Pergamon

Tetrahedron: *Asymmetry* 11 (2000) 2547–2553

TETRAHEDRON: *ASYMMETRY*

Stereoselective synthesis of (–)-deacetylanisomycin

Pierre Hutin, Mansour Haddad and Marc Larchevêque*

Laboratoire de Synthèse Organique associé au CNRS, ENSCP, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

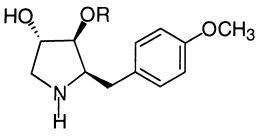
Received 2 May 2000; accepted 26 May 2000

Abstract

A concise synthesis of (–)-deacetylanisomycin has been achieved via the stereocontrolled reductive alkylation of a protected trihydroxynitrile derived from tartaric acid. The resulting aminotriol was selectively *O*-mesylated on the primary hydroxyl group and cyclised in situ to give the target molecule.

1. Introduction

Polyhydroxylated pyrrolidines and piperidines have received much attention since many representatives have been reported to exhibit interesting physiological effects. Among them, (–)-anisomycin **1** is an antibiotic that was first isolated from fermentation broths of *Streptomyces griseolus* and *Streptomyces roseochromogenes* in 1954.[1] The structure and relative stereochemistry of anisomycin were first studied chemically[2] and then determined by X-ray crystallographic analysis.[3] The absolute stereochemistry was established as (2*R*,3*S*,4*S*) by chemical correlation studies.[4] Anisomycin possesses strong and selective activities against pathogenic protozoa and fungi due to the fact that it specifically blocks peptide bond formation on eukariyotic ribosomes.[5] These properties have been used successfully in the clinical treatment of amoebic dysentery and *trichomonas vaginitis*.[6] Both anisomycin and its deacetylated derivative **2** have also been employed as fungicides in the eradication of bean mildew and other fungal plant infections.[7] It was also recently reported that anisomycin and some of its analogues were active against human tumoural cells in vitro,[8] and in 1995 several derivatives were patented due to their improved in vivo stability and activity.[9]



1 R = Ac, (-)-Anisomycin

2 R = H, (-)-Deacetylanisomycin

* Corresponding author. Fax: (33) 1 43 25 79 75; e-mail: larchm@ext.jussieu.fr

0957-4166/00/$ - see front matter
PII: S0957-4166(00)00216-0

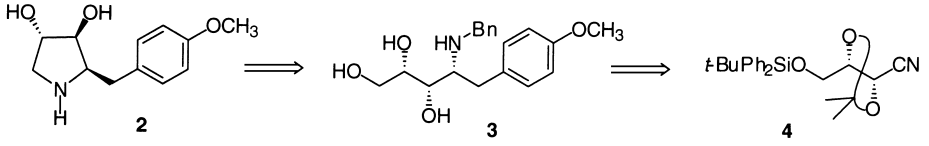
The diverse biological activities of **1** have attracted considerable synthetic interest.[10] In most of the previously reported syntheses, anisomycin was obtained by transformation of **2**,[11d,12] notably via a conformation-controlled regioselective acetylation of its *N*-benzyl derivative.[11b]

Various chiral pool starting materials were used to access deacetylanisomycin. Among them, tartaric acid was especially interesting due to the presence of two hydroxyl groups with the requisite relative stereochemistry.[11] However, the syntheses starting from this compound were frequently non-stereoselective and often proceeded in low overall yields.

We wish to report here a concise synthesis of (–)-deacetylanisomycin based on the stereoselective reductive alkylation of a protected trihydroxynitrile derived from tartaric acid.

