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Preparative Synthesis of Vanillin and Vanillal Alkanoates

E. A. Dikusar, O. G. Vyglazov, K. L. Moiseichuk, N. A. Zhukovskaya, and N. G. Kozlov

Institute of Physical Organic Chemistry, Belarussian National Academy of Sciences, Minsk, Belarus
Tereza Inter Limited Liability Company, Moscow, Russia

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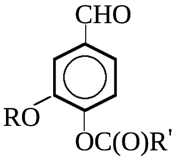
Abstract—Procedures for preparing vanillin and vanillal alkanoates were developed.

Vanillin (4-hydroxy-3-methoxybenzaldehyde, **Ia**) and its homolog, vanillal (4-hydroxy-3-ethoxybenzaldehyde, **Ib**) are widely used in food and perfume industries [1–3]. Vanillin can also be used as a synthetic precursor of biologically active substances [4, 5]. However, new processes in food industry demand new aroma chemicals that would have vanilla smell but be more heat-resistant than vanillin and stable in a wide range of pH in the presence of enzymes. These requirements stimulate chemists to prepare new vanillin and vanillal derivatives; many of them appeared to exhibit stronger vanilla smell, compared to the initial compounds, with diverse tints.

Here we report convenient synthetic routes to vanillin (**IIa**–**IIm**) and vanillal (**IIIa**–**IIIg**) esters.



II a–m, III a–g

II, R = Me, R' = H (**a**), Me (**b**), Et (**c**), Pr (**d**), Me_2CH (**e**), Bu (**f**), Me_2CHCH_2 (**g**), C_5H_{11} (**h**), C_6H_{13} (**i**), C_7H_{15} (**j**), $C_{12}H_{25}$ (**k**), CH_2Cl (**l**), 4-$MeC_6H_4O(CH_2)_2$ (**m**); **III**, R = Et, R' = H (**a**), Me (**b**), Et (**c**), Pr (**d**), Me_2CH (**e**), Bu (**f**), Me_2CHCH_2 (**g**).

Some of them were characterized [6–13], but the lack of some esters in the homologous series of the vanillin and vanillal derivatives and incompleteness of the available physicochemical data for the previously described compounds stimulated us to make this study, aimed to develop new flavor additives derived from vanillin and vanillal.

The formates were prepared by the reactions of vanillin **Ia** and vanillal **Ib** with formic acid in the presence of dicyclohexylcarbodiimide [14], which is a simpler procedure compared to the known routes [11]. The other esters **IIb**–**IIm** and **IIIb**–**IIIg** were prepared by reactions of **Ia** and **Ib** with alkanecarboxylic acid chlorides in the presence of pyridine [15, 16]. To simplify the production process and improve the purity of the target products for their use in formulations for perfume and food industry, the esters were also prepared by the Schotten–Baumann reaction [9, 17]. The resulting esters **IIb**–**IIe** and **IIIb**–**IIIe** (Tables 1, 2) do not require additional purification. They are free of benzene and pyridine impurities and can be directly used in the perfume industry.

The organoleptic assessment of the scents of **IIa**–**IIg** and **IIIa**–**IIIg** was made by the Tasting Council at the Accredited Checkout and Analytical Laboratory of the Tereza Inter Limited Liability Company (Moscow, Russia). Esters **IIa**–**IIg** and **IIIa**–**IIIg** have pronounced vanilla smell with various intense tints (Table 3). Esters **IIh**–**IIm** have no odor.

EXPERIMENTAL

The IR spectra of the compounds were recorded on a Protege-460 IR Fourier spectrometer (Nicolet) from the samples prepared as thin films or KBr pellets; the UV spectra, on a Specord UV-Vis spectrophotometer from 1×10^{-4} M solutions in 1-butanol; the ^{1}H NMR spectra, on a BS-587A spectrometer (100 MHz, Tesla) from 5% solutions in $CDCl_3$, with octamethyltetracyclosiloxane as internal reference; and the mass spectra, on a Chrommas GC/MS Hewlett–Packard 5890/5972 gas chromatograph–mass spectrometer equipped with an HP-5MS column, at an ionizing electron energy of 70 eV.

Alkanecarboxylic acid chlorides were prepared by refluxing the corresponding carboxylic acids with a 1.5-fold excess of $SOCl_2$ in benzene.

