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Preparative Synthesis of 3- and 4-(3-Alkoxy-4-acyloxyphenylmethylamino)benzoic Acids

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Abstract—Reduction of 3- and 4-[(3-alkoxy-4-acyloxyphenyl)methylideneamino]benzoic acids (*E* isomers) with sodium triacetoxyhydridoborate in benzene gave the corresponding 3- and 4-(3-alkxy-4-acyloxyphenylmethyl)benzoic acids in preparative yields.

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We previously reported on the synthesis of *E*-isomeric 3- and 4-[(3-alkoxy-4-acyloxyphenyl)methylideneamino]benzoic acids (Schiff bases **I**) by condensation of 3- and 4-aminobenzoic acids with esters derived from vanillin and vanillal [1, 2]. We now report on the reduction of compounds **I** with sodium triacetoxyhydridoborate in boiling benzene. The reactions were complete in 0.5–1 h, and the corresponding aromatic amino acids **II**–**V** were isolated in almost quantitative yield (91–94%). Mild temperature conditions of the reduction process and moderate acidity [3] allowed us to avoid side reduction or hydrolysis of the ester groups.

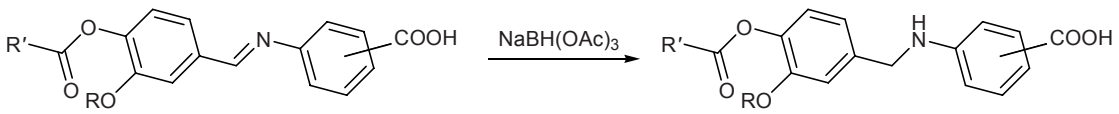
The structure of compounds **II**–**V** was confirmed by elemental analysis, IR and ^{1}H NMR spectra, and alkalimetric determination of molecular weight. According to the ^{1}H NMR data, the purity of the isolated products was 97 ± 1%. The IR and ^{1}H NMR spectra of amino acids **IIa**–**IIu**, **IIIa**–**IIIi**, **IVa**–**IVu**, and **Va**–**Vi** contained absorption bands and resonance signals indicating the presence of the corresponding ester groups in their molecules [1, 2, 4]. The nitro groups in compounds **IIu** and **IVu** gave rise to characteristic absorption bands in the IR spectra at 1533–1540 and 1348–1346 cm^{-1}. The IR spectra of all compounds **II**–**V** lack absorption band in the region 1631–1624 cm^{-1}, which are typical of C=N bond in initial Schiff bases **I** [4].

In the ^{1}H NMR spectra of **IIa**–**IIu** and **IVa**–**IVu**, protons in the methoxy group resonated as a singlet at δ 3.74–3.80 ppm, while protons in the ethoxy groups of **IIIa**–**IIIi** and **Va**–**Vi** gave rise to a triplet at δ 0.90–1.30 ppm (CH_3) and a quartet at δ 3.80–4.20 ppm (CH_2). Signals from the CH_2N protons were broadened singlets in the region δ 4.20–4.50 ppm, and aromatic proton signals were located in the region δ 6.80–8.00 ppm. No signals were observed in the ^{1}H NMR spectra of **II**–**V** at δ 8.45–8.50 ppm, i.e., in the region typical of HC=N proton of initial compounds **I** [4].

EXPERIMENTAL

The IR spectra were recorded in KBr on a Nicolet Protégé-460 spectrometer with Fourier transform. The ^{1}H NMR spectra were measured on a Tesla BS-587A

Scheme 1.



