limate was determined in a scintillation counter[24] and had an average value of 520 d.p.m./mg.

B. 12,12′-Bifluoradenyl (XXIV) (55 mg.) was boiled with 10 ml. of the stock solution in a nitrogen atmosphere for 65 hours. (The concentration of hydrocarbon in the cold solution was determined by means of its ultraviolet absorption to be 2.6×10^{-4} *M*. The solubility of the dimer in the boiling solvent is estimated to be at least 10^{-3} *M* since on cooling considerable quantities of crystals separate from solution). The cold solution was filtered and the crystals washed with benzene and sublimed to give material of m.p. 307° dec. A 1-mg. sample of this material showed no activity as measured by the scintillation counter.

9-Phenylfluorene.—A solution of 218 mg. (0.79 mmole) of 9-*o*-chlorophenylfluorene (X) and 72 mg. (0.88 mmole) of sodium acetate in 50 ml. of alcohol was hydrogenated at room temperature and atmospheric pressure using 65 mg. of 5% palladized carbon as catalyst. The hydrogen absorption was rapid and ceased at 100 mole %. The catalyst was removed by filtration, and the filtrate was evaporated to give material which recrystallized readily from ethanol and after sublimation (80° (0.05 mm.)) had a m.p. of 147–148° (reported[25] m.p. 146°); $\lambda_{\max}^{\text{cyclohexane}}$ 265 mμ (ϵ 20,300), 293 (6,320), 304 (10,300).

1-Phenylfluorene.—A solution of 1-phenylfluorenone[26] (354 mg., 1.38 mmoles) in 25 ml. of benzene–10 ml. ethanol, was hydrogenated at room temperature and atmospheric pressure using 73 mg. of 5% palladized carbon as catalyst. The total hydrogen uptake ceased at 180 mole %, after which the reaction mixture was filtered and the filtrate was evaporated. Chromatography of the oily residue (331 mg·) on 8 g. of neutral alumina using hexane as the eluent resulted in an oil which on sublimation (80° (0.1 mm.)) crystallized on the cold finger; m.p. 38–41°; $\lambda_{\max}^{\text{cyclohexane}}$ 256 mμ (ϵ 27,400), 302 (4,570).

Anal. Calcd. for $C_{19}H_{14}$: C, 94.2; H, 5.8. Found: C, 93.9; H, 5.9.

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[24] We wish to express our appreciation to Mr. I. M. Whittemore of the Donner Laboratories, University of California, Berkeley, for his assistance with the radioactivity analyses in these experiments.

[25] A. Kliegl, *Ber.*, **38**, 288 (1905).

[26] We wish to thank B. L. Smolinsky for preparing this compound according to the directions of Stiles and Libby[4] by heating the peroxide of 1-carboxyfluorenone in benzene.

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[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF ARTHRITIS AND METABOLIC DISEASES, NATIONAL INSTITUTES OF HEALTH]

The Anomeric 2,3,4-Tri-*O*-benzoyl-D-ribopyranosyl Fluorides and 2,3,5-Tri-*O*-benzoyl D-ribofuranosyl Fluorides. A Novel Transformation from the D-Ribopyranose to the D-Ribofuranose Series

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Brief treatment of β-D-ribopyranose tetrabenzoate with liquid hydrogen fluoride gives both anomeric 2,3,4-tri-*O*-benzoyl-D-ribopyranosyl fluorides, the *cis* or α-anomer being sufficiently stable to debenzoylate to α-D-ribopyranosyl fluoride. Longer treatment of β-D-ribopyranose tetrabenzoate or 2,3,4-tri-*O*-benzoyl-β-D-ribopyranosyl fluoride with hydrogen fluoride affords 3,4-di-*O*-benzoyl-β-D-ribopyranosyl fluoride, a topic of the succeeding paper. From this long treatment of β-D-ribopyranose tetrabenzoate with hydrogen fluoride a second di-*O*-benzoylpentosyl fluoride was obtained. Benzoylation of the substance led to the isolation of a third tri-*O*-benzoylpentosyl fluoride which was converted to the known β-D-ribofuranose tetrabenzoate. The third tri-*O*-benzoylpentosyl fluoride was also synthesized from 1,3,5-tri-*O*-benzoyl-α-D-ribofuranose. From 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose a fourth tri-*O*-benzoylpentosyl fluoride, convertible to β-D-ribofuranose tetrabenzoate and to methyl β-D-ribofuranoside, was obtained. It is tentatively concluded that the third and fourth tri-*O*-benzoyl-D-pentosyl fluorides are, respectively, the α- and β-anomers of 2,3,5-tri-*O*-benzoyl-D-ribofuranosyl fluoride.

Through a number of earlier researches in this Laboratory, extending over a period of some twelve years, the preparation and properties of a number of benzoylated aldopyranosyl and aldofuranosyl bromides and chlorides have been investigated.[2] We have recently turned our attention to some of the benzoylated glycosyl fluorides of the ribose and arabinose series. The present paper will deal with results obtained in the D-ribose series; the paper immediately following will describe work in the L-ribose and L-arabinose series.

