay* K10 (*General Procedure*). An appropriate aldehyde was added to a suspension of clay *K10* in CH_2Cl_2 (10 ml). A soln. of diol **1** in CH_2Cl_2 (20 ml) was added dropwise with stirring. The solvent was distilled off. The mixture was stored at r.t. for 7 d. Then, AcOEt (20 ml) was added. The catalyst was filtered off, the solvent was evaporated, and the residue was separated on a SiO_2 column.

2.1. *Reaction of* **1** *with 2,3,4-Trimethoxybenzaldehyde* (**2a**). The reaction of **1** (0.600 g) and **2a** (0.700 g) for 7 d in the presence of clay *K10* (2.6 g) gave 0.047 g of starting aldehyde **2a** (conversion is 93%) and products **3a** ((5*S*)/(5*R*) 67:33; 0.485 g, 40%), **4a** (0.361 g, 20%), and **5a** (0.150 g, 13%). Compound **6a** was not isolated in pure form, estimated yield of the product by NMR and GC/MS was *ca.* 0.036 g (3%). Spectral characteristics of compounds **3a**, **4a**, and **5a** were in agreement with those reported in [13].

2.2. *Reaction of* **1** *with 2,4,5-Trimethoxybenzaldehyde* (**2b**). The reaction of **1** (0.700 g) and **2b** (0.800 g) for 7 d in the presence of clay *K10* (2.3 g) gave 0.160 g of starting aldehyde **2b** (80% conversion) and products **3b** ((5*S*)/(5*R*) 67:33; 0.652 g, 55%) and **6b** (0.288 g, 25%). Spectral characteristics of compounds **3b** and **6b** were in agreement with those described in [13].

2.3. *Reaction of* **1** *with 2,5-Dimethoxybenzaldehyde* (**2e**). The reaction of **1** (0.400 g) and **2e** (0.400 g) for 7 d in the presence of clay *K10* (1.6 g) gave 0.127 g of starting aldehyde **2e** (conversion is 68%) and **3e** ((5*S*)/(5*R*) 50:50; 0.238 g, 43%) and **5e**, which was not isolated in pure form; estimated yield by NMR and GC/MS was *ca.* 0.052 g, 7%. Yields based on **2e**.

*(2*S,*4*S,*4a*R,*8*R,*8a*R*)-2-(2,5-Dimethoxyphenyl)-3,4,4a,5,8,8a-hexahydro-4,7-dimethyl-2*H*-chromene-4,8-diol* ((5*S*)-**3e**). ^{1}H-NMR ($CDCl_3$): 1.50 (*s*, Me(17)); 1.69 (*dd*, *J*(4a,4e) = 13.1, *J*(4a,3a) = 11.3, H_a–C(4)); 1.75 (*ddd*, *J*(4e,4a) = 13.1, *J*(4e,3a) = 2.9, *J*(4e,6a) = 0.9, H_e–C(4)); 1.76–1.81 (*m*, H_a–C(6)); 1.80 (*m*, all $J \leq 2.5$, Me(18)); 2.11–2.16 (*m*, CH_2(7)); 3.72, 3.75 (2*s*, 2 MeO); 3.79 (*dd*, *J*(1e,10e) = 2.4, *J*(1e,6a) = 2.0, H_e–C(1)); 3.88 (br. *s*, H_e–C(10)); 4.75 (*dd*, *J*(3a,4a) = 11.3, *J*(3a,4e) = 2.9, H_a–C(3)); 5.60–5.64 (*m*, H–C(8)); 6.70 (*dd*, *J*(14,13) = 8.8, *J*(14,16) = 3.0, H–C(14)); 6.73 (*d*, *J*(13,14) = 8.8,

H–C(13)); 6.95 (*d*, *J*(16,14) = 3.0, H–C(16)). ^{13}C-NMR ($CDCl_3$): 20.65 (*q*, C(18)); 22.68 (*t*, C(7)); 22.85 (*q*, C(17)); 38.45 (*d*, C(6)); 41.79 (*t*, C(4)); 55.59, 55.92 (2*q*, C(19), C(20)); 70.58 (*d*, C(10)); 71.06 (*s*, C(5)); 71.79 (*d*, C(3)); 77.60 (*d*, C(1)); 111.28 (*d*, C(13)); 111.77 (*d*, C(14)); 113.14 (*d*, C(16)); 124.55 (*d*, C(8)); 131.35 (*s*, C(9)); 132.03 (*s*, C(11)); 149.77 (*s*, C(12)); 153.79 (*s*, C(15)). HR-MS: 334.1776 (M^+, $C_{19}H_{26}O_5^+$; calc. 334.1775).

*(2*S*,4*R*,4a*R*,8*R*,8a*R*)-2-(2,5-Dimethoxyphenyl)-3,4,4a,5,8,8a-hexahydro-4,7-dimethyl-2*H*-chromene-4,8-diol* ((5*R*)-**3e**). ^{1}H-NMR ($CDCl_3$/CD_3OD): 1.13 (*s*, Me(17)); 1.53 (*dd*, *J*(4a,4e) = 14.1, *J*(4a,3a) = 11.4, H_a–C(4)); 1.62 – 1.70 (*m*, H_e–C(4), H_a–C(6)); 1.75 (*m*, all $J \leq 2.5$, Me(18)); 1.91 – 1.96 (*m*, CH_2(7)); 3.68, 3.70 (2*s*, 2 MeO); 3.82 (br. *s*, H_e–C(10)); 4.17 (*dd*, *J*(1e,10e) = 2.4, *J*(1e,6a) = 2.0, H_e–C(1)); 5.05 (*dd*, *J*(3a,4a) = 11.4, *J*(3a,4e) = 2.8, H_a–C(3)); 5.50 – 5.54 (*m*, H–C(8)); 6.65 (*dd*, *J*(14,13) = 8.8, *J*(14,16) = 3.0, H–C(14)); 6.70 (*d*, *J*(13,14) = 8.8, H–C(13)); 6.92 (*d*, *J*(16,14) = 3.0, H–C(16)). ^{13}C-NMR ($CDCl_3$/CD_3OD): 20.61 (*q*, C(18)); 24.40 (*t*, C(7)); 27.82 (*q*, C(17)); 37.63 (*d*, C(6)); 40.44 (*t*, C(4)); 55.51, 55.83 (2*s*, C(19), C(20)); 70.13 (*d*, C(3)); 70.17 (*d*, C(10)); 70.42 (*s*, C(5)); 75.06 (*d*, C(1)); 111.29 (*d*, C(13)); 111.49 (*d*, C(14)); 113.19 (*d*, C(16)); 123.68 (*d*, C(8)); 131.69 (*s*, C(9)); 132.66 (*s*, C(11)); 149.82 (*s*, C(12)); 153.67 (*s*, C(15)). HR-MS: 334.1776 (M^+, $C_{19}H_{26}O_5^+$; calc. 334.1775).

2.4. *Reaction of* **1** *with 3,4-Dimethoxybenzaldehyde* (**2f**). The reaction of **1** (0.400 g) and **2f** (0.400 g) for 7 d in the presence of clay *K10* (1.6 g) gave 0.107 g of starting aldehyde **2f** (73% conversion) and products **3f** ((5*S*)/(5*R*) 75 :25; 0.336 g, 57%), **4f** (0.115 g, 13%), and **5f** (0.030 g, 5%).

*(2*S*,4*S*,4a*R*,8*R*,8a*R*)-2-(3,4-Dimethoxyphenyl)-3,4,4a,5,8,8a-hexahydro-4,7-dimethyl-2*H*-chromene-4,8-diol* ((5*S*)-**3f**). ^{1}H-NMR ($CDCl_3$): 1.50 (*s*, Me(17)); 1.65 (*ddd*, *J*(4e,4a) = 13.4, *J*(4e,3a) = 2.7, *J*(4e,6) = 1.1, H_e–C(4)); 1.79 (*m*, all $J \leq 2.5$, Me(18)); 1.77 – 1.83 (*m*, H_a–C(6)); 1.93 (*dd*, *J*(4a,4e) = 13.4, *J*(4a,3a) = 12.0, H_a–C(4)); 2.13 – 2.19 (*m*, CH_2(7)); 3.79 (*dd*, *J*(1e,6a) = 2.4, *J*(1e,10e) = 2.1, H_e–C(1)); 3.82, 3.84 (2*s*, 2 MeO); 3.90 (br. *s*, H_e–C(10)); 4.35 (*dd*, *J*(3a,4a) = 12.0, *J*(3a,4e) = 2.7, H_a–C(3)); 5.63 (*tq*, *J*(8,7) = 3.8, *J*(8,18) = 1.5, H–C(8)); 6.79 (*d*, *J*(15,16) = 8.2, H–C(15)); 6.81 (*d*, *J*(12,16) = 1.9, H–C(12)); 6.85 (*dd*, *J*(16,15) = 8.2, *J*(16,12) = 1.9, H–C(16)). ^{13}C-NMR ($CDCl_3$): 20.63 (*q*, C(18)); 22.64 (*t*, C(7)); 27.03 (*q*, C(17)); 38.37 (*d*, C(6)); 42.74 (*t*, C(4)); 55.76, 55.80 (2*q*, C(19), C(20)); 70.50 (*d*, C(10)); 71.04 (*s*, C(5)); 77.39 (*d*, C(3)); 77.75 (*d*, C(1)); 109.62 (*d*, C(12)); 111.06 (*d*, C(15)); 118.25 (*d*, C(16)); 124.52 (*d*, C(8)); 131.37 (*s*, C(9)); 134.37 (*s*, C(11)); 148.52 (*s*, C(14)); 148.81 (*s*, C(13)). HR-MS: 334.1770 (M^+, $C_{19}H_{26}O_5^+$; calc. 334.1774).