I **IIa–IIu**, **IIIa–IIIi**, **IVa–IVu**, **Va–Vi**

II, **III**, C_6H_4-3-COOH; **IV**, **V**, C_6H_4-4-COOH; **II**, **IV**, R = Me, R′ = Me (**a**), Et (**b**), Pr (**c**), *i*-Pr (**d**), $Me(CH_2)_6$ (**e**), $Me(CH_2)_8$ (**f**), $Me(CH_2)_{11}$ (**g**), $Me(CH_2)_{16}$ (**h**), H_2C=CH (**i**), H_2C=C(Me) (**j**), $PhCH_2$ (**k**), $MeCH(Ph)CH_2$ (**l**), 4-$MeC_6H_4O(CH_2)_2$ (**m**), Ph (**n**), 4-MeC_6H_4 (**o**), 2-ClC_6H_4 (**p**), 4-ClC_6H_4 (**q**), 2,4-$Cl_2C_6H_3$ (**r**), 2,4-$Cl_2C_6H_3OCH_2$ (**s**), 4-BrC_6H_4 (**t**), 3-$O_2NC_6H_4$ (**u**); **III**, **V**, R = Et, R′ = Me (**a**), Et (**b**), Pr (**c**), *i*-Pr (**d**), Me_2CHCH_2 (**e**), Ph (**f**), 4-MeC_6H_4 (**g**), 2-ClC_6H_4 (**h**), 4-ClC_6H_4 (**i**).

spectrometer (operating frequency 100 MHz) from 5% solutions in DMSO-d_6 using tetramethylsilane as internal reference. The molecular weights were determined by alkalimetric titration of carboxy groups with a 0.1 N solution of sodium hydroxide in the presence of phenolphthalein as indicator.

3- and 4-(3-Alkoxy-4-acyloxyphenylmethylamino)benzoic acids IIa–IIu, IIIa–IIIi, IVa–IVu, and Va–Vi (*general procedure***).** A solution of 5 mmol of the corresponding Schiff base **I**, 10 mmol of $NaBH_4$, and 30 mmol of glacial acetic acid in 50 ml of anhydrous benzene was heated for 0.5–1 h under reflux. The hot solution was filtered, the filtrate was cooled and left to stand for 10–15 h at 23–25°C, and the precipitate was filtered off, washed with a small amount of benzene, dried in air, and purified by recrystallization from benzene.

IR spectra of **II–V**, ν, cm^{-1}: 3650–2000 (several bands, OH); 3406–3376 (N–H); 3100–3000, 880–600 (C–H_{arom}); 2990–2840 (C–H_{aliph}); 1770–1714 (C=O, ester); 1690–1650 (C=O, acid); 1607–1380 (C=C_{arom}); 1290–1000 (C–O).

3-(4-Acetyloxy-3-methoxyphenylmethylamino)benzoic acid (IIa). Yield 91%, mp 142–143°C (from benzene). Found, %: C 65.03; H 5.49; N 4.12. *M* 316.1. $C_{17}H_{17}NO_5$. Calculated, %: C 64.75; H 5.43; N 4.44. *M* 315.3.

3-(3-Methoxy-4-propionyloxyphenylmethylamino)benzoic acid (IIb). Yield 92%, mp 132–133°C (from benzene). Found, %: C 65.88; H 5.95; N 4.03. *M* 327.8. $C_{18}H_{19}NO_5$. Calculated, %: C 65.64; H 5.81; N 4.25. *M* 329.4.

3-(4-Butanoyloxy-3-methoxyphenylmethylamino)benzoic acid (IIc). Yield 91%, mp 93–94°C (from benzene). Found, %: C 66.85; H 6.29; N 3.90. *M* 344.0. $C_{19}H_{21}NO_5$. Calculated, %: C 66.46; H 6.16; N 4.08. *M* 343.4.

3-[3-Methoxy-4-(2-methylpropanoyloxy)phenylmethylamino]benzoic acid (IId). Yield 91%, mp 114–115°C (from benzene). Found, %: C 66.80; H 6.26; N 3.84. *M* 343.7. $C_{19}H_{21}NO_5$. Calculated, %: C 66.46; H 6.16; N 4.08. *M* 343.4.

3-(3-Methoxy-4-octanoyloxyphenylmethylamino)benzoic acid (IIe). Yield 92%, mp 72–73°C (from benzene). Found, %: C 69.47; H 7.42; N 3.19. *M* 397.5. $C_{23}H_{29}NO_5$. Calculated, %: C 69.15; H 7.32; N 3.51. *M* 399.5.

3-(4-Decanoyloxy-3-methoxyphenylmethylamino)benzoic acid (IIf). Yield 93%, mp 69–70°C (from benzene). Found, %: C 70.45; H 7.94; N 3.05. *M* 422.8. $C_{25}H_{33}NO_5$. Calculated, %: C 70.23; H 7.78; N 3.28. *M* 427.5.

