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THIYLATION OF (*R*)-4-MENTHEN-3-ONE AND ITS DERIVATIVES

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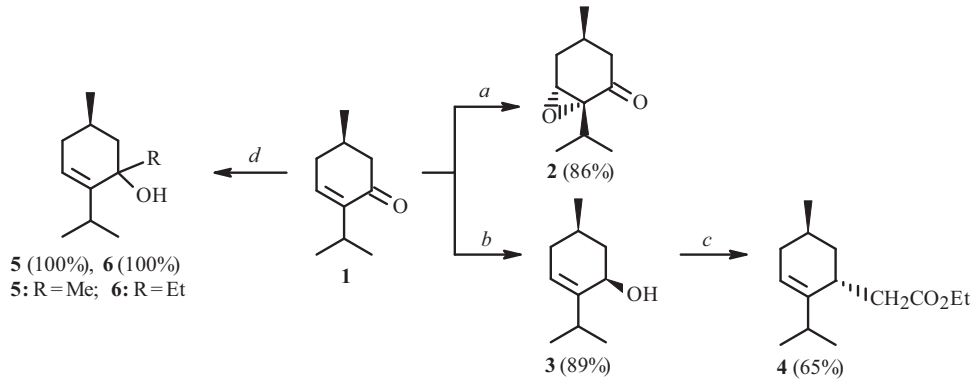
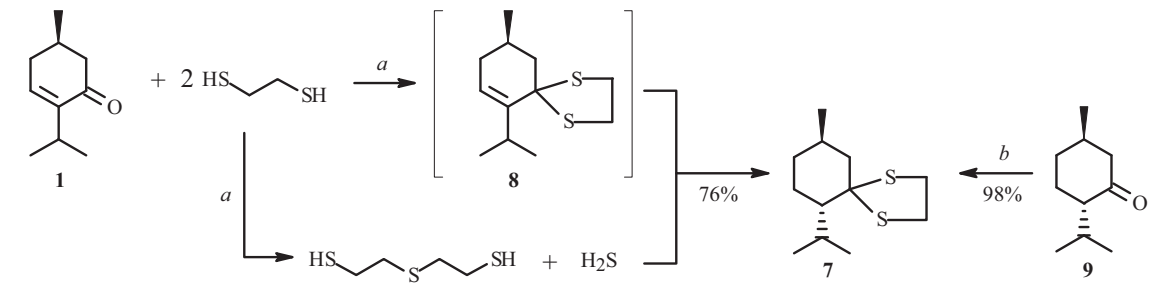
*Thiylation of (*R*)-4-menthen-3-one and its derivatives was studied. New sulfides and sulfoxides of the menthane series were synthesized.*

Keywords: (*R*)-4-menthen-3-one and its derivatives, thiylation and oxidation, sulfides and sulfoxides of the menthane series.

We have previously reported pathways for transforming the available optically pure (*R*)-4-menthen-3-one (**1**) via ozonolysis [1] and showed that enone **1** was significantly less reactive than ordinary cyclic α,β-unsaturated ketones in 1,2- and 1,4-addition reactions of organometallic reagents [2] and inert to Michael reactions and pyrazoline formation [3].



a. H_2O_2, NaOH; *b*. *i*-Bu_2AlH, CH_2Cl_2, –78°C; *c*. $MeC(OEt)_3$, AcOH, 130°C; *d*. MeLi or EtLi, Et_2O, –78°C



a. TsOH, PhH, 80°C; *b*. $HSCH_2CH_2SH$, $BF_3{\cdot}Et_2O$, AcOH

In continuation of research on the reactivity, we studied thiylation of **1** itself and its derivatives such as the epoxide **2** [4], (1*R*,3*R*)-menthen-3-ol (**3**) [5], the product of Claisen orthoester rearrangement **4** [6], and enols **5** and **6**, which were products of 1,2-addition of MeLi or EtLi to cycloenone **1** [2]. The results acquired a special significance because it is known [7–9] that S-containing derivatives of mono- and bicyclic monoterpenoids exhibit various types of biological activity.

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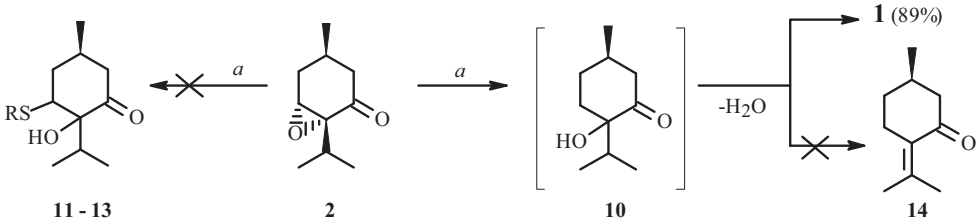
We performed a series of experiments on electrophilic (with catalysis by $ZnCl_2$ or $BF_3 \cdot OEt_2$) and nucleophilic (in the presence of K_2CO_3 or AcONa) addition of thiols [PhSH, *n*-$C_{12}H_{25}SH$, $HS(CH_2)_2SH$] to (*R*)-4-menthen-3-one (**1**) in various solvents at 20 or 55°C. As a result, enone **1** seemed to be less reactive toward catalyzed thiylation involving thiols (PhSH or *n*-$C_{12}H_{25}SH$) than (–)-carvone [10–12]. This was probably due to the steric influence of the *i*-Pr group.

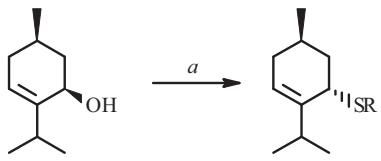
The inertness of menthenone **1** to electrophilic addition of $HS(CH_2)_2SH$ under $ZnCl_2$ or $BF_3 \cdot OEt_2$ catalysis conditions provided a basis for the method developed by us for purifying (*R*)-4-menthen-3-one from a (–)-menthone impurity [13]. However, saturated dithiolane **7** could be prepared under more forcing conditions (TsOH, 80°C, 24 h) through the action of $HS(CH_2)_2SH$ on **1** whereas PhSH was inert under these conditions. Apparently, the initially formed allyl dithiolane **8** was reduced further to its saturated analog **7** through the action of H_2S [14], which was released by thermal decomposition of $HS(CH_2)_2SH$ as before [15]. This was confirmed by the presence in the reaction mixture of $HS(CH_2)_2S(CH_2)_2SH$ and elemental S. The mass spectrum of the reaction mixture showed molecular ions for 153.0 $[M - H]^-$, 171.0 ($[M - H]^- + H_2O$), and 120.0 $([M - H]^- - SH)^+$. The ^{13}C NMR spectrum had resonances at 34.78 and 26.62 ppm [16] that were indicative of the formation of $HS(CH_2)_2S(CH_2)_2SH$. The stereochemistry of S-containing product **7** was confirmed by NMR spectroscopy and convergent synthesis from (–)-menthone (**9**) by the literature method [17].