*(2*S*,4*R*,4a*R*,8*R*,8a*R*)-2-(3,4-Dimethoxyphenyl)-3,4,4a,5,8,8a-hexahydro-4,7-dimethyl-2*H*-chromene-4,8-diol* ((5*R*)-**3f**). ^{1}H-NMR ($CDCl_3$): 1.22 (*s*, Me(17)); 1.61 (*ddd*, *J*(4e,4a) = 14.2, *J*(4e,3a) = 2.7, *J*(4e,6) = 1.3, H_e–C(4)); 1.68 (br. *t*, *J*(6a,7) = 9, H_a–C(6)); 1.76 (*dd*, *J*(4a,4e) = 14.2; *J*(4a,3a) = 11.7, H_a–C(4)); 1.79 (*m*, all $J \leq 2.5$, Me(18)); 1.97 – 2.03 (*m*, CH_2(7)); 3.82, 3.83 (2*s*, MeO(19), MeO(20)); 3.92 (br. *s*, H_e–C(10)); 4.23 (*dd*, *J*(1e,6a) = 2.4, *J*(1e,10e) = 2.0, H_e–C(1)); 4.72 (*dd*, *J*(3a,4a) = 11.7, *J*(3a,4e) = 2.7, H_a–C(3)); 5.55 – 5.59 (*m*, H–C(8)); 6.77 (*d*, *J*(15,16) = 8.2, H–C(15)); 6.82 (*d*, *J*(12,16) = 1.9, H–C(12)); 6.85 (*dd*, *J*(16,15) = 8.2, *J*(16,12) = 1.9, H–C(16)). ^{13}C-NMR ($CDCl_3$): 20.73 (*q*, C(18)); 24.53 (*t*, C(7)); 28.29 (*q*, C(17)); 38.07 (*d*, C(6)); 41.87 (*t*, C(4)); 55.75, 55.80 (2*q*, C(19)), C(20)); 70.48 (*d*, C(10)); 70.78 (*s*, C(5)); 75.29 (*d*, C(1)); 75.65 (*d*, C(3)); 109.62 (*d*, C(12)); 111.10 (*d*, C(15)); 118.09 (*d*, C(16)); 123.88 (*d*, C(8)); 131.84 (*s*, C(9)); 135.12 (*s*, C(11)); 148.30, 148.76 (2*s*, C(13), C(14)). HR-MS: 334.1770 (M^+, $C_{19}H_{26}O_5^+$; calc. 334.1774).

*(2*R*,4*S*,4a*R*,6*S*,7*R*,8a*R*,9*S*)-2,9-Bis(3,4-dimethoxyphenyl)hexahydro-4,7-dimethyl-2*H*-4,6-(epoxymethano)chromen-8(8a*H*)-one* (**4f**). $[\alpha]_D^{20} = -10$ ($c = 0.26$). ^{1}H-NMR ($CDCl_3$): 1.10 (*d*, *J*(18,9) = 7.5, Me(18)); 1.44 (*s*, Me(17)); 1.74 (*dd*, *J*(4a,4e) = 13.8, *J*(4a,3a) = 12.0, H_a–C(4)); 1.85 (*m*, all $J \leq 3.1$, H_e–C(8)); 2.01 (*dd*, *J*(4e,4a) = 13.8, *J*(4e,3a) = 2.6, H_e–C(4)); 2.27 (*ddd*, *J*(7a,7e) = 14.2, *J*(7a,6e) = 3.3, *J*(7a,8e) = 3.1, H_a–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,6e) = 3.1, *J*(7e,8e) = 3.1, *J*(7e,9e) = 1.8, H_e–C(7)); 2.53 (*qdd*, *J*(9e,18) = 7.5, *J*(9e,8e) = 2.2, *J*(9e,7e) = 1.8, H_e–C(9)); 3.85 (*s*, MeO–C(14), MeO–C(23)), 3.90 (*s*, MeO–C(13), MeO–C(22)); 4.43 (*d*, *J*(1a, 6e) = 5.8, H_a–C(1)); 5.05 (*d*, *J*(19,8e) = 2.1, H–C(19)); 5.09 (*dd*, *J*(3a,4a) = 12.0, *J*(3a,4e) = 2.6, H_a–C(3)); 6.78 (*d*, *J*(21,25) = 1.9, H–C(21)); 6.81 (*dd*, *J*(25,24) = 8.2, *J*(25,21) = 1.9, H–C(25)); 6.83 (*d*, *J*(15,16) = 8.2, H–C(15)); 6.85 (*d*, *J*(24,25) = 8.2, H–C(24)); 6.94 (*dd*, *J*(16,15) = 8.2, *J*(16,12) = 2.1, H–C(16)); 7.01 (*d*, *J*(12,16) = 2.1, H–C(12)). ^{13}C-NMR ($CDCl_3$): 17.56 (*q*, C(18)); 22.07 (*q*, C(17)); 22.48 (*t*, C(7)); 41.18 (*d*, C(6)); 42.47(*d*, C(8)); 43.39 (*d*, C(9)); 46.07 (*t*, C(4)); 55.81 (2*q*, *M*eO–C(13), MeO–C(22)); 55.87 (2*q*, MeO–C(14), MeO–C(23)); 69.25 (*d*, C(3)); 72.99 (*s*,

C(5)); 75.69 (*d*, C(19)); 76.34 (*d*, C(1)); 109.42 (*d*, C(21)); 109.57 (*d*, C(12)); 110.93 (*d*, C(15)); 111.11 (*d*, C(24)); 118.10 (*d*, C(25)); 118.22 (*d*, C(16)); 132.82 (*s*, C(20)); 134.67 (*s*, C(11)); 148.09 (*s*, C(23)); 148.34 (*s*, C(14)); 148.75 (*s*, C(13), 148.88 (*s*, C(22)); 209.74 (*s*, C(10)). HR-MS: 482.2299 (M^+, $C_{28}H_{34}O_7^+$; calc. 482.2299).

*(2*S*,4a*S*,8*R*,8a*R*)-2-(3,4-Dimethoxyphenyl)-3,4,4a,5,8,8a-hexahydro-7-methyl-4-methylidene-2*H*-chromen-8-ol* (**5f**). $[\alpha]_D^{30} = -38$ ($c = 0.36$). ^{1}H-NMR ($CDCl_3$): 1.81 (br. *s*, Me(18)); 1.96 (*dddq*, *J*(7e,7a) = 17.8, *J*(7e,6a) = 6.4, *J*(7e,8) = 5.1, *J*(7e,18) = 1.5, H_e–C(7)); 2.31 (*dd*, *J*(4e,4a) = 14.1, *J*(4e,3a) = 2.8, H_e–C(4)); 2.35 (*ddm*, *J*(7a,7e) = 17.8, *J*(7a,6a) = 10.8, H_a–C(7)); 2.49 – 2.56 (*m*, H–C(6), H_a–C(4)); 3.72 (*dd*, *J*(1e,6a) = 2.4, *J*(1e,10e) = 2.0, H_e–C(1)); 3.83, 3.86 (2s, 2 MeO); 3.92 (br. *s*, H_e–C(10)); 4.32 (*dd*, *J*(3a,4a) = 11.6, *J*(3a,4e) = 2.8, H_a–C(3)); 4.80 (*dd*, *J*(17,17′) = 2.4, *J*(17,6a) = 2.0, H–C(17)); 4.90 (*dd*, *J*(17′,17) = 2.4, *J*(17′,6a) = 2.0, H–C(17′)); 5.60 – 5.64 (*m*, H–C(8)); 6.81 (*d*, *J*(15,16) = 8.2, H–C(15)); 6.86 (*d*, *J*(12,16) = 1.8, H–C(12)); 6.89 (*dd*, *J*(16,15) = 8.2, *J*(16,12) = 1.8, H–C(16)). ^{13}C-NMR ($CDCl_3$): 20.84 (*q*, C(18)); 26.22 (*t*, C(7)); 36.75 (*d*, C(6)); 38.37 (*t*, C(4)); 55.77, 55.81 (2*q*, C(19), C(20)); 70.33 (*d*, C(10)); 80.53 (*d*, C(3)); 80.62 (*d*, C(1)); 109.50 (*d*, C(12)); 109.69 (*t*, C(17)); 111.02 (*d*, C(15)); 118.12 (*d*, C(16)); 124.39 (*d*, C(8)); 131.49 (*s*, C(9)); 134.70 (*s*, C(11)); 146.86 (*s*, C(5)); 148.48, 148.80 (2*s*, C(13), C(14)). HR-MS: 316.1668 (M^+, $C_{19}H_{24}O_4^+$; calc. 316.1669).

2.5. *Reaction of* **1** *with 2,4-Dimethoxybenzaldehyde* (**2g**). The reaction of **1** (0.400 g) and **2g** (0.400 g) for 7 d in the presence of clay *K10* (1.6 g) gave 0.082 g of starting aldehyde **2g** (80% conversion) and products **3g** ((5*S*)/(5*R*) 67:33; 0.143 g, 22%), **4g** (0.068 g, 7%), and **6g** (0.028 g, 5%).

