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A SYNTHESIS OF L-RISTOSAMINE AND A DERIVATIVE OF ITS C-4 EPIMER

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ABSTRACT

A synthesis of L-ristosamine from L-rhamnal is described, involving the sequence of reactions: methoxymercuration, tosylation, azide displacement, and reduction, which gave methyl α-L-ristosaminide (**10**). Acid hydrolysis then afforded L-ristosamine hydrochloride. Trifluoroacetylation of the hydrochloride of **10** followed by saponification and oxidation with ruthenium tetraoxide gave methyl 2,3,6-trideoxy-3-trifluoroacetamido-α-L-*erythro*-hexopyranosid-4-ulose (**17**). Borohydride reduction of **17** gave a separable, 1:1 mixture of methyl 2,3,6-trideoxy-3-trifluoroacetamido-α-L-*ribo*- and -α-L-*xylo*-hexopyranoside.

INTRODUCTION

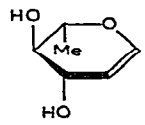
In 1974, we reported[1] a structural investigation of L-ristosamine (3-amino-2,3,6-trideoxy-L-*ribo*-hexopyranose) isolated from the antibiotic ristomycin-A, and later[2] the first definitive synthesis. Other syntheses (without experimental details) have been reported[3–5]. A new semisynthetic analogue of the anticancer antibiotic daunomycin has been prepared[5,6] *via* a glycosylation reaction involving a derivative of L-ristosamine. Syntheses of D-ristosamine have also been described[7–9].

We now describe preparative syntheses of L-ristosamine and of a derivative of its C-4 epimer 3-amino-2,3,6-trideoxy-L-*xylo*-hexopyranose, starting from L-rhamnal.

RESULTS AND DISCUSSION

Methoxymercuration[10,11] of L-rhamnal (**1**) gave methyl 2-acetoxymercurio-2-deoxy-α-L-rhamnopyranoside (**2**, 69%). Compound **2** was described by Marsh *et al.*[12] in 1967, but no physical data were recorded. The high values (9–9.5 Hz) of $J_{3,4}$ and $J_{4,5}$ in the ^{1}H-n.m.r. spectrum of **2** and its 3,4-diacetate (**3**) indicate the $^1C_4$-L

conformation for each compound, and the low value (1–1.5 Hz) of $J_{1,2}$ indicates MeO-1 and AcOHg-2 to be *trans*-diaxial.



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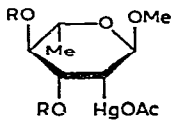

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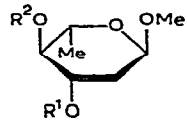
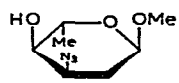
3 R = Ac



4 $R^1 = R^2 = H$
5 $R^1 = R^2 = Ts$
6 $R^1 = Ts, R^2 = H$
7 $R^1 = H, R^2 = Ts$



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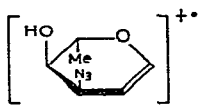
Reductive demercuration of **2** with methanolic sodium borohydride gave methyl 2,6-dideoxy-α-L-*arabino*-hexopyranoside[13] (**4**) which, with 1.1 equivalents of tosyl chloride in pyridine, gave methyl 2,6-dideoxy-3,4-di-*O*-toluene-*p*-sulphonyl-α-L-*arabino*-hexopyranoside (**5**, ~4%) and a 4:1 mixture {51%, m.p. 79–81°, $[\alpha]_D^{23}$ −110° (*c* 1, chloroform)} of methyl 2,6-dideoxy-3-*O*-toluene-*p*-sulphonyl-α-L-*arabino*-hexopyranoside (**6**) and probably the corresponding 4-tosylate (**7**), which could not be separated by column chromatography*. The signal for H-3 in the n.m.r. spectrum of the mixture of **6** and **7** was shifted to lower field by 0.9 p.p.m. (Table I), indicating the main component to be the 3-tosylate (**6**). Treatment of the mixture of **6** and **7** with sodium azide in *N*,*N*-dimethylformamide gave crystalline methyl 3-azido-2,3,6-trideoxy-α-L-*ribo*-hexopyranoside (**8**, 36%). The location of the azido group at position 3 in **8** was proved by mass spectrometry. Although no molecular ion was detected, the base peak had *m/e* 155.0689, corresponding to the $[M-MeOH]^+$ ion (**9**). Loss of N_3 from **9** to give the ion *m/e* 113.0605 (30%) was consistent with the allylic azide structure of **9**. The high value (9 Hz) observed for $J_{4,5}$ in **8** (Table I) indicates the $^1C_4$-L conformation.



