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ACYLGLYCEROLS FROM THE SLIME MOULD, *LYCOGALA EPIDENDRUM*

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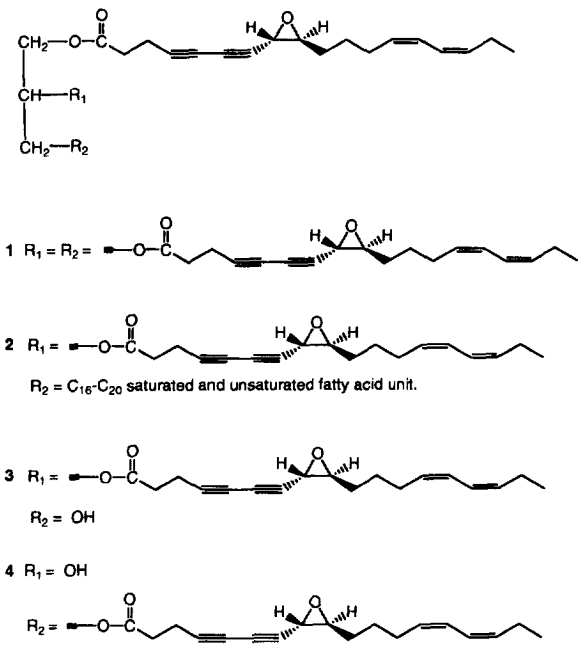
Key Word Index—*Lycogala epidendrum*; Myxomycetes; slime mould; triacylglycerols; diacylglycerols; 3,4-*bis*(indol-3-yl)pyrrole-2,5-dicarboxylic acid derivatives; acetylene; modified Mosher's method.

Abstract—From the slime mould *Lycogala epidendrum*, four unusual new acylglycerols, lycogarides D–G, were isolated. Their structures were determined by spectroscopic and chemical methods. Also, the known lycogalic acid dimethyl esters A and B were obtained.

INTRODUCTION

Slime moulds (Myxomycetes) are microorganisms of the division Mycota on the borderline between the plant and animal kingdom. It is difficult to collect slime moulds in large amounts and, thus, only a few of the more than 500 species have been chemically investigated so far [1, 2]. However, *Lycogala epidendrum* has been studied previously [3–5]. In one study, three novel triacylglycerols, lycogarides A–C, were isolated [3], while in two other studies, which were independent from each other, the same three 3,4-*bis*(indol-3-yl)pyrrole-2,5-dicarboxylic acid derivatives, lycogalic acid dimethyl esters A–C, were obtained [4, 5].

In the present paper, we describe the isolation and structural elucidation of two unusual new triacylglycerols, lycogarides D (**1**) and E (**2**), two new diacylglycerols, lycogarides F (**3**) and G (**4**), along with the known lycogalic acid dimethyl esters A (**5**) and B (**6**), from *L. epidendrum*.

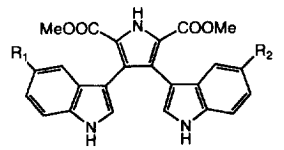


RESULTS AND DISCUSSION

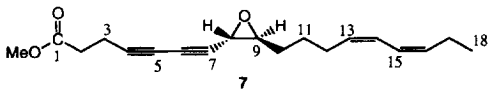
An ethyl acetate extract of *L. epidendrum* was chromatographed by flash column chromatography on silica gel. The 10 fractions collected were further purified by preparative TLC on silica gel, and by preparative HPLC, to give **1**–**4** and **5**–**6**.

The molecular formula, $C_{57}H_{68}O_9$, of **1** was determined by elemental analysis (Found: C, 76.18; H, 7.96. $C_{57}H_{68}O_9$ requires: C, 76.30; H, 7.64) and quasi-molecular ion peaks at *m/z* 919 $[M + Na]^+$ and *m/z* 935 $[M + K]^+$ in its (+)-FAB-mass spectrum. It was obvious from the ^1H and ^{13}C NMR spectra that **1** was a symmetrical triacylglycerol [δ_H 4.36 (*dd*, J = 12.0 and 4.0 Hz, 2H); 4.19 (*dd*, J = 12.0 and 6.0 Hz, 2H); 5.29 (*m*). δ_C 170.5 (*s*, 2C); 170.2 (*s*); 69.2 (*d*); 62.2 (*t*, 2C)]. In order to determine further the structure a methanol–benzene solution of **1** was treated with 0.5 M sodium methoxide to yield the methyl ester (**7**).

