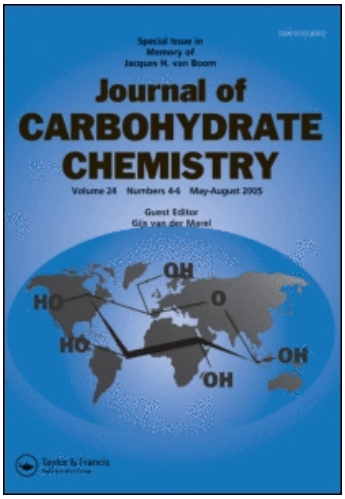

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SYNTHESIS OF ANELLATED ANHYDROPYRANOSES ON THE BASIS OF 1,6-ANHYDRO-3-DEOXY-4-METHYLSULFANYL-3-[(METHYLSULFANYL)METHYLENE]-β-D-*ERYTHRO*-HEXOPYRANOS-2-ULOSE

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SYNTHESIS OF ANELLATED ANHYDROPYRANOSES ON THE BASIS OF 1,6-ANHYDRO-3-DEOXY-4-METHYLSULFANYL-3-[(METHYLSULFANYL)METHYLENE]-β-D-*ERYTHRO*-HEXOPYRANOS-2-ULOSE

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Dedicated to Professor Dr. Peter Köll on the occasion of his 60th birthday.

