Russian Journal of Organic Chemistry, Vol. 41, No. 7, 2005, pp. 992–996. Translated from Zhurnal Organicheskoi Khimii, Vol. 41, No. 7, 2005, pp. 1015–1019.

Esters Derived from Vanillin and Vanillal and Aromatic and Functionalized Aliphatic Carboxylic Acids

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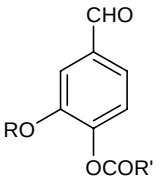
Received October 6, 2004

Abstract—Reactions of vanillin and vanillal with aromatic and functionally substituted aliphatic carboxylic acid chlorides in the presence of pyridine afforded the corresponding previously unknown esters.

Natural phytogenic aromatic hydroxy aldehydes, such as vanillin (4-hydroxy-3-methoxybenzaldehyde, **Ia**) and its nearest homolog vanillal (3-ethoxy-4-hydroxybenzaldehyde, **Ib**), are widely used in food and fragrance industries [1, 2]. Annual production of these compounds exceeds 15000 tons [3, 4]. In addition, vanillin, vanillal, and their derivatives are convenient synthons for the preparation of biologically active compounds [5, 6].

The goal of the present work was to synthesize new esters derived from vanillin and vanillal, on the one hand, and aromatic and functionally substituted aliphatic carboxylic acids, on the other. Esters **IIIa**–**IIIu** and **IVa**–**IVe** were obtained by reactions of compounds **Ia** and **Ib** with the corresponding acid chlorides **II** in dry methylene chloride in the presence of pyridine. Chlorides derived from the following carboxylic acids were used: capric, stearic, acrylic, methacrylic, oleic, benzoic, *p*-toluic, phenylacetic, 2-phenylbutyric, cinnamic, 2-(*p*-tolyloxy)propionic, succinic, *o*-chlorobenzoic, *p*-chlorobenzoic, *o*,*p*-dichlorobenzoic, *o*,*p*-dichlorophenoxyacetic, bromoacetic, 2,3-dibromo-3-phenylpropionic, *p*-bromobenzoic, *m*-nitrobenzoic, and *p*-nitrobenzoic. The yields of esters **IIIa**–**IIIu** and **IVa**–**IVe** were 80 to 90%.



IIIa–IIIu, **IVa–IVe**

III, R = Me, R' = C_9H_{19} (**a**), $C_{17}H_{35}$ (**b**), CH_2=CH (**c**), CH_2=C(Me) (**d**), *cis*-Me$(CH_2)_7$CH=CH$(CH_2)_7$ (**e**), Ph (**f**), *p*-MeC_6H_4 (**g**), $PhCH_2$ (**h**), PhCH(Me)CH_2 (**i**), *trans*-PhCH=CH (**j**), *p*-$MeC_6H_4O(CH_2)_2$ (**k**), $XCO(CH_2)_2$ (X = 2-MeO-4-$OCHC_6H_3O$) (**l**), *o*-ClC_6H_4 (**m**), *p*-ClC_6H_4 (**n**), *o*,*p*-$Cl_2C_6H_3$ (**o**), *o*,*p*-$Cl_2C_6H_3OCH_2$ (**p**), $BrCH_2$ (**q**), PhCHBrCHBr (**r**), *p*-BrC_6H_4 (**s**), *m*-$O_2NC_6H_4$ (**t**), *p*-$O_2NC_6H_4$ (**u**); **IV**, R = Et, R' = Ph (**a**), *p*-MeC_6H_4 (**b**), $XCO(CH_2)_2$ (X = 2-EtO-4-$OCHC_6H_3O$) (**c**), *o*-ClC_6H_4 (**d**), *p*-ClC_6H_4 (**e**).

Compounds **IIIa**–**IIIu** and **IVa**–**IVe** contain aldehyde and ester moieties, methoxy or ethoxy group, and substituents in the acid fragment. Therefore, they can be involved in further chemical transformations. Esters **IIIa**–**IIIu** and **IVa**–**IVe** attract interest as potential antimicrobial and radioprotecting agents [7, 8]. The structure of products **IIIa**–**IIIu** and **IVa**–**IVe** was confirmed by the data of elemental analysis, determination of their molecular weights by cryoscopy, and ^{1}H NMR, IR, and UV spectroscopy. According to the ^{1}H NMR data, their purity was 98±1%.

