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The synthesis of mycobacterial dimycoloyl diarabinoglycerol based on defined synthetic mycolic acids

Omar T. Ali[a,1], Mohsin O. Mohammed[a,2], Paul J. Gates[c], Mark S. Baird[a,*],
Juma'a R. Al Dulayymi[a,b]

[a] School of Chemistry, Bangor University, Bangor, Gwynedd, LL57 2UW, UK
[b] School of Natural Sciences, Bangor University, Bangor, Gwynedd, LL57 2UW, UK
[c] School of Chemistry, Bristol University, Bristol, BS8 1TS, UK

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ABSTRACT

Complex mixtures of natural dimycoloyl diarabinoglycerols isolated from mycobacteria have been shown to be both potent immune signalling agents and potentially valuable antigens in the serodiagnosis of mycobacterial infections. We now report the highly stereocontrolled synthesis of diacyl L-glycerol-(1′→1)-β-D-arabinofuranosyl-α-D-arabinofuranosides based on simple fatty acids and single defined synthetic mycolic acids. NMR analysis confirmed that the synthetic core was identical to that in natural mixtures.

1. Introduction

The cells of Mycobacteria and some other organisms contain complex mixtures of characteristic long chain β-hydroxy acids, mycolic acids (MA, **1**) (Scheme 1). The proximal group Y is often a *cis*- or a *trans*-cyclopropane with a methyl substituent on the adjacent carbon to the cyclopropane moiety, in a distal position in relation to the carboxylic group. The distal group X is often a *cis*-cyclopropane (α-MA), a -CH (CH_3)CH(OCH_3)- (methoxy-MA), or a –CH(CH_3)CO- fragment (keto-MA). MA may be bound to the wall, generally as penta-arabinose tetramycolates. They may also not be wall bound, when they are generally present as sugar esters such as trehalose dimycolate, trehalose monomycolate, glucose and glycerol mycolates (Brennan, 2003). Arabinose mycolate was isolated from firmly bound lipids of Mycobacteria over 50 years ago (Azuma and Yamamura, 1962; 1963; Azuma et al., 1965, 1968a, 1968b and 1969). Oligosaccharide fragments from *Mycobacterium tuberculosis* have been extensively studied by mass spectrometry and nuclear magnetic resonance and by degradation (Besra et al., 1995; Uenishi et al., 2010; Miyauchi et al., 2011; Daffé et al., 1993; McNeil et al., 1991). Two-dimensional NMR has been applied in whole cells (Lee et al., 2005). The synthesis of the penta-arabinofuranyl and related fragments of *M. tuberculosis* has been described (Liu et al., 2010; Ayers et al., 1998; Mereyala et al., 1998; Backus et al., 2014; Ishiwata et al., 2006a, 2006b). Such fragments have also been found to be of value in the treatment of cancer (Sunakawa et al., 2006). Smaller fragments such as glycerol mycolate, (Kremer et al., 2005; Andersen et al., 2009a, 2009b; Bhowruth et al., 2009; Hattori et al., 2011 and 2014) and arabinoglycerol mycolate (**2**), (Watanabe et al., 1999; Mohammed et al., 2015) have also been reported and, in the former case, have significant biological activity.

In 1992, a new glycolipid, 5-mycoloyl-β-arabinofuranosyl-(1→2)-5-mycoloyl-α-arabinofuranosyl-(1→1′)-glycerol (dimycoloyl diarabinoglycerol, DMAG) (**3**), was isolated from the *Mycobacterium avium* – *Mycobacterium intracellulare* complex (MAC) (Watanabe et al., 1992). High IgM titres against the glycolipid **3** were observed in ELISA assays of serum from individuals who were culture positive for MAC infection, implying that this serodiagnosis detects the disease in an active phase (Honda et al., 1993). A similar glycolipid mixture has been isolated from *Mycobacterium bovis* Bacille Calmette-Guérin or *Mycobacterium marinum* and from *M. tuberculosis* (Rombouts et al., 2012). The DMAG from *M. marinum* (Mma_DMAG) was rich in keto- and methoxy MA rather than α-MA, and lacked *trans*-cyclopropane MA. It was found to induce the secretion of pro-inflammatory cytokines (TNF-α, IL-8, IL-1β) in human macrophage THP-1 cells and to trigger the expression of ICAM-1 and CD40 cell surface antigens. In addition, various genes encoding pro-inflammatory factors were up-regulated after exposure to Mma_DMAG. A range of other genes related to immune and inflammatory responses were modulated, suggesting that DMAG may

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[*] Corresponding author.
E-mail address: chs028@bangor.ac.uk (M.S. Baird).
[1] Current address: College of Education for Pure Sciences, Chemistry Department, Mosul University, Iraq.
[2] Current address: College of Science, Chemistry Dept., Kirkuk University, Iraq.

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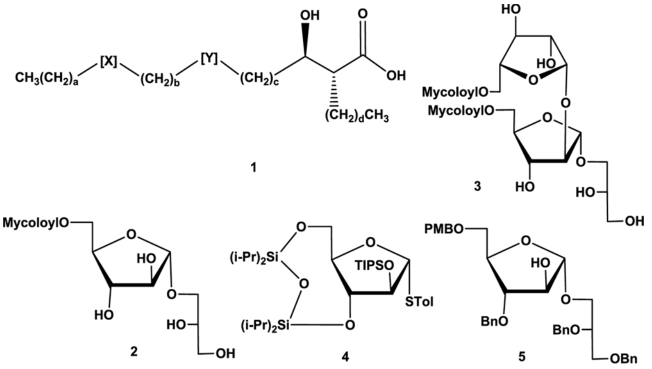


Scheme 1. Structures **1** – **5**; natural mixtures of mycolic acids comprise a range of different values of a – d.

drive host-pathogen interactions and participate in the immunopathogenesis of mycobacterial infections (Elass et al., 2012).

We now report the synthesis of a set of diacyl and dimycoloyl diarabinoglycerols by coupling fragments **4** and **5**, producing the diarabinoglycerol framework as a single β-isomer, followed by esterification and deprotection.

2. Experimental

2.1. General

Chemicals used were obtained from commercial suppliers (Sigma, Aldrich, and Alfa Aesar) or prepared from them by the methods described. Solvents which were required to be dry, e.g. ether, tetrahydrofuran were dried over sodium wire and benzophenone under nitrogen, while dichloromethane and HMPA were dried over calcium hydride. Petroleum spirit (petrol) was of boiling point 40–60 °C. All reagents and solvents used were of reagent grade unless otherwise stated. Silica gel (Merck 7736) and silica gel plates used for column and thin layer chromatography were obtained from Aldrich; separated components were detected using variously UV light, I_2 and phosphomolybdic acid solution in IMS followed by charring. Anhydrous $MgSO_4$ was used to dry organic solutions. Infra-red (IR) spectra were carried out on a Perkin-Elmer 1600 F.T.I.R. spectrometer as liquid films or KBr disc (solid). Melting points were measured using a Gallenkamp melting point apparatus. NMR spectra were carried out on a Bruker Avance 400 or 500 spectrometers. $[\alpha]_D$ values were recorded in $CHCl_3$ on a POLAAR 2001 optical activity polarimeter. Mass spectra were recorded on a Bruker MALDI-TOF MS to an accuracy of 1 d.p.; accurate mass values were carried out by the EPSRC Mass Spectrometry Service in Swansea University or in Bristol University.

2.2. 2',3'-Di-O-benzyl-L-glycerol-(1'→1)-2-O-Benzoyl-3,5-O-(tetraisopropylsiloxane-1,3-diyl)-α-D-arabinofuranoside (8)

Molecular sieves 4 Å (5.6 g) were added to a stirred solution of α-D-arabinofuranoside **(6)** (Reddy et al., 2012; D'Souza et al., 2000) (15.4 g, 0.0255 mol) and 2',3'-di-*O*-benzyl-L-glycerol **(7)** (Ashton et al., 1985) (6.9 g, 0.025 mol) in dry CH_2Cl_2 (25 mL) at rt under nitrogen. The mixture was stirred for 30 min then cooled to −35 °C and *N*-iodosuccinimide (9.38 g, 0.0383 mol) was added, followed by silver trifluoromethanesulfonate (1.17 g, 0.00460 mol). The mixture was stirred at −35 °C until the colour turned a red/dark brown colour and TLC showed no starting material, then quenched by the addition of triethylamine (2 mL), diluted with CH_2Cl_2 (50 mL), filtered through celite and the solvent was evaporated. Chromatography on silica eluting with hexane/ethyl acetate (10:1) afforded the title compound **8** as a colourless thick oil (17 g, 91%) [MALDI–Found $(M + Na)^+$: 773.3; $C_{41}H_{58}NaO_9Si_2$, requires: 773.3], $[\alpha]^{22}_{D}$ +2.6 (*c* 4.3, $CHCl_3$); δ_H (400 MHz, $CDCl_3$): 8.01 – 7.97 (2H, m), 7.55 (1H, t, *J* 7.4 Hz), 7.41 (2H, t, *J* 7.7 Hz), 7.35 – 7.15 (10H, m), 5.41 (1H, br.dd, *J* 1.4, 4.9 Hz), 4.98 (1H, br.d, *J* 1.0 Hz), 4.67 (2H, br.s), 4.50 (2H, br.s), 4.45 (1H, dd, *J* 5.0, 7.4 Hz), 4.04 – 3.95 (2H, incl. br. dd *J* 3.0, 9.9 Hz at 3.99), 3.92 (1H, dd, *J* 5.5, 13.2 Hz), 3.86 – 3.76 (2H, m), 3.67 – 3.59 (2H, incl. br. dd *J* 4.2, 10.0 Hz at 3.63), 3.58 (1H, dd, *J* 5.0, 10.2 Hz), 1.32 – 0.75 (28H, m); δ_C (101 MHz, $CDCl_3$): 165.5, 138.7, 138.3, 133.2, 129.7, 128.4, 128.3, 128.2, 127.8, 127.6, 127.5, 127.4, 105.6, 84.4, 81.2, 76.2, 73.4, 72.3, 70.3, 67.7, 61.8, 31.6, 22.6, 17.5, 17.4, 17.3, 17.0, 16.9, 13.4, 13.2, 12.8, 12.5; ν_{max}: 3065, 3031, 2945, 2868,1717, 1105, 884, 712 cm^{-1}.

2.3. 2',3'-Di-O-benzyl-L-glycerol-(1'→1)-2-O-allyl-3-O-benzyl-5-O-tert-butyldiphenylsilyl-α-D-arabinofuranoside (9)

(i) Sodium methoxide in methanol (10 mL, 0.1 M) was added to a stirred solution of compound **(8)** (15.6 g, 0.0207 mol) in dry CH_3OH:CH_2Cl_2 (25 mL, 1:1) at rt and the mixture was stirred for 0.5 h then neutralized with Amberlite IR-120 (H^+), the resin was filtered off and the solvent was removed; chromatography on silica eluting with petrol/ethyl acetate (5:1) afforded 2',3'-di-*O*-benzyl-L-glycerol-(1'→1)-3,5-*O*-(tetraisopropylsiloxane-1,3-diyl)-α-D-arabinofuranoside as a thick colourless oil (12 g, 89%) [Found–MALDI $(M + Na)^+$: 669.3, $C_{34}H_{54}NaO_8Si_2$, requires 669.3], $[\alpha]^{20}_{D}$ -40 (*c* 0.10, $CHCl_3$) which showed δ_H (400 MHz, $CDCl_3$): 7.35 – 7.17 (10H, m), 4.79 (1H, br.d, *J* 2.4 Hz), 4.63 (2H, br.s), 4.49 (2H, br.s), 4.14 – 4.04 (2H, m), 3.89 (1H, dd, *J* 3.1, 12.7 Hz), 3.86 (1H, br.d, *J* 3.7 Hz), 3.84 – 3.79 (1H, m), 3.77 (1H, br.dd, *J* 3.7, 7.2 Hz), 3.72 (1H, p, *J* 4.8 Hz), 3.57 (2H, d, *J* 4.8 Hz), 3.54 (1H, dd, *J* 4.4, 10.5 Hz), 1.80 (1H, br s), 1.12 – 0.72 (28H, m); δ_C (101 MHz, $CDCl_3$): 138.5, 138.4, 128.3, 128.3, 127.8, 127.7, 127.6, 107.5, 82.6, 80.8, 76.9, 73.4, 72.2, 70.2, 67.9, 61.4, 31.6, 22.6, 17.4, 17.3, 17.1, 17.05, 17.0, 13.5, 13.1, 12.8, 12.5; ν_{max}: 3402,3062, 2946, 2867, 1467, 1035, 884, 695 cm^{-1}.

(ii) A solution of the above α-D-arabinofuranoside (11.9 g, 0.0183 mol) in dry DMF (20 mL) was added dropwise to a stirred suspension of NaH (0.88 g, 0.036 mol, 60% dispersion in mineral oil) at 0 °C under nitrogen. The mixture was stirred for 10 min, when allyl bromide (2.66 g, 1.90 mL, 0.022 mol) was added, stirred at 0 °C for 2 h, then quenched by slow addition of CH_3OH (1 mL) and evaporated under reduced pressure to give an oil. This was diluted with ethyl acetate (100 mL), and washed with water (50 mL), brine (50 mL), dried and evaporated under reduced pressure. Chromatography on silica eluting with petrol/ethyl acetate (5:1) gave 2',3'-di-*O*-benzyl-L-glycerol-(1'→1)-2-*O*-allyl-3,5-*O*-(tetraisopropyl-siloxane-1,3-diyl)-α-D-arabinofuranoside as a colourless thick oil (9.5 g, 75%) [Found–MALDI $(M + Na)^+$: 709.3, $C_{37}H_{58}NaO_8Si_2$, requires:709.3], $[\alpha]^{22}_{D}$ +72 (*c* 0.10, $CHCl_3$); δ_H (400 MHz, $CDCl_3$): 7.44 – 7.05 (10H, m), 5.81 (1H, ddt, *J* 5.4, 10.6, 17.3 Hz), 5.20 (1H, dd, *J* 1.6, 17.3 Hz), 5.09 (1H, dd, *J* 1.4, 10.6 Hz), 4.84 (1H, br.d, *J* 2.4 Hz), 4.63 (2H, br.s), 4.49 (2H, br.s), 4.14 (1H, dd, *J* 6.0, 8.3 Hz), 4.05 – 3.93 (2H, m), 3.92 – 3.81 (3H, m), 3.80 – 3.77 (2H, incl. br. dd *J* 3.5, 8.5 Hz at 3.78), 3.76 – 3.70 (1H, m), 3.64 – 3.55 (2H, incl. br. dd *J* 4.1, 10.7 Hz at 3.58), 3.54 (1H, dd, *J* 3.4, 9.3 Hz), 1.11 – 0.83 (28H, m); δ_C (101 MHz, $CDCl_3$): 138.6, 138.3, 134.3, 128.3, 128.2, 127.7, 127.6, 127.55, 127.5, 116.8, 106.0, 89.5, 80.5, 77.1, 76.1, 73.4, 72.1, 71.4, 70.4, 67.5, 61.5, 17.5, 17.3, 17.2, 17.1, 17.05, 17.0, 13.5, 13.1, 12.8, 12.5; ν_{max}: 3082, 3069, 2927, 2867.

(iii) Tetrabutylammonium fluoride (26.2 mL, 0.0904 mol, 1.0 M) was added dropwise to a stirred solution of the above α-D-arabinofuranoside (9.0 g, 0.01 mol) in anhydrous THF (25 mL) at 0 °C under nitrogen. The mixture was allowed to reach rt and stirred for 2 h, then diluted with ethyl acetate (100 mL), washed with sat. aq. NH_4Cl (50 mL) and brine (50 mL). The organic layer was dried and concentrated to give a residue; chromatography on silica eluting with hexane/ethyl acetate (3:1) gave 2',3'-di-*O*-benzyl-L-glycerol-(1'→1)-2-*O*-allyl-α-D-arabino-furanoside as a colourless thick oil (5.5 g, 95%) [Found–MALDI $(M + Na)^+$: 467.2, $C_{25}H_{32}NaO_7$, requires: 467.2], $[\alpha]^{20}_{D}$ +80 (*c* 0.10, $CHCl_3$); which showed δ_H (400 MHz, $CDCl_3$): 7.33 –

7.19 (10H, m), 5.81 (1H, ddt, *J* 5.6, 10.8, 17.2 Hz), 5.22 (1H, dd, *J* 1.5, 17.2 Hz), 5.14 (1H, dd, *J* 1.3, 10.8 Hz), 5.00 (1H, br.s), 4.61 (1H, d, *J* 11.9 Hz), 4.57 (1H, d, *J* 11.9 Hz), 4.48 (2H, br.s), 4.04 – 3.92 (4H, m), 3.84 – 3.77 (2H, incl. br. dd *J* 5.7, 10.3 Hz at 3.81), 3.72 (1H, br.dd, *J* 4.8, 9.7 Hz), 3.68 (1H, br.d, *J* 3.1 Hz), 3.63 (1H, dd, *J* 3.7, 11.8 Hz), 3.58 – 3.54 (1H, m), 3.53 – 3.49 (2H, incl. br.d, *J* 5.1 Hz at 3.52), 1.80 (2H, br s); δ_C (101 MHz, CDCl$_3$): 138.1, 137.9, 133.6, 128.4, 128.3, 127.8, 127.75, 127.7, 117.9, 105.6, 86.9, 86.5, 76.5, 75.3, 73.5, 72.1, 70.6, 69.6, 66.7, 62.4; ν_{max}: 3437, 3031, 2940, 2867, 1651, 1454, 1055, 668 cm^{-1}.