When β-D-ribopyranose tetrabenzoate[3] (I) was treated with liquid hydrogen fluoride at room temperature for ten minutes, two crystalline tri-*O*-benzoylpentosyl fluorides were obtained, a levorotatory isomer in 59% yield and a dextrorotatory isomer in 12% yield. On fusion with a mixture of benzoic acid and anhydrous calcium benzoate both isomers gave β-D-ribopyranose tetrabenzoate (I); with barium methoxide they were both converted to methyl β-D-ribopyranoside (V). These facts demonstrate that the two fluorides are D-ribopyranose derivatives. That they are anomers (II and III) is evidenced through comparison (Tables I and II) of their rotations with those of the corresponding 2,3,4-tri-*O*-benzoyl-α-D-ribopyranosyl and 2,3,4-tri-*O*-benzoyl-β-D-ribopyranosyl halides reported in earlier work.[4] As expected[5–8] the α-anomer is more weakly dextrorotatory than the corresponding α-chloride while the β-anomer is more weakly levorotatory than the corresponding β-chloride. In the transformations mentioned above the α-(*cis*)-fluoride reacts with simple inversion while the displacement of the halogen in the β-(*trans*)-fluoride involves neighboring group participation, the products in both cases having the substituents at C_1 and C_2 in a *trans* relationship.

[1] Chemical Foundation Fellow 1958–1960.

[2] For reviews and specific references see: H. G. Fletcher, Jr., *Record Chem. Progr. Kresge-Hooker Sci. Lib.*, **19**, 147 (1958), and L. J. Haynes and F. J. Newth, *Advances in Carbohydrate Chem.*, **10**, 207 (1955).

[3] R. Jeanloz, H. G. Fletcher, Jr., and C. S. Hudson, THIS JOURNAL, **70**, 4052 (1948).

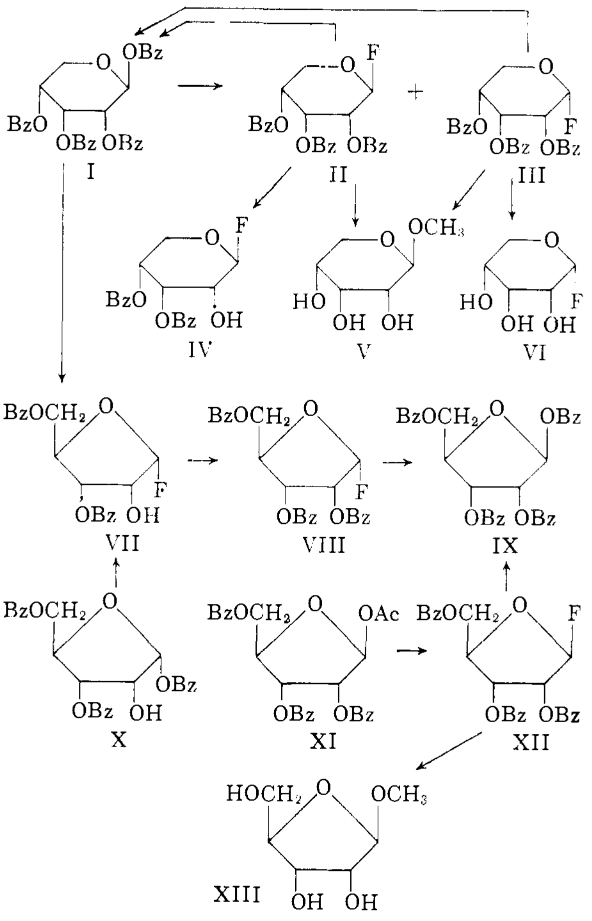
[4] R. K. Ness, H. G. Fletcher, Jr., and C. S. Hudson, *ibid.*, **73**, 959 (1951).

[5] D. H. Brauns, *ibid.*, **45**, 2381 (1923).

[6] D. H. Brauns, *ibid.*, **46**, 1484 (1924).

[7] C. S. Hudson, *ibid.*, **46**, 462 (1924).

[8] A. K. Bose and B. G. Chatterjee, *J. Org. Chem.*, **23**, 1425 (1958).



In passing, it may be noted that the proportions of the two anomers formed from β-D-ribopyranose tetrabenzoate is not markedly different from that found[4] in the preparation of the corresponding bromides and chlorides.

TABLE I

BENZOYLATED α-D-RIBOPYRANOSYL HALIDES

	M.p., °C.	$[\alpha]^{20}$D CHCl$_3$[a]	$[M]^{20}$D	Differences
2,3,4-Tri-*O*-benzoyl-α-D-ribopyranosyl bromide[b]	164–166	+78°	+41,000	
2,3,4-Tri-*O*-benzoyl-α-D-ribopyranosyl chloride[b]	203–204	+60	+28,900	12,100
2,3,4-Tri-*O*-benzoyl-α-D-ribopyranosyl fluoride (III)	205–206	+38.3	+17,800	11,100

[a] The rotations of the bromide and chloride were measured in absolute chloroform (ref. 4), that of the more stable fluoride in U.S.P. chloroform. [b] Ref. 4.

