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SOME ESTERS OF LEVOGLUCOSAN

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ABSTRACT

It is shown that esterification of levoglucosan with octanoyl or hexadecanoyl chloride under limiting conditions provides a mixture of the theoretically possible esters. These compounds have been separated, their ratios determined, and their properties recorded.

INTRODUCTION

Fatty acid esters of carbohydrates, particularly of 1,4-anhydro-D-glucitol and sucrose, are used, or have been suggested for use, as non-ionic surfactants. We are interested in the development of levoglucosan (1,6-anhydro-β-D-glucopyranose, **1**) for various applications, and have investigated its long-chain fatty acid esters. The initial experiments were aimed at opening the 1,6-anhydro ring with simultaneous esterification at O-1, to obtain a D-glucosyl monoester, but this proved to be more difficult than expected. Attempts were also made first to block O-2 and O-4 in levoglucosan with benzeneboronic acid[1], esterify O-3, and then remove the blocking group, to produce a monoester. This approach also proved unsatisfactory, because of partial decomposition of the boronic ester, and was modified in favor of selective esterification of levoglucan.

Many methods are applicable[2,3] for the esterification of **1**, and the literature contains examples of a variety of esters, particularly the di- and tri-acetates, benzoates, methanesulfonates, and their derivatives. However, we could find no examples of mono-esters of long-chain (C_8 to C_{20}) fatty acids that would be expected to be more suitable for our purpose. We now provide an account of our investigation on the synthesis of such compounds, and on selective esterification of levoglucosan.

RESULTS AND DISCUSSION

Addition of an acid chloride to a solution of **1** in anhydrous pyridine cooled to 0° (or below) resulted in an immediate, exothermic reaction. Generally, the reaction

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TABLE I

SELECTED ^{1}H-N.M.R. PARAMETERS[a] FOR SOME ESTERS OF LEVOGLUCOSAN

Compound	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*endo	*H-6*exo
2[b]	5.46(s)	4.60(m)	4.86(m)	4.65(m)	4.65(m)	4.11(d)	3.78(dd)
3[b]	5.47(s)	4.56(m)	3.77(s)	4.62(m)	4.62	4.18(d)	3.77(m)
4[c]	5.45(s)	4.73(s)	4.89(m)	4.73	4.73(m)	4.10(d)	3.76(dd)
5[d]	5.45(s)	← 3.50(s), 4.80(s), 4.68(s) → protons unspecified			4.59(d)	4.12(d)	3.89(dd)
6[d]	5.46(s)	← 4.67(s), 4.60(s), 3.73(s) → protons unspecified			4.61(d)	4.20(d)	3.77(dd)
7[c]	5.44(s)	4.56(s)	3.70(s)	4.66(s)	4.57(d)	4.18(d)	3.75(dd)
8[b]	5.50(s)	← 4.74(s), 3.79(s), 3.56(d) → protons unspecified			4.59(d)	4.24(d)	3.81(dd)
9[b]	5.43(s)	← 4.58(s), 3.76(s), 3.65(s) → protons unspecified			4.59(d)	4.23(d)	3.71(dd)
10[b]	5.45(s)	← 4.58(m), 4.61(m) → protons unspecified			4.61(d)	4.09(d)	3.80(dd)
11[b]	5.45(s)	← 4.56(m), 3.75(s) → protons unspecified			4.64(d)	4.19(d)	3.76(dd)
13[d]	5.47(s)	← 4.60, 3.66, 3.79(m) → protons unspecified			4.60	4.25(d)	3.79(m)

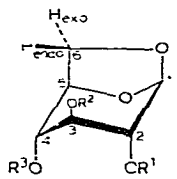
[a]All values in p.p.m. from Me_4Si. All spectra for solutions in $CDCl_3$. [b]100 MHz. [c]60 MHz. [d]360 MHz. [e]250 MHz.

was complete within 15 minutes of the initial addition. Processing consisted in removal of the pyridine under vacuum, followed by chromatographic separation.

