JOURNAL
OF
THE CHEMICAL SOCIETY

PERKIN TRANSACTIONS I
Organic and Bio-organic Chemistry

A Possible Model for a New Chiral Glyceride Synthesis. Part 2.[1] Synthesis of 1,3-Di-*O*-aroyl- and 1-*O*-Aroyl-3-*O*-tosyl-*sn*-glycerols from 2,5-*O*-Methylene-D-mannitol

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1,3-Di-*O*-aroyl- and 1-*O*-aroyl-3-*O*-tosyl-*sn*-glycerols have been prepared from D-mannitol *via* 2,5-*O*-methylene-D-mannitol. Some 1,3-diglycerides have also been synthesised from 3-*O*-aroyl-*sn*-glycerols. The optical rotations and the structure of the 1,3-diglycerides have also been confirmed.

We have previously described the synthesis of 1-*O*-aroyl-2-*O*-tosyl-*sn*-glycerols.[1] We now report the preparation of 1,3-di-*O*-aroyl- (4) and 1-*O*-aroyl-3-*O*-tosyl-*sn*-glycerols (12) which are required as intermediates in the synthesis of triglycerides and of di-*O*-aroyl-*sn*-glycerol-3-iodohydrins.

The synthesis of 1,3-di-*O*-acyl-*sn*-glycerols (4) from 3-*O*-acyl-*sn*-glycerols (2) by the action of an acyl chloride leads to mixtures which are difficult to separate (Scheme 1).[2-4] Since attempts to increase the yield using a variety of conditions were unsuccessful, we have investigated a new method (Scheme 2). The optical rotations of enantiomers from these two methods are equivalent, that would show any partial racemisation, in particular when the methylene group was eliminated. But the position of aroyl groups and the optical rotations of 1,3-diglycerides (12) and (13) were confirmed by an unambiguous method.

