Sucrochemistry. Part 33.† The Selective Pivaloylation of Sucrose

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The pivaloylation of sucrose by pivaloyl chloride (2,2-dimethylpropanoyl chloride) has been studied under a variety of conditions and shown to be selective for certain hydroxy groups. There exists two principal, but divergent, reaction pathways lying between sucrose and its octapivalate in which the orders of acylation of the eight hydroxy groups are as follows (a) 6,6'-OH > 1'-OH > 4'-OH > 2-OH > 4-OH > 3'-OH > 3-OH; (b) 6,6'-OH > 1'-OH > 3'-OH > 3-OH > 4'-OH > 2-OH and 4-OH. With the exception of the 1',3',6,6'-tetra- and the 1',2,3',4,4',6,6'-hepta-pivalate, all of the intermediary esters in these two reaction pathways have been isolated in yields in the range 30—52% depending upon the conditions employed.

Selective acylation of carbohydrates has been widely exploited in the monosaccharide field,[1] but its application to disaccharides has not always been successful, inasmuch as the mixtures are invariably more complex and the yields of components often low after extensive chromatographic fractionation. However, selective hepta-acylations of maltose,[2] cellobiose,[3] and lactose [4] have been successful owing to the very low reactivity of 3-HO towards acid chlorides, resulting in each case in the isolation of the 1,2,2',3',4',6,6'-heptaesters in good yield. A more detailed study of the selective benzoylation of methyl β-lactoside [5] revealed that the order of acylation of the hydroxy groups was 6'-HO > 3'-HO > 6-HO > 2-HO > 2'-HO > 4'-HO > 3-HO and many of the intermediary esters were isolated in reasonable yield. These observations suggested that those hydroxy groups that were adjacent or near to the interglycosidic linkage (namely, 6-HO, 2'-HO, and 3-HO) have lower reactivities, presumably due to the greater steric hindrance, than those at the periphery of the molecule. The abnormally high reactivity of 3'-HO has been related to its *cis*-relationship to 4'-HO which is known to cause enhancement of reactivity towards acylation by acid chlorides.[5,6]

The selective di- and tri-molar tosylation of sucrose (1) has been described,[7] but the derived 6,6'-di- and 1',6,6'-tritosylates were obtained pure only with difficulty after chromatography. More recently this drawback has been overcome by the use of sterically hindered sulphonyl chlorides, such as mesitylenesulphonyl chloride [8,9] and 2,4,6-tri-isopropylbenzenesulphonyl chloride.[9] The greater selectivity of these reagents gives high yields of the 1',6,6'-triesters, which were obtained crystalline directly and without the need for chromatography.[8,9] The use of hindered carboxylic acid chlorides might also be expected to show a similar selectivity, and we have therefore investigated the selective pivaloylation of sucrose (1) using pivaloyl chloride (2,2-dimethylpropanoyl chloride), which has the advantage of being both cheap and readily available. Its high selectivity towards primary hydroxy groups of nucleosides [10] has previously been noted and, since our preliminary report, the selective pivaloylation of various simple glycosides has been reported.[11]

Preliminary experiments using an excess of pivaloyl chloride quickly established that the acylation readily proceeded well beyond the substitution of the primary hydroxy groups. Indeed, when sucrose was treated with 20 equivalents of the reagent at 70 °C in pyridine for 24 h, the crystalline octapivalate (2) was isolated in 90% yield without difficulty. However, when the same reaction was conducted initially at −40 °C and then at room temperature for 24 h, two major and two minor products were isolated by chromatographic fractionation, of which fraction A (40% yield) was the octapivalate (2). Fraction B was a minor component (1%) obtained as a syrup whose ^{1}H n.m.r. spectrum (Table 1) indicated that it was a heptapivalate. Comparison of its spectrum with that of (2) showed that the double doublet due to 2-H [present at δ 5.24 in the spectrum of the octaester(2)] was not present in the low-field region of the spectrum whereas all of the resonances due to 3-H, 4-H, 3'-H, and 4'-H were present to low field of δ 5. However, when trichloroacetyl isocyanate [12] was added to the n.m.r. solution the monocarbamate (18) was formed *in situ* and the 2-H resonance appeared in the n.m.r. spectrum at δ 5.39 as a double doublet together with a singlet resonance at δ 9.35 due to NH. This result confirmed that B was the 1',3,3',4,4',6,6'-heptapivalate (17).

Fraction C, another minor component (1.5%), was an isomeric heptapivalate whose ^{1}H n.m.r. spectrum (Table 1) showed that the 3-H resonance was absent from the low-field region (δ *ca.* 5.8). Further evidence for the 1',2,3',4,4',6,6'-heptapivalate (50) was provided by the ^{1}H n.m.r. spectrum of its 3-*O*-mesylate (51) in which 3-H appeared as a triplet at δ 5.44 ($J_{2,3} = J_{3,4} = 10$ Hz).

Component D was the major product of the reaction and was isolated crystalline in 52% yield. Its ^{1}H n.m.r. spectrum (Table 1) suggested it was the 1',2,3,3',4',6,6'-heptapivalate (33) since the 4-H resonance, normally present at δ *ca.* 5.3, appeared as a triplet at δ 3.64 ($J_{3,4} = J_{4,5} = 10$ Hz) indicating that 4-HO was unsubstituted. Further proof of the identity of D was provided by reaction of its 4-*O*-mesylate ester (34) with sodium benzoate in *N*,*N*-dimethylformamide (DMF) which afforded the octaester (52) of *galacto*-sucrose. The derived ^{1}H n.m.r. coupling constants for (52) ($J_{1,2}$ 4.0; $J_{2,3}$ 10.4; $J_{3,4}$ 3.0; $J_{4,5}$ 1.5 Hz) were indicative of the *galacto*-configuration (Table 1) and *O*-deacylation afforded the known [13] β-D-fructofuranosyl α-D-galactopyranoside (53) in 59% overall yield from the heptapivalate (33). The heptapivalate (33) could be isolated in about the same yield by reaction of sucrose (1) with 12 equivalents of pivaloyl chloride in pyridine at room temperature for 72 h.

Lesser substituted sucrose esters were obtained by conducting the reaction either at lower reaction temperatures or with lower molar ratios of acid chloride. For example, when the 20 molar reaction above was conducted at −40 °C for 1—2 h, none of the octapivalate could be detected, but the heptapivalate (33) was present as a major component along with several other components. When the mixture was fractionated on silica gel five fractions E, F, G, H, and I were obtained, each of which was apparently pure as judged by t.l.c. Fraction E was the heptapivalate (33) which was obtained in 25% yield,