The di- and tri-acetates of **1** have been reported[3], and the p.m.r. spectrum of 2,3,4-tri-*O*-acetyl-1,6-anhydro-β-D-glucopyranose (**2**) is known[4,5]. We prepared samples of these compounds to use for p.m.r. comparison. Under the reaction conditions employed, we were unable to obtain any monoacetates of **1**. Even under severely limiting conditions, involving a large excess of **1** relative to acetyl chloride, only two esters were obtained, namely, **2** and 2,4-di-*O*-acetyl-1,6-anhydro-β-D-hexopyranose (**3**). Compound **2** was identical with authentic samples, and the structure of **3** was deduced from comparison of the melting point and optical rotation with those reported by Shapiro *et al.*[3], who unequivocally determined the structures of the 2,3- 2,4- and 3,4-diacetates of **1**. The p.m.r. spectrum of **3** has, however, to the best of our knowledge, never been reported (see Table I and Experimental section). An interesting feature of it is the very large, upfield shift (1.09 p.p.m.) in the resonance position of H-3 of **3** on replacement of an acetate group by a hydroxyl group.

Treatment of **1** with octanoyl chloride in anhydrous pyridine under limiting conditions (3-fold excess of **1**) yielded a mixture of octanoic esters. A total yield of 27.6%, based on the initial amount of acid chloride used, was obtained. After the removal of pyridine under vacuum, and chromatographic separation, six distinct compounds were obtained. Of the total products separated, there were 16% of tri-

octanoate, 51% of different dioctanoates, and 33% of the two monooctanoates. The p.m.r. spectrum of 1,6-anhydro-2,3,4-tri-*O*-octanoyl-β-D-glucopyranose (**4**) (listed partially in Table I and completely in the Experimental section) was closely similar to that of **2**.



1 $R^1 = R^2 = R^3 = H$
2 $R^1 = R^2 = R^3 = Ac$
3 $R^1 = R^3 = Ac$, $R^2 = H$
4 $R^1 = R^2 = R^3 = a$
5*† 1 of the R groups = H, 2 of the R groups = a
6*† 1 of the R groups = H, 2 of the R groups = a
7 Tentatively assigned as $R^1 = R^3 = a$, $R^2 = H$
8† $R^1 = a$, $R^2 = R^3 = H$
9*† 2 of the R groups = H, 1 of the R groups = a
10 $R^1 = R^2 = R^3 = b$
11* 1 of the R groups = H, 2 of the R groups = b
12*† 2 of the R groups = H, 1 of the R groups = b
13*† 2 of the R groups = H, 1 of the R groups = b

a = $-C(=O)-(CH_2)_6-Me$

b = $-C(=O)-(CH_2)_2-Me$

* Absolute assignment is at present impossible
† These compounds are chromatographically different

The three dioctanoates theoretically possible, namely, **5**, **6**, and **7**, were obtained in the ratios of 1.7:19.9:1; they were chromatographically different, but the elemental analysis of each agreed with that calculated for $C_{22}H_{38}O_7$. The absolute stereochemistry of these compounds has eluded us, as the pyranose ring seems to assume a conformation (consistent with crystal studies reported by Leung *et al.*[6]) resulting in negligible observable coupling between H-1, 2, 3, 4, and 5. At 360 MHz, the resonances due to H-2, 3, and 4 of **5** are observed as slightly broadened singlets. Decoupling each of these in turn caused no observable change in the remaining spectrum.

In the spectrum of **6**, two of the three unassigned protons appear as singlets, and the third, at δ 3.73, is a broad singlet partially overlapping the doublet of doublets due to H-6-*exo*. A well defined doublet at δ 3.15 (*J* 4.68 Hz), due to the free OH, disappears on addition of D_2O. Irradiation of the resonances at δ 4.59 and 4.67 caused no change in the remaining spectrum, and irradiation at δ 3.73 resulted in collapse of the doublet at δ 3.15.

We were unable to decouple the spectrum of **7**; however, addition of D_2O caused collapse of the multiplet at δ 3.07, indicating that it was an OH resonance. The appearance of this spectrum is, however, almost identical with that of **6**.