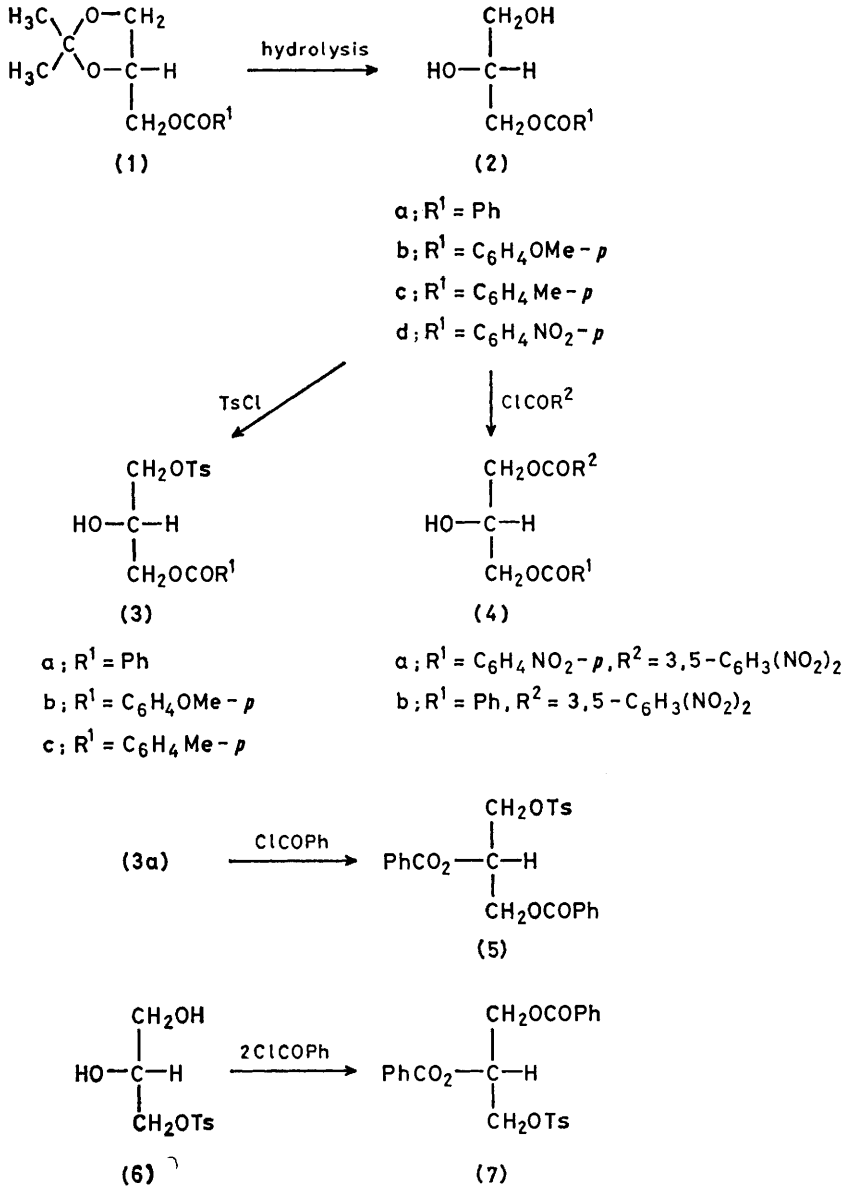
RESULTS AND DISCUSSION

Preparation of 1,3-*Di*-O-*aroyl*-sn-*glycerols from* 1-O-*Aroyl*-sn-*glycerols.*—The original method [2] gives large quantities of by-products (1,2-diglycerides and triglycerides). Treatment of 1-*O*-aroyl-*sn*-glycerol with 0.5, 0.75, or 1 equiv. of acid chloride or tosyl chloride at room temperature for 18 h did not improve the overall yield, and the reaction time (4—48 h) had no influence. Column chromatography gave the following products: 1,3-diglycerides (40—55%), 1,2-diglycerides (5%), and triglycerides (10—30%).

Synthesis of 1,3-*Diglycerides from* 2,5-O-*Methylene*-D-*mannitol.*—2,5-*O*-Methylene-D-mannitol was obtained from D-mannitol *via* 1,3:2,5:4,6-tri-*O*-methylene-D-mannitol, and *via* 1,6-di-*O*-acetyl-3,4-di-*O*-acetoxymethyl-2,5-*O*-methylene-D-mannitol.[5] The action of 2 mol of acid chloride on the methylene derivative in pyridine gave the 1,6-di-*O*-aroyl-2,5-*O*-methylene-D-mannitol (8). Oxidation of this compound with lead(IV) acetate in ethyl acetate, and reduction of the aldehyde with sodium borohydride in the same solvent gave the 2,2′-*O*-methylenebis(1-*O*-aroyl-*sn*-glycerol). The latter was converted into 2,2′-*O*-methylenebis(1,3-di-*O*-aroyl-*sn*-glycerol) with 2 mol of a second acid chloride ($ClCOR^2$), or into 2,2′-*O*-methylenebis(1-*O*-aroyl-3-*O*-tosyl-*sn*-glycerol) with 2 mol of tosyl chloride. The hydrolysis of compounds (10) or (11) in acetic acid with hydrochloric acid gives the 1,3-diglycerides contaminated with impurities.

To increase the yield of 1,3-diglycerides, reactions were carried out at different temperatures, for different periods of time, and with different ratios of acetic acid, water, and hydrochloric acid. Hydrolysis with 96% sulphuric acid or 38% hydrochloric acid in ethanol–water gave the same results. In relation to the report of Gigg,[6] hydrolysis could be effected by hydrogen chloride in methanol, but under these conditions facile transposition of aroyl groups occurs.[7,8] Products were isolated by chromatography. The hydrolysis of 2,2′-*O*-methylenebis(1-*O*-benzoyl-3-*O*-*p*-nitrobenzoyl-*sn*-glycerol) (11a), effected under suitable conditions for the formation of by-products, gave, after treatment and chromatography, three products: A (36%), 1,3-diglyceride (50%), and B (12%). Compound (A) was characterised as 1-*O*-benzoyl-2-*O*-acetyl-3-*O*-*p*-nitrobenzoyl-*sn*-glycerol on the basis of n.m.r. acetyl-methyl signal. An identical sample of (A) was also prepared by

treatment of 1-*O*-benzoyl-3-*O*-*p*-nitrobenzoyl-*sn*-glycerol with acetyl chloride. Compound (B), on the basis of its t.l.c. behaviour was a 1,2- or 2,3-diglyceride (one spot). To confirm this hypothesis, compound (B) was treated with a third acid chloride (*p*-$MeOC_6H_4COCl$). The crude product, after the usual work-up, was chromatographed