EXPERIMENTAL

The IR spectra were recorded on a Nicolet Protege-460 Fourier spectrometer from samples prepared as thin films or KBr pellets. The UV spectra were measured on a Specord UV-Vis spectrophotometer from 10^{-4} M solutions in methanol. The ^{1}H NMR spectra were obtained on a Tesla BS-587A instrument (100 MHz) from 5% solutions in $CDCl_3$; the chemical shifts were measured relative to octamethylcyclotetrasiloxane as internal reference. The molecular weights were determined by cryoscopy in benzene. Carboxylic acid chlorides **II** were prepared by treatment of the corresponding acid with 1.5 equiv of thionyl chloride in benzene under reflux.

1070-4280/05/4107-0992

Esters IIIa–IIIu and IVa–IVe (*general procedure*). Hydroxy aldehyde **Ia** or **Ib**, 0.2 mol, was dissolved in 500 ml of dry methylene chloride, 0.25 mol of anhydrous pyridine was added, and 0.2 mol of the corresponding carboxylic acid chloride **II** (0.1 mol of succinoyl dichloride) was added in small portions under continuous shaking. The mixture was heated for 1 h under reflux, the solvent was distilled off on a water bath, the residue was dissolved in 500 ml of benzene, and the benzene solution was washed with three portions of water and three portions of a 5% solution of sodium hydrogen carbonate and dried over calcium chloride. The solvent was distilled off, and the residue was recrystallized from benzene–hexane or distilled under reduced pressure. The solvents, methylene chloride and benzene, may be reused after distillation over P_2O_5 through a Vigreaux column.

4-Formyl-2-methoxyphenyl decanoate (IIIa). Yield 86%, mp 35–36°C. IR spectrum, ν, cm^{-1}: 3067, 3050, 3014 (C–H_{arom}); 1764, 1720, 1695, 1681 (C=O); 1601, 1589, 1510, 1420, 1464, 1383 (C–C_{arom}); 1473 (CH_2); 921, 884, 841, 783, 745, 725, 714 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 206 (8000), 224 (15000), 260 (7000), 310 (3000). ^{1}H NMR spectrum, δ, ppm: 0.89 t (CH_3, ^3J = 5.5 Hz), 1.20–1.50 m [$(CH_2)_6$], 1.82 t (CH_2, ^3J = 5.5 Hz), 2.60 t (CH_2C=O, ^3J = 7.4 Hz), 3.89 s (CH_3O), 7.10–7.55 m (C_6H_3), 9.94 s (CHO). Found, %: C 70.91; H 8.67. *M* 291.8. $C_{18}H_{26}O_4$. Calculated, %: C 70.56; H 8.55. *M* 306.4.

4-Formyl-2-methoxyphenyl octadecanoate (IIIb). Yield 89%, mp 32–33°C. IR spectrum, ν, cm^{-1}: 3110, 3072, 3014 (C–H_{arom}); 1765, 1704 (C=O); 1601, 1504, 1466, 1422, 1390 (C–C_{arom}); 1475 (CH_2); 964, 915, 865, 835, 780, 734, 645, 585 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 205 (8000), 223 (14000), 260 (6000), 310 (3000). ^{1}H NMR spectrum, δ, ppm: 0.88 t (CH_3, ^3J = 4.7 Hz), 1.15–2.05 m [$(CH_2)_{15}$], 2.67 t (CH_2C=O, ^3J = 7.3 Hz), 3.89 s (CH_3O), 7.10–7.60 m (C_6H_3), 9.94 s (CHO). Found, %: C 75.03; H 10.24. *M* 392.1. $C_{26}H_{42}O_4$. Calculated, %: C 74.60; H 10.11. *M* 418.6.