On comparing the p.m.r. spectrum of **3** with those of **5**, **6**, **7**, it appeared that that of **7** most closely approximates that of **3** with respect to pyranose-ring protons. Hence, we have tentatively assigned **7** as 1,6-anhydro-2,4-di-*O*-octanoyl-β-D-hexopyranose, but we are unable to assign, unequivocally, structures to the remaining two spectra (of **5** and **6**).

Also noteworthy is the fact that one of these esters is formed in very much higher proportions than the other two. Jeanloz *et al.*[2] speculated that OH-2 and OH-4 are similar in reactivity, and slightly more reactive than OH-3. It initially seemed to us that the most likely major product would be the 2,4-dioctanoate, but, if our assignment of the spectrum of **7** is correct, it would appear that the 2,4-dioctanoate is not the most prevalent product. Models indicate that, for steric reasons, a 2,3- or 3,4-diester might be favored.

The remaining two compounds, **8** and **9**, obtained in the ratio of 2.25:1, gave the correct elemental analysis for mono-octanoates, and were chromatographically and magnetically different. Both solidified on long standing, to produce waxy solids of low melting point. On repetition of this reaction, although the total quantity of these mono-esters isolated remained essentially the same, their ratio differed greatly, and, in one reaction, only one of these compounds, **8**, was obtained. On studying the p.m.r. spectra, it was seen that these two compounds are strikingly similar, but subtly different. H-1 of **8** is observed at nearly 0.1 p.p.m. lower field than that observed for H-1 in **9**. This may indicate that the ester group is resident on C-2, as a slight down-field shift in H-1 would be expected, due to a β-substituent effect on replacing OH-2 by an ester[7]. Again, decoupling of the resonances at δ 4.74, 3.79, and 3.57 caused no change in the remaining spectrum. Deuterium replacement indicated that the coupling observed at resonance δ 3.57 is due to an OH and H attached to the same carbon atom. We thus tentatively suggest that compound **8** is 1,6-anhydro-2-*O*-octanoyl-β-D-glucopyranose.

Treatment of **1** with hexadecanoyl (palmitoyl) chloride differed from the aforedescribed reaction, in that it could not be conducted at 0°, because, on introducing palmitoyl chloride to cold pyridine, solidification occurred. The reaction was therefore conducted at room temperature, and the mixture was stirred overnight. Initially, on completion of the reaction, the pyridine was removed as a copper (II) complex by addition of a saturated solution of aqueous copper sulfate, and the mixture was then extracted with chloroform. When this method of processing was used, only two compounds were recovered in appreciable amount, namely, 1,6-anhydro-2,3,4-tri-*O*-palmitoyl-β-D-glucopyranose (**10**) and dipalmitate **11**. These were obtained in the ratio of ~4:3 and constituted ~70% of the total recoverable material expected (based on the initial quantity of acid chloride used). Traces of materials that appeared to be two monopalmitates (~1.0 mg) were observed at R_F 0.24 and 0.17.

Removal of the residual pyridine under vacuum as already described, instead of using copper sulfate, left a white solid. Chromatographic separation produced four major fractions, **10** (40%), **11** (28%), **12** (19%), and **13** (12%), a 99% yield of esters being isolated, based on the initial quantity of acid chloride used. As observed previously, g.l.c. analysis showed spots, occurring slightly above and below that due to **11**, which were presumed to be those of two other dipalmitates, isolated in small quantity (~1.5 mg) (see Experimental section). The p.m.r. spectrum of **10** was similar to those of **4** and **2** (see Table I and Experimental section), and was assigned accordingly. As with **5**, **6**, and **7**, decoupling experiments did not provide elucidation of the stereochemistry (similarly, for **13**). Compound **12** appeared, from the p.m.r. spectrum, to be a monoester; however, an impurity was observable in the p.m.r. spectrum (reflected in the results of microanalysis), and attempts to remove it chromatographically were unsuccessful.

It appears from this investigation that, owing to the high reactivity of the hydroxyl groups in **1**, high yields of mono-esters are not achievable by simply increasing the chain length of the acid chloride. Steric hindrance is not large enough to prevent polyesterification.