SCHEME 1

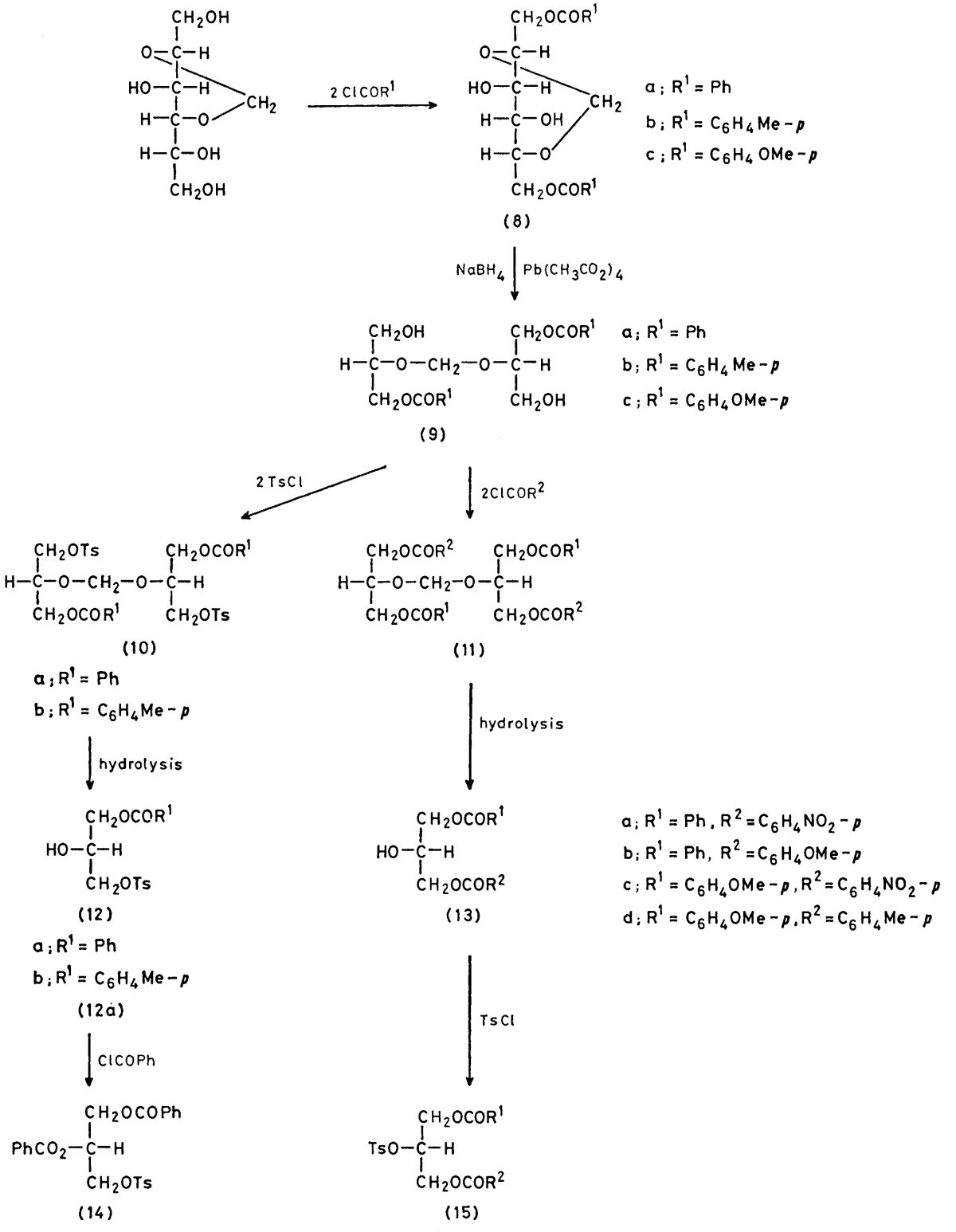
compound (11a), after elimination of the acetyl ester, was maintained at 80 °C for 20 d without isomerisation.