3-(3-Methoxy-4-tridecanoyloxyphenylmethylamino)benzoic acid (IIg). Yield 94%, mp 58–59°C (from benzene). Found, %: C 71.87; H 8.38; N 2.63. *M* 470.1. $C_{28}H_{39}NO_5$. Calculated, %: C 71.61; H 8.37; N 2.98. *M* 469.6.

3-(3-Methoxy-4-octadecanoyloxyphenylmethylamino)benzoic acid (IIh). Yield 92%, mp 64–65°C (from benzene). Found, %: C 73.82; H 9.20; N 2.23. *M* 541.5. $C_{33}H_{49}NO_5$. Calculated, %: C 73.43; H 9.15; N 2.60. *M* 539.8.

3-(4-Acryloyloxy-3-methoxyphenylmethylamino)benzoic acid (IIi). Yield 91%, mp 173–174°C (from benzene). Found, %: C 66.36; H 5.28; N 4.04. *M* 325.6. $C_{18}H_{17}NO_5$. Calculated, %: C 66.05; H 5.23; N 4.28. *M* 327.3.

3-[3-Methoxy-4-(2-methylprop-2-enoyloxy)phenylmethylamino]benzoic acid (IIj). Yield 91%, mp 159–160°C (from benzene). Found, %: C 67.17; H 5.66; N 3.87. *M* 340.3. $C_{19}H_{19}NO_5$. Calculated, %: C 66.85; H 5.61; N 4.10. *M* 341.4.

3-[3-Methoxy-4-(phenylacetyloxy)phenylmethylamino]benzoic acid (IIk). Yield 92%, mp 141–142°C (from benzene). Found, %: C 70.93; H 5.49; N 3.20. *M* 390.5. $C_{23}H_{21}NO_5$. Calculated, %: C 70.58; H 5.41; N 3.58. *M* 391.4.

3-[3-Methoxy-4-(3-phenylbutanoyloxy)phenylmethylamino]benzoic acid (IIl). Yield 91%, mp 62–63°C (from benzene). Found, %: C 71.89; H 6.18; N 3.02. *M* 420.0. $C_{25}H_{25}NO_5$. Calculated, %: C 71.58; H 6.01; N 3.34. *M* 419.5.

3-{3-Methoxy-4-[3-(4-methylphenyl)propanoyloxy]phenylmethylamino}benzoic acid (IIm). Yield 94%, mp 136–137°C (from benzene). Found, %: C 69.28; H 6.04; N 2.97. *M* 437.1. $C_{25}H_{25}NO_6$. Calculated, %: C 68.95; H 5.79; N 3.22. *M* 435.5.

3-(4-Benzoyloxy-3-methoxyphenylmethylamino)benzoic acid (IIn). Yield 94%, mp 158–159°C (from benzene). Found, %: C 70.34; H 5.18; N 3.35. *M* 378.2. $C_{22}H_{19}NO_5$. Calculated, %: C 70.02; H 5.07; N 3.71. *M* 377.4.

3-[3-Methoxy-4-(4-methylbenzoyloxy)phenylmethylamino]benzoic acid (IIo). Yield 92%, mp 184–185°C (from benzene). Found, %: C 70.95; H 5.42; N 3.26. *M* 392.2. $C_{23}H_{21}NO_5$. Calculated, %: C 70.58; H 5.41; N 3.58. *M* 391.4.

3-[4-(2-Chlorobenzoyloxy)-3-methoxyphenylmethylamino]benzoic acid (IIp). Yield 93%, mp 136–137°C (from benzene). Found, %: C 64.43; H 4.54; Cl 8.19; N 3.11. *M* 403.7. $C_{22}H_{18}ClNO_5$. Calculated, %: C 64.16; H 4.41; Cl 8.61; N 3.40. *M* 411.8.

3-[4-(4-Chlorobenzoyloxy)-3-methoxyphenylmethylamino]benzoic acid (IIq). Yield 93%, mp 160–161°C (from benzene). Found, %: C 64.46; H 4.50; Cl 8.23; N 3.03. *M* 410.2. $C_{22}H_{18}ClNO_5$. Calculated, %: C 64.16; H 4.41; Cl 8.61; N 3.40. *M* 411.8.