EXPERIMENTAL

General. — All t.l.c. assays were conducted on Baker-flex silica gel IB2-F (J. T. Baker Chemical Company). In all instances, t.l.c. visibilization was achieved either by u.v. absorbance or by spraying with (*a*) 1:2:37 anisaldehyde–sulfuric acid–ethanol, or (*b*) 10% dodecaphosphomolybdic acid in ethanol. Silica used for column chromatography was supplied by E. Merck (silica gel 60, Cat. No. 7734; 70–230 mesh, ASTM), as was the silica used for p.l.c. plates (Cat. No. 7748, PF 254 + 366). P.m.r. (100 and 360 MHz) spectra were recorded at Colorado State University and 250-MHz spectra at Montana State University, and 60-MHz spectra were recorded with a Varian EM 360 spectrometer. Infrared spectra were recorded with a Nicolet MX-1 instrument, and mass spectra with a Varian M.A.T. III spectrometer.

Acetylation of levoglucosan. — To a solution of levoglucosan (1.042 g, 6.4 mmol) in anhydrous pyridine (5 mL), cooled to 0°, was added acetyl chloride (0.500 g). After 10 min, t.l.c. analysis of the mixture showed three spots, at R_F 0.45, 0.58, and 0.66, on a plate of silica eluted with 3:2:8 methanol–1,2-dichloroethane–ethyl acetate; the spot at R_F 0.45 was levoglucosan. The t.l.c. pattern of the mixture remained unchanged after 1 h; another portion of acetyl chloride (0.500 g) was then added, and, within 0.5 h, only one (elongated) spot was observable. The mixture was evaporated under vacuum, and the residue was passed through a column (3.5 × 23 cm) of silica, using 1:1 ethyl acetate–pet. ether (b.p. 30–60°), to provide three components. The first compound (**2**), R_F 0.79, was crystalline; yield 0.701 g (2.4 mmol). Recrystallization from methanol, and then cyclohexane, produced needle-like crystals, m.p. 110–111° (an authentic sample had m.p. 110–111°); ν_{max}^{KBr} 2989, 2921 (CH), 1754, 1733 (C=O), 1367, 1249, 1235, 1218, 1150, 1117, 1050, and 889

cm^{-1} (all strong); ^{1}H-n.m.r. (100 MHz, $CDCl_3$–Me_4Si): δ 5.46 (s, 1 H, H-1), 4.86 (m, 1 H, H-3, $J_{2,3}$ ~1.5, $J_{3,4}$ 1.5 Hz), 4.65 (m, 2 H, H-4,5), 4.60 (m, 1 H, H-2), 4.11 (d, 1 H, H-6*endo*, $J_{6endo,exo}$ 7.57 Hz), 3.78 (dd, 1 H, H-6*exo*, $J_{6endo,exo}$ 7.57, $J_{5,6exo}$ 5.61 Hz), and 2.18, 2.15, and 2.12 (3 s, 3 H each, Ac-3, 2, and 4, respectively); this n.m.r. spectrum is in good agreement with that reported by Budesinsky *et al.*[5]; *m/z*: parent 288 (0.5), 245 (1), 243 (2), 230 (20), 229 (18), 187 (41), 179 (13), 141 (52), 128 (30), 127 (28), and 116 (100%).

Anal. Calc. for $C_{12}H_{16}O_8$: C, 50.00; H, 5.59. Found: C, 50.03; H, 5.50.

The second component (3), R_F 0.74, yielded a solid having a sharp melting point after crystallization from methanol and recrystallization from chloroform–cyclohexane[3]: recrystallized, yield 0.325 g (1.13 mmol); m.p. 129–130° (uncorr.) (lit.[2] 132–133°); ν_{max}^{KBr} 3498 (OH), 2976, 2920 (CH), 1741 (C=O), 1374, 1239, 1140, and 1087 cm^{-1} (all very strong): ^{1}H-n.m.r. (100 MHz, $CDCl_3$–Me_4Si): δ 5.47 (s, 1 H, H-1), 4.62 (m, 2 H, H-4,5), 4.56 (m, 1 H, H-2), 4.18 (d, 1 H, H-6*endo*, $J_{6endo,exo}$ 7.09 Hz), 3.77 (m, 2 H, H-6*exo*,3, $J_{5,6exo}$ 5.37, $J_{6endo,exo}$ 7.80 Hz), 3.06 (broad s, 1 H, OH), and 2.16 and 2.15 (2 s, Ac-4 and 2, respectively); *m/z*: parent 246 (3), 202 (6), 157 (20), 156 (28), 114 (100), 111 (39), 101 (49), and 96 (76%).