*(2*S*,4*S*,4a*R*,8*R*,8a*R*)-2-(2,4-Dimethoxyphenyl)-3,4,4a,5,8,8a-hexahydro-4,7-dimethyl-2*H*-chromene-4,8-diol* ((5*S*)-**3g**). ^{1}H-NMR ($CDCl_3$/CD_3OD): 1.41 (*s*, Me(17)); 1.56 (*ddd*, *J*(4e,4a) = 13.3, *J*(4e,3a) = 2.6, *J*(4e,6a) = 0.9, H_e–C(4)); 1.71 (*m*, all $J \leq 2.5$, Me(18)); 1.68 – 1.76 (*m*, H_a–C(4), H_a–C(6)); 2.04 – 2.10 (*m*, CH_2(7)); 3.68, 3.69 (2*s*, 2 MeO); 3.74 (br. *s*, H_e–C(10)); 4.67 (*dd*, *J*(3a,4a) = 11.7, *J*(3a,4e) = 2.6, H_a–C(3)); 5.53 – 5.57 (*m*, H–C(8)); 6.32 (*d*, *J*(13,15) = 2.3, H–C(13)); 6.37 (*dd*, *J*(15,16) = 8.4, *J*(15,13) = 2.3, H–C(15)); 7.16 (*d*, *J*(16,15) = 8.4, H–C(16)). The signal of H_e–C(1) was overlapped by that of the MeO group of (3.69 ppm). ^{13}C-NMR ($CDCl_3$/CD_3OD): 20.39 (*q*, C(18)); 22.55 (*t*, C(7)); 26.36 (*q*, C(17)); 38.23 (*d*, C(6)); 41.22 (*t*, C(4)); 55.05, 55.12 (2*q*, C(19), C(20)); 69.98 (*d*, C(10)); 70.63 (*s*, C(5)); 71.30 (*d*, C(3)); 77.79 (*d*, C(1)); 98.00 (*d*, C(13)); 104.40 (*d*, C(15)); 122.98 (*s*, C(11)); 124.24 (*d*, C(8)); 127.00 (*d*, C(16)); 131.10 (*s*, C(9)); 156.59 (*s*, C(12)); 159.81 (*s*, C(14)). HR-MS: 334.1778 (M^+, $C_{19}H_{26}O_5^+$; calc. 334.1775).

The NMR spectra of (5*R*)-**3g** were recorded for the mixture (5*S*)-**3g**/(5*R*)-**3g** 1:1.

*(2*S*,4*R*,4a*R*,8*R*,8a*R*)-2-(2,4-Dimethoxyphenyl)-3,4,4a,5,8,8a-hexahydro-4,7-dimethyl-2*H*-chromene-4,8-diol* ((5*R*)-**3g**). ^{1}H-NMR ($CDCl_3$/CD_3OD): 1.14 (*s*, Me(17)); 1.57 – 1.66 (*m*, CH_2(4), H_a–C(6)); 1.75 (*m*, all $J \leq 2.5$, Me(18)); 1.93 – 1.97 (*m*, CH_2(7)); 3.72 (*s*, 2 MeO); 3.82 (br. *s*, H_e–C(10)); 4.16 (*dd*, *J*(1e,10e) = 2.3, *J*(1e,6a) = 2.0, H_e–C(1)); 5.03 (*dd*, *J*(3a,4a) = 8.4, *J*(3a,4e) = 6.1, H_a–C(3)); 5.52 – 5.55 (*m*, H–C(8)); 6.35 – 6.37 (*m*, H–C(13)); 6.40 (*dd*, *J*(15,16) = 8.4, *J*(15,13) = 2.3, H–C(15)); 7.20 (*d*, *J*(16,15) = 8.4, H–C(16)); the signal of H–C(13) was overlapped by those of the major isomer **3g**. ^{13}C-NMR ($CDCl_3$/CD_3OD): 20.61 (*q*, C(18)); 24.43 (*t*, C(7)); 27.87 (*q*, C(17)); 37.72 (*d*, C(6)); 40.62 (*t*, C(4)); 55.12, 55.20 (2*q*, C(19), C(20)); 69.86 (*d*, C(3)); 70.18 (*d*, C(10)); 70.47 (*s*, C(5)); 75.19 (*d*, C(1)); 98.09 (*d*, C(13)); 104.42 (*d*, C(15)); 123.69 (*d*, C(8)); 127.06 (*d*, C(16)); 131.78 (*s*, C(9)); 156.68 (*s*, C(12)); 159.72 (*s*, C(14)). HR-MS: 334.1778 (M^+, $C_{19}H_{26}O_5^+$; calc. 334.1775).

*(2*R*,4*S*,4a*R*,6*S*,7*R*,8a*R*,9*S*)-2,9-Bis(2,4-dimethoxyphenyl)hexahydro-4,7-dimethyl-2*H*-4,6-(epoxymethano)chromen-8(8a*H*)-one* (**4g**). $[\alpha]_D^{27} = -56.71$ ($c = 1.34$). ^{1}H-NMR ($CDCl_3$): 1.07 (*d*, *J*(18,9) = 7.6, Me(18)); 1.39 (*s*, Me(17)); 1.55 (*dd*, *J*(4a,4e) = 13.9, *J*(4a,3a) = 11.8, H_a–C(4)); 1.93 – 1.96 (*m*, all $J \leq 3.0$, H_e–C(8)); 2.06 (*dd*, *J*(4e,4a) = 13.9, *J*(4e,3a) = 2.5, H_e–C(4)); 2.19 (*ddd*, *J*(7a,7e) = 14.1, *J*(7a,6) = 3.2, *J*(7a,8e) = 3.0, H_a–C(7); 2.30 (*dddd*, *J*(6,1a) = 5.8, *J*(6,7a) = 3.2, *J*(6,7e) = 3.0, *J*(6,8e) = 0.7, H–C(6); 2.42 (*dm*, *J*(7e,7a) = 14.1, H_e–C(7)); 2.47 (br. *q*, *J*(9,18) = 7.6, H_e–C(9)); 3.765 (*s*, MeO–C(21)); 3.776, 3.784 (2*s*, MeO–C(14), MeO–C(23)); 3.805 (*s*, MeO–C(12)); 4.41 (*d*, *J*(1a,6) = 5.8, H_a–C(1)); 5.28 (*d*, *J*(19,8e) = 2.0, H–C(19)); 5.42 (*dd*, *J*(3a,4a) = 11.8, *J*(3a,4e) = 2.5, H_a–C(3)); 6.41 (*d*, *J*(22,24) = 2.4, H–C(22)); 6.42 (*d*, *J*(13,15) = 2.4, H–C(13)); 6.47 (*dd*, *J*(15,16) = 8.4, *J*(15,13) = 2.4, H–C(15)); 6.55 (*dd*, *J*(24,25) = 8.4, *J*(24,22) = 2.4, H–C(24)); 7.28 (*d*, *J*(25,24) = 8.4, H–C(25)); 7.41 (*d*, *J*(16,15) = 8.4, H–C(16)). ^{13}C-NMR ($CDCl_3$): 17.67 (*q*, C(18)); 22.07 (*q*, C(17)); 22.46 (*t*, C(7)); 39.45 (*d*, C(8)); 41.47 (*d*, C(6)); 43.89 (*d*, C(9)); 45.44 (*t*, C(4)); 55.10 (*q*, MeO–C(21)); 55.23, 55.28 (2*q*, MeO–C(14),

MeO–C(23)); 55.43 (*q*, MeO–C(12)); 64.58 (*d*, C(3)); 70.75 (*d*, C(19)); 72.93 (*s*, C(5)); 76.44 (*d*, C(1)); 98.21, (*d*, C(13), C(22)); 104.06 (*d*, C(24)); 104.19 (*d*, C(15)); 121.07 (*s*, C(20)); 123.58 (*s*, C(11)); 126.93 (*d*, C(16)); 128.44 (*d*, C(25)); 156.13 (*s*, C(21)); 157.16 (*s*, C(12)); 159.74 (*s*, C(23)); 159.78 (*s*, C(14)); 210.34 (*s*, C(10)). HR-MS: 482.2296 (M^+, $C_{28}H_{34}O_7^+$; calc. 482.2299).

*(2*S*,4*S*,4a*R*,8*S*,8a*R*)-2-(2,4-Dimethoxyphenyl)-3,4,4a,5,8,8a-hexahydro-4,7-dimethyl-2*H*-4,8-epoxychromene* (**6g**). $[\alpha]_D^{23} = -4.76$ ($c = 0.42$). ^{1}H-NMR ($CDCl_3$): 1.36 (*s*, Me(17)); 1.55 (*dd*, *J*(4a,4e) = 13.0, *J*(4a,3a) = 10.6, H_a–C(4)); 1.75 (*m*, all $J \leq 2.5$, Me(18)); 1.90 (*dd*, *J*(4e,4a) = 13.0, *J*(4e,3a) = 4.1, H_e–C(4)); 2.06 (br. *d*, *J*(6,7) = 5.6, H–C(6)); 2.36 (*dddq*, *J*(7a,7e) = 18.7, *J*(7a,6) = 5.6, *J*(7a,8) = 3.5, *J*(7a,18) = 2.5, H_a–C(7)); 2.53 (*dm*, *J*(7e,7a) = 18.7 , H_e–C(7)); 3.769, 3.772 (2*s*, 2 MeO); 4.25 (br. *s*, H_e–C(10)); 4.42 (br. *s*, H–C(1)); 5.13–5.16 (*m*, H–C(8)); 5.40 (*dd*, *J*(3a,4a) = 10.6, *J*(3a,4e) = 4.1, H_a–C(3)); 6.41 (*d*, *J*(13,15) = 2.4, H–C(13)); 6.47 (*dd*, *J*(15,16) = 8.4, *J*(15,13) = 2.4, H–C(15)); 7.34 (*d*, *J*(16,15) = 8.4, H–C(16)). ^{13}C-NMR ($CDCl_3$): 20.90 (*q*, C(18)); 21.50 (*q*, C(17)); 28.22 (*t*, C(4)); 45.61 (*t*, C(7)); 45.65 (*d*, C(6)); 55.21, 55.23 (2*q*, 2 MeO); 68.24 (*d*, C(3)); 80.22 (*d*, C(10)); 81.07 (*d*, C(1)); 83.36 (*s*, C(5)); 98.22 (*d*, C(13); 104.30 (*d*, C(15)); 120.64 (*d*, C(8)); 123.03 (*s*, C(11)); 127.36 (*d*, C(16)); 139.90 (*s*, C(9)); 157.19 (*s*, C(12)); 159.91 (*s*, C(14)). HR-MS: 316.1670 (M^+, $C_{19}H_{24}O_4^+$; calc. 316.1669).