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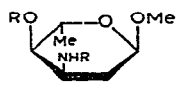
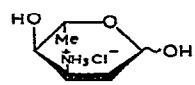


10 R = H
11 R = H (HCl salt)
13 R = Bz



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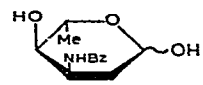

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Catalytic hydrogenation of **8** gave extremely hygroscopic, crystalline methyl 3-amino-2,3,6-trideoxy-α-L-*ribo*-hexopyranoside (**10**), the mass spectrum of which was identical with that of methyl α-L-ristosaminide isolated[1] from ristomycin-A. The

*Marsh *et al.*[12] recorded m.p. 86.5–86.9°, $[\alpha]_D$ −116° (chloroform), for **6**, but experimental conditions were not given.

TABLE I

^{1}H-N.M.R. (100 MHz) DATA

Compound	*Solvent*	*Chemical shifts* (δ, *p.p.m.*)								
		H-1	*H-2e*	*H-2a*	*H-3*	*H-4*	*H-5*	*Me-5*	*Others*	
4	$CDCl_3$	4.68	2.11	1.65	3.82	—	3.59	1.28	OMe	3.31
2	D_2O	5.42	3.56	—	4.51	3.50	4.11	1.67	OAc	2.38
									OMe	3.70
3	$CDCl_3$	4.99	3.29	—	5.57	4.83	3.91	1.20	OAc	2.03
									OMe	3.31
5	$CDCl_3$	4.63	2.42	1.80	~4.75	4.42	3.75	1.23	OMe	3.22
									OTs	2.41; 2.43
6	$CDCl_3$	4.66	2.11	1.78	~4.71	—	3.62	1.24	OMe	3.27
								1.18[a]	OTs	2.43
8	$CDCl_3$	4.66	2.20	1.97	4.02	~3.4	3.86	1.28	OMe	3.39
									OH	2.56
10	D_2O	4.80	2.07–2.18			3.2–4.0		1.31	OMe	3.39

[a]Me-5 signal of the 4-tosylate **7**; ratio of **6** and **7** (from integrated intensities) is ~4:1.

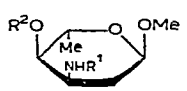
Compound	*Solvent*	*First-order coupling constants* (*Hz*)								
		$J_{1,2e}$	$J_{1,2a}$	$J_{2e,3}$	$J_{2a,3}$	$J_{2e,2a}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	*Others*
4	$CDCl_3$	~1[a]	3.5	5.4	11.5	12.8	9.4	9.4	6.0	
2	D_2O	~1[a]	—	5.2	—	—	9.0	9.5	6.2	
3	$CDCl_3$	~1.5	—	6.5	—	—	9.0	9.5	6.2	
5	$CDCl_3$	~1.5	3.7	5.5	11.0	13.5	9.5	9.5	6.0	
6	$CDCl_3$	~1.6	3.5	5.8	11.5	13.0	9.0	9.2	6.0	
8	$CDCl_3$	1.7	4.0	3.6	4.1	15.0	~4.0	9.0	6.0	$J_{CH,OH}$ ~9
10	D_2O	2.7	2.7	—	—	—	—	—	6.0	

[a]Estimated from the line width.

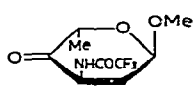
hydrochloride (**11**) of **10** was identical with the product obtained[1] by methanolysis of ristomycin-A. Acid hydrolysis of **11** gave L-ristosamine hydrochloride (**12**).

Schotten–Baumann benzoylation of **10** and hydrolysis of the resulting dibenzoyl derivative **13** with hydrochloric acid yielded a product that was identical with *N*-benzoyl-L-ristosamine (**14**) prepared[1] from ristomycin-A.