Structure and Optical Purity of Compounds (12) *and* (13).—If one of the aroyl groups is transposed to carbon 2, during the hydrolysis, without racemisation [this hypothesis could not be neglected (see above)], the action of an acid chloride $ClCOR^1$ or $ClCOR^2$ on the resulting 1,2-diglyceride gives a triglyceride. This triglyceride will be the same as the one which would be obtained from a 1,3-diglyceride *without* transposition. Therefore 1,3-diglycerides (13) were treated with tosyl chloride to give triglycerides (15) which were also prepared from 1,2-diglycerides (16).[1] The physical data are identical. But, the weak optical rotations of the tosyl esters (0.2° to 2.4°) do not prove their optical purity. In one case, to give two fractions (17) and (18) (Scheme 4), which were characterised by comparing their retention times (h.p.l.c.) with those of authentic triglycerides. Confirmation was obtained from the i.r. and n.m.r. spectra, and the optical rotations. Compound (B) was shown to be a mixture of 1,2- and 2,3-di-*O*-aroyl-*sn*-glycerols.

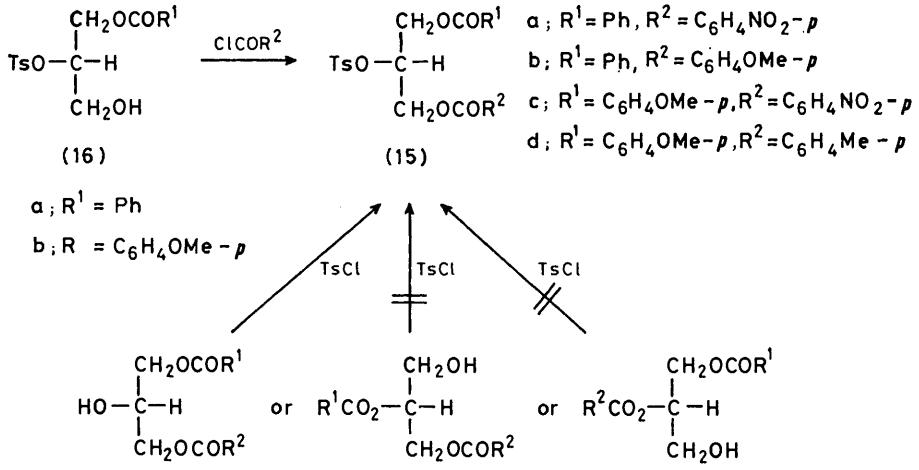
The solid-state isomerisation [9] of 1,2- or 2,3-diglycerides into 1,3-diglycerides does not occur with aroyl substituents. The crude product from the hydrolysis of

the two enantiomers of 1-*O*-benzoyl-3-*O*-tosyl-*sn*-glycerol (3a) and (12a) were treated with benzoyl chloride. The higher rotations of resulting triesters (5) and (14) and of triester (7) prepared from 3-*O*-tosyl-*sn*-glycerol (6) are equivalent.

Though we have emphasised the difficulties, this route gives a high yield (70%), without chromatography, of 1,3-diglycerides (12a) and (12b) on a 50-g scale, and offers an easy route to diaroyl-3-iodohydrins.



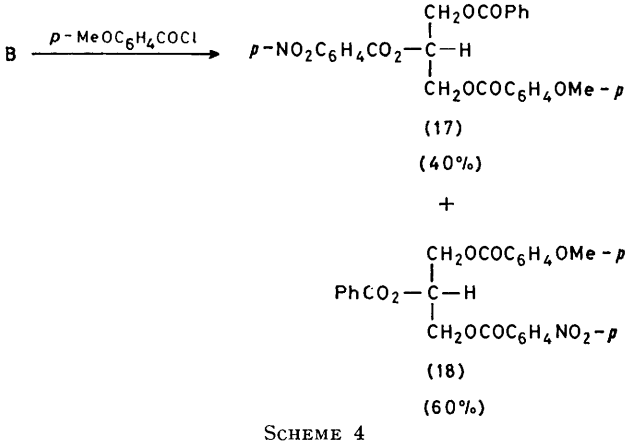
SCHEME 2



SCHEME 3

EXPERIMENTAL

M.p.s were determined with a hot-stage apparatus. I.r. spectra were recorded on a Perkin-Elmer 325 spectrometer (KBr discs for solids). ^{1}H N.m.r. spectra were obtained on a Varian T60 spectrometer with deuteriochloroform as solvent and tetramethylsilane as internal reference.