2.6. *Reaction of* **1** *with 2,3-Dimethoxybenzaldehyde* (**2h**). The reaction of **1** (0.400 g) and **2h** (0.400 g) for 7 d in the presence of clay *K10* (1.6 g) gave 0.028 g of starting aldehyde **2h** (93% conversion) and products **3h** ((5*S*)/(5*R*) 67:33; 0.314 g, 42%), **4h** (0.126 g, 12%), and **5h** (0.060 g, 8%).

*(2*S*,4*S*,4a*R*,8*R*,8a*R*)-2-(2,3-Dimethoxyphenyl)-3,4,4a,5,8,8a-hexahydro-4,7-dimethyl-2*H*-chromene-4,8-diol* ((5*S*)-**3h**). ^{1}H-NMR ($CDCl_3$): 1.50 (*s*, Me(17)); 1.64 (*ddd*, *J*(4e,4a) = 13.3, *J*(4e,3a) = 2.6, *J*(4e,6a) = 1.0, H_e–C(4)); 1.79 (*m*, all $J \leq 2.5$, Me(18)); 1.78–1.82 (*m*, H_a–C(6)); 1.88 (*dd*, *J*(4a,4e) = 13.3, *J*(4a,3a) = 11.8 , H_a–C(4)); 2.14–2.19 (*m*, CH_2(7)); 3.802 (*s*, H–C(19)); 3.812 (*s*, H–C(20)); 3.87 (br. *s*, H_e–C(10)); 4.74 (*dd*, *J*(3a,4a) = 11.8, *J*(3a,4e) = 2.6, H_a–C(3)); 5.61–5.65 (*m*, H–C(8)); 6.79 (*dd*, *J*(14,15) = 8.0, *J*(14,16) = 1.6, H–C(14)); 6.93 (*dd*, *J*(16,15) = 7.8, *J*(16,14) = 1.6, H–C(16)); 7.00 (*dd*, *J*(15,14) = 8.0, *J*(15,16) = 7.8, H–C(15)); the signal of the H_e–C(1) was overlapped by that of the MeO groups, (3.805 ppm). ^{13}C-NMR ($CDCl_3$): 20.65 (*q*, C(18)); 22.69 (*t*, C(7)); 26.82 (*q*, C(17)); 38.35 (*d*, C(6)); 42.10 (*t*, C(4)); 55.62 (*q*, C(20)); 60.80 (*q*, C(19)); 70.51 (*d*, C(10)); 71.00 (*s*, C(5)); 72.55 (*d*, C(3)); 77.69 (*d*, C(1)); 111.50 (*d*, C(14)); 118.52 (*d*, C(16)); 124.14 (*d*, C(15)); 124.59 (*d*, C(8)); 131.33 (*s*, C(9)); 135.68 (*s*, C(11)); 145.69 (*s*, C(12)); 152.30 (*s*, C(13)). HR-MS: 334.1775 (M^+, $C_{19}H_{26}O_5^+$; calc. 334.1775).

*(2*S*,4*R*,4a*R*,8*R*,8a*R*)-2-(2,3-Dimethoxyphenyl)-3,4,4a,5,8,8a-hexahydro-4,7-dimethyl-2*H*-chromene-4,8-diol* (5*R*)-**3h**. The NMR spectra of (5*R*)-**3h** were recorded for the mixture (5*S*)-**3h**/(5*R*)-**3h** 1.0:0.9 ^{1}H-NMR ($CDCl_3$): 1.20 (*s*, Me(17)); 1.61 (*ddd*, *J*(4e,4a) = 14.3, *J*(4e,3a) = 2.8, *J*(4e,6a) = 1.2, H_e–C(4)); 1.70 (br. *dd*, *J*(6a,7a) = 9.8, *J*(6a,7e) = 7.5, H_a–C(6)); 1.80 (*m*, all $J \leq 2.5$, Me(18)); 1.80 (*dd*, *J*(4a,4e) = 14.3, *J*(4a,3a) = 11.7, H_a–C(4)); 2.00–2.05 (*m*, CH_2(7)); 3.80 (*s*, Me(19)); 3.82 (*s*, Me(20)); 3.91 (br. *s*, H_e–C(10)); 4.27 (*dd*, *J*(1e,10e) = 2.4, *J*(1e,6a) = 2.1, H_e–C(1)); 5.07 (*dd*, *J*(3a,4a) = 11.7, *J*(3a,4e) = 2.8, H_a–C(3)); 5.57–5.60 (*m*, H–C(8)); 6.78 (*dd*, *J*(14,15) = 8.0, *J*(14,16) = 1.6, H–C(14)); 6.92 (*d*, *J*(16,14) = 1.6, H–C(16)); 6.98 (*dd*, *J*(15,14) = 8.0, *J*(15,16) = 7.8, H–C(15)). ^{13}C-NMR ($CDCl_3$): 20.78 (*q*, C(18)); 24.55 (*t*, C(7)); 28.32 (*q*, C(17)); 37.86 (*d*, C(6)); 41.05 (*t*, C(4)); 55.60 (*q*, C(20)); 60.78 (*q*, C(19)); 70.50 (*d*, C(10)); 71.09 (*s*, C(5)); 71.30 (*d*, C(3)); 75.16 (*d*, C(1)); 111.39 (*d*, C(14)); 118.79 (*d*, C(16)); 124.01 (*d*, C(8)); 124.12 (*d*, C(15)); 131.92 (*s*, C(9)); 136.32 (*s*, C(11));145.91 (*s*, C(12)); 152.44 (*s*, C(13)). HR-MS: 334.1775 (M^+, $C_{19}H_{26}O_5^+$; calc. 334.1775).

*(2*R*,4*S*,4a*R*,6*S*,7*R*,8a*R*,9*S*)-2,9-Bis(2,3-dimethoxyphenyl)hexahydro-4,7-dimethyl-2*H*-4,6-(epoxymethano)chromen-8(8a*H*)-one* (**4h**). $[\alpha]_D^{26} = -19.2$ ($c = 0.31$). ^{1}H-NMR ($CDCl_3$): 1.08 (*d*, *J*(18,9) = 7.6, Me(18)); 1.50 (*s*, Me(17)); 1.96 (*dd*, *J*(4e,4a) = 14.7, *J*(4e,3a) = 2.4, H_e–C(4)); 1.99–2.02 (*m*, H–C(8)); 2.13 (*dd*, *J*(4a,4e) = 14.7, *J*(4a,3a) = 13.0, H_a–C(4)); 2.36 (*ddd*, *J*(7a,7e) = 14.1, *J*(7a,6e) = 3.2, *J*(7a,8) = 3.6, H_a–C(7)); 2.43 (*dm*, *J*(7e,7a) = 14.1, H_e–C(7)); 2.48 (br. *q*, *J*(9,18) = 7.6, H_e–C(9)); 2.64–2.68 (*m*, H–C(6)); 3.797 (*s*, MeO–C(12)); 3.808 (*s*, MeO–C(21)); 3.814, 3.816 (2*s*, MeO–C(13), MeO–C(22)); 4.54 (*d*, *J*(1a,6) = 5.3, H_a–C(1)); 5.05 (br. *s*, H–C(19)); 5.22 (*dd*, *J*(3a,4a) = 13.0, *J*(3a,4e) = 2.4, H_a–C(3)); 6.80 (*dd*, *J*(23,24) = 8.0, *J*(23,25) = 1.6. H–C(23)); 6.81 (*dd*, *J*(14,15) = 8.0, *J*(14,16) = 1.6. H–C(14)); 6.98 (*dd*, *J*(25,24) = 8.0, *J*(25,23) = 1.6, H–C(25)); 7.03 (*dd*, *J*(24,23) = *J*(24,25) = 8.0, H–C(24)); 7.12 (*dd*. *J*(15,14) = *J*(15,16) = 8.0, H–C(15)); 7.66 (*dd*, *J*(16,15) = 8.0, *J*(16,14) = 1.6. H–C(16)). ^{13}C-NMR ($CDCl_3$): 17.70 (*q*, C(18)); 23.02 (*q*, C(17)); 24.37 (*t*, C(7)); 39.10 (*d*, C(6)); 41.83 (*d*, C(8)); 42.98 (*d*, C(9)); 47.53 (*t*, C(4)); 55.49, 55.55 (2*q*, MeO–C(13), MeO–C(22)); 60.17 (*q*,

MeO–C(21)); 60.76 (*q*, MeO–C(12)); 65.54 (*d*, C(3)); 71.20 (*d*, C(19)); 73.12 (*s*, C(5)); 76.37 (*d*, C(1)); 111.18 (*d*, C(23)); 111.28 (*d*, C(14)); 119.76 (*d*, C(25)); 119.82 (*d*, C(16)); 123.71 (*d*, C(24)); 124.40 (*d*, C(15)); 133.69 (*s*, C(20)); 135.74 (*s*, C(11)); 144.97 (*s*, C(21)); 145.34 (*s*, C(12)); 151.74 (*s*, C(13)); 151.88 (*s*, C(22)); 212.51 (*s*, C(10)). HR-MS: 482.2305 (M^+, $C_{28}H_{34}O_7^+$; calc. 482.2299).