4-Formyl-2-methoxyphenyl acrylate (IIIc). Yield 80%, bp 140–141°C (0.5 mm), d_{20}^{20} = 1.3428, n_D^{20} = 1.5555. IR spectrum, ν, cm^{-1}: 3110, 3080, 3045, 3010 (=C–H, C–H_{arom}); 1767, 1751, 1701 (C=O); 1640 (C=C); 1601, 1503, 1466, 1423, 1404, 1391 (C–C_{arom}); 920, 895, 875, 835, 800, 780, 734 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 208 (12000), 219 (18000), 254 (9000), 303 (4000). ^{1}H NMR spectrum, δ, ppm: 3.90 s (CH_3O), 5.80–6.85 m ($CH=CH_2$), 7.15–7.65 m (C_6H_3), 9.96 s (CHO). Found, %: C 64.32; H 5.09. *M* 193.4. $C_{11}H_{10}O_4$. Calculated, %: C 64.07; H 4.89. *M* 206.2.

4-Formyl-2-methoxyphenyl methacrylate (IIId). Yield 82%, mp 46–47°C. IR spectrum, ν, cm^{-1}: 3100, 3080, 3040, 3015 (=C–H, C–H_{arom}); 1768, 1750, 1700 (C=O); 1645 (C=C); 1600, 1505, 1465, 1423, 1405, 1390 (C–C_{arom}); 920, 895, 875, 830, 800, 780, 735 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 207 (13000), 220 (18000), 255 (9000), 300 (4000). ^{1}H NMR spectrum, δ, ppm: 2.08 t (CH_3, ^3J = 0.9 Hz), 3.90 s (CH_3O), 5.77 t (=CH, ^3J = 1.1 Hz), 6.37 t (=CH, ^3J = 0.9 Hz), 7.15–7.65 m (C_6H_3), 9.93 s (CHO). Found, %: C 65.88; H 5.67. *M* 208.5. $C_{12}H_{12}O_4$. Calculated, %: C 65.45; H 5.49. *M* 220.2.

4-Formyl-2-methoxyphenyl (*Z*)-8-octadecenoate (IIIe). Yield 88%, d_{20}^{20} = 1.1563, n_D^{20} = 1.5040. IR spectrum, ν, cm^{-1}: 3080, 3040, 3015 (C–H_{arom}); 3006 (=CH); 1767, 1703 (C=O); 920, 860, 820, 785, 733 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 202 (6000), 218 (17000), 255 (6000), 309 (3000). ^{1}H NMR spectrum, δ, ppm: 0.88 t (CH_3, ^3J = 4.6 Hz), 1.05–2.15 m [$(CH_2)_5$, $(CH_2)_6$], 2.57 t (CH_2C=O, ^3J = 6.1 Hz), 3.88 s (CH_3O), 5.35 t (2H, =CH, ^3J = 4.0 Hz), 7.00–7.50 m (C_6H_3), 9.93 s (CHO). Found, %: C 75.19; H 10.02. *M* 394.7. $C_{26}H_{40}O_4$. Calculated, %: C 74.96; H 9.68. *M* 416.6.

4-Formyl-2-methoxyphenyl benzoate (IIIf). Yield 90%, mp 71–72°C. IR spectrum, ν, cm^{-1}: 3110, 3094, 3066, 3050, 3035, 3010 (C–H_{arom}); 1734, 1695, 1681 (C=O); 1601, 1503, 1465, 1452, 1426, 1398 (Ar); 940, 872, 856, 817, 806, 734, 702, 677, 587, 550 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 204 (23000), 220 (30000), 258 (18000), 308 (6000). ^{1}H NMR spectrum, δ, ppm: 3.88 s (CH_3O), 7.20–7.70 and 8.05–8.30 m (C_6H_3, C_6H_5), 9.97 s (CHO). Found, %: C 70.57; H 5.03. *M* 248.4. $C_{15}H_{12}O_4$. Calculated, %: C 70.31; H 4.72. *M* 256.3.