3-[4-(2,4-Dichlorobenzoyloxy)-3-methoxyphenylmethylamino]benzoic acid (IIr). Yield 92%, mp 153–154°C (from benzene). Found, %: C 55.48; H 3.91; Cl 15.34; N 2.88. *M* 440.8. $C_{22}H_{17}Cl_2NO_5$. Calculated, %: C 55.18; H 3.84; Cl 15.89; N 3.14. *M* 446.3.

3-[4-(2,4-Dichlorophenoxyacetyloxy)-3-methoxyphenylmethylamino]benzoic acid (IIs). Yield 91%, mp 179–180°C (from benzene). Found, %: C 58.32; H 4.17; Cl 14.30; N 2.81. *M* 474.0. $C_{23}H_{19}Cl_2NO_6$. Calculated, %: C 58.00; H 4.02; Cl 14.89; N 2.94. *M* 476.3.

3-[4-(4-Bromobenzoyloxy)-3-methoxyphenylmethylamino]benzoic acid (IIt). Yield 94%, mp 157–158°C (from benzene). Found, %: C 58.27; H 4.13; Br 17.18; N 2.69. *M* 454.5. $C_{22}H_{18}BrNO_5$. Calculated, %: C 57.91; H 3.98; Br 17.51; N 3.07. *M* 456.3.

3-[3-Methoxy-4-(3-nitrobenzoyloxy)phenylmethylamino]benzoic acid (IIu). Yield 92%, mp 195–196°C (from benzene). Found, %: C 62.78; H 4.39; N 6.10. *M* 425.9. $C_{22}H_{18}N_2O_7$. Calculated, %: C 62.56; H 4.30; N 6.63. *M* 422.4.

3-(4-Acetoxy-3-ethoxyphenylmethylamino)benzoic acid (IIIa). Yield 93%, mp 117–118°C (from benzene). Found, %: C 65.91; H 5.87; N 3.96. *M* 329.1. $C_{18}H_{19}NO_5$. Calculated, %: C 65.64; H 5.81; N 4.25. *M* 329.4.

3-(3-Ethoxy-4-propanoyloxyphenylmethylamino)benzoic acid (IIIb). Yield 93%, mp 133–134°C (from benzene). Found, %: C 66.80; H 6.22; N 3.87. *M* 342.8. $C_{19}H_{21}NO_5$. Calculated, %: C 66.46; H 6.16; N 4.08. *M* 343.4.

3-(4-Butanoyloxy-3-ethoxyphenylmethylamino)benzoic acid (IIIc). Yield 92%, mp 127–128°C (from benzene). Found, %: C 67.58; H 6.49; N 3.58. *M* 356.2. $C_{20}H_{23}NO_5$. Calculated, %: C 67.21; H 6.49; N 3.92. *M* 357.4.

3-[3-Ethoxy-4-(2-methylpropanoyloxy)phenylmethylamino]benzoic acid (IIId). Yield 92%, mp 125–126°C (from benzene). Found, %: C 67.47; H 6.58; N 3.74. *M* 358.0. $C_{20}H_{23}NO_5$. Calculated, %: C 67.21; H 6.49; N 3.92. *M* 357.4.

3-(3-Ethoxy-4-(3-methylbutanoyloxy)phenylmethylamino]benzoic acid (IIIe). Yield 93%, mp 87–88°C (from benzene). Found, %: C 68.14; H 6.83; N 3.57. *M* 369.3. $C_{21}H_{25}NO_5$. Calculated, %: C 67.91; H 6.78; N 3.77. *M* 371.4.

3-(4-Benzoyloxy-3-ethoxyphenylmethylamino)benzoic acid (IIIf). Yield 93%, mp 144–145°C (from benzene). Found, %: C 70.86; H 5.53; N 3.22. *M* 390.2. $C_{23}H_{21}NO_5$. Calculated, %: C 70.58; H 5.41; N 3.58. *M* 391.4.

3-[3-Ethoxy-4-(4-methylbenzoyloxy)phenylmethylamino]benzoic acid (IIIg). Yield 93%, mp 174–175°C (from benzene). Found, %: C 71.35; H 5.78; N 3.07. *M* 403.5. $C_{24}H_{23}NO_5$. Calculated, %: C 71.10; H 5.72; N 3.45. *M* 405.4.