*(2*S*,4a*S*,8*R*,8a*R*)-2-(2,3-Dimethoxyphenyl)-3,4,4a,5,8,8a-hexahydro-7-methyl-4-methylene-2*H*-chromen-8-ol* **5h**. $[\alpha]_D^{26} = -32.1$ ($c = 0.46$). ^{1}H-NMR ($CDCl_3$): 1.81 (*m*, all $J \leq 2.5$, Me(18)); 1.95 (*dddq*, J(7e,7a) = 17.8, J(7e,6a) = 6.4, J(7e,8) = 5.2, J(7e,18) = 1.5, H_e–C(7)); 2.30 (*dd*, J(4e,4a) = 14.0, J(4e,3a) = 3.0, H_e–C(4)); 2.38 (*dddqd*, J(7a,7e) = 17.8, J(7a,6a) = 10.8, J(7a,8) = 2.5, J(7a,18) = 2.5, J(7a,10e) = 1.5, H_a–C(7)); 2.50 (*ddt*, J(4a,4e) = 14.0, J(4a,3a) = 11.5, J(4a,17) = 2.0, H_a–C(4)); 2.53 (*ddd*, J(6a,7a) = 10.8, J(6a,7e) = 6.4, J(6a,1e) = 2.1, H_a–C(6)); 3.75 (*dd*, J(1e,10e) = 2.4, J(1e,6a) = 2.1, H_e–C(1)); 3.81 (*s*, MeO–C(16)); 3.83 (*s*, MeO–C(15)); 3.89 (br. *s*, H_e–C(10)); 4.70 (*dd*, J(3a,4a) = 11.5, J(3a,4e) = 3.0, H_a–C(3)); 4.79 (*dd*, J(17,17′) = 2.0, J(17,4a) = 2.0, H–C(17)); 4.89 (*dd*, J(17′,17) = 2.0, J(17′,4a) = 2.0, H′-C(17)); 5.61 – 5.65 (*m*, H–C(8)); 6.81 (*dd*, J(14,15) = 7.8, J(14,16) = 1.9, H–C(14)); 6.99 (*dd*, J(16,15) = 7.8, J(16,14) = 1.9, H–C(16)); 7.02 (*dd*, J(15,14) = 7.8, J(15,16) = 7.8, H–C(15)). ^{13}C-NMR ($CDCl_3$): 20.87 (*q*, C(18)); 26.27 (*t*, C(7)); 36.80 (*d*, C(6)); 37.59 (*t*, C(4)); 55.65 (*q*, C(20)); 60.89 (*q*, C(19)); 70.37 (*d*, C(10)); 75.77 (*d*, C(3)); 80.46 (*d*, C(1)); 109.52 (*t*, C(17)); 111.49 (*d*, C(14)); 118.53 (*d*, C(16)); 124.17 (*d*, C(15)); 124.48 (*d*, C(8)); 131.48 (*s*, C(9)); 135.96 (*s*, C(11)); 145.86 (*s*, C(12)); 147.03 (*s*, C(5)); 152.39 (*s*, C(13)). HR-MS: 316.1667 (M^+, $C_{19}H_{24}O_4^+$; calc. 316.1669).

2.7. *Reaction of* **1** *with 2-Methoxybenzaldehyde* (**2i**). The reaction of **1** (0.350 g) and **2i** (0.284 g) for 7 d in the presence of clay *K10* (1.3 g) gave compounds **3i** ((5*S*)/(5*R*) 75 :25; 0.328 g, 52%), **4i** (0.060 g, 14%), and **5i** (0.014 g, 5%).

The NMR spectra of (5*S*)-**3i** were recorded for the mixture (5*S*)-**3i**/(5*R*)-**3i** 3 :2.

*(2*S*,4*S*,4a*R*,8*R*,8a*R*)-2-(2-Methoxyphenyl)-3,4,4a,5,8,8a-hexahydro-4,7-dimethyl-2*H*-chromene-4,8-diol* (5*S*)-**3i**. ^{1}H-NMR ($CDCl_3$/CD_3OD): 1.51 (*s*, Me(17)); 1.67 – 1.86 (*m*, CH_2(4), H_a–C(6)); 1.81 (*m*, all $J \leq 2.5$, Me(18)); 2.14 – 2.21 (*m*, CH_2(7)); 3.81 (*s*, MeO); 3.84 (br. *s*, H_e–C(10)); 4.84 (*dd*, J(3a,4a) = 11.4, J(3a,4e) = 3.0, H_a–C(3)); 5.64 – 5.67 (*m*, H–C(8)); 6.84 (*dd*, J(13,14) = 8.3, J(13,15) = 0.8, H–C(13)); 6.92 (*td*, J(15,14(16)) = 7.5, J(15,13) = 0.8, H–C(15)); 7.20 (*ddd*, J(14,13) = 8.3, J(14,15) = 7.5, J(14,16) = 1.8, H–C(14)), 7.35 (*dd*, J(16,15) = 7.5, J(16,14) = 1.8, H–C(16)). The signal of the H_e–C(1) was overlapped by that of the MeO group. ^{13}C-NMR ($CDCl_3$ + CD_3OD): 20.79 (*q*, C(18)); 23.03 (*t*, C(7)); 26.67 (*q*, C(17)); 38.70 (*d*, C(6)); 41.46 (*t*, C(4)); 55.51 (*q*, MeO); 70.37 (*d*, C(10)); 70.96 (*s*, C(5)); 72.01 (*d*, C(3)); 78.30 (*d*, C(1)); 110.54 (*d*, C(13)); 121.00 (*d*, C(15));124.68 (*d*, C(8)); 126.60 (*d*, C(16)); 128.46 (*d*, C(14)); 130.90 (*s*, C(11)); 131.52 (*s*, C(9)); 155.82 (*s*, C(12)). HR-MS: 304.1670 (M^+, $C_{18}H_{24}O_4^+$; calc. 304.1669).

*(2*S*,4*R*,4a*R*,8*R*,8a*R*)-2-(2-Methoxyphenyl)-3,4,4a,5,8,8a-hexahydro-4,7-dimethyl-2*H*-chromene-4,8-diol* ((5*R*)-**3i**). ^{1}H-NMR ($CDCl_3$ /CD_3OD): 1.19 (*s*, Me(17)); 1.62 (*dd*, J(4a,4e) = 14.4, J(4a,3a) = 11.3, H_a–C(4)); 1.67 – 1.75 (*m*, H_e–C(4), H_a–C(6)); 1.81 (*m*, all $J \leq 2.5$, Me(18)); 1.99 – 2.05 (*m*, CH_2(7)); 3.79 (*s*, MeO); 3.85 (br. *s*, H_e–C(10)); 4.22 (*dd*, J(1e,6a) = 2.3, J(1e,10e) = 2.0, H_e–C(1)); 5.16 (*dd*, J(3a,4a) = 11.3, J(3a,4e) = 2.8, H_a–C(3)); 5.58 – 5.61 (*m*, H–C(8)); 6.84 (*dd*, J(13,14) = 8.3, J(13,15) = 0.8, H–C(13)); 6.92 (*td*, J(15,14(16)) = 7.5, J(15,13) = 0.8, H–C(15)); 7.19 (*ddd*, J(14,13) = 8.3, J(14,15) = 7.5, J(14,16) = 1.8, H–C(14)), 7.35 (*dd*, J(16,15) = 7.5, J(16,14) = 1.8, H–C(16)). ^{13}C-NMR ($CDCl_3$/CD_3OD): 20.87 (*q*, C(18)); 24.81 (*t*, C(7));27.99 (*q*, C(17)); 38.01 (*d*, C(6)); 40.72 (*t*, C(4)); 55.40 (*q*, MeO); 70.37 (*d*, C(10)); 70.55 (*d*, C(3)); 70.55 (*s*, C(5)); 75.64 (*d*, C(1)); 110.58 (*d*, C(13)); 120.97 (*d*, C(15));124.01 (*d*, C(8)); 126.69 (*d*, C(16)); 128.31 (*d*, C(14));131.50 (*s*, C(11));132.12 (*s*, C(9)); 155.95 (*s*, C(12)). HR-MS: 304.1670 (M^+, $C_{18}H_{24}O_4^+$; calc. 304.1669).

*(2*R*,4*S*,4a*R*,6*S*,7*R*,8a*R*,9*S*)-Hexahydro-2,9-bis(2-methoxyphenyl)-4,7-dimethyl-2*H*-4,6-(epoxymethano)chromen-8(8a*H*)-one* (**4i**). $[\alpha]_D^{27} = -56.8$ ($c = 1.2$). ^{1}H-NMR ($CDCl_3$): 1.10 (*d*, J(18,9) = 7.5, Me(18)); 1.50 (*s*, Me(17)); 2.01 (*dd*, J(4e,4a) = 14.8, J(4e,3a) = 2.8, H_e–C(4)); 2.03 (*m*, all $J \leq 3.5$, H_e–C(8)); 2.08 (*dd*, J(4a,4e) = 14.8, J(4a,3a) = 12.2, H_a–C(4)); 2.35 (*dm*, J(7a,7e) = 14.3, H_a–C(7)); 2.42 (*dm*, J(7e,7a) = 14.3, H_e–C(7)); 2.49 (br. *q*, J(9e,Me(18)) = 7.5, H_e–C(9)); 2.63 – 2.67 (*m*, H_e–C(6)); 3.79 (*s*, 2 MeO); 4.55 (*d*, J(1a, 6e) = 5.2, H_a–C(1)); 5.09 (br. *s*, H–C(19)); 5.27 (*dd*, J(3a,4a) = 12.2, J(3a,4e) = 2.8, H_a–C(3)); 6.80 (*d*, J(13,14) = J(22,23) = 8.2, H–C(13), H–C(22)), 6.96 (*t*, J(24,23(25)) = 7.5, H–C(24)); 7.06 (*t*, J(15,14(16)) = 7.5, H–C(15)); 7.19 (*ddd*, J(23,22) = 8.2, J(23,24) = 7.5, J(23,25) = 1.8, H–C(23)); 7.22 (*ddd*, J(14,13) = 8.2, J(14,15) = 7.5, J(14,16) = 1.8, H–C(14)); 7.37 (*dd*, J(25,24) = 7.5,

J(25,23) = 1.8, H–C(25)); 8.08 (*dd*, *J*(16,15) = 7.5, *J*(16,14) = 1.8, H–C(16)). ^{13}C-NMR ($CDCl_3$): 17.79 (*q*, C(18)); 23.15 (*q*, C(17)); 24.33 (*t*, C(7)); 39.22 (*d*, C(6)); 40.71 (*d*, C(8)); 43.16 (*d*, C(9)); 46.91 (*t*, C(4)); 54.97, 55.17 (2*q*, 2 MeO); 65.20 (*d*, C(3)); 70.68 (*d*, C(19));73.08 (*s*, C(5)); 76.44 (*d*, C(1)); 109.57 (*d*, C(22)); 109.64, (*d*, C(13)); 120.45 (*d*, C(15));121.06 (*d*, C(24)); 127.72 (*d*, C(23)); 127.77 (*d*, C(25)); 127.79 (*d*, C(16)); 127.97 (*d*, C(14)); 128.34 (*s*, C(20)); 130.53 (*s*, C(11)); 155.21 (*s*, C(21)); 155.37 (*s*, C(12)); 212.73 (*s*, C(10)). HR-MS: 422.2086 (M^+, $C_{26}H_{30}O_5^+$; calc. 422.2088).

