FLUORINATED SULPHONIC ESTERS OF SUGARS: THEIR SYNTHESIS AND REACTIONS WITH PYRIDINE*

LAURANCE D. HALL AND DIANE C. MILLER

Department of Chemistry, The University of British Columbia, Vancouver, British Columbia, V6T 1W5 (Canada)

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ABSTRACT

1,2:5,6-Di-O-isopropylidene- α -D-allofuranose (1), 1,2:5,6-di-O-isopropylidene- α -D-glucofuranose (2), and 1,2:3,4-di-O-isopropylidene- α -D-galactopyranose (3) have been separately treated in pyridine solution with trifluoromethanesulphonic anhydride, 2,2,2-trifluoroethanesulphonyl chloride, and pentafluorobenzenesulphonyl chloride. Both 1 and 2 afforded the anticipated sulphonic esters. Although 3 also gave the 2,2,2-trifluoroethanesulphonic and pentafluorobenzenesulphonic esters, the reaction with trifluoromethanesulphonic anhydride yielded 6-deoxy-1,2:3,4-di-O-isopropylidene-6-pyridino- α -D-galactopyranose trifluoromethanesulphonate.

INTRODUCTION

Sulphonic esters of carbohydrate derivatives $provide^{3-5}$ a simple method for activating hydroxyl groups for a wide diversity of reactions. The vast majority of studies have involved either methanesulphonates or toluene-*p*-sulphonates, although it was noted by Tipson⁶, more than twenty years ago, that the reactivity, towards a nucleophile, of a sugar benzenesulphonate should be enhanced by attachment of an electron-withdrawing substituent to the aromatic moiety. Few such studies have been reported^{7,8}. The well-known high reactivity of fluorinated alkyl- and aryl-sulphonates prompted a study of selected carbohydrate derivatives.

Three classes of fluorinated sulphonates have been examined, namely trifluoromethanesulphonates (triflates, CF_3SO_3R), 2,2,2-trifluoroethanesulphonates (tresylates, $CF_3CH_2SO_3R$), and pentafluorobenzenesulphonates (pentaflates, $C_6F_5SO_3R$) derived from 1,2:5,6-di-O-isopropylidene- α -D-allofuranose¹⁰ (1), 1,2:5,6di-O-isopropylidene- α -D-glucofuranose¹¹ (2), and 1,2:3,4-di-O-isopropylidene- α -Dgalactopyranose¹² (3).

^{*}Studies of Specifically Fluorinated Carbohydrate Derivatives: Part XVII. For Part XVI, see Ref. 1. For a preliminary communication, see Ref. 2. A full account of this study was given at the 58th Conference of the Chemical Institute of Canada, Toronto, May 25–28, 1975; Abstract No. 302.

RESULTS AND DISCUSSION

Although the fluorinated sulphonyl reagents are not difficult to handle, the yields of products were significantly improved by working under anhydrous conditions and in an atmosphere of dry nitrogen.

Reaction of 1 and 2 with trifluoromethanesulphonic (triflic) anhydride gave



high yields of the corresponding trifluoromethanesulphonates 4 and 5 which were stable, crystalline substances. The stability of solutions for n.m.r. studies was enhanced by the addition of a little anhydrous sodium carbonate. Reaction of 3 under similar conditions gave the pyridinium salt 7 in high yield rather than the desired triflate 6 (see below).

For reactions with 2,2,2-trifluoroethanesulphonyl chloride, 1, 2, and 3 were rapidly converted into the respective, crystalline, tresyl derivatives 8, 9, and 10.

The conversion of 1, 2, and 3 into the corresponding pentaflates 11, 12, and 13 by reaction with pentafluorobenzenesulphonyl chloride was less satisfactory. Yields were <40% and, for the conversion $2\rightarrow 12$, an analytically pure sample could not be obtained. Our experience suggests that pentaflates may be substantially less-convenient derivatives than the triflates or tresylates. Also trifluoromethanesulphonyl chloride does not give satisfactory yields of sugar triflates.

The conversion of 3 into the pyridinium salt 7 after ~ 1.5 h at -15° indicates the enhanced reactivity of these fluorinated sulphonate derivatives. When the corresponding tosyl derivative 16 was heated with pyridine under reflux for ~ 24 h, the pyridinium toluene-*p*-sulphonate 18 was obtained in only $\sim 30\%$ yield.