Compared with ordinary benzoylated aldopyranosyl chlorides the two new anomeric fluorides are relatively stable substances. They failed to react with aqueous dioxane or with a suspension of calcium benzoate in boiling benzene or acetonitrile. However, as with other anomeric pairs the *cis*-halide III was more stable than the *trans*-halide II. The former anomer, for instance, gave a lower yield of β-D-ribopyranose tetrabenzoate than did the latter when fused with benzoic acid–calcium benzoate as mentioned above. Moreover, attempts to debenzoylate the more reactive β-anomer resulted in loss of fluorine while the α-anomer afforded α-D-ribopyranosyl fluoride (VI) in crystalline form.

TABLE II

BENZOYLATED β-D-RIBOPYRANOSYL HALIDES

	M.p., °C.	$[\alpha]^{20}$D CHCl$_3$[a]	$[M]^{20}$D	Differences
2,3,4-Tri-*O*-benzoyl-β-D-ribopyranosyl bromide[b]	152–154	−202°	−106,000	
2,3,4-Tri-*O*-benzoyl-β-D-ribopyranosyl chloride[b]	162–163	−147	−70,700	35,300
2,3,4-Tri-*O*-benzoyl-β-D-ribopyranosyl fluoride (II)	139–140	−51.5	−23,900	46,800

[a] The rotations of the bromide and chloride were measured in absolute chloroform (ref. 4), that of the more stable fluoride in U.S.P. chloroform. [b] Ref. 4.

While the action of liquid hydrogen fluoride on β-D-ribopyranose tetrabenzoate (I) at room temperature for ten minutes gave the normal 2,3,4-tri-*O*-benzoyl-D-ribopyranosyl fluorides (II and III), prolongation of the reaction to twenty-four hours led to the isolation in small yield of two other new substances. The first of these, which could also be made through the action of hydrogen fluoride on 2,3,4-tri-*O*-benzoyl-β-D-ribopyranosyl fluoride (II), is shown in the succeeding paper to be, most probably, 3,4-di-*O*-benzoyl-β-D-ribopyranosyl fluoride (IV). The second, obtained from the mother liquors from the first on long standing, was isomeric with it, being a di-*O*-benzoylpentosyl fluoride. The same substance was obtained by treatment of 1,3,5-tri-*O*-benzoyl-α-D-ribofuranose (X)[9,10] with hydrogen fluoride. Benzoylation with benzoyl chloride in 2,4,6-trimethylpyridine gave a crystalline, dextrorotatory tri-*O*-benzoylpentosyl fluoride which, on fusion with benzoic acid–calcium benzoate, afforded the known β-D-ribofuranose tetrabenzoate[11] (IX). Assuming no acyl migration in the conversion of X to VII, it appears, then, that the new substance is a 3,5-di-*O*-benzoyl-D-ribofuranosyl fluoride; the dextrorotation of the halide, $[\alpha]^{20}$D +52.8°, suggests that it may be the α-anomer VII. Comparison of its molecular rotation with those of the previously prepared and much less stable bromide[10] and chloride[9] (Table III) indicates that the fluoride and bromide may be α-anomers while the chloride may be a β-anomer.

From the well-known 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose (XI)[11,12] the action of hydrogen fluoride in ether solution[13] gave a second 2,3,5-tri-*O*-benzoyl-D-ribofuranosyl fluoride. Fu-

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[9] R. K. Ness and H. G. Fletcher, Jr., THIS JOURNAL, **78**, 4710 (1956).

[10] R. K. Ness and H. G. Fletcher, Jr., *ibid.*, **76**, 1663 (1954).

[11] R. K. Ness, H. W. Diehl and H. G. Fletcher, Jr., *ibid.*, **76**, 763 (1954).

[12] F. Weygand and F. Wirth, *Chem. Ber.*, **85**, 1000 (1952).

[13] It may be noted that hydrogen fluoride in ether solution, a much milder fluorinating agent than hydrogen fluoride alone, was without apparent effect on 1,3,5-tri-*O*-benzoyl-α-D-ribofuranose.

TABLE III

3,5-DI-*O*-BENZOYL-D-RIBOFURANOSYL HALIDES

	M.p., °C., dec.	$[\alpha]^{20}D$	$[M]^{20}D$
Bromide[a]	104–105	+96°[b]	40,000
Chloride[c]	123–124	+ 1.2[d]	450
Fluoride (VII)	132–133	+52.8 ($CHCl_3$)	19,000

[a] Ref. 10. [b] Measured in absolute chloroform after 3 minutes; the substance mutarotates in this solvent. [c] Ref. 9. [d] Calculated from the observed rotation in methylene chloride after 5 minutes; *cf*. ref. 9.

sion of this substance with benzoic acid–calcium benzoate afforded β-D-ribofuranose tetrabenzoate (IX); treatment with sodium methoxide gave methyl β-D-ribofuranoside (XIII).