Anal. Calc. for $C_{10}H_{14}O_7$: C, 48.78; H, 5.73. Found: C, 48.97; H, 5.83.

The third component was unreacted levoglucosan.

Reaction of levoglucosan with octanoyl chloride. — To a solution of levoglucosan (1.0 g, 6.2 mmol) in anhydrous pyridine (6 mL), cooled to 0°, was added octanoyl chloride (1.053 mL, 6.2 mmol); the mixture was kept for 3 h at 0°, when t.l.c. showed no further change. The pyridine hydrochloride was filtered off, the filtrate evaporated, and the residue subjected to high vacuum overnight (to remove the remaining pyridine). A light-yellow, sticky residue remained. T.l.c. of this material showed 5 spots, at R_F 0.14, 0.21, 0.54, 0.64, and 0.86, on elution with 1:1 ethyl acetate–pet. ether (b.p. 30–60°). The spot at R_F 0.14 proved to be that of levoglucosan. Separation by chromatography in a column (2 × 100 cm) of silica eluted with 1:1 hexane–ethyl acetate gave the following products.

Trioctanoate **4**. — This was obtained as a colorless oil, R_F 0.86, yield, 0.135 g; ν_{max}^{KBr} 2956, 2927, 2853 (CH), 1736 (C=O, broad), 1169, 1141, and 1053 cm^{-1} (strong); ^{1}H-n.m.r. (60 MHz, $CDCl_3$–Me_4Si): δ 5.46 (s, 1 H, H-1), 4.89 (m, 1 H, H-3), 4.73 (m, 3 H, H-5,2,4), 4.10 (d, 1 H, H-6*endo*, $J_{6exo,endo}$ 7.0 Hz), 3.76 (dd, 1 H, H-6*exo*, $J_{6exo,endo}$ 7.0, $J_{5,6exo}$ ~5.0 Hz), 2.40 (t, 6 H, -CH_2-CO-), 1.35 (m, 30 H, -CH_2-), and 0.90 (m, 9 H, 3 CH_3).

Anal. Calc. for $C_{30}H_{52}O_8$: C, 66.64; H, 9.69. Found: C, 66.79; H, 9.85.

Dioctanoates. — The material with R_F 0.54–0.64 was rechromatographed on a column (2 × 100 cm) of silica eluted with 1:3 ethyl acetate–pet. ether, to yield 3 fractions, **5**, **6**, and **7**, with the following R_F values and yields; 0.36 (0.025 g), 0.44 (0.284 g), and 0.54 (0.015 g), respectively. Fractions **5** and **7** were light-yellow oils, and fraction **6** solidified on long standing to a waxy material, m.p. 33–34°.

Physical data. — Compound **5**. ^{1}H-n.m.r. (360 MHz, $CDCl_3$–Me_4Si): δ 5.45 (s, 1 H, H-1), 4.79 (s, 1 H), 4.67 (s, 1 H), 4.59 (d, 1 H, H-5, $J_{5,6exo}$ 5.42 Hz), 4.12

(d, 1 H, H-6*endo*, $J_{5,6endo}$ 6.75 Hz), 3.79 (dd, 1 H, H-6*exo*, $J_{6exo,endo}$ 6.75, $J_{5,6exo}$ 5.42 Hz), 3.50 (s, 1 H), 2.42 (t, 2 H, -CO-CH_2-), 2.36 (t, 2 H, -CO-CH_2-), 1.15 (m, 4 H, -CO-CH$_2$-CH_2-), 1.28 (m, 16 H, -CH$_2$-), and 0.91 (t, 6 H, 2 CH_3).