Table 1. Properties of esters **IIa–IIm** and **IIIa–IIIg**

Ester	Yield, %	T_m, °C	Found, %		Formula	Calculated, %		*M*	
			C	H		C	H	found	calculated
IIa	70	54–55	60.08	4.43	$C_9H_8O_4$	60.00	4.48	180	180.2
IIb	92	78–79	62.05	5.43	$C_{10}H_{10}O_4$	61.85	5.19	194	194.2
IIc	79	35–36	63.64	5.79	$C_{11}H_{12}O_4$	63.46	5.77	208	208.2
IId*	81	–	65.12	6.42	$C_{12}H_{14}O_4$	64.86	6.31	222	222.2
IIe	89	29–30	65.07	6.46	$C_{12}H_{14}O_4$	64.86	6.31	222	222.2
IIf*	84	–	66.29	7.02	$C_{13}H_{16}O_4$	66.09	6.83	236	236.3
IIg*	84	–	66.27	7.04	$C_{13}H_{16}O_4$	66.09	6.83	236	236.3
IIh*	85	–	67.39	7.41	$C_{14}H_{18}O_4$	67.18	7.25	250	250.3
IIi*	82	–	68.45	7.80	$C_{15}H_{20}O_4$	68.16	7.63	264	264.3
IIj*	77	–	69.18	8.03	$C_{16}H_{22}O_4$	69.04	7.91	278	278.3
IIk	75	–	72.54	9.37	$C_{21}H_{32}O_4$	72.38	9.26	348	348.5
IIl*	78	–	52.63	4.08	$C_{10}H_9ClO_4$	52.53	3.97	228	228.6
IIm	76	63–64	69.02	5.97	$C_{18}H_{18}O_5$	68.78	5.77	314	314.3
IIIa	73	47–48	62.03	5.28	$C_{10}H_{10}O_4$	61.85	5.19	194	194.2
IIIb	87	33–34	63.72	5.84	$C_{11}H_{12}O_4$	63.46	5.77	208	208.2
IIIc	84	45–47	65.07	6.44	$C_{12}H_{14}O_4$	64.86	6.31	222	222.2
IIId*	92	–	66.34	7.07	$C_{13}H_{16}O_4$	66.09	6.83	236	236.3
IIIe	93	45–46	66.29	7.01	$C_{13}H_{16}O_4$	66.09	6.83	236	236.3
IIIf*	92	–	67.41	7.45	$C_{14}H_{18}O_4$	67.18	7.25	250	250.3
IIIg*	82	–	67.49	7.41	$C_{14}H_{18}O_4$	67.18	7.25	250	250.3

* T_m, °C (*p*, mm Hg), d^{20}_{20}, n^{20}_D: 137–138 (0.5), 1.2101, 1.5281 (**IId**); 129–130 (**I**), 1.1807, 1.5273 (**IIf**); 129–130 (0.5), 1.1825, 1.5235 (**IIg**); 155–156 (0.5), 1.1228, 1.5068 (**IIh**); 163–164 (0.5), 1.1033, 1.5092 (**IIi**); 170–171 (0.5), 1.0949, 1.5079 (**IIj**); 145–146 (0.5), 1.2009, 1.5272 (**IIId**); 150–151 (0.5), 1.1129, 1.5213 (**IIIf**); 132–133 (0.5), 1.0954, 1.5180 (**IIIg**).