(iv) *tert*-Butylchlorodiphenylsilane (9.2 g, 0. 033 mol) was added to a stirred solution of the above α-D-arabinofuranoside (15 g, 0.033 mol) in dry DMF (100 mL), followed by the addition of imidazole (5.7 g, 0.084 mol) at 0 °C under nitrogen. The mixture was allowed to reach rt and stirred for 25 min, then diluted with ethyl acetate (100 mL) and water (25 mL). The aqueous layer was re-extracted with ethyl acetate (2 × 100 mL). The combined organic layers were washed with water (100 mL), brine (100 mL), dried and the solvent was evaporated under reduced pressure. Chromatography on silica eluting with hexane/ ethyl acetate (4:1) afforded 2',3'-di-*O*-benzyl-L-glycerol-(1'→1)-2-*O*-allyl-5-*O*-*tert*-butyldiphenylsilyl-α-D-arabinofuranoside as a colourless thick oil (15 g, 65%) [MALDI–Found (M + NH$_4$)$^+$: 700.3661; C$_{41}$H$_{54}$O$_7$SiN requires: 700.3664], $[\alpha]^{22}_D$ +26.5 (*c* 1.27, CHCl$_3$); δ_H (400 MHz, CDCl$_3$): 7.66 – 7.55 (4H, m), 7.41 – 7.17 (16H, m), 5.77 (1H, ddt, *J* 5.5, 10.7, 17.2 Hz), 5.18 (1H, dd, *J* 1.0, 17.2 Hz), 5.11 (1H, dd, *J* 0.5, 10.7 Hz), 4.95 (1H, br.s), 4.62 (1H, d, *J* 12.1 Hz), 4.58 (1H, d, *J* 12.1 Hz), 4.48 (2H, br.s), 4.11 – 3.98 (2H, incl. br. dd *J* 3.5, 9.6 Hz at 4.03), 3.97 – 3.87 (2H, incl. br. d *J* 5.4 Hz at 3.93), 3.83 – 3.75 (3H, incl. br. dd *J* 5.5, 10.5 Hz at 3.79), 3.74 – 3.69 (1H, m), 3.66 (1H, dd, *J* 6.5, 10.2 Hz), 3.60–346 (3H, incl. br. q *J* 4.7 Hz at 3.54), 2.62 (1H, br s), 1.02 (9H, s); δ_C (101 MHz, CDCl$_3$): 138.3, 138.0, 135.6, 135.5, 134.0, 133.3, 133.2, 129.7, 128.4, 128.3, 127.75, 127.7, 127.65, 127.6, 127.55, 117.3, 106.0, 87.8, 84.9, 76.6, 76.5, 73.4, 72.0, 70.6, 69.9, 66.8, 64.3, 26.8, 19.2; ν_{max}: 3445, 3069, 3031, 2930, 2859,1590, 1471, 1110, 858, 740 cm^{-1}.

(v) A solution of the above α-D-arabinofuranoside (9.7 g, 0.014 mol) in dry DMF (100 mL) was added dropwise to a stirred suspension of NaH (0.68 g, 0.028 mol, 60% dispersion in mineral oil) at 0 °C under nitrogen atmosphere. The mixture was stirred for 30 min, then benzyl bromide (2.5 mL, 3.6 g, 0.021 mol) in dry DMF (5 mL) was added. The mixture was stirred at rt for 10 h then quenched slowly with CH$_3$OH (10 mL) and H$_2$O (15 mL) and diluted with ether (200 mL). The aqueous layer was extracted with ether (2 × 100 mL). The combined extracts were washed with water (100 mL), brine (100 mL), dried and the solvent was evaporated under reduced pressure. Chromatography on silica eluting with petrol/ethyl acetate (5:1) gave the title compound **9** as a colourless thick oil (8.1 g, 72%) [MALDI–Found (M + NH$_4$)$^+$: 790.4132; C$_{48}$H$_{60}$O$_7$SiN requires: 790.4134], $[\alpha]^{22}_D$ +28 (*c* 3.9, CHCl$_3$); δ_H (400 MHz, CDCl$_3$): 7.79–756 (4H, incl. br. dd *J* 3.9, 10.8 Hz at 7.66), 7.47 – 7.14 (21H, m), 5.84 (1H, ddt, *J* 5.5, 10.7, 17.2 Hz), 5.24 (1H, dd, *J* 1.3, 17.2 Hz), 5.16 (1H, dd, *J* 0.9, 10.7 Hz), 5.01 (1H, br.s), 4.70 (1H, d, *J* 12.0 Hz), 4.66 (1H, d, *J* 12.0 Hz), 4.59 (1H, d, *J* 11.9 Hz), 4.54 – 4.48 (3H, m), 4.13 (1H, br.q, *J* 4.6 Hz), 4.03 – 3.89 (4H, m), 3.85 (1H, dd, *J* 5.1, 10.2 Hz), 3.82 – 3.73 (3H, incl. br. dd *J* 4.8, 8.1 Hz at 3.79), 3.67 – 3.56 (3H, m), 1.04 (9H, s); δ_C (101 MHz, CDCl$_3$): 138.6, 138.3, 138.0, 135.7, 135.6, 134.1, 133.5, 133.4, 129.6, 129.5, 128.3, 128.2, 127.7, 127.65, 127.6, 127.55, 127.5, 127.45, 127.4, 117.2, 106.4, 88.0, 77.0, 73.3, 72.1, 72.0, 70.6, 70.3, 67.0, 63.7, 26.8, 19.3; ν_{max}: 3068, 3031, 2929, 2859, 1588, 1454, 1027, 823, 738 cm^{-1}.

2.4. 2',3'-Di-O-benzyl-L-glycerol-(1'→1)-3-O-benzyl-5-p-methoxybenzyl-α-D-arabinofuranoside (5)

(i) Tetrabutylammonium fluoride (7.0 mL, 7.0 mmol, 1.0 M) was added dropwise to a stirred solution of α-D-arabinofuranoside **(9)** (5.2 g, 0.0067 mol) in anhydrous THF (50 mL) at 0 °C under nitrogen. The mixture was allowed to reach rt and stirred for 16 h then diluted with ethyl acetate (100 mL) and water (50 mL). The aqueous layer was re-extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with sat. aq. NH$_4$Cl (50 mL), brine (50 mL), dried and concentrated. Chromatography on silica eluting with petrol/ethyl acetate (5:1) to give 2',3'-di-*O*-benzyl-L-glycerol-(1'→1)-2-*O*-allyl-3-*O*-benzyl-α-D-arabinofuranoside as a colourless thick oil (3.3 g, 91%) [MALDI–Found (M + NH$_4$)$^+$: 552.2948; C$_{32}$H$_{42}$O$_7$N requires: 552.2956], $[\alpha]^{22}_D$ +36 (*c* 3.3, CHCl$_3$); δ_H (400 MHz, CDCl$_3$): 7.38 – 7.28 (15H, m), 5.87 (1H, ddt, *J* 5.6, 10.7, 17.2 Hz), 5.27 (1H, dd, *J* 1.5, 17.2 Hz), 5.20 (1H, dd, *J* 1.1, 10.7 Hz), 5.03 (1H, br.s), 4.70 (2H, br.s), 4.66 (1H, d, *J* 11.8 Hz), 4.58 – 4.49 (3H, m), 4.13 (1H, br.p, *J* 3.4 Hz), 4.01 (1H, br.dd, *J* 4.4, 11.8 Hz), 3.99 – 3.95 (2H, incl. br. d *J* 10.6 Hz at 3.98), 3.94 (1H, br.dd, *J* 2.6, 6.2 Hz), 3.86 (1H, dd, *J* 5.2, 10.3 Hz), 3.82 (1H, dd, *J* 5.3, 9.6 Hz), 3.79 (1H, br.d, *J* 9.7 Hz), 3.67 – 3.63(2H, incl. br. dd *J* 6.3, 7.4 Hz at 3.64), 3.63 – 3.59 (2H, incl. br. d *J* 10.5 Hz at 3.62), 1.82 (1H, br s); δ_C (101 MHz, CDCl$_3$): 138.6, 138.2, 137.8, 133.9, 128.4, 128.35, 128.3, 127.8, 127.75, 127.7, 127.6, 127.5, 117.6, 106.4, 87.6, 82.8, 82.2, 76.9, 73.4, 72.3, 72.2, 70.7, 70.1, 67.1, 62.2; ν_{max}: 3453, 3063, 3031, 2923, 2870, 1603, 1453, 1064, 850, 739 cm^{-1}.

(ii) The above α-D-arabinofuranoside (3.1 g, 0.0057 mol) in dry DMF (10 mL) was added dropwise to a stirred suspension of NaH (0.25 g, 0.010 mol, 60% dispersion in mineral oil) at 0 °C under nitrogen, then stirred for 30 min, when freshly prepared *p*-methoxybenzyl bromide (1.4 g, 0.0069 mol) was added. The mixture was stirred at 0 °C for 2 h then quenched with slow addition of CH$_3$OH (1 mL) and evaporated; the oily residue was diluted with ethyl acetate (50 mL). The organic layer was washed with water (25 mL), brine (25 mL), dried and evaporated. Chromatography on silica eluting with petrol/ethyl acetate (5:1) gave 2',3'-Di-*O*-benzyl-L-glycerol-(1'→1)-2-*O*-allyl-3-*O*-benzyl-5-*p*-methoxy-benzyl-α-D-arabinofuranoside as a thick colourless oil (2.9 g, 76%) [MALDI–Found (M + NH$_4$)$^+$: 672.3526; C$_{40}$H$_{50}$O$_8$N requires: 672.3531], $[\alpha]^{22}_D$ +41 (*c* 1.6, CHCl$_3$); δ_H (400 MHz, CDCl$_3$): 7.37 – 7.26 (15H, m), 7.24 (2H, d, *J* 8.7 Hz), 6.86 (2H, d, *J* 8.6 Hz), 5.86 (1H, ddt, *J* 5.5, 10.7, 17.2 Hz), 5.25 (1H, dd, *J* 1.6, 17.2 Hz), 5.18 (1H, dd, *J* 1.3, 10.7 Hz), 5.03 (1H, br.s), 4.71 (1H, d, *J* 12.1 Hz), 4.68 (1H, d, *J* 12.1 Hz), 4.61 (1H, d, *J* 11.9 Hz), 4.54 (3H, br.s), 4.51 (1H, d, *J* 11.7 Hz), 4.47 (1H, d, *J* 11.7 Hz), 4.22 – 4.15 (1H, m), 4.03 – 3.91 (3H, m), 3.88 (1H, dd, *J* 5.2, 10.5 Hz), 3.86 (1H, br.d, *J* 6.5 Hz), 3.84 – 3.75 (4H, incl. s at 3.8 for O*CH$_3$*), 3.66 – 3.58 (4H, m), 3.55 (1H, dd, *J* 5.2, 10.7 Hz); δ_C (101 MHz, CDCl$_3$): 138.7, 138.3, 138.0, 134.1, 130.2, 129.4, 128.8, 128.4, 128.3, 127.75, 127.7, 127.6, 127.5, 127.45, 117.4, 113.7, 106.4, 88.1, 83.7, 80.8, 73.4, 73.0, 72.2, 70.8, 70.4, 69.3, 67.2, 55.3; ν_{max}: 3064, 3030, 2912, 2864, 1612, 1513, 1454, 1106, 820, 738 cm^{-1}.

(iii) Palladium (II) chloride (0.30 g, 0.0017 mol) was added to a stirred solution of the above α-D-arabinofuranoside (5.7 g, 0.0087 mol) in dry CH$_2$Cl$_2$:MeOH (0.6:5, 5 mL) at rt. The mixture was stirred for 16 h then quenched with triethylamine (1 mL) and evaporated under reduced pressure. Chromatography on silica eluting with petrol/ethyl acetate (4:1) gave the title compound **5** as a pale yellow thick oil (4.5 g, 84%) [MALDI–Found (M + NH$_4$)$^+$: 632.3209; C$_{37}$H$_{46}$O$_8$N requires: 632.3218], $[\alpha]^{22}_D$ +60 (*c* 4.6, CHCl$_3$); δ_H (400 MHz, CDCl$_3$): 7.38 – 7.26 (15H, m), 7.23 (2H, d, *J* 8.5 Hz), 6.89 (2H, d, *J* 8.6 Hz), 5.03 (1H, br.s), 4.74 (1H, d, *J* 12.1 Hz), 4.68 (1H, d, *J* 12.1 Hz), 4.66 (1H, d, *J* 11.9 Hz), 4.58 (1H, d, *J* 11.9 Hz), 4.51 (2H, br.s), 4.49 (1H, d, *J* 11.7 Hz), 4.44 (1H, d, *J* 11.7 Hz), 4.26 (1H, br.d, *J* 2.4 Hz), 4.18 (1H, d, *J* 10.8 Hz), 3.89 (1H, dd, *J* 5.4, 10.4 Hz), 3.87 (1H, br.d, *J* 3.1 Hz), 3.85 – 3.79 (4H, incl. s at 3.82 for O*CH$_3$*), 3.68 – 3.63 (3H, m), 3.61 (1H, dd, *J* 5.5, 10.2 Hz), 3.49 (1H, dd, *J* 2.1, 10.4 Hz), 3.39 (1H, d, *J* 10.8 Hz); δ_C (101 MHz, CDCl$_3$): 159.5, 138.8, 138.4, 137.8, 129.5, 129.1, 128.4, 128.3, 128.2, 127.75, 127.7, 127.65, 127.55, 127.45, 127.4, 113.9, 109.4, 85.4, 83.6, 77.5, 76.9, 73.4, 73.3, 72.2, 71.9, 70.4, 69.4, 67.4, 55.2; ν_{max}: 3433, 3063, 3031, 2912, 2867, 1611, 1513, 1454, 1248, 1098, 820, 738, 699 cm^{-1}.

2.5. 2′,3′-Di-O-benzyl-L-glycerol-(1′→1)-2-O-(triisopropylsilyl)-3,5-O-(tetraiso-propylsiloxane-1,3-diyl)-β-D-arabinofuranosyl-(1→2)-3-O-benzyl-5-p-methoxybenzyl-α-D-arabinofuranoside (10)

Molecular sieves 4 Å (5 g) was added to a stirred solution of -D-arabinofuranoside **(5)** (4.3 g, 0.0069 mol) and α-D-arabinofuranoside **(4)** (11.4 g, 0.0174 mol) in dry CH_2Cl_2 (50 mL) at rt under nitrogen. The mixture was stirred for 30 min then cooled to −78 °C and *N*-iodo-succinimide (6.4 g, 0.026 mol) was added followed by the addition of silver trifluoromethanesulfonate (0.71 g, 0.0028 mol). The mixture was stirred until the colour turned red/dark brown at -60 °C, quenched with triethylamine (4 mL) until the colour turned yellow, then diluted with CH_2Cl_2 (100 mL) and filtered through celite. The solvent was evaporated. The residue was purified by chromatography on silica eluting with hexane/ethyl acetate (4:1) affording the title compound **10** as a yellow thick oil (6.9 g, 86%) [MALDI–Found $(M + NH_4)^+$:1162.6495; $C_{63}H_{100}O_{13}Si_3N$ requires: 1162.6497], $[\alpha]^{22}_{D}$ +4.5 (*c* 0.97, $CHCl_3$); δ_H (400 MHz, $CDCl_3$): 7.28 – 7.18 (15H, m), 7.15 (2H, d, *J* 8.5 Hz), 6.78 (2H, d, *J* 8.5 Hz), 4.96 (1H, br.s), 4.79 (1H, br.d, *J* 4.3 Hz), 4.63 (1H, d, *J* 12.0 Hz), 4.59 (2H, d, *J* 12.0 Hz), 4.44 (2H, br.s), 4.43 (1H, d, *J* 12.0 Hz), 4.39 (2H, br.s), 4.34 (1H, br.dd, *J* 5.7, 7.3 Hz), 4.20 – 4.17 (1H, br.m), 4.15 (1H, dd, *J* 4.7, 9.2 Hz), 4.12 (1H, br.t, *J* 5.1 Hz), 3.87 (1H, d, *J* 5.7 Hz), 3.86 (1H, d, *J* 6.8 Hz), 3.84 – 3.76 (3H, m), 3.75 – 3.70 (4H, incl. s at 3.73 for O*CH₃*), 3.56 (1H, dd, *J* 3.9, 9.7 Hz), 3.53 (1H, br.d, *J* 5.3 Hz), 3.51 – 3.47 (2H, incl. br. dd *J* 4.6, 10.5 Hz at 3.49), 3.45 (1H, dd, *J* 5.9, 10.8 Hz), 1.04 – 0.92 (49H, m); δ_C (101 MHz, $CDCl_3$): 159.1, 138.8, 138.4, 138.0, 130.2, 129.3, 128.3, 128.25, 128.2, 127.7, 127.65, 127.6, 127.5, 127.4, 127.3, 113.7, 106.2, 100.6, 85.9, 84.4, 82.0, 81.5, 79.4, 79.1, 77.05, 73.3, 72.9, 72.2, 72.15, 70.6, 69.8, 67.4, 66.6, 55.2, 18.0, 17.95, 17.6, 17.5, 17.4, 17.3, 17.2, 17.1, 17.0, 16.9, 13.4, 13.3, 13.0, 12.7, 12.4; ν_{max}: 3064, 3031, 2943, 2867, 1513,1248, 736, 695 cm^{-1}.