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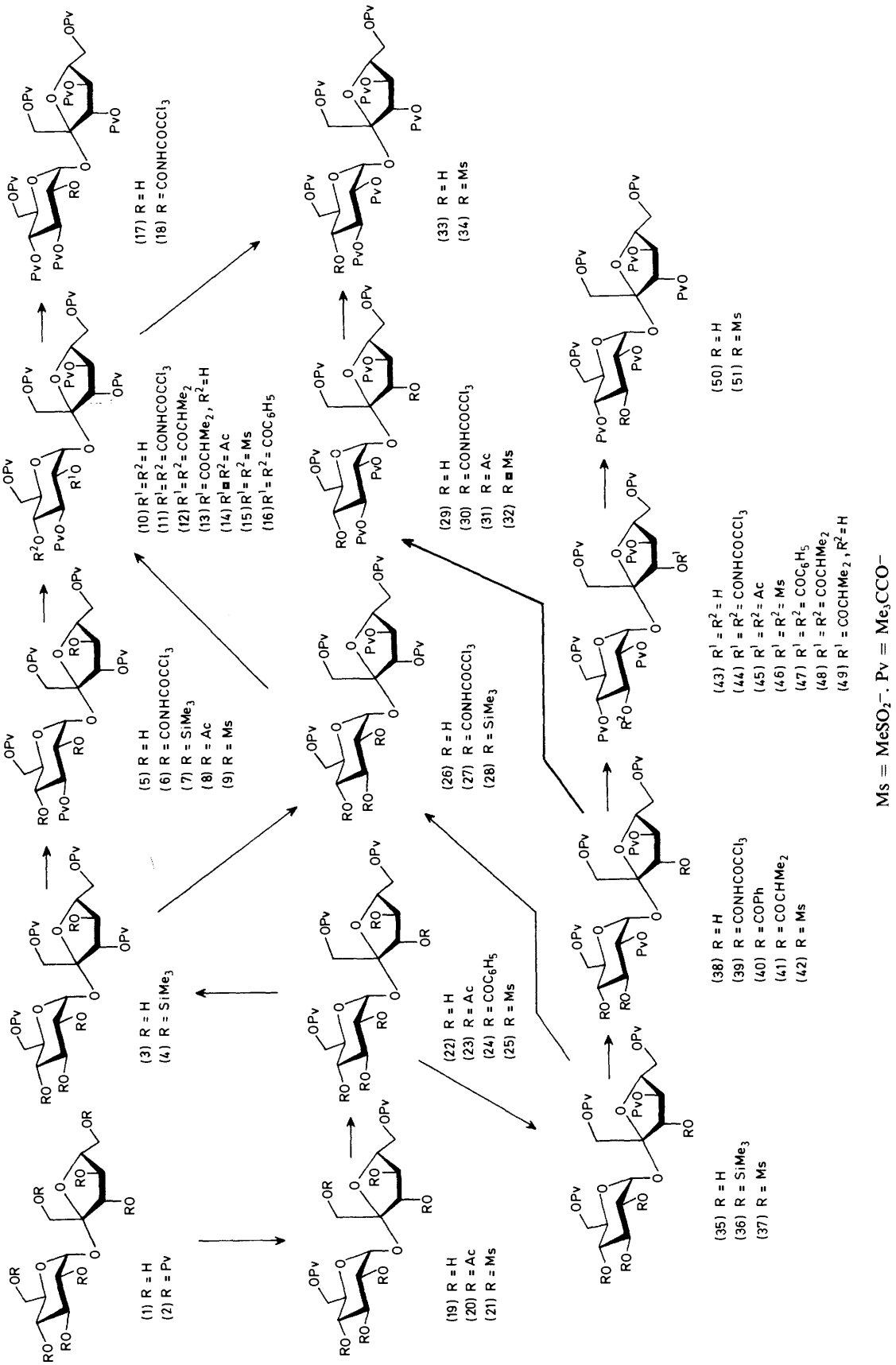
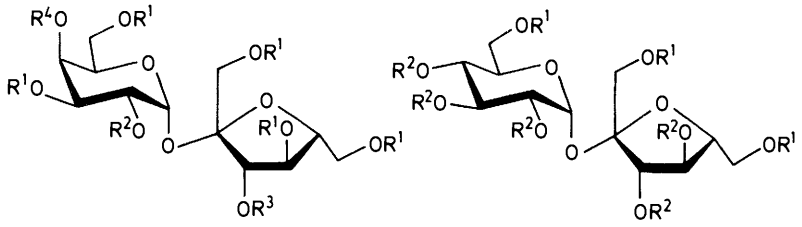

(1) R = H
(2) R = Pv
(3) R = H
(4) R = SiMe3
(5) R = H
(6) R = CONHCOCCl3
(7) R = SiMe3
(8) R = Ac
(9) R = Ms
(10) R1 = R2 = H
(11) R1 = R2 = CONHCOCCl3
(12) R1 = R2 = COCHMe2
(13) R1 = COCHMe2, R2 = H
(14) R1 = R2 = Ac
(15) R1 = R2 = Ms
(16) R1 = R2 = COC6H5
(17) R = H
(18) R = CONHCOCCl3
(19) R = H
(20) R = Ac
(21) R = Ms
(22) R = H
(23) R = Ac
(24) R = COC6H5
(25) R = Ms
(26) R = H
(27) R = CONHCOCCl3
(28) R = SiMe3
(29) R = H
(30) R = CONHCOCCl3
(31) R = Ac
(32) R = Ms
(33) R = H
(34) R = Ms
(35) R = H
(36) R = SiMe3
(37) R = Ms
(38) R = H
(39) R = CONHCOCCl3
(40) R = COPh
(41) R = COCHMe2
(42) R = Ms
(43) R1 = R2 = H
(44) R1 = R2 = CONHCOCCl3
(45) R1 = R2 = Ac
(46) R1 = R2 = Ms
(47) R1 = R2 = COC6H5
(48) R1 = R2 = COCHMe2
(49) R1 = COCHMe2, R2 = H
(50) R = H
(51) R = Ms
Ms = MeSO2−. Pv = Me3CCO−



(52) $R^1 = R^2 = R^3 = Pv, R^4 = COPh$
(53) $R^1 = R^2 = R^3 = R^4 = H$
(54) $R^1 = R^3 = Pv, R^2 = Ms, R^4 = COPh$
(55) $R^1 = R^2 = Pv, R^3 = Ms, R^4 = COPh$
(56) $R^1 = CPh_3, R^2 = H$
(57) $R^1 = CPh_3, R^2 = COPh$
(58) $R^1 = H, R^2 = COPh$

but fraction F, a semi-crystalline solid, proved to be composed of two components with almost identical chromatographic mobility. Recrystallisation of fraction F afforded a highly crystalline hexapivalate (10) in 33% yield. The other component of fraction F was obtained as a syrup by evaporation of the mother liquors and was an isomeric hexapivalate (43). The structure of the major hexapivalate (10) was apparent from its ^1H n.m.r. spectrum (Table 1) in which the 2-H and 4-H resonances occupied high-field positions (δ *ca.* 3.56), whilst all of the other resonances due to ring hydrogen atoms were at low field and were readily recognised by their multiplicities and coupling constants. When the n.m.r. solution was treated with trichloroacetyl isocyanate, two NH singlet resonances appeared at δ 8.32 and 9.33, indicative of a diol, and the 2-H and 4-H resonances moved to low-field positions overlapping at δ *ca.* 5.33. Hence this showed that the major hexapivalate was the 1′,3,3′,4′,6,6′-isomer (10). The mass spectrum of the derived bistrimethylsilyl ether showed ionic fragments at *m/z* 499 (Pv_4fruf^+) and 475 ($Pv_2Tms_2glcp^+$), due to the fructofuranosyl and glucopyranosyl oxycarbonium ions resulting from A_1 cleavage of the glycosidic bonds, showing that both of the trimethylsilyl groups were located on the same sugar residue. A fragment ion at *m/z* 373 resulted from the loss of the elements of pivalic acid from the ion at *m/z* 475 and strongly suggested the presence of a pivaloyl group at O-3 of the glucopyranosyl unit.[14] The 2,4-diol (10) was further characterised by the formation of its crystalline di-*O*-acetate (14), the syrupy di-*O*-mesylate (15), and the syrupy di-*O*-benzoate (16). Furthermore treatment of the diol (10) with isobutyryl chloride afforded a mixture from which the crystalline di-*O*-isobutyrate (12) and the 2-*O*-isobutyrate (13) were isolated.

Upon treatment of the 2,4-di-*O*-mesylate (15) with sodium benzoate in DMF, only the 4-mesyloxy group was displaced to give the crystalline 2-*O*-mesyl-*galacto*-sucrose derivative (54) in excellent yield. The ^1H n.m.r. parameters (Table 1) were in complete accord with its structure.

The isomeric hexapivalate in fraction F was clearly the 1′,2,4,4′,6,6′-isomer (43), since its ^1H n.m.r. spectrum showed the 3-H triplet and 3′-H doublet at high field (δ 4.27 and 4.00 respectively) which, upon the addition of trichloroacetyl isocyanate, shifted to higher field (δ 5.95 and 5.85 respectively) (Table 1). This *in situ* reaction also resulted in the development of two NH resonances at low field as expected for a 3,3′-diol. The formation of a crystalline derivative of the 3,3′-diol (43) was accomplished by its conversion into the 3,3′-di-isobutyrate (48) which was also accompanied by some of the syrupy 3′-isobutyrate (49). The diacetate (45), the dimesylate (46), and the dibenzoate (47) were all obtained as syrups, whose n.m.r. parameters are recorded in Table 1.