SCHEME 4

Optical rotations were measured with a Jouan micropolarimeter (*c*, g per 100 ml; precision ±5%). H.p.l.c. was performed with the following apparatus; Dosapro Milton Roy pump; injection system, septum-syringe; detector, Seive spectrophotometer; column 20 cm × 4.6 mm internal diameter; packing phase, Lichrosorb SI 60, 5 μm (Merck); solvent, dichloromethane–methanol (200 : 0.5) (for diglycerides) and dichloroethane or heptane–ethyl acetate (95 : 5) (for triglycerides). Preparative chromatography was performed with columns of silica gel (Lobar, Merck), a low-pressure pump (maximum pressure 6 bar, maximum flow rate 1 400 ml h^{-1}), a spectrophotometer Seive detector, and a Gilson fraction collector (T.D.C. 220). Silica gel F_{254} (Merck) was used for t.l.c., and spots were detected by u.v. fluorescence. Microanalyses were provided by Service Central de Microanalyse, Thiais, France. All solvents were reagent grade. Anhydrous sodium sulphate was used for drying. The physical and analytical data of new compounds are given in Tables 1 and 2.

1-O-*Aroyl*-3-O-*tosyl*-sn-*glycerols* (3) *and* 1,3-*Di*-O-*aroyl*-sn-*glycerols* (4).—The 3-*O*-aroyl-*sn*-glycerols (2a—d) were prepared according to the literature.[1,10] The procedure described gives the maximum yield of 1,3-diglycerides. Acid chloride or tosyl chloride (0.02 mol) in pyridine (0.1 mol) was added dropwise to a stirred and cooled solution of 3-*O*-aroyl-*sn*-glycerol (2) (0.02 mol) in pyridine (0.1 mol). The mixture was maintained for 1 h at 0 °C and then set aside at room temperature for an additional 17 h. After dilution with water, the organic phase was extracted with chloroform, and the extracts were washed successively with 2N-sulphuric acid, saturated aqueous sodium hydrogencarbonate, and water. The solution was dried and the solvent removed. The 1,3-diglycerides (3c), (4a), and (4b) were purified by chromatography [dichloromethane–diethyl ether (90 : 10)]. The first fraction gave the triglyceride: 1,2-*di*-O-*tosyl*-3-O-p-*methylbenzoyl*-sn-*glycerol* had m.p. 101 °C (from ethanol) (10%); 1,2-*di*-

TABLE 1

Compd.	M.p. (°C) or B.p. [mmHg]	[α]/° 589 nm	578 nm	546 nm	436 nm	Solvent	*c*	Found (%) C	H	N	S	Formula	Required (%) C	H	N	S
(1c)	132 [4 mm]	+12.4	+12.7	+14.7	+27.8	Pyridine	3.7	66.95	7.25			$C_{14}H_{18}O_4$	67.20	7.20		
(2c)	54	−15	−15.9	−18.4	−32.5	Pyridine	1.3	62.85	6.65			$C_{11}H_{14}O_4$	62.86	6.67		
(3a)	85	+3.2	+3.4	+3.8	+6.9	$CHCl_3$	4.3	58.45	5.20		9.0	$C_{17}H_{18}O_6S$	58.29	5.14		9.14
(3b)	82	+3.7	+3.9	+4.4	+8.1	$CHCl_3$	2.7	56.85	5.30		8.35	$C_{18}H_{20}O_7S$	56.84	5.26		8.42
(3c)	87	+4.8	+5.1	+5.9	+10.4	$CHCl_3$	3.3	59.35	5.50		8.80	$C_{18}H_{20}O_6S$	59.34	5.50		8.79
(4a)	136	+3.2	+3.4	+3.9	+8	Pyridine	2.5	46.95	3.05	9.75		$C_{17}H_{13}N_3O_{11}$	46.90	2.99	9.66	
(4b)	97	+5.2	+5.4	+6.1	+12.1	Pyridine	2	52.25	3.70	7.30		$C_{17}H_{14}N_2O_9$	52.31	3.59	7.18	

O-(3,5-*dinitrobenzoyl*)-3-O-p-*nitrobenzoyl*-sn-*glycerol* had m.p. 155 °C (crude product) (25%); and 1,2-*di*-O-(3,5-*dinitrobenzoyl*)-3-O-*benzoyl*-sn-*glycerol* had m.p. 84 °C (crude product) (30%). The second fraction gave the 1,3-*diglyceride* contaminated with a minor fraction of 1,2-diglyceride. The 1,3-diglycerides were recrystallised from ethanol–water (yield 40—45%) (Table 1). The third fraction gave the 1,2-*diglyceride* as an oil. The 1,3-diglyceride (3a) was purified by four fractional crystallisations from methanol–water (50 : 50), m.p. 82 °C, and was recrystallised from acetic acid–water (80 : 20), m.p. 85 °C. acid–water–HCl (62 : 2 : 5)]. The mixture was stirred for 4—7 h, then diluted with water. After evaporation of acetic acid under reduced pressure, the organic phase was extracted with chloroform, washed (saturated $NaHCO_3$ and water), dried, and the solvent was removed. The 1,3-diglycerides (12a) and (12b) were crystallised from carbon tetrachloride and were used without further purification (m.p.s 83—84 °C). Recrystallisation from ethanol–water (90 : 10) yielded products with m.p.s 85 °C (12a) and 86 °C (12b). For the other 1,3-diglycerides (13a—d), the oil was chromatographed [CH_2Cl_2–diethyl ether (90 : 10)]. The