2.6. 2′,3′-Di-O-benzyl-L-glycerol-(1′→1)-β-D-arabinofuranosyl-(1→2)-3-O-benzyl-5-p-methoxybenzyl-α-D-arabinofuranoside (11)

TBAF (17.1 mL, 0.0202 mol, 1.0 M) was added dropwise with stirring to α-D-arabinofuranoside **(10)** (6.5 g, 0.0056 mol) in dry THF (100 mL) at 0 °C under nitrogen. The mixture was stirred at rt for 6 h, then diluted with ethyl acetate (100 mL) and water (10 mL). The aqueous layer was re-extracted with ethyl acetate (3 × 25 mL). The combined organic layers were washed with sat. aq. NH_4Cl (25 mL), brine (25 mL), and concentrated; chromatography on silica eluting with dichloro-methane/methanol (20:1) gave the title compound **11** as a thick colourless oil (4.0 g, 95%) [MALDI–Found $(M + NH_4)^+$: 764.3639; $C_{42}H_{54}O_{12}N$ requires: 764.3641], $[\alpha]^{24}_{D}$ +16 (*c* 0.50, $CHCl_3$); δ_H (400 MHz, $CDCl_3$): 7.28 – 7.17 (15H, m), 7.15 (2H, d, *J* 8.6 Hz), 6.79 (2H, d, *J* 8.6 Hz), 4.96 (1H, br.s), 4.94 (1H, br.d, *J* 4.7 Hz), 4.60 (2H, br.s), 4.56 (1H, d, *J* 11.9 Hz), 4.44 (3H, br.s), 4.40 (1H, d, *J* 11.6 Hz), 4.33 (1H, d, *J* 11.6 Hz), 4.23 (1H, m), 4.06 (1H, br.p, *J* 3.6 Hz), 4.01 (1H, dd, *J* 2.7, 6.1 Hz), 3.95 (1H, t, *J* 7.2 Hz), 3.87 (1H, br.dd, *J* 5.9, 10.6 Hz), 3.79 (1H, br.dd, *J* 4.8, 10.5 Hz), 3.76 (1H, br.dd, *J* 3.3, 6.8 Hz), 3.73 – 3.69 (4H, incl. s at 3.7 for O*CH₃*), 3.61 – 3.47 (6H, m), 3.39 (1H, dd, *J* 3.9, 10.9 Hz), 2.70 (2H, br s), 2.28 (1H, br s); δ_C (101 MHz, $CDCl_3$): 159.3, 138.5, 138.2, 137.8, 129.8, 129.7, 128.4, 128.35, 128.3, 127.8, 127.7, 127.6, 127.55, 127.5, 113.8, 106.2, 101.0, 86.5, 82.9, 82.4, 81.2, 78.1, 76.9, 75.0, 73.4, 73.1, 72.3, 72.2, 70.1, 68.6, 67.3, 62.3, 55.3; ν_{max}: 3430, 3063, 3031, 2923, 2868, 1612, 1514, 1100, 740, 699 cm^{-1}.

2.7. 2′,3′-Di-O-benzyl-L-glycerol-(1′→1)-5-O-tert-butyldiphenylsilyl-β-D-arabinofuranosyl-(1→2)-3-O-benzyl-5-p-methoxybenzyl-α-D-arabinofuranoside

tert-Butylchlorodiphenylsilane (1.39 mL, 1.47 g, 0.00535 mol) was added with stirring to arabinofuranoside **(11)** (4.0 g, 0.005 mol) in dry DMF (5 mL), followed by the addition of imidazole (0.73 g, 0.010 mol) at 0 °C under nitrogen. The mixture was allowed to reach rt, stirred for 30 min, then diluted with ethyl acetate (25 mL) and water (5 mL). The aqueous layer was re-extracted with ethyl acetate (2 × 25 mL). The combined organic layers were washed with water (10 mL), brine (10 mL), dried and evaporated under reduced pressure. Chromatography on silica eluting chloroform/methanol (20:1) afforded the title compound as a colourless thick oil (4.1 g, 77%) [MALDI–Found $(M + NH_4)^+$: 1002.4816; $C_{58}H_{72}O_{12}SiN$, requires: 1002.4818], $[\alpha]^{22}_{D}$ -6.3 (*c* 0.38, $CHCl_3$); δ_H (400 MHz, $CDCl_3$): 7.69 – 7.63 (4H, m), 7.46 – 7.16 (21H, m), 7.11 (2H, dd, *J* 2.9, 8.0 Hz), 6.85 (2H, d, *J* 8.0 Hz), 5.03 (1H, br.d, *J* 4.5 Hz), 5.02 (1H, br.s), 4.69 (1H, d, *J* 12.0 Hz), 4.66 (1H, d, *J* 12.0 Hz), 4.56 – 4.48 (4H, m), 4.45 (1H, d, *J* 11.6 Hz), 4.40 (1H, d, *J* 11.6 Hz), 4.31 – 4.29 (1H, m), 4.25 (1H, d, *J* 11.7 Hz), 4.14 (1H, br.p, *J* 5.1 Hz), 4.01 – 3.84 (4H, m), 3.82 (1H, br.dd, *J* 3.8, 9.1 Hz), 3.79 – 3.75 (4H, incl. s at 3.77 for O*CH₃*), 3.71 (1H, dd, *J* 6.6, 10.0 Hz), 3.65 – 3.60 (3H, incl. br. dd *J* 4.9, 8.9 Hz at 3.63), 3.54 (1H, dd, *J* 3.3, 10.8 Hz), 3.46 (1H, dd, *J* 4.9, 10.8 Hz), 2.43 (1H, d, *J* 9.4 Hz), 2.16 (1H, d, *J* 2.7 Hz), 1.07 (9H, s); δ_C (101 MHz, $CDCl_3$): 159.2, 138.6, 138.3, 137.8, 135.8, 135.7, 135.6, 135.5, 133.1, 133.0, 130.0, 129.95, 129.9, 129.6, 129.5, 128.4, 128.35, 128.3, 128.2, 128.0, 127.9, 127.85, 127.8, 127.7, 127.65, 127.6, 127.55, 127.5, 113.8, 106.3, 100.8, 85.9, 83.8, 81.6, 81.4, 78.2, 77.4, 77.0, 73.4, 73.0, 72.3, 72.2, 70.2, 69.1, 67.3, 66.1, 55.3, 26.9, 19.2; ν_{max}: 3438, 3067, 3031, 2930, 2859, 1612, 1513, 1248, 739, 700 cm^{1}.

2.8. 2′,3′-Di-O-benzyl-L-glycerol-(1′→1)-2,3-di-O-benzyl-5-O-tert-butyldiphenylsilyl-β-D-arabinofuranosyl-(1→2)-3-O-benzyl-5-p-methoxybenzyl-α-D-arabinofuranoside (12)

α-D-arabinofuranoside (section **4.7**) (4.0 g, 0.0040 mol) in dry DMF (5 mL) was added dropwise to a stirred suspension of NaH (0.39 g, 0.016 mol, 60% dispersion in mineral oil) at 0 °C under nitrogen. The mixture was stirred for 0.5 h then benzyl bromide (1.44 mL, 2.08 g, 0.012 mol) in dry DMF (5 mL) was added. The mixture was stirred at rt for 10 h, then quenched with CH_3OH (1 mL) and H_2O (5 mL) and diluted with ether (25 mL). The aqueous layer was extracted with ether (2 × 25 mL). The combined organic layers were washed with water (25 mL), brine (25 mL), dried and evaporated. Chromatography on silica eluting with petrol/ethyl acetate (4:1) gave the title compound **12** as a colourless thick oil (4.3 g, 90%) [MALDI–Found $(M + NH_4)^+$: 1182.5751; $C_{72}H_{84}O_{12}SiN$ requires: 1182.5757], $[\alpha]^{22}_{D}$ -11 (*c* 0.38, $CHCl_3$); δ_H (400 MHz, $CDCl_3$): 7.68 – 7.64 (4H, m), 7.42 – 7.16 (31H, m), 7.08 (2H, dd, *J* 1.6, 8.0 Hz), 6.85 (2H, d, *J* 8.0 Hz), 5.08 (1H, d, *J* 4.4 Hz), 5.04 (1H, br.s), 4.70 (1H, d, *J* 12.1 Hz), 4.66 (1H, d, *J* 12.1 Hz), 4.64 (2H, br.s), 4.56 (1H, d, *J* 11.7 Hz), 4.52 (2H, br.s), 4.48 (1H, d, *J* 11.7 Hz), 4.44 (2H, d, *J* 11.5 Hz), 4.41 (2H, d, *J* 11.5 Hz), 4.29 (1H, br.d, *J* 1.9 Hz), 4.20 (1H, br.d, *J* 5.9 Hz), 4.17 (2H, br.dd, *J* 5.0, 6.1 Hz), 4.11 (1H, br.q, *J*, 6.5 Hz), 4.05 (1H, br.dd, *J* 4.5, 6.1 Hz), 3.89 (1H, dd, *J* 5.2, 10.4 Hz), 3.84 – 3.78 (6H, incl. s at 3.79 for O*CH₃*), 3.61 (3H, br.dd, *J* 4.8, 9.4 Hz), 3.53 (1H, br.dd, *J* 2.8, 9.5 Hz), 3.49 (1H, br.dd, *J* 4.7, 9.5 Hz), 1.05 (9H, s); δ_C (101 MHz, $CDCl_3$): 159.1, 138.7, 138.4, 138.2, 137.9, 137.7, 135.6, 135.5, 133.2, 133.1, 130.3, 129.8, 129.3, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.75, 127.7, 127.6, 127.55, 127.5, 127.4, 113.7, 106.0, 100.3, 85.4, 84.6, 84.1, 84.0, 82.0, 81.6, 77.1, 73.3, 72.8, 72.4, 72.3, 72.25, 72.2, 70.4, 69.9, 67.2, 66.2, 55.2, 26.8, 19.2; ν_{max}: 3065, 3031, 2930, 2860, 1612, 1513, 1248, 738, 699 cm^{-1}.

2.9. 2′,3′-Di-O-benzyl-L-glycerol-(1′→1)-2,3-di-O-benzyl-β-D-arabinofuran- osyl-(1→2)-3-O-benzyl-5-p-methoxybenzyl-α-D-arabinofuranoside (13)

TBAF (3.5 mL, 0.0038 mol, 1.0 M) was added dropwise to a stirred solution of α-D-arabinofuranoside **(12)** (4.1 g, 0.0035 mol) in dry THF (25 mL) at 0 °C under nitrogen. The mixture was allowed to reach rt and stirred for 6 h then diluted with ethyl acetate (15 mL) and water (5 mL). The aqueous layer was re-extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with sat. aq. NH_4Cl (25 mL), brine (25 mL), dried and concentrated; chromatography on silica eluting with petrol /ethyl acetate (5:2) gave the title compound **13** as a colourless thick oil (3.0 g, 93%) [MALDI–Found $(M + NH_4)^+$: 944.4574; $C_{56}H_{66}O_{12}N$ requires: 944.4580], $[\alpha]_D^{22}$ -7.1 (*c* 0.79, $CHCl_3$); δ_H (400 MHz, $CDCl_3$): 7.29 – 7.18 (25H, m), 7.16 (2H, d, *J* 8.7 Hz), 6.78 (2H, d, *J* 8.7 Hz), 4.97 (1H, d, *J* 4.5 Hz), 4.95 (1H, br.d, *J* 1.1 Hz), 4.64 (1H, d, *J* 11.7 Hz), 4.60 (2H, br.s), 4.53 (1H, d, *J* 11.5 Hz), 4.51 (1H, d, *J* 11.5 Hz), 4.47 – 4.43 (4H, m), 4.39 (1H, d, *J* 11.9 Hz), 4.38 (1H, d, *J* 11.9 Hz), 4.35 (1H, d, *J* 11.7 Hz), 4.21 (1H, br.dd, *J* 1.4, 3.5 Hz), 4.18 (1H, d, *J* 6.8 Hz), 4.09 (1H, br.p, *J* 4.1 Hz), 4.02 (1H, br.dd, *J* 3.5, 6.5 Hz), 3.95 (1H, dd, *J* 4.5, 7.3 Hz), 3.93 – 3.88 (1H, m), 3.79 (1H, dd, *J* 5.2, 10.4 Hz), 3.74 – 3.68 (4H, incl. s at 3.71 for OCH_3), 3.59 – 3.50 (5H, m), 3.48 (1H, br.d, *J* 3.7 Hz), 3.43 (1H, dd, *J* 4.9, 10.8 Hz), 2.22 (1H, br.dd, *J* 5.1, 7.8 Hz); δ_C (101 MHz, $CDCl_3$): 159.2, 138.6, 138.3, 138.1, 137.9, 137.6, 130.0, 129.5, 128.5, 128.45, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.75, 127.7, 127.65, 127.6, 127.55, 127.5, 113.8, 106.1, 100.1, 86.3, 84.1, 83.3, 82.0, 81.0, 80.7, 77.0, 73.4, 73.0, 72.6, 72.4, 72.2, 70.3, 69.1, 67.4, 63.4, 55.2; ν_{max}: 3491, 3063, 3031, 2925, 2869, 1612, 1513, 1454, 1248, 738, 699 cm^{-1}.

2.10. 2′,3′-Di-O-benzyl-L-glycerol-(1′→1)-2,3-di-O-benzyl-β-D-arabinofuran-osyl-(1→2)-3-O-benzyl-α-D-arabinofuranoside (14)

Cerium ammonium nitrate (CAN) (3.5 g, 0.0064 mol) was added with stirring to furanoside **(13)** (2.0 g, 0.002 mol) in CH_3CN: H_2O (9:1, 15 mL) at 0 °C. The mixture was allowed to reach rt, stirred for 1 h, then diluted with chloroform (25 mL), washed with aq. $NaHCO_3$ (15 mL), dried and evaporated under reduced pressure. Chromatography on silica eluting with petrol/ethyl acetate (5:2) gave the title compound **14** as a colourless thick oil (1.5 g, 89%) [MALDI–Found $(M + Na)^+$: 829.4; $C_{48}H_{54}NaO_{11}$ requires: 829.4], $[\alpha]_D^{21}$ -4.3 (*c* 0.83, $CHCl_3$); δ_H (400 MHz, $CDCl_3$): 7.64 – 6.67 (25H, m), 4.97 (1H, br.d, *J* 4.6 Hz), 4.95 (1H, br.s), 4.67 (1H, d, *J* 11.6 Hz), 4.64 (2H, br.s), 4.62 (1H, d, *J* 11.6 Hz), 4.55 (1H, d, *J* 11.6 Hz), 4.50 – 4.46 (5H, m), 4.2 – 4.17 (2H, br. dd *J* 5.6, 8.1 Hz), 4.16 (1H, br.dd, *J* 2.2, 5.6 Hz), 4.09 – 4.04 (1H, m), 4.00 (1H, dd, *J* 4.6, 7.3 Hz), 3.97 – 3.92 (1H, m), 3.80 (1H, dd, *J* 5.2, 10.2 Hz), 3.76 (1H, br.d, *J* 6.4 Hz), 3.73 (1H, br.dd, *J* 3.9, 8.3 Hz), 3.63 (1H, dd, *J* 2.9, 10.2 Hz), 3.60 – 3.48 (5H, m), 1.30 (2H, br s); δ_C (101 MHz, $CDCl_3$): 138.5, 138.2, 137.9, 137.8, 137.4, 128.5, 128.4, 128.35, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.65, 127.6, 127.55, 127.5, 106.3, 100.5, 86.4, 84.0, 83.0, 82.7, 81.9, 80.4, 76.9, 73.3, 72.6, 72.5, 72.3, 72.2, 70.1, 67.2, 63.2, 62.0; ν_{max}: 3463, 3063, 3031, 2922, 2872, 1454, 1107, 738, 698 cm^{-1}.