4-Formyl-2-methoxyphenyl *p*-methylbenzoate (IIIg). Yield 87%, mp 91–92°C. IR spectrum, ν, cm^{-1}: 3109, 3072, 3011 (C–H_{arom}); 1736, 1701, 1686 (C=O); 1609, 1598, 1502, 1465, 1426, 1399 (C–C_{arom}); 938, 882, 870, 852, 837, 804, 782, 747, 731, 687, 645, 636, 606, 583, 548 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 208 (25000), 221 (25000), 253 (27000), 308 (6000). ^{1}H NMR spectrum, δ, ppm: 2.44 s (CH_3), 3.86 s (CH_3O), 7.15–7.55 m and 7.90–8.15 m (C_6H_3, C_6H_4), 9.95 s (CHO). Found, %: C 71.35; H 5.41. *M* 262.7. $C_{16}H_{14}O_4$. Calculated, %: C 71.10; H 5.22. *M* 270.3.

4-Formyl-2-methoxyphenyl phenylacetate (IIIh). Yield 89%, bp 179–180°C (0.5 mm), d_{20}^{20} = 1.2835,

n_D^{20} = 1.5810. IR spectrum, ν, cm^{-1}: 3110, 3090, 3080, 3040, 3010 (C–H_{arom}); 1764, 1700 (C=O); 1600, 1499, 1480, 1420, 1390 (C–C_{arom}); 1470 (CH_2); 900, 880, 830, 780, 720, 703, 660 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 210 (15000), 218 (16000), 256 (8000), 308 (4000). ^{1}H NMR spectrum, δ, ppm: 3.79 s (CH_2), 3.89 s (CH_3O), 7.10–7.50 m (C_6H_3, C_6H_5), 9.89 s (CHO). Found, %: C 71.30; H 5.44. $C_{16}H_{14}O_4$. *M* 260.1. Calculated, %: C 71.10; H 5.22. *M* 270.3.

4-Formyl-2-methoxyphenyl 2-phenylbutyrate (IIIi). Yield 85%, mp 69–70°C. IR spectrum, ν, cm^{-1}: 3113, 3080, 3061, 3040, 3025 (C–H_{arom}); 1756, 1702, 1689 (C=O); 1601, 1501, 1451, 1425, 1396, 1362 (C–C_{arom}); 1467 (CH_2); 930, 885, 843, 810, 765, 733, 700, 652 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 210 (16000), 255 (8000), 307 (4000). ^{1}H NMR spectrum, δ, ppm: 1.42 d (CH_3, ^3J = 7.4 Hz), 2.88 d (CH_2, ^3J = 7.4 Hz), 3.38 q (CH, ^3J = 7.4 Hz), 3.79 s (CH_3O), 6.90–7.45 m (C_6H_3, C_6H_5), 9.89 s (CHO). Found, %: C 72.68; H 6.30. *M* 283.9. $C_{18}H_{18}O_4$. Calculated, %: C 72.47; H 6.08. *M* 298.3.

4-Formyl-2-methoxyphenyl cinnamate (IIIj). Yield 84%, mp 59–60°C. IR spectrum, ν, cm^{-1}: 3110, 3090, 3025, 3010 (C–H_{arom}); 3060 (=CH); 1738, 1725, 1700, 1688 (C=O); 1636 (C=C); 1600, 1580, 1503, 1470, 1453, 1425, 1391 (C–C_{arom}); 976, 920, 875, 863, 840, 780, 766, 740, 707, 680, 645 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 206 (32000), 220 (41000), 280 (38000). ^{1}H NMR spectrum, δ, ppm: 3.90 s (CH_3O), 7.10–7.90 m (CH=CH, C_6H_3, C_6H_5), 9.96 s (CHO). Found, %: C 72.53; H 5.19. *M* 273.0. $C_{17}H_{14}O_4$. Calculated, %: C 72.33; H 5.00. *M* 282.3.