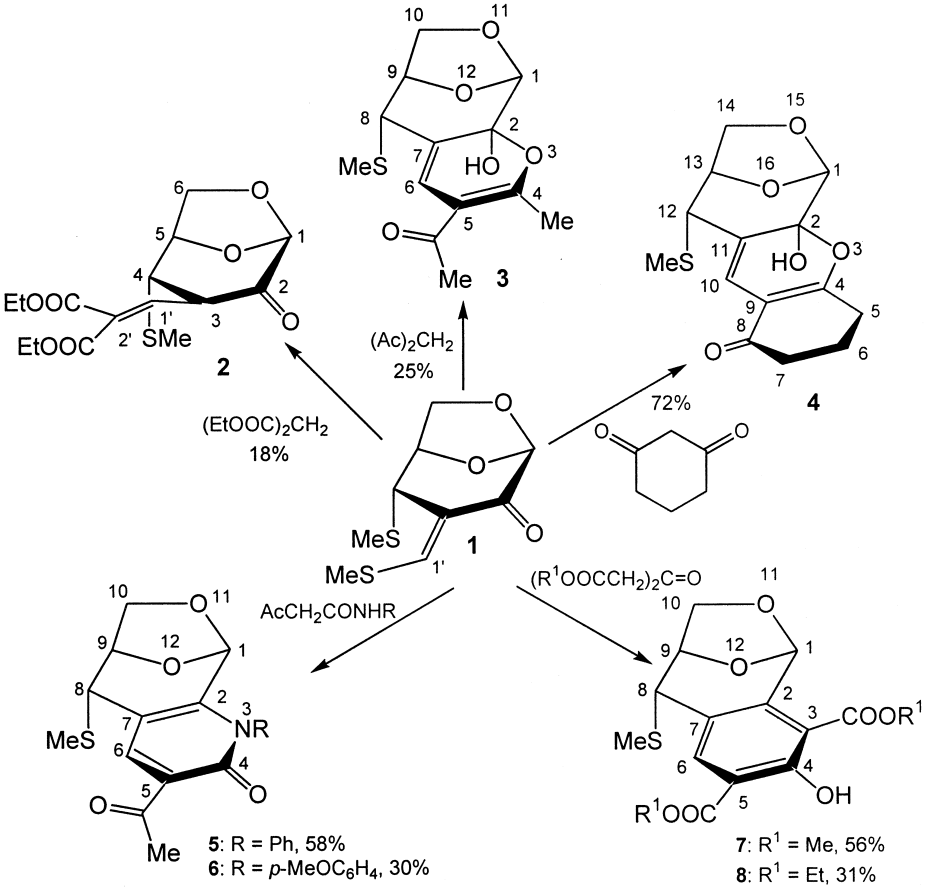
ABSTRACT

(*Z*)-1,6-Anhydro-3-deoxy-4-methylsulfanyl-3-[(methylsulfanyl)methylene]-β-D-*erythro*-hexopyranos-2-ulose (**1**) reacted with diethyl malonate, 1,3-diketones, *N*-aryl-3-oxobutyramides and dialkyl 3-oxoglutarate, respectively, in the presence of potassium carbonate and crown ether to yield diethyl 2-(1,6-anhydro-4-methylsulfanyl—D-*arabino*-hex-2-ulopyranos-3-ylmethylene) malonate (**2**), 1-{(1*R*,2*S*,8*S*,9*R*)-2-hydroxy-4-methyl-8-methylthio-3,11,12-trioxatricyclo7.2.1.$0^{2,7}$dodeca-4,6-dien-5-yl}ethanone (**3**), (1*R*,2*S*,12*S*,13*R*)-2-hydroxy-12-methylthio-3,15,16-trioxatetracyclo[11.2.1. $0^{2,11}$.$0^{4,9}$] hexadeca-4(9),10-dien-8-one (**4**), (1*R*,8*S*,9*R*)-5-acetyl-3-aryl-8-methylthio-11,12-dioxa-3-azatricyclo-[7.2.1.$0^{2,7}$]dodeca-2(7),5-dien-4-ones (**5**,**6**) and dialkyl (1*R*,8*S*,-9*R*)-4-hydroxy-8-methylthio-11,12-dioxatricyclo[7.2.1.$0^{2,7}$]dodeca-2(7),3,5-triene-3,5-dicarboxylates (**7**,**8**), respectively.

INTRODUCTION

During the past decade the development of new synthetic pathways for the preparation of anellated pyranoses has become a topic of great interest in synthetic organic chemistry[1–4] because of the relevance of these compounds particularly as anti-inflammatory drugs, spruce budworm antifeedants and herbicidin nucleoside antibiotics.[5–7]

Continuing our studies[8] concerning the preparation of polycyclic compounds on the basis of levoglucosenone, we report in this paper the reactions of β-methylthioenulose derivatives of levoglucosenone **1**[8] with several salts derived from diethyl malonate, 1,3-diketones, *N*-aryl-3-oxobutyramides and dialkyl 3-oxoglutarates, respectively. By utilizing the push-pull substituted exocyclic double bond in compound **1**, the formation of various heterocyclic and carbocyclic anellated 1,6-anhydropyranoses could be observed (Scheme 1).



Scheme 1.

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RESULTS AND DISCUSSION

Treatment of (*Z*)-1,6-anhydro-3-deoxy-4-methylthio-3-[(methylthio)methylene]-β-D-*erythro*-hexopyranos-2-ulose (**1**) at room temperature with diethyl malonate and potassium carbonate in tetrahydrofuran in the presence of crown ether resulted in the substitution of the methylthio group in the branch to yield the branched-chain ulose **2**. However, the expected further attack of the enolic hydroxyl group on carbon atom 2 was not observed due to the small enolization tendency of this compound. The IR and NMR spectra showed the presence of three carbonyl groups in the molecule indicating the open-chain structure. In a NOESY experiment the corresponding correlations between H-3–H-1, H-1′–H-4 and H-1′–MeS were found confirming the (*R*)-configuration at C-3.

In contrast to the reaction of **1** with malonate, treatment of **1** with 2,4-pentanedione and 1,3-cyclohexanedione resulted in the formation of 1-{(1*R*,2*S*,8*S*,9*R*)-2-hydroxy-4-methyl-8-methylthio-3,11,12-trioxatricyclo[7.2.1.$0^{2,7}$]dodeca-4,6-dien-5-yl}ethanone (**3**) and (1*R*,2*S*,12*S*,13*R*)-2-hydroxy-12-methylthio-3,15,16-trioxatetracyclo-[11.2.1.$0^{2,11}$.$0^{4,9}$]hexadeca-4(9),10-dien-8-one (**4**), respectively. It can be assumed that these compounds originated from the substitution of the exocyclic methylthio group at C-1′ by the anion derived from the 1,3-diketone followed by an attack of the enolic hydroxyl group of the β-diketone part on the C-2. The structures of **3** and **4** were unequivocally determined by IR, NMR and mass spectral analyses. In a NOESY experiment of **4**, correlations were found between OH–H-1 and OH–MeS demonstrating the (*S*)-configuration at C-2.