Compound **6**. ν_{max}^{KBr} 3489 (OH); 2929, 2919, 2845 (CH); 1733, 1718 (C=O); 1181, 1138, and 1022 cm^{-1}; ^{1}H-n.m.r. (360 MHz, CDCl$_3$–Me$_4$Si); δ 5.46 (s, 1 H, H-1), 4.67 (s, 1 H), 4.61 (d, 1 H, H-5, $J_{5,6exo}$ 7.35 Hz), 4.60 (s, 1 H), 4.20 (d, 1 H, H-6*endo*, $J_{6exo,endo}$ 6.05 Hz), 3.77 (dd, 1 H, H-6*exo*, $J_{6exo,endo}$ 6.05, $J_{5,6exo}$ 7.35 Hz), 3.73 (broad s, 1 H), 3.15 (d, 1 H, OH, J 4.68 Hz), 2.30 (m, 4 H, -CO-CH_2-), 1.56 (m, 4 H, -CO-CH$_2$-CH_2-), 1.20 (m, 16 H, -CH$_2$-), and 0.79 (t, 6 H, 2 CH$_3$).

Compound **7**. ^{1}H-n.m.r. (250 MHz, CDCl$_3$–Me$_4$Si); δ 5.44 (s, 1 H, H-1), 4.66 (m, 1 H, H-4), 4.57 (d, 1 H, H-5, $J_{5,6exo}$ 6.20 Hz), 4.56 (s, 1 H, H-2), 4.18 (d, 1 H, H-6*endo*, $J_{6exo,endo}$ 7.54 Hz), 3.75 (dd, 1 H, H-6*exo*, $J_{6exo,endo}$ 7.54, $J_{5,6exo}$ 6.20 Hz), 3.70 (broad s, 1 H, H-3), 3.07 (m, 1 H, OH), 2.37 (t, 2 H, -CO-CH_2-), 2.39 (t, 2 H, -CO-CH_2-), 1.57 (t, 2 H, -CO-CH$_2$-CH_2-), 1.56 (t, 2 H, -CO-CH$_2$-CH_2-), 1.25 (m, 16 H, -CH_2-), and 0.86 (t, 6 H, 2 CH_3).

Anal. Calc. for $C_{22}H_{38}O_7$: C, 63.74; H, 9.24. Found: **5**: C, 63.99; H, 9.26. **6**: C, 63.77; H, 9.23. **7**: C, 63.79; H, 9.25.

Mono-octanoates. Two fractions, **8** and **9**, obtained from the initial chromatographic column, having R_F values of 0.30 (0.097 g) and 0.18 (0.043 g), respectively, on silica plates eluted with 1:1 ethyl acetate–pet. ether (b.p. 30–60°), proved to be mono-octanoate derivatives of levoglucosan. Both **8** and **9** solidified on long standing, to give waxy solids. **8** was reddish in color, and **9** remained yellow. The quantities of these two materials that were obtained seemed to vary substantially from one reaction to the next, despite attempts to maintain similar conditions.

Compound **8**: ν_{max}^{KBr} 3331 (OH); 2929, 2919, 2853 (CH); 1733 (C=O); 1170, 1061, 1009, and 927 cm^{-1} (all strong); ^{1}H-n.m.r. (100 MHz, CDCl$_3$–Me$_4$Si): δ 5.50 (s, 1 H, H-1), 4.73 (s, 1 H), 4.59 (d, 1 H, H-5, $J_{5,6exo}$ 4.98 Hz), 4.24 (d, 1 H, H-6*endo*, $J_{6exo,endo}$ 7.94 Hz), 3.81 (dd, 1 H, H-6*exo*, $J_{6exo,endo}$ 7.97, $J_{5,6exo}$ 4.98 Hz), 3.79 (bs, 1 H), 3.56 (d, 1 H, J 6.39 Hz), 2.75 (bs, 1 H, OH), 2.40 (t, 2 H, CO-CH_2-O), 1.66 (t, 2 H, CO-CH$_2$-CH_2-), 1.28 (m, 8 H, -CH_2-), and 0.88 (t, 3 H, CH_3).