3-[4-(2-Chlorobenzoyloxy)-3-ethoxyphenylmethylamino]benzoic acid (IIIh). Yield 94%, mp 119–120°C (from benzene). Found, %: C 65.01; H 4.79; Cl 8.05; N 2.92. *M* 422.7. $C_{23}H_{20}ClNO_5$. Calculated, %: C 64.87; H 4.73; Cl 8.32; N 3.29. *M* 425.9.

3-[4-(4-Chlorobenzoyloxy)-3-ethoxyphenylmethylamino]benzoic acid (IIIi). Yield 93%, mp 139–140°C (from benzene). Found, %: C 65.10; H 4.82; Cl 8.11; N 2.97. *M* 425.0. $C_{23}H_{20}ClNO_5$. Calculated, %: C 64.87; H 4.73; Cl 8.32; N 3.29. *M* 425.9.

4-(4-Acetoxy-3-methoxyphenylmethylamino)benzoic acid (IVa). Yield 92%, mp 203–204°C (from benzene). Found, %: C 65.08; H 5.52; N 4.10. *M* 314.3. $C_{17}H_{17}NO_5$. Calculated, %: C 64.75; H 5.43; N 4.44. *M* 315.3.

4-(3-Methoxy-4-propanoyloxyphenylmethylamino)benzoic acid (IVb). Yield 92%, mp 176–177°C (from benzene). Found, %: C 65.83; H 5.99; N 3.88. *M* 328.3. $C_{18}H_{19}NO_5$. Calculated, %: C 65.64; H 5.81; N 4.25. *M* 329.4.

4-(4-Butanoyloxy-3-methoxyphenylmethylamino)benzoic acid (IVc). Yield 91%, mp 127–128°C (from benzene). Found, %: C 66.92; H 6.20; N 3.84. *M* 342.8. $C_{19}H_{21}NO_5$. Calculated, %: C 66.46; H 6.16; N 4.08. *M* 343.4.

4-[3-Methoxy-4-(2-methylpropanoyloxy)phenylmethylamino]benzoic acid (IVd). Yield 93%, mp 218–219°C (from benzene). Found, %: C 66.64; H 6.25; N 3.87. *M* 342.6. $C_{19}H_{21}NO_5$. Calculated, %: C 66.46; H 6.16; N 4.08. *M* 343.4.

4-(3-Methoxy-4-octanoyloxyphenylmethylamino)benzoic acid (IVe). Yield 91%, mp 125–126°C

(from benzene). Found, %: C 69.60; H 7.38; N 3.24. *M* 401.2. $C_{23}H_{29}NO_5$. Calculated, %: C 69.15; H 7.32; N 3.51. *M* 399.5.

4-(4-Decanoyloxy-3-methoxyphenylmethylamino)benzoic acid (IVf). Yield 92%, mp 165–166°C (from benzene). Found, %: C 70.56; H 7.92; N 3.00. *M* 426.2. $C_{25}H_{33}NO_5$. Calculated, %: C 70.23; H 7.78; N 3.28. *M* 427.5.

4-(3-Methoxy-4-tridecanoyloxyphenylmethylamino)benzoic acid (IVg). Yield 93%, mp 114–115°C (from benzene). Found, %: C 71.95; H 8.43; N 2.60. *M* 466.8. $C_{28}H_{39}NO_5$. Calculated, %: C 71.61; H 8.37; N 2.98. *M* 469.6.

4-(3-Methoxy-4-octadecanoyloxyphenylmethylamino)benzoic acid (IVh). Yield 91%, mp 92–93°C (from benzene). Found, %: C 73.78; H 9.27; N 2.17. *M* 540.3. $C_{33}H_{49}NO_5$. Calculated, %: C 73.43; H 9.15; N 2.60. *M* 539.8.

4-(4-Acryloyloxy-3-methoxyphenylmethylamino)benzoic acid (IVi). Yield 93%, mp 146–147°C (from benzene). Found, %: C 66.40; H 5.29; N 4.11. *M* 326.0. $C_{18}H_{17}NO_5$. Calculated, %: C 66.05; H 5.23; N 4.28. *M* 327.3.