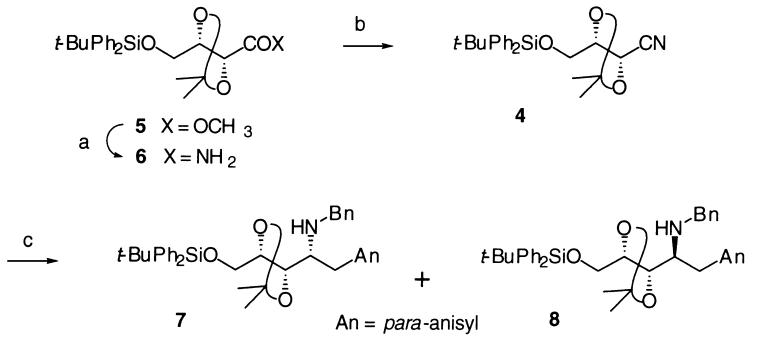
2. Results and discussion

A retrosynthetic analysis indicated that the aminotriol **3** would be a suitable intermediate to access deacetylanisomycin (Scheme 1). We thought that such an aminotriol could be obtained by the addition of the appropriate Grignard reagent to the nitrile **4**, followed by sodium borohydride reduction of the intermediate metalloimine. Such a reductive alkylation was known to give essentially *anti* 2-aminoalcohols when applied to *O*-silylated cyanohydrins.[13] However, we have recently shown that the same reaction applied to *syn* 3-substituted 2,3-dialkoxynitriles afforded the all *syn*-protected aminodiols, mainly.[14]



Scheme 1.

The nitrile **4** was prepared by oxidation of the monosilylated 2,3-*O*-isopropylidenethreitol into the aldehyde, followed by transformation into the nitrile via an oxime.[15] Alternatively, it was obtained by the transformation of the ester **5** (easily prepared in three steps from tartaric acid)[16,17] into primary amide **6** by reaction with ammonia in ethanol, followed by dehydration with a trifluoroacetic anhydride/pyridine mixture (Scheme 2).

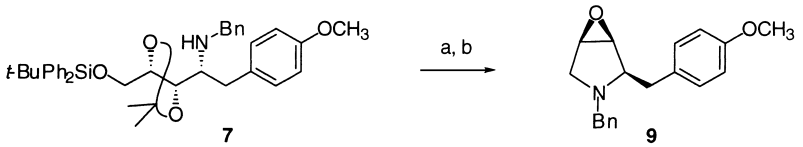


Scheme 2. (a) NH_3/EtOH, 90%; (b) $(CF_3CO_2)_2O$, pyridine, CH_2Cl_2, 87%; (c) (i) 4-MeOBnMgCl, ether; (ii) $BnNH_2$, MeOH; (iii) $NaBH_4$, 80% (**7**+**8**) from **4**

Condensation of 4-methoxybenzylmagnesium chloride with **4** afforded an intermediate metalloimine which was transformed in situ into the primary imine by methanolysis. In order to obtain a *N*-benzylamine directly, the unsubstituted imine was transiminated using benzylamine before reduction.[18] After reaction with sodium borohydride, the *syn* and *anti* diastereomeric *N*-benzylamines **7** and **8** were isolated in an 81:19 ratio with 80% overall yield from **4**.

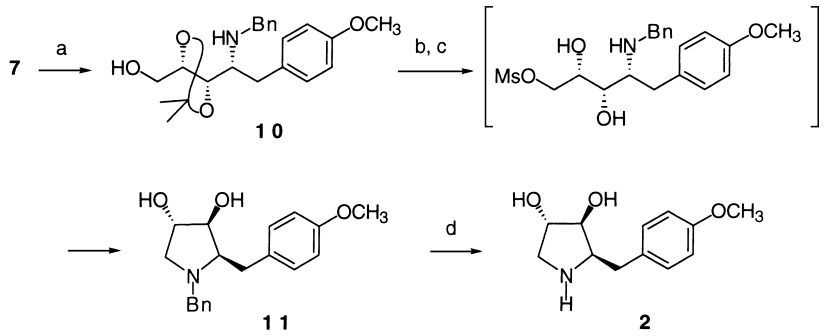
With **7** in hand, we turned our attention towards its ring closure to give the pyrrolidine. To this end, **7** was deprotected by acidic hydrolysis in order to remove both the silylether protection and the acetonide. The resulting *N*-benzyl aminotriol **3** was treated according to two methods. In the first experiment, we attempted to achieve an intramolecular Mitsunobu reaction according to the method previously reported by Vogel.[19]

