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Short Report

Synthesis of *N*-Methyl-*N*-formyltyramine, a New β-Phenethylamide Derivative Isolated from *Cyathobasis fruticulosa* (Bunge) Aellen

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Este trabalho descreve a síntese da *N*-metil-*N*-formiltiramina, um novo derivado β-fenetilamídico isolado de *Cyathobasis fructiculosa* (Bunge) Aellen. O produto natural foi preparado em seis etapas com bom rendimento, partindo-se do 4-hidroxibenzaldeído.

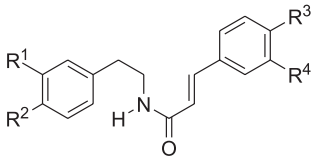
The synthesis of *N*-methyl-*N*-formyltyramine, a novel β-phenethylamide derivative isolated from *Cyathobasis fructiculosa* (Bunge) Aellen, is reported. The natural product was prepared in six steps and good overall yield from 4-hydroxybenzaldehyde.

Keywords: synthesis, β-phenethylamide derivative, *Cyathobasis fructiculosa*, natural product

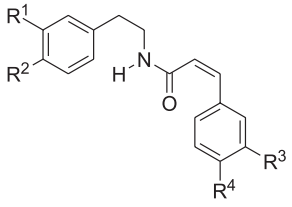
Introduction

β-Phenethylamides, exemplified by compounds **1** and **2**,[1] constitute a relatively widespread family of natural products, the members of which have been found mainly as soluble constituents of cell-wall fractions of higher plants.[2] Several amides, structurally related to them, have been found in different plant species,[3] and *N-trans*-feruloyltyramine (**3**) has demonstrated to have an ubiquitous occurrence.[4,5]

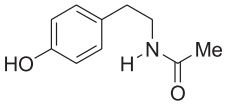
There is no definite conclusion yet about the functions of the β-phenethylamides; however, it has been discussed their possible role in plant growth processes, as well as their participation in self defense, due to their antimicrobial and antiviral effects.[6] In addition, β-phenethylamides such as **4**-**7** have been informed to display interesting biological activities, ranging from DNA strand scission[7] to anti-mutagenic and anticarcinogenic,[8] and including inhibition of the lipopolysaccharide-induced nitric oxide production in macrophages,[9] as well as inhibition of acetyl-cholinesterase.[10] Noteworthy, *N*-acetyl tyramine (**8**) is an inducible phytoalexin found in soybean seeds,[11] while Paik and coworkers reported the isolation of the unusual compounds **9**-**11** from *Xenorhabdus nematophilus*, a bacterial strain which grows symbiotic with a nematode. These β-phenethylamides were shown to be cytotoxic against five human cancer cell lines.[12]



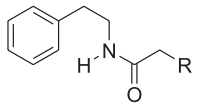
1 R^1= R^2= H, R^3-R^4= OCH_2O
3 R^1= H, R^2= R^3= OH, R^4= OMe
5 R^1= R^4= OMe, R^2= R^3= OH
7 R^1= R^4= H, R^2= R^3= OH



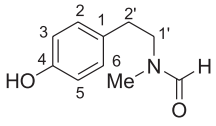
2 R^1= R^2= H, R^3-R^4= OCH_2O
4 R^1= H, R^2= R^4= OH, R^3= OMe
6 R^1= R^3= OMe, R^2=R^4= OH



8



9 R= Ph
10 R= Et
11 R= $CHMe_2$



12

Very recently, Topçu and coworkers[13] isolated *N*-methyl-*N*-formyltyramine (**12**) from the aerial parts and roots of *Cyathobasis fruticulosa* (Bunge) Aellen (Chenopodiaceae), the only species of the genus *Cyathobasis* of the Turkish flora, which grows most commonly in Central Anatolia. In view of the potential interest of this type of compounds, we decided to prepare **12**, and herein we disclose a short synthesis of the natural product from commercial 4-hydroxybenzaldehyde (**13**).