More-vigorous reaction conditions (pyridine, reflux, 25 h) were required to effect the conversions $1\rightarrow 17$ and $4\rightarrow 17$ in 70% yield. Under similar conditions, the tosyl derivative 14 did not react. As would be anticipated, the above reactions were

7 447 5.54 5.22 5.43 5.60 4.75 5.08 0.74 1.68 1.18 7 447 5.54 5.22 5.43 5.60 4.75 5.08 0.74 1.68 1.18 9 $J_{1,2}$ 5.32 5.31 5.43 5.60 4.75 5.08 0.74 1.68 1.18 18 4.52 5.59 5.31 5.43 5.60 4.75 $J_{6,6}$ 13.6 $J_{m,p}$ 7.8 $J_{0,p}$ 1.24 18 4.52 5.39 5.31 5.48 5.60 4.58 5.19 0.59 1.75 1.24 20 4.48 5.54 5.35 $J_{5,6}$ $J_{5,6}$ $J_{6,6}$ $J_{m,p}$ 7.8 $J_{0,p}$ 0.59 20 4.48 5.32 $J_{5,6}$ $J_{5,6}$ $J_{6,6}$ $J_{0,m}$ 6.6 $J_{m,p}$ 7.8 $J_{0,p}$ 21 $J_{1,2}$ $J_{2,3}$ $J_{2,6}$ $J_{5,6}$ $J_{6,6}$ $J_{6,6}$ $J_{0,m}$ $J_{0,p}$ $J_{0,p}$	Compound	H-I	H-2	Н-3	H-4	H-5	9-H	9-H	Pyridine			Others
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18 4.52 5.59 5.31 5.48 5.60 4.58 5.19 0.59 1.75 1.24 $J_{1,2}$ $J_{2,3}$ $Z_{2,4}$ $J_{5,6}$ $Z_{4,6}$ $J_{5,6}$ $J_{5,6}$ $Z_{5,6}$ $J_{5,6}$ $Z_{5,6}$ $Z_{1,1}$ 0.54 1.66 $J_{m,p}$ Z_{0} $J_{0,p}$ 0.5 20 4.48 5.54 5.33 5.56 4.52 5.11 0.54 1.66 1.16 $J_{0,p}$ $U_{0,p}$ Z_{0} 20 4.48 5.54 5.33 5.56 4.52 5.11 0.54 1.60 $J_{m,p}$ Z_{0} 21 3.41 4.44 4.37 5.37 6.53 6.04 5.90 0.94 1.61 1.09 $1_{1,2}$ $3.2_{1,2}$ 0 $J_{3,6}$ 4.5 $J_{5,6}$ 4.56 $J_{6,6'}$ 8.5 $J_{m,p}$ 7.6 $J_{0,p}$ 1.09 21 3.41 4.33 5.33 6.54 $J_{5,6}$ $J_{6,6'}$ 8.5 $J_{0,m}$	2	4,47 J _{1,2} 5	5.54 J _{2,3} 2.4	5.22 J _{3,4} 7.8	5,43 J _{4,5} 1.6	5.60 J _{5,6} 3	4.75 J _{5,6} , 8.8	5.08 J _{6,6} , 13.6	0.74 J _{orm} 6.6	1.68 J _{m,p} 7.8	1.18 J _{0,P} 1.2	Ţ
20 4.48 5.54 5.28 5.35 5.56 4.52 5.11 0.54 1.66 1.16 $J_{1,2}$ 4.7 $J_{2,3}$ 2.3 $J_{3,4}$ 8.0 $J_{4,5}$ 1.7 $J_{5,6}$ 2.5 $J_{5,6'}$ 9.2 $J_{6,6'}$ 13.4 $J_{0,m}$ 6.8 $J_{m,p}$ 7.6 $J_{0,p}$ 1.2 17 3.41 4.44 4.37 5.37 6.53 6.04 5.90 0.94 1.61 1.09 $J_{1,2}$ 3.5 $J_{2,3}$ 0 $J_{3,4}$ 4 $J_{4,5}$ 9 $J_{5,6}$ 4.5 $J_{5,6'}$ 6 $J_{6,6'}$ 8.5 $J_{0,m}$ 6.8 $J_{m,p}$ 7.8 $J_{0,p}$ 1.3 19 3.09 4.35 $J_{3,3}$ 0.75 1.60 1.07 $J_{3,6}$ 4.5 $J_{5,6}$ 4.5 $J_{5,6'}$ 6 $J_{6,6'}$ 8.5 $J_{0,m}$ 6.8 $J_{m,p}$ 7.6 $J_{0,p}$ 1.3	18	4.52 J _{1,2} 4.7	5.59 J _{2,3} 2.2	5.31 J _{3,4} 7.6	5.48 J4,5 1.6	5.60 J _{3,6} 2.4	4.58 J _{3,6} , 9.6	5.19 J _{6,6} , 13.6	0.59 J _{0,m} 6.0	1.75 J _{m.p} 8.0	1.24 J _{0,P} ~0	٩
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19 3.09 4.35 4.35 5.38 6.54 6.07 5.93 0.75 1.60 1.07 $J_{1,2}$ 3.5 $J_{2,3}$ 0 $J_{3,4}$ 4 $J_{4,5}$ 9 $J_{5,6}$ 4.5 $J_{5,6'}$ 6 $J_{6,6'}$ 8.5 $J_{0,m}$ 6.8 $J_{m,p}$ 7.6 $J_{0,p}$ 1.1	17	3.41 J _{1,2} 3.5	4,44 J _{2,3} 0	4.37 J _{3,4} 4	5.37 J4.5 9	6.53 J _{5,6} 4.5	6.04 J _{5,6} ' 6	5.90 J _{6,6} , 8.5	0.94 J _{0.m} 6.8	1.61 J _{m,p} 7.8	1.09 J _{o,p} 1.3	-
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FLUORINATED ESTERS