The melting points and rotations of the two 2,3,5-tri-*O*-benzoyl-D-ribofuranosyl fluorides may be compared in Table IV. While the difference between the rotations of a given anomeric pair of glycosyl fluorides must, of course, be less than that between pairs of other halides, the difference found here (Table IV) is surprisingly small compared with the differences between the corresponding D-ribopyranosyl fluorides or the 2,3,4,6-tetra-*O*-acetyl-D-glucopyranosyl fluorides. As far as we know, no other anomeric pair of glycofuranosyl fluorides is available for comparison. Several possible reasons may be suggested to explain this small rotatory difference. In the first place, the relative contribution of C_4 to the rotations of the pyranosyl fluorides II and III may be smaller than in the furanosyl fluorides VIII and XII. In the second place, the rotatory difference between the pyranosyl fluorides may be due in some part to conformational differences, a factor which probably plays a much smaller role in the two furanosyl fluorides. It is hoped that data from another sugar series may be obtained to throw some light on this question. In any case, in the absence of other evidence, one may tentatively assign the α-configuration VIII to that isomer derived *via* VII from β-D-ribofuranose tetrabenzoate and the β-configuration (XII) to that derived from 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose.

TABLE IV

SOME ANOMERIC PAIRS OF ACYLATED GLYCOSYL FLUORIDES

Fluoride	M.p., °C.	$[\alpha]^{20}D$ $CHCl_3$	$[M]^{20}D$	Difference
2,3,5-Tri-*O*-benzoyl-α-D-ribofuranosyl	82–83	+123°	+57,100	8,500
2,3,5-Tri-*O*-benzoyl-β-D-ribofuranosyl	82–83	+105	+48,600	
2,3,4-Tri-*O*-benzoyl-α-D-ribopyranosyl	205–206	+ 38.3	+17,800	41,700
2,3,4-Tri-*O*-benzoyl-β-D-ribopyranosyl	139–140	− 51.5	−23,900	
2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl[a]	108	+ 90.1	+31,600	24,210
2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl[b]	98	+ 21.9[c]	+ 7,390	

[a] D. H. Brauns, THIS JOURNAL, **45**, 833 (1923). [b] B. Helferich and R. Gootz, *Ber*., **62**, 2505 (1929). [c] 18°.

The mechanism of the conversion of β-D-ribopyranose tetrabenzoate to 3,5-di-*O*-benzoyl-α-D-ribofuranosyl fluoride would seem to involve at the least a series of steps; speculation on this point seems pointless in our present state of knowledge. Suffice it to say that the yield of the product and the rotation of the starting material appear at this time to rule out the possibility that VII arose from any known D-ribofuranose contaminant in I.

Experimental[14]

The Anomeric 2,3,4-Tri-*O*-benzoyl-D-ribopyranosyl Fluorides (II and III).—β-D-Ribopyranose tetrabenzoate[3] (20.0 g.) was dissolved in 20 ml. of liquid hydrogen fluoride in a polyethylene container and the solution kept at room temperature for 10 min. A stream of air was then introduced, the major part of the hydrogen fluoride being removed in 10 min. The residue, dissolved in 150 ml. of methylene chloride, was washed with saturated aqueous sodium bicarbonate (3 × 200 ml.) and then with water (3 × 200 ml.). Moisture was removed with sodium sulfate, the solution filtered through a layer of decolorizing carbon and then concentrated *in vacuo* at 40° (bath) to a clear colorless sirup. The product was extracted with several batches of boiling ether (total 500 ml.) and during this treatment crystallized in part, the insoluble, needle-shaped crystals of the α-anomer (3.6 g.) being filtered off. The ether extract, concentrated to a volume of 250 ml. and kept at room temperature, deposited 4.90 g. of the β-anomer as prismatic crystals. Cooling the ethereal mother liquor overnight at 0° gave a mixture of needles and prisms; the former were separated by swirling the solution and then decanting rapidly. The mother liquor was further concentrated and another crop of needles separated in similar fashion.

The combined crops of the α-anomer (5.0 g.) were recrystallized from ethyl acetate (35 ml.) giving 1.74 g. of product melting at 202–204°. On concentration, the mother liquor from this recrystallization afforded 0.8 g. of the β-anomer and 1.17 g. of the α-anomer. Recrystallization of the latter gave 0.23 g. of nearly pure material (m.p. 201–203°); total yield of α-fluoride 12%. The combined crops of the nearly pure α-anomer were recrystallized twice from ethyl acetate–pentane (1:1) giving pure 2,3,4-tri-*O*-benzoyl-α-D-ribopyranosyl fluoride melting at 205–206° and rotating in chloroform (*c* 0.56) $[\alpha]^{20}D$ +38.3°.[15]

Anal. Calcd. for $C_{26}H_{21}O_7F$: C, 67.24; H, 4.56. Found: C, 67.03; H, 4.68.