The availability of **11** allowed the preparation of hitherto unknown derivatives of 3-amino-2,3,6-trideoxy-L-*xylo*-hexopyranose. Conversion of **11** into methyl di-*N*,*O*-trifluoroacetyl-α-L-ristosaminide (**15**) followed by Zemplén deacetylation gave methyl *N*-trifluoroacetyl-α-L-ristosaminide[5] (**16**). Oxidation of **16** with ruthenium tetraoxide gave crystalline methyl 2,3,6-trideoxy-3-trifluoroacetamido-α-L-*erythro*-hexopyranosid-4-ulose (**17**, 40%). Reduction of **17** with sodium borohydride gave a 1:1 mixture of **16** and its C-4 epimer methyl 2,3,6-trideoxy-3-trifluoroacetamido-α-L-*xylo*-hexopyranoside (**18**), which was separated by p.l.c. The ^{13}C-n.m.r. spectra (see Experimental) of **16** and **18** clearly indicate the change of configuration at C-4; relative to those for **16**, the signals of C-4 and C-2 in **18** were shifted upfield as a result of a 2,4-diaxial interaction, the signal for C-3 was unchanged, and that for C-6 was shifted upfield by 1.1 p.p.m. Similar differences have been recorded[14] for methyl α-L-fucoside and methyl 6-deoxy-α-L-glucoside.



15 $R^1 = R^2 = CF_3CO$
16 $R^1 = CF_3CO$, $R^2 = H$



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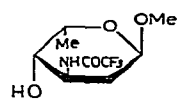

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EXPERIMENTAL

General. — Melting points were determined on a Kofler hot-stage and are uncorrected. Optical rotations were measured with Schmidt–Haensch and Bendix NPL polarimeters. ^{1}H-N.m.r. spectra (100 MHz) were recorded with a Jeol MH-100 instrument and ^{13}C-n.m.r. spectra with a Varian XL-100-FT-15 instrument at 60° for 25% solutions in $CDCl_3$. Mass spectra (70 eV) were recorded with an AEI MS-902 spectrometer and i.r. spectra with a Unicam SP-200 G instrument. T.l.c. and column chromatography were performed on silica gel G (Merck) with benzene–methanol mixtures *A*, 85:15; *B*, 9:1; and *C*, 4:1; and with *D*, propan-2-ol–25% ammonia–water (6:2:1). Concentrations were carried out under diminished pressure at 40°.

Methyl 2-acetoxymercurio-2,6-dideoxy-α-L-mannopyranoside (**2**). — To a solution of L-rhamnal[15] (**1**; 12.4 g, 9.52 mmol) in methanol (50 ml) was added a solution of mercury(II) acetate (31 g, 9.72 mmol) in methanol (170 ml)[10,11]. After storage at room temperature for 2 h, the mixture was filtered and concentrated, and the residue was crystallised from methanol (30 ml) to give **2** (27.7 g, 69%), m.p. 150–152° (from acetone), $[\alpha]_D^{23}$ −5° (*c* 0.57, methanol); ν_{max}^{KBr} 1575 cm^{-1} (C=O of HgOAc)[11],

Anal. Calc. for $C_9H_{16}HgO_6$: OMe, 7.37. Found: OMe, 7.35.

The 3,4-diacetate (**3**) of **2** was a colourless syrup, $[\alpha]_D^{23}$ +26° (*c* 4.16, chloroform), R_F 0.9 (solvent *A*); ν_{max}^{film} 1580 (C=O of HgOAc) and 1732 cm^{-1} (OAc).

Anal. Calc. for $C_{13}H_{20}HgO_8$: OMe, 6.14. Found: OMe, 6.08.

*Tosylation of methyl 2,6-dideoxy-α-*L*-arabino-hexopyranoside* (**4**). — To a solution of **2** (26 g, 6.2 mmol) in methanol (500 ml) was added sodium borohydride (3.5 g, 9.3 mmol) portionwise at 0–5°. After storage at room temperature for 1 h, the mixture was treated with Celite, filtered, and concentrated, and a solution of the residue in chloroform was washed with water, dried ($MgSO_4$), and concentrated. Mercury and sodium salts were removed by column chromatography (solvent *A*), and **4** (7.33 g, 73.2%) was obtained as a colourless, thick syrup, $[\alpha]_D^{23}$ −146° (*c* 0.73, acetone), lit.[13] $[\alpha]_D$ −152.5 ±2° (*c* 0.7, acetone).