4-Formyl-2-methoxyphenyl 3-(*p*-tolyloxy)propionate (IIIk). Yield 81%, mp 63–64°C. IR spectrum, ν, cm^{-1}: 3120, 3085, 3032, 3015 (C–H_{arom}); 1773, 1704 (C=O); 1599, 1511, 1396, 1376 (C–C_{arom}); 1462 (CH_2); 955, 910, 890, 880, 850, 827, 818, 781, 731, 590 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 204 (15000), 221 (20000), 260 (7000), 306 (3000). ^{1}H NMR spectrum, δ, ppm: 2.28 s (CH_3), 3.06 t (CH_2O, ^3J = 6.3 Hz), 3.86 s (CH_3O), 4.35 t (CH_2C=O, ^3J = 6.3 Hz), 6.63–7.52 m (C_6H_3, C_6H_4), 9.90 s (CHO). Found, %: C 69.02; H 5.97. *M* 303.6. $C_{18}H_{18}O_5$. Calculated, %: C 68.78; H 5.77. *M* 314.3.

Bis(4-formyl-2-methoxyphenyl) succinate (IIIl). Yield 84%, mp 130–131°C. IR spectrum, ν, cm^{-1}: 3110, 3073, 3050, 3010 (C–H_{arom}); 1756, 1704 (C=O); 1601, 1592, 1508, 1502, 1455, 1424, 1396 (C–C_{arom}); 1472 (CH_2); 944, 917, 881, 868, 836, 803, 781, 735, 671, 587 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 204 (50000), 220 (70000), 258 (39000), 305 (15000). ^{1}H NMR spectrum, δ, ppm: 3.04 s [4H, $(CH_2)_2$], 3.84 s (6H, CH_3O), 7.12–7.55 m (6H, C_6H_3), 9.90 s (2H, CHO). Found, %: C 62.63; H 5.02. *M* 372.7. $C_{20}H_{18}O_8$. Calculated, %: C 62.18; H 4.70. *M* 386.4.

4-Formyl-2-methoxyphenyl *o*-chlorobenzoate (IIIm). Yield 86%, mp 91–92°C. IR spectrum, ν, cm^{-1}: 3095, 3067, 3020 (C–H_{arom}); 1746, 1701, 1686 (C=O); 1600, 1590, 1505, 1468, 1455, 1430, 1421, 1390 (C–C_{arom}); 961, 876, 856, 814, 790, 741, 710, 683, 650, 630, 595 (δC–H_{arom}); 550 (C–Cl). UV spectrum, λ_{max}, nm (ε): 208 (27000), 219 (23000), 255 (12000), 304 (4000). ^{1}H NMR spectrum, δ, ppm: 3.90 s (CH_3O), 7.15–7.55 m and 8.00–8.25 m (C_6H_3, C_6H_4), 9.97 s (CHO). Found, %: C 62.24; H 4.06; Cl 11.92. *M* 281.1. $C_{15}H_{11}ClO_4$. Calculated, %: C 61.98; H 3.81; Cl 12.20. *M* 290.7.

4-Formyl-2-methoxyphenyl *p*-chlorobenzoate (IIIn). Yield 84%, mp 98–99°C. IR spectrum, ν, cm^{-1}: 3105, 3093, 3074, 2999 (C–H_{arom}); 1743, 1703 (C=O); 1593, 1501, 1480, 1463, 1422, 1400, 1391 (C–C_{arom}); 958, 873, 858, 847, 817, 780, 748, 730, 678, 637, 588 (δC–H_{arom}); 522 (C–Cl). UV spectrum, λ_{max}, nm (ε): 204 (25000), 220 (21000), 252 (15000), 303 (4000). ^{1}H NMR spectrum, δ, ppm: 3.93 s (CH_3O), 7.20–7.60 m and 8.05–8.25 m (C_6H_3, C_6H_4), 9.98 s (CHO). Found, %: C 62.16; H 4.01; Cl 11.98. *M* 282.4. $C_{15}H_{11}ClO_4$. Calculated, %: C 61.98; H 3.81; Cl 12.20. *M* 290.7.