*(2*S*,4a*S*,8*R*,8a*R*)-3,4,4a,5,8,8a-Hexahydro-2-(2-methoxyphenyl)-7-methyl-4-methylidene-2*H*-chromen-8-ol* (**5i**). $[\alpha]_D^{27} = -80$ (*c* = 0.28). ^{1}H-NMR ($CDCl_3$): 1.84 (*m*, all $J \leq 2.5$, Me(18)); 1.96 (*dddq*, *J*(7e,7a) = 17.8, *J*(7e,6a) = 6.4, *J*(7e,8) = 5.0, *J*(7e,Me(18) = 1.5, H_e–C(7)); 2.34 (*dddd*, *J*(4a,4e) = 14.1, *J*(4a,3a) = 11.0, *J*(4a,17) = 2.0, *J*(4a,17′) = 1.7, H_a–C(4)); 2.40 (*dd*, *J*(4e,4a) = 14.1, *J*(4e,3a) = 3.4, H_e–C(4)); 2.53 (*ddd*, *J*(6a,7a) = 10.8, *J*(6a,7e) = 6.4, *J*(6a,1e) = 2.4, H_a–C(6)); 3.75 (*dd*, *J*(1e,6) = 2.4, *J*(1e,10e) = 2.1, H_e–C(1)); 3.81 (*s*, MeO); 3.92 (br. *s*, H_e–C(10)); 4.77 (*dd*, *J*(3a,4a) = 11.0, *J*(3a,4e) = 3.4, H_a–C(3)); 4.80 (*dd*, *J*(17,17′) = 2.2, *J*(17,4a) = 2.0, H–C(17)); 4.89 (*dd*, *J*(17′,17) = 2.2, *J*(17′,4a) = 1.7, H'–C(17)); 5.64 (*dm*, *J*(8,7e) = 5.0, H–C(8)); 6.83 (*dd*, *J*(13,14) = 8.2, *J*(13,15) = 1.0, H–C(13)); 6.94 (*td*, *J*(15,14(16)) = 7.5, *J*(15,13) = 1.0, H–C(15)); 7.21 (*ddd*, *J*(14,13) = 8.2, *J*(14,15) = 7.5, *J*(14,16) = 1.8, H–C(14)); 7.42 (*dd*, *J*(16,15) = 7.5, *J*(16,14) = 1.8, H–C(16)). ^{13}C-NMR ($CDCl_3$): 20.91 (*q*, C(18)); 26.33 (*t*, C(7)); 36.92 (*d*, C(6)); 37.41 (*t*, C(4)); 55.27 (*q*, MeO); 70.48 (*d*, C(10)); 74.87 (*d*, C(3)); 80.48 (*d*, C(1)); 109.38 (*t*, C(17));110.22 (*d*, C(13)); 120.73 (*d*, C(15)); 124.51 (*d*, C(8)); 126.26 (*d*, C(16)); 128.10 (*d*, C(14)); 130.93 (*s*, C(11)); 131.57 (*s*, C(9)); 147.30 (*s*, C(5)); 155.58 (*d*, C(12)). HR-MS: 286.1563 (M^+, $C_{18}H_{22}O_3^+$; calc. 286.1561).

2.8. *Reaction of* **1** *with 4-Methoxybenzaldehyde* (**2j**). The reaction of **1** (0.050 g) and **2j** (0.040 g) for 7 d in the presence of clay *K10* (1.3 g) gave compounds **3j** ((5*S*)/(5*R*) 75 : 25; 0.075 g, 84%).

The NMR spectra of (5*S*)-**3j** were recorded for the mixture (5*S*)-**3j**/(5*R*)-**3j** 2 : 1.

*(2*S*,4*S*,4a*R*,8*R*,8a*R*)-3,4,4a,5,8,8a-Hexahydro-2-(4-methoxyphenyl)-4,7-dimethyl-2*H*-chromene-4,8-diol* ((5*S*)-**3j**). ^{1}H-NMR ($CDCl_3$): 1.53 (*s*, Me(17)); 1.62 (*ddd*, *J*(4e,4a) = 13.4, *J*(4e,3a) = 2.7, *J*(4e,6) = 1.1, H_e–C(4)); 1.82 (*m*, all $J \leq 2.0$, Me(18)); 1.87 – 1.93 (*m*, H_a–C(6)); 1.95 (*dd*, *J*(4a,4e) = 13.4, *J*(4a,3a) = 12.0, H_a–C(4)); 2.18 – 2.23 (*m*, CH_2(7)); 3.78 (*s*, MeO); 3.81 – 3.84 (*m*, H_e–C(1), H_e–C(10)); 4.46 (*dd*, *J*(3a,4a) = 12.0, *J*(3a,4e) = 2.7, H_a–C(3)); 4.85 (*s*, 2 OH); 5.67 (*tq*, *J*(8,7) = 3.8, *J*(8,18) = 1.5, H–C(8)); 6.88 (*d*, *J*(13,12) = *J*(15,16) = 8.8, H–C(13), H–C(15)); 7.26 (*d*, *J* = 8.8, H–C(12), H–C(16)). ^{13}C-NMR ($CDCl_3$): 21.26 (*q*, C(18)); 24.05 (*t*, C(7)); 27.16 (*q*, C(17)); 39.69 (*d*, C(6)); 43.88 (*t*, C(4)); 55.67 (*q*, MeO); 71.32 (*d*, C(10)); 71.61 (*s*, C(5)); 78.68 (*d*, C(3)); 79.52 (*d*, C(1)); 114.65 (*d*, C(13), C(15)); 125.43 (*d*, C(8)); 128.38 (*d*, C(12), C(16)); 132.60 (*s*, C(9)); 135.82 (*s*, C(11)); 160.59 (*s*, C(14)). HR-MS: 304.1668 (M^+, $C_{18}H_{24}O_4^+$; calc. 304.1669).

*(2*S*,4*R*,4a*R*,8*R*,8a*R*)-3,4,4a,5,8,8a-Hexahydro-2-(4-methoxyphenyl)-4,7-dimethyl-2*H*-chromene-4,8-diol* ((5*R*)-**3j**). ^{1}H-NMR ($CDCl_3$): 1.24 (*s*, Me(17)); 1.59 (*ddd*, *J*(4e,4a) = 14.3, *J*(4e,3a) = 2.7, *J*(4e,6) = 1.3, H_e–C(4)); 1.76 – 1.82 (*m*, H_a–C(6)); 1.81 (*dd*, *J*(4a,4e) = 14.3, *J*(4a,3a) = 11.7, H_a–C(4)); 1.82 (*m*, all $J \leq 2.5$, Me(18)); 2.01 – 2.07 (*m*, CH_2(7)); 3.77 (*s*, MeO); 3.82 (br. *s*, H_e–C(10)); 4.27 (*dd*, *J*(1e,6) = 2.4, *J*(1e,10e) = 2.0, H_e–C(1)); 4.74 (*dd*, *J*(3a,4a) = 11.7, *J*(3a,4e) = 2.7, H_a–C(3)); 4.85 (br. *s*, 2OH); 5.60 – 5.63 (*m*, H–C(8)); 6.87 (*d*, *J*(13,12) = *J*(15,16) = 8.8, H–C(13), H–C(15)); 7.25 (*d*, *J* = 8.8, H–C(12), H–C(16)). ^{13}C-NMR ($CDCl_3$): 21.26 (*q*, C(18)); 25.67 (*t*, C(7)); 28.31 (*q*, C(17)); 38.72 (*d*, C(6)); 43.01 (*t*, C(4)); 55.67 (*q*, MeO); 71.26 (*s*, C(5)); 71.27 (*d*, C(10)); 77.10 (*d*, C(3)); 77.12 (*d*, C(1)); 114.62 (*d*, C(13), C(15)); 124.86 (*d*, C(8)); 128.43 (*d*, C(12), C(16)); 133.08 (*s*, C(9)); 136.20 (*s*, C(11)); 160.50 (*s*, C(14)). HR-MS: 304.1668 (M^+, $C_{18}H_{24}O_4^+$; calc. 304.1669).

2.10. *Reaction of* **1** *with 2,4-Dihydroxybenzaldehyde* (**2k**). The reaction of **1** (0.600 g) and **2k** (0.500 g) for 7 d in the presence of clay *K10* (2.2 g) gave, after CC, 0.300 g of **2k** (40% conversion) and compound **3k** ((5*S*)/(5*R*) 70 : 30; 0.363 g, 82%).

The NMR spectra of (5*S*)-**3k** were recorded for the mixture (5*S*)-**3k**/(5*R*)-**3k** in a ratio 1 : 0.4 resp.