The yields of the hexapivalates (10) and (43) could be improved to 45 and 35% respectively by carrying out the pivaloylation of sucrose with 7 moles of the reagent, when the 2,4-diol (10) was isolated directly by crystallisation from the crude reaction product prior to chromatography to isolate the 3,3′-diol (43).

Fraction G was a minor hexapivalate isolated crystalline in 4% yield. Inspection of its ^1H n.m.r. spectrum showed that the resonances due to 3′-H (doublet) and 4-H (triplet) were not present in the downfield region of the spectrum, but upon addition of trichloroacetyl isocyanate to the n.m.r. solution they were shifted to δ 5.83 and 5.19 respectively (Table 1). Hence G was the 1′,2,3,4′,6,6′-hexapivalate (29) and was further characterised as the crystalline diacetate (31) and dimesylate (32). The latter underwent selective nucleophilic displacement with sodium benzoate in DMF at C-4 to give the 3′-*O*-mesyl-*galacto*-sucrose derivative (55) in good yield.

Fraction H was a minor component (4.5%) which did not crystallise. Since its ^1H n.m.r. spectrum (Table 1) showed that it was a pentapivalate with only three resonances in the low-field region of the spectrum, namely the 1-H doublet (δ 5.50), the 3-H triplet (δ 5.44), and the 3′-H doublet (δ 5.40), it was therefore assigned as the 1′,3,3′,6,6′-pentapivalate (5). In agreement with this structure, the addition of trichloroacetyl isocyanate to the n.m.r. solution caused the 2-H, 4-H, and 4′-H resonances to appear below δ 5 and three NH resonances were observed to lower field (Table 1). The mass spectrum of the derived tris-trimethylsilyl ether (7) showed fragments at *m/z* 487 ($Pv_3Tmsfruf^+$) and 475 ($Pv_2Tms_2glcp^+$) due to the two oxycarbonium ions resulting from the cleavage of the two glycosidic bonds. The ion at *m/z* 475 lost the elements of pivalic acid to give a strong ion at *m/z* 373 indicating the presence of a pivaloyl group at C-3. The pentapivalate could be prepared in improved yield (30%) by carrying out the reaction with 5 molar equivalents of acid chloride in a mixture of chloroform and pyridine.

Fraction I was isolated crystalline in 11% yield. Its ^1H n.m.r. spectrum indicated that it was a pentapivalate, and the only resonances to low field of δ 5 were the 1-H doublet (δ 5.89), the 2-H double doublet (δ 4.97), and the 4′-H triplet (δ 5.49), suggesting that the product was the 1′,2,4′,6,6′-pentapivalate (38). Addition of trichloroacetyl isocyanate to the n.m.r. solution resulted in the appearance of three NH singlets, indicative of a triol, and the appearence of the resonances due to 3-H, 4′-H, and 4-H to low field of δ 5 (Table 1). The yield of (38) could be improved to *ca.* 30% by treatment of sucrose with 6 equivalents of the acid chloride at −40 °C for 4 h and then at room temperature.

When the pivaloylation was repeated with 5 molar equivalents of acid chloride at −70 °C in a mixture of pyridine and chloroform at least eight components had been formed after one hour. The mixture was fractionated chromatographically to give five chromatographically pure components of which the first two fractions (J and K) were shown to be the penta-

Table 1. First-order ^{1}H n.m.r. parameters (δ; J/Hz) at 220 MHz [a,b]

	(2)	(3)	(5)	(6) [d,e]	(8) [f]	(9) [g]	(10) [h]	(11) [d,j]	(12)	(13)	(14)	(15)	(16)	(17)	(18) [d,k]
1-H	5.98d	5.56d	5.50d	4.69d	5.81d	6.01d	5.54d	5.69d	5.82d	5.76d	5.73d	5.99d	6.02d	5.57d	5.72d
2-H	5.24dd		3.55dd	5.31dd	5.17dd	4.85dd	3.56m	5.33dd	5.30dd	5.21dd	5.29dd	4.84dd	5.74dd	3.68m	5.39dd
3-H	5.89t		5.44t	5.77t	5.82t	5.96t	5.48t	5.79t	5.88t	5.80t	5.76t	5.89t	6.34t	5.57t	5.75t
4-H	5.61t		3.57t	5.33t	5.44t	5.08t	3.56m	5.33t	5.56t	3.59t	5.47t	5.06t	5.89t	5.49t	5.51t
5-H	4.80m							4.67dt				4.65dt	4.88dt		
1′-H$_a$							4.49d			4.49d	4.40d	4.44d	4.55d	4.76d	
1′-H$_b$							4.40d	4.14d		4.33d	4.23d	4.34d	4.25d	4.62d	3.90d
3′-H	5.91d	5.44d	5.40d	} 5.54cm	5.69d	5.54d	5.72d	5.64d	5.88d	5.87d	5.83d	5.87d	5.83d	5.67d	5.70d
4′-H	5.79t		4.39t		5.54t	5.79t	5.61t	5.54t	5.76t	5.74t	5.71t	5.69t	5.76t	5.60t	5.55t
5′-H	5.20m							4.25q							
$J_{1,2}$	4.0	4.0	4.0	3.5	3.5	4.0	3.5	3.5	3.8	3.7	3.5	3.5	4	3.5	4
$J_{2,3}$	10		10	10	10	10	10	10.5	10.5	10	10.5	10	10.5	10	10
$J_{3,4}$	10		10	10	9	10	10	10	10	10	10	10	10	9	10
$J_{4,5}$	10		10	10	9	9.5	10	10	10	10	10	10	10	9	10
$J_{3',4'}$	8	7.5	7		4	7.5	6	5	7.5	7	6.5	7	7	5.5	6
$J_{4',5'}$	8		7		4	7.5	6	5	7.5	7	6.5	7	7	5.5	6

	(20) [l]	(21) [c,m]	(23) [n]	(24)	(25) [o]	(26) [d,p]	(27)	(29)	(30) [d,q]	(31) [r]	(32) [s]	(33)	(34) [c,t]	(35)	(37) [u]	(38)
1-H	5.91d	5.96d	5.87d	6.28d	6.07d	5.64d	5.85d	5.93d	6.08d	6.04d	6.38d	5.84d	5.67d	5.70d	6.03d	5.89d
2-H	5.07dd	4.43dd	5.17dd	5.70dd	4.64dd	3.68dd	5.40dd	5.06dd	4.62dd	5.17dd	5.44dd	5.13dd	4.92dd		4.68dd	4.97dd
3-H	5.82t	5.14t	5.84t	6.52t	5.44t	4.07t	5.88t	5.81t	5.86t	5.92t	6.12t	5.80t	5.57t		5.45t	4.23t
4-H	5.44t	4.91t	5.35t	6.04t	5.05t	3.61t	5.46t	3.44t	5.19t	5.55t	5.46t	3.64t	4.92t		5.06t	3.54t
5-H																
1′-H$_a$												4.43d	3.93d			
1′-H$_b$	4.28d									4.32d		4.33d	4.05d			
3′-H	5.63d	} 5.34m	5.71d	6.10d	} 5.51cm	5.80d	5.67d		5.83d	5.86d	5.83d	5.90d	5.57d		5.49d	4.1m
4′-H	5.52t		5.58t	6.02t		5.83t	5.56t	5.45t	5.58t	5.71t	6.07t	5.79t	5.36t	5.66t	5.66t	5.49t
5′-H	4.13q		4.18q													