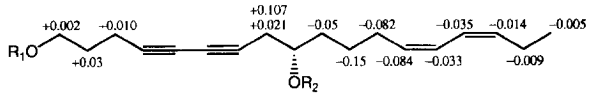
Compound **7** was a colourless oil and had the molecular formula $C_{19}H_{24}O_3$ ($[M]^+$ at *m/z* 300.1716) as determined by HR mass spectrometry. The IR spectrum indicated the presence of alkyne (ν_{max} 2257 cm^{-1}) and ester (ν_{amx} 1742 cm^{-1}) groups. The ^1H NMR spectrum showed signals for ester methyl [δ_H 3.70 (*s*)], a conjugated diene system [δ_H 5.39 (*br dt*, J = 11.0 and 7.5 Hz); 6.28 (*tq*, J = 11.0 and 1.5 Hz); 6.18 (*tq*, J = 11.0 and 1.5 Hz); 5.47 (*br dt*, J = 11.0 and 7.5 Hz)], two oxygenated methines [δ_H 3.12 (*d*, J = 2.2 Hz); 3.09 (*td*, J = 5.0 and 2.2 Hz)] and a primary methyl [δ_H 1.0 (*t*, J = 7.5 Hz)]. The ^{13}C NMR



	R_1	R_2
5	H	H
6	OH	H



7



	R_1	R_2
8	OH	OH
9	TBDMS	OH
10	TBDMS	(*S*)-MTPA
11	TBDMS	(*R*)-MTPA

Fig. 1. $\Delta\delta$ [$\delta_S - \delta_R$ (ppm)] for the MTPA esters (compounds **10** and **11**).

spectrum displayed 19 carbons: methyl ester [δ_C 171.7 (*s*), 51.9 (*q*)], conjugated diene [δ_C 134.3, 130.5, 124.3 and 122.6 (all *d*)], two oxygenated methines (δ_C 60.5 and 45.3), four singlets (δ_C 78.7, 73.0, 68.3 and 65.1), six methylenes and a methyl. The IR spectrum did not show the presence of hydroxyl groups and the mass spectral data indicated that there can only be one further oxygen in addition to those of the ester group. Thus, the two oxygenated methines (δ_C 60.5 and 45.3) must belong to a disubstituted epoxide and the four singlets (δ_C 78.7, 73.0, 68.3 and 65.1) to two triple bonds. The vicinal coupling (J = 2.2 Hz) between the epoxide protons indicated a *trans*-fused epoxide and the 13*Z*,15*Z*-configuration follows from the vicinal coupling (J = 11.0 Hz) between olefinic protons.

The partial structure of **7** from C-6 to C-18 was derived from the above information together with the analysis of phase-sensitive DQF-COSY and HMQC spectra. Long-range correlations observed in an HMBC experiment confirmed this part structure and established the C-1 to C-5 part structure as follows: all four C-2 methylene protons [δ_H 2.55 (*m*, 2H)] and C-3 [δ_H 2.60 (*m*, 2H)] correlate with the ester carbonyl carbon and the alkyne carbon at δ_C 78.7 (C-4). To complete the structure there must be a bond between C-5 and C-6 forming a conjugated triple bond system, thus giving the planar structure and relative configuration of **7**.