TABLE I

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accompanied by inversion of configuration at C-3. The 3-triflate 5 also reacted with pyridine, but did not give the pyridinium salt. This reaction is being further studied.

The isolation of 10 and 13 in the galactose series indicates clearly that the tresylate and pentaflate have substantially lower reactivity with respect to displacement by pyridine than the triflate. The solvolysis rates⁹ in aqueous ethanol follow the sequence tosylate (1)<tresylate (100)<triflate (4000). Nonaflates (O-SO₂C₄F₉) appear¹³ to have even higher reactivity than triflates.

The n.m.r. spectra of the pyridinium salts 7 and 17–20 were well-resolved when measured for solutions in acetone- d_6 ; the parameters are summarised in Table I.

The markedly enhanced reactivity of secondary triflates as compared to tosylates should be widely exploitable in carbohydrate chemistry, especially in conjunction with the use of dipolar aprotic solvents. We are currently evaluating the potential of these derivatives.

EXPERIMENTAL

All solutions were concentrated under diminished pressure, using a Buchi rotary evaporator. Melting points were measured with a Hoover Unimelt (6406-K) instrument and are uncorrected. Optical rotations were measured on acetone solutions at ambient temperature with a Perkin-Elmer 141 polarimeter. T.l.c. was performed on Silica Gel G (Merck), using toluene-ether (1:2) and detection by charring with H_2SO_4 .

¹H-N.m.r. spectra were measured with a Varian XL-100 (15) instrument operating in the Fourier transform mode with a Varian Computer (620 L, 16K); acetone- d_6 was used as solvent and its resonance provided the deuterium lock signal. ¹⁹F-N.m.r. spectra were measured with a T-60 instrument operating at 56.4 MHz. Tetramethylsilane was used as internal reference for the ¹H shifts (τ values), and CFCl₃ (freon 11) for the ¹⁹F shifts (ϕ_c values).

All ¹H-n.m.r. spectra showed the requisite number of methyl resonances centred within the general region τ 8.6–8.7, and individual values are not stated.

All reactions were performed in anhydrous solvents under an atmosphere of dry nitrogen; solvents were dried, distilled, and then stored over molecular sieves.

Trifluoromethanesulphonic anhydride (98% by g.l.c.) and 2,2,2-trifluoroethanesulphonyl (tresyl) chloride (98%) were obtained from Willow-Brook Laboratories Inc. (Waukesha, Wisconsin, U.S.A.), and were used without further purification. Both reagents appear to be stable indefinitely when kept at -10° . Pentafluorobenzenesulphonyl chloride (99%) was obtained from Aldrich Chemical Co., and was used without purification; it is stable for at least several months at room temperature.