2.11. 2′,3′-Di-O-benzyl-L-glycerol-(1′→1)-2,3-di-O-benzyl-5-O-methane-sulfonyl-β-D-arabinofuranosyl-(1→2)-3-O-benzyl-5-O-methane-sulfonyl-α-D-arabino-furanoside (15)

Methanesulfonyl chloride (1.98 g, 1.36 mL, 17.1 mmol) and DMAP (0.10 g, 0.86 mmol) were added to a stirred solution of α-D-arabinofuranoside **(14)** (1.4 g, 1.7 mmol) in dry pyridine (10 mL) under nitrogen at rt. The mixture was stirred for 16 h then quenched with H_2O (3 mL). The organic layer was diluted with CH_2Cl_2 (10 mL) and washed with 1 N HCl (4 × 10 mL), sat. aq. $NaHCO_3$ (4 × 10 mL), dried and evaporated under reduced pressure to give a thick oil. Chromato-graphy on silica eluting with petrol/ethyl acetate (4:1) gave compound **15** as a colourless thick oil (1.4 g, 85%) [MALDI–Found $(M + Na)^+$: 985.3109; $C_{50}H_{58}NaO_{15}S_2$ requires: 985.3115]; $[\alpha]_D^{22}$ +2.8 (*c* 1.3, $CHCl_3$); δ_H (400 MHz, $CDCl_3$): 7.36 – 7.16 (25H, m), 5.01 (1H, br.d, *J* 4.4 Hz), 4.93 (1H, br.s), 4.70 (1H, d, *J* 11.7 Hz), 4.67 (1H, d, *J* 11.7 Hz), 4.63 (2H, br.s), 4.58 (1H, d, *J* 11.7 Hz), 4.51 (1H, d, *J* 11.7 Hz), 4.46 (4H, br.s), 4.32 (1H, br.q, *J* 4.6 Hz), 4.25 – 4.13 (5H, m), 4.13 – 4.07 (3H, m), 4.00 (1H, br.dd, *J* 4.4, 6.9 Hz), 3.80 (1H, dd, *J* 5.2, 10.3 Hz), 3.74 (1H, br.p, *J* 5.1 Hz), 3.60 – 3.50 (3H, incl. br. dd, *J* 4.6, 7.2 at 3.56), 2.85 (3H, s), 2.84 (3H, s); δ_C (101 MHz, $CDCl_3$): 138.5, 138.2, 137.7, 137.6, 137.2, 128.6, 128.5, 128.4, 128.35, 128.3, 128.1, 128.0, 127.95, 127.9, 127.8, 127.75, 127.7, 127.6, 127.55, 127.5, 106.4, 101.2, 85.9, 83.5, 81.1, 80.9, 78.4, 76.9, 73.3, 72.7, 72.6, 72.4, 72.3, 69.9, 69.8, 69.0, 67.3, 37.5, 37.4; ν_{max}: 3087, 3031, 2929, 2867, 1606, 1454, 1046,738, 697 cm^{-1}.

2.12. 2′,3′-Di-O-benzyl-L-glycerol-(1′→1)-2,3-di-O-benzyl-5-O-alkanoate-β-D-arabinofuranosyl-(1→2)-3-O-benzyl-5-O-alkanoate-α-D-arabino-furanosides (16a-e)

2.12.1. General procedure

Cesium hydrogencarbonate was added to a stirred solution of α-D-arabinofuranoside **(15)** and the selected fatty acid in dry THF:DMF (5:1, 1 mL) at rt under nitrogen. The mixture was stirred at 70 °C for 4 days then diluted with ethyl acetate (25 mL) and water (5 mL). The aqueous layer was re-extracted with ethyl acetate (2 × 10 mL). The combined organic layers were washed with water (10 mL) and brine (10 mL) and evaporated under reduced pressure to give a thick oil. Chromatography on silica eluting with hexane/ethyl acetate (5:1) afforded the title compounds **(16a-e)**. Full analytical data is presented here for **16a**; that for **16b** – **16e** is provided in the Supplementary Data.

2.12.1.1. ′,3′-Di-O-benzyl-L-glycerol-(1′→1)-2,3-di-O-benzyl-5-O-palmitate-β-D-arabinofuranosyl-(1→2) -3-O-benzyl-5-O-palmitate-α-D-arabinofuranoside (16a). $CsHCO_3$ (66 mg, 0.34 mmol), α-D-arabinofuranoside **(15)** (33.0 mg, 0.034 mmol) and palmitic acid (22 mg, 0.085 mmol) gave **(16a)** as a colourless thick oil (41 mg, 92%) [MALDI–Found $(M + Na)^+$: 1305.8; $C_{80}H_{114}NaO_{13}$ requires: 1305.8], $[\alpha]_D^{22}$-7.6 (*c* 0.58, $CHCl_3$); δ_H (400 MHz, $CDCl_3$): 7.37 – 7.16 (25H, m), 5.01 (1H, d, *J* 4.2 Hz), 4.95 (1H, br.s), 4.66 (1H, d, *J* 11.6 Hz), 4.63 (3H, br.s), 4.56 (1H, d, *J* 11.6 Hz), 4.48 (1H, d, *J* 11.6 Hz), 4.47 (2H, br.s), 4.45 (1H, d, *J* 11.8 Hz), 4.41 (1H, d, *J* 11.8 Hz), 4.30 (1H, br.d, *J* 2.0 Hz), 4.25 – 4.15 (3H, m), 4.11 (1H, br.dd, *J* 3.1, 6.6 Hz), 4.09 – 4.01 (3H, m), 3.99 (1H, dd, *J* 4.3, 6.6 Hz), 3.90 (1H, br.dd, *J* 2.5, 5.8 Hz), 3.82 (1H, dd, *J* 5.2, 10.4 Hz), 3.74 (1H, br.p, *J* 5.0 Hz), 3.61 – 3.50 (3H, incl. br. dd *J* 4.7, 8.5 Hz at 3.56), 2.33 – 2.21 (2H, m), 2.18 (2H, dt, *J* 2.1, 7.4 Hz), 1.64 – 1.01 (52H, m), 0.84 (6H, t, *J* 6.8 Hz); δ_C (101 MHz, $CDCl_3$): 173.5, 173.4, 138.6, 138.3, 137.8, 137.7, 137.4, 128.5, 128.4, 128.35, 128.3, 128.0, 127.8, 127.75, 127.7, 127.65, 127.6, 127.5, 106.1, 100.5, 85.6, 84.3, 83.8, 82.5, 80.1, 78.9, 73.4, 72.6, 72.5, 72.4, 72.3, 70.2, 67.3, 66.0, 63.7, 34.0, 31.9, 29.7, 29.65, 29.6, 29.5, 29.4, 29.35, 29.3, 29.25, 29.2, 29.1, 24.9, 24.8, 22.7, 14.1; ν_{max}: 3065, 3031, 2924, 2853, 1741, 1732, 1455, 1114, 737, 698 cm^{-1}.

2.13. L-Glycerol-(1′→1)-5-O-alkanoate-β-D-arabinofuranosyl-(1→2)-5-O-alkanoate-α-D-arabinofuranosides (17)

2.13.1. General procedure

Palladium hydroxide on activated charcoal was added to a stirred solution of α-D-arabinofuranoside **(16a-e)** in CH_2Cl_2:MeOH:THF (1:1:1.5, 1 mL) at rt under hydrogen. The mixture was stirred for 36 h, filtered through celite and evaporated under reduced pressure to give a residue. Chromatography on silica eluting with chloroform/methanol (10:1) afforded furanosides **(17a-e)**.

2.13.1.1. L-Glycerol-(1′→1)-5-O-palmitate-β-D-arabinofuranosyl-(1→2)-5-O-palmitate-α-D-arabinofuranoside (17a). $Pd(OH)_2$-C/20% (25 mg, 0.75 fold by weight) and furanoside **(16a)** (33 mg, 0.025 mmol) gave **(17a)** as a colourless thick oil (18 mg, 82%) [MALDI–Found $(M + Na)^+$: 855.5804; $C_{45}H_{84}NaO_{13}$ requires: 855.5810]; $[\alpha]^{21}_{D}$ +14 (*c* 0.30, $CHCl_3$), which showed δ_H (400 MHz, $CDCl_3$ + few drops CD_3OD): 5.06 (1H, br.d, *J* 4.5 Hz), 5.02 (1H, br.d, *J* 1.9 Hz), 4.45 (1H, dd, *J* 7.2, 11.9 Hz), 4.38 – 3.30 (1H, m), 4.28 (1H, br.dd, *J* 4.1, 6.8 Hz), 4.26 – 4.21 (1H, m), 4.20 – 4.15 (2H, incl. br. dd, *J* 1.9, 9.6 Hz at 4.18), 4.15 – 4.10 (2H, m), 4.07 (2H, incl. br. dd, *J* 5.4, 8.3 Hz at 4.07), 4.04 (1H, br.d, *J* 7.0 Hz), 4.00 (1H, dd, *J* 4.8, 10.3 Hz), 3.91 – 3.85 (2H, m), 3.77 (2H, dd, *J* 6.0, 10.7 Hz), 3.71 (1H, br.d, *J* 2.9 Hz), 3.67 (2H, br.t, *J* 6.0 Hz), 2.36 (4H, t, *J* 7.6 Hz), 1.46 – 1.08 (53H, m), 0.89 (6H, t, *J* 6.8 Hz); δ_C (101 MHz, $CDCl_3$ + few drops CD_3OD): 173.5, 173.4, 138.6, 138.3, 137.8, 137.7, 137.4, 128.5, 128.4, 128.35, 128.3, 128.0, 127.8, 127.75, 127.7, 127.65, 127.6, 127.5, 106.1, 100.5, 85.6, 84.3, 83.8, 82.5, 80.1, 78.9, 77.0, 73.4, 72.6, 72.5, 72.4, 72.3, 70.2, 67.3, 66.0, 63.7, 34.0, 31.9, 29.7, 29.65, 29.6, 29.5, 29.45, 29.4, 29.3, 29.25, 29.2, 29.1, 24.9, 24.8, 22.7, 14.1; ν_{max}: 3436, 2918, 2850, 1738, 1643, 1469, 1219, 1116, 1041, 927 cm^{-1}.

2.13.1.2. L-Glycerol-(1'→1)-5-O-stearate-β-D-arabinofuranosyl-(1→2)-5-O-stearate-α-D-arabinofuranoside (17b). Pd$(OH)_2$-C/20% (34 mg, 0.75 fold by weight) and α-D-arabino-furanoside **(16b)** (45 mg, 0.033 mmol) gave **(17b)** as a colourless thick oil (24 mg, 81%) [MALDI–Found $(M + Na)^+$: 911.6430; $C_{49}H_{92}NaO_{13}$ requires: 911.6436], $[\alpha]^{25}_{D}$ -3.4 (*c* 0.71, $CHCl_3$); δ_H (400 MHz, $CDCl_3$ + few drops CD_3OD): 5.01 (1H, br.d, *J* 4.3 Hz), 5.00 (1H, br.s), 4.33 – 4.29 (1H, m), 4.27 (1H, br.d, *J* 5.7 Hz), 4.20 – 4.15 (2H, m), 4.13 (1H, br.d, *J* 7.0 Hz), 4.04 (1H, dd, *J* 5.9, 10.6 Hz), 4.00 (1H, br.dd, *J* 2.6, 6.6 Hz), 3.98 – 3.88 (3H, incl. br. dd *J* 4.9, 9.0 Hz at 3.96), 3.86 – 3.78 (1H, m), 3.74 (1H, dd, *J* 5.8, 10.6 Hz), 3.63 (1H, br.dd, *J* 3.9, 11.8 Hz), 3.6 – 3.53 (2H, incl. br.dd, *J* 3.0, 10.8 Hz at 3.58), 2.33 (4H, t, *J* 7.5 Hz), 1.36 – 1.17 (65H, m), 0.86 (6H, t, *J* 6.3 Hz); δ_C (101 MHz, $CDCl_3$): 173.5, 173.3, 138.6, 138.3, 137.8, 137.7, 137.4, 128.5, 128.4, 128.3, 128.2, 128.0, 127.8, 127.7, 127.65, 127.6, 127.55, 127.5, 106.1, 100.4, 85.6, 84.3, 83.8, 82.5, 80.1, 78.8, 77.0, 73.4, 72.5, 72.4, 72.3, 72.2, 70.2, 67.3, 65.9, 63.7, 34.0, 31.9, 29.7, 29.65, 29.6, 29.5, 29.4, 29.35, 29.3, 29.2, 29.15, 29.1, 24.9, 24.8, 22.7, 14.1; ν_{max}: 3430, 2917, 2849, 1737, 1643, 1467, 1214, 1172, 1041, 719 cm^{-1}.

2.13.1.3. L-Glycerol-(1'→1)-5-O-behenate-β-D-arabinofuranosyl-(1→2)-5-O-behenate-α-D-arabinofuranoside (17c). Pd$(OH)_2$-C/ 20% (75 mg, 0.75 fold by weight) and furanoside **(16c)** (100 mg, 0.0688 mmol) gave **(17c)** as a colourless thick oil (60 mg, 87%) [MALDI–Found $(M + Na)^+$: 1023.7682; $C_{57}H_{108}NaO_{13}$ requires: 1023.7688], $[\alpha]^{22}_{D}$ -2.3 (*c* 0.44, $CHCl_3$), which showed δ_H (400 MHz, $CDCl_3$ + few drops CD_3OD): 4.97 (1H, br.d, *J* 4.7 Hz), 4.96 (1H, br.s), 4.30 – 4.21 (2H, incl. br. dd *J* 8.4, 11.2 Hz at 4.25), 4.16 (1H, dd, *J* 3.2, 11.9 Hz), 4.14 – 4.06 (2H, m), 4.03 – 3.97 (2H, m), 3.96 – 3.88 (3H, m), 3.78 (1H, br.p, *J* 5.1 Hz), 3.71 (1H, dd, *J* 6.0, 10.4 Hz), 3.63 – 3.59 (1H, m), 3.57 (1H, dd, *J* 4.3, 11.5 Hz), 3.53 (1H, dd, *J* 4.8, 11.2 Hz), 2.31 (4H, t, *J* 7.6 Hz), 1.34 – 1.14 (81H, m), 0.83 (6H, t, *J* 6.6 Hz); δ_C (126 MHz, $CDCl_3$ + few drops CD_3OD): 174.2, 173.9, 105.9, 101.9, 88.5, 80.3, 80.1, 75.8, 75.5, 70.4, 69.5, 65.5, 63.6, 63.2, 34.0, 33.9, 31.8, 29.5, 29.45, 29.4, 29.3, 29.2, 29.15, 29.1, 29.0, 24.7, 22.5, 13.8; ν_{max}: 3419, 2956, 2917, 1738, 1732, 1464, 1215, 1171, 1048, 881, 720 cm^{-1}.