Furthermore, the reactions of **1** with *N*-phenyl-3-oxobutyramide and *N*-(*p*-methoxy)-3-oxobutyramide in the presence of potassium carbonate did not afford the corresponding pyran derivatives but the substituted pyridones **5** and **6** were isolated as crystalline products. NMR data and an X-ray structure analysis of **5** (see Figure 1) confirmed the structures represented in Scheme 1. A COLOC spectrum of **5** allowed the assignment of all ^{13}C NMR signals.

In a similar way the benzoanellated anhydro sugars **7** and **8** could be obtained by the reaction of **1** with dimethyl and diethyl 3-oxoglutarate, respectively. The chemical shifts of the carbon atoms were assigned unambiguously with the help of ^{13}C,^{1}H correlation experiments, and clearly confirm the postulated structures. As expected the signals of C-6 and H-6 were found in the typical region for aromatic nuclei (δ = 134.5, 134.3 and δ = 8.07, 8.04).

In summary, the described procedure represents a method for the synthesis of anellated pyranose derivatives with potential biological activity.

EXPERIMENTAL

General Procedures. Melting points were determined with a Boëtius apparatus and are corrected. IR spectra were recorded with a Nicolet 205 FT-IR spec-

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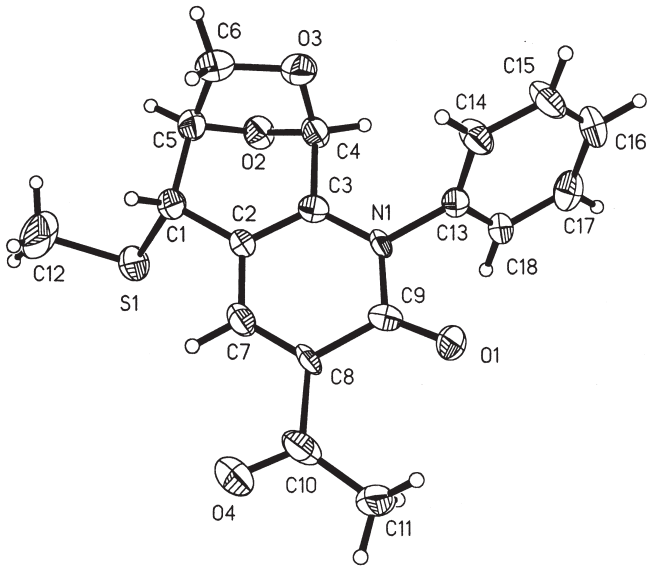

Figure 1. ORTEP drawing of **5**.

trometer. Specific optical rotations were measured with a Gyromat HP (Dr. Kernchen). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker instruments ARX 300 and AC 250 with $CDCl_3$ or DMSO-d_6 as solvent. The calibration of spectra was carried out by means of solvent peaks (DMSO-d_6: δ ^{1}H = 2.50; δ ^{13}C = 39.7; $CDCl_3$: δ ^{1}H = 7.25; δ ^{13}C = 77.0). The ^{13}C NMR signals were assigned by DEPT and/or two-dimensional ^{1}H,^{13}C correlation experiments. The mass spectra were recorded on an AMD 402/3 spectrometer (AMD Intectra GmbH). For chromatography Merck silica gel 60 (230–400 mesh) was used. The X-ray analysis for compound **5** was performed at 223 K on a Siemens P4 four-circle diffractometer using Mo-K_α radiation with graphite monochromator. The crystals are monoclinic: a = 9.443(3) Å, b = 9.330(3) Å, c = 10.393(3) Å, β = 113.36(2)° , V = 840.6(5) Å^3, space group $P2_1$, Z = 2, $C_{18}H_{17}NO_4S$, M = 343.39, F(000): 360, μ = 0.214 mm^{-1}, d_{calc} = 1.357 Mg/m≥, crystal size 0.40 × 0.20 × 0.04 mm^3, temperature 223 K. The intensities of 2153 independent reflections with $2\Theta < 45°$ were measured using the ω-scan technique. The structure was solved by direct methods (SHELXS-86, G.M. Sheldrick, Universität Göttingen, 1986) and refined by the full matrix least squares method of the SHELXL-97 program to w$R2$ = 0.1518, S = 1.029 ($R1$ = 0.0593 for 1632 reflections with $I > 2\sigma$) . Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-151210. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. code +(1223) 336–033; e-mail: deposit@ccdc.cam.ac.uk).