TABLE 2

Compd.	M.p. (°C)	[α]/° 589 nm	578 nm	546 nm	436 nm	Solvent	*c*	Found (%) C	H	N	S	Formula	Required (%) C	H	N	S
(8a) [a]	121	−69.6	−73	−81.3	−143	$CHCl_3$	1.14									
(8b)	147	−76.5	−81.4	−95.3	−163	$CHCl_3$	0.53	64.2	6.35			$C_{23}H_{26}O_8$	64.19	6.05		
(8c)	143	−67.2	−71.3	−83.7	−143	$CHCl_3$	0.48	59.8	5.95			$C_{23}H_{26}O_{10}$	59.74	5.63		
(9a) [a]	106	−61	−63.3	−71.4	−118	$CHCl_3$	1.44									
(9b)	139	−52.3	−54.9	−62.2	−102	$CHCl_3$	1.1	63.55	6.75			$C_{23}H_{28}O_6$	63.89	6.48		
(9c)	122	−48	−50	−57.3	−95.5	$CHCl_3$	0.88	59.40	6.1			$C_{23}H_{28}O_{10}$	59.48	6.03		
(10a)	89	−8.3	−8.7	−9.9	−17	$CHCl_3$	5.6	58.85	5.05		8.95	$C_{35}H_{36}O_{12}S_2$	58.90	5.06		8.99
(10b)	96	−10.5	−11.1	−12.7	−22	$CHCl_3$	2.1	59.9	5.4		8.75	$C_{37}H_{42}O_{12}S_2$	59.84	5.66		8.63
(11a)	106	−4.3	−4.7	−5.4	−7.6	$CHCl_3$	2.1	59.9	4.25	4.0		$C_{35}H_{30}N_2O_{14}$	59.83	4.27	3.99	
(11b)	86	+2	+2.1	+2.4	+5	$CHCl_3$	1.8	66.0	5.35			$C_{37}H_{36}O_{12}$	66.07	5.36		
(11c)	116	−7.1	−7.4	−9	−14.8	$CHCl_3$	3.4	58.5	4.40	3.65		$C_{37}H_{34}N_2O_{16}$	58.27	4.45	3.67	
(11d)	75	−0.7	−0.8	−0.9	−1.8	$CHCl_3$	4.9	67.05	5.8			$C_{39}H_{40}O_{12}$	66.86	5.71		
(12a)	85	−3.3	−3.4	−4	−7	$CHCl_3$	6	58.45	5.20		9.0	$C_{17}H_{18}O_6S$	58.28	5.14		9.14
(12b)	86	−4.8	−5.2	−5.9	−10.6	$CHCl_3$	2.9	59.45	5.4		8.85	$C_{18}H_{20}O_6S$	59.34	5.50		8.79
(13a)	104	−3.9	−4.4	−4.8	−7.7	$CHCl_3$	1.4	59.20	4.4	4.05		$C_{17}H_{15}NO_7$	59.13	4.35	4.06	
(13b)	46	−0.8	−0.9	−1	−1.6	Pyridine	2.3	65.60	5.7			$C_{18}H_{16}O_6$	65.46	5.45		
(13c)	80	−2.8	−3.1	−3.4	−6.7	$CHCl_3$	1.6	57.40	4.75	3.9		$C_{18}H_{17}NO_8$	57.60	4.53	3.73	
(13d)	88	+1	+1.1	+1.2	+2.2	$CHCl_3$	5	66.25	5.85			$C_{19}H_{20}O_6$	66.28	5.81		
(15a) [b]	145	−2.3	−2.4	−2.6	−4.6	Pyridine	1.7	57.55	4.20	2.75	6.4	$C_{24}H_{21}NO_9S$	57.72	4.21	2.81	6.41
(15a) [c]	143	−2.4	−2.4	−2.9	−4.9	Pyridine	1.9									
(15b) [b]	118	+0.8	+0.9	+1	+1.8	Pyridine	1.6	61.55	5.0		6.6	$C_{23}H_{24}O_8S$	61.98	4.96		6.61
(15b) [c]	116	−0.6	−0.7	−0.8	−1.5	Pyridine	2.5									
(15c) [b]	132	−1.6	−1.8	−2.1	−3.7	Pyridine	2.3	56.25	4.3	2.65	6.1	$C_{25}H_{23}NO_{10}S$	56.71	4.35	2.65	6.05
(15c) [c]	134	−2.1	−2.2	−2.5	−4.3	Pyridine	1.7									
(15d) [b]	114	+0.3	+0.3	+0.4	+0.6	Pyridine	1.4	62.65	5.25		6.25	$C_{26}H_{26}O_8S$	62.65	5.22		6.43
(15d) [c]	115	+0.2	+0.2	+0.3	+0.4	Pyridine	1.9									
(17) [d]	143	−4.2	−4.6	−5.3	−11.3	$CHCl_3$	0.6									
(17) [c]	144	−1.4	−1.6	−2	−5.5	$CHCl_3$	1.6	62.4	4.1	3.15		$C_{25}H_{21}NO_9$	62.63	4.38	2.92	
(18) [c]	93	−18.2	−19.4	−23	−45.2	$CHCl_3$	0.5	62.4	4.45	3.35		$C_{25}H_{21}NO_9$	62.63	4.38	2.92	
(18) [d]	91	−17.5	−18.5	−21.5	−43.4	$CHCl_3$	0.4									
(5)	113	+12.1	+12.3	+14.1	+26.1	Pyridine	1.5	63.4	4.9		6.85					
(14)	112	−11.9	−12.3	−14.3	−26.1	Pyridine	1.3	63.45	4.9		6.9	$C_{24}H_{22}O_7S$	63.44	4.85		7.05
(7)	114	−12.1	−12.6	−14.5	−27.2	Pyridine	1.4	63.35	4.8		7.0					