However, this approach failed to give any cyclised compound. In the second attempt, we tried to transform selectively the primary alcohol into the chloride according to the method described by Appel (triphenylphosphine–carbon tetrachloride).[20] In this case, the major product (obtained in low yield) was identified as the epoxide **9** (Scheme 3). We then decided to use another strategy involving activating the primary alcohol before elimination of the acetonide moiety. First, the amine **7** was desilylated with tetrabutylammonium fluoride to give the compound **10**. This was then regioselectively mesylated on the primary alcohol and the acetonide was then cleaved in an acidic medium. After base treatment, the resulting aminodiol cyclized directly to give *N*-benzyl deacetylanisomycin **11** in 80% overall yield from **10** (Scheme 4). This compound was deprotected by catalytic hydrogenation to give (–)-deacetylanisomycin **2**, the spectral data of which were in all respects identical to those reported.[2,11b]



7 **9**

Scheme 3. (a) 2N HCl, MeOH; (b) $(C_6H_5)_3P$, CCl_4



10 **11** **2**

Scheme 4. (a) Bu_4NF, THF, 80%; (b) MsCl, Et_3N, cat. DMAP, CH_2Cl_2; (c) 10% HCl in THF then $NaHCO_3$, 80% from **10**; (d) H_2, 10% Pd/C, AcOEt, 90%

In summary, this synthesis demonstrates that the reductive alkylation of 2,3-dialkoxynitriles offers efficient access to deacetylanisomycin and could be applied to other polyhydroxylated pyrrolidines.

3. Experimental

Infrared spectra were taken on a FT Nicolet 210 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded at 200 and 50 MHz, respectively, in $CDCl_3$ using a Bruker AC-200 E apparatus. Chemical shifts are expressed in ppm from internal TMS. Flash chromatography was performed using silica gel 60 (Merck, 230–400 mesh). Optical rotations were measured on a Perkin–Elmer 141 polarimeter.

3.1. (4S,5S)-5-tert-Butyl(diphenyl)silyloxymethyl-4-carbamoyl-2,2-dimethyl-1,3-dioxolane **6**

To a solution of methyl *O*-isopropylidene-L-threonate[15] (3.8 g, 20 mmol) in CH_2Cl_2 (100 ml), was added successively triethylamine (4.8 ml, 48 mmol), *tert*-butyldiphenylsilyl chloride (6.6 g, 24 mmol) and 4-dimethylaminopyridine (0.49 g, 4 mmol). The mixture was stirred for 15 h and then concentrated under vacuo. The crude mixture was diluted in Et_2O (100 ml) and washed with 1 M HCl (40 ml). The aqueous layer was extracted with Et_2O (50 ml) and the combined organic layers were washed with saturated $NaHCO_3$, dried over $MgSO_4$ and concentrated. The residue was then placed in a thick flask and diluted in absolute ethanol (150 ml) saturated with NH_3. The flask was corked and allowed to stand at room temperature for 3 days. Excess of the solvent was evaporated and the crude product was purified by flash chromatography (cyclohexane:AcOEt, 60:40) to give the amide **6** (5.05 g, 60%): $[\alpha]_D^{22}$ –12.2 (*c* 5.25, $CHCl_3$); IR (neat) ν_{max} 3430, 3200, 1680 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.08 (s, 9H, $(CH_3)_3$), 1.46 (s, 3H, CH_3), 1.51 (s, 3H, CH_3), 3.9 (dd, J = 3.9 and 11.4 Hz, 1H, CH_2-O), 4.06 (dd, J = 2.2 and 11.4 Hz, 1H, CH_2-O), 4.22 (ddd, J = 2.2, 3.9 and 7.8 Hz, 1H, CH-O), 4.54 (d, J = 7.8 Hz, 1H, CH-O), 6.25 (m, 1H, NH), 6.56 (m, 1H, NH), 7.35–7.45 (m, 6H, Ph), 7.7–7.8 (m, 4H, Ph); ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.4, 26.3, 26.9, 27.1, 63.5, 75.2, 80.3, 110.8, 127.8, 129.8, 133.4, 135.8, 174.1; MS (EI) *m*/*z* 398 (2%), 356 (100%), 199 (50%), 77 (7%), 43 (44%). Anal. calcd for $C_{23}H_{31}NO_4Si$: C, 66.79; H, 7.55; N, 3.39. Found: C, 64.74; H, 7.49; N, 3.30.