2.13.1.4. L-Glycerol-(1'→1)-5-O-(R)-2-((R)-1-hydroxydocosyl) hexacosanoate-β-D-arabinofuranosyl-(1→2)-5-O-(R)-2-((R)-1-hydroxydocosyl)hexa-cosanoate-α-D-arabinofuranoside (17d). Pd$(OH)_2$-C/20% (23 mg, 0.75 fold by weight) and α-D-arabino-furanoside **(16d)** (30 mg, 0.013 mmol) gave **(17d)** as a colourless thick oil (17 mg, 74%) [MALDI–Found $(M + Na)^+$: 1728.5; $C_{105}H_{204}NaO_{15}$ requires: 1728.5], $[\alpha]^{22}_{D}$ +8 (*c* 0.3, $CHCl_3$); δ_H (400 MHz, $CDCl_3$ + few drops CD_3OD): 4.98 (1H, br.d, *J* 5.7 Hz), 4.97 (1H, br.s), 4.40 (1H, dd, *J* 4.7, 11.6 Hz), 4.34 (1H, dd, *J* 4.8, 11.4 Hz), 4.22 (1H, dd, *J* 5.6, 11.6 Hz), 4.20 (1H, dd, *J* 6.4, 12.0 Hz), 4.13 (1H, dd, *J* 6.1, 10.7 Hz), 4.10 (1H, br.q, *J* 6.9 Hz), 4.05 – 3.98 (4H, incl. br. d *J* 11.2 Hz at 4.02), 3.85 – 3.76 (1H, m), 3.71 (1H, dd, *J* 6.4, 10.6 Hz), 3.68 – 3.62 (2H, br.m), 3.61 (1H, d, *J* 4.1 Hz), 3.57 (1H, dd, *J* 4.2, 9.6 Hz), 3.54 (1H, br.dd, *J* 3.2, 10.3 Hz), 2.46 – 2.37 (2H, m), 1.64 – 1.01 (171H, m), 0.86 (12H, t, *J* 6.8 Hz); δ_C (101 MHz, $CDCl_3$ + few drops CD_3OD): 175.1, 175.0, 105.8, 101.5, 87.6, 80.7, 79.5, 77.2, 76.4, 76.1, 72.8, 72.5, 70.4, 69.5, 65.4, 63.7, 63.3, 63.2, 53.3, 52.6, 34.8, 34.7, 31.9, 29.7, 29.6, 29.55, 29.5, 29.45, 29.4, 29.3, 29.2, 29.1, 27.4, 27.3, 25.4, 25.2, 22.6, 14.0; ν_{max}: 3416, 2927, 2854, 1728, 1719, 1466, 1215, 1121, 1044, 759, 669 cm^{-1}.

2.13.1.5. L-Glycerol-(1'→1)-5-O-(R)-2-((R)-1-hydroxy-18-((1R,2S)-2-((17S,18S)-17-methoxy-18-methylhexatriacontyl)cyclopropyl)-octadecyl) tetracosanoate-β-D-arabinofuranosyl-(1→2)-5-O-(R)-2-((R)-1-hydroxy-18-((1R,2S)-2-((17S,18S)-17-methoxy-18-methylhexatria-contyl) cyclopropyl)octadecyl)-tetracosanoate-α-D-arabinofurano-side (17e). Pd $(OH)_2$-C/20% (33 mg, 0.75 fold by weight) was added with stirring to compound **(16e)** (43 mg, 0.013 mmol) in CH_2Cl_2:MeOH (1:1, 1 mL) at rt under hydrogen. After 36 h, the mixture was filtered through celite and evaporated to give a residue. Chromatography on silica eluting with chloroform/methanol (10:1) gave **(17e)** as a colourless thick oil (27 mg, 73%) [MALDI–Found $(M + Na)^+$: 2793.6; $C_{179}H_{348}NaO_{17}$ requires: 2793.6], $[\alpha]^{22}_{D}$ +13 (*c* 0.36, $CHCl_3$); δ_H (400 MHz, $CDCl_3$ + few drops CD_3OD): 4.98 (1H, br.d, *J* 4.7 Hz), 4.82 (1H, br.s), 4.40 (1H, dd, *J* 4.4, 12.2 Hz), 4.37 – 4.31 (2H, incl. br. dd *J* 4.7, 11.6 Hz at 4.34), 4.22 (1H, dd, *J* 5.6, 11.5 Hz), 4.15 (1H, br.dd, *J* 5.6, 11.7 Hz), 4.10 (1H, br.dd, *J* 4.1, 9.0 Hz), 4.07 – 3.94 (6H, br.m), 3.89 (1H, br.dd, *J* 2.6, 4.7 Hz), 3.85 – 3.77 (1H, m), 3.72 (1H, dd, *J* 5.5, 11.5 Hz), 3.69 – 3.51 (6H, m), 3.38 (1H, dd, *J* 4.2, 8.5 Hz), 3.32 (6H, s), 2.99 – 2.90 (2H, m), 2.47 – 2.37 (2H, m), 1.66 – 0.96 (288H, m), 0.86 (12H, t, *J* 6.9 Hz), 0.83 (6H, d, *J* 6.9 Hz), 0.66 – 0.58 (4H, m), 0.53 (2H, dt, *J* 4.1, 8.6 Hz), -0.36 (2H, br.q, *J* 5.1 Hz); δ_C (101 MHz, $CDCl_3$ + few drops CD_3OD): 175.1, 175.0, 105.8, 101.5, 87.7, 85.5, 80.6, 79.5, 77.2, 76.4, 76.0, 72.6, 72.4, 70.3, 69.3, 65.4, 63.3, 63.1, 57.6, 53.2, 52.6, 35.2, 32.2, 31.8, 30.4, 30.1, 29.8, 29.7, 29.6, 29.5, 29.3, 29.2, 29.1, 29.0, 28.6, 27.4, 27.35, 27.3, 26.0, 25.3, 25.2, 22.6, 15.6, 14.7, 13.9, 10.8; ν_{max}: 3397, 2920, 2851, 1730, 1467, 1171, 1099, 1046, 721 cm^{-1}.

2.14. 2',3'-Di-O-benzyl-L-glycerol-(1'→1)-2,3-di-O-benzyl-5-O-mycolate-β-D-arabinofuranosyl-(1→2)-3-O-benzyl-5-O-mycolate-α-D-arabinofuranoside (18f-h)

2.14.1. General procedure

1-Ethyl-3-(3-dimethylaminopropyl)carbodi-imide hydrochloride (EDCI) in dry CH_2Cl_2 (1 mL) was added to a stirred solution of furanoside **(14)**; molecular sieves 4 Å, DMAP and mycolic acids **(f–h)** (R' = TBDMS) in dry CH_2Cl_2 (1 mL) at rt under nitrogen and stirred for 5 days. The precipitate was washed with CH_2Cl_2 (10 mL), the solvent was evaporated and the residue was purified by chromato-graphy on silica eluting with hexane/ethyl acetate (5:1) to afford compounds **(18f-h)**. Full data is presented here for **18f;** that for **18 g** and **18 h** is in the Supplementary Data.

2.14.1.1. 2',3'-Di-O-benzyl-L-glycerol-(1'→1)-2,3-di-O-benzyl-5-O-(R)-2-((R)-1-((tert-butyldimethylsilyl)oxy)-16-((1S,2R)-2-((S)-20-methyl-19-oxooctatria-contyl)cyclopropyl)hexadecyl)hexacosanoate-β-D-arabinofuranosyl-(1→2)-3-O-benzyl-5-O-(R)-2-((R)-1-((tert-butyldimethylsilyl)oxy)-16-((1S,2R)-2-((S)-20-methyl-19-

oxooctatriacontyl)cyclopropyl)hexa-decyl)hexacosanoate-α-D-arabinofuranoside (18f). EDCI (77 mg; 0.40 mmol), molecular sieves 4 Å (50 mg), arabinofuranoside **(14)** (33 mg, 0.040 mmol), DMAP (49 mg; 0.40 mmol) and (*R*)-2-((*R*)-1-((*tert*-butyldimethylsilyl)oxy)-16-((1*S*,2*R*)-2-((*S*)-20-methyl-19-oxooctatriacontyl)-cyclopropyl)hexadecyl) hexacosanoic acid (108 mg, 0.0790 mmol)[29] gave the title compound as a colourless thick oil (0.13 g, 97%) [MALDI–Found (M + Na)$^+$: 3496.1; $C_{228}H_{406}NaO_{17}Si_2$ requires: 3496.1], $[\alpha]^{21}_{D}$ +4.2 (*c* 0.38, $CHCl_3$); δ_H (400 MHz, $CDCl_3$): 7.38 – 7.18 (25H, m), 5.03 (1H, br.d, *J* 4.2 Hz), 4.97 (1H, br.s), 4.72 (1H, d, *J* 11.6 Hz), 4.68 (3H, d, *J* 11.6 Hz), 4.62 (1H, d, *J* 11.7 Hz), 4.56 – 4.48 (4H, m), 4.43 (1H, d, *J* 11.7 Hz), 4.37 (1H, br.d, *J* 2.0 Hz), 4.29 – 4.11 (6H, m), 4.06 (1H, t, *J* 6.0 Hz), 4.00 (1H, br.dd, *J* 4.3, 6.5 Hz), 3.96 – 3.81 (4H, m), 3.78 (1H, br.p, *J* 4.7 Hz), 3.67 – 3.54 (3H, incl. br. dd *J* 4.4, 10.4 Hz at 3.60), 2.53 (4H, incl. sextet *J* 6.8 Hz at 2.53), 2.42 (4H, dt, *J* 1.0, 7.2 Hz), 1.61 – 1.12 (288H, m), 1.06 (6H, d, *J* 6.9 Hz), 0.89 (12H, t, *J* 6.8 Hz), 0.85 (9H, s), 0.84 (9H, s), 0.71 – 0.62 (4H, m), 0.57 (2H, dt, *J* 4.1, 8.4 Hz), 0.04 (3H, s), 0.02 (3H, s), 0.01 (3H, s), -0.01 (3H, s), -0.32 (2H, br.q, *J* 5.1 Hz); δ_C (101 MHz, $CDCl_3$): 215.2, 174.3, 174.1, 138.6, 138.3, 137.9, 137.7, 137.5, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.65, 127.6, 127.5, 127.4, 105.9, 100.2, 84.9, 84.6, 83.6, 83.3, 80.1, 79.1, 77.1, 73.4, 73.2, 73.1, 72.5, 72.4, 72.2, 70.3, 67.2, 66.3, 64.3, 51.5, 51.4, 46.3, 41.1, 33.7, 33.0, 31.9, 30.2, 29.9, 29.85, 29.8, 29.75, 29.7, 29.65, 29.6, 29.55, 29.5, 29.45, 29.4, 29.35, 29.3, 28.7, 27.8, 27.7, 27.4, 27.3, 25.9, 25.8, 24.0, 23.9, 23.7, 22.7, 16.4, 15.8, 14.1, 10.9, -4.4, -4.5, -4.7, -4.8; ν_{max}: 3088, 3063, 2922, 2852, 1739, 1713, 1465, 1115, 758, 698 cm^{-1}.

2.15. De-protection of silyl group in MA fragment: (18f-h)

2.15.1. General procedure

TBAF (1.0 M in THF) was added dropwise with stirring to compounds **(18f-h)** in dry THF (1 mL) at 0 °C under nitrogen then diluted with ethyl acetate (10 mL) and water (1 mL). The aqueous layer was re-extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with sat.aq. NH_4Cl (5 mL), brine (5 mL), dried and the concentrated. Chromatography on silica eluting with hexane /ethyl acetate (10:1) afforded compounds **(16f-h) (R' = H).** Full data is presented here for **16f;** that for **16 g** and **16 h** is in the Supplementary Data.

2.15.1.1. 2',3'-Di-O-benzyl-L-glycerol-(1'→1)-2,3-di-O-benzyl-5-O-(R)-2-((R)-1-hydroxy-16-((1S,2R)-2-((S)-20-methyl-19-oxooctatriacontyl)cyclopropyl)hexa-decyl)hexacosanoate-β-D-arabinofuranosyl-(1→2)-3-O-benzyl-5-O-(R)-2-((R)-1-hydroxy-16-((1S,2R)-2-((S)-20-methyl-19-oxooctatriacontyl)cyclopropyl)-hexadecyl)hexacosanoate-α-D-arabinofuranoside (16f). TBAF (0.56 mL, 1.9 mmol, 1.0 M) and arabinofuranoside **(18f)** (98 mg, 0.028 mmol) gave the title compound as a colourless thick oil (45 mg, 38%); [MALDI–Found (M + Na)$^+$: 3267.9; $C_{216}H_{378}NaO_{17}$ requires: 3267.9], $[\alpha]^{22}_{D}$ +7.1 (*c* 0.34, $CHCl_3$); δ_H (400 MHz, $CDCl_3$): 7.39 – 7.22 (25H, m), 5.01 (1H, br.d, *J* 4.3 Hz), 4.97 (1H, br.s), 4.71 (2H, d, *J* 11.5 Hz), 4.67 (2H, m), 4.62 (1H, d, *J* 11.5 Hz), 4.56 – 4.50 (3H, m), 4.51 (1H, d, *J* 11.6 Hz), 4.45 (1H, d, *J* 11.6 Hz), 4.32 (1H, br.d, *J* 1.7 Hz), 4.30 – 4.21 (5H, m), 4.17 – 4.08 (2H, incl. br. p *J* 6.0 Hz at 4.12), 4.02 (1H, br.dd, *J* 4.4, 6.3 Hz), 3.99 – 3.93 (1H, m), 3.84 (1H, dd, *J* 5.3, 10.3 Hz), 3.81 – 3.76 (1H, br.p, *J* 5.3 Hz), 3.59 (5H, incl. br. dd, *J* 4.5, 10.8 Hz at 3.59), 2.56 – 2.46 (4H, incl. sextet, *J* 6.8 Hz at 2.51), 2.42 (4H, dt, *J* 1.1, 7.6 Hz), 1.65 – 1.11 (290H, m), 1.06 (6H, d, *J* 6.9 Hz), 0.89 (12H, t, *J* 6.8 Hz), 0.71 – 0.61 (4H, m), 0.60 – 0.53 (2H, dt, *J* 4.0, 8.5 Hz), -0.32 (2H, br.q, *J* 5.1 Hz); δ_C (101 MHz, $CDCl_3$): 215.2, 175.0, 138.5, 138.3, 137.7, 137.3, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.75, 127.7, 127.6, 127.5, 105.9, 100.4, 85.5, 84.4, 83.7, 82.8, 80.3, 78.9, 77.2, 73.4, 72.7, 72.6, 72.5, 72.4, 72.2, 72.1, 70.2, 67.2, 66.1, 63.7, 51.9, 51.6, 46.3, 41.1, 35.4, 35.3, 33.0, 31.9, 30.3, 30.2, 29.8, 29.75, 29.7, 29.65, 29.6, 29.55, 29.5, 29.45, 29.4, 29.35, 29.3, 29.2, 28.7, 27.5, 27.4, 27.3, 25.7, 23.7, 22.7, 16.4, 15.8, 14.1, 10.9; ν_{max}: 3501, 3063, 2920, 2852, 1736, 1714, 1465, 1116, 757, 698 cm^{-1}.

2.16. L-Glycerol-(1'→1)-5-O-mycolate-β-D-arabinofuranosyl-(1→2)-5-O-mycolate-α-D-arabinofuranoside (17f-h)

2.16.1. General procedure

Palladium hydroxide on activated charcoal was added to a stirred solution of α-D-arabinofuranoside **(16f-h)** in CH_2Cl_2:MeOH (1:1, 1 mL) at rt under hydrogen. The mixture was stirred for 36 h then filtered off through celite and the solvent was evaporated under reduced pressure to give a residue which was purified by column chromatography on silica eluting with chloroform/methanol (10:1) affording the title compounds **(17f-h).** Full data is presented here for **17f**; that for **17 g** and **17 h** is in the Supplementary Data.

2.16.1.1. L-Glycerol-(1'→1)-5-O–(R)-2-((R)-1-hydroxy-16-((1S,2R)-2-((S)-20-methyl-19-oxoocta-triacontyl)cyclopropyl)hexadecyl)hexacosanoate-β-D-arabinofuranosyl-(1→2)-5-O-(R)-2-((R)-1-hydroxy-16-((1S,2R)-2-((S)-20-methyl-19-oxooctatriacontyl)cyclopropyl)-hexadecyl)-hexacosanoate-α-D-arabinofuranoside (17f). ($Pd(OH)_2$-C/20% (26 mg, 0.75 fold by weight) and α-D-arabinofuranoside **(16f)** (35 mg, 0.010 mmol) gave **(17f)** as a colourless thick oil (22 mg, 71%) [MALDI–Found (M + Na)$^+$: 2817.6; $C_{181}H_{348}NaO_{17}$, requires: 2817.6], $[\alpha]^{22}_{D}$ +7.4 (*c* 0.38, $CHCl_3$); δ_H (400 MHz, $CDCl_3$ + few drops CD_3OD): 4.97 (1H, br.d, *J* 4.4 Hz), 4.96 (1H, br.s), 4.38 (1H, dd, *J* 4.7, 11.6 Hz), 4.33 (1H, br.dd, *J* 6.9, 11.4 Hz), 4.20 (1H, dd, *J* 6.0, 11.5 Hz), 4.18 (1H, dd, *J* 5.4, 11.5 Hz), 4.11 (1H, br.q, *J* 5.5 Hz), 4.08 – 3.92 (5H, m), 3.82 – 3.75 (1H, br.m), 3.69 (1H, br.dd, *J* 6.3, 10.5 Hz), 3.66 – 3.62 (3H, m), 3.57 (1H, br.dd, *J* 4.5, 11.4 Hz), 3.52 (1H, dd, *J* 3.4, 10.4 Hz), 2.60 – 2.40 (4H, incl. sextet *J* 6.8 Hz at 2.48), 2.38 (4H, br.t, 7.3 Hz), 1.67 – 1.05 (295H, m), 1.01 (6H, d, *J* 6.9 Hz), 0.84 (12H, t, *J* 6.8 Hz), 0.65 – 0.56 (4H, m), 0.52 (2H, dt, *J* 4.1, 8.5 Hz), -0.37 (2H, br.q, *J* 5.1 Hz); δ_C (101 MHz, $CDCl_3$ + few drops CD_3OD): 215.9, 175.1, 175.0, 105.8, 101.5, 87.6, 80.7, 79.5, 77.2, 76.4, 76.1, 72.7, 72.5, 70.3, 69.4, 65.4, 63.2, 53.3, 52.6, 46.3, 41.1, 34.8, 34.7, 32.9, 31.8, 30.2, 30.1, 29.7, 29.6, 29.55, 29.5, 29.45, 29.4, 29.35, 29.3, 29.25, 29.2, 29.1, 29.0, 28.6, 27.4, 27.3, 27.2, 25.3, 25.2, 23.6, 22.6, 16.2, 15.7, 14.0, 10.8; ν_{max}: 3420, 2919, 2851, 1733, 1714, 1467, 1120, 1046, 721 cm^{-1}.