[a] See ref. 11. [b] From 1,2-diglycerides. [c] From 1,3-diglycerides. [d] From B (see Experimental section).

P.l.c. in chloroform with double development yielded the 1,3-*diglyceride* (3b), which was crystallised from ethanol–water (90 : 10).

2,2′-O-*Methylenebis*(1-O-*aroyl*-3-O-*tosyl*-sn-*glycerols*) (10) *and* 2,2′-O-*Methylenebis*(1,3-*di*-O-*aroyl*-sn-*glycerols* (11).—2,2′-*O*-Methylenebis(3-*O*-aroyl-*sn*-glycerols) (9) were prepared from D-mannitol by the method of Brundish [11] and recrystallised from carbon tetrachloride (9a) or ethanol (9b,c). Then a solution of acid chloride or chloride (0.1 mol) in dry pyridine (0.5 mol) was added to a stirred and cooled solution of 2,2′-*O*-methylenebis(3-*O*-aroyl-*sn*-glycerol) (9) (0.05 mol) in pyridine (0.05 mol). The mixture was set aside at room temperature for 48 h and worked up in the usual way to give the 2,2′-O-*methylenebis*(*glycerol*) (10) or (11) which was recrystallised from ethanol or from ethyl acetate–ethanol (50 : 50) (11c), yield 75% (Table 2).

1-O-*Aroyl*-3-O-*tosyl*-sn-*glycerols* (12) *and* 1,3-*Di*-O-*aroyl*-sn-*glycerols* (13).—The bis(glycerol) (10) or (11) was dissolved in the minimum volume of acetic acid–water (62 : 2) at 40—50 °C. The solution was cooled to room temperature and concentrated hydrochloric acid was added [acetic

first eluted component was the 1,3-*di*-O-*aroyl*-2-O-*acetyl*-sn-*glycerol*. The second component to be eluted was the 1,3-*di*-O-*aroyl*-sn-*glycerol* contaminated with a minor fraction of the 1,2- and 2,3-di-*O*-aroyl derivatives. The third fraction was a mixture of 1,2- and 2,3-diglycerides. The crude 1,3-diglycerides were crystallised from ethanol–water (yields 55—70%). The 1,3-diglyceride (13b) crystallised after two years (Table 2).