To establish the absolute configuration of **1** the modified Mosher's method, with 2-methoxy-2-phenyl-2-(trifluoromethyl) acetic acid (MTPA) esters, was used [6–8]. Compound **1** was treated with $LiAlH_4$ in dry diethyl ether, which resulted in the alcohol (**8**) being formed. The primary alcohol group of **8** was then protected by making the *tert*-butyldimethylsilyl (TBDMS) ether (**9**) and this was then converted into the (*S*)- and (*R*)-MTPA esters **10** and **11**. The proton signals of **10** and **11** were assigned by a phase-sensitive DQF-COSY experiment and the $\Delta\delta$ ($\delta_S - \delta_R$) (ppm) values obtained for the respective protons are shown in Fig. 1. The systematic arrangement of positive and negative $\Delta\delta$s, confirmed the *S*-configuration for the hydroxyl group at C-9. Thus, the structure and absolute configuration of lycogaride D was established as shown for **1**.

The spectral data (^{1}H and ^{13}C NMR, IR and UV) for **2** were similar to those for **1**. From the ^{1}H and ^{13}C NMR data for the glycerol unit, it was clear that **2** is an unsymmetrical triacylglycerol [δ_H 4.36 (*dd*, J = 12.0 and 4.0 Hz); 4.31 (*dd*, J = 12.0 and 4.0 Hz); 4.18 (*dd*, J = 12.0 and 6.0 Hz); 4.14 (*dd*, J = 12.0 and 6.0 Hz); 5.29 (*m*). δ_C 62.4 (*t*), 61.6 (*t*) and 69.4 (*d*)]. Methanolysis of **2** yielded two equivalents of **7** and one equivalent of a mixture of C_{16}–C_{20} saturated and unsaturated fatty acid methyl esters. The mixture consisted of esters of C_{16} (16%), C_{18} (16%), C_{20} (4%)-anoic acids, C_{18}-enoic acids (21%), C_{18}-dienoic acids (34%) and several other minor components (9%). The mixture constitution was determined by GC-mass spectral analysis. The above information leads to structure **2** for lycogaride E.

The (+)-FAB-mass spectrum of **3** showed two quasi-molecular ion peaks at *m/z* 651 $[M + Na]^+$ and *m/z* 667 $[M + K]^+$ corresponding to a molecular formula of $C_{39}H_{48}O_7$. The IR spectrum showed the presence of hydroxyl (ν_{max} 3460 cm^{-1}), alkyne (ν_{max} 2255 cm^{-1}) and ester (ν_{max} 1742 cm^{-1}) groups. The ^{1}H and ^{13}C NMR data for **3** showed signals characteristic of an unsymmetrical diacylglycerol [glycerol unit: δ_H 3.76 (*m*, 2H); 4.27 (*dd*, J = 12.1 and 5.9 Hz); 4.40 (*dd*, J = 12.1 and 4.1 Hz); 5.13 (*m*); δ_C 62.55 (*t*), 61.30 (*t*), and 72.63 (*d*). Ester carbonlys: δ_C 171.17 and 170.83 (1 : 1 intensity ratio)]. The NMR data also reveals that the diacylglycerol fatty acid units are identical to those of **1** and this was confirmed by 2D-experiments (phase-sensitive DQF-COSY, HMQC and HMBC). The above data indicates that lycogaride F is a diacylglycerol with structure **3**.

Compound **4**, $C_{39}H_{48}O_7$ {(+)-FAB-mass spectrum: *m/z* 651 $[M + Na]^+$, 667 $[M + K]^+$}, was isomeric with **3**. It was clear from the NMR data that **4** is the corresponding symmetrical diacylglycerol of **3**. Thus, there are ^{1}H NMR signals for the glycerol unit at δ_H 4.23 (*dd*, J = 11.6 and 4.3 Hz, 2H); 4.18 (*dd*, J = 11.6 and 6.0 Hz, 2H) and 4.11 (*m*) and ^{13}C NMR signals at δ_C 68.0 (*d*) and 65.4 (*t*, 2C). There is also a two-carbon ester carbonyl signal at δ_C 171.2. Lycogaride G was therefore assigned structure **4**.

The known lycogalic acid dimethyl esters A (**5**) and B (**6**), were identified by comparison of their spectroscopic data with those for the authentic compounds [4, T. Hashimoto, unpublished data].