It was found during the study of the thiylation of epoxyketone **2** by *n*-$C_{12}H_{25}SH$ [or $HS(CH_2)_2SH$ or $HSCH_2CO_2H$] that it occurred analogously to transformations of carvone 1,2-oxide [18] and was accompanied by regeneration of starting (*R*)-4-menthen-3-one probably through dehydration of intermediate ketoalcohol **10** and not formation of hydroxysulfides **11**–**13**. In turn, the production of **1** and not (*R*)-pulegone (**14**) was confirmed by GC and spectral data, i.e., the presence in the PMR spectrum of a resonance for olefinic proton HC=C–C=O at 5.6 ppm and the opposite phases of the resonances for the C atoms of the multiple bond of the α,β-unsaturated ketone **1** in the ^{13}C NMR spectrum in JMOD mode.



R = *n*-$C_{12}H_{25}$ (**11**), CH_2CO_2H (**12**), $(CH_2)_2SH$ (**13**)
a. RSH, EtONa

Thiylation of (1*R*,3*R*)-menthen-3-ol (**3**), in contrast with **1**, occurred smoothly under $ZnCl_2$ catalysis conditions even at room temperature with substitution of the hydroxyl group by sulfide function. Formation of sulfides **15**–**20** was accompanied (according to PMR and capillary GC data) by complete configuration inversion of the O-containing asymmetric center, as was noted earlier for *cis*-verbenol [19].

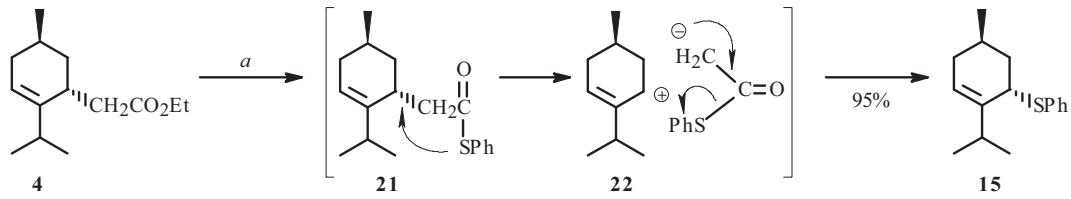


R = Ph (**15**), *n*-C_6H_{13} (**16**), *n*-$C_{12}H_{25}$ (**17**), *n*-$C_{16}H_{33}$ (**18**), $(CH_2)_2SH$ (**19**), CH_2CO_2H (**20**)
a. RSH, $ZnCl_2$, CH_2Cl_2

The stereochemistry of the reaction products, terpene sulfides **15**–**20**, was established by PMR data. Thus, the SSCC of the C-1 proton in the spectrum of **3** (^3J = 8.4 and 5.3 Hz) implied the equatorial orientation of the hydroxyl function whereas the small SSCC (H–H) (^3J = 5.4 and 6.3 Hz) of the C-6 protons in sulfides **16**–**18** and C-1 protons in sulfides **15**, **19**, and **20** were indicative of the axial orientation of the S-containing substituent. Therefore, thiylation of **3** was accompanied by complete configuration inversion of the OH-containing asymmetric center.

The reaction of orthoester Claisen rearrangement product of (1*R*,3*R*)-menthen-3-ol, i.e., acetate **4**, with PhSH with $ZnCl_2$ catalysis went without configuration inversion of the asymmetric center on C-1 and formed sulfide **15**, which was prepared earlier from **3**. The reaction occurred through an S_Ni mechanism according to the following proposed scheme. Acetate **4** was transformed initially into intermediate **21** that then dissociated to form contact ion pair **22**. The components of this pair were situated very close to each other. Therefore, attack of the nucleophile (PhS^-) was forced to occur from the same

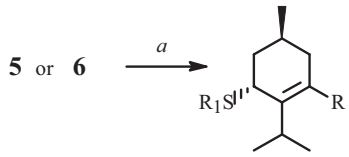
side where the leaving group ($^{-}CH_2CO_2Et$) was previously located. The contact ion pair decomposed so rapidly that PhS^{-} attacked frontally at the carbonium ion before it managed to convert into the planar state. As a result, sulfide **15** was formed [20, 21].



4 **21** **22** **15**

a. PhSH, $ZnCl_2$, CH_2Cl_2

Thiylation of tertiary allyl alcohols **5** and **6** in the presence of catalytic amounts of $ZnCl_2$ also occurred with OH substitution. In contrast with **3**, the reaction was accompanied by allyl rearrangement to form secondary terpene sulfides **23**–**25**, the PMR spectra of which lacked a resonance for the olefinic proton and retained other resonances of the starting enols **5** and **6**. The small SSCC for the C-1 proton (^3J = 1.4 and 4.3 Hz) in **23**–**25** indicated that the thioalkyl groups had the axial orientation.

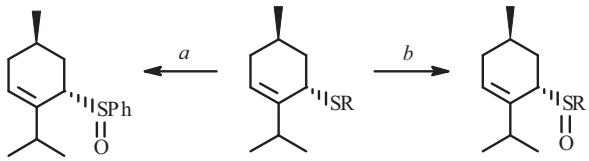


23 - 25

23: R = Me, R_1 = *n*-$C_{12}H_{25}$
24: R = Me, R_1 = $(CH_2)_2SH$
25: R = Et, R_1 = Ph

a. PhSH, $ZnCl_2$, CH_2Cl_2

Sulfides **15**, **16**, and **18** gave a series of menthene sulfoxides **26**–**28** upon oxidation by H_2O_2 (30%) in AcOH and *m*-CPBA in CH_2Cl_2.



26 **15, 16, 18** **26, 27, 28**

15, 26: R = Ph
16, 27: R = *n*-C_6H_{13}
18, 28: *n*-$C_{16}H_{33}$

a. *m*-CPBA, CH_2Cl_2; *b*. H_2O_2, AcOH

Thus, we studied the reactivity of available monoterpenoid (*R*)-4-menthenone and its derivatives in electrophilic and nucleophilic thiylation reactions and demonstrated their potential in the synthesis of new potentially biologically active sulfides and sulfoxides of the menthane series.