1,3-*Di*-O-*aroyl*-2-O-*tosyl*-sn-*glycerols* (15).—Tosyl chloride (1.5 mmol) in pyridine (7.5 mmol) was added to a cooled solution of the 1,3-diglyceride (13) (1.5 mmol) in pyridine (7.5 mmol). In the same way, the appropriate acid chloride (1.5 mmol) was added to a solution of the 1,2-diglyceride (16). The mixture was set aside at room temperature for 48 h. The usual work-up gave *tosyl esters* (15) which were recrystallised from ethanol [(15b,d)] or from ethyl acetate [(15a,c)] (yields 70—75%) (Table 2).

1-O-*Benzoyl*-2-O-*acetyl*-3-O-p-*nitrobenzoyl*-sn-*glycerol*.—2,2′-*O*-Methylenebis(1-*O*-benzoyl-3-*O*-*p*-nitrobenzoyl-*sn*-glycerol) (11a) (5 g) in acetic acid (122 ml) and water (3 ml)

was stirred with hydrochloric acid (10 ml) for 14 h. The work-up described above gave an oil which was column-chromatographed. The first fraction, A, afforded the *acetyl ester* (1.35 g) which was recrystallised from ethanol, m.p. 72 °C, $[\alpha]_{589}$ −6.5°, $[\alpha]_{578}$ −6.7°, $[\alpha]_{546}$ −7.8°, $[\alpha]_{436}$ −13.9° (*c* 0.9 in $CHCl_3$), δ 2.1 (Me). The identical acetyl ester was isolated from 1-*O*-benzoyl-3-*O*-*p*-nitrobenzoyl-*sn*-glycerol (13a) by the action of acetyl chloride in pyridine, m.p. 72 °C; $[\alpha]_{589}$ −5.8°, $[\alpha]_{578}$ −6°, $[\alpha]_{546}$ −7.3°, $[\alpha]_{436}$ −12° (*c* 0.9 in $CHCl_3$); δ 2.1 (Me) (Found: C, 58.69; H, 4.28; N, 3.91. $C_{19}H_{17}NO_8$ requires C, 58.91; H, 4.39; N, 3.62%).

1-O-*Benzoyl*-2-O-p-*nitrobenzoyl*-3-O-p-*methoxybenzoyl*-sn-*glycerol* (17) *and* 1-O-p-*Methoxybenzoyl*-2-O-*benzoyl*-3-O-p-*nitrobenzoyl*-sn-*glycerol* (18).—According to the procedure described above, chromatography yielded a third fraction B as an oil (0.9 g) which was treated with *p*-methoxybenzoyl chloride in pyridine. After the usual treatment, chromatography [CH_2Cl_2–diethyl ether (90 : 10)] gave as the first component 1-O-*benzoyl*-2-O-p-*nitrobenzoyl*-3-O-p-*methoxybenzoyl*-sn-*glycerol* (17) and as the second component 1-O-p-*methoxybenzoyl*-2-O-*benzoyl*-3-O-p-*nitrobenzoyl*-sn-*glycerol* (18). The identical triesters (17) and (18) were also prepared from the corresponding 1,3-diglycerides (13b,c) (Table 2).

Di-O-*benzoyl*-O-*tosyl*-sn-*glycerols* (5), (7), *and* (14).—Treatment of 1,3-diglycerides (3a) or (12a) (0.53 g, 1.5 mmol) with benzoyl chloride (0.21 g, 1.5 mmol) in pyridine gave *triglycerides* (5) or (14). 1,2-Di-*O*-benzoyl-3-*O*-tosyl-*sn*-glycerol (7) was obtained from 3-*O*-tosyl-*sn*-glycerol (6) {m.p. 62 °C, $[\alpha]_{589}$ −6.6°, $[\alpha]_{578}$ −7°, $[\alpha]_{546}$ −8°, $[\alpha]_{436}$ −12.3° (*c* 1.1 in pyridine) (Found: C, 49.10; H, 5.79; S, 13.05. $C_{10}H_{14}O_5S$ requires C, 48.78; H, 5.69; S, 13.01%) (lit.,[12])} (0.49 g, 2 mmol) which was treated with benzoyl chloride (0.56 g, 4 mmol) in pyridine, m.p. 114 °C (from ethanol) (Table 2).

[8/844 *Received*, 4*th May*, 1978]

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