The combined crops of prismatic crystals (11.5 g.) were recrystallized from ether (350 ml.) giving 7.87 g. of the β-anomer melting at 138–139°. A second crop (0.82 g.) of equal purity was obtained: total yield 9.69 g. (59%). Two further recrystallizations from ether of a sample raised its melting point to 139–140°. The pure β-anomer rotated in chloroform $[\alpha]^{20}D$ −51.5° (*c* 0.84).

Anal. Calcd. for $C_{26}H_{21}O_7F$: C, 67.24; H, 4.56. Found: C, 67.49; H, 4.81.

β-D-Ribopyranose Tetrabenzoate (I) from 2,3,4-Tri-*O*-benzoyl-β-D-ribopyranosyl Fluoride (II).—A mixture of 2,3,4-tri-*O*-benzoyl-β-D-ribopyranosyl fluoride (200 mg.), 5.0 g. of benzoic acid and 0.5 g. of anhydrous calcium benzoate was heated to 145–150° (bath) and stirred at this temperature for 2 hr. The somewhat darkened reaction mixture was then cooled, dissolved in methylene chloride and washed, first with saturated aqueous sodium bicarbonate, and then with water. Moisture was removed with sodium sulfate, the solution filtered through a layer of decolorizing carbon and the filtrate concentrated *in vacuo*. From a mixture of ether (3–4 ml.) and pentane (10 ml.) the residue gave 160 mg. (66%) of β-D-ribopyranose tetrabenzoate, m.p. 129–131° and $[\alpha]^{20}D$ −101.5° ($CHCl_3$, *c* 0.34).

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(14) Melting points are corrected.

(15) This substance, like all other fluorine-containing derivatives described here, gave with concentrated sulfuric acid a positive test for fluorine; see B. Fetkenheuer, *Wiss. Veröffentl. Siemens-Konzern*, **1**, 177 (1922); *C. A.*, **17**, 1398 (1923).

Under the same conditions, 200 mg. of the α-fluoride III gave only about 1 mg. of β-D-ribopyranose tetrabenzoate. Increasing the reaction time to 6 hr. and use of a larger excess of calcium benzoate failed to increase this yield.

Methyl β-D-Ribopyranoside (V). (a) From 2,3,4-Tri-*O*-benzoyl-β-D-ribopyranosyl Fluoride (II).—2,3,4-Tri-*O*-benzoyl-β-D-ribopyranosyl fluoride (500 mg.) was dissolved in a mixture of methylene chloride (5 ml.) and anhydrous methanol (10 ml.) and 1.5 *N* barium methoxide added dropwise. The solution became neutral within a few minutes after the addition of each drop of the alkaline solution, indicating solvolysis of the fluoride. When a total of 15 drops of the barium methoxide solution had been added the solution was left overnight at room temperature. It was then neutralized with carbon dioxide, concentrated *in vacuo* and the residue freed of methyl benzoate by extraction with pentane. The remainder was extracted with hot ethyl acetate (3 × 10 ml.); concentration of the extract afforded a sirup which crystallized on scratching. Recrystallization from a mixture of ethyl acetate (4 ml.) and pentane (10 ml.) afforded 113 mg. (69%) of nearly pure methyl β-D-ribopyranoside melting at 84–85°. A further recrystallization from the same mixture of solvents gave the pure glycoside melting at 84–85° and rotating $[\alpha]^{20}_{\text{D}}$ −105° in water (*c* 0.53). Jackson and Hudson[16] reported methyl β-D-ribopyranoside to melt at 83° (uncor.) and rotate $[\alpha]^{20}_{\text{D}}$ −105.2° (water, *c* 0.47).

(b) From 2,3,4-Tri-*O*-benzoyl-α-D-ribopyranosyl Fluoride (III).—2,3,4-Tri-*O*-benzoyl-α-D-ribopyranosyl fluoride (300 mg.) was suspended in a mixture of 10 ml. of absolute methanol and 0.74 ml. of 1.76 *N* sodium methoxide. After 2 hr. at room temperature the solid had dissolved and the solution was boiled under reflux for 1 hr., some darkening taking place. The alkali was neutralized with carbon dioxide and the solution concentrated *in vacuo* to give a solid mass which was extracted with pentane to remove methyl benzoate. The remainder was then extracted with hot ethyl acetate (3 × 5 ml.). Evaporation of the extracts gave a brown sirup which crystallized on seeding. Recrystallization from ether–pentane afforded 40 mg. (38%) of crystals melting at 79–81° either alone or in admixture with authentic methyl β-D-ribopyranoside.