4-Formyl-2-methoxyphenyl *o,p*-dichlorobenzoate (IIIo). Yield 87%, mp 102–103°C. IR spectrum, ν, cm^{-1}: 3095, 3080, 3068, 3040, 3027 (C–H_{arom}); 1746, 1705, 1689 (C=O); 1598, 1584, 1556, 1508, 1470, 1465, 1417, 1392, 1379 (C–C_{arom}); 961, 937, 900, 871, 852, 845, 835, 802, 784, 735, 675, 642, 588 (δC–H_{arom}); 559, 526 (C–Cl). UV spectrum, λ_{max}, nm (ε): 212 (32000), 255 (15000), 306 (3000). ^{1}H NMR spectrum, δ, ppm: 3.90 s (CH_3O), 7.00–7.65 m and 7.95–8.55 m (H_{arom}), 9.97 s (CHO). Found, %: C 55.85; H 3.28; Cl 21.56. *M* 311.8. $C_{15}H_{10}Cl_2O_4$. Calculated, %: C 55.41; H 3.10; Cl 21.81. *M* 325.1.

4-Formyl-2-methoxyphenyl *o,p*-dichlorophenoxyacetate (IIIp). Yield 81%, mp 115–116°C. IR spectrum, ν, cm^{-1}: 3106, 3085, 3077, 3055, 3038, 3020 (C–H_{arom}); 1769, 1699, 1686 (C=O); 1600, 1504, 1680, 1425, 1396, 1380 (C–C_{arom}); 1470 (CH_2); 960, 946, 923, 862, 840, 823, 801, 751, 735, 716, 697, 680, 648, 583 (δC–H_{arom}); 557, 536 (C–Cl). UV spectrum, λ_{max}, nm (ε): 206 (27000), 222 (17000), 257 (5000), 280 (5000), 295 (5000), 308 (4000). ^{1}H NMR spectrum, δ,

ppm: 3.87 s (CH_3O), 4.98 s (CH_2), 6.85–7.55 m (H_{arom}), 9.93 s (CHO). Found, %: C 54.49; H 3.64; Cl 19.78. *M* 334.6. $C_{16}H_{12}Cl_2O_5$. Calculated, %: C 54.11; H 3.41; Cl 19.96. *M* 355.2.

4-Formyl-2-methoxyphenyl bromoacetate (IIIq). Yield 83%, mp 43–44°C. IR spectrum, ν, cm^{-1}: 3080, 3017 (C–H_{arom}); 1786, 1701 (C=O); 1602, 1503, 1423, 1391 (C–C_{arom}); 1466 (CH_2); 960, 920, 880, 850, 814, 781, 733, 680, 635, 590 (δC–H_{arom}); 540 (C–Br). UV spectrum, λ_{max}, nm (ε): 207 (13000), 230 (13000), 278 (8000), 308 (8000). ^{1}H NMR spectrum, δ, ppm: 3.90 s (CH_3O), 4.36 s (CH_2), 7.20–7.60 m (C_6H_3), 9.95 s (CHO). Found, %: C 44.17; H 3.47; Br 28.89. *M* 265.4. $C_{10}H_9BrO_4$. Calculated, %: C 43.98; H 3.32; Br 29.26. *M* 273.1.

4-Formyl-2-methoxyphenyl 1,2-dibromo-2-phenylpropionate (IIIr). Yield 80%, mp 82–83°C. IR spectrum, ν, cm^{-1}: 3100, 3090, 3025, 3010 (C–H_{arom}); 1785, 1700 (C=O); 1599, 1510, 1396, 1375 (C–C_{arom}); 955, 910, 890, 880, 850, 826, 818, 780, 730, 590 (δC–H_{arom}), 540 (C–Br). UV spectrum, λ_{max}, nm (ε): 209 (17000), 257 (9000), 308 (6000). ^{1}H NMR spectrum, δ, ppm: 2.29 s (CH), 3.89 s (CH_3O), 4.95–5.55 m (CH), 6.95–8.45 m (C_6H_3, C_6H_5), 9.95 s (CHO). Found, %: C 46.32; H 3.28; Br 35.92. *M* 410.5. $C_{17}H_{14}Br_2O_4$. Calculated, %: C 46.19; H 3.19; Br 36.15. *M* 442.1.