1,2:5,6-Di-O-isopropylidene-3-O-triffyl- α -D-allofuranose (4). — To a cooled ($\sim -15^{\circ}$) solution of 1 (0.5 g, 1.92 mmol) in pyridine (0.6 ml, 7.43 mmol) and CH₂Cl₂ (40 ml), triffic anhydride (0.38 ml, 2.3 mmol) was slowly added. After 1 h, t.l.c. showed the reaction to be complete. The reaction mixture was poured onto a mixture of ice and sodium hydrogen carbonate. The aqueous layer was extracted

with CH_2Cl_2 (3×50 ml), and the combined CH_2Cl_2 solutions were dried, and rapidly and repeatedly concentrated with toluene to remove any residual pyridine. The brown residue was extracted with light petroleum (b.p. 30-60°) (3×50 ml), and the combined extracts were filtered and cooled. The colourless needles which were collected, after careful evaporation of additional solvent were 4 (~100%), m.p. 40°, $[\alpha]_D^{25} + 64$ (c 2.1).

Anal. Calc. for C₁₃H₁₉F₃O₈S: C, 39.80; H, 4.88. Found: C, 40.02; H, 5.00.

¹H-N.m.r. data: τ 4.05 (H-1), 5.05 (H-2), 4.78 (H-3), 5.81 (H-4), 6.12 (H-5), 5.81 (H-6); $J_{1,2}$ 4.02, $J_{2,3}$ 4.69, $J_{3,4}$ 6.7 Hz. ¹⁹F: ϕ_{C} +78.8 p.p.m.

A similar result was obtained using only pyridine as solvent: the reaction took \sim 3 h for completion and the product was obtained in 80% yield.

1,2:5,6-Di-O-isopropylidene-3-O-triflyl- α -D-glucofuranose (5). — In a manner similar to that described above, a solution of 2 (1 g, 3.8 mmol) in pyridine at -10° , when treated with triflic anhydride (0.7 ml, 4.2 mmol), gave 5 (~100%). When recrystallised from light petroleum (b.p. 30-60°), the product was a white powder m.p. 70°, $[\alpha]_{D}^{25} - 35^{\circ}$ (c 2).

Anal. Calc. for C₁₃H₁₉F₃O₈S: C, 39.80; H, 4.88. Found: C, 39.71; H, 4.85.

¹H-N.m.r. data: τ 3.84 (H-1), 5.00 (H-2), 4.66 (H-3), ~5.9 (m, H-4,5,6); $J_{1,2}$ 4, $J_{2,3}$ 0, $J_{3,4}$ 2 Hz. ¹⁹F: $\phi_{\rm C}$ +77 p.p.m.

6-Deoxy-1,2:3,4-di-O-isopropylidene-6-pyridino- α -D-galactopyranose trifluoromethanesulphonate (7). — A solution of 3 (1.75 g, 6.7 mmol) in CH₂Cl₂ (15 ml) was added during 10 min to a cooled ($\sim -15^{\circ}$) solution of triflic anhydride (1.2 ml, 7.2 mmol) in pyridine. After 1.5 h, the reaction mixture was worked-up in the usual fashion to yield 7 (2.83 g, 90%). Recrystallisation from aqueous ethanol-light petroleum gave white platelets, m.p. 217–218° (dec.), $[\alpha]_{\rm D}^{25} - 35^{\circ}$ (c 2.5).

Anal. Calc. for C₁₈H₂₄F₃NO₈S: C, 45.86; H, 5.13; N, 2.97. Found: C, 45.95; H, 5.32; N, 2.96.

The n.m.r. data are listed in Table I.

1,2:5,6-Di-O-isopropylidene-3-O-tresyl- α -D-allofuranose (8). — A solution of 1 (2 g, 7.7 mmol) in pyridine (0.94 ml, 11.6 mmol) and CH₂Cl₂ (40 ml) was treated with tresyl chloride (0.94 ml, 9.9 mmol), using a procedure parallel to that described above for the preparation of 4. The stirred mixture was allowed to warm up to room temperature overnight. The usual work-up and recrystallisation of the product from light petroleum gave very fine, white needles of 8 (3.2 g, 89%), m.p. 55-56°, $[\alpha]_D^{25}$ + 66° (c 2.1).