$J_{1,2}$	4	4	3.5	3.5	4	3.5	3.5	4	4	3.5	3.5	3.5	3.5	3.0	3.5	3.5
$J_{2,3}$	10.5	9.5	10	10	10	9.5	10	10	10	9.5	10	10.5	10		10	10
$J_{3,4}$	10.5	10	10	10	10	9.5	10	10	10	9.0	10	10	10		10	10
$J_{4,5}$	10.5	10	9	10	10	9.5	10	10	10	9.0	10	10	8.5		10	
$J_{3',4'}$	4.5		5.5	6	6	7	5	7.5	6	7	8	8	8	6	6.5	7.5
$J_{4',5'}$	4.5		5.5	6	6	7	5	7.5	6	7	8	8	8	6	6.5	7.5
	(39) [d,v]	(40)	(41)	(42) [w]	(43)	(44) [x]	(45) [y]	(46) [z]	(47)	(48)	(49)	(50) [c]	(51) [α]	(52)	(54) [β]	(55) [γ]
1-H	6.08d	6.45d	6.04d	5.95d	5.92d	6.14d	6.04d	6.11d	6.15d	6.09d	6.02d	5.53d	5.95d	6.19d	6.17d	6.30d
2-H	4.80dd	5.54dd	5.21dd	4.94dd	4.93dd	4.76dd	5.08dd	5.11dd	5.44dd	5.23dd	4.94dd	5.2m	5.19dd	5.87dd	5.47dd	5.68dd
3-H	5.91t	6.44t	5.94t	5.41t		5.95t	5.90t	5.50t	6.26t	5.95t			5.44t	5.92dd	5.81dd	5.88dd
4-H	5.27t	6.02t	5.60t	5.04t	5.15t	5.39t	5.50t	5.61t	5.76t	5.61t	5.28t	5.2m	5.64t	6.27dd	6.19d	6.21d
5-H		4.90dt							5.26dt	4.81t				5.10m	5.04m	4.88m
1′-H_a			4.41d					5.67d		5.73d	5.70d					
1′-H_b			4.28d			4.32d		5.60d		5.59d	5.49d					
3′-H	5.82d	6.17d	5.93d	5.44d	4.00m	5.85d	5.81d	5.52d	6.13d	5.93d	5.92d	5.46d	5.92d	5.98d	5.90d	5.66d
4′-H	5.56t	5.96t	5.82t	5.70t	5.05t	5.55t	5.67t	5.82t	5.95t	5.84t	5.82t	5.34t	5.78t	5.82t	5.72t	6.00t
5′-H																4.17m
$J_{1,2}$	4	4	3.5	3.5	3.5	4	3.5	3.8	3.0	3.7	3.5	4	4	4	4	4
$J_{2,3}$	10	10	9.5	10	10	10.5	10	9.5	10.5	10.5	10		10	10.5	10.5	11.0
$J_{3,4}$	10	10	9.5	10	10	10	10	9.5	10	9.5	10		10	3	4	3
$J_{4,5}$	10	9.5	9.5	10	10	10	10	10	10	10	10		10	*ca.* 1.5	*ca.* 1	*ca.* 1
$J_{3',4'}$	6	7.5	7.5	8	7.5	6.5	6.5	8	7	8	8	6	8	8.5	7.5	8
$J_{4',5'}$	6	7.5	7.5	8	7.5	6.5	6.5	8	7	8	8	6	8	8.5	7.5	8

[a] In each case the appropriate number of CMe_3 resonances were observed in the region δ 1—1.3. In the case of isobutyryl esters the $CHMe_2$ resonances occurred in the same region, with additional $CHMe_2$ multiplets in the region δ 2.3—2.6. In most cases the resonances due to 6-H and 6′-H were not observed as discrete resonances nor could they be assigned with confidence. In cases where the 1′-H_a and 1′-H_b resonances could be assigned, $J_{1'a,1'b}$ was *ca.* 12—12.5 Hz. [b] Unless otherwise stated [$^2H_6$]benzene was used as solvent. [c] In $CDCl_3$. [d] Prepared *in situ* from the previous sample by the addition of an excess of trichloroacetyl isocyanate to the n.m.r. solution. [e] NH singlets at δ 7.46, 7.16, and 7.04. [f] *O*-Acetyl singlets at δ 1.82, 1.86, and 1.91. [g] *O*-Mesyl singlets at δ 2.30, 2.48, and 2.53. [h] OH doublets at δ 2.52 and 3.33. [j] NH singlets at δ 9.33 and 8.32. [k] NH singlet at δ 9.35. [l] *O*-Acetyl singlets at δ 1.63, 1.72 (× 2), 1.77, 1.88, and 1.91. [m] *O*-Mesyl singlets at δ 3.12, 3.17, 3.19 (× 2), and 3.23 (× 2). [n] *O*-Acetyl singlets at δ 1.63, 1.70, and 1.90 (× 2). [o] *O*-Mesyl singlets at δ 2.49, 2.58, 2.60, and 2.75. [p] NH singlets at δ 8.68, 8.69, and 9.71. [q] NH singlets at δ 8.56 and 9.49. [r] *O*-Acetyl singlets at δ 1.72 and 2.22. [s] In [$^2H_5$]pyridine, *O*-mesyl singlets at δ 3.20 and 3.50. [t] *O*-Mesyl singlet at δ 2.98. [u] *O*-Mesyl singlets at δ 3.59, 3.60, 3.73, and 3.78. [v] NH singlets at δ 8.62, 8.69, and 9.28. [w] *O*-Mesyl singlets at δ 2.47 (× 2) and 2.68. [x] NH singlets at δ 8.43 and 9.34. [y] *O*-Acetyl singlets at δ 1.70 and 1.85. [z] *O*-Mesyl singlets at δ 2.32 and 2.38. [α] *O*-Mesyl singlet at δ 2.23. [β] *O*-Mesyl resonance at δ 2.48. [γ] *O*-Mesyl resonance at δ 2.69.

pivalates (5) and (38) respectively, isolated in 10 and 23% yield.

The following fraction L was a minor product isolated in 1% yield, the ^{1}H n.m.r. spectrum of which was indicative of another pentapivalate. Since the resonances due to 2-H, 3-H, and 4-H were clearly recognised to high field (δ 3.68, 4.07, and 3.61 respectively) the implication was that the pivaloyl groups were located at the 1′-, 3′-, 4′-, 6-, and 6′-position as in (26). Indeed the 3′-H and 4′-H resonances formed a second-order multiplet at δ 5.8, and upon addition of trichloroacetyl isocyanate the 2-H, 3-H, and 4-H resonances shifted downfield into the δ 5.4—5.9 region and the 3′-H and 4′-H resonances shifted slightly upfield and were better separated (Table 1). The mass spectrum of the tristrimethylsilyl ether (28) displayed ions at *m/z* 499 (Pv_4fruf^+) and 463 ($PvTms_3glcp^+$) due to the fructofuranosyl and glucopyranosyl ions, respectively, which showed quite conclusively that four of the five pivaloyl groups were located on one of the sugar moieties. These data clearly indicated that L was the 1′,3′,4′,6,6′-pentapivalate (26).

The penultimate fraction M, obtained in 4.4% yield, was recognised as a tetrapivalate from its ^{1}H n.m.r. spectrum (Table 1). The only resonances to low field of δ 5 were two doublets due to 1-H and 3′-H which indicated that M was the 1′,3′,6,6′-tetrapivalate (3). Further support for this structure was provided by the mass spectrum of the derived tetrakistrimethylsilyl ether (4) which showed two ions at *m/z* 487 ($Pv_3Tmsfruf^+$) and 463 ($PvTms_3glcp^+$), thereby confirming the presence of three pivaloyl groups on one ring and one on the other.

The final fraction N contained the major product of the reaction, isolated in 33% yield, and was a tetrapivalate as shown by its ^{1}H n.m.r. spectrum. Since the only resonances to low field of δ 5 were 1-H (δ 5.70) and 4′-H (δ 5.66), the compound was assigned as the 1′,4′,6,6′-tetrapivalate (35) which was confirmed by the mass spectrum of its tetrakistrimethylsilyl ether (36) which showed, as above, glycosyloxy ions at *m/z* 487 and 463.