EXPERIMENTAL

IR spectra were recorded in a thin layer on an IR Prestige-21 instrument (Shimadzu). NMR spectra were taken in $CDCl_3$ with TMS internal standard on a Bruker Avance III 500 spectrometer (operating frequency 500.13 MHz for PMR and 125.20 MHz for ^{13}C NMR). PMR and ^{13}C NMR spectra were analyzed and resonances were assigned using two-dimensional COSY (H–H), HSQC, and HMBC correlation spectroscopy. Chromatographic analysis was performed on Chrom-5 instruments using columns (1.2 m long) with stationary phase silicone SE-30 (5%) + OV-225 (3%) on a Chromaton N-AW-DMCS (0.16–0.20 mm, operating temperature 50–300°C) and on a GC-9A instrument (Shimadzu) (quartz capillary column, 25 m long with stationary phase OV-101, operating temperature 80–280°C) with He carrier gas. Optical rotation was measured on a PerkinElmer 241-MC polarimeter. Melting points were determined on a Kofler apparatus, modification S 30A/G. Column chromatography was carried out over silica gel L (60–200 μm) (Sorbfil, Russia). Sorbfil plates (Russia) were used for TLC.

Mass spectra were measured on a LC MS 2010 EV instrument (Shimadzu) (syringe injection, sample solution in MeCN at flow rate 60 μL/min) using electrospray ionization (ESI) with simultaneous recording of positive and negative ions at capillary potentials 4.5 and 3.5 kV, respectively; capillary interface temperature 230°C; and nebulizer gas (dry N_2) flow rate 1.5 L/min; and on a MAT95XP high-resolution spectrometer (Thermo Finnigan) with the Xcalibur data processing system (chromatographic sample injection, HP-5MS column, 25 m long) by electron impact (ionizing electron energy 70 eV, ionizing chamber temperature 250°C). Chromatography used petroleum ether (PE) with bp 40–70°C. Solvents were dried by standard methods. Elemental analyses of newly synthesized compounds agreed with those calculated.

Procedure for Reaction of (*R*)-4-Menthen-3-one (1) with $HS(CH_2)_2SH$. A mixture of **1** (1.00 g, 6.6 mmol), $HS(CH_2)_2SH$ (1.20 g, 12.8 mmol), *p*-TsOH (0.05 g), and PhH (60 mL) was refluxed with a Dean-Stark trap for 24 h [additional *p*-TsOH (0.10 g) was added 12 h of refluxing]; cooled to room temperature; diluted with hexane (80 mL); washed sequentially with NaOH solution (5%, 3 × 10 mL), H_2O (3 × 10 mL), and saturated NaCl solution (2 × 10 mL); dried over Na_2SO_4, and evaporated. The residue (1.20 g) was purified by column chromatography (SiO_2, PE) to afford (6*S*,9*R*)-6-(1-methylethyl)-9-methyl-1,4-dithiaspiro[4,5]decane (**7**, 1.12 g, 76%), R_f 0.77 (PE–EtOAc 2:1). $[\alpha]_D^{20}$ –13.0° (*c* 1.01; EtOH), lit. $[\alpha]_D^{21}$ –13.4° (*c* 0.97; EtOH) [17]. IR spectrum (KBr, ν, cm^{-1}): 758 (C–S–C). PMR spectra were identical to those described before [17]. ^{13}C NMR spectrum (125.20 MHz, $CDCl_3$, δ, ppm): 18.35 (q, C-3″), 21.79 (q, CH_3-9), 24.21 (q, C-2″), 27.73 (d, C-9, C-1″), 32.22 (d, C-7), 38.57 (t, C-8), 39.11 (t, C-2, C-3), 51.92 (d, C-6), 55.77 (t, C-10), 74.92 (s, C-5).

Procedure for Thiylation of (1*R*,4*R*,6*R*)-4-Methyl-1-(1-methylethyl)-7-oxabicyclo[4.1.0]heptan-2-one (2). Sodium thiolate prepared from Na (0.18 g, 7.8 mg-at) and the appropriate thiol (7.8 mmol) [*n*-$C_{12}H_{25}SH$ or $HS(CH_2)_2SH$ or $HSCH_2CO_2H$] was treated with **2** (1.00 g, 6.0 mmol) in anhydrous EtOH (40 mL), stirred and refluxed for 5 h, cooled to 20°C, diluted with H_2O (25 mL), and extracted with Et_2O (3 × 30 mL). Then, the combined organic extract was washed with saturated NH_4Cl solution (3 × 20 mL), dried over Na_2SO_4, and evaporated. The residue (1.20 g) was purified by column chromatography (SiO_2, PE:EtOAc, 20:1) to afford **1** (0.75 g, 89%), bp 86–88°C (12 mm Hg), $[\alpha]_D^{20}$ –67.1° (*c* 4.95; $CHCl_3$), lit. $[\alpha]_D^{20}$ –67.5° (*c* 5.3; $CHCl_3$) [22]. IR spectrum (KBr, ν, cm^{-1}): 1672 (C=C–C=O). PMR and ^{13}C NMR spectral data were identical to those described before [22].

Procedure for Thiylation of (1*R*,5*R*)-5-Methyl-2-(1-methylethyl)cyclohex-2-en-1-ol (3). A solution of **3** (2.0 mmol) in anhydrous CH_2Cl_2 (10 mL) was stirred at room temperature, treated sequentially with the appropriate thiol (2.5 mmol) [PhSH or *n*-$C_6H_{13}SH$ or *n*-$C_{12}H_{25}SH$ or *n*-$C_{16}H_{33}SH$ or $HSCH_2CO_2H$ or $HS(CH_2)_2SH$] in anhydrous CH_2Cl_2 (10 mL) and $ZnCl_2$ (0.03 g, 0.2 mmol), stirred for 8 h, diluted with H_2O (20 mL), and extracted with CH_2Cl_2 (3 × 30 mL). The extract was dried over $MgSO_4$ and evaporated. Then, the products were isolated by column chromatography (SiO_2, PE).