A solution of toluene-*p*-sulphonyl chloride (9.2 g, 48.3 mmol) in pyridine (25 ml) was added with cooling to a solution of **4** in pyridine (20 ml). After storage for 5 days at 0—5°, t.l.c. (solvent *B*) indicated an almost complete conversion of **4** (R_F 0.25) into two products (R_F 0.68 and 0.88). Solid sodium hydrogen carbonate (3 g) and crushed ice were added and the mixture was concentrated to dryness. The residue was extracted with chloroform (3 × 20 ml), and the combined extracts were washed with aqueous 3% sodium hydrogen carbonate and water, dried ($MgSO_4$), and concentrated to give a yellow syrup that was chromatographed with solvent *B* to give the following products.

Methyl 2,6-dideoxy-3,4-di-*O*-toluene-*p*-sulphonyl-α-L-*arabino*-hexopyranoside (**5**) as a syrup (0.9 g, 4.3%), $[\alpha]_D^{23}$ −80° (*c* 1.27, chloroform), R_F 0.88.

Anal. Calc. for $C_{21}H_{26}O_8S_2$: S, 13.63. Found: S, 13.42.

An ~4:1 mixture (7.1 g, 51.3%) of methyl 2,6-dideoxy-3-*O*-toluene-*p*-sulphonyl-α-L-*arabino*-hexopyranoside (**6**) and methyl 2,6-dideoxy-4-*O*-toluene-*p*-sulphonyl-α-L-*arabino*-hexopyranoside (**7**), m.p. 79–81°, $[\alpha]_D^{23}$ −110° (*c* 1, chloroform), R_F 0.68.

Anal. Calc. for $C_{14}H_{20}O_6S$: S, 10.13. Found: S, 9.99.

*Methyl 3-azido-2,3,6-trideoxy-α-*L*-ribo-hexopyranoside* (**8**). — A solution of the above mixture of **6** and **7** (5.5 g, 17.4 mmol) and sodium azide (5.5 g, 84 mmol) in *N,N*-dimethylformamide (30 ml) was stirred at 100–120° for 20 h, and then cooled, diluted with water (150 ml), and extracted with chloroform. The extract was dried ($MgSO_4$) and concentrated, and traces of *N,N*-dimethylformamide were removed at 60–70° (bath)/1 mmHg; some **8** sublimed under these conditions. Recrystallisation of the residue from light petroleum gave **8** (1.17 g, 36%), m.p. 77–78°, $[\alpha]_D^{23}$ −300° (*c* 0.57, chloroform); ν_{max}^{KBr} 2100 cm^{-1} (C–N); R_F 0.5 (solvent *B*). Mass spectrum: *m/e* 155.0698 (100%, $M^+ - MeOH$), 129 (6), 113.0605 (40, $M^+ - MeOH - N_3$), 100 (85), 71 (40), 69 (35), and 59 (60). Metastable: *m/e* 82.4 (155 $\xrightarrow{42}$ 113).

Anal. Calc. for $C_7H_{13}N_3O_3$: C, 44.91; H, 6.99; N, 22.44. Found: C, 45.68; H, 6.97; N, 22.21.

*Methyl 3-amino-2,3,6-trideoxy-α-*L*-ribo-hexopyranoside hydrochloride* (**11**, *methyl α-*L*-ristosaminide hydrochloride*). — A solution of **8** (307 mg) in methanol (15 ml) was hydrogenated (20°, 1 atmos.) in the presence of 10% palladium-on-carbon

for 4 h. The filtered mixture was concentrated, and the residue was dried in a vacuum desiccator over calcium chloride to give methyl α-L-ristosaminide (**10**; 224 mg, 84.2%) as a very hygroscopic foam, $[\alpha]_D^8$ −192° (*c* 1.2, chloroform), R_F 0.2 (solvent *C*) and 0.8 (solvent *D*), identical with the product of natural origin[1].