3.2. (4S,5S)-5-tert-Butyl(diphenyl)silyloxymethyl-4-cyano-2,2-dimethyl-1,3-dioxolane **4**

To a cooled (–30°C) solution of CH_2Cl_2 (100 ml) containing the amide **6** (5 g, 12.1 mmol) and pyridine (3.9 ml, 48.4 mmol), was added dropwise trifluoroacetic anhydride (3.4 ml, 24.2 mmol) and the mixture was warmed to room temperature with stirring for 4 h. At the end of the reaction, the solvent was removed and the residue was taken up with a mixture of ether:petroleum ether (20:80). The mixture was stirred for 5 min and filtrated. Drying ($MgSO_4$) followed by concentration gave a crude product which was purified by flash chromatography (cyclohexane:AcOEt, 95:5) to give the nitrile **4** (4.17 g, 87%) as a viscous syrup which crystallised upon standing: $[\alpha]_D^{22}$ –2.9 (*c* 2.54, cyclohexane), lit.[15] $[\alpha]_D^{26}$ –3.65 (*c* 2.5, cyclohexane); mp 74–76°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.10 (s, 9H, $(CH_3)_3C$), 1.47 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 3.77 (dd, J = 5.7 and 11 Hz, 1H, CH_2-O), 3.86 (dd, J = 3.8 and 11 Hz, 1H, CH_2-O), 4.5 (dt, J = 3.8 and 5.7 Hz, 1H, CH-O), 4.78 (d, J = 5.7 Hz, 1H, CH-O), 7.4–7.5 (m, 6H, Ph), 7.65–7.75 (m, 4H, Ph); ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.3, 25.2, 26.8, 26.9, 62.9, 65.2, 80.4, 113.2, 118.4, 128.0, 128.1, 130.1, 130.2, 132.8, 135.6, 135.7; MS (EI) *m*/*z* 380 (5%), 338 (31%), 250 (100%), 239 (7%), 91 (13%), 77 (7%), 57 (8%), 43 (22%).

3.3. (2S,3S,4R)-4-Benzylamino-1-O-tert-butyl(diphenyl)silyl-2,3-O-isopropylidene-5-(4-methoxyphenyl)pentan-1,2,3-triol 7

Nitrile **4** (1.98 g, 5 mmol) was placed in anhydrous Et_2O (40 ml) and cooled to –13°C. A 1.25 M solution of 4-methoxybenzylmagnesium chloride in THF (6 ml, 7.5 mmol) was added dropwise and the reaction was allowed to warm to room temperature. Stirring was continued for 4 h before being cooled to –13°C. Anhydrous methanol (10 ml) and benzylamine (1.1 ml, 10 mmol) were added successively and the mixture was stirred for 45 min at room temperature. Sodium borohydride (380 mg, 10 mmol) was then added. The resultant mixture was stirred overnight and water (50 ml) was added. The mixture was extracted with Et_2O (3×60 ml, and the combined organic layers were washed with brine. After usual work-up, the residue was subjected to column chromatography (cyclohexane:AcOEt, 90:10) to give the amine **7** (1.80 g, 60%) as the major isomer: $[\alpha]_D^{22}$ –17.3 (*c* 2.38, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (s, 9H, $(CH_3)_3C$), 1.38 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 2.73 (dd, J=7.7 and 12.8 Hz, 1H, CH_2-Ph), 2.84 (ddd, J=2.8, 6.2 and 7.7 Hz, 1H, CH-N), 2.93 (dd, J=6.2 and 12.8 Hz, 1H, CH_2-Ph), 3.60 (dd, J=4 and 10.9 Hz, 1H, CH_2-O), 3.65 (dd, J=4.9 and 10.9 Hz, 1H, CH_2-O), 3.77 (d, J=13.2 Hz, 1H, CH_2-N), 3.78 (s, 3H, CH_3-O), 3.89 (d, J=13.2 Hz, 1H, CH_2-N), 4.07 (dd, J=2.8 and 7.9 Hz, 1H, CH-O), 4.28 (m, 1H, CH-O), 6.79 (d, J=8.6 Hz, 2H, Ph), 7.08 (d, J=8.6 Hz, 2H, Ph), 7.2–7.4 (m, 11H, Ph), 7.55 (m, 4H, Ph); ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.2, 26.7, 27.2, 27.4, 37.2, 51.8, 55.2, 58.6, 64.3, 77.5, 78.7, 108.6, 114.0, 126.9, 127.7, 128.1, 128.3, 129.7, 130.3, 131.4, 133.2, 133.3, 135.7, 140.9, 158.0; MS (CI, NH_3) m/z 610 (MH^+, 100%), 488 (35%). Anal. calcd for $C_{38}H_{47}NO_4Si$: C, 74.84; H, 7.77; N, 2.30. Found: C, 74.29; H, 7.98; N, 2.22.