Finally, when the pivaloylation was conducted with 3 molar equivalents of the reagent at −40 °C for 3 h, a mixture of two major and several minor components was formed. The major components were isolated by chromatography, yielding fractions O (42% yield) and P (22% yield).

The ^{1}H n.m.r. spectrum of O indicated that it was a tripivalate since there were three discrete resonances in the region δ 1.2—1.3 (CMe_3), but the remaining spectrum was largely overlapped and not capable of first-order analysis. However, it was significant that there were no resonances below δ 5, which indicated that none of the pivaloyl groups were located on the secondary hydroxy groups. Consequently the triester was tentatively assigned as the 1′,6,6′-tripivalate (22) which was further characterised by conversion into its syrupy pentaacetate (23) and pentabenzoate (24) and the crystalline pentamesylate (25). The structure of the tripivalate was finally confirmed by an unequivocal synthesis of the pentabenzoate (24) from 1′,6,6′-tri-*O*-tritylsucrose (56) which was benzoylated to give (57)[15] followed by sequential *O*-detritylation and pivaloylation. The resulting syrupy 2,3,3′,4,4′-pentabenzoate (24) was indistinguishable (i.r. and t.l.c.) from that derived from fraction O.

The second fraction P was crystalline and its ^{1}H n.m.r. spectrum indicated that it was a dipivalate and that the ester groups were located at primary positions. The mass spectrum of the hexakistrimethylsilyl ether showed a single glycosyloxycarbonium ion at *m/z* 463, suggesting that the two pivalate groups were located on separate sugar moieties. The most likely structure for P is therefore the 6,6′-dipivalate (19) since the 1′-OH is substantially less reactive than those at the 6- and 6′-position.

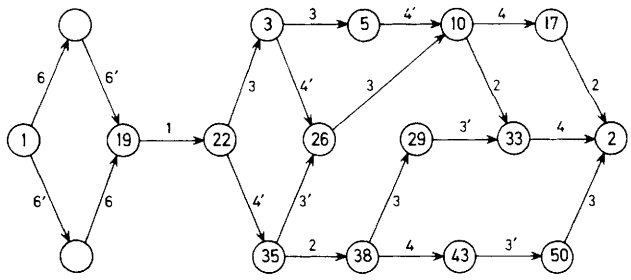


Figure. Sequence of reactions in the pivaloylation of sucrose

The pattern of reactivity of sucrose towards pivaloyl chloride is outlined in the Figure. It does not appear to follow the course which might have been predicted on the basis of other studies on the selective acylation of sucrose with other acid chlorides. For example the tetramolar tosylation of sucrose with tosyl chloride afforded the 1′,2,6,6′-tetratosylate in 32% yield [16] and Ball *et al.*[17] have isolated the 2,6,6′-tritosylate in addition to the 1′,6,6′-triester from the selective trimolar tosylation of sucrose. We have recently shown that the selective tosylation of 6,6′-di-*O*-tritylsucrose gives a mixture of the 1′,2-ditosylate and the 1′-tosylate [18] and 1,6,6′-tri-*O*-tritylsucrose gave the 2-*O*-tosyl derivative on selective monotosylation.[19] Similarly we have recently shown that 1′,6,6′-tri-*O*-mesitylsulphonylsucrose affords the 2-*O*-tosylate upon selective monotosylation.[16] The enhanced reactivity of the 2-OH is related to the vicinal *cis*-oxygen at C-1,[6] but in the present case the tetrapivaloylation of sucrose leads mainly to the 1′,4′,6,6′-tetrapivalate (35) with the 1′,3′,6,6′-isomer (3) as a minor product. The 1′,2,6,6′-isomer has not been detected in the reaction mixtures, and had it been a substantial product we are confident that it would have been isolated.

Of the pentapivalates isolated, the 1′,2,4′,6,6′- and the 1′,3,3′,6,6′-isomer, (38) and (5) respectively, were the major components, with the 1′,3′,4′,6,6′-isomer (26) being present in small amounts. Obviously the former must arise from the 1′,4′,6,6′-tetrapivalate (35) which itself is a major tetraester. The pentapivalate (5) must arise directly from the 1′,3′,6,6′-tetrapivalate (3) which has only been isolated in *ca.* 4% yield. The formation of a relatively good yield of (5) suggests that the yield of its direct precursor (3) could be considerably improved, although we have not found conditions for this as yet. The two major pentapivalates (38) and (5) serve as precursors of the two major hexapivalates, the 1′,2,4,4′,6,6′-isomer (43) and the 1′,3,3′,4′,6,6′-isomer (10) respectively, although the minor pentaester (26) could also serve as a precursor of (10), but this is probably only a minor pathway. The minor 1′,2,3,4′,6,6′-hexapivalate (29) has only been isolated in 4% yield and would appear to lie on a minor reaction pathway between the 1′,2,4′,6,6′-pentapivalate (38) and the major heptapivalate (33), and consequently it seems more reasonable that (33) must arise mainly from the 1′,3,3′,4′,6,6′-hexapivalate (10). The rather low yield (*ca.* 2%) of the 1′,2,3′,-4,4′,6,6′-heptapivalate (50) is puzzling, since it lies directly between the major hexapivalate (43) and the octapivalate (2).

The possibility that the observed products could arise from acyl migration cannot be completely ruled out, but it is generally thought that acylations carried out under these conditions are kinetically controlled.[1] Furthermore, in the present work the pivalates have been subjected to benzoylation, acetylation, mesylation, and isobutyrylation (Table 2), yet in none of these reactions, the conditions of which were similar to the conditions used in pivaloylation reactions, was migration of a pivaloyl group observed.