*(2*S*,4*S*,4a*R*,8*R*,8a*R*)-2-(2,4-Dihydroxyphenyl)-3,4,4a,5,8,8a-hexahydro-4,7-dimethyl-2*H*-chromene-4,8-diol* ((5*S*)-**3k**). ^{1}H-NMR ($CDCl_3$/CD_3OD): 1.51 (*s*, Me(17)); 1.62 (*ddd*, *J*(4e,4a) = 13.4, *J*(4e,3a) = 2.7, *J*(4e,6) = 1.0, H_e–C(4)); 1.80 (*m*, all $J \leq 2.5$, Me(18)); 1.87 – 1.92 (*m*, H_a–C(6)); 2.01 (*dd*, *J*(4a,4e) = 13.4, *J*(4a,3a) = 12.1, H_a–C(4)); 2.16 – 2.22 (*m*, CH_2(7)); 3.83 (*dd*, *J*(1e,10e) = 2.4, *J*(1e,6a) = 2.1, H_e–C(1)); 3.85 (br. *s*, H_e–C(10)); 4.69 (*dd*, *J*(3a,4a) = 12.1, *J*(3a,4e) = 2.7, H_a–C(3)); 5.64 – 5.68 (*m*, H–C(8)); 6.28 – 6.33 (*m*, H–C(13), H–C(15)); 6.92 (*d*, *J* (16,15) = 8.1, H–C(16)). ^{13}C-NMR ($CDCl_3$/CD_3OD): 21.01 (*q*,

C(18)); 23.34 (*t*, C(7)); 26.76 (*q*, C(17)); 38.48 (*d*, C(6)); 41.59 (*t*, C(4)); 70.24 (*d*, C(10)); 70.86 (*s*, C(5)); 76.27 (*d*, C(3)); 78.56 (*d*, C(1)); 103.76 (*d*, C(13)); 107.48 (*d*, C(15)); 119.10 (*s*, C(11)); 124.78 (*d*, C(8)); 127.99 (*d*, C(16)); 131.82 (*s*, C(9)); 156.02 (*s*, C(12)); 157.90 (*s*, C(14)). HR-MS: 306.1459 (M^+, $C_{17}H_{22}O_5^+$; calc. 306.1462).

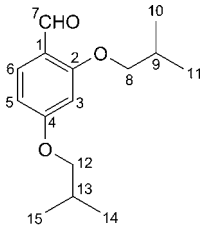
*(2*S*,4*R*,4a*R*,8*R*,8a*R*)-2-(2,4-Dihydroxyphenyl) – 3,4,4a,5,8,8a-hexahydro-4,7-dimethyl-2 H-chromene-4,8-diol* ((5*R*)-**3k**). ^{1}H-NMR ($CDCl_3$/CD_3OD): 1.22 (*s*, Me(17)); 1.59 (*ddd*, *J*(4e,4a) = 14.3, *J*(4e,3a) = 3.0, *J*(4e,6a) = 1.2, H_e–C(4)); 1.75 – 1.80 (*m*, H_a–C(6)); 1.80 (*m*, all $J \leq 2.5$, Me(18)); 1.88 (*dd*, *J*(4a,4e) = 14.3, *J*(4a,3a) = 11.8, H_a–C(4)); 2.05 – 2.10 (*m*, CH_2(7)); 3.86 (br. *s*, H_e–C(10)); 4.27 (*dd*, *J*(1e,6a) = 2.1, *J*(1e,10e) = 2.4, H_e–C(1)); 4.96 (*dd*, *J*(3a,4a) = 11.8, *J*(3a,4e) = 3.0, H_a–C(3)); 5.59 – 5.62 (*m*, H–C(8)); 6.28 – 6.33 (*m*, H–C(13), H–C(15)); 6.87 (*d*, *J*(16,15) = 8.1, H–C(16)). ^{13}C-NMR ($CDCl_3$/CD_3OD): 21.10 (*q*, C(18)); 25.03 (*t*, C(7)); 27.93 (*q*, C(17)); 37.53 (*d*, C(6)); 40.87 (*t*, C(4)); 70.14 (*d*, C(10)); 70.55 (*s*, C(5)); 75.70 (*d*, C(3)); 76.03 (*d*, C(1)); 103.98 (*d*, C(13)); 107.52 (*d*, C(15)); 119.14 (*s*, C(11)); 124.02 (*d*, C(8)); 127.99 (*d*, C(16)); 132.47 (*s*, C(9)); 156.27 (*s*, C(12)); 157.86 (*s*, C(14)). HR-MS: 306.1459 (M^+, $C_{17}H_{22}O_5^+$; calc. 306.1462).

2.11. *Synthesis of* Compound (**2l**). 2,4-Diisobutoxybenzaldehyde **2l** was synthesized from 2,4-dihydroxybenzaldehyde as described in [18]. A stirred mixture of 2,4-dihydroxybenzaldehyde (0.400 g), K_2CO_3 (1.6 g), and KI (1.66 g) in DMF (20 ml) was heated to 50°. 1-Bromo-2-methylpropane (1.6 g) was then added dropwise. The mixture was stirred for 24 h at 50°, then cooled, and filtered. The org. layer was washed with sat. NH_4Cl soln. (30 ml) and brine (30 ml), and dried (Na_2SO_4). The org. extract, which contained mixture of starting 2,4-dihydroxybenzaldehyde (6% by GC/MS), mono-alkylated product (38% by GC/MS), and desired aldehyde **2l** (56% by GC/MS) was washed twice with 10% soln. NaOH (30 ml) and H_2O (2 × 30 ml), and then dried (Na_2SO_4). The org. extract was concentrated *in vacuo* and yielded **2l** (0.45 g, 62%). ^{1}H-NMR ($CDCl_3$; for atom numbering, see *Fig. 3*): 1.01, 1.03 (2*d*, *J*(10(11),9) = *J*(14(15),13) = 6.7, Me(10), Me(11), Me(14), Me(15)); 2.01 – 2.19 (*m*, H–C(9), H–C(13)); 3.75, 3.78 (2*d*, *J*(8, 9) = *J*(12, 13) = 6.4, CH_2(8), CH_2(12)); 6.39 (*d*, *J*(3,5) = 2.2 H–C(3)); 6.48 (*ddd*, *J*(5,6) = 8.7, *J*(5,3) = 2.2, *J*(5,7) = 0.7, H–C(5)); 7.76 (*d*, *J*(6,5) = 8.7, H–C(6)); 10.33 (*d*, *J*(7,5) = 0.7, H–C(7)). ^{13}C-NMR ($CDCl_3$): 19.01, 19.06 (2*q*, C(10), C(11), C(14), C(15)); 28.10, 28.15 (2*d*, C(9), C(13)); 74.55, 74.58 (2*t*, C(8), C(12)); 98.79 (*d*, C(3)); 106.21 (*d*, C(5)); 118.85 (*s*, C(1)); 129.98 (*d*, C(6)); 163.32 (*s*, C(2)); 165.77 (*s*, C(4)); 188.07 (*d*, C(7)). HR-MS: 250.1563 (M^+, $C_{15}H_{22}O_3^+$; calc. 250.1564).

2.12. *Reaction of* **1** *with* **2l**. The reaction of **1** (0.168 g) and **2l** (0.250 g) for 7 d in the presence of clay *K10* (0.840 g) gave compounds **3l** ((5*S*)/(5*R*) 67:33; 0.150 g, 36%), **5l** (0.056, 14%), and **6l** (0.016 g, 4%).

The NMR spectra of (5*S*)-**3l** were recorded for the mixture (5*S*)-**3l**/(5*R*)-**3l** 1.0:0.5.

*(2*S*,4*S*,4a*R*,8*R*,8a*R*)-2-[2,4-Bis(2-methylpropoxy)phenyl]-3,4,4a,5,8,8a-hexahydro-4,7-dimethyl-2*H*-chromene-4,8-diol* ((5*S*)-**3l**). ^{1}H-NMR ($CDCl_3$/CD_3OD): 0.891, 0.935 (2*d*, *J*(*Me*$_2$CHCH$_2$O–C(12), Me$_2$C*H*CH$_2$O–C(12)) = *J*(*Me*$_2$CHCH$_2$O–C(14), Me$_2$C*H*CH$_2$O–C(14)) = 6.7, 2 *Me*$_2$CHCH$_2$); 1.59 – 1.67 (*m*, CH_2(4)); 1.70 (*m*, all $J \leq 2.5$, Me(18)); 1.69 – 1.73 (*m*, H–C(6)); 1.88 – 2.03 (*m*, 2 Me$_2$C*H*CH$_2$); 2.02 – 2.08 (*m*, CH_2(7)); 3.55 – 3.59 (*m*, 2 Me$_2$CHC*H*$_2$); 3.68 (*dd*, *J*(1e,10e) = 2.4, *J*(1e,6a) = 2.1, H_e–C(1)); 3.74 (br. *s*, H_e–C(10)); 4.70 (*dd*, *J*(3a,4a) = 11.1, *J*(3a,4e) = 3.2, H_a–C(3)); 5.52 – 5.55 (*m*, H–C(8)); 6.28 (*d*, *J*(13,15) = 2.3, H–C(13)); 6.33 (*dd*, *J*(15,16) = 8.4, *J*(15,13) = 2.3, H–C(15)); 7.12 (*d*, *J*(16,15) = 8.4, H–C(16)). ^{13}C-NMR ($CDCl_3$/CD_3OD): 18.84, 18.89 (4*q*, 2 *Me*$_2$CHCH$_2$); 20.35 (*q*, C(18)); 22.55 (*t*, C(7)); 26.19 (*q*, C(17)); 27.96, 28.13 (2*d*, 2 Me$_2$*C*HCH$_2$); 38.19 (*d*, C(6)); 41.33 (*t*, C(4)); 69.93 (*d*, C(10)); 70.57 (*s*, C(5)); 71.63 (*d*, C(3)); 74.28 (*t*, 2 Me$_2$CH*C*H$_2$); 77.90 (*d*, C(1)); 98.99 (*d*, C(13)); 104.95 (*d*, C(15));



2l

Fig. 3. *Structure and trivial atom numbering of aldehyde* **2l**

122.88 (*s*, C(11)); 124.21 (*d*, C(8)); 126.44 (*d*, C(16)); 131.04 (*s*, C(9)); 155.83 (*s*, C(12)); 159.32 (*s*, C(14)). HR-MS: 418.2719 (M^+, $C_{25}H_{38}O_5^+$; calc. 418.2714).