3.4. (2S,3S,4R)-4-Benzylamino-2,3-O-isopropylidene-5-(4-methoxyphenyl)pentan-1,2,3-triol **10**

To a stirred solution of compound **7** (3.6 g, 5.90 mmol) in THF (50 ml) at 23°C was added a 1 M solution of tetrabutylammonium fluoride in THF (8.85 ml, 8.85 mmol). The mixture was stirred 3 h before being diluted with water (75 ml). The product was extracted with ethyl acetate (2×50 ml), dried over $MgSO_4$, and the solvent was evaporated in vacuo. Flash chromatography (cyclohexane:AcOEt, 60:40) yielded the title compound (1.75 g, 80%) as a white solid: $[\alpha]_D^{22}$ +46 (*c* 1.05, CH_2Cl_2); mp 82–83°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.42 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 2.43 (dd, J=11.6 and 14.4 Hz, 1H, CH-Ph), 3.10–3.20 (m, 2H, CH-Ph and CH-N), 3.55 (dd, J=8.6 and 10.7 Hz, 1H, CH_2-N), 3.66 (dd, J=13.1 Hz, 1H, CH_2-N), 3.80 (s, 3H, CH_3-O), 3.86 (dd, J=3.6 and 10.7 Hz, 2H, CH-O), 3.99 (dd, J=3.5 and 8.6 Hz, 1H, CH-O), 4.09 (dt, J=3.6 and 8.6 Hz, 1H, CH-O), 6.80 (d, J=6.56 Hz, 2H, Ph), 6.81–6.98 (m, 4H, Ph), 7.20–7.22 (m, 3H, Ph); ^{13}C NMR (50 MHz, $CDCl_3$) δ 26.8, 34.5, 52.4, 55.1, 57.9, 62.8, 76.1, 81.0, 108.2, 114.1, 127.2, 128.0, 128.4, 129.7, 129.8, 138.3, 158.3; MS (CI, NH_3) m/z 372 (MH^+, 100%). Anal. calcd for $C_{22}H_{29}NO_4$: C, 71.14; H, 7.86; N, 3.77. Found: C, 71.01; H, 7.95; N, 3.60.

3.5. (2R,3S,4S)-N-Benzyl-3,4-dihydroxy-2-(4-methoxybenzyl)pyrrolidine **11**

Alcohol **10** (1.86 g, 5 mmol), triethylamine (1.4 ml, 10 mmol) and 4-dimethylaminopyridine (30 mg, 0.25 mmol) were dissolved in anhydrous CH_2Cl_2 (40 ml), and the mixture was cooled to 0°C under argon. Mesyl chloride (0.39 ml, 5 mmol) was added dropwise. The mixture was stirred at room temperature for 4 h, and another amount of mesyl chloride (0.195 ml, 2.5 mmol) was added. The solution was stirred for 12 h, and water (50 ml) was added. The organic phase was