4-[3-Methoxy-4-(2-methylprop-2-enoyloxy)-phenylmethylamino]benzoic acid (IVj). Yield 92%, mp 181–182°C (from benzene). Found, %: C 67.08; H 5.73; N 3.90. *M* 340.4. $C_{19}H_{19}NO_5$. Calculated, %: C 66.85; H 5.61; N 4.10. *M* 341.4.

4-[3-Methoxy-4-(phenylacetyloxy)phenylmethylamino]benzoic acid (IVk). Yield 93%, mp 167–168°C (from benzene). Found, %: C 70.90; H 5.56; N 3.18. *M* 389.8. $C_{23}H_{21}NO_5$. Calculated, %: C 70.58; H 5.41; N 3.58. *M* 391.4.

4-[3-Methoxy-4-(3-phenylbutanoyloxy)phenylmethylamino]benzoic acid (IVl). Yield 92%, mp 123–124°C (from benzene). Found, %: C 71.90; H 6.09; N 3.10. *M* 418.3. $C_{25}H_{25}NO_5$. Calculated, %: C 71.58; H 6.01; N 3.34. *M* 419.5.

4-{3-Methoxy-4-[3-(4-methylphenyloxy)propanoyloxy]phenylmethylamino}benzoic acid (IVm). Yield 92%, mp 199–200°C (from benzene). Found, %: C 69.12; H 5.87; N 2.90. *M* 434.8. $C_{25}H_{25}NO_6$. Calculated, %: C 68.95; H 5.79; N 3.22. *M* 435.5.

4-(4-Benzoyloxy-3-methoxyphenylmethylamino)-benzoic acid (IVn). Yield 94%, mp 216–217°C (from benzene). Found, %: C 70.25; H 5.11; N 3.28. *M* 376.4. $C_{22}H_{19}NO_5$. Calculated, %: C 70.02; H 5.07; N 3.71. *M* 377.4.

4-[3-Methoxy-4-(4-methylbenzoyloxy)phenylmethylamino]benzoic acid (IVo). Yield 93%, mp 234–235°C (from benzene). Found, %: C 70.86; H 5.48; N 3.32. *M* 390.3. $C_{23}H_{21}NO_5$. Calculated, %: C 70.58; H 5.41; N 3.58. *M* 391.4.

4-[4-(2-Chlorobenzoyloxy)-3-methoxyphenylmethylamino]benzoic acid (IVp). Yield 92%, mp 194–195°C (from benzene). Found, %: C 64.58; H 4.50; Cl 8.31; N 3.17. *M* 410.6. $C_{22}H_{18}ClNO_5$. Calculated, %: C 64.16; H 4.41; Cl 8.61; N 3.40. *M* 411.8.

4-[4-(4-Chlorobenzoyloxy)-3-methoxyphenylmethylamino]benzoic acid (IVq). Yield 94%, mp 268–269°C (from benzene). Found, %: C 64.52; H 4.53; Cl 8.19; N 3.12. *M* 410.8. $C_{22}H_{18}ClNO_5$. Calculated, %: C 64.16; H 4.41; Cl 8.61; N 3.40. *M* 411.8.

4-[4-(2,4-Dichlorobenzoyloxy)-3-methoxyphenylmethylamino]benzoic acid (IVr). Yield 93%, mp 205–206°C (from benzene). Found, %: C 55.25; H 3.97; Cl 15.47; N 2.92. *M* 444.6. $C_{22}H_{17}Cl_2NO_5$. Calculated, %: C 55.18; H 3.84; Cl 15.89; N 3.14. *M* 446.3.

4-[4-(2,4-Dichlorophenoxyacetyloxy)-3-methoxyphenylmethylamino]benzoic acid (IVs). Yield 91%, mp 185–186°C (from benzene). Found, %: C 58.45; H 4.10; Cl 14.46; N 2.64. *M* 474.7. $C_{23}H_{19}Cl_2NO_6$. Calculated, %: C 58.00; H 4.02; Cl 14.89; N 2.94. *M* 476.3.