{[(1*S*,5*R*)-5-Methyl-2-(1-methylethyl)cyclohex-2-en-1-yl]thio}benzene (15). Yield 0.29 g (62%) of **15**. R_f 0.74 (PE–EtOAc 2:1), $[\alpha]_D^{20}$ +1.8° (*c* 0.35; CH_2Cl_2). IR spectrum (KBr, ν, cm^{-1}): 736 (C–S–C), 810 (C–S), 1583 (Ar), 1653 (C=C). Mass spectrum (ESI), *m/z* ($I_{rel.}$, %), MeCN–H_2O 95:5, $(Scan)^+$: 247.0 ($[M + H]^+$, 2.6), 137.0 ($[M – SPh]^+$, 100). ^1H NMR spectrum (500.13 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.88 (3H, d, J = 6.8, H-3″), 0.98 (3H, d, J = 6.7, CH_3-5′), 1.03 (3H, d, J = 6.8, H-2″), 1,38 (1H, ddd, ^2J = 13.1, ^3J = 6.3, ^3J = 11.4, H_a-6′), 1.84 (1H, ddd, ^2J = 10.4, ^3J = 2.7, ^3J = 2.0, H_a-4′), 2.00–2.18 (1H, m, H_e-4′, H-5′), 2.10–2.14 (1H, m, H_e-6′), 2.51 (1H, sept, J = 6.8, H-1″), 3.73 (1H, dd, ^2J = 5.6, ^3J = 6.3, H_e-1′), 5.56 (1H, dd, ^2J = 2.7, ^3J = 4.8, H-3′), 7.13 (1H, t, J = 7.8, H-4), 7.22 (2H, d, J = 7.3, H-2, H-6), 7.32 (2H, t, J = 7.1, H-3, H-5). ^{13}C NMR spectrum (125.20 MHz, $CDCl_3$, δ, ppm): 21.63 (q, C-3″), 21.75 (q, C-2″), 23.53 (q, CH_3-5′), 29.69 (d, C-5′), 31.79 (d, C-1″), 34.03 (t, C-6′), 37.69 (t, C-4′), 48.75 (d, C-1′), 122.94 (d, C-3′), 126.25 (d, C-4), 128.87 (d, C-3, C-5), 130.61 (d, C-2, C-6), 137.56 (s, C-1), 142.29 (s, C-2′).

(4*R*,6*S*)-6-(Hexylthio)-4-methyl-1-(1-methylethyl)cyclohexene (16). Yield 0.39 g (80%) of **16**. R_f 0.77 (PE–EtOAc 2:1), $[\alpha]_D^{20}$ +2.3° (*c* 1.01; CH_2Cl_2). IR spectrum (KBr, ν, cm^{-1}): 725 (C–S–C), 810 (C–S), 1635 (C=C). Mass spectrum (ESI), *m/z* ($I_{rel.}$, %), MeCN–H_2O 95:5, $(Scan^+)$: 255.0 ($[M + H]^+$, 25.8), 169.0 ($[M – C_6H_{13}]^+$, 3.1), 137.0 ($[M – SC_6H_{13}]^+$, 100). ^1H NMR spectrum (500.13 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.82 (3H, d, J = 6.8, H-3″), 0.91 (3H, d, J = 6.8, H-2″), 0.96 (3H, t, J = 6.7, H-6′), 0.98 (3H, d, J = 6.7, CH_3-4), 1.25–1.35 (2H, m, H-4′), 1.35–1.48 (1H, m, H_a-3), 1.52–1.73 (6H, m, H-2′, H-3′, H-5′), 1.90–2.05 (1H, m, H-4), 1.91 (1H, ddd, ^2J = 12.8, ^3J = 1.4, ^3J = 1.4, H_a-5), 2.30–2.45 (1H, m, H-1″), 2.30–2.50 (1H, m, H_e-3), 2.40–2.62 (1H, m, H_e-5), 2.42–2.63 (2H, m, H-1′), 3.26 (1H, dd, ^2J = 7.9, ^3J = 4.2, H_e-6), 5.50 (1H, d, J = 2.6, H-2). ^{13}C NMR spectrum (125.20 MHz, $CDCl_3$, δ, ppm): 13.92 (q, C-6′), 20.74 (q, C-2″), 21.77 (t, C-5′), 22.95 (q, CH_3-4), 23.51 (q, C-3″), 28.79 (t, C-3′), 29.49 (d, C-1′), 29.60 (t, C-4′), 29.71 (d, C-4), 29.94 (t, C-2′), 32.60 (t, C-1′), 34.06 (t, C-5), 41.12 (t, C-3), 45.08 (d, C-6), 121.92 (d, C-2), 143.12 (s, C-1).

(4*R*,6*S*)-6-(Dodecylthio)-4-methyl-1-(1-methylethyl)cyclohexene (17). Yield 0.85 g (64%) of **17**. R_f 0.65 (hexane–EtOAc 2:1), $[\alpha]_D^{20}$ +1.1° (*c* 0.56; $CHCl_3$). IR spectrum (KBr, ν, cm^{-1}): 721 (C–S–C), 810 (C–S), 1658 (C=C). Mass spectrum (ESI), *m/z* ($I_{rel.}$, %), MeCN–H_2O 95:5, ($Scan^+$): 339.0 ($[M + H]^+$, 1.5), 137.0 ($[M - SC_{12}H_{25}]^+$, 100]. ^1H NMR spectrum (500.13 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.88 (3H, t, J = 6.4, H-12′), 0.97 (3H, d, J = 6.7, CH_3-4), 1.00 (3H, d, J = 6.8, H-3″), 1.07 (3H, d, J = 6.8, H-2″), 1.22–1.30 (12H, m, H-4′, H-5′, H-6′, H-7′, H-8′, H-9′), 1.32–1.65 (10H, m, H-1′, H-2′, H-3′, H-10′, H-11′), 1.88 (1H, dd, ^2J = 12.1, ^3J = 3.4, H_a-3), 1.98–2.10 (1H, m, H_e-3), 2.12–2.18 (2H, m, H_a-5, H-4), 2.30–2.43 (1H, m, H_e-5), 2.48 (1H, sept, J = 6.6, H-1″), 3.29 (1H, dd, ^2J = 6.4, ^3J = 5.2, H_e-6), 5.50 (1H, dd, ^2J = 4.9, ^3J = 2.2, H-2). ^{13}C NMR spectrum (125.20 MHz, $CDCl_3$, δ, ppm): 14.12 (q, C-12′), 21.51 (q, C-3″), 21.85 (q, C-2″), 22.69 (t, C-11′), 23.62 (q, CH_3-4), 28.77 (t, C-3′), 29.01 (t, C-9′), 29.54 (t, C-4′, C-5′, C-6′, C-7′, C-8′), 29.82 (d, C-4), 30.06 (t, C-2′), 31.50 (d, C-1″), 31.92 (t, C-10′), 32.70 (t, C-1′), 34.13 (t, C-5), 38.27 (t, C-3), 45.12 (d, C-6), 121.43 (d, C-2), 143.23 (s, C-1).