α-D-Ribopyranosyl Fluoride (VI) from 2,3,4-Tri-*O*-benzoyl-α-D-ribopyranosyl Fluoride (III).—To 460 mg. of 2,3,4-tri-*O*-benzoyl-α-D-ribopyranosyl fluoride, suspended in a mixture of 10 ml. of anhydrous methanol and 5 ml. of methylene chloride, was added 0.08 ml. of 1.74 *N* sodium methoxide. After standing at room temperature overnight the solid had dissolved and the solution was still alkaline. The mixture was then neutralized with carbon dioxide, concentrated *in vacuo* and the residue extracted with pentane (3 × 15 ml.) to remove methyl benzoate. The pentane-insoluble material was extracted with hot ethyl acetate (3 × 15 ml.); concentration of this extract *in vacuo* afforded a crystalline residue. Recrystallization from methanol (5 ml.)–ether (5 ml.)–pentane (30 ml.) yielded 87 mg. (58%) of α-D-ribopyranosyl fluoride as colorless blades melting at 100–150° dec. and rotating $[\alpha]^{20}_{\text{D}}$ +90.5° in methanol (*c* 0.32). Further recrystallization failed to change this rotation.

Anal. Calcd. for $C_5H_9O_4F$: C, 39.48; H, 5.96. Found: C, 39.49; H, 6.05.

On standing in a glass container for about a week at room temperature the α-D-ribopyranosyl fluoride decomposed to a sirup having the typical sharp odor of hydrogen fluoride. Paper chromatography showed the product to be mainly ribose.

3,4-Di-*O*-benzoyl-β-D-ribopyranosyl Fluoride (IV) from β-D-Ribopyranose Tetrabenzoate (I) and from 2,3,4-Tri-*O*-benzoyl-β-D-ribopyranosyl Fluoride (II).—Ten grams of β-D-ribopyranose tetrabenzoate was dissolved in 28 ml. of anhydrous liquid hydrogen fluoride and the solution left at room temperature for 24 hr. The hydrogen fluoride was then removed with a stream of air and the residue dissolved in methylene chloride. The solution was washed with saturated aqueous sodium bicarbonate, then with water, dried over sodium sulfate and concentrated *in vacuo* to yield 6.35 g. of a colorless sirup which was dissolved in *ca.* 15 ml. of ether and cooled to −5°. Sufficient pentane was added to produce a slight turbidity; on standing for 2 weeks at −6° the solution deposited material which, recrystallized from ether (*ca.* 3 ml.), was obtained as colorless prisms (35 mg.) melting at 144–145°. A second recrystallization from ether gave 25 mg. (0.4%) of pure product melting at 150–151° and rotating $[\alpha]^{20}_{\text{D}}$ −50.6° in chloroform (*c* 0.074).

Anal. Calcd. for $C_{19}H_{17}O_6F$: C, 63.33; H, 4.76. Found: C, 63.14; H, 4.99.

A similar treatment of 2,3,4-tri-*O*-benzoyl-β-D-ribopyranosyl fluoride with liquid hydrogen fluoride at room temperature for 6 hr. afforded the same 3,5-di-*O*-benzoyl-β-D-ribopyranosyl fluoride in 4.7% yield, the melting point and mixed melting point of the preparations from the two sources being identical.

3,5-Di-*O*-benzoyl-α-D-ribofuranosyl Fluoride (VII) from β-D-Ribopyranose Tetrabenzoate (I).—The mother liquor of the preparation of 3,4-di-*O*-benzoyl-β-D-ribopyranosyl fluoride from β-D-ribopyranose tetrabenzoate was kept at −5° for about 2 months to give a crystalline deposit which was recrystallized from a mixture of 5 ml. of ether and 5 ml. of pentane to yield 200 mg. (3.1%) of 3,5-di-*O*-benzoyl-α-D-ribofuranosyl fluoride as prismatic needles melting at 132–133° (gas evoln.). A further recrystallization failed to change this melting point and afforded material showing $[\alpha]^{20}_{\text{D}}$ +52.8° in chloroform (*c* 0.44).

Anal. Calcd. for $C_{19}H_{17}O_6F$: C, 63.33; H, 4.76. Found: C, 62.97; H, 4.85.

3,5-Di-*O*-Benzoyl-α-D-ribofuranosyl Fluoride (VII) from 1,3,5-Tri-*O*-benzoyl-α-D-Ribofuranose (X).—One gram of 1,3,5-tri-*O*-benzoyl-α-D-ribofuranose[9,10] was dissolved in 5 ml. of liquid hydrogen fluoride and the solution kept at room temperature for 30 min. The hydrogen fluoride was then blown off with a stream of air and the residue dissolved in methylene chloride. After washing with aqueous sodium bicarbonate and then with water the solution was dried with sodium sulfate, filtered through a layer of decolorizing carbon and evaporated to a sirup (0.71 g.). From ether–pentane the product crystallized on standing at 5° for 24 hr. Recrystallized from a mixture of ether (*ca.* 5 ml.), benzene (5 ml.) and a little pentane, the product (0.13 g., 17%) was obtained as prismatic needles melting at 130–131° and rotating $[\alpha]^{20}_{\text{D}}$ +51.3° in chloroform (*c* 0.50). A second recrystallization failed to change the melting point, giving material of $[\alpha]^{20}_{\text{D}}$ +51.7° ($CHCl_3$, *c* 0.34). A mixed melting point with material prepared from β-D-ribopyranose tetrabenzoate was undepressed; the infrared spectra of the samples from the two sources were identical.