It is interesting to note that, from *L. epidendrum* studied here, both 3,4-bis(indol-3-yl)pyrrole-2,5-dicarboxylic acid derivatives and acetylenic acylglycerols were isolated, whereas in previous investigations on this species only one or the other of these types of compounds has been reported.

EXPERIMENTAL

General. TLC prep. TLC: Merck precoated silica gel 60 F_{254}, visualized under UV light (254 nm) and by spraying with 30% H_2SO_4 and heating. R_f values refer to *n*-hexane–EtOAc (1:1) as eluent. Flash CC: silica gel 60 (40–63 μm). HPLC: Chemcosorb 5Si-U 10 × 250 mm (B).

Spectral data. NMR spectra (^{1}H, 600, 400 MHz; ^{13}C, 150, 100, 50 MHz) were recorded for $CDCl_3$ solns relative to TMS at δ_H 0 and $CDCl_3$ at δ_C 77.0. Multiplicities were determined by DEPT expts. IR spectra were measured for $CHCl_3$ solns, UV spectra in dioxane and EtOH, and $[\alpha]_D$ in $CHCl_3$ and MeOH. EIMS were measured at 70 eV. (+)-FAB-MS: matrix of *m*-nitrobenzyl alcohol. CIMS were obtained at 70 eV with CH_4 as reagent gas.

Slime mould. Lycogala epidendrum was collected in Tokushima (Japan) in November 1994. A voucher specimen is deposited at the Faculty of Pharmaceutical Sciences, Tokushima Bunri University.

Extraction and isolation. Fresh material (210 g) was extracted (× 2) with EtOAc to yield 4.95 g crude extract. This was then subjected to flash CC on silica gel using an *n*-hexane–EtOAc gradient to give 10 frs. Frs 3 and 4 were combined (446 mg) and purified further by prep. TLC [*n*-hexane–EtOAc (3:1)] to give **2** (97 mg, R_f 0.74). Fr 5 (1.80 g) was chromatographed by prep. TLC [*n*-hexane–EtOAc (7:3)] to give **2** (1.25 g) and **1** (213 mg, R_f 0.62). Frs 6 (2.20 g) and 7 (75 mg) consisted entirely of **1**. Fr. 8 (30 mg) was further purified by HPLC [*n*-hexane–EtOAc (2:3), CH_2Cl_2–MeOH (99:1)] to give **3** (8 mg, R_f 0.37), **4** (11 mg, R_f 0.31) and **5** (19 mg, R_f 0.24). Chromatography by prep. TLC (EtOAc) and final purification by HPLC [*n*-hexane–EtOAc (1:3)] of fr. 9 (192 mg) yielded **5** (22 mg) and **6** (108 mg, R_f 0.11).

Lycogaride D (**1**). Oil. $[\alpha]_D$ −48.5° ($CHCl_3$; *c* 5.09). (+)-FAB-MS: *m/z* 919 $[M + Na]^+$, 935 $[M + K]^+$. UV λ_{max} (dioxane) nm (log ε): 239 (4.77). Elemental analysis (Found: C, 76.18; H, 7.96. $C_{57}H_{68}O_9$ requires: C, 76.30; H, 7.64). IR ν_{max} cm^{-1}: 2934; 2257 (alkyne), 1746 (C=O). ^{1}H NMR (400 MHz): δ6.28 (*t*, *J* = 11.0 Hz, 3H), 6.18 (*t*, *J* = 11.0 Hz, 3H), 5.46 (*dt*, *J* = 11.0, 7.5 Hz, 3H), 5.39 (*dt*, *J* = 11.0, 7.5 Hz, 3H), 5.29 (*m*), 4.36 (*dd*, *J* = 12.0, 4.0 Hz, 4H), 4.19 (*dd*, *J* = 12.0, 6.0 Hz, 4H), 3.12 (*br s*, 3H), 3.08 (*m*, 3H), 2.58 (*m*, 12H), 2.20 (*m*, 12H), 1.55 (*m*, 12H), 0.99 (*t*, *J* = 7.5 Hz, 12H). ^{13}C NMR (100 MHz): δ170.5 (*s*, 2C), 170.2 (*s*), 134.0 (*d*, 3C), 130.4 (*d*, 3C), 124.1 (*d*, 3C), 122.5 (*d*, 3C), 78.4 (*s*, 3C), 73.1 (*s*, 3C), 69.2 (*d*), 68.0 (*s*, 3C), 65.1 (*s*, 3C), 62.2 (*t*, 2C), 60.3 (*d*, 3C), 45.0 (*d*, 3C), 32.5 (*t*), 32.3 (*t*, 2C), 30.9 (*t*, 3C), 26.7 (*t*, 3C), 25.3 (*t*, 3C), 20.6 (*t*, 3C), 14.9 (*t*, 3C), 14.0 (*q*, 3C).