Compound **9**. ν_{max}^{KBr} 3376 (OH); 2959, 2925, 2854 (CH); 1728 (C=O); 1465, 1387, 1322, 1142, 1053, and 914 cm^{-1}; ^{1}H-n.m.r. (100 MHz, CDCl$_3$–Me$_4$Si): δ 5.43 (bs, 1 H, H-1), 4.58 (bs, 2 H, H-5, H-?) 4.23 (d, 1 H, H-6*endo*, $J_{6exo,endo}$ 7.33 Hz), 3.71 (dd, 1 H, H-6*exo*, $J_{5,6exo}$ 3.63, $J_{6exo,endo}$ 7.33 Hz), 3.76 (bs, 1 H), 3.65 (bs, 1 H), 3.38 (bs, 2 H, OH, ?), 2.38 (t, 2 H, -CO-CH_2-), 1.64 (t, 2 H, -CO-CH$_2$-CH_2-), 1.28 (m, 8 H, -CH$_2$-), and 0.88 (t, 3 H, CH$_3$).

Anal. Calc. for $C_{14}H_{24}O_6$: C, 58.32; H, 8.39. Found: **8**: C, 58.39; H, 8.41. **9**: C, 58.41; H, 8.28.

Mass-spectral data. — *Compound* **4**. The parent ion should have a mass of 540 m.u., but this was not observed; the highest countable mass was 200 m.u. Other peaks, above this, were observed, but accurate counting was impossible. Nothing above 350 m.u. was observed; 200 (16), 150 (21), 146 (34), 145 (16), 144 (16), 129 (39), 128 (100), 116 (34), 110 (34), and 100 (100%).

Compound **6**. The parent ion should have been 414 m.u.; however, accurate counting above 200 m.u. proved impossible. Peaks in the order of 400 m.u. were observed.

Compound **8**. The parent ion should be 288 m.u., but the highest countable peak was 277 m.u. The next, well defined peaks were observed at 147 m.u. (30), 125 (54), 113 (97), and 99 (100%).

Compound **9**. The parent ion should be 288 m.u., but the highest mass observed was 198 (5%); 144 (12), 126 (100), 119 (80), and 96 (33%).

Reaction of levoglucosan with palmitoyl chloride. — A solution of levoglucosan (1.315 g, 8.11 mmol) in anhydrous pyridine (~6 mL) was cooled to 0°. Addition of palmitoyl chloride (2.23 g, 1 equiv.) caused instant solidification. The mixture was allowed to warm to room temperature, and was stirred overnight. The excess of pyridine was removed by addition of a saturated solution of aqueous $CuSO_4$, followed by extraction with chloroform. The extract was dried (anhydrous sodium sulfate), and evaporated; yield 1.353 g of a greenish solid. T.l.c. on plates of silica eluted with 1:1 ethyl acetate–pet. ether (b.p. 30–60°) showed 4 spots, R_F 0.74, 0.64, 0.24, and 0.17. A spot at R_F 0.17 was levoglucosan. Separation was effected on a column (2 × 30 cm) of silica with elution with the same solvent, to yield two major fractions, R_F 0.74 (0.896 g) and R_F 0.64 (0.447 g), with traces at R_F 0.24 and 0.17 (only ~2 mg of each was isolated). Recrystallization from hexane yielded two white solids, **10** and **11**.

Physical data. — *Compound* **10**. R_F 0.74; m.p. 68–69°; ν_{max}^{KBr} 2926, 2850 (CH), 1740 (C=O), 1470, 1167, and 1106 cm^{-1} (all strong); ^{1}H-n.m.r. (100 MHz, $CDCl_3$–Me_4Si): δ 5.45 (s, 1 H, H-1), 4.85 (m, 1 H, H-3, w/2 6 Hz), 4.61 (m, 3 H, H-2,4,5, w/2 ~8 Hz), 4.09 (d, 1 H, H-6*endo*, $J_{6exo,endo}$ 8.96 Hz), 3.80 (dd, 1 H, H-6*exo*, $J_{6exo,endo}$ 8.96, $J_{5,6exo}$ 3.98 Hz), 2.35 (m, 6 H, -CO-CH_2-), 1.62 (m, 6 H, -CO-CH_2-CH_2-), 1.26 (m, 30 H, -CH_2-), and 0.88 (t, 9 H, 3 CH_3).