Anal. Calc. for C₁₄H₂₁F₃O₈S: C, 41.38; H, 5.21. Found: C, 41.73; H, 5.28.

¹H-N.m.r. data: τ 4.12 (H-1), 5.1 (H-2), 4.51 (H-3), ~5.8 (m, H-4,6), 5.64 H-5), 4.94 (CF₃CH₂); $J_{1,2}$ 3.7, $J_{2,3}$ 4.7, $J_{3,4}$ 7.3, $J_{H,F}$ 9.3 Hz. ¹⁹F: ϕ_{C} +63.2 p.p.m.

1,2:5,6-Di-O-isopropylidene-3-O-tresyl- α -D-glucofuranose (9). — The reaction of a solution of 2 (1 g, 3.9 mmol) in pyridine (0.47 ml, 5.8 mmol) and CH₂Cl₂ (40 ml) with tresyl chloride (0.47 ml, 5 mmol) was conducted as described above to yield 9 as white needles (1.4 g, 90%), m.p. 90–91°, $[\alpha]_D^{25} - 39°$ (c 2.7).

Anal. Calc. for C₁₄H₂₁F₃O₈S: C, 41.38; H, 5.21. Found: C, 41.72; H, 5.44.

¹H-N.m.r. data: τ 3.92 (H-1), 5.11 (H-2), 4.81 (H-3), 5.8 (m, H-4,6), 6.04 (H-5), 5.34 (CF₃CH₂); $J_{1,2}$ 3.7, $J_{2,3}$ 0, $J_{3,4}$ 2.0, $J_{F,H}$ 9.3 Hz. ¹⁹F: ϕ_{C} + 63.2 p.p.m.

1,2:3,4-Di-O-isopropylidene-6-O-tresyl- α -D-galactopyranose (10). — The reaction of a solution of 3 (2.3 g, 8.9 mmol) in pyridine (14 mmol) and CH₂Cl₂ (40 ml) with tresyl chloride (1.15 ml, 12 mmol) at ~ -15° for 1.5 h was followed by the usual work-up. Recrystallisation of the product from light petroleum gave 10 (3.2 g, 89%) as fine, white needles, m.p. 93–94°, $[\alpha]_{D}^{25} - 52^{\circ}$ (c 1.7).

Anal. Calc. for C₁₄H₂₁F₃O₈S: C, 41.38; H, 5.21. Found: C, 41.30; H, 5.10.

¹H-N.m.r. data: τ 4.41 (H-1), 5.54 (H-2), 4.26 (H-3), 5.60 (H-4), 4.80 (H-5), 5.43 (H-6), 5.53 (H-6), 5.37 (CF₃CH₂); $J_{1,2}$ 4.8, $J_{2,3}$ 2.0, $J_{3,4}$ 7.5, $J_{4,5}$ 1.5, $J_{5,6}$ 4.5, $J_{5,6'}$ 6.5, $J_{6,6'}$ 11.5, $J_{F,H}$ 9.25 Hz. ¹⁹F: ϕ_{C} +63.6 p.p.m.

Reactions with pentafluorobenzenesulphonyl chloride. — None of the reactions attempted with this reagent were satisfactory, the yields being invariably low (~40%). Reactions conducted with a 3-molar excess of reagent gave no significant improvement in yield, neither did variations in reaction time (3-48 h), nor temperature $(-20 \rightarrow +80^{\circ})$.

The carbohydrate (1, 2, or 3) (1.4 g, 4.2 mmol) and pyridine (0.7 ml, 8.7 mmol) was treated with pentafluorobenzenesulphonyl chloride (1.57 g, 6.25 mmol) and followed by the usual work-up. The following compounds were thereby obtained.

1,2:5,6-Di-O-isopropylidene-3-O-pentaflyl- α -D-allofuranose (11), m.p. 103–104°, $[\alpha]_D^{25} + 64^\circ$ (c 1.9).

Anal. Calc. for C₁₈H₁₉F₅O₈S: C, 44.09; H, 3.91. Found: C, 44.04; H, 3.95.