General Procedure for the Reaction of (*Z*)-1,6-Anhydro-3-deoxy-4-methylsulfanyl-3-[(methylsulfanyl)methylene]-β-D-*erythro*-hexopyranos-2-ulose (1) with Diethyl malonate, 1,3-Diketones, *N*-Aryl-3-oxobutyramides and Dialkyl 3-oxoglutarate, respectively. A mixture of **1** (116 mg, 0.50 mmol), diethyl malonate, 1,3-diketones, *N*-aryl-3-oxobutyramides and dialkyl 3-oxoglutarates, respectively, (0.75 mmol), K_2CO_3 (120 mg), 18-crown-6 (100 mg) and THF (10 mL) was stirred at 22°C up to the disappearance of **1** (10–12 h, TLC control). The suspension was filtered and the filtrate was concentrated. The residue was purified by column chromatography (toluene/ethyl acetate 2–4:1)

Diethyl 2-(1,6-Anhydro-4-methylsulfanyl-β-D-*arabino*-hex-2-ulopyranos-3-yl-methylene)malonate (2). Compound **2** was obtained as a colourless syrup (31 mg, 18%); R_f = 0.44 (toluene/ethyl acetate 4:1); $[\alpha]_D^{24}$ −295.8 (*c* 1.0, chloroform); IR(capillary) 1731, 1697 (C═O); 1553 (C═C); ^{1}H NMR (300.1 MHz, $CDCl_3$) δ 1.20 (t, 3H, CH_2CH_3); 1.24 (t, 3H, CH_2CH_3); 2.50 (s, 3H, SCH_3); 3.23 (dd, 1H, J_{3-4} = 3.6 Hz, $J_{3-1'}$ = 1.3 Hz, H-3); 3.77–3.82 (m, 2H, J_{5-6e} = 1.5 Hz, H-4, H-6e); 3.98 (dd, 1H, J_{6a-6e} = 7.6 Hz, J_{5-6a} = 5.2 Hz, H-6a); 4.10–4.30 (m, 4H, 2× CH_2CH_3); 5.12–5.17 (m, 2H, H-1, H-5); 7.72 (d, 1H, H-1′). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 184.9 (C-2); 168.6, 168.2 (2× *C*OOEt); 147.9 (C-1′); 126.0 (C-2′); 100.8 (C-1); 74.5 (C-5); 68.3 (C-6); 61.9, 61.8 (2× CH_2CH_3); 50.5 (C-3); 43.9 (C-4); 17.8 (SCH_3); 14.0, 13.8 (2× CH_2CH_3). Mass spectrum, CI: *m/z* (%) = 344.8 (100, $M^{+\Sigma}$).

Anal. Calcd for $C_{15}H_{20}O_7S_2$ (344.38): C, 52.32; H, 5.85; S, 9.31. Found: C, 53.10; H, 5.85; S, 9.11.