Methanolysis of **1**. To a soln of **1** (171 mg) in dry benzene (4 ml) and dry MeOH (10 ml) was added 0.5M NaOMe (2.5 ml). The mixt. was stirred at room temp. for 30 min. The solvents were then evapd and the product purified by prep. TLC [*n*-hexane–EtOAc (1:3)] to give a single Me ester (**7**) (131 mg).

Methyl ester **7**. Oil. $[\alpha]_D$ −49.7° ($CHCl_3$; *c* 2.98), HRMS: *m/z* 300.1716 $[M]^+$ calc. for $C_{19}H_{24}O_3$: 300.1725. EIMS *m/z* (rel. int.): 300 $[M]^+$ (4), 285 (4), 271 (10), 231 (15), 197 (21), 169 (36), 129 (85), 106 (68), 79 (100), 67 (65), 41 (49). UV λ_{max} (dioxane) nm (log ε): 248 (4.05). IR ν_{max} cm^{-1}: 2936; 2257 (alkyne), 1742 (C=O). ^{1}H NMR (600 MHz): δ6.28 (*tq*, *J* = 11.0, 1.5 Hz, H-14), 6.18 (*tq*, *J* = 11.0, 1.5 Hz, H-15), 5.47 (*br dt*, *J* = 11.0, 7.5 Hz, H-16), 5.39 (*br dt*, *J* = 11.0, 7.5 Hz, H-13), 3.70 (*s*, OMe), 3.12 (*d*, *J* = 2.2 Hz, H-8), 3.09 (*td*, *J* = 5.0, 2.2 Hz, H-9), 2.60 (*m*, 2H-3), 2.55 (*m*, 2H-2), 2.22 (*br q*, *J* = 7.5 Hz, 2H-12), 2.19 (*quin. d*, *J* = 7.5, 1.5 Hz, 2H-17), 1.57 (*m*, 2H-11), 1.53 (*m*, 2H-10), 1.0 (*t*, *J* = 7.5 Hz, 3H-18). ^{13}C NMR (150 MHz): δ171.7 (*s*, C-1), 134.3 (*d*, C-16), 130.5 (*d*, C-13), 124.3 (*d*, C-14), 122.6 (*d*, C-15), 78.7 (*s*, C-4), 73.0, 68.3, 65.1 (all *s*, C-5/6/7), 60.5 (*d*, C-9), 51.9 (*q*, OMe), 45.3 (*d*, C-8), 32.5 (*t*, C-3), 31.1 (*t*, C-11), 26.9 (*t*, C-12), 25.4 (*t*, C-10), 20.8 (*t*, C-17), 15.1 (*t*, C-2), 14.1 (*q*, C-18).