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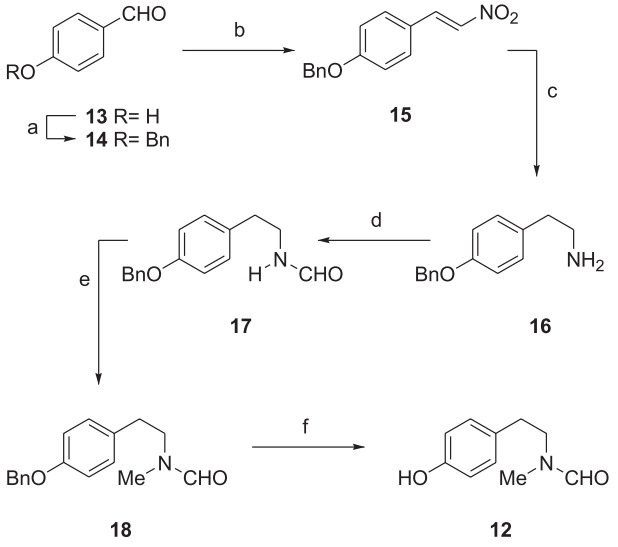
Results and Discussion

Williamson etherification of **13** with benzyl chloride provided 99% of aldehyde **14** (Scheme), which was subjected to a Henry condensation with nitromethane in the presence of ethylenediammonium diacetate as base,[14] furnishing 90% of nitrostyrene **15**. In turn, this was submitted to reduction with lithium aluminum hydride, giving β-phenethylamine **16**, as an oil which easily darkened upon contact with air; therefore, this was immediately amidated in refluxing ethyl formate, providing formamide **17** in 44% overall yield. Noteworthy, the ^{1}H and ^{13}C NMR spectra of **17** exhibited signals of two conformers, even at 70 ºC in DMSO-d_6.



Scheme. a: BnCl, K_2CO_3, EtOH, reflux (99%); b: $MeNO_2$, $(H_3NCH_2CH_2NH_3)^{++}$. $2AcO^-$, ^{t}BuOH, 60 ºC, 18 h (90%); c: $LiAlH_4$, THF, reflux, 3 h; d: HCO_2Et, reflux, 8 h (44%, 2 steps); e: 1. NaH, DMF, 65 ºC, 10 min; 2. MeI, 45 ºC (79%); f: H_2, 1 atm, 10% Pd/C, 4 h (92%).

Next, **17** was *N*-methylated with methyl iodide, and the resulting amide **18** obtained in 79% yield was subjected to a final 10% Pd/C mediated catalytic hydrogenation, furnishing 92% of synthetic **12**, the spectral data of which fully agreed with those previously reported for the natural product.[13] Clear signals of the two conformers of **12** and **18** were also observed in their ^{1}H and ^{13}C NMR spectra. Interestingly, despite that the use of benzyl ether intermediates required additional protection and deprotection steps, increasing the length of the sequence, it allowed convenient manipulation of amine and amide reaction intermediates.

In conclusion, a simple synthesis of **12** was achieved in six steps from commercial 4-hydroxybenzaldehyde. Protection of the starting phenol as a benzyl ether allowed convenient manipulation of the reaction intermediates without sacrificing efficiency of the synthetic sequence.

Experimental

General procedures

Melting points (uncorrected) were taken on an Ernst Leitz Wetzlar model 350 hot-stage microscope. FT-IR spectra were determined with a Shimadzu IR Prestige 21 spectrophotometer. The ^{1}H and ^{13}C NMR spectra were acquired in $CDCl_3$ employing TMS as internal standard, with a Bruker AC200-E spectrometer operating at 200.13 and 50.33 MHz, respectively; coupling constants (*J*) are expressed in Hertz. HRMS data were obtained from Kent Electronics (UK). The reactions were carried out under dry argon atmospheres, employing oven-dried glassware. All new compounds gave single spots on TLC plates run in different hexane-EtOAc solvent systems. Spots were visualized by exposure to UV light (254 and 365 nm), followed by spraying with ethanolic *p*-anisaldehyde/sulfuric acid reagent and careful heating. Flash column chromatographies were carried out with silica gel 60 H, eluting with hexane-EtOAc mixtures under positive pressure and employing gradient techniques.