1-{(1*R*,2*S*,8*S*,9*R*)-2-Hydroxy-4-methyl-8-methylthio-3,11,12-trioxatricyclo[7.2.1.0^{2,7}] dodeca-4,6-dien-5-yl}ethanone (3). Compound **3** was obtained as a colourless syrup (35 mg, 25%); R_f = 0.18 (toluene/ethyl acetate 2:1); $[\alpha]_D^{24}$ −33.1 (*c* 1.0, chloroform); IR(KBr) 3423 (OH); 1678 (C═O); 1604, 1559 (C═C); ^{1}H NMR (250.1 MHz, $CDCl_3$) δ 2.17 (s, 3H, SCH_3); 2.34 (s, 3H, $COCH_3$); 2.39 (s, 3H, CH_3); 3.31 (d, 1H, J_{8-9} =1.5 Hz, H-8); 3.65 (s, 1H, OH); 3.80 (dd, 1H, J_{9-10e} = 1.2 Hz, H-10e); 3.92 (dd, 1H, $J_{10a-10e}$ = 7.6 Hz, J_{9-10a} = 5.3 Hz, H-10a); 4.72 (ddd, 1H, H-9); 5.32 (s, 1H, H-1); 6.50 (s, 1H, H-6). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 195.1 (*C*OCH_3); 164.8 (C-4); 122.8 (C-6); 119.7 (C-5); 113.2 (C-7); 102.1 (C-1); 93.9 (C-2); 76.7 (C-9); 68.2 (C-10); 50.1 (C-8); 29.6 (CO*C*H_3); 20.9 (CH_3); 15.0 (SCH_3). Mass spectrum, EI: *m/z* (%) = (282.8, $[M-1]^{+\Sigma}$), 43.0 (100).

(1*R*,2*S*,12*S*,13*R*)-2-Hydroxy-12-methylthio-3,15,16-trioxatetracyclo[11.2.1. 0^{2,11}.0^{4,9}] hexadeca-4(9),10-dien-8-one (4). Recrystallization of the residue from dichloromethane/*n*-hexane yielded **4** as colourless crystals (106 mg, 72%); mp 144–147°C (decomp.); R*f* = 0.14 (toluene/ethyl acetate 2:1); $[\alpha]_D^{24}$ −100.8 (*c* 0.25, chloroform); IR(KBr) 3427 (OH); 1735 (C═O); 1651, 1629 (C═C); ^{1}H NMR (300.1 MHz, $CDCl_3$) δ 2.03 (m, 2H, H-6); 2.15 (s, 3H, SCH_3);

2.42 (m, 2H), 2.60 (m, 2H) (H-5, H-7); 3.30 (d, 1H, J_{12-13} = 1.5 Hz, H-12); 3.80 (dd, 1H, J_{13-14e} = 1.5 Hz, H-14e); 3.90 (dd, 1H, $J_{14a-14e}$ = 7.8 Hz, J_{13-14a} = 5.5 Hz, H-14a); 4.01 (s, 1H, OH); 4.71 (ddd, 1H, H-13); 5.32 (s, 1H, H-1); 6.56 (s, 1H, H-10). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 195.0 (C-8); 170.3 (C-4); 121.3 (C-9); 118.9 (C-10); 111.1 (C-11); 102.1 (C-1); 94.2 (C-2); 76.9 (C-13); 68.2 (C-14); 50.5 (C-12); 36.4, 28.2 (C-5, C-7); 20.4 (C-6); 15.0 (SCH_3). Mass spectrum, EI: *m/z* (%) = 296.0 (2, $M^{+\Sigma}$), 175.0 (100).

Anal. Calcd for $C_{14}H_{16}O_5S$ (296.33): C, 56.74; H, 5.44; S, 10.82. Found: C, 56.51; H, 5.42; S, 10.74.