A solution of **10** (120 mg) in methanol was treated with 1.2M hydrochloric acid in methanol (0.95 ml) and then concentrated, and portions of methanol were evaporated from the residue to remove excess of hydrochloric acid. The residue crystallised to give **11** (135 mg, 92%), m.p. 154–157°. Recrystallisation from a small amount of ethanol gave material, m.p. 165–168°, $[\alpha]_D^{20}$ −160° (*c* 0.23, methanol): lit.[1], for methyl α-L-ristosaminide hydrochloride obtained by the methanolysis of ristomycin-A, m.p. 168–170°, $[\alpha]_D^{20}$ −157° (*c* 1, methanol). T.l.c. also showed the identity of synthetic and natural **11**; R_F 0.8 (solvent *D*).

*3-Amino-2,3,6-trideoxy-*L*-*ribo*-hexopyranose hydrochloride* (**12**, *L-ristosamine hydrochloride*). — Compound **11** (198 mg) was hydrolysed with 0.1M hydrochloric acid (5 ml) at 100° for 1 h. The solution was neutralised with Dowex 2 x4 (HO^-) resin, filtered, and lyophilized to give extremely hygroscopic **12**, (166 mg, 73.6%), $[\alpha]_D^{25}$ −44.5→−49° (3 h; *c* 1.66, 0.1M HCl). The product isolated[1] from ristomycin-A had $[\alpha]_D^{21}$ −34.3° (*c* 0.57, water), and an R_F value (0.93, solvent *D*) identical with that of **12**.

*3-Benzamido-2,3,6-trideoxy-*L*-ribo-hexopyranose* (**14**, *N-benzoylristosamine*). — A solution of **10** (68.3 mg) and sodium hydrogen carbonate (47.5 mg) in water (2.5 ml) was stirred with a solution of benzoyl chloride (0.55 ml) in dry tetrahydrofuran (1.1 ml) for 30 min and then deionized with AG 50W-x12 (H^+) and Dowex 2 x4 (HO^-) resins, diluted with water (10 ml), and extracted with ether (3 × 5 ml). The combined extracts were dried ($MgSO_4$), and concentrated to give a colourless, chromatographically homogeneous syrup (49 mg, 43.5%), R_F 0.54 (solvent *A*), which was identical with methyl *N*-benzoyl-α-L-ristosaminide[1]. The foregoing product (49 mg) was hydrolysed with 0.1M hydrochloric acid at 100° for 1 h, when dissolution occurred. Concentration of the mixture gave **14** (32 mg, 69%), m.p. 126–128° alone and 128–130° in admixture with authentic[1] **14**, $[\alpha]_D^{23}$ −10° (10 min; *c* 0.7, ethanol); lit.[1] m.p. 131–133°, $[\alpha]_D^{26}$ −14→−11° (after 10 min; *c* 1, ethanol).

*Methyl di-*N,O*-benzoyl-α-*L*-ristosaminide* (**13**). — Compound **11** (100 mg) was conventionally treated with benzoyl chloride (0.12 ml) and pyridine (1.5 ml) to give **13** (180 mg, 96.3%), m.p. 150–151° (from 96% ethanol), $[\alpha]_D^{20}$ −181° (*c* 0.66, chloroform), R_F 0.48 (solvent *B*).

Anal. Calc. for $C_{21}H_{23}NO_5$: N, 3.79. Found: N, 3.76.

*Methyl di-*N,O*-trifluoroacetyl-α-*L*-ristosaminide* (**15**). — A suspension of **11** (357 mg, 1.8 mmol) in ether (9 ml) at 0° was stirred with trifluoroacetic anhydride (1.43 ml, 11.2 mmol). On storage of the mixture at room temperature for 4 h, **11** completely dissolved. The mixture was concentrated, and light petroleum (2 × 2 ml) was evaporated from the residue, which was then dried *in vacuo* to constant weight over calcium chloride and potassium hydroxide, to give **15** as a light-yellow syrup (624 mg, 97.7%), $[\alpha]_D^{25}$ −90° (*c* 0.55, methanol), R_F 0.72 (solvent *A*); ν_{max}^{film} 1795 (amide I), 1540 (amide II), and 1730 cm^{-1} (C=O).

Anal. Calc. for $C_{11}H_{13}F_6NO_5$: F, 32.28. Found: F, 32.34.