(4*R*,6*S*)-6-(Hexadecylthio)-4-methyl-1-(1-methylethyl)cyclohexene (18). Yield 0.58 g (76%) of **18**. R_f 0.85 (PE–EtOAc 2:1), $[\alpha]_D^{20}$ +1.0° (*c* 1.12; CH_2Cl_2). IR spectrum (KBr, ν, cm^{-1}): 719 (C–S–C), 810 (C–S), 1664 (C=C). Mass spectrum (ESI), *m/z* ($I_{rel.}$, %), MeCN–H_2O 95:5, ($Scan^+$): 395.0 ($[M + H]^+$, 1.6), 137.0 ($[M - SC_{16}H_{33}]^+$, 100). ^1H NMR spectrum (500.13 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.88 (3H, t, J = 6.7, H-16′), 0.97 (3H, d, J = 6.7, CH_3-4), 1.01 (3H, d, J = 6.8, H-3″), 1.06 (3H, d, J = 6.8, H-2″), 1.24–1.33 (16H, m, H-5′, H-6′, H-7′, H-8′, H-9′, H-10′, H-11′, H-12′), 1.26–1.35 (2H, m, H-15′), 1.35–1.42 (6H, m, H-4′, H-13′, H-14′), 1.45–1.68 (6H, m, H-1′, H-2′, H-3′), 1.90 (1H, ddd, ^2J = 11.0, ^3J = 3.2, ^3J = 2.1, H_a-3), 2.12–2.18 (1H, m, H_a-5), 2.18–2.20 (3H, m, H-4, H_e-5, H_e-3), 2.47–2.58 (1H, m, H-1″), 3.28 (1H, dd, ^2J = 6.8, ^3J = 5.4, H_e-6), 5.52 (1H, dd, ^2J = 2.7, ^3J = 5.6, H-2). ^{13}C NMR spectrum (125.20 MHz, $CDCl_3$, δ, ppm): 14.09 (q, C-16′), 21.49 (q, C-3″), 21.84 (q, C-2″), 22.67 (t, C-15′), 23.59 (q, CH_3-4), 28.71 (t, C-13′), 28.81 (t, C-3′), 29.20 (t, C-11′), 29.36 (t, C-12′), 29.68 (t, C-4′, C-5′, C-6′, C-7′, C-8′, C-9, C-10′), 29.91 (d, C-4), 30.04 (t, C-2′), 31.46 (t, C-14′), 31.46 (d, C-1″), 32.67 (t, C-1′), 33.97 (t, C-5), 38.21 (t, C-3), 45.12 (d, C-6), 121.37 (d, C-2), 143.18 (s, C-1).

2-{[(1*S*,5*R*)-5-Methyl-2-(1-methylethyl)cyclohex-2-en-1-yl]thio}ethanethiol (19). Yield 0.90 g (76%) of **19**. R_f 0.45 (PE–EtOAc 2:1), $[\alpha]_D^{20}$ –1.2° (*c* 5.4; $CHCl_3$). IR spectrum (KBr, ν, cm^{-1}): 810 (C–S), 1615 (C=C), 2528 (S–H). Mass spectrum (ESI), *m/z* ($I_{rel.}$, %), MeCN–H_2O 95:5, ($Scan^+$): 137.0 ($[M - S(CH_2)_2SH]^+$, 100). ^1H NMR spectrum (500.13 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.89 (3H, d, J = 6.7, CH_3-5′), 1.04 (3H, d, J = 6.9, H-3″), 1.13 (3H, d, J = 6.9, H-2″), 1.48 (1H, dd, ^2J = 12.9, ^3J = 2.0, H_a-6′), 1.55 (1H, s, SH), 1.59 (1H, ddd, ^2J = 17.7, ^3J = 11.0, ^3J = 3.1, H_a-4′), 1.89 (1H, dd, ^2J = 12.9, ^3J = 4.2, H_e-6′), 2.13 (1H, dd, ^2J = 17.7, ^3J = 4.9, H_e-4′), 2.43 (1H, sept, J = 6.9, H-1″), 2.67–2.82 (4H, m, H-1, H-2), 3.31 (1H, dd, ^2J = 4.2, ^3J = 2.0, H_e-1′), 5.50 (1H, dd, ^2J = 4.9, ^3J = 3.1, H-3′). ^{13}C NMR spectrum (125.20 MHz, $CDCl_3$, δ, ppm): 21.41 (q, C-3″), 21.91 (q, C-2″), 23.49 (d, C-5′), 23.58 (q, CH_3-5′), 25.20 (q, C-1), 31.59 (d, C-1″), 34.04 (t, C-6′), 38.55 (t, C-4′), 38.64 (t, C-2), 45.49 (d, C-1′), 121.87 (d, C-3′), 142.98 (s, C-2′).

{[(1*S*,5*R*)-5-Methyl-2-(1-methylethyl)cyclohex-2-en-1-yl]thio}acetic Acid (20). Yield 0.38 g (43%) of **20**. R_f 0.54 (PE–EtOAc 2:1), $[\alpha]_D^{20}$ –1.3° (*c* 2.73; $CHCl_3$). IR spectrum (KBr, ν, cm^{-1}): 810 (C–S), 1618 (C=C), 3750–3320 (CO_2H). Mass spectrum (ESI), *m/z* ($I_{rel.}$, %), MeCN–H_2O 95:5, ($Scan^-$): 227.0 ($[M - H]^-$, 100); ($Scan^+$):137.0 ($[M - SCH_2CO_2H]^+$, 100). ^1H NMR spectrum (500.13 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.93 (3H, d, J = 6.7, CH_3-5′), 0.98 (3H, d, J = 6.7, H-3″), 1.12 (3H, d, J = 6.7, H-2″), 1.47 (1H, ddd, ^2J = 13.3, ^3J = 13.2, ^3J = 3.5, H_a-6′), 1.58 (1H, dd, ^2J = 17.7, ^3J = 10.5, H_a-4′), 1.89 (1H, dd, ^2J = 13.3, ^3J = 1.4, H_e-6′), 1.98–2.08 (1H, m, H-5′), 2.12 (1H, dd, ^2J = 17.7, ^3J = 5.4, H_e-4′), 2.42 (1H, sept, J = 6.7, H-1″), 3.19 (1H, d, J = 14.7, H-2), 3.32 (1H, d, J = 14.7, H-2), 3.54 (1H, dd, ^2J = 3.5, ^3J = 1.4, H_e-1′), 5.89 (1H, dd, ^2J = 5.4, ^3J = 3.5, H-3′), 11.2 (1H, br. s, H-1). ^{13}C NMR spectrum (125.20 MHz, $CDCl_3$, δ, ppm): 21.34 (q, C-2″), 21.67 (q, C-3″), 23.35 (d, C-5′), 23.51 (q, CH_3-5′), 31.36 (d, C-1″), 33.91 (t, C-2, C-6′), 37.22 (t, C-4′), 45.12 (d, C-1′), 122.97 (d, C-3′), 141.98 (s, C-2′), 177.33 (s, C-1).