(1*R*,8*S*,9*R*)-5-Acetyl-8-methylthio-3-phenyl-11,12-dioxa-3-azatricyclo-[7.2.1.0^{2,7}] dodeca-2(7),5-dien-4-one (5). Compound **5** was obtained after a reaction time of 6–8 h (TLC control) and recrystallization from dichloromethane/*n*-hexane as colourless needles (96 mg, 56%); mp 195–198 °C; R_f = 0.26 (toluene/ethyl acetate 2:1); $[\alpha]_D^{24}$ −221.3 (*c* 0.3, chloroform); IR(KBr) 1683, 1666 (C═O); 1535, 1488 (C═C); ^{1}H NMR (300.1 MHz, $CDCl_3$) δ 2.18 (s, 3H, SCH_3); 2.65 (s, 3H, $COCH_3$); 3.48 (d, 1H, J_{8-9} = 1.0 Hz, H-8); 3.67 (dd, 1H, J_{9-10e} = 1.8 Hz, H-10e); 3.98 (dd, 1H, $J_{10a-10e}$ = 7.9 Hz, J_{9-10a} = 6.1 Hz, H-10a); 4.96 (ddd, 1H, H-9); 5.36 (s, 1H, H-1); 7.28 (m, 2H, Ph); 7.54 (m, 3H, Ph); 8.32 (s, 1H, H-6). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 196.8 (C═O); 160.5 (C-4); 147.4 (C-2); 145.4 (C-6); 135.5 [C-1(Ph)]; 128.9 (C-5); 130.0, 129.7, 128.1, 128.0 [C-2,3,5,6 (Ph)]; 129.6 [C-4 (Ph)]; 107.6 (C-7); 95.0 (C-1); 77.9 (C-9); 67.6 (C-10); 45.7 (C-8); 30.8 (CO*C*H_3); 14.0 (SCH_3). Mass spectrum, EI: *m/z* (%) = 342.9 (6, M^+), 265.9 (100).

Anal. Calcd for $C_{18}H_{17}NO_4S$ (343.39): C, 62.92; H, 4.99; N, 4.08; S, 9.34. Found: C, 62.94; H, 5.06; N, 4.15; S, 9.34.

(1*R*,8*S*,9*R*)-5-Acetyl-3-(4-methoxyphenyl)-8-methylthio-11,12-dioxa-3-azatricyclo[7.2.1.0^{2,7}] dodeca-2(7),5-dien-4-one (6). Compound **6** was obtained after a reaction time of 6–8 h (TLC control) and recrystallization from dichloromethane/*n*-hexane as yellow crystals (57 mg, 30%); mp 102–106 °C; R_f = 0.24 (toluene/ethyl acetate 2:1); $[\alpha]_D^{24}$ −185.4 (*c* 0.5, chloroform); IR(KBr) 1680, 1663 (C═O); 1591, 1540 (C═C); ^{1}H NMR (250.1 MHz, $CDCl_3$) δ 2.18 (s, 3H, SCH_3); 2.65 (s, 3H, $COCH_3$); 3.47 (d, 1H, J_{8-9} = 0.8 Hz H-8); 3.66 (dd, 1H, J_{9-10e}= 1.8 Hz, H-10e); 3.84 (s, 3H, OCH_3); 3.98 (dd, 1H, $J_{10a-10e}$ = 7.9 Hz, J_{9-10a} = 6.1 Hz, H-10a); 4.96 (ddd, 1H, H-9); 5.44 (s, 1H, H-1); 8.30 (s, 1H, H-6); 7.00–7.08 [m, 2H, H-2,6 (4-$CH_3OC_6H_4$)]; 7.13–7.25 [m, 2H, H-3,5 (4-$CH_3OC_6H_4$)]. ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 197.0 (C═O); 160.9, 160.3 [C-4, C-4 (4-$CH_3OC_6H_4$)]; 147.9 (C-2); 145.4 (C-6); 129.5, 129.0 [C-3,5 (4-$CH_3OC_6H_4$)]; 127.9, 127.8 [C-5, C-1 (4-$CH_3OC_6H_4$)]; 115.3, 114.9 [C-2,6 (4-$CH_3OC_6H_4$)]; 107.6 (C-7); 95.1 (C-1); 77.9 (C-9); 67.6 (C-10); 55.5 (OCH_3); 47.7 (C-8); 30.9 (CO*C*H_3); 14.0 (SCH_3). Mass spectrum, EI: *m/z* (%) = 373.0 (6, M^+), 296.1 (100).

Anal. Calcd for $C_{19}H_{19}NO_5S$ (373.42): N, 3.75; S, 8.59. Found: N, 3.52; S, 7.99.