Preparation of alcohol **8**. Compound **1** (133 mg) dissolved in 10 ml dry Et_2O was added slowly dropwise over 20 min to $LiAlH_4$ (155 mg) in 15 ml dry Et_2O and the mixt. stirred at 0–5° for 3 hr. After work-up, the mixt. was purified by HPLC [*n*-hexane–EtOAc (1:4), CH_2Cl_2–EtOAc (2:3)] to give **8** (15 mg) as an oil. $[\alpha]_D$ −11.6° (MeOH; *c* 0.65). HRCIMS: *m/z* 275.2003 $[M + H]^+$ calculated for $C_{18}H_{27}O_2$: 275.2011. CIMS *m/z* (rel. int.): 275 $[M + H]^+$ (96), 257 (100), 229 (43), 215 (66), 197 (78), 187 (44), 171 (63), 153 (63), 95 (79). UV λ_{max} (EtOH) nm (log ε): 228 (3.68). IR ν_{max} cm^{-1}: 3390 (OH), 2934. ^{1}H NMR (400 MHz): δ6.27 (*t*, *J* = 11.0 Hz), 6.20 (*t*, *J* = 11.0 Hz), 5.44 (*m*, 2H), 3.70–3.80 (*m*), 3.75 (*t*, *J* = 6.2 Hz), 2.49 (*dd*, *J* = 17.0, 4.8 Hz), 2.39 (*m*), 2.40 (*t*, *J* = 7.3 Hz), 2.10–2.25 (*m*, 4H), 1.78 (*quin.*, *J* = 6.6 Hz), 1.35–1.60 (*m*, 4H), 1.0 (*t*, *J* = 7.3 Hz). ^{13}C NMR (50 MHz): δ134.0, 131.2, 124.0, 122.8 (all *d*), 77.3, 73.8 (both *s*), 69.9 (*d*), 67.5, 65.5 (both *s*), 61.4 (*d*), 35.9, 30.9, 28.2, 27.2, 25.6, 20.8, 15.7 (all *t*), 14.1 (*q*).

Preparation of (R)- and (S)-MTPA esters. (*i*) *TBDMS ether of alcohol* **8**. A soln of **8** (15 mg) in dry CH_2Cl_2 (3 ml) was treated with Et_3N (0.04 ml), DMAP (1 mg) and TBDMS-Cl (15 mg). The mixt. was stirred at room temp. for 14 hr. The residue obtained after evapn of solvent was purified by prep. TLC [*n*-hexane–EtOAc (4:1) to give TBDMS ether **9** (16 mg). (*ii*) *(S)-MTPA ester of* **9**. To a soln of **9** (8 mg) in dry CH_2Cl_2 (4 ml) was added (*S*)-MTPA (11 mg), DCC (16 mg) and DMAP (2 mg) and the mixt. stirred at room temp. for 16 hr. The product obtained after evapn of solvent was purified by prep. TLC [*n*-hexane–EtOAc (4:1)] to give (*S*)-MTPA ester **10** (13 mg). (*iii*) *(R)-MTPA ester of* **9**. The same procedure as described above was employed for (*R*)-MTPA (11 mg), yielding the (*R*)-MTPA ester **11** (11 mg).

Lycogaride E (**2**). Oil. $[\alpha]_D$ −34.1° ($CHCl_3$; *c* 4.13). UV λ_{max} (dioxane) nm (log ε): 239 (4.69) IR ν_{amx} cm^{-1}: 2928; 2257 (alkyne), 1744 (C=O), ^{1}H NMR of glycerol unit (400 MHz): δ4.36 (*dd*, *J* = 12.0, 4.0 Hz), 4.31 (*dd*, *J* = 12.0, 4.0 Hz), 4.18 (*dd*, *J* = 12.0, 6.0 Hz), 4.14 (*dd*, *J* = 12.0, 6.0 Hz), 5.29 (*m*). ^{13}C NMR of glycerol unit (100 MHz): δ62.4 (*t*), 61.6 (*t*), 69.4 (*d*).

Methanolysis of **2**. The same procedure used for the methanolysis of **1** was employed for **2** (128 mg) to give two equivalents of Me ester **7** (70 mg) and one equivalent of a mixt. of C_{16}–C_{20} satd and unsatd fatty acid Me

esters (40 mg). The mixt. consisted of Me esters of C_{16} (16%), C_{18} (16%), C_{20} (4%)-anoic acids, C_{18}-enoic acids (21%), C_{18}-dienoic acids (34%) and several other minor components (9%). Identification was achieved by comparison of GC-MS fragmentation patterns with those of authentic specimens; approx. yields were determined from TlC peak areas.