Procedure for Thiylation of Products of 1,2-Addition of Organolithium Reagents to (*R*)-4-Menthen-3-one (1). A suspension of MeLi or EtLi prepared from Li (0.31 g, 44.3 mmol) and alkylhalide (44.3 mmol) (MeI or EtBr) in anhydrous Et_2O (30 mL) (–78°C, Ar) was treated dropwise with **1** (0.50 g, 3.3 mmol) in anhydrous Et_2O (20 mL) (–78°C, Ar), stirred for 6 h (–78°C, Ar), treated with saturated NH_4Cl solution (10 mL) over 1 h, adjusted to room temperature, and extracted with Et_2O (3 × 50 mL). The combined organic extract was washed with saturated NaCl solution (3 × 5 mL) until the pH was 7, dried over Na_2SO_4, and evaporated. The resulting tertiary allyl alcohols (**5** and **6**) were used without further purification in the next step. For this, the residues (0.54 g of **5** or 0.60 g of **6**) after evaporation were dissolved in anhydrous CH_2Cl_2 (10 mL), treated sequentially at room temperature with stirring with the appropriate thiol (2.5 mmol) [PhSh or *n*-$C_{12}H_{25}SH$ or $HS(CH_2)_2SH$] in anhydrous CH_2Cl_2 (10 mL) and $ZnCl_2$ (0.03 g, 0.2 mmol), stirred for 8 h, diluted with H_2O (20 mL), and extracted with CH_2Cl_2 (3 × 30 mL). The extract was dried over $MgSO_4$ and evaporated. Then, products were isolated by column chromatography (SiO_2, PE).

(1*R*,5*S*)-3,5-Dimethyl-2-(1-methylethyl)cyclohex-2-en-1-yl Dodecyl Sulfide (23). Yield 0.40 g (57%) of **23** per enone **1**. R_f 0.75 (PE–EtOAc 2:1), $[\alpha]_D^{20}$ +17.6° (*c* 3.34; $CHCl_3$). IR spectrum (KBr, ν, cm^{-1}): 721 (C–S–C), 806 (C–S), 1631 (C=C). Mass spectrum (ESI), *m/z* ($I_{rel.}$, %), MeCN–H_2O 95:5, ($Scan^-$): 351.0 ($[M - H]^+$, 26.25); ($Scan^+$): 201.0 ($[([M + H]^+ - C_{11}H_{20}]^+$, 6.6). ^1H NMR spectrum (500.13 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.93 (3H, t, J = 6.5, H-12′), 1.06 (3H, d, J = 6.7, CH_3-5), 1.18–1.60 (20H, m, H-2′, H-3′, H-4′, H-5′, H-6′, H-7′, H-8′, H-9′, H-10′, H-11′), 1.19 (3H, d, J = 6.7, H-3″), 1.23 (3H, d, J = 6.7, H-2″), 1.62–1.80 (2H, m, H_a-4, H_a-6), 1.72 (3H, s, CH_3-3), 1.89 (1H, dd, ^2J = 13.2, ^3J = 4.7, H_e-6), 2.10–2.40 (1H, m, H-5), 2.16 (1H, dd, ^2J = 17.4, ^3J = 5.6, H_e-4), 2.57–2.70 (1H, m, H-3″), 2.78–2.83 (2H, m, H-1′), 3.41 (1H, dd, ^2J = 4.2, ^3J = 1.6, H_e-1). ^{13}C NMR spectrum (125.20 MHz, $CDCl_3$, δ, ppm): 14.04 (q, C-12′), 19.33 (q, CH_3-3), 20.35 (q, C-3″), 21.87 (q, C-2″), 22.64 (q, CH_3-5), 22.64 (t, C-11′), 23.62 (d, C-5), 28.49 (t, C-2′), 29.06–29.76 (t, C-3′, C-4′, C-5′, C-6′, C-7′, C-8′, C-9′), 30.68 (d, C-1″), 31.88 (t, C-10′), 32.51 (t, C-1′), 37.66 (t, C-6), 39.09 (t, C-4), 44.36 (d, C-1), 130.17 (s, C-3), 134.00 (s, C-2).

2-{[**(1*R*,5*S*)-3,5-Dimethyl-2-(1-methylethyl)cyclohex-2-en-1-yl]thio}ethanethiol (24).** Yield 0.60 g (56%) of **24** per enone **1**. R_f 0.63 (PE–EtOAc 2:1), $[\alpha]_D^{20}$ +6.0° (*c* 0.63; $CHCl_3$). IR spectrum (KBr, ν, cm^{-1}): 739 (C–S–C), 1634 (C=C), 2566 (S–H). ^1H NMR spectrum (500.13 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.88 (3H, d, J = 6.6, CH_3-5′), 1.01 (3H, d, J = 6.4, H-2″), 1.03 (3H, d, J = 6.4, H-3″), 1.60–1.78 (2H, m, H_a-6′, H_a-4′), 1.70 (1H, dd, ^2J = 12.7, ^3J = 4.0, H_e-6′), 1.60 (3H, s, CH_3-3′), 1.82 (1H, s, SH), 1.95 (1H, dd, ^2J = 15.4, ^3J = 5.3, H_e-4′), 2.09–2.20 (1H, m, H-3″, H-5′), 2.54–2.78 (4H, m, H-1, H-2), 3.29 (1H, dd, ^2J = 4.1, ^3J = 1.2, H_e-1′). ^{13}C NMR spectrum (125.20 MHz, $CDCl_3$, δ, ppm): 19.60 (q, CH_3-3′), 20.55 (q, C-3″), 21.90 (q, CH_3-5′), 22.64 (q, C-2″), 23.64 (d, C-1″), 24.99 (t, C-1), 30.79 (d, C-5′), 36.71 (t, C-2), 37.93 (t, C-6′), 41.55 (t, C-4′), 44.75 (d, C-1′), 131.14 (s, C-3′), 133.54 (s, C-2′).