Dimethyl (1*R*,8*S*,9*R*)-4-Hydroxy-8-methylthio-11,12-dioxatricyclo[7.2.-1.0^{2,7}] dodeca-2(7),3,5-triene-3,5-dicarboxylate (7). Recrystallization of the residue from dichloromethane/*n*-hexane yielded **7** as colourless powder (95 mg, 56%); mp 119–120 °C; R_f = 0.45 (toluene/ethyl acetate 4:1); $[\alpha]_D^{24}$ −226.4 (*c* 0.45, chloroform); IR(KBr) 3433 (OH); 1735, 1721 (C═O); 1676, 1617 (C═C); ^{1}H NMR (300.1 MHz, $CDCl_3$) δ 2.06 (s, 3H, SCH_3); 3.61 (d, 1H, J_{8-9} = 1.2 Hz, H-8); 3.62 (dd, 1H, J_{9-10e} = 2.0 Hz, H-10e); 3.97 (s, 3H, OCH_3); 3.95 (s, 3H, OCH_3); 4.04 (dd, 1H, $J_{10a-10e}$ = 8.0 Hz, J_{9-10a} = 6.2 Hz, H-10a); 5.00 (ddd, 1H, H-9); 6.18 (s, 1H, H-1); 8.07 (s, 1H, H-6); 11.32 (s, 1H, OH). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 169.3 (5-$COOCH_3$); 167.9 (3-$COOCH_3$); 158.3 (C-4); 141.2 (C-2); 134.5 (C-6); 121.6 (C-7); 118.2, 113.2 (C-3, C-5); 96.9 (C-1); 78.2 (C-9); 67.8 (C-10); 52.6, 52.3 (2× OCH_3); 46.0 (C-8); 13.3 (SCH_3). Mass spectrum, EI: *m/z* (%) = 339.8 (10, M^+), 263.0 (100).

Anal. Calcd for $C_{15}H_{16}O_7S$ (340.34): S, 9.42. Found: S, 9.42.

Diethyl (1*R*,8*S*,9*R*)-4-Hydroxy-8-methylthio-11,12-dioxatricyclo[7.2.1.0^{2,7}] dodeca-2(7),3,5-triene-3,5-dicarboxylate (8). Compound **8** was obtained as a colourless syrup (57 mg, 31%); R_f = 0.35 (toluene/ethyl acetate 8:1); $[\alpha]_D^{24}$ −231.1 (*c* 0.25, chloroform); IR(capillary) 3381 (OH); 1731, 1739 (C═O); 1676, 1616 (C═C); ^{1}H NMR (250.1 MHz, $CDCl_3$) δ 1.40 (t, 3H, CH_2CH_3); 1.41 (t, 3H, CH_2CH_3); 2.07 (s, 3H, SCH_3); 3.60–3.62 (m, 2H, J_{9-10e} = 1.8 Hz, H-8, H-10e); 4.01 (dd, 1H, $J_{10a-10e}$ = 8.0 Hz, J_{9-10a} = 6.2 Hz, H-10a); 4.35–4.50 (m, 4H, 2× CH_2CH_3); 4.99 (ddd, 1H, H-9); 6.20 (s, 1H, H-1); 8.04 (s, 1H, H-6); 11.35 (s, 1H, OH). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 169.1 (5-*C*OOEt); 165.4 (3-*C*OOEt); 158.4 (C-4); 140.9 (C-2); 134.3 (C-6); 121.5 (C-7); 118.8, 113.9 (C-3, C-5); 97.0 (C-1); 78.2 (C-9); 67.9 (C-10); 62.1, 62.0 (2× CH_2CH_3); 46.1 (C-8); 14.3, 14.1 (2× CH_2CH_3); 13.5 (SCH_3). Mass spectrum, EI: *m/z* (%) = 368.1 (7, M^+), 291.1 (100).

Anal. Calcd for $C_{17}H_{20}O_7S$ (368.40): C, 55.43; H, 5.47; S, 8.70. Found: C, 55.14; H, 5.80; S, 8.33.

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