*E-1-Benzyloxy-4-(2'-nitrovinyl)-benzene (**15**)*

Benzyl chloride (0.52 mL, 4.54 mmol) was added to a stirred suspension of 4-hydroxybenzaldehyde (**13**, 482 mg, 3.95 mmol) and K_2CO_3 (818 mg, 5.92 mmol) in absolute EtOH (4 mL). The slurry was refluxed until complete consumption of the starting material (by TLC), and the solvent was then evaporated under reduced pressure. After addition of H_2O (5 mL), the aqueous phase was extracted with EtOAc (3 x 25 mL) and the combined organic extracts were successively washed with 10% Na_2CO_3 (2 x 10 mL) and brine (10 mL). The organic phase was dried (Na_2SO_4), concentrated *in vacuo* and chromatographed, to give **14** (830 mg, 99%), as a solid; mp 66-68 ºC (lit. 72 ºC);[15] IR (KBr) ν_{max}/cm^{-1}: 3034, 2830, 2740, 1690, 1600, 1577, 1508, 1454, 1312, 1258, 1160, 1022, 1005, 830, 738, 697; ^{1}H NMR δ 5.15 (s, 2H, $C_6H_5CH_2O$-), 7.07 (d, *J* 8.6, 2H, H-3 and H-5), 7.33-7.45 (m, 5H, $C_6H_5CH_2O$-), 7.83 (d, *J* 8.6, 2H, H-2 and H-6), 9.88 (s, 1H, C*H*O); ^{13}C NMR δ 70.2 ($C_6H_5CH_2O$-), 115.1 (C-3 and C-5), 127.4 (*m*-$C_6H_5CH_2O$-), 128.2 (*p*-$C_6H_5CH_2O$-), 128.6 (*o*-$C_6H_5CH_2O$-), 130.1 (*C*-1), 131.9 (C-2, and C-6), 135.9 (*ipso*-$C_6H_5CH_2O$-), 163.6 (*C*-4), 190.6 (Ar*C*HO). Without further purification, a solution of aldehyde **14** (258 mg, 1.21 mmol), $MeNO_2$ (0.2 mL, 3.64 mmol) and anhydrous $[NH_3CH_2CH_2NH_3]^{2+}$. $2AcO^-$ (22 mg, 0.12 mmol) in dry ^{t}BuOH (3.7 mL) was heated at 65 ºC. After 18 h, the mixture was diluted with EtOAc (40 mL) and successively washed with water (3 x 15 mL) and brine

(2 x 15 mL). The organic phase was dried (Na_2SO_4), most of the solvent was removed under reduced pressure, and the resulting yellow solution was crystallized on settling, affording nitrostyrene derivative **15** (249 mg, 90%), as a solid; mp 116-118 ºC (lit. 120 ºC, EtOH);[15] IR (KBr) ν_{max}/cm^{-1}: 3109, 2941, 2875, 2217, 1600, 1509, 1492, 1341, 1252, 1175, 1003, 969, 828, 752, 699; ^{1}H NMR δ 5.13 (s, 2H, $C_6H_5CH_2O$-), 7.03 (d, *J* 8.8, 2H, H-3 and H-5), 7.30-7.43 (m, 5H, $C_6H_5CH_2O$-), 7.51 (d, *J* 8.6, 2H, H-2 and H-6), 7.52 (d, *J* 13.4, 1H, ArCH=C*H*NO$_2$), 7.98 (d, *J* 13.4, 1H, ArC*H*=CHNO$_2$); ^{13}C NMR δ 70.1 ($C_6H_5CH_2O$-), 115.7 (C-3 and C-5), 122.7 (*C*-1), 127.3 (*m*-$C_6H_5CH_2O$-), 128.2 (*p*-$C_6H_5CH_2O$-), 128.6 (*o*-$C_6H_5CH_2O$-), 131.1 (C-2 and C-6), 135.0 (Ar*C*H=CHNO$_2$), 135.9 (*ipso*-$C_6H_5CH_2O$-), 138.8 (ArCH=*C*HNO$_2$), 161.9 (*C*-4); HRMS (CI) Found: 256.09755 (M$^+$ + 1). Calc. for $C_{15}H_{14}NO_3$: 256.09736.