Lycogaride F (**3**). Oil. $[\alpha]_D$ −78.1° ($CHCl_3$; *c* 0.51). (+)-FAB-MS *m/z*: 651 $[M + Na]^+$, 667 $[M + K]^+$. UV λ_{max} (dioxane) nm (log ε): 249 (4.22), IR ν_{amx} cm^{-1}: 3460 (OH); 2934; 2255 (alkyne), 1742 (C=O). ^1H NMR (600 MHz): δ6.28 (*tq*, *J* = 11.0, 1.5 Hz, 2H), 6.18 (*tq*, *J* = 11.0, 1.5 Hz, 2H), 5.47 (*br td*, *J* = 11.0, 7.5 Hz, 2H), 5.39 (*br dt*, *J* = 11.0, 7.5 Hz, 2H), 5.13 (*m*), 4.40 (*dd*, *J* = 12.1, 4.1 Hz), 4.27 (*dd*, *J* = 12.1, 5.9 Hz), 3.76 (*m*, 2H), 3.13 (*d*, *J* = 2.0 Hz, 2H), 3.09 (*br dt*, *J* = 5.0, 2.0 Hz, 2H), 2.60 (*m*, 8H), 2.22 (*br q*, *J* = 7.5 Hz, 4H), 2.19 (*quin. d*, *J* = 7.5, 1.5 Hz, 4H), 1.98 (*br s*, OH),1.56 (*m*, 8H), 1.00 (*t*, *J* = 7.5 Hz, 6H). ^{13}C NMR (150 MHz): δ171.2, 170.8 (both *s*), 134.3, 130.5, 124.3, 122.7 (all 2C *d*), 78.6, 78.5, 73.2, 73.2 (all *s*), 72.6 (*d*), 68.2, 68.2, 65.3, 65.4 (all *s*), 62.6, 61.3 (both *t*), 60.6, 60.6, 45.3, 45.3 (all *d*), 32.8, 32.6 (both *t*), 31.1, 26.9, 25.5, 20.8 (all 2C *t*), 15.2, 15.1 (both *t*), 14.2 (*q*, 2C).

Lycogaride G (**4**). Oil. $[\alpha]_D$ −33.7° ($CHCl_3$; *c* 0.36). (+)-FAB-MS: *m/z* 651 $[M + Na]^+$, 667 $[M + K]^+$. UV λ_{max} (dioxane) nm (log ε): 247 (4.32). IR ν_{amx} cm^{-1}: 3480 (OH); 2934; 2255 (alkyne), 1742 (C=O). ^1H NMR (600 MHz): δ6.28 (*tq*, *J* = 11.0, 1.5 Hz, 2H), 6.18 (*tq*, *J* = 11.0, 1.5 Hz, 2H), 5.47 (*br dt*, *J* = 11.0, 7.5 Hz, 2H), 5.39 (*br dt*, *J* = 11.0, 7.5 Hz, 2H), 4.23 (*dd*, *J* = 11.6, 4.3 Hz, 2H), 4.18 (*dd*, *J* = 11.6, 6.0 Hz, 2H), 4.11 (*m*), 3.13 (*d*, *J* = 2.2 Hz, 2H), 3.09 (*br td*, *J* = 4.9, 2.2 Hz, 2H), 2.61 (*m*, 8H), 2.39 (*d*, *J* = 5.1 Hz), 2.22 (*br q*, *J* = 7.5 Hz, 4H), 2.19 (*quin. d*, *J* = 7.5, 1.5 Hz, 4H), 1.56 (*m*, 8H), 1.0 (*t*, *J* = 7.5 Hz, 6H). ^{13}C NMR (150 MHz): δ171.2 (*s*, 2C), 134.3, 130.5, 124.3, 122.7 (all 2C *d*), 78.5, 73.2, 68.2, 68.0 (all 2C *s*), 68.0 (*d*), 65.4 (*t*, 2C), 60.6, 45.3 (both *d*), 32.6, 31.1, 26.9, 25.4, 20.8, 15.2 (all 2C *t*), 14.1 (*q*, 2C).

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