Evaporation of the mother liquor from the above preparation gave a sirup which could not be induced to crystallize. In attempts to improve the yield in the above reaction it was repeated at −10°, at room temperature for 5 hr. and in methylene chloride. No improvement was noted. Hydrogen fluoride in ether failed to change the starting material.

2,3,5-Tri-*O*-benzoyl-α-D-ribofuranosyl Fluoride (VIII) from 3,5-Di-*O*-benzoyl-α-D-ribofuranosyl Fluoride (VII). 3,5-Di-*O*-benzoyl-α-D-ribofuranosyl fluoride (70 mg.) was added to an ice-cold mixture of 0.045 ml. of benzoyl chloride and 1 ml. of anhydrous 2,4,6-trimethylpyridine and the mixture kept overnight at room temperature. Two drops of water was then added and, after a lapse of 15 min., the mixture was dissolved in methylene chloride. The solution was washed successively with cold 3 *N* sulfuric acid, cold, saturated, aqueous sodium bicarbonate and water. Moisture was removed with sodium sulfate, the solution filtered through decolorizing carbon and then concentrated *in vacuo* to a sirup. Dissolved in a little ether–pentane and kept at −5° for 2 days, this material deposited 61 mg. (68%) of crystals melting at 79–82° and showing $[\alpha]^{20}_{\text{D}}$ +122° ($CHCl_3$, *c* 0.26). Two recrystallizations from ether–pentane raised the melting point to 82–83° and the rotation to $[\alpha]^{20}_{\text{D}}$ +123° ($CHCl_3$, *c* 0.23).

Anal. Calcd. for $C_{26}H_{21}O_7F$: C, 67.24; H, 4.56. Found: C, 67.38; H, 4.68.

β-D-Ribofuranose Tetrabenzoate (IX) from 2,3,5-Tri-*O*-benzoyl-α-D-ribofuranosyl Fluoride (VIII).—2,3,5-Tri-*O*-benzoyl-α-D-ribofuranosyl fluoride (20 mg.), mixed with 200 mg. of calcium benzoate and 3.0 g. of benzoic acid was heated at 150° (bath) and stirred for 2 hr., slight darkening of the mixture taking place. The cooled mixture was then dissolved in methylene chloride and the solution washed with aqueous sodium bicarbonate. Moisture was removed with sodium sulfate, the solution filtered through decolorizing carbon and concentrated *in vacuo* to a sirup which crystallized on scratching. Recrystallization from ether–pentane gave 13 mg. (53%) of β-D-ribofuranose tetrabenzoate melting at 118–

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[16] E. L. Jackson and C. S. Hudson, THIS JOURNAL, **63**, 1229 (1941).

120°. After one further recrystallization the product melted at 120–121° either alone or in admixture with authentic β-D-ribofuranose tetrabenzoate.[11]

2,3,5-Tri-*O*-benzoyl-β-D-ribofuranosyl Fluoride (XII) from 1-*O*-Acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose (XI).—1-*O*-Acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose[10,12] (2.0 g.) was added to 40 ml. of 6 *N* hydrogen fluoride in ether. In the course of 30 min. at room temperature the ester dissolved; after 4 hr. the solvent and hydrogen fluoride was removed with a stream of air and the residue dissolved in methylene chloride. The solution was washed successively with cold aqueous sodium bicarbonate and water, dried with sodium sulfate, filtered through decolorizing carbon and evaporated *in vacuo* to give 1.92 g. of sirup. This material was dissolved in a mixture of 15 ml. of ether and 15 ml. of pentane. When cooled to +5° it gave 1.23 g. (67%) of prismatic needles melting at 81–83° and rotating $[\alpha]^{20}_D$ +102° ($CHCl_3$, *c* 0.78). Two additional recrystallizations from ether–pentane afforded pure 2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl fluoride melting at 82–83° and rotating $[\alpha]^{20}_D$ +105° ($CHCl_3$, *c* 0.61).[17]

Anal. Calcd. for $C_{26}H_{21}O_7F$: C, 67.24; H, 4.56. Found: C, 67.34; H, 4.78.

When the above reaction was attempted using liquid hydrogen fluoride at room temperature for varying periods of time, no crystalline product could be isolated.

β-D-Ribofuranose Tetrabenzoate (IX) from 2,3,5-Tri-*O*-benzoyl-β-D-ribofuranosyl Fluoride (XII).—A mixture of 100 mg. of 2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl fluoride, 250 mg. of anhydrous calcium benzoate and 3.0 g. of benzoic acid was heated to 150° (bath) and stirred at that temperature for 1 hr. The product was isolated as described earlier for the preparation from the α-fluoride, 60 mg. (49%) of crude β-D-ribofuranose tetrabenzoate being obtained. Recrystallization gave pure β-D-ribofuranose tetrabenzoate melting at 120–121° either alone or in admixture with authentic material.