** Cl, %: found 15.39, calculated 15.51 (**IIl**).

Table 2. ^{1}H, IR, and UV spectra of esters **IIa–IIm** and **IIIa–IIIg**

Ester	^{1}H NMR spectrum, δ, ppm	IR spectrum, ν, cm^{-1}	UV spectrum, λ_{max}, nm (ε)
IIa	3.91 s (3H, MeO), 7.20–7.57 m (3H, C_6H_3), 8.27 s [1H, OC(O)H], 9.95 s (1H, CHO)	3110, 3077, 3060, 3045, 3020, 2995, 2960, 2928, 2847, 2805, 2749, 1757, 1685, 1801, 1473, 1455, 1426, 1392, 1275, 1204, 1197, 1154, 1124, 1097, 1029, 962, 875, 867, 821, 733, 679, 632, 590, 574	205 (9000), 223 (14 000), 260 (8000), 308 (3000)
IIb	2.32 s (3H, Me), 3.92 s (3H, MeO), 7.18 d, 7.48 m (3H, C_6H_3), 9.92 s (1H, CHO)	3090, 3070, 3055, 3017, 2965, 2945, 2920, 2848, 2805, 2755, 1758, 1690, 1599, 1507, 1471, 1427, 1396, 1377, 1280, 1220, 1209, 1155, 1126, 1033, 1014, 907, 862, 830, 739, 680, 600, 580	206 (8000), 224 (15 000), 261 (8000), 309 (3000)
IIc	1.25 t (3H, $MeCH_2$), 2.52 q (2H, CH_2), 3.84 s (3H, MeO), 7.13 d, 7.42 m (3H, C_6H_3), 9.88 s (1H, CHO)	3115, 3070, 3017, 2968, 2940, 2875, 2855, 2800, 2745, 1766, 1700, 1602, 1504, 1466, 1423, 1393, 1275, 1180, 1182, 1145, 1120, 1032, 912, 870, 40, 780, 733, 645, 580	205 (8000), 223 (14 000), 260 (8000), 310 (3000)
IId	1.02 t (3H, Me), 1.63 m (2H, CH_2), 2.51 t (2H, CH_2), 3.84 s (3H, MeO), 7.15 d, 7.40 m (3H, C_6H_3), 9.90 (1H, CHO)	3117, 3071, 3015, 2968, 2939, 2874, 2853, 2800, 2743, 1765, 1701, 1601, 1503, 1465, 1423, 1391,1272, 1181, 1145, 1120, 1031, 913, 865, 840, 780, 733, 647, 582	206 (8000), 224 (15 000), 260 (7000), 310 (3000)

Table 2. (Contd.)