*N-[2'-(4-Benzyloxyphenyl)-ethyl]-formamide (**17**)*

A solution of nitrostyrene **15** (128 mg, 0.497 mmol) in THF (0.5 mL) was introduced *via* cannula during 5 min into an ice-cooled suspension of $LiAlH_4$ (113 mg, 2.98 mmol) in THF (1.5 mL). The system was submitted to reflux for 3 h, then cooled to room temperature and treated with $Na_2SO_4.10H_2O$. The slurry was diluted with Et_2O (40 mL) and the resulting ethereal suspension was filtered trough Celite. Solvent removal under reduced pressure furnished crude amine **16**, as a yellowish oil. IR (film) ν_{max}/cm^{-1}: 3361, 3033, 2927, 2865, 1610, 1511, 1454, 1381, 1241, 1177, 1026, 829, 739, 697; ^{1}H NMR δ 1.93 (bs, 2H, N*H*$_2$ *J* 6.8, 2H, ArC*H*$_2$CH$_2$N), 2.92 (t, *J* 6.8, 2H, ArCH$_2$C*H*$_2$N), 5.04 (s, 2H, $C_6H_5CH_2O$-), 6.92 (d, *J* 8.5, 2H, H-2 and H-6), 7.11 (d, *J* 8.5, 2H, H-3 and H-5), 7.31-7.41 (m, 5H, $C_6H_5CH_2O$-); ^{13}C NMR δ 38.6 (Ar*C*H$_2$CH$_2$N), 43.2 (ArCH$_2$*C*H$_2$N), 69.8 ($C_6H_5CH_2O$-), 114.7 (C-3 and C-5), 127.3 (*m*-$C_6H_5CH_2O$-), 127.7 (*p*-$C_6H_5CH_2O$-), 128.4 (*o*-$C_6H_5CH_2O$-), 129.6 (C-2 and C-6), 131.7 (C-1), 136.9 (*ipso*-$C_6H_5CH_2O$-), 157.1 (C-4). Without further purification, the crude amine **16** (112 mg, 0.443 mmol) was dissolved in freshly distilled HCO_2Et (3 mL), and was refluxed until complete consumption of the starting amine. The solvent was removed under vacuum, and the oily residue was chromatographed to give formamide derivative **17** (51 mg, 44%), as a white solid; mp 99-101 ºC; IR (KBr) ν_{max}/cm^{-1}: 3231, 3035, 2928, 2886, 1653, 1510, 1379, 1232, 1111, 1010, 959, 821, 753, 699, 563; ^{1}H NMR δ major conformer 2.78 (t, *J* 6.7, 2H, ArCH$_2$CH$_2$N), 3.54 (t, *J* 6.7, 2H, ArCH$_2$CH$_2$NH), 5.05 (s, 2H, $C_6H_5CH_2O$-), 5.46 (bs, 1H, NHCHO), 6.93 (d, *J* 8.6, 2H, H-2 and H-6), 7.11 (d, *J* 8.6, 2H, H-3 and H-5), 7.31-7.44 (m, 5H, $C_6H_5CH_2O$-), 8.13 (s, 1H, -NHCHO); ^{13}C NMR δ 34.4 (Ar*C*H$_2$CH$_2$N), 39.1 (ArCH$_2$*C*H$_2$N), 69.9 ($C_6H_5CH_2O$-), 114.9 (C-3 and C-5), 127.3 (*m*-$C_6H_5CH_2O$-), 127.8 (*p*-$C_6H_5CH_2O$-), 128.4 (*o*-$C_6H_5CH_2O$-), 129.5 (C-2 and C-6), 131.7 (*C*-1), 136.9 (*ipso*-$C_6H_5CH_2O$-), 157.4 (*C*-4), 169.9 (NH*C*HO); HRMS (CI) Found: 256.13390 (M$^+$ + 1). Calc. for $C_{16}H_{18}NO_2$: 256.13375.

*N-[2'-(4-Hydroxy-phenyl)-ethyl]-N-methyl-formamide (N-methyl-N-formyltyramine, **12**)*