Methyl N-*trifluoroacetyl*-α-L-*ristosaminide* (**16**). — Zemplén deacetylation of **15** (320 mg) in methanol (3 ml) gave syrupy **16** (0.3 g), which was purified by column chromatography with solvent *A* to give syrupy material (224.5 mg, 96.3%), $[\alpha]_D^{20}$ −64° (*c* 1, methanol), R_F 0.52 (solvent *B*); ν_{max}^{film} 3360 (OH), 1730 (amide I), and 1555 cm^{-1} (amide II); lit.[5] $[\alpha]_D^{25}$ −61.9° (*c* 0.5, benzene).

Anal. Calc. for $C_9H_{14}F_3NO_4$: F, 22.16. Found: F, 22.11.

Methyl 2,3,6-trideoxy-3-trifluoroacetamido-α-L-erythro-*hexopyranosid-4-ulose* (**17**). — To a mixture of **16** (206 mg, 0.8 mmol), anhydrous potassium carbonate (25.8 mg), and potassium periodate (223.6 mg) in water (3.8 ml) was added a freshly prepared solution of ruthenium tetraoxide (12 mg) in carbon tetrachloride (2 ml) with stirring at room temperature in the dark. After 24 h, the mixture was treated with further amounts of the reagents mentioned above. After 48 h, the mixture was filtered, the organic layer was washed with water, and the aqueous layer was extracted with carbon tetrachloride (6 × 2 ml). The combined organic solutions were dried ($MgSO_4$) and concentrated to give **17** as white needles (82 mg, 40%), m.p. 116–117°, $[\alpha]_D^{24}$ −227° (*c* 0.53, carbon tetrachloride), R_F 0.81 (solvent *A*); ν_{max}^{KBr} 1745 (ketone, C=O), 1705 (amide I), and 1550 cm^{-1} (amide II). Mass spectrum: *m/e* 255 (1%, M^+), 224 (4), 197 (1), 183.0494 (100, $C_6H_8F_3NO_2$), 168 (10), 152 (10), 111 (40), 86 (51), 69 (15), and 59 (14).

Anal. Calc. for $C_9H_{12}F_3NO_4$: F, 22.33. Found: F, 22.14.

Transformation of **11**, obtained from ristomycin-A by methanolysis, through the route **15**→**16**→**17** gave a product having m.p. 115–118°, $[\alpha]_D^{24}$ −248° (*c* 0.42, carbon tetrachloride), R_F 0.8 (solvent *A*).

Methyl 2,3,6-trideoxy-3-trifluoroacetamido-α-L-xylo-*hexopyranoside* (**18**). — To a solution of **17** (98 mg) in 1,4-dioxane (1 ml) and water (1 ml) at 5°, sodium borohydride (10 mg) was added portionwise. After storage at room temperature for 30 min, the mixture was diluted with water, neutralised to pH 6 with AG 50W-x12 (H^+) resin, and concentrated. Methanol (3 × 5 ml) was evaporated from the residue, which was then dried over P_2O_5 to give a light-yellow syrup (92 mg, 92.8%) that was shown by t.l.c. and ^{13}C-n.m.r. spectroscopy to be a 1:1 mixture of **16** and **18**. Fractionation of the mixture by p.l.c. (solvent *B*) gave (*1*) **16**, R_F 0.52 (solvent *B*); ^{13}C-n.m.r. data: δ 98.0 (C-1), 32.9 (C-2), 48.3 (C-3), 72.9 (C-4), 64.4 (C-5), 17.7 (C-6), and 55.1 (MeO-1); and (*2*) **18** as a colourless syrup, $[\alpha]_D^{24}$ −25° (*c* 0.28, methanol), R_F 0.42 (solvent *B*); ^{13}C-n.m.r. data: δ 98.7 (C-1), 27.1 (C-2), 48.3 (C-3), 67.5 (C-4), 62.5 (C-5), 16.6 (C-6), and 55.1 (MeO-1). Mass spectrum: *m/e* 239 (0.3%, $M^+ - 18$), 226 (12, $M^+ - 31$), 225 (22), 207 (15), 199 (4), 183.0490 (20, $C_6H_8F_3NO_2$), 168 (8), 155 (100), 140 (22), 113 (45), 100 (10), 95 (5), 86 (50), 84 (20), 69 (20), 59 (95), and 58 (90); metastables: *m/e* 225→207, 199→155, 155→86, and 113→95.

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