4-Formyl-2-methoxyphenyl *p*-bromobenzoate (IIIs). Yield 84%, mp 108–109°C. IR spectrum, ν, cm^{-1}: 3100, 3085, 3060, 3020 (C–H_{arom}); 1738, 1689 (C=O); 1587, 1507, 1483, 1468, 1421, 1399, 1381 (C–C_{arom}); 868, 844, 813, 780, 749, 677, 590 (δC–H_{arom}); 550 (C–Br). UV spectrum, λ_{max}, nm (ε): 206 (24000), 222 (21000), 255 (28000), 306 (5000). ^{1}H NMR spectrum, δ, ppm: 3.88 s (CH_3O), 7.20–7.75 m and 7.95–8.15 m (C_6H_3, C_6H_4), 9.97 s (CHO). Found, %: C 54.08; H 3.45; Br 23.61. *M* 322.6. $C_{15}H_{11}BrO_4$. Calculated, %: C 53.76; H 3.31; Br 23.84. *M* 335.2.

4-Formyl-2-methoxyphenyl *m*-nitrobenzoate (IIIt). Yield 82%, mp 114–115°C. IR spectrum, ν, cm^{-1}: 3110, 3084, 3030, 3005 (C–H_{arom}); 1747, 1703, 1685 (C=O); 1616, 1601, 1501, 1479, 1462, 1421, 1396 (C–C_{arom}); 1533, 1350 (NO_2); 958, 920, 909, 857, 818, 742, 732, 714, 657 (δCH_{arom}). UV spectrum, λ_{max}, nm (ε): 220 (40000), 258 (17000), 305 (4000). ^{1}H NMR spectrum, δ, ppm: 3.91 s (CH_3O); 7.00–7.90 m, 8.30–8.65 m, and 8.85–9.10 m (C_6H_3, C_6H_4); 10.00 s (CHO). Found, %: C 60.11; H 3.87; N 4.33. $C_{15}H_{11}NO_6$. *M* 291.8. Calculated, %: C 59.80; H 3.68; N 4.65. *M* 301.3.

4-Formyl-2-methoxyphenyl *p*-nitrobenzoate (IIIu). Yield 84%, mp 189–190°C. IR spectrum, ν, cm^{-1}: 3110, 3080, 3055, 3020 (C–H_{arom}); 1746, 1703, 1689 (C=O); 1600, 1501, 1460, 1420, 1399 (C–C_{arom}); 1526, 1350 (NO_2); 955, 880, 851, 820, 780, 730, 711, 645 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 221 (37000), 260 (20000), 305 (4000). ^{1}H NMR spectrum, δ, ppm: 3.91 s (CH_3O), 7.15–7.45 m and 8.35–8.45 m (C_6H_3, C_6H_4), 10.00 s (CHO). Found, %: C 60.04; H 3.80; N 4.48. *M* 294.0. $C_{15}H_{11}NO_6$. Calculated, %: C 59.80; H 3.68; N 4.65. *M* 301.3.

2-Ethoxy-4-formylphenyl benzoate (IVa). Yield 89%, mp 68–69°C. IR spectrum, ν, cm^{-1}: 3095, 3077, 3053, 3010 (C–H_{arom}); 1739, 1697 (C=O); 1601, 1586, 1512, 1451, 1432, 1397, 1380 (C–C_{arom}); 1477 (CH_2); 938, 879, 866, 823, 798, 782, 706, 675, 582 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 204 (21000), 222 (31000), 258 (17000), 308 (5000). ^{1}H NMR spectrum, δ, ppm: 1.30 t (CH_3, ^3J = 7.4 Hz), 4.12 q (CH_2O, ^3J = 7.4 Hz), 7.15–7.70 m and 8.10–8.35 m (C_6H_3, C_6H_5), 9.94 s (CHO). Found, %: C 71.39; H 5.37. *M* 263.4. $C_{16}H_{14}O_4$. Calculated, %: C 71.10; H 5.22. *M* 270.3.