Compound **11**. R_F 0.64; m.p. 84–85°; ν_{max}^{KBr} 3485 (OH); 2952, 2919, 2850 (CH); 1736, 1719 (C=O); 1466, 1268, 1180, 1140, 913, and 721 cm^{-1}; ^{1}H-n.m.r. (100 MHz, $CDCl_3$–Me_4Si): δ 5.45 (s, 1 H, H-1), 4.64 (m, 2 H, H-5, H-?), 4.56 (m, 1 H), 4.19 (d, 1 H, H-6*endo*, $J_{6exo,endo}$ 7.57 Hz), 3.76 (dd, 1 H, H-6*exo*, $J_{6exo,endo}$ 7.57, $J_{5,6exo}$ 5.43 Hz), 3.75 (s, 1 H), 3.10 (bs, 1 H, OH), 2.38 (bt, 4 H, -CO-CH_2-), 1.61 (m, 4 H, -CO-CH_2CH_2-), 1.25 (m, 20 H, -CH_2-), and 0.88 (m, 6 H, CH_3).

Because of the ready solubility of levoglucosan and its mono-esters in water, the method of processing was altered. If the excess of pyridine is removed under vacuum, a white, waxy solid remains. On dissolution in ethyl acetate, t.l.c. on silica plates with 1:1 ethyl acetate–hexane showed the presence of seven compounds, R_F 0.90, 0.87 (trace), 0.85, 0.82 (trace), 0.52, 0.40, and 0.02. A white solid, insoluble in ethyl acetate, which proved to be unreacted levoglucosan (R_F 0.02), was also obtained. Separation on silica columns and p.l.c. plates provided four desired compounds. A total of 0.296 g of the di- and tri-palmitic esters was obtained. These were isolated *via* p.l.c. plates, to yield the tripalmitate **10** (40%) and the dipalmitate **11** (28%). Traces of two other compounds, presumed to be dipalmitates (R_F 0.87 and

0.82), were obtained (~1.5 mg of each), along with 0.156 g (20%) and 0.102 g (12%) of the mono-esters **12** and **13**.

Physical data for the two mono-esters. — *Compound* **12**. R_F 0.52; m.p. 67–68°; ν_{max}^{KBr} 3412 (OH); 2917, 2951 (CH); 1732 (C=O); 1479, 1167, 1144, 1060, 1006, and 924 cm^{-1}. The ^{1}H-n.m.r. spectrum of this compound seemed to indicate that a mono-ester derivative had been formed. However, both the n.m.r. spectrum and the micro-analysis showed an apparent impurity not removable by recrystallization or chromatography.

Compound **13**. R_F 0.40; m.p. 54–58°; ν_{max}^{KBr} 3412, 3355 (OH); 2933, 2850 (CH); 1737 (C=O); 1489, 1167, 891, and 813 cm^{-1}; ^{1}H-n.m.r. (360 MHz, $CDCl_3$–Me_4Si): δ 5.47 (s, 1 H, H-1), 4.60 (s, 2 H, H-5, H-?), 4.25 (d, 1 H, H-6*endo*, $J_{6endo,exo}$ 7.33 Hz), 3.79 (m, 2 H, H-6*exo*, H-?), 3.66 (s, 1 H), 2.71 (bs, 2 H, OH), 2.37 (t, 2 H, CO-CH_2-), 1.63 (t, 2 H, -CO-CH_2-CH_2-), 1.25 (m, 8 H, -CH_2), and 0.88 (t, 3 H, CH_3).

Anal. Calc. for $C_{20}H_{36}O_6$: C, 64.49; H, 9.74. Found: C, 64.55; H, 9.87.

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