2.17. 2',3'-Di-O-acetyl-L-glycerol-(1'→1)-2,3-di-O-acetyl-5-O-behenate-β-D-arabinofuranosyl-(1→2)-3-O-acetyl-5-O-behenate-α-D-arabinofuranoside (DMAG penta-acetate analogue from 16c)

Acetic anhydride (0.02 g, 0.20 mmol, 0.02 mL) was added to a stirred solution of α-D-arabinofuranoside **(16c)** (20 mg, 0.019 mmol) in dry pyridine (2 mL) at rt and stirred for 18 h under nitrogen. The solvent was evaporated and the product was purified by chromatography eluting with petrol/ethyl acetate (2:1) to afford the title compound **(23)** (20 mg, 83%) [MALDI–Found (M + Na)$^+$: 1233.8210; $C_{67}H_{118}NaO_{18}$ requires: 1233.8216], $[\alpha]^{23}_{D}$ -13 (*c* 0.62, $CHCl_3$), which showed δ_H (400 MHz, $CDCl_3$): 5.40 (1H, br.d, *J* 4.7 Hz), 5.34 (1H, dd, *J* 5.3, 6.3 Hz), 5.21 (1H, br.p, *J* 4.8 Hz), 4.95 (2H, br.dd, *J* 4.7, 6.6 Hz), 4.91 (1H, br.s), 4.37 (1H, dd, *J* 4.6, 11.6 Hz), 4.29 (1H, dd, *J* 4.4, 7.6 Hz), 4.27 – 4.10 (7H, m), 3.82 (1H, dd, *J* 5.2, 11.0 Hz), 3.60 (1H, dd, *J* 4.5, 10.9 Hz), 2.42 – 2.29 (4H, m), 2.11 – 2.09 (12H, m), 2.08 (3H, s), 1.70 – 0.99 (76H, m), 0.89 (6H, t, *J* 6.7 Hz); δ_C (101 MHz, $CDCl_3$): 173.4, 173.3, 170.6, 170.4, 170.2, 170.1, 169.9, 105.0, 99.4, 83.9, 80.6, 79.1, 77.5, 75.6, 69.8, 65.3, 65.2, 63.6, 62.5, 34.1, 34.0, 31.9, 31.6, 29.7, 29.65, 29.5, 29.35, 29.3, 29.2, 24.9, 24.8, 22.7, 22.6, 21.0, 20.8, 20.7, 20.6, 20.4, 14.1; ν_{max}: 2918, 2850, 1742, 1736, 1466, 1224, 1167, 1045, 755, 721 cm^{-1}.

2.18. 2',3'-Di-O-benzyl-L-glycerol-(1'→1)-2,3-di-O-benzyl-5-O-behenate-β-D-arabinofuranosyl-(1→2)-3-O-benzyl-5-p-methoxy-benzyl-α-D-arabinofuranoside (19)

EDCI (13.6 mg, 0.070 mmol) in dry CH_2Cl_2 (1 mL) was added dropwise to a stirred solution of α-D-arabinofuranoside **(13)** (13.2 mg, 0.0142 mmol), DMAP (8.6 mg, 0.070 mmol) and behenic acid (7.1 mg, 0.020 mmol) in dry CH_2Cl_2 (1 mL) at 0 °C under nitrogen, and stirred for 48 h. The precipitate was washed with CH_2Cl_2 (10 mL). The solvent was evaporated and the residue was purified by chromatography eluting with hexane/ethyl acetate (5:1) to give compound **(19)** as a colourless thick oil (15 mg, 85%) [Found $(M + NH_4)^+$: 1266.7800; $C_{78}H_{108}O_{13}N$, requires: 1266.7815], $[\alpha]^{22}_{D}$ -2.2 (*c* 0.92, $CHCl_3$); δ_H (400 MHz, $CDCl_3$): 7.30 – 7.17 (25H, m), 7.15 (2H, d, *J* 8.6 Hz), 6.77 (2H, d, *J* 8.6 Hz), 5.00 (1H, br.d, *J* 4.1 Hz), 4.95 (1H, br.s), 4.61 (1H, d, *J* 12.1 Hz), 4.60 (2H, br.s), 4.58 (1H, d, *J* 12.1 Hz), 4.51 (1H, d, *J* 11.6 Hz), 4.46 – 4.41 (3H, m), 4.37 (3H, br.d, *J* 11.7 Hz), 4.36 (1H, d, *J* 11.7 Hz), 4.25 (1H, br.d, *J* 1.9 Hz), 4.17 – 4.10 (2H, m), 4.07 – 3.98 (3H, m), 3.95 (1H, br.q, *J* 6.6 Hz), 3.89 (1H, br.dd, *J* 2.4, 6.0 Hz), 3.80 (1H, dd, *J* 5.1, 10.4 Hz), 3.74 – 3.68 (4H, incl. s at 3.72 for OCH_3), 3.57 – 3.50 (3H, incl. br. dd, *J* 5.0, 8.5 Hz at 3.53), 3.49 – 3.42 (2H, incl. br. dd *J* 4.2, 11.1 Hz at 3.47), 2.13 (2H, dt, *J* 3.6, 7.7 Hz), 1.53 – 1.02 (38H, m), 0.81 (3H, t, *J* 6.7 Hz); δ_C (101 MHz, $CDCl_3$): 173.4, 159.2, 138.7, 138.3, 138.0, 137.8, 137.5, 130.2, 129.4, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.65, 127.6, 127.55, 127.5, 127.4, 113.7, 106.0, 100.5, 85.9, 84.4, 83.8, 82.6, 81.5, 78.9, 77.0, 73.4, 72.9, 72.5, 72.4, 72.3, 72.2, 70.3, 69.6, 67.2, 66.0, 55.2, 34.0, 31.9, 29.8, 29.7, 29.65, 29.6, 29.5, 29.4, 29.3, 29.1, 24.8, 22.7, 14.1; ν_{max}: 3062, 3031, 2924, 2859, 1741, 1612, 1513, 1454, 1248, 1110,738, 699 cm^{-1}.

2.19. 2',3'-Di-O-benzyl-L-glycerol-(1'→1)-2,3-di-O-benzyl-5-O-behen-ate-β-D-arabinofuranosyl-(1→2)-3-O-benzyl-5-O-(2R)-2-(1-((tert-butyldimethylsilyl)oxy)-16-((1S,2R)-2-((S)-20-methyl-19-oxo-octatria-contyl)cyclopropyl)hexadecyl) hexacosanoate)-α-D-arabinofuran-oside (20)

(i) Cerium ammonium nitrate (CAN) (13 mg, 0.023 mmol) was added to a stirred solution of compound **(19)** (15 mg, 0.012 mmol) in CH_3CN:H_2O:THF (9:1:0.2, 1 mL)at 0 °C. The mixture was allowed to reach room temperature and stirred at ambient temperature for 16 h. The mixture was diluted with chloroform (20 mL), washed with aq. $NaHCO_3$ (10 mL), dried and the solvent was evaporated under reduced pressure. Column chromatography on silica eluting with petrol/ethyl acetate (4:1) gave 2',3'-di-*O*-benzyl-L-glycerol-(1'→1)-2,3-di-*O*-benzyl-5-*O*-behenate-β-D-arabinofuranosyl-(1→2)-3-*O*-benzyl-α-D-arabinofuranoside as a colourless thick oil (8.4 mg, 62%) [NSI–Found $(M + Na)^+$: 1151.7; $C_{70}H_{96}NaO_{12}$, requires: 1151.7]; $[\alpha]^{22}_{D}$ -11 (*c* 0.27, $CHCl_3$), which showed δ_H (400 MHz, $CDCl_3$): 7.39 – 7.25 (25H, m), 5.04 (1H, br.d, *J* 4.1 Hz), 4.98 (1H, br.s), 4.71 (1H, d, *J* 11.5 Hz), 4.69 (3H, br.s), 4.62 (1H, d, *J* 11.5 Hz), 4.54 – 4.49 (5H, m), 4.33 (1H, br.d, *J* 1.3 Hz), 4.21 (2H, incl. br. d, *J* 6.0 Hz at 4.21), 4.18 – 4.12 (2H, incl. br. dd, *J* 4.3, 7.2 Hz at 4.15), 4.11 (1H, br.dd, *J* 3.6, 7.9 Hz), 4.08 (1H, br.d, *J* 2.5 Hz), 4.05 (1H, dd, *J* 4.2, 6.6 Hz), 3.86 (1H, dd, *J* 5.2, 10.3 Hz), 3.82 – 3.76 (2H, incl. br. dd *J* 4.3, 9.7 Hz at 3.8), 3.66 – 3.58 (4H, incl. br. dd, *J* 4.7, 11.8 Hz at 3.6), 2.25 (2H, dt, *J* 0.9, 7.3 Hz), 1.36 – 1.18 (39H, m), 0.90 (3H, t, *J* 6.8 Hz); δ_C (101 MHz, $CDCl_3$): 173.5, 138.3, 137.9, 137.7, 137.4, 136.9, 128.5, 128.4, 128.3, 128.25, 128.1, 128.0, 127.9, 127.75, 127.7, 127.6, 127.55, 127.5, 106.0, 100.4, 85.1, 83.8, 83.5, 83.4, 82.5, 78.9, 73.3, 72.6, 72.4, 72.2, 70.1, 67.2, 66.0, 62.3, 34.0, 31.9, 29.7, 29.65, 29.6, 29.5, 29.4, 29.3, 29.1, 24.8, 22.7, 14.1; ν_{max}: 3414, 3062, 3032, 2915, 2852, 1737, 1467, 735, 697 cm^{-1}.

(ii) EDCI (5.5 mg, 0.035 mmol) in dry CH_2Cl_2 (1 mL) was added dropwise with stirring to the above furanoside (8.1 mg, 0.007 mmol), DMAP (4.3 mg, 0.035 mmol) and (2*R*)-2-(1-((*tert*-butyldimethylsilyl)oxy)-16-((1*S*,2*R*)-2-((*S*)-20-methyl-19-oxooctatriacontyl)cyclopropyl)hexadecyl)hexa-cosanoic acid (14.3 mg, 0.010 mmol) (Mizutani et al., 1989) in dry CH_2Cl_2 (1 mL) at 0 °C under nitrogen. The mixture was stirred for 48 h, then worked up and purified as above affording the title compound **(20)** (11 mg, 63%) [Found $(M + Na)^+$: 2485.0183; $C_{160}H_{272}NaO_{15}Si$, requires: 2485.0188]; δ_H (400 MHz, $CDCl_3$): 7.34 – 7.18 (25H, m), 4.99 (1H, br.d, *J* 4.2 Hz), 4.93 (1H, br.s), 4.65 (2H, d, *J* 11.5 Hz), 4.62 (2H, br.s), 4.56 (1H, d, *J* 11.6 Hz), 4.51 – 4.43 (4H, m), 4.40 (1H, d, *J* 11.6 Hz), 4.31 (1H, br.d, *J* 2.0 Hz), 4.24 – 4.14 (4H, m), 4.13 – 4.00 (3H, m), 3.97 (1H, dd, *J* 4.5, 6.4 Hz), 3.92 – 3.84 (2H, m), 3.80 (1H, dd, *J* 5.0, 10.4 Hz), 3.73 (1H, br.p, *J* 4.7 Hz), 3.58 – 3.53 (3H, incl. br.dd, *J* 4.3, 10.4 Hz at 3.56), 2.55 – 2.43 (2H, m), 2.37 (2H, t, *J* 7.5 Hz), 2.18 (2H, td, *J* 2.1, 7.3 Hz), 1.56 – 1.11 (182H, m), 1.01 (3H, d, *J* 6.9 Hz), 0.85 (9H, t, *J* 6.7 Hz), 0.81 (9H, s), 0.66 – 0.58 (2H, m), 0.52 (1H, dt, *J* 3.9, 8.6 Hz), -0.01 (3H, s), -0.03 (3H, s), -0.37 (1H, br.q, *J* 5.1 Hz); δ_C (101 MHz, $CDCl_3$): 215.2, 174.4, 173.3, 138.6, 138.3, 137.8, 137.7, 137.4, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.65, 127.6, 127.55, 127.5, 127.4, 106.0, 100.3, 85.4, 84.7, 83.7, 82.6, 80.1, 78.9, 77.1, 73.4, 73.2, 72.6, 72.5, 72.4, 72.2, 70.3, 67.2, 66.0, 64.2, 51.5, 46.3, 41.1, 34.0, 33.7, 33.0, 31.9, 30.2, 29.9, 29.7, 29.7, 29.6, 29.55, 29.5, 29.45, 29.4, 29.35, 29.3, 29.1, 28.7, 27.7, 27.4, 27.3, 25.8, 24.8, 23.9, 23.7, 22.7, 16.4, 15.8, 14.1, 10.9, -4.4, -4.8; ν_{max}: 3086, 3061, 2923, 2851, 1737, 1715, 1464, 1117, 757, 697 cm^{-1}.