Anhydrous DMF (1.0 mL) was added to a 50% NaH dispersion in mineral oil (10 mg, 0.207 mmol), and the system was heated 10 min at 65 ºC, and cooled to room temperature. Then, a solution of formamide **17** (44 mg, 0.172 mmol) in DMF (1.0 mL) was introduced, the system was warmed to 65-70 ºC for 10 min, cooled to -10 ºC, and treated with MeI (38 μL, 0.602 mmol). The reaction was warmed to 45 ºC until complete consumption of the starting material; brine (5 mL) was added and the reaction product was extracted with Et_2O (5 x 10 mL). Drying (Na_2SO_4) and concentration of the organic phase, followed by flash chromatography furnished **18** (37 mg, 79%), as a yellowish waxy solid; mp 56-58 ºC; IR (KBr) ν_{max}/cm^{-1}: 2929, 2855, 1675, 1515, 1455, 1397, 1242, 1179, 1016, 819, 746, 698; ^{1}H NMR δ *Z*-form 2.74-2.81 (m, 2H, ArC*H*$_2$CH$_2$N), 2.84 (s, 3H, NC*H*$_3$), 3.53 (t, *J* 6.9, 1H, ArCH$_2$C*H*$_2$N), 5.03 (s, 2H, $C_6H_5CH_2O$-), 6.91 (m, 2H, H-3 and H-5), 7.14 (d, *J* 8.6, 2H, H-2 and H-6), 7.31-7.45 (m, 5H, $C_6H_5CH_2O$-), 8.01 (s, 1H, -NC*H*O); *E*-form 2.74-2.81 (m, 2H, ArC*H*$_2$CH$_2$N), 2.88 (s, 3H, NC*H*$_3$), 3.43 (t, *J* 6.8, 2H, ArCH$_2$C*H*$_2$N), 5.03 (s, 2H, $C_6H_5CH_2O$-), 6.91 (m, 2H, H-3 and H-5), 7.04 (d, *J* 8.6, 2H, H-2 and H-6), 7.31-7.45 (m, 5H, $C_6H_5CH_2O$-), 7.80 (s, 1H, NC*H*O); ^{13}C NMR δ *Z*-form 32.3 (C-2'), 35.0 (N*C*H$_3$), 46.1 (C-1'), 70.1 ($C_6H_5CH_2O$-), 114.9 (C-3 and C-5), 127.3 (*m*-$C_6H_5CH_2O$-), 127.8 (*p*-$C_6H_5CH_2O$-), 128.4 (*o*-$C_6H_5CH_2O$-), 129.6 (C-2 and C-6), 130.8 (C-1), 136.9 (*ipso*-$C_6H_5CH_2O$-), 157.4 (C-4), 162.3 (N*C*HO); *E*-form 29.7 (C-2'), 33.9 (N*C*H$_3$), 51.4 (C-1'), 70.1 ($C_6H_5CH_2O$-), 115.1 (C-3 and C-5), 127.3 (*m*-$C_6H_5CH_2O$-), 127.8 (*p*-$C_6H_5CH_2O$-), 128.4 (*o*-$C_6H_5CH_2O$-), 129.6 (C-2 and C-6), 129.9 (C-1), 137.0 (*ipso*-$C_6H_5CH_2O$-), 157.6 (C-4), 162.5 (N*C*HO). Without further purification, **18** (45 mg, 0.168 mmol) was dissolved in EtOH (5.7 mL), 10% Pd/C (9 mg) was added, and the black suspension was vigorously stirred 4 h under a H_2 atmosphere. The catalyst was removed by filtration trough a short pad of Celite, the filtrate was concentrated under vacuum and chromatographed affording **12** (28 mg, 92%), as a solid; mp 111-113 ºC ($CHCl_3$) [lit. 112-114 ºC (MeOH)];[13] IR (KBr) ν_{max}/cm^{-1}: 3141, 3135, 2945, 2924, 2882, 1657, 1652, 1614, 1595, 1509, 1446, 1394, 1239,

1172, 1072, 816, 768, 655; ^{1}H NMR δ *Z*-form 2.71-2.80 (m, 2H, ArC*H*$_2$CH$_2$N), 2.86 (s, 3H, NC*H*$_3$), 3.55 (t, *J* 7.1, 2H, ArCH$_2$C*H*$_2$N), 6.75 (d, *J* 8.2, 2H, H-3 and H-5), 6.92 (t, *J* 8.2, 2H, H-2 and H-6), 7.97 (s, 2H, ArOH and NC*H*O); *E*-form 2.71-2.80 (m, 2H, ArC*H*$_2$CH$_2$N), 2.90 (s, 3H, NC*H*$_3$), 3.42 (t, *J* 6.5, 2H, ArCH$_2$C*H*$_2$N), 6.72 (d, *J* 8.0, 2H, H-3 and H-5), 7.03 (t, *J* 8.0Hz, 2H, H-2 and H-6), 7.66 (s, 1H, NC*H*O), 7.97 (s, 2H, ArOH and NC*H*O); ^{13}C NMR δ *Z*-form 32.0 (C-2'), 34.9 (NCH$_3$), 45.9 (C-1'), 115.4 (C-3 and C-5), 129.0 (C-1), 129.5 (C-2 and C-6), 155.2 (C-4), 162.8 (N*C*HO); *E*-form 29.9 (C-2'), 33.4 (N*C*H$_3$), 51.7 (C-1'), 115.7 (C-3 and 5), 128.2 (C-1), 129.6 (C-2 and C-6), 155.3 (C-4), 163.2 (-N*C*HO); HRMS (CI) Found: 180.10254 (M^+ + 1). Calc. for $C_{10}H_{14}NO_2$: 180.10245.

Acknowledgments

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