Table 2. Derivatives of partially pivaloylated sucroses

	M.p. (°C)	$[\alpha]_D$ (°)	Mol. formula	Elemental analysis: Found C	Found H	Found S	Requires C	Requires H	Requires S
1′,2,3,3′,4′,6,6′-Heptapivalate (33)									
4-Mesylate (34)	76—77 [a]	+53 [b]	$C_{48}H_{80}O_{20}S$	56.8	8.1	3.2	57.2	7.9	3.2
1′,2,3′,4,4′,6,6′-Heptapivalate (50)									
3-Mesylate (51)	syrup	+48 [b]	$C_{48}H_{80}O_{20}S$	57.1	8.3	3.8	57.2	7.9	3.2
1′,3,3′,4′,6,6′-Hexapivalate (10)									
2,4-Di-isobutyrate (12) [c]	77—79 [a]	+51 [b]	$C_{50}H_{82}O_{19}$	61.0	8.4	—	60.9	8.3	—
2-Isobutyrate (13) [c]	syrup	+41 [b]	$C_{46}H_{76}O_{18}$	60.3	8.5	—	60.3	8.3	—
2,4-Diacetate (14)	82—83 [a]	+50 [b]	$C_{46}H_{74}O_{19}$	59.3	8.0	—	59.4	8.0	—
2,4-Dimesylate (15)	syrup	+47 [b]	$C_{44}H_{74}O_{21}S_2$	52.8	7.6	6.7	52.7	7.4	6.4
2,4-Dibenzoate (16)	syrup	+26 [b]	$C_{56}H_{78}O_{19}$	63.4	7.5	—	63.8	7.4	—
1′,2,3,4′,6,6′-Hexapivalate (29)									
3′,4-Diacetate (31)	79—80 [a]	+59 [d]	$C_{46}H_{74}O_{19}$	59.1	8.1	—	59.4	8.0	—
3′,4-Dimesylate (32)	139—140 [a]	+48 [d]	$C_{44}H_{74}O_{21}S_2$	52.4	7.5	6.7	52.7	7.4	6.4
1′,2,4,4′,6,6′-Hexapivalate (43)									
3,3′-Diacetate (45)	syrup	+56 [b]	$C_{46}H_{74}O_{19}$	59.1	8.1	—	59.4	8.0	—
3,3′-Dimesylate (46)	syrup	+38 [b]	$C_{44}H_{74}O_{21}S_2$	52.5	7.8	6.2	52.7	7.4	6.4
3,3′-Dibenzoate (47)	syrup	+39 [b]	$C_{56}H_{78}O_{19}$	64.2	7.5	—	63.8	7.4	—
3,3′-Di-isobutyrate (48) [c]	67—68 [a]	+51 [b]	$C_{50}H_{82}O_{19}$	61.4	8.4	—	60.9	8.3	—
3′-Isobutyrate (49)	syrup	+41 [b]	$C_{46}H_{76}O_{18}$	60.0	8.2	—	60.3	8.3	—
1′,3,3′,6,6′-Pentapivalate (5)									
2,4,4′-Triacetate (8)	syrup	+34 [d]	$C_{43}H_{68}O_{19}$	58.3	7.6	—	58.1	7.7	—
2,4,4′-Trimesylate (9)	syrup	+37 [d]	$C_{40}H_{68}O_{22}S_3$	48.5	6.9	9.7	48.2	6.8	9.6
1′,2,4′,6,6′-Pentapivalate (38)									
3,3′,4-Tribenzoate (40)	syrup	+7 [d]	$C_{58}H_{74}O_{19}$	64.4	6.8	—	64.8	6.9	—
3,3′,4-Tri-isobutyrate (41)	syrup	+54 [d]	$C_{49}H_{80}O_{19}$	60.8	8.2	—	60.5	8.2	—
3,3′,4-Trimesylate (42)	syrup	+48 [d]	$C_{40}H_{68}O_{22}S_3$	48.5	6.9	9.7	48.2	6.8	9.6
1′,4′,6,6′-Tetrapivalate (35)									
2,3,3′,4-Tetramesylate (37)	syrup	+36 [d]	$C_{36}H_{62}O_{23}S_4$	43.9	6.3	12.9	43.6	6.3	12.9
1′,6,6′-Tripivalate (22)									
2,3,3′,4,4′-Penta-acetate (23)	syrup	+57 [d]	$C_{37}H_{56}O_{19}$	54.9	7.0	—	55.2	7.0	—
2,3,3′,4,4′-Pentabenzoate (24)	syrup	+11 [d]	$C_{62}H_{66}O_{19}$	67.3	6.0	—	66.8	5.9	—
2,3,3′,4,4′-Pentamesylate (25)	162—163 [e]	+38 [d]	$C_{32}H_{56}O_{24}S_5$	39.2	5.8	15.9	39.0	5.7	16.3
6,6′-Dipivalate (19)									
1′,2,3,3′,4,4′-Hexa-acetate (20)	syrup	+65 [d]	$C_{34}H_{50}O_{14}$	53.5	6.6	—	53.5	6.6	—
1′,2,3,3′,4,4′-Hexamesylate (21)	205—207 [e]	+42 [d]	$C_{28}H_{50}O_{25}S_6$	35.0	5.1	19.5	34.4	5.1	19.6

[a] From light petroleum. [b] In methanol. [c] Mixture of products obtained after reaction with isobutyryl chloride–pyridine; separated by chromatography. [d] In chloroform. [e] From methanol.

Experimental

General.—Column chromatography was performed on silica gel G (Merck 7734) using dry-packed columns.[20] T.l.c. was performed on silica gel G layers deposited on either sheets of aluminium or plastic. Optical rotations were, unless otherwise stated, measured in methanol at a concentration of 1 g per 100 ml in a 1 dm cell. N.m.r. spectra were recorded on a Perkin-Elmer R-34 spectrometer operating at 220 MHz and mass spectra were determined on an A.E.I. MS-30 spectrometer. Acylations with acetic anhydride, benzoyl chloride, isobutyryl chloride, and mesyl chloride were carried out in the conventional way using an excess of the reagent in pyridine as solvent. The reaction mixtures were then processed by decomposition with ice–water and extraction of the product with either chloroform or diethyl ether (hereafter referred to as ether). The physical properties of the products are mostly reported in Table 2. Light petroleum refers to that fraction boiling in the range 40—60 °C unless otherwise stated.

Reaction of Sucrose with Pivaloyl Chloride under Various Conditions.—(a). A stirred solution of sucrose (10 g, 29.24 mmol) in anhydrous pyridine (150 ml) was cooled to *ca.* −40 °C (acetone–solid carbon dioxide) and pivaloyl chloride (70 ml, 583 mmol) was added slowly from a dropping funnel during *ca.* 1 h. The stirred reaction mixture was maintained at −40 °C for 6 h and then stored at room temperature for a further 24 h, when t.l.c. [ether–light petroleum (1 : 1)] suggested the presence of two major and several minor components. The reaction mixture was quenched by the addition of ice–water, and the precipitated syrup was then extracted with chloroform and the extract washed sequentially with dilute hydrochloric acid, saturated aqueous sodium hydrogen carbonate, and water and then dried ($MgSO_4$). The extract was then concentrated to dryness and fractionated chromatographically using, initially, ether–light petroleum (1 : 8) (500 ml) as the eluant. Subsequently the composition of the eluting solvent was then changed to 1 : 5 (1 000 ml) which gave the following fractions.

Fraction A, which contained the faster moving component 1,3,4,6-*tetra*-O-*pivaloyl*-β-D-*fructofuranosyl* 2,3,4,6-*tetra*-O-*pivaloyl*-α-D-*glucopyranoside* (*sucrose octapivalate*) (2)* (12 g, 40%), m.p. 128—130 °C (ethanol); $[\alpha]_D$ +61° (Found: C, 61.3; H, 8.4. $C_{52}H_{86}O_{19}$ requires C, 61.5; H, 8.5%); *m/z* 499 (25%), 397 (3), 295 (11), 211 (15), 109 (6), 85 (40, Me_3CCO^+), 81 (1), and 57 (100, Me_3C^+).

Fraction B was obtained by changing the eluting solvent to

* The octapivalate (2) could be isolated directly in 90% yield without the need for chromatography by conducting the reaction at 70 °C for 24 h.

a 1 : 4 mixture (200 ml) which afforded syrupy 1,3,4,6-*tetra*-O-*pivaloyl*-β-D-*fructofuranosyl* 3,4,6-*tri*-O-*pivaloyl*-α-D-*glucopyranoside* (17) (0.3 g, 1%), $[\alpha]_D$ +43° (Found: C, 60.6; H, 8.8. $C_{47}H_{78}O_{18}$ requires C, 60.6; H, 8.4%); *m/z* 499 (1.6%), 415 (1.3), 313 (1), 295 (4), 211 (5.6), 109 (3.9), 85 (32, Me_3CCO^+), and 57 (100, Me_3C^+).

Fraction C was obtained as a syrup (0.4 g, 1.5%) by elution with a 1 : 3 mixture of the eluting solvent (200 ml) and subsequently identified as 1,3,4,6-*tetra*-O-*pivaloyl*-β-D-*fructofuranosyl* 2,4,6-*tri*-O-*pivaloyl*-α-D-*glucopyranoside* (50), $[\alpha]_D$ +49° (Found: C, 60.3; H, 8.4. $C_{47}H_{78}O_{18}$ requires C, 60.6; H, 8.4%); *m/z* (of trimethylsilyl ether) 499 (14%), 487 (3), 295 (11), 283 (9), 211 (5), 109 (5), 85 (32, Me_3CCO^+), and 57 (100, Me_3C^+).

Fraction D was eluted using the same solvent as above and was characterised as 1,3,4,6-*tetra*-O-*pivaloyl*-β-D-*fructofuranosyl* 2,3,6-*tri*-O-*pivaloyl*-α-D-*glucopyanoside* (33) (14 g, 52%),* m.p. 100—102 °C (light petroleum, b.p. 100—120 °C); $[\alpha]_D$ +50° (Found: C, 60.9; H, 8.6. $C_{47}H_{78}O_{18}$ requires C, 60.6; H, 8.4%); *m/z* 499 (3%), 415 (1), 313 (5), 295 (5), 211 (4), 109 (4), 85 (31, Me_3CCO^+), and 57 (100, Me_3C^+).