4-[4-(4-Bromobenzoyloxy)-3-methoxyphenylmethylamino]benzoic acid (IVt). Yield 93%, mp 298–299°C (from benzene). Found, %: C 58.14; H 4.10; Br 17.22; N 2.87. *M* 455.6. $C_{22}H_{18}BrNO_5$. Calculated, %: C 57.91; H 3.98; Br 17.51; N 3.07. *M* 456.3.

4-[3-Methoxy-4-(3-nitrobenzoyloxy)phenylmethylamino]benzoic acid (IVu). Yield 93%, mp 232–233°C (from benzene). Found, %: C 62.87; H 4.42; N 6.43. *M* 422.0. $C_{22}H_{18}N_2O_7$. Calculated, %: C 62.56; H 4.30; N 6.63. *M* 422.4.

4-(4-Acetoxy-3-ethoxyphenylmethylamino)benzoic acid (Va). Yield 94%, mp 182–183°C (from benzene). Found, %: C 65.98; H 5.93; N 3.99. *M* 328.9. $C_{18}H_{19}NO_5$. Calculated, %: C 65.64; H 5.81; N 4.25. *M* 329.4.

4-(3-Ethoxy-4-propanoyloxyphenylmethylamino)benzoic acid (Vb). Yield 92%, mp 159–160°C (from benzene). Found, %: C 66.76; H 6.28; N 3.85. *M* 342.3. $C_{19}H_{21}NO_5$. Calculated, %: C 66.46; H 6.16; N 4.08. *M* 343.4.

4-(4-Butanoyloxy-3-ethoxyphenylmethylamino)-benzoic acid (Vc). Yield 91%, mp 145–146°C (from

benzene). Found, %: C 67.61; H 6.40; N 3.72. *M* 356.8. $C_{20}H_{23}NO_5$. Calculated, %: C 67.21; H 6.49; N 3.92. *M* 357.4.

4-[3-Ethoxy-4-(2-methylpropanoyloxy)phenylmethylamino]benzoic acid (Vd). Yield 91%, mp 186–187°C (from benzene). Found, %: C 67.40; H 6.61; N 3.70. *M* 358.6. $C_{20}H_{23}NO_5$. Calculated, %: C 67.21; H 6.49; N 3.92. *M* 357.4.

4-[3-Ethoxy-4-(2-methylbutanoyloxy)phenylmethylamino]benzoic acid (Ve). Yield 92%, mp 144–145°C (from benzene). Found, %: C 68.07; H 6.84; N 3.41. *M* 370.5. $C_{21}H_{25}NO_5$. Calculated, %: C 67.91; H 6.78; N 3.77. *M* 371.4.

4-(4-Benzoyloxy-3-ethoxyphenylmethylamino)benzoic acid (Vf). Yield 94%, mp 215–216°C (from benzene). Found, %: C 70.94; H 5.57; N 3.31. *M* 390.8. $C_{23}H_{21}NO_5$. Calculated, %: C 70.58; H 5.41; N 3.58. *M* 391.4.

4-[3-Ethoxy-4-(4-methylbenzoyloxy)phenylmethylamino]benzoic acid (Vg). Yield 92%, mp 201–202°C (from benzene). Found, %: C 71.45; H 5.81; N 3.03. *M* 404.1. $C_{24}H_{23}NO_5$. Calculated, %: C 71.10; H 5.72; N 3.45. *M* 405.4.

4-[4-(2-Chlorobenzoyloxy)-3-ethoxyphenylmethylamino]benzoic acid (Vh). Yield 93%, mp 213–214°C (from benzene). Found, %: C 65.13; H 4.70; Cl 8.10; N 2.98. *M* 423.3. $C_{23}H_{20}ClNO_5$. Calculated, %: C 64.87; H 4.73; Cl 8.32; N 3.29. *M* 425.9.

4-[4-(4-Chlorobenzoyloxy)-3-ethoxyphenylmethylamino]benzoic acid (Vi). Yield 93%, mp 207–208°C (from benzene). Found, %: C 65.14; H 4.88; Cl 8.10; N 2.90. *M* 424.2. $C_{23}H_{20}ClNO_5$. Calculated, %: C 64.87; H 4.73; Cl 8.32; N 3.29. *M* 425.9.

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