¹H-N.m.r. data: τ 4.17 (H-1), 5.18 (H-2), 5.08 (H-3), 6.08 (m, H-4,5,6); $J_{1,2}$ 3.5, $J_{2,3}$ 4.6, $J_{3,4}$ 7.29 Hz. ¹⁹F: ϕ_C + 136 (ortho), + 148 (meta), and + 164 p.pm. (para).

1,2:5,6-Di-O-isopropylidene-3-O-pentaflyl- α -D-glucofuranose (12), m.p. 132–136°; an acceptably pure specimen was not obtained even after chromatography on a neutral alumina column (Brockman I; 80–200 mesh) using toluene-ether.

¹H-N.m.r. data: τ 3.7 (H-1), 4.8 (H-2,3), 5.8 (m, H-4,5,6); $J_{1,2}$ 3.6, $J_{2,3}$ 3.6 Hz. ¹⁹F: $\phi_{\rm C}$ +135, +148, +163 p.p.m.

1,2:3,4-Di-O-isopropylidene-6-O-pentaflyl- α -D-galactopyranose (13), m.p. 103–104°, $[\alpha]_D^{25}$ -47.5° (c 2.3).

Anal. Calc. for C₁₈H₁₉F₅O₈S: C, 44.09; H, 3.91. Found: C, 44.21; H, 3.88.

¹H-N.m.r. data: τ 4.78 (H-1), 5.66 (H-2), 5.35 (H-3), 5.71 (H-4), 5.94 (H-5), 5.42 (m, H-6); $J_{1,2}$ 5.1, $J_{2,3}$ 2.5, $J_{3,4}$ 8.1, $J_{4,5}$ 1.8, $J_{5,6} \sim 5.4$, $J_{5,6'} \sim 6.3$ Hz. ¹⁹F: $\phi_{\rm C}$ +135, +147.2, +162.4 p.p.m.

6-Deoxy-1,2:3,4-di-O-isopropylidene-6-pyridino- α -D-galactopyranose toluene-psulphonate (18). — A solution of the 6-O-tosyl derivative 16 (5 g, 1.2 mmol) in pyridine (~50 ml) was heated under reflux for 24 h; t.l.c. then indicated that 95% of 16 had reacted. Work-up in the usual fashion gave a crude product (2 g, ~33%) which was recrystallised from aqueous ethanol to give 18, m.p. 204-205°, $[\alpha]_D^{25} - 25^\circ$ (c 0.5).

Anal. Calc. for C₂₄H₃₂NO₈S: C, 58.28; H, 6.52.; N, 2.83. Found: C, 58.37; H, 6.69; N, 2.80.

¹H-N.m.r. data given in Table I.

6-Deoxy-1,2:3,4-di-O-isopropylidene-6-pyridino-α-D-galactopyranose iodide (20). — To a solution of 7 or 18 in acetone, a 3-molar excess of sodium iodide was added. The mixture was heated under reflux for 1 h and the usual work-up gave 20 (~100%). Recrystallisation from methanol gave 20 as a pale-yellow powder, m.p. 250° (dec.), $[\alpha]_{D}^{25} - 30^{\circ}$ (c 0.27).

Anal. Calc. for C₁₇H₂₄INO₅: C, 45.45; H, 5.38; N, 3.12. Found: C, 45.47; H, 5.37; N, 3.00.

Salts of 3-deoxy-1,2:5,6-di-O-isopropylidene-3-pyridino- α -D-glucofuranose trifluoromethanesulphonate. — A solution of 1 (1 g, 2.8 mmol) and triflic anhydride (0.74 ml, 4.4 mmol) in pyridine (~40 ml) was heated at reflux temperature for 25 h. After the usual work-up and a single treatment with charcoal-Celite, a very hygroscopic, brown, crystalline material was obtained (1.2 g, 71%), which was proved to be the triflate salt 17 by ¹H-n.m.r. and ¹⁹F-n.m.r. spectroscopy (ϕ_c +81.6 p.p.m.).

Likewise, 4 was converted into 17.

A sample of 17 was quantitatively converted into the iodide 19 as described previously; m.p. 190–193° (from aqueous ethanol), $[\alpha]_D^{25} - 3^\circ$ (c 0.39).

Anal. Calc. for C₁₇H₂₄INO₅: C, 45.45; H, 5.38; N, 3.12. Found: C, 44.96; H, 5.46; N, 3.03.

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