(b). To a cooled (−40 °C) solution of sucrose (10 g, 29.24 mmol) in anhydrous pyridine (150 ml) was added pivaloyl chloride (70 ml, 583 mmol) dropwise during *ca.* 1 h. The reaction mixture was stirred at −40 °C for a further 1 h and then processed as above to give a syrup which contained at least six components (t.l.c.; ether–light petroleum, 1 : 1). Chromatographic fractionation using various ether–light petroleum mixtures as eluant gave the following fractions.

Fraction E was obtained using a 1 : 3 mixture (500 ml) and was identical with the above heptapivalate (33) (6.8 g, 25%).

Fraction F was also eluted with the same mixture of solvents as above (1 000 ml) and was a mixture of two components. It was obtained as a syrupy solid which was recrystallised from light petroleum to give 1,3,4,6-*tetra*-O-*pivaloyl*-β-D-*fructofuranosyl* 3,6-*di*-O-*pivaloyl*-α-D-*glucopyranoside* (10) (8 g, 33%),† m.p. 144 °C; $[\alpha]_D$ +54° (Found: C, 59.2; H, 8.4. $C_{42}H_{70}O_{17}$ requires C, 59.6; H, 8.3%); *m/z* (bistrimethylsilyl ether derivative) 499 (12%), 475 (1), 373 (4), 295 (13), 283 (2), 271 (9), 211 (6), 109 (6), 85 (27, Me_3CCO^+), and 57 (100, Me_3C^+).

The other component of fraction F was isolated pure as a syrup (2.5 g, 10%)† simply by evaporation of the light petroleum mother liquors from the crystallisation of (10), and was identified as 1,4,6-*tri*-O-*pivaloyl*-β-D-*fructofuranosyl* 2,4,6-*tri*-O-*pivaloyl*-α-D-*glucopyranoside* (43), $[\alpha]_D$ +45.5° (Found: C, 59.7; H, 8.1. $C_{42}H_{70}O_{17}$ requires C, 59.6; H, 8.3%); *m/z* 415 (1.6%), 211 (3.4), 109 (2), 85 (22, Me_3CCO^+), and 57 (100, Me_3C^+).

Fraction G was a minor component obtained as a syrup (1 g, 4%) by elution with a 1 : 1 mixture of solvents (300 ml). It was crystallised from light petroleum and was identified as 1,4,6-*tri*-O-*pivaloyl*-β-D-*fructofuranosyl* 2,3,6-*tri*-O-*pivaloyl*-α-D-*glucopyranoside* (29), m.p. 102—103 °C; $[\alpha]_D$ +49° (Found: C, 60.0; H, 8.6. $C_{42}H_{70}O_{17}$ requires C, 59.6; H, 8.3%); *m/z* 415 (2%), 313 (0.7), 295 (0.5), 211 (3), 109 (2), 85 (22, Me_3CCO^+), 81 (1.4), 57 (100, Me_3C^+).

Fraction H was another minor product isolated as a syrup (1 g, 4.5%)‡ by further elution with the same solvent mixture (300 ml). It was subsequently characterised as 1,3,6-*tri*-O-*pivaloyl*-β-D-*fructofuranosyl* 3,6-*di*-O-*pivaloyl*-α-D-*glucopyranoside* (5), $[\alpha]_D$ +36° (Found: C, 58.1; H, 8.2. $C_{37}H_{62}O_{16}$ requires C, 58.3; H, 8.1%); *m/z* (tristrimethylsilyl derivative) 487 (14%), 475 (3), 373 (3), 313 (1), 295 (25), 211 (8), 85 (30, Me_3CCO^+), and 57 (100, Me_3C^+).

Fraction I was obtained as a white solid by elution with a 2 : 1 mixture (200 ml) of the solvents (2.1 g, 11%)§ and was identified as 1,4,6-*tri*-O-*pivaloyl*-β-D-*fructofuranosyl* 2,6-*di*-O-*pivaloyl*-α-D-*glucopyranoside* (38), m.p. 120—121 °C (light petroleum or cyclohexane); $[\alpha]_D$ +61° (Found: C, 58.0; H, 8.3. $C_{37}H_{62}O_{16}$ requires C, 58.3; H, 8.1%); *m/z* (tristrimethylsilyl ether) 487 (18%), 475 (3), 373 (3), 313 (1), 295 (3), 211 (5), 85 (30, Me_3CCO^+), and 57 (100, Me_3C^+).

(c). A stirred solution of sucrose (6.84 g, 20 mmol) in a mixture of anhydrous pyridine (100 ml) and chloroform (50 ml) was cooled to *ca.* −70 °C (acetone–solid carbon dioxide) and pivaloyl chloride (12 ml, 100 mmol) was added slowly during *ca.* 30 min. After 1 h t.l.c. [chloroform–methanol (10 : 1)] showed at least eight components. The reaction mixture was then processed in the usual way to give a syrupy mixture which was fractionated on silica gel using dichloromethane–methanol mixtures.

Fraction J was eluted with an 80 : 1 mixture (200 ml) and identified as the pentapivalate (5) (1.5 g, 10%) which had previously been isolated.

Fraction K was isolated by elution with a 60 : 1 mixture (500 ml) and was identified as the isomeric pentapivalate (38) (3.5 g, 23%) which had been previously isolated.

Fraction L was a minor syrupy component (0.25 g, 1%) eluted with a 50 : 1 mixture (100 ml) and identified as 1,3,4,6-tetra-*O*-pivaloyl-β-D-fructofuranosyl 6-*O*-pivaloyl-α-D-glucopyranoside (26), $[\alpha]_D$ +25° (*c* 1 in chloroform) (Found: C, 57.5; H, 8.0. $C_{37}H_{62}O_{16}$ requires C, 58.3; H, 8.1%); *m/z* (tristrimethylsilyl ether) 499 (18%), 463 (1), 373 (3), 295 (17), 281 (1), 271 (7), 211 (8), 109 (7), 85 (37, Me_3CCO^+), and 57 (100, Me_3C^+).

Fraction M was a further minor fraction eluted with a 40 : 1 mixture (100 ml) and obtained as a syrup (0.5 g, 4.4%) and subsequently identified as 1,3,6-*tri*-O-*pivaloyl*-β-D-*fructofuranosyl* 6-O-*pivaloyl*-α-D-*glucopyranoside* (3), $[\alpha]_D$ +26° (*c* 1 in chloroform) (Found: C, 56.8; H, 8.1. $C_{32}H_{54}O_{15}$ requires C, 56.6; H, 8.0%); *m/z* (tetrakistrimethylsilyl ether) 487 (20%), 463 (0.4), 373 (3), 211 (5), 109 (10), 85 (25, Me_3CCO^+), and 57 (100, Me_3C^+).

Fraction N was obtained by elution with a 30 : 1 mixture (800 ml) to give a syrup (4 g, 35%) which was subsequently crystallised from chloroform to give 1,4,6-*tri*-O-*pivaloyl*-β-D-*fructofuranosyl* 6-O-*pivaloyl*-α-D-*glucopyranoside* (35), m.p. 85—88 °C; $[\alpha]_D$ +32.5° (*c* 1 in chloroform) (Found: C, 56.4; H, 8.2. $C_{32}H_{54}O_{15}$ requires C, 56.6; H, 8.0%); *m/z* (tetrakistrimethylsilyl ether) 487 (8%), 463 (0.1), 373 (1.1), 109 (1.3), 85 (7, Me_3CCO^+), 73 (34), and 57 (100, Me_3C^+).