2.20. 2',3'-Di-O-benzyl-L-glycerol-(1'→1)-2,3-di-O-benzyl-5-O-behenate-β-D-arabinofuranosyl-(1→2)-3-O-benzyl-5-O-(R)-2-((R)-1-hydroxy-16-((1S, 2R)-2-((S)-20-methyl-19-oxooctatriacontyl) cyclopropyl) hexadecyl) hexacosan-oate)-α-D-arabinofuranoside (21)

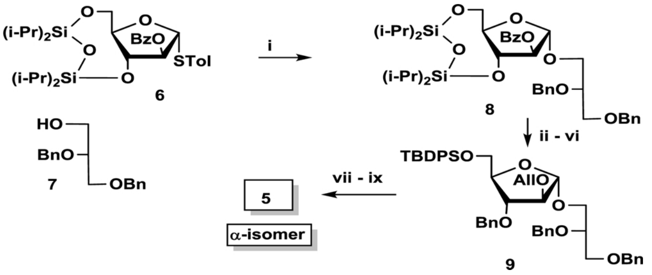
The protected glycolipid α-D-arabinofuranoside **(20)** (10 mg, 0.004 mmol) was dissolved in dry THF (10 mL) in a dry polyethylene vial equipped with an acid proof rubber septum, followed by addition of pyridine (0.1 mL) at room temperature under nitrogen. The mixture was cooled to 0 °C, and then hydrogen fluoride-pyridine complex as (70% w, 1.5 mL) was added dropwise. The mixture was stirred at 43 °C for 24 h, then neutralized by pouring it slowly into sat. aq. $NaHCO_3$ and stirred until no more CO_2 was liberated. The aqueous layer was re-extracted with chloroform (3 × 10 mL). The combined organic layers were evaporated; chromatography on silica eluting with hexane/ethyl acetate (10:1) afforded compound **(21)** as a colourless thick oil (6.5 mg, 68%) [NSI–Found $(M + Na)^+$: 2371.9; $C_{154}H_{258}NaO_{15}$, requires: 2371.9. NSI–Found $(M + NH_4)^+$: 2367.0; $C_{154}H_{262}NO_{15}$, requires: 2367.0]; δ_H (400 MHz, $CDCl_3$): 7.36 – 7.23 (25H, m), 5.03 (1H, br.d, *J* 4.3 Hz), 4.97 (1H, br.s), 4.70 (2H, d, *J* 11.4), 4.67 (1H, br.s), 4.65 (1H, d, *J* 11.9 Hz), 4.60 (1H, d, *J* 11.6 Hz), 4.56 – 4.49 (4H, m), 4.46 (1H, d, *J* 11.6 Hz), 4.34 (1H, br.d, *J* 1.7 Hz), 4.31 – 4.24 (3H, incl. br. dd, *J* 4.3, 8.1 Hz at 4.27), 4.22 (1H, br.dd, *J* 6.0, 8.6 Hz), 4.18 – 4.07 (4H, m), 4.07 – 4.00 (1H, m), 3.98 – 3.91 (1H, m), 3.85 (1H, dd, *J* 5.3, 10.2 Hz), 3.79 (1H, br.p, *J* 5.1 Hz), 3.65 – 3.55 (4H, incl. br. dd, *J* 4.4, 10.0 Hz at 3.60), 2.56 – 2.47 (1H, m), 2.44 – 2.38 (3H, m), 2.26 – 2.17 (2H, m), 1.61 – 1.10 (182H, m), 1.06 (3H, d, *J* 6.9 Hz), 0.87 (9H, t, *J* 6.3 Hz), 0.69 – 0.63 (2H, m), 0.57 (1H, dt, *J* 4.1, 8.4 Hz), -0.32 (1H, br.q, *J* 5.1 Hz); δ_C (101 MHz, $CDCl_3$): 215.2, 175.0, 173.4, 138.5, 138.2, 137.8, 137.7, 137.3, 128.5, 128.4, 128.35, 128.3, 128.2, 128.1, 127.8, 127.75, 127.7, 127.65, 127.6, 127.55, 127.5, 106.0, 100.4, 85.6, 84.6, 83.8, 82.6, 80.2, 78.9, 77.2, 73.4, 72.6, 72.5, 72.4, 72.3, 72.2, 70.2, 67.2, 66.0, 63.7, 51.8, 46.3, 41.3, 41.1, 35.3, 34.0, 33.7, 33.0, 31.9, 30.2, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 28.7, 27.7, 27.4, 27.3, 25.6, 24.8, 23.7, 22.7, 22.6, 20.4, 19.4, 16.4, 15.8, 14.3, 14.1, 11.4, 10.9; ν_{max}: 3503, 3061, 2921, 2853, 1738, 1717, 1466, 1117, 758, 697 cm^{-1}.

2.21. L-glycerol-(1'→1)-5-O-behenate-β-D-arabinofuranosyl-(1→2)-5-O-(R)-2-((R)-1-hydroxy-16-((1S,2R)-2-((S)-20-methyl-19-oxooctatriacontyl)cyclopropyl)hexadecyl)hexacosanoate)-α-D-arabino-furanoside (22)

Pd(OH)$_2$-C/20% (20 mg) was added with stirring to furanoside **(21)** **(R' = H)** (6.5 mg, 2.7 mmol) in CH$_2$Cl$_2$:MeOH:THF (2:1:1.5, 3 mL) at rt under hydrogen, then stirred for 36 h, filtered through celite and the solvent evaporated under reduced pressure. Chromatography on silica eluting with chloroform/ methanol (10:1) gave **(22)** as a colourless thick oil (4.1 mg, 78%) [Found (M + Na)$^+$: 1921.7019; $C_{119}H_{228}NaO_{15}$, requires: 1921.7005]; δ_H (400 MHz, CDCl$_3$ + few drops CD$_3$OD): 4.92 (1H, br.d, *J* 5.8 Hz), 4.91 (1H, br.s), 4.30 (1H, br.dd, *J* 2.4, 7.1 Hz), 4.28 (1H, br.d, *J* 2.7 Hz), 4.20 – 4.11 (3H, m), 4.07 – 4.00 (3H, m), 3.97 (1H, br.q, *J* 5.2 Hz), 3.94 – 3.85 (4H, m), 3.52 – 3.46 (4H, m), 3.33 – 3.29 (3H, incl. br.dd, *J* 2.5, 4.1 Hz at 3.32), 3.23 (1H, br.dd, *J* 2.9, 4.3 Hz), 2.49 – 2.39 (2H, m), 2.38 – 2.31 (4H, m), 2.30 – 2.23 (2H, m), 1.57 – 1.02 (181H, m), 0.97 (3H, d, *J* 6.8 Hz), 0.79 (9H, t, *J* 6.9 Hz), 0.59 – 0.52 (2H, m), 0.48 (1H, dt, *J* 3.8, 11.8 Hz), -0.42 (1H, br.q, *J* 4.4 Hz); δ_C (101 MHz, CDCl$_3$): 216.1, 175.0, 174.4, 105.8, 101.6, 87.8, 80.3, 80.0, 77.2, 76.4, 75.4, 72.4, 70.4, 69.3, 65.7, 63.3, 63.1, 52.6, 46.2, 41.1, 34.7, 34.0, 32.9, 31.8, 30.1, 29.6, 29.5, 29.45, 29.4, 29.35, 29.3, 29.25, 29.2, 29.15, 29.1, 29.0, 28.6, 27.3, 27.2, 25.3, 24.7, 23.6, 22.5, 16.2, 15.6, 13.9, 10.7; ν_{max}: 3421, 2920, 2852, 1735, 1715, 1468, 1121, 1045, 722 cm^{-1}.

3. Results and discussion

The donor fragment **4**, was prepared by known methods (Ishiwata et al., 2006a). The acceptor fragment **5** was prepared as in Scheme 2. Compound **6** (Reddy et al., 2012; D'Souza et al., 2000) was subjected to a glycosidation reaction with **7** (Ashton et al., 1985) using *N*-iodosuccinimide and silver triflate in dichloromethane at −35 °C to give the α- isomer **8** in 91% yield. The proton NMR of the product showed a downfield signal as a broad doublet at δ 4.98 (*J* 1.0 Hz), while the ^{13}C NMR showed a peak at δ 105.6 due to the carbon at position **1**, both indicating the α- anomer (Mizutani et al., 1989). Deprotection of the benzoyl group followed by protection of the resulting alcohol as an allyl ether using allyl bromide and sodium hydride, then removal of the silyl protecting group gave a diol at C-3 and C-5 positions in 63% overall yield. Two different groups were required at these positions in the DMAG's acceptor. The presence of a *p*-methoxybenzyl group at the C-5 position on the acceptor was found to give good β-selectivity when coupling with the donor to form a disaccharide (Liu et al., 2010). Therefore, the primary alcohol was first protected as a TBDPS ether, while the secondary alcohol was protected with a benzyl group to give compound **9**. Replacement of the TBDPS group with a PMB group, followed by removal of the allyl group from C-2 led to the acceptor fragment **5** (Scheme 2). The fragment **5** might be obtained in higher yield through the desilylation and debenzoylation of 8 followed by formation and nucleophilic opening of a 2,3-anhydro-α-*D*-lyxofuranoside as reported by Liu (Liu et al., 2010).

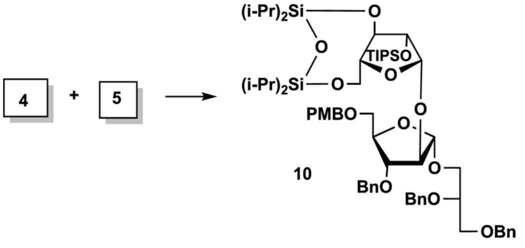


Scheme 2. (i) **7**, NIS/AgOTf, CH$_2$Cl$_2$, −35 °C, 91%; (ii) NaOCH$_3$, CH$_3$OH:CH$_2$Cl$_2$ (1:1), R.T., 1 h, 89%; (iii) NaH, allyl bromide, DMF, 0 °C /R.T., 1 h, 75%; (iv) TBAF, THF, 0 °C /R.T., 16 h, 95%; (v) *t*-BuPh$_2$SiCl, imidazole, DMF, 0 °C /R.T., 1/2 h, 65%; (vi) NaH, BnBr, DMF, 0 °C /R.T. 2 h, 72%; (vii) TBAF, THF, 0 °C /R.T.,16 h, 91%; (viii) NaH, PMBBr, DMF, 0 °C /R.T. 2 h, 76%; (ix) PdCl$_2$, CH$_3$OH:CH$_2$Cl$_2$ (1:1), R.T., 16 h, 84%.

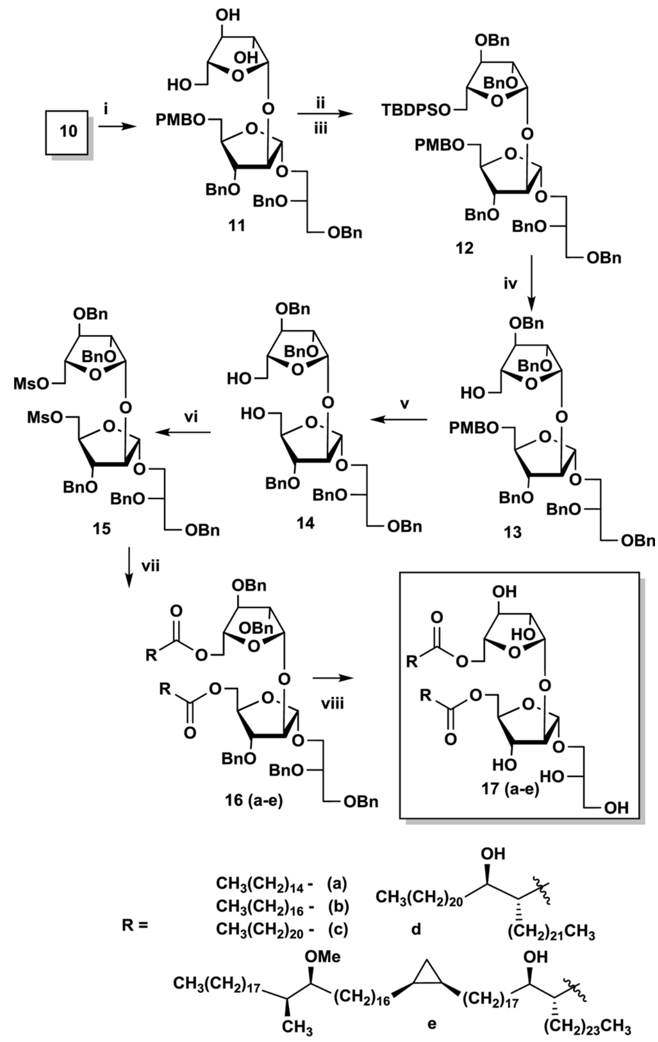
Coupling of arabinogylcerol **5** to arabinose **4** proceeded in high yield to give only the β-diastereomer at the newly formed acetal **10** (Scheme 3). The proton NMR showed characteristic acetal signals at 4.96 (1H, br. s) and 4.79 (1H, br. d, *J* 4.3 Hz) for the pre-formed acetals; the ^{13}C NMR showed signals at δ 106.2 and 100.6 corresponding to the α and β anomeric carbons respectively (Mizutani et al., 1989). With other combinations of protecting groups, such glycosylation reactions have been reported to produce mixtures of α and β isomers (Crich et al., 2007; Liu et al., 2010). Ishiwata (Ishiwata et al., 2006a) reported a strategy for β-selective glycosylation using donors protected with 3,5-TIDPS. An enhancement of β-selectivity was achieved by utilising a donor with an eight-membered ring protection as in **4**. The best α/β-ratio of (1:20) from the disaccharide was realised. By using a PMB protection in acceptor **5**, we observed only the β-isomer.

The silyl groups were removed from compound **10**. The resulting triol **11** was first converted into the diol by protection of the primary alcohol as a TBDPS ether, followed by benzylation of the secondary alcohols to give **12**. Removal of the TBDPS group from the top primary alcohol to give **13**, followed by removal of the PMB group from the lower primary alcohol gave diol **14**. Compound **14** was converted into the corresponding dimesylate **15** and esterified with simple fatty acids, a model β-hydroxy-acid (Hameed et al., 2014), or a single synthetic methoxy-MA (Baols et al., 2014), to give protected DMAGs compounds **16a-e**, and after debenzylation, DMAGs **17a-e** **(**Scheme 4**)**. The sequence of deprotection and protection steps was chosen to overcome loss of selectivity in the acylation step, and also meant that the final deprotection only entailed the removal of benzyl groups.

Alternatively, the diol **14** was coupled directly to protected synthetic MAs (Salah, 2013; Koza et al., 2009; Al Dulayymi et al., 2005; Koza et al., 2013), followed by deprotection as in Scheme 5:



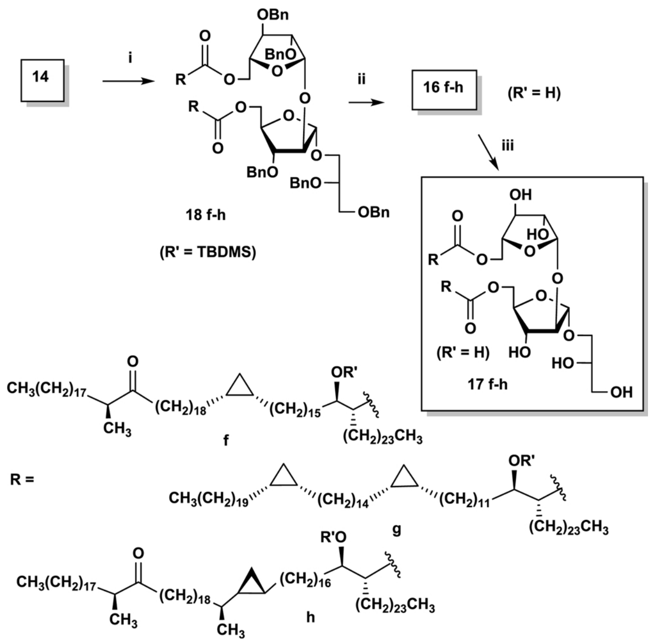
Scheme 3. Synthesis of **10**, using NIS/AgOTf, molecular sieve, −78 °C, then Et$_3$N, (86%).



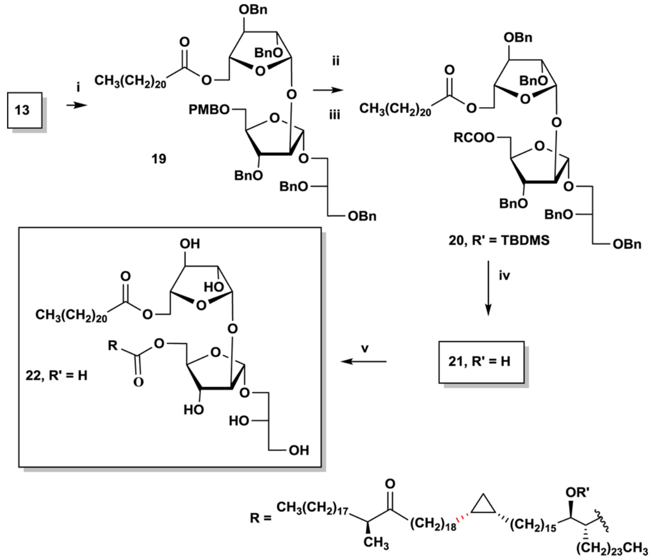
Scheme 4. (i) TBAF, THF, 0 °C /R.T., 6 h, 95%; (ii) *t*-BuPh$_2$SiCl, imidazole, DMF, 0 °C /R.T., 2 h, 77%; (iii) NaH, BnBr, DMF, 0 °C /R.T., 2 h, 90%; (iv) TBAF, THF, 0 °C /R.T., 6 h, 93%; (v) CAN/ CH$_3$CN:H$_2$O (9:1), 0 °C /R.T., 1 h, 89%; (vi) CH$_3$SO$_2$Cl, DMAP, pyridine, 16 h, 85%; (vii) RCOOH, CsHCO$_3$, THF:DMF (5:1), 70 °C, 4 days, (a: 92%; b: 89%; c: 87%; d: 55%; e: 54%); (viii) (Pd(OH)$_2$-C/20%), H$_2$, CH$_3$OH:CH$_2$Cl$_2$:THF (1:1:1.5), R.T., 36 h, (a: 82%; b: 81%; c: 87%; d: 74%; e: 73%).

Using the intermediate alcohol **13**, it was also possible to selectively esterify with different acids at each primary alcohol position of the DMAG sugar moiety. Thus esterification of **13** led to a mono-acyl diarabinoglycerol **19**, esterified only on the top arabinose, which could then be selectively deprotected and acylated on the lower arabinose to give **22 (R' = H)** (Scheme 6).