{[**(1*R*,5*S*)-3-Ethyl-5-methyl-2-(1-methylethyl)cyclohex-2-en-1-yl]thio}benzene (25).** Yield 0.60 g (51%) of **25** per enone **1**. R_f 0.73 (PE–EtOAc 2:1), $[\alpha]_D^{20}$ –1.7° (*c* 4.0; $CHCl_3$). IR spectrum (KBr, ν, cm^{-1}): 741 (C–S–C), 1582 (Ar), 1654 (C=C). Mass spectrum (ESI), *m/z* ($I_{rel.}$, %), MeCN–H_2O 95:5, ($Scan^+$): 166.0 ($[M + H]^+ - SPh]^+$, 15.11). ^1H NMR spectrum (500.13 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.96 (3H, d, J = 6.6, CH_3-5′), 1.04 (3H, t, J = 6.8, $C\underline{H}_3CH_2$-3′), 1.14 (3H, d, J = 6.8, H-2″), 1.27 (3H, d, J = 6.8, H-3″), 1.53 (1H, dd, ^2J = 13.2, ^3J = 4.2, H_a-4′), 1.63 (1H, dd, ^2J = 17.6, ^3J = 10.4, H_a-6′), 1.82 (1H, dd, ^2J = 13.2, ^3J = 1.4, H_e-4′), 2.12 (2H, q, J = 6.8, $CH_3C\underline{H}_2$-3′), 2.18 (1H, dd, ^2J = 17.6, ^3J = 6.0, H_e-6′), 2.20–2.36 (1H, m, H-5′), 2.83 (1H, sept, J = 6.8, H-1″), 3.88 (1H, dd, ^2J = 4.2, ^3J = 1.5, H_e-1′), 7.21 (1H, t, J = 7.7, H-4), 7.30 (2H, t, J = 7.6, H-3, H-5), 7.51 (2H, d, J = 7.6, H-2, H-6). ^{13}C NMR spectrum (125.20 MHz, $CDCl_3$, δ, ppm): 13.28 (q, $\underline{C}H_3CH_2$-3), 21.25 (q, C-3″), 22.03 (q, C-2″), 23.41 (q, CH_3-5′), 23.77 (d, C-5′), 26.43 (t, $CH_3\underline{C}H_2$-3), 30.51 (d, C-1″), 37.55 (t, C-4′), 38.47 (t, C-6′), 47.43 (d, C-3′), 126.09 (d, C-4), 127.53 (d, C-3, C-5), 129.12 (d, C-2, C-6), 132.74 (s, C-1′), 137.08 (s, C-1), 137.80 (s, C-2′).

Procedure for Thiylation of Ethyl [(1*R*,5*R*)-5-methyl-2-(1-methylethyl)cyclohex-2-en-1-yl]acetate (4). A solution of **4** (0.40 g, 1.8 mmol) in anhydrous CH_2Cl_2 (5 mL) was stirred at room temperature, treated sequentially with PhSH (0.20 g, 1.8 mmol) in anhydrous CH_2Cl_2 (10 mL) and $ZnCl_2$ (0.03 g, 0.2 mmol), stirred for 10 h, diluted with H_2O (25 mL), and extracted with CH_2Cl_2 (3 × 40 mL). The extract was dried over Na_2SO_4 and evaporated to afford **15** (0.42 g, 95%). R_f 0.74 (PE:EtOAc, 2:1), $[\alpha]_D^{20}$ +1.7° (*c* 2.2, CH_2Cl_2). PMR and ^{13}C NMR spectra were identical to those for **15** prepared from (1*R*,3*R*)-menthen-3-ol (**3**).

Procedure for Oxidation of Sulfides 15, 16, and 18. *a*. Sulfides (0.50 mmol) (**15** or **16** or **18**) dissolved in glacial AcOH (3 mL) were treated dropwise at 0°C with H_2O_2 solution (0.12 mL, 30%, 1.00 mmol), heated to room temperature, stirred for 4 h, diluted with H_2O (25 mL), and extracted with EtOAc (3 × 15 mL). The combined organic extract was washed sequentially with saturated solutions of $NaHCO_3$ (2 × 3 mL) and NaCl (2 × 3 mL), dried over Na_2SO_4, and evaporated.

b. Sulfide **16** (0.12 g, 0.46 mmol) was dissolved in CH_2Cl_2 (3 mL), treated dropwise at 0°C with *m*-CPBA (0.21 g, 0.92 mmol, 75% solution) in CH_2Cl_2 (2 mL), heated to room temperature, stirred for 8 h, diluted with H_2O (30 mL), and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extract was washed sequentially with saturated solutions of $NaHCO_3$ (3 × 5 mL) and NaCl (2 × 3 mL), dried over Na_2SO_4, and evaporated.

{[(1*S*,5*R*)-5-Methyl-2-(1-methylethyl)cyclohex-2-en-1-yl]sulfanyl}benzene (26). Yield 0.19 g (88%) of **26** (by method *a*) and 0.10 g (87%) (by method *b*). R_f 0.47 (PE–EtOAc 2:1), $[\alpha]_D^{20}$ +31.0° (*c* 0.28; CH_2Cl_2). IR spectrum (KBr, ν, cm^{-1}): 1076 (SO), 1584 (Ar), 1635 (C=C). Mass spectrum (EI, 70 eV), *m/z* ($I_{rel.}$, %): 77.0 ($[M^+ - C_{10}H_{17}SO]^+$, 39.3), 125.0 ($[M^+ - C_{10}H_{17}]^+$, 11.4), 137.1 ($[M^+ - SOPh]^+$, 100.0), 186.0 ($[M + H]^+ - Ph]^+$, 1.4). ^1H NMR spectrum (500.13 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.83 (3H, d, J = 6.7, CH_3-5′), 0.97 (3H, d, J = 6.8, H-2″), 1.10 (3H, d, J = 6.8, H-3″), 1.18 (1H, ddd, ^2J = 14.4, ^3J = 5.6, ^3J = 14.2, H_a-6′), 1.55 (1H, d, ^2J = 18.4, ^3J = 3.1, H_a-4′), 1.98 (1H, ddd, ^2J = 14.4, ^3J = 1.6, ^3J = 3.2, H_e-6′), 2.05–2.11 (1H, m, H-5′), 2.23 (1H, ddd, ^2J = 18.4, ^3J = 4.7, ^3J = 2.0, H_e-4′), 2.64 (1H, sept, J = 6.8, H-1″), 3.84 (1H, dd,