(d). To a stirred solution of sucrose (6.84 g, 20 mmol) in anhydrous pyridine (100 ml) at *ca.* −40 °C was added pivaloyl chloride (7.2 ml, 60 mmol) dropwise during *ca.* 1 h. The reaction mixture was then stirred at between −30 and

* The heptapivalate was subsequently obtained in 50% yield from a similar reaction using 12 molar equivalents of acid chloride with an extension of the room temperature ' standing ' period to 72 h.

† The yield of (10) could be improved to 45% by repeating the reaction with 7 molar equivalents of pivaloyl chloride at −40 °C for *ca.* 8 h and was isolated crystalline without recourse to chromatography. In addition a 35% yield of the hexapivalate (43) could be obtained from the same reaction mixture but only after chromatography.

‡ The yield of the pentapivalate (5) was improved to *ca.* 30% by treating a suspension of sucrose in a mixture of chloroform and pyridine (1 : 2) with 5 molar equivalents of pivaloyl chloride at room temperature, followed by isolation in the usual way and chromatography.

§ The yield of the pentapivalate (38) could be improved to about 30% by treating a solution of sucrose in anhydrous pyridine with 6 molar equivalents of pivaloyl chloride at −40 °C for 4 h and then at room temperature for 20 h.

−40 °C for 3 h and then processed in the usual way to give a syrup which contained one major and several minor components according to t.l.c. [chloroform–methanol (3 : 1)]. The mixture was then fractionated chromatographically in the usual way and the following fractions were obtained.

Fraction O was the major component and was obtained as a syrup (5 g, 42%) by elution with chloroform–methanol (15 : 1; 1 l) and was shown to be the 1,6-*di*-O-*pivaloyl*-β-D-*fructofuranosyl* 6-O-*pivaloyl*-α-D-*glucopyranoside* (22), $[\alpha]_D$ +57° (Found: C, 54.6; H, 8.1. $C_{27}H_{46}O_{14}$ requires C, 54.6; H, 7.7%); *m/z* (pentakistrimethylsilyl ether) 475 (39%), 463 (1), 373 (9), 361 (7), 283 (12), 271 (45), 211 (5), 109 (28), 85 (31), and 57 (100).

Fraction P was eluted with a 10 : 1 mixture of the two solvents (500 ml), giving initially a syrup (3 g, 22%)* which was later crystallised from chloroform–acetone. It was identified as 6-*O*-pivaloyl-β-D-fructofuranosyl 6-*O*-pivaloyl-α-D-glucopyranoside (19), m.p. 155—156 °C; $[\alpha]_D$ +48° (*c* 1 in chloroform); *m/z* (hexakistrimethylsilyl ether) 463 (11%), 373 (24), 361 (16), 331 (6), 283 (10), 271 (82), 211 (3), 109 (11), 85 (36), and 73 (100, Me_3Si^+).

1,3,4,6-*Tetra*-O-*pivaloyl*-β-D-*fructofuranosyl* 4-O-*Benzoyl*-2,3,6-*tri*-O-*pivaloyl*-α-D-*galactopyranoside* (52).—To a solution of the 4-*O*-mesylate (34) (1 g, 1 mmol) in dry DMF (15 ml) was added an excess of sodium benzoate (1 g, 7 mmol) and the mixture was heated and stirred for 48 h at 125—130 °C. Examination of the reaction mixture by t.l.c. [ether–light petroleum (2 : 3)] indicated the complete conversion of starting material into a faster moving single product. The reaction mixture was then cooled and poured into ice–water and the precipitated syrup was extracted into ether. The extract was then washed well with water and dried ($MgSO_4$) and finally concentrated to dryness to give the 4-O-*benzoate* (52) (0.8 g, 80%), m.p. 100—102 °C (light petroleum); $[\alpha]_D$ +55° (Found: C, 62.7; H, 7.9. $C_{54}H_{82}O_{19}$ requires C, 62.7; H, 7.9%); *m/z* 519 (14%), 499 (10), 417 (2), 295 (12), 211 (10), 109 (5), 85 (33), and 57 (100).

β-D-*Fructofuranosyl* α-D-*Galactopyranoside* (53).—A stirred solution of the 4-*O*-benzoate (52) (1 g, 0.98 mmol) in methanol was treated with a few drops of methanolic sodium methoxide and the mixture was kept at room temperature for 24 h and then passed through a small pad of silica gel to remove the sodium methoxide. Evaporation of the solution then gave *galacto*-sucrose (53) (0.31 g, 80%), m.p. 176—178 °C (methanol); $[\alpha]_D$ +79° (*c* 0.8 in methanol) (lit.,[13] m.p. 179 °C; $[\alpha]_D$ +78.5°) (Found: C, 42.1; H, 6.5. Calc. for $C_{12}H_{22}O_{11}$: C, 42.1; H, 6.4%).

1,3,4,6-*Tetra*-O-*pivaloyl*-β-D-*fructofuranosyl* 4-O-*Benzoyl*-2-*O*-*mesyl*-3,6-*di*-O-*pivaloyl*-α-D-*galactopyranoside* (54).—A solution of the 2,4-dimesylate (15) (2 g, 2 mmol) in dry DMF (30 ml) containing sodium benzoate (2 g, 14 mmol) was heated at *ca.* 130 °C for 48 h, when t.l.c. (ether–light petroleum) indicated the complete conversion of the starting material into a faster moving compound. The reaction mixture was then processed as above to give the crystalline 4-O-*benzoate* (54) (2 g, 98%), m.p. 151—155 °C; $[\alpha]_D$ +48.9° (Found: C, 58.4; H, 7.6; S, 3.2. $C_{50}H_{76}O_{20}S$ requires C, 58.4; H, 7.4; S, 3.1%); *m/z* 513 (30%), 499 (14), 411 (1), 295 (15), 211 (12), 109 (11), 85 (45), 81 (2), and 57 (100).

* The yield of the dipivalate (19) could be improved to 40% by reaction of sucrose in anhydrous pyridine with 2.2 molar equivalents of pivaloyl chloride at room temperature for 12 h.

3-O-*Mesyl*-1,4,6-*tri*-O-*pivaloyl*-β-D-*fructofuranosyl* 4-O-*Benzoyl*-2,3,6-*tri*-O-*pivaloyl*-α-D-*galactopyranoside* (55).—A solution of 3′,4-dimesylate (32) (3 g, 2.9 mmol) in dry DMF (50 ml) containing sodium benzoate (3 g, 20.8 mmol) was heated and stirred at 130 °C for 48 h and then processed as above to give the 4-O-*benzoate* (55) as a syrup, $[\alpha]_D$ +45° (*c* 1 in chloroform) (Found: C, 58.7; H, 7.5; S, 2.8. $C_{50}H_{76}O_{20}S$ requires C, 58.4; H, 7.4; S, 3.1%); *m/z* 519 (4.7%), 493 (7), 298 (12), 211 (8), 109 (11), 85 (31), and 57 (100).

3,4-*Di*-O-*benzoyl*-1,6-*di*-O-*pivaloyl*-β-D-*fructofuranosyl* 2,3,4-*Tri*-O-*benzoyl*-6-O-*pivaloyl*-α-D-*glucopyranoside* (24).—To a solution of sucrose 2,3,3′,4,4′-pentabenzoate (58)[14] (0.5 g, 0.7 mmol) in dry pyridine (10 ml) was added pivaloyl chloride (3 ml, 25 mmol) and the solution was kept at room temperature for 24 h. The reaction mixture was then processed in the usual way and the product was extracted with ether to give the *octaester* (24) as a syrup (0.5 g, 64%), $[\alpha]_D$ +11° (Found: C, 67.0; H, 6.3. $C_{62}H_{66}O_{19}$ requires C, 66.8; H, 5.9%). The product was identical (i.r. and t.l.c.) with that prepared by benzoylation of the 1′,6,6′-tripivalate (22) (see Table 2); *m/z* 559 (1.4%), 539 (0.7), 315 (3.6), 211 (3.3), 122 (3), 109 (3), 105 (100), 85 (10), 81 (2), and 57 (35).

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