Product **16c** was converted into its penta-acetate (**23**) (Table 1) by reaction with acetic anhydride in pyridine. The NMR spectra of this (Supplementary Information) could then be compared directly with those reported for the penta-acetate of the natural mixture (Elass et al., 2012). As seen in Table 1, there is a very good agreement between the signals for the diarabinoglycerol fragments of natural and synthetic molecules.



Scheme 5. Synthesis of DMAG glycolipid: (i) RCOOH (R' = TBDMS), EDCI, DMAP, CH$_2$Cl$_2$ (f: 97%; g: 84%; h: 91%); (ii) TBAF, THF (f: 38%; g: 64%; h: 31%); (iii) (Pd(OH)$_2$-C/20%), H$_2$, CH$_3$OH:CH$_2$Cl$_2$:THF (1:1:1.5), R.T., 36 h, (f: 71%; g: 70%; h: 72%).

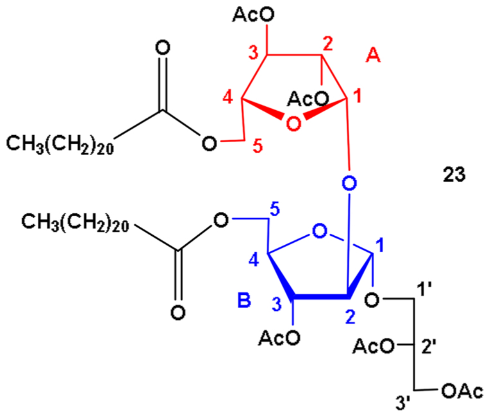


Scheme 6. (i) Behenic acid, EDCI, DMAP, CH$_2$Cl$_2$, 0 °C, 48 h, 85%; (ii) CAN/ CH$_3$CN:H$_2$O:THF (9:1:0.2), 0 °C /R.T., 16 h, 62%; (iii) RCOOH (R' = TBDMS), EDCI, DMAP, CH$_2$Cl$_2$, 0 °C, 48 h, 63%; (iv) HF-pyridine complex, pyridine, THF, 43 °C, 24 h, 68%; (v) (Pd(OH)$_2$-C/20%), H$_2$, CH$_3$OH:CH$_2$Cl$_2$:THF (1:2:1.5), R.T., 36 h, 78%.

4. Conclusion

By appropriate use of protecting groups, the skeleton of diarabinoglycerol can be produced with essentially complete stereocontrol. Esterification with simple fatty acids or with individual mycolic acids provides the corresponding diacyl- and dimycoloyl diarabinoglycerols. The NMR spectra of these, in the sugar region, match very well to those reported for natural mixtures, confirming the stereochemistry of the arabinose units and establishing the absolute stereochemistry of the glycerol unit. These compounds will allow the effect of the detailed structure of DMAG on its biological activity to be determined.

Table 1
Comparison of diarabinoglycerol fragment of carbon and proton NMR spectra of synthetic and natural DMAG penta-acetates 23.[20]



23

Natural DMAG peracetate[20]					Synthetic DMAG penta-acetate analogue 23 from 16c	
Glycerol		^{13}C *δ/ppm*		^1H *Shift, Class, J/Hz*	^1H *Shift, Class, J/Hz*	^{13}C *δ/ppm*
		C1’	65.3	3.60 (dd, *J* 4.5, 11.0), 3.80 (dd, *J* 5.2, 11.0)	3.60 (dd, *J* 4.5, 11.0), 3.80 (dd, *J* 5.2, 11.0)	65.3
		C2’	69.8	5.20	5.21(m)	69.8
		C3’	62.8	4.25 (dd, *J* 4.0, 11.7), 4.17 (dd, *J* 5.2, 11.7)	4.37 (dd, *J* 4.6, 11.6), 4.20 (m)	62.6
Arabinose A	C1		99.5	5.39 (d, *J* 4.7)	5.40 (br.d, *J* 4.7)	99.4
	C2		77.2	4.98 (dd, *J* 4.7, 6.6)	4.95 (br.dd, *J* 4.7, 6.6)	77.5
	C3		75.4	5.34 (dd, *J* 5.1, 6.6)	5.34 (dd, *J* 5.3, 6.3)	75.6
	C4		79.0	4.12 (dt, *J* 4.6, 5.1, 7.8)	4.12 (m)	79.1
	C5		65.2	4.38 (dd, *J* 4.6, 11.6), 4.22 (dd, *J* 7.8, 11.6)	4.37 (dd, 4.6, 11.6), 4.20 (m)	65.2
Arabinose B	C1		105	4.91 (s)	4.91 (br.s)	105
	C2		84.0	4.22 (m)	4.21 (m)	84.0
	C3		77.5	4.98	4.95 (br.dd, *J* 4.7, 6.6)	77.5
	C4		80.8	4.17	4.17 (m)	80.6
	C5		63.8	4.18, 4.30 (dd, *J* 2.7,10.3)	4.18 (m)	63.6

Conflict of interest

I confirm that there is no conflict of interest for any of the authors of this paper.

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References

Al Dulayymi, J.R., Baird, M.S., Roberts, E., 2005. The synthesis of a single enantiomer of a major α-mycolic acid of *M. Tuberculosis*. Tetrahedron 61, 11939–11951.

Andersen, C.S., Agger, E.M., Rosenkrands, I., Gomes, J.M., Bhowruth, V., Gibson, K.J.C., Petersen, R.V., Minnikin, D.E., Besra, G.S., Andersen, P., 2009a. A simple mycobacterial monomycolated glycerol lipid has potent immunostimulatory activity. J. Immunol. 182, 424–432.

Andersen, C.S., Rosenkrands, I., Olsen, A.W., Nordly, P., Christensen, D., Lang, R., Kirschning, C., Gomes, J.M., Bhowruth, V., Minnikin, D.E., Besra, G.S., Follmann, F., Andersen, P., Agger, E.M., 2009b. Novel generation mycobacterial adjuvant based on liposome-encapsulated monomycoloyl glycerol from Mycobacterium bovis Bacillus calmette-Guérin. J. Immunol. 183, 2294–2302.

Ashton, W.T., Canning, L.F., Reynolds, G.F., Tolman, R.L., Karkas, J.D., Liou, R., Davies, M.E.M., DeWitt, C.M., Perry, H.C., Field, A.K., 1985. Synthesis and antiherpetic activity of (*S*)-, (*R*)-, and (+/-)-9-[(2,3-dihydroxy-1-propoxy)lmethyl]guanine, linear isomers of 2’-nor-2’-deoxyguanosine. J. Med. Chem. 28, 926–933.

Ayers, J.D., Lowary, T.L., Morehouse, C.B., Besra, G.S., 1998. Synthetic arabinofuranosyl oligosaccharides as Mycobacterial arabinosyltransferase substrates. Bioorg. Med. Chem. Lett. 8, 437–442.

Azuma, I., Yamamura, Y., 1962. Studies on the firmly bound lipids of human tubercle Bacillus. I. isolation of arabinose mycolate. J. Biochem. 52, 200–206.

Azuma, I., Yamamura, Y., 1963. Studies on the firmly bound lipids of human tubercle Bacillus. Ii. Isolation of arabinose mycolate and identification of its chemical structure. J. Biochem. 53, 275–281.

Azuma, I., Kimura, H., Yamamura, Y., 1965. Isolation of arabinose mycolate from wax d fraction of human tubercle Bacillus *aoyama B* strain. J. Biochem. 57, 571–572.

Azuma, I., Kimura, H., Yamamura, Y., 1968a. Chemical and immunological properties of polysaccharides of wax D extracted from Mycobacterium tuberculosis strain Aoyama B. J. Bacteriol. 95, 567–568.

Azuma, I., Yamamura, Y., Fukushi, K., 1968b. Fractionation of mycobacterial cell wall. Isolation of arabinose mycolate and arabinogalactan from cell wall fraction of Mycobacterium tuberculosis strain Aoyama B. J. Bacteriol. 96, 1885–1887.

Azuma, I., Yamamura, Y., Misaki, A., 1969. Isolation and characterization of arabinose mycolate from firmly bound lipids of Mycobacteria. J. Bacteriol. 98, 331–333.

Backus, M., Dolan, A., Barry, S., Joe, M., McPhie, P., Boshoff, M., Lowary, L., Davis, B., Barry, C., 2014. The three Mycobacterium tuberculosis antigen 85 isoforms have unique substrates and activities determined by non-active site regions. J. Biol. Chem. 289, 25041–25053.

Baols, K.S., Thesis, Ph D., University, Bangor, 2014. Synthesis of Mixed Cord Factors and Related Compounds.

Besra, G.S., Khoo, K.-H., McNeil, M.R., Dell, A., Morris, H.R., Brennan, P.J., 1995. A new interpretation of the structure of the mycolyl-arabinogalactan complex of Mycobacterium tuberculosis as revealed through characterization of oligoglycosylalditol fragments by fast-atom bombardment mass spectrometry and 1H nuclear magnetic resonance spectroscopy. Biochemistry 34, 4257–4266.

Bhowruth, V., Minnikin, D.E., Agger, E.M., Andersen, P., Bramwell, V.W., Perrie, Y., Besra, G.S., 2009. Adjuvant properties of a simplified C32 monomycolyl analogue. Bioorg. Med. Chem. Lett. 19, 2029–2032.

Brennan, P.J., 2003. Structure, function, and biogenesis of the cell wall of Mycobacterium tuberculosis. Tuberculosis 83, 91–97.

Crich, D., Pedersen, C.M., Bowers, A.A., Wink, D.J., 2007. On the Use of 3,5-Di-*O*-benzylidene and 3,5-Di-*O*-(di-*tert*-butylsilylene)-2-*O*-benzylarabinothiofuranosides and their Sulfoxides as Glycosyl Donors for the Synthesis of β-Arabinofuranosides: Importance of the Activation Method. J. Org. Chem. 72, 1553–1565.

D'Souza, F.W., Ayres, J.D., McCarren, P.R., Lowary, T.L., 2000. Arabinofuranosyl oligosaccharides from mycobacteria: synthesis and effect of glycosylation on ring conformation and hydroxymethyl group rotamer populations. J. Am. Chem. Soc. 122, 1251–1260.

Daffé, M., McNeil, M., Brennan, P.J., 1993. Major structural features of the cell wall arabinogalactans of *Mycobacterium, Rhodococcus, and Nocardia* spp. Carbohydr. Res. 249, 383–398.

Elass, E., Rombouts, Y., Coddeville, B., Maes, E., Blervaque, R., Hot, D., Kremer, L., Guérardel, Y., 2012. Structural determination and toll-like receptor 2-dependent proinflammatory activity of dimycolyl-diarabino-glycerol from Mycobacterium marinum. J. Biol. Chem. 287, 34432–34444.

Hameed, R.T., Thesis, Ph D., University, Bangor, 2014. Synthesis of Mycobacterial Cord Factors and Related Compounds.

Hattori, Y., Matsunaga, I., Komori, T., Urakawa, T., Nakamura, T., Fujiwara, N., Hiromatsu, K., Harashima, H., Sugita, M., 2011. Glycerol monomycolate, a latent tuberculosis-associated mycobacterial lipid, induces eosinophilic hypersensitivity responses in guinea pigs. Biochem. Biophys. Res. Commun. 409, 304–307.

Hattori, Y., Morita, D., Fujiwara, N., Mori, D., Nakamura, T., Harashima, H., Yamasaki, S., Sugita, M., 2014. Glycerol monomycolate is a novel ligand for the human, but not mouse macrophage inducible C-type lectin. Mincle. J. Biol. Chem. 289, 15405–15412.

Honda, I., Kawajiri, K., Watanabe, M., Tioda, I., Kawamata, K., Minnikin, D.E., 1993. Evaluation of the use of 5-mycoloyl-ß-arabinofuranosyl-(1→2)-5-mycoloyl-α-arabinofuranosyl-(1→1′)-glycerol in serodiagnosis of Mycobacterium avium-intracellulare complex infection. Res. Microbiol. 144, 229–235.

Ishiwata, A., Akao, H., Ito, Y., Sunagawa, M., Kusunose, N., Kashiwazaki, Y., 2006a. Synthesis and TNF-alpha inducing activities of mycoloyl-arabinan motif of mycobacterial cell wall components. Bioorg. Med. Chem. 14, 3049–3061.

Ishiwata, A., Akao, H., Ito, Y., 2006b. Stereoselective synthesis of a fragment of mycobacterial arabinan. Organic Letts. 8 (24), 5525–5528.

Koza, G., Theunissen, C., Al-Dulayymi, J.R., Baird, M.S., 2009. The synthesis of single enantiomers of mycobacterial ketomycolic acids containing *cis*-cyclopropanes. Tetrahedron 65, 10214–10229.

Koza, G., Muzael, M., Schubert-Rowles, R.R., Theunissen, C., Al Dulayymi, J.R., Baird, M.S., 2013. The synthesis of methoxy and keto mycolic acids containing methyl-*trans*-cyclopropanes. Tetrahedron 69, 6285–6296.

Kremer, L., de Chastellier, C., Dobson, G., Gibson, K.J.C., Bifani, P., Balor, S., Gorvel, J.P., Locht, C., Minnikin, D.E., Besra, G.S., 2005. Identification and structural characterization of an unusual mycobacterial monomeromycolyl-diacylglycerol. Mol. Microbiol. 57, 1113–1126.

Lee, R.E.B., Li, W., Chatterjee, D., Lee, R.E., 2005. Rapid structural characterization of the arabinogalactan and lipoarabinomannan in live mycobacterial cells using 2D and 3D HR-MAS NMR: structural changes in the arabinan due to ethambutol treatment and gene mutation are observed. Glycobiology 15, 139–151.

Liu, C., Richards, M.R., Lowary, T.L., 2010. Probing the effect of acylation on arabinofuranose ring conformation in di- and trisaccharide fragments of mycobacterial arabinogalactan. J. Org. Chem. 75, 4992–5007.

McNeil, M., Daffé, M., Brennan, P.J., 1991. Location of the mycolyl ester substituents in the cell walls of mycobacteria. J. Biol. Chem. 266, 13217–13223.

Mereyala, H.B., Hotha, S., Gurjar, M.K., 1998. Synthesis of pentaarabinofuranosyl structure motif A of Mycobacterium tuberculosis. Chem. Commun. (Camb.) 685–686.

Miyauchi, M., Murata, M., Shibuya, K., Koga-Yamakawa, E., Uenishi, Y., Kusunose, N., Sunagawa, M., Yano, I., Kashiwazaki, Y., 2011. Arabino-mycolates derived from cell-wall skeleton of *Mycobacterium bovis* BCG as a prominent structure for recognition by host immunity. Drug Discov. Today Ther. Strateg. 5, 130–135.

Mizutani, K., Kasai, R., Nakamura, M., Tanaka, O., Matsuura, H., 1989. N.M.R. Spectral study of α- and β-L-arabinofuranosides. Carbohydr. Res. 185, 27–38.

Mohammed, M.O., Baird, M.S., Al Dulayymi, J.R., 2015. Mycolyl arabino glycerols from synthetic mycolic acids. Tetrahedron Lett. 56, 3268–3272.

Reddy, K.C., Padmaja, N., Pathak, V., Pathak, A.K., 2012. Concise synthesis of an arabinofuranose hexasaccharide present in the cell wall of Mycobacterium tuberculosis. Tetrahedron Lett. 53, 2461–2464.

Rombouts, Y., Brust, B., Ojha, A.K., Maes, E., Coddeville, B., Elass-Rochard, E., Kremer, L., Guerardel, Y., 2012. Exposure of Mycobacteria to Cell Wall-inhibitory Drugs Decreases Production of Arabinoglycerolipid Related to Mycolyl-arabinogalactan-peptidoglycan Metabolism. J. Biol. Chem. 287, 11060–11069.

Salah, A.D., 2013. Development of a Method for Detecting TB-antibodies in Patient Serum. PhD Thesis. Bangor University.

Sunakawa, J., Uenishi, Y., Kususe, N., Ito, Y., Ishiwata, A., Arao, H., Yan, I., Fujita, Y., JP2006312604.

Uenishi, Y., Kusunose, N., Yano, I., Sunagawa, M., 2010. Isolation and identification of arabinose mycolates of Cell Wall Skeleton (CWS) derived from Mycobacterium bovis BCG Tokyo 172 (SMP-105). J. Microbiol. Meth. 80, 302–305.

Watanabe, M., Kudoh, S., Yamada, Y., Iguchi, K., Minnikin, D.E., 1992. A new glycolipid from *Mycobacterium avium-Mycobacterium intracellulare* complex. Biochim. Biophys. Acta 1165, 53–60.

Watanabe, M., Ohta, A., Sasaki, S., Minnikin, D.E., 1999. Structure of a new Glycolipid from the Mycobacterium avium-Mycobacterium intracellulare complex. J. Bacteriol. 181, 2293–2297.