^{2}J = 5.5, ^{3}J = 1.6, H_e-1′), 5.88 (1H, dd, ^{2}J = 4.7, ^{3}J = 3.1, H-3′), 7.41 (1H, t, J = 7.4, H-4), 7.56 (2H, t, J = 7.4, H-3, H-5), 7.86 (2H, d, J = 7.3, H-2, H-6). ^{13}C NMR spectrum (125.20 MHz, $CDCl_3$, δ, ppm): 20.86 (q, C-3′′), 21.87 (q, C-2′′, CH_3-5′), 22.48 (d, C-5′), 32.15 (d, C-1′′), 32.71 (t, C-6′), 33.53 (t, C-4′), 64.66 (d, C-1′), 128.43 (d, C-2, C-6), 128.59 (d, C-3′), 129.33 (d, C-3, C-5), 131.35 (d, C-4), 133.34 (s, C-1), 135.41 (s, C-2′).

(4*R*,6*S*)-6-(Hexylsulfanyl)-4-methyl-1-(1-methylethyl)cyclohexene (27). Yield 0.11 g (97%) of **27** by method *a*. R_f 0.57 (PE–EtOAc 2:1), $[\alpha]_D^{20}$ –1.0° (*c* 0.47; CH_2Cl_2). IR spectrum (KBr, ν, cm^{-1}): 1119 (SO), 1655 (C=C). Mass spectrum (EI, 70 eV), *m/z* ($I_{rel.}$, %): 137.1 ($[M^+ – SOC_6H_{13}]^+$, 100.0), 269.1 ($[M – H]^–$, 3.1). ^{1}H NMR spectrum (500.13 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.88 (3H, t, J = 6.9, H-6′), 0.97 (3H, d, J = 6.5, CH_3-4), 1.01 (3H, d, J = 6.7, H-3′′), 1.12 (3H, d, J = 6.7, H-2′′), 1.27–1.36 (4H, m, H-4′, H-5′), 1.36–1.47 (2H, m, H-3′), 1.38–1.46 (1H, m, H_a-5), 1.66 (1H, dd, ^{2}J = 10.9, ^{3}J = 7.8, H_a-3), 1.82–1.90 (2H, m, H-2′), 2.03–2.13 (1H, m, H-4), 2.31 (1H, d, J = 10.9, H_e-3), 2.34 (1H, d, J = 11.9, H_e-5), 2.67 (1H, sept, J = 6.7, H-1′′), 2.88 (1H, dd, ^{2}J = 13.5, ^{3}J = 7.5, H-1′), 2.93 (1H, dd, ^{2}J = 13.5, ^{3}J = 8.8, H-1′), 3.72 (1H, d, J = 5.1, H_e-6), 5.88 (1H, dd, ^{2}J = 3.7, ^{3}J = 3.8, H-2). ^{13}C NMR spectrum (125.20 MHz, $CDCl_3$, δ, ppm): 13.92 (q, C-6′), 20.86 (q, C-3′′), 21.26 (t, C-2′), 21.92 (t, C-5′), 21.93 (q, C-2′′), 23.18 (d, C-4), 23.45 (q, CH_3-4), 28.36 (t, C-3′), 31.29 (t, C-4′), 31.98 (d, C-1′′), 32.80 (t, C-5), 33.60 (t, C-3), 52.46 (t, C-1′), 63.35 (d, C-6), 127.39 (d, C-2), 135.91 (s, C-1).

(4*R*,6*S*)-6-(Hexadecylsulfanyl)-4-methyl-1-(1-methylethyl)cyclohexene (28). Yield 0.17 g (85%) of **28** by method *a*. R_f 0.77 (PE–EtOAc 2:1), mp 60–62° (from hexane), $[\alpha]_D^{20}$ –2.5° (*c* 0.89; CH_2Cl_2). IR spectrum (KBr, ν, cm^{-1}): 1118 (SO), 1652 (C=C). Mass spectrum (EI, 70 eV, *m/z* ($I_{rel.}$, %): 137.1 ($[M^+ – SOC_{16}H_{33}]^+$, 100.0). ^{1}H NMR spectrum (500.13 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.80 (3H, m, J = 6.1, H-16′), 0.95 (3H, d, J = 6.8, H-3′′), 0.97 (3H, d, J = 6.7, CH_3-4), 1.07 (3H, d, J = 6.8, H-2′′), 1.12–1.30 (24H, m, H-3′, H-4′, H-5′, H-6′, H-7′, H-8′, H-9′, H-10′, H-11′, H-12′, H-13′, H-14′), 1.33–1.45 (4H, m, H-2′, H-15′), 1.68 (1H, ddd, ^{2}J = 16.4, ^{3}J = 10.2, ^{3}J = 2.6, H_a-3), 1.91–2.08 (1H, m, H-4), 2.20–2.32 (1H, m, H_a-5), 2.21–2.32 (1H, m, H_e-3), 2.61 (1H, sept, J = 6.8, H-1′′), 2.71–2.92 (3H, m, H_e-5, H-1′), 3.63 (1H, d, J = 5.0, H_e-6), 5.81 (1H, dd, ^{2}J = 5.3, ^{3}J = 2.6, H-2). ^{13}C NMR spectrum (125.20 MHz, $CDCl_3$, δ, ppm): 14.10 (q, C-16′), 20.86 (q, C-3′′), 21.91 (q, C-2′′), 22.66 (t, C-15′), 23.44 (q, CH_3-4), 28.66 (t, C-3′), 28.94 (d, C-4), 29.12 (t, C-2′), 29.25 (t, C-12′), 29.34 (t, C-13′), 29.66 (t, C-4′, C-5′, C-6′, C-7′, C-8′, C-9′, C-10′, C-11′), 31.90 (t, C-14′), 31.97 (d, C-1′′), 32.79 (t, C-5), 33.42 (t, C-3), 52.47 (t, C-1), 63.34 (d, C-6), 127.35 (d, C-2), 135.92 (s, C-1).

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