2-Ethoxy-4-formylphenyl *p*-methylbenzoate (IVb). Yield 87%, mp 103-104°C. IR spectrum, ν, cm^{-1}: 3074, 3053, 3040, 3010 (C–H_{arom}); 1732, 1698 (C=O); 1609, 1603, 1590, 1512, 1431, 1399, 1378 (C–C_{arom}); 1476 (CH_2); 870, 838, 825, 789, 777, 747, 686, 647, 636, 610, 586, 578 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 208 (24000), 220 (24000), 253 (28000), 307 (6000). ^{1}H NMR spectrum, δ, ppm: 1.27 t (CH_3, ^3J = 7.3 Hz), 2.41 s (CH_3), 4.08 q (CH_2O, ^3J = 7.3 Hz), 7.10–7.55 m and 7.75–8.15 m (C_6H_3, C_6H_4), 9.90 s (CHO). Found, %: C 72.13; H 5.91. *M* 271.9. $C_{17}H_{16}O_4$. Calculated, %: C 71.82; H 5.67. *M* 284.3.

Bis(2-ethoxy-4-formylphenyl) succinate (IVc). Yield 82%, mp 114–115°C. IR spectrum, ν, cm^{-1}: 3110, 3090, 3073, 3060, 3020 (C–H_{arom}); 1763, 1701 (C=O); 1601, 1500, 1435, 1414, 1393, 1371 (C–C_{arom}); 1477 (CH_2); 949, 914, 897, 875, 840, 812, 790, 671, 588, 580 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 205 (50000), 220 (70000), 258 (40000), 305 (14000). ^{1}H NMR spectrum, δ, ppm: 1.35 t (6H, CH_3, ^3J = 7.4 Hz), 3.02 s [4H, $(CH_2)_2$], 4.08 q (4H, CH_2O, ^3J = 7.4 Hz), 7.10–7.50 m (6H, C_6H_3), 9.90 s (2H, CHO). Found, %: C 64.04; H 5.57. *M* 397.6. $C_{22}H_{22}O_8$. Calculated, %: C 63.76; H 5.35. *M* 414.4.

2-Ethoxy-4-formylphenyl *o*-chlorobenzoate (IVd). Yield 85%, mp 83–84°C. IR spectrum, ν, cm^{-1}: 3090, 3076, 3066, 3050, 3020 (C–H_{arom}); 1746, 1696

(C=O); 1505, 1436, 1392 (C–C_{arom}); 1470 (CH_2); 900, 878, 862, 823, 814, 783, 739, 712, 681, 655, 590 (δC–H_{arom}); 535 (C–Cl). UV spectrum, λ_{max}, nm (ε): 208 (28000), 220 (23000), 255 (12000), 305 (4000). ^{1}H NMR spectrum, δ, ppm: 1.37 t (CH_3, ^3J = 7.4 Hz), 4.16 q (CH_2O, ^3J = 7.4 Hz), 7.20–7.60 m and 7.95–8.15 m (C_6H_3, C_6H_4), 9.94 s (CHO). Found, %: C 63.27; H 4.42; Cl 11.25. *M* 295.8. $C_{16}H_{13}ClO_4$. Calculated, %: C 63.06; H 4.30; Cl 11.63. *M* 304.7.

2-Ethoxy-4-formylphenyl *p*-chlorobenzoate (IVe). Yield 83%, mp 84–85°C. IR spectrum, ν, cm^{-1}: 3095, 3080, 3050, 3015 (C–H_{arom}); 1745, 1696 (C=O); 1597, 1503, 1436, 1398 (C–C_{arom}); 1470 (CH_2); 902, 872, 862, 842, 822, 744, 676, 637, 587 (C–H_{arom}); 520 (C–Cl). UV spectrum, λ_{max}, nm (ε): 205 (25000), 220 (20000), 252 (15000), 304 (4000). ^{1}H NMR spectrum, δ, ppm: 1.32 t (CH_3, ^3J = 7.4 Hz), 4.13 q (CH_2O, ^3J = 7.4 Hz), 7.25–7.60 m and 7.95–8.20 m (C_6H_3, C_6H_4), 9.96 s (CHO). Found, %: C 63.30; H 4.51; Cl 11.37. *M* 293.9. $C_{16}H_{13}ClO_4$. Calculated, %: C 63.06; H 4.30; Cl 11.63. *M* 304.7.

This study was performed under financial support by the Belarus Republican Foundation for Basic Research (project no. Kh 03-079).

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