separated and washed with brine (30 ml), dried ($MgSO_4$), and the solvent was evaporated to give the expected *O*-mesylated intermediate as a colourless oil which was used in the next step without purification. Thus, the crude product was diluted in THF (30 ml) in the presence of 10% HCl (20 ml) and refluxed for 12 h. After cooling to 0°C, the solution was basified (pH = 10), and the mixture was stirred for 2 h. The solution was extracted with CH_2Cl_2 (2×40 ml) and the organic extract dried ($MgSO_4$) and evaporated in vacuo. The residue obtained was finally purified by flash chromatography (CH_2Cl_2:MeOH, 90:10) to give a solid (1.25 g, 80%): $[\alpha]_D^{22}$ –82.1 (*c* 1.13, CH_2Cl_2); mp 81–82°C (lit.[11a] mp 80–82°C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.16 (dd, J = 3.8 and 10.9 Hz, 1H, CH-N), 2.80–2.95 (m, 3H, CH-N and CH_2-Ph), 3.35 and 4.12 (dd AB system, J = 12.9 Hz, 2H, CH_2-Ph), 3.37 (dd, J = 6.2 and 10.9 Hz, 1H, CH-N), 3.62–3.65 (m, 1H, CH-O), 3.78 (s, 3H, CH_3-O), 4.05–4.09 (m, 1H, CH-O), 6.83 (d, J = 8.7 Hz, 2H, Ph), 7.22 (d, J = 8.7 Hz, 2H, Ph), 7.24–7.34 (m, 5H, Ph); ^{13}C NMR (50 MHz, $CDCl_3$) δ 32.6, 55.10, 58.2, 59.8, 68.0, 75.6, 78.2, 113.8, 127.2, 128.3, 129.0, 130.1, 131.0, 137.9, 157.9; MS (CI, NH_3) m/z 192 (14.8%), 314 (MH^+, 100%); MS (EI) m/z 380 (5%), 338 (31%), 250 (100%), 239 (7%), 91 (13%), 77 (7%), 57 (8%), 43 (22%).

3.6. (2R,3S,4S)-3,4-Dihydroxy-2-(4-methoxybenzyl)pyrrolidine, (–)-deacetylanisomycin **2**

The pyrrolidine **11** (625 mg, 2 mmol) was dissolved in absolute ethanol (30 ml) containing palladium on activated carbon (10%) as catalyst (100 mg) and hydrogenated at atmospheric pressure for 15 h. The catalyst was removed by filtration through Celite and the solvent was evaporated to dryness to give **2** as a solid (400 mg, 90%): $[\alpha]_D^{22}$ –29 (*c* 1.25, EtOH), lit.[21]: $[\alpha]_D^{20}$ –20 (*c* 1.0, EtOH); mp 173–174°C (lit.[11d] mp 176–177°C); ^{1}H NMR (400 MHz, CD_3OD) δ 2.54 (dd, J = 1.8 and 12.3 Hz, 1H, CH-N), 2.72 (dd, J = 6.6 and 13.5 Hz, 1H, CH-Ph), 2.89 (dd, J = 8.2 and 13.5 Hz, 1H, CH-Ph), 3.18–3.22 (m, 1H, CH-N), 3.28 (dd, J = 5.6 and 12.4 Hz, 1H, CH-N), 3.71 (d, J = 2.8 Hz, 1H, CH-O), 3.75 (s, 3H, CH_3-O), 4.07 (d, J = 5.3 Hz, 1H, CH-O), 4.87 (s, 3H, NH, OH), 6.73 (d, J = 8.7 Hz, 2H, Ph), 7.10 (d, J = 8.7 Hz, 2H, Ph); ^{13}C NMR (50 MHz, CD_3OD) δ 34.4, 53.5, 55.6, 64.2, 78.0, 78.6, 114.8, 131.0, 132.9, 159.6; MS (CI, NH_3) m/z 224 (MH^+, 100%), 206 (12%), 188 (26%).

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