(2S,4R,4aR,8R,8aR)-2-[2,4-Bis(2-methylpropoxy)phenyl]-3,4,4a,5,8,8a-hexahydro-4,7-dimethyl-2H-chromene-4,8-diol ((5*R*)-**3l**). ^{1}H-NMR ($CDCl_3$/CD_3OD): 0.890 (2*d*), 0.922, 0.929 (all *d*, *J* = 6.7, 2 *Me*$_2$CHCH$_2$); 1.09 (*s*, Me(17)); 1.52 (*ddd*, *J*(4e,4a) = 14.1, *J*(4e,3a) = 2.8, *J*(4e,6a) = 1.4, H$_e$–C(4)); 1.55 – 1.61 (*m*, H$_a$–C(6)); 1.62 – 1.68 (*m*, H$_a$–C(4)); 1.69 (br. *s*, Me(18)); 1.88 – 2.03 (*m*, 2 Me$_2$C*H*CH$_2$); 3.58 – 3.62 (*m*, 2 Me$_2$CHC*H*$_2$); 3.74 (br. *s*, H$_e$–C(10)); 4.09 (*dd*, *J*(1e,10e) = 2.4, *J*(1e,6a) = 2.1, H$_e$–C(1)); 5.00 (*dd*, *J*(3a,4a) = 11.6, *J*(3a, 4e) = 2.8, H$_a$–C(3)); 5.46 – 5.49 (*m*, H–C(8)); 6.29 (*d*, *J*(13,15) = 2.3, H–C(13)); 6.32 (*dd*, *J*(15,16) = 8.4, *J*(15,13) = 2.3, H–C(15)); 7.10 (*d*, *J*(16,15) = 8.4, H–C(16)). ^{13}C-NMR ($CDCl_3$/CD_3OD): 18.84 (2*q*), 18.94, 18.97 (2*q*, 2 *Me*$_2$CHCH$_2$); 20.41 (*q*, C(18)); 24.34 (*t*, C(7)); 27.64 (*q*, C(17)); 27.96, 27.98 (2*d*, 2 Me$_2$C*H*CH$_2$); 37.57 (*d*, C(6)); 40.22 (*t*, C(4)); 69.89 (*d*, C(10)); 70.24 (*s*, C(5)); 70.29 (*d*, C(3)); 73.94 (*t*, 2 Me$_2$CHC*H*$_2$); 75.26 (*d*, C(1)); 99.34 (*d*, C(13)); 104.95 (*d*, C(15)); 123.14 (*s*, C(11)); 123.57 (*d*, C(8)); 127.13 (*d*, C(16)); 131.62 (*s*, C(9)); 156.44 (*s*, C(12)); 159.38 (*s*, C(14)). HR-MS: 418.2719 (M^+, $C_{25}H_{38}O_5^+$; calc. 418.2714).

(2S,4aS,8R,8aR)-2-[2,4-Bis(2-methylpropoxy)phenyl]-3,4,4a,5,8,8a-hexahydro-7-methyl-4-methylidene-2H-chromen-8-ol (**5l**). $[\alpha]_D^{27} = -18$ ($c = 0.01$). ^{1}H-NMR ($CDCl_3$): 0.99 (*d*, *J*(*Me*$_2$CHC*H*$_2$O–C(14), Me$_2$CHCH$_2$–C(14)) = 6.7, *Me*$_2$CHCH$_2$O–C(14)); 1.019, 1.022 (2*d*, *J*(*Me*$_2$CHCH$_2$O–C(16), Me$_2$C*H*CH$_2$O–C(16)) = *J*(*Me*$_2$CHCH$_2$O–C(16), Me$_2$C*H*CH$_2$O–C(16)) = 6.7, *Me*$_2$CHCH$_2$O–C(16)); 1.83 (*m*, all *J* ≤ 2.5, Me(18)); 1.94 (*dddq*, *J*(7e,7a) = 17.9, *J*(7e,6a) = 6.3, *J*(7e,8) = 5.2, *J*(7e,18) = 1.5, H$_e$–C(7)); 1.98 – 2.15 (*m*, 2 Me$_2$C*H*CH$_2$); 2.32 – 2.41 (*m*, H$_a$–C(7), CH$_2$(4)); 2.52 (*ddd*, *J*(6a,7a) = 10.8, *J*(6a,7e) = 6.3, *J*(6a,1e) = 2.3, H$_a$–C(6)); 3.67 (*d*, *J*(23,24) = 6.4, Me$_2$CHC*H*$_2$O–C(14)); 3.67 – 3.71 (*m*, Me$_2$CHC*H*$_2$O–C(16)); 3.74 (*dd*, *J*(1e,6a) = 2.3, *J*(1e,10e) = 2.1, H$_e$–C(1)); 3.91 (br. *s*, H$_e$–C(10)); 4.68 (*dd*, *J*(3a,4a) = 8.4, *J*(3a, 4e) = 5.6, H$_a$–C(3)); 4.76, 4.87 (2*m*, all *J* ≤ 2.5, CH$_2$(17)); 5.61 – 5.64 (*m*, H–C(8)); 6.39 (*d*, *J*(15, 13) = 2.3, H–C(15)); 6.43 (*dd*, *J*(13, 12) = 8.4, *J*(13, 15) = 2.3, H–C(13)); 7.27 (*d*, *J*(12, 13) = 8.4, H–C(12)). ^{13}C-NMR ($CDCl_3$): 19.17 (*q*, *Me*$_2$CHCH$_2$O–C(14)); 19.22, 19.27 (2*q*, *Me*$_2$CHCH$_2$O–C(16)); 20.91 (*q*, C(18)); 26.35 (*t*, C(7)); 28.20 (*d*, Me$_2$C*H*CH$_2$O–C(14)); 28.29 (*d*, Me$_2$C*H*CH$_2$O–C(16)); 37.00 (*d*, C(6)); 37.60 (*t*, C(4)); 70.54 (*d*, C(10)); 74.21 (*t*, Me$_2$CHC*H*$_2$O–C(14)); 74.43 (*t*, Me$_2$CHC*H*$_2$O–C(16)); 75.37 (*d*, C(3)); 80.73 (*d*, C(1)); 99.33 (*d*, C(13)); 104.98 (*d*, C(15)); 109.09 (*t*, C(17)); 123.20 (*s*, C(11)); 124.55 (*d*, C(8)); 126.68 (*d*, C(12)); 131.56 (*s*, C(9)); 147.67 (*s*, C(5)); 156.32 (*s*, C(16)); 159.62 (*s*, C(14)). HR-MS: 400.2613 (M^+, $C_{25}H_{36}O_4^+$; calc. 400.2608).

(2S,4R,4aR,8S,8aR)-3,4,4a,5,8,8a-Hexahydro-2-[2,4-bis(2-methylpropoxy)phenyl]-4,7-dimethyl-2H-4,8-epoxychromene (**6l**). $[\alpha]_D^{23} = -2.85$ ($c = 0.14$). ^{1}H-NMR ($CDCl_3$): 0.99 (*d*, *J*(*Me*$_2$C*H*CH$_2$O–C(14)) = 6.7, *Me*$_2$CHCH$_2$O–C(14)); 1.02 (*d*, *J*(*Me*$_2$C*H*CH$_2$O–C(16)) = 6.7, *Me*$_2$CHCH$_2$O–C(16)); 1.35 (*s*, C(17)); 1.57 (*dd*, *J*(4a,4e) = 13.0, *J*(4a,3a) = 10.6, H$_a$–C(4)); 1.75 (*m*, all *J* ≤ 2.5, Me(18)); 1.92 (*dd*, *J*(4e,4a) = 13.0, *J*(4e, 3a) = 4.1, H$_e$–C(4)); 1.98 – 2.16 (*m*, 2 Me$_2$C*H*CH$_2$); 2.35 (*dddq*, *J*(7a,7e) = 18.7, *J*(7a,6) = 5.5, *J*(7a,8) = 3.5, *J*(7a,18) = 2.5, H$_a$–C(7)); 2.52 (*dm*, *J*(7e,7a) = 18.7, H$_e$–C(7)); 3.66 – 3.71 (*m*, 2 Me$_2$CHC*H*$_2$); 4.23 (br. *s*, H$_e$–C(10)); 4.42 (br. *s*, H–C(1)); 5.13 – 5.16 (*m*, H–C(8)); 5.42 (*dd*, *J*(3a,4a) = 10.6, *J*(3a,4e) = 4.1, H$_a$–C(3)); 6.39 (*d*, *J*(15, 13) = 2.3, H–C(15)); 6.44 (*dd*, *J*(13, 12) = 8.4, *J*(13, 15) = 2.3, H–C(13)); 7.31 (*d*, *J*(12, 13) = 8.4, H–C(12)). ^{13}C-NMR ($CDCl_3$): 19.18 (*q*, *Me*$_2$CHCH$_2$O–C(14)), 19.33, 19.36 (2*q*, *Me*$_2$CHCH$_2$); 20.91 (*q*, C(18)); 21.58 (*q*, C(17)); 28.22 (*d*, 2 Me$_2$C*H*CH$_2$); 28.23 (*t*, C(7)); 45.64 (*d*, C(6)); 45.66 (*t*, C(4)); 68.45 (*d*, C(3)); 74.38, 74.42 (2*t*, 2 Me$_2$CHC*H*$_2$); 80.25 (*d*, C(10)); 81.05 (*d*, C(1)); 83.31 (*s*, C(5)); 99.42 (*d*, C(13)); 104.90 (*d*, C(15)); 120.65 (*d*, C(8)); 122.92 (*s*, C(11)); 127.17 (*d*, C(12)); 139.93 (*s*, C(9)); 156.67 (*s*, C(16)); 159.50 (*s*, C(14)). HR-MS: 400.2611 (M^+, $C_{25}H_{36}O_4^+$; calc. 400.2608).

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