When 2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl fluoride, dissolved in benzene, was boiled with calcium benzoate for 24 hr. a yield of 38% of β-D-ribofuranose tetrabenzoate was obtained. In boiling acetonitrile or in benzene at room temperature no reaction was observed.

Methyl β-D-Ribofuranoside (XIII) from 2,3,5-Tri-*O*-benzoyl-β-D-ribofuranosyl Fluoride (XII).—2,3,5-Tri-*O*-benzoyl-β-D-ribofuranosyl fluoride (400 mg.) was dissolved in 10 ml. of methanol and 1.0 ml. of 1.74 *N* sodium methoxide added to the solution which was then boiled under reflux for 1.5 hr. The cooled solution was neutralized with carbon dioxide, evaporated to dryness and the residue extracted with pentane (3 × 15 ml.) to remove methyl benzoate. The remainder was then extracted with hot ethyl acetate (4 × 5 ml.) and the combined extracts concentrated to a sirup which crystallized when seeded with methyl β-D-ribofuranoside. Recrystallization from a mixture of ether (10 ml.) and pentane (5 ml.) gave the pure product (60 mg., 42%) which rotated $[\alpha]^{20}_D$ −48.5° (H_2O, *c* 0.41) and melted at 77–78° either alone or in admixture with authentic methyl β-D-ribofuranoside.

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[17] Except for their rotations, the two anomeric 2,3,5-tri-*O*-benzoyl-D-ribofuranosyl fluorides are remarkably alike in their physical properties, the melting points, X-ray diffraction patterns and infrared spectra being essentially identical. A mixture of the two was found to melt at 80–82° and the proton magnetic resonance spectra of the two differed.

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2,3,4-Tri-*O*-benzoyl-β-L-arabinopyranosyl Fluoride and a Transformation from the L-Arabinopyranose to the L-Ribopyranose Series Induced by Hydrogen Fluoride

BY CHRISTIAN PEDERSEN[1] AND HEWITT G. FLETCHER, JR.

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Brief treatment of β-L-arabinopyranose tetrabenzoate with anhydrous hydrogen fluoride affords a crystalline 2,3,4-tri-*O*-benzoyl-L-arabinopyranosyl fluoride which is probably the β-L-anomer. More prolonged treatment of either β-L-arabinopyranose tetrabenzoate or of the above-mentioned fluoride leads to the formation of 3,4-di-*O*-benzoyl-β-L-ribopyranosyl fluoride, the enantiomorph of a substance prepared earlier through the action of hydrogen fluoride on β-D-ribopyranose tetrabenzoate and on 2,3,4-tri-*O*-benzoyl-β-D-ribopyranosyl fluoride. 3,4-Di-*O*-benzoyl-β-L-ribopyranosyl fluoride was characterized through conversion to 2,3,4-tri-*O*-benzoyl-β-L-ribopyranosyl fluoride, methyl β-L-ribopyranoside and 3,4-di-*O*-benzoyl-2-*O*-methylsulfonyl-β-L-ribopyranosyl fluoride.

By way of extension of the work on benzoylated glycosyl fluorides described in the preceding paper,[2] we have now turned our attention to the L-arabinopyranose series.

When β-L-arabinopyranose tetrabenzoate (I)[3] is treated for a brief period (thirty minutes) at −15° with liquid hydrogen fluoride there is obtained in 38% yield a crystalline tri-*O*-benzoylpentosyl fluoride. Fusion of this halide with a mixture of benzoic acid and calcium benzoate converts it in good yield to α-L-arabinopyranose tetrabenzoate (III),[3] the *trans* - ester which would be expected from either of the anomeric tri-*O*-benzoyl-L-arabinopyranosyl fluorides. Attempts to remove the benzoyl groups without loss of the fluorine were unsuccessful.

The configuration at C_1 of the new crystalline fluoride cannot be stated with certainty. However, its molecular rotation, +48,800, is not very different from that of 2,3,4-tri-O-acetyl-β-L-arabinopyranosyl fluoride, +38,500,[4] and it may provisionally be assigned the β-L-configuration (II) normally encountered with such compounds in the arabinose series.

When β-L-arabinopyranose tetrabenzoate (I) was treated with liquid hydrogen fluoride at room temperature for six hours the fluoride mentioned above was not isolated. In its place was obtained in 36% yield a crystalline substance with the analysis of a di-*O*-benzoylpentosyl fluoride. The same compound was obtained in 44% yield by a

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[1] Chemical Foundation Fellow 1958–1960.

[2] C. Pedersen and H. G. Fletcher, Jr., THIS JOURNAL, **82**, 941 (1960).

[3] H. G. Fletcher, Jr., and C. S. Hudson, *ibid.*, **69**, 1145 (1947).

[4] D. H. Brauns, *ibid.*, **46**, 1484 (1924).