Ester	^{1}H NMR spectrum, δ, ppm	IR spectrum, ν, cm^{-1}	UV spectrum, λ_{max}, nm (ε)
IIe	1.30 s, 1.40 s, 2.88 s, 2.88 m (7H, *i*-Pr), 3.90 s (3H, MeO), 7.21 d, 7.50 m (3H, C_6H_3), 9.96 s (1H, CHO)	3115, 3075, 3015, 2976, 2940, 2878, 2845, 2800, 2745, 1763, 1701, 1601, 1503, 1468, 1423, 1389, 1270, 1202, 1180, 1150, 1121, 1191, 1033, 960, 914, 865, 815, 780, 734, 650, 580, 550	206 (9000), 223 (15 000), 261 (7000), 311 (3000)
IIf	0.96 t (3H, Me), 1.20–1.90 m [4H, $(CH_2)_2$], 2.62 t (2H, CH_2), 3.96 s (3H, OMe), 7.15 d, 7.38 m (3H, C_6H_3), 9.90 s (1H, CHO)	3074, 3012, 2962, 2936, 2874, 2860, 2736, 1764, 1701, 1601, 1503, 1466, 1423, 1391, 1371, 1322, 1284, 1272, 1198, 1181, 1149, 1119, 1092, 1082, 1032, 964, 913, 866, 835, 781, 733, 645, 585, 548	206 (7000), 224 (14 000), 261 (7000), 310 (3000)
IIg	1.06 d (6H, Me_2C), 1.35–2.90 m (3H, CH and CH_2), 3.96 s (3H, OMe), 7.12 d, 7.42 m (3H, C_6H_3), 9.91 s (1H, CHO)	3117, 3070, 3010, 2957, 2934, 2870, 2855, 2743, 1766, 1704, 1601, 1503, 1466, 1424, 1390, 1322, 1272, 1200, 1145, 1120, 1032, 965, 915, 866, 835, 780, 735, 645, 585, 545	206 (8000), 223 (14 000), 260 (7000), 310 (3000)
IIh	0.90 t (3H, Me), 1.12–1.90 m [6H, $(CH_2)_3$], 2.58 m (2H, CH_2), 3.88 s (3H, OMe), 7.13 d, 7.44 m (3H, C_6H_3), 9.95 s (1H, CHO)	3110, 3070, 3010, 2958, 2935, 2872, 2856, 2743, 1765, 1704, 1602, 1503, 1465, 1424, 1392, 1321, 1271, 1200, 1144, 1120, 1033, 965, 915, 867, 835, 781, 736, 645, 585, 544	207 (8000), 223 (14 000), 260 (7000), 311 (3000)
IIi	0.96 t (3H, Me), 1.15–1.88 m [8H, $(CH_2)_4$], 2.51 m (2H, CH_2), 3.86 s (3H, OMe), 7.12 d, 7.45 m (3H, C_6H_3), 9.91 s (1H, CHO)	3109, 3070, 3015, 2958, 2936, 2872, 2857, 2744, 1764, 1704, 1601, 1503, 1464, 1424, 1390, 1322, 1271, 1201, 1144, 1120, 1032, 965, 914, 867, 835, 782, 736, 644, 585, 545	207 (7000), 224 (14 000), 261 (7000), 310 (3000)
IIj	0.92 t (3H, Me), 1.32 m [8H, $(CH_2)_4$], 1.79 m (2H, CH_2), 2.60 m (2H, CH_2), 3.88 s (3H, OMe), 7.14 d, 7.47 m (3H, C_6H_3), 9.90 s (1H, CHO)	3108, 3070, 3016, 2957, 2935, 2872, 2856, 2746, 1763, 1703, 1602, 1504, 1464, 1424, 1391, 1323, 1271, 1202, 1145, 1120, 1031, 965, 915, 867, 834, 782, 735, 644, 585, 544	208 (7000), 224 (14 000), 262 (7000), 310 (3000)
IIk	0.89 t (3H, Me), 1.30 m [18H, $CH_2)_9$], 1.75 m (2H, CH_2), 2.59 m (2H, CH_2), 3.87 s (3H, OMe), 7.16 d, 7.41 m (3H, C_6H_3), 9.91 s (1H, CHO)	3115, 3072, 3015, 2955, 2935, 2870, 2855, 2741, 1766, 1703, 1601, 1503, 1466, 1422, 1390, 1325, 1272, 1199, 1145, 1120, 1032, 964, 915, 866, 835, 780, 734, 645, 585	206 (7000), 223 (14 000), 260 (7000), 310 (3000)
IIl	3.88 s (3H, MeO, 4.39 s (2H, CH_2), 7.24 d, 7.50 m (3H, C_6H_3), 9.89 s (1H, CHO)	3095, 3070, 3050, 3015, 2970, 2942, 2922, 2845, 2805, 2755, 1770, 1692, 1600, 1507, 1471, 1427, 1396, 1377, 1280, 1220, 1209, 1155, 1126, 1033, 1014, 908, 862, 830, 739, 680, 600, 580	208 (8000), 224 (16 000), 261 (7000), 310 (3000)
IIm	2.28 s (3H, Me), 3.06 t (2H, CH_2O), 3.86 s (3H, OMe), 4.35 t (2H, $CH_2C{=}O$), 6.63–7.52 m (7H, C_6H_3 and C_6H_4), 9.90 s (1H, CHO)	3120, 3085, 3032, 3015, 2995, 2933, 2882, 2857, 2831, 2817, 2790, 2729, 1773, 1704, 1599, 1511, 1462, 1396, 1376, 1327, 1290, 1248, 1209, 1179, 1131, 1042, 1028, 955, 910, 890, 880, 850, 827, 818, 781, 731, 590, 514	204 (15 000), 221 (20 000), 260 (7000), 306 (3000)
IIIa	1.46 t (3H, Me), 4.18 q (2H, CH_2), 7.22 d, 7.51 m (3H, C_6H_3), 8.32 s [1H, OC(O)H], 9.97 s (1H, CHO)	3110, 3081, 3015, 2988, 2940, 2840, 2813, 2744, 1733, 1698, 1599, 1505, 1439, 1391, 1276, 1197, 1160, 1138, 1098, 1040, 895, 868, 851, 824, 800, 745, 618, 590	205 (8000), 222 (15 000), 261 (8000), 308 (3000)
IIIb	1.41 t (3H, $MeCH_2$), 2.32 s [3H, MeC(O)], 4.11 q (2H, CH_2), 7.20 d, 7.45 m (3H, C_6H_3), 9.92 s (1H, CHO)	3080, 2982, 2934, 2907, 2880, 2850, 2830, 2736, 1768, 1694, 1600, 1592, 1509, 1479, 1441, 1392, 1370, 1320, 1288, 1273, 1210, 1197, 1156, 1040, 1011, 973, 900, 870, 832, 800, 786, 745, 726, 667, 632, 586, 528	204 (8000), 224 (15 000), 261 (8000), 309 (3000)

Table 2. (Contd.)

Ester	^{1}H NMR spectrum, δ, ppm	IR spectrum, ν, cm^{-1}	UV spectrum, λ_{max}, nm (ε)
IIIc	1.35 m (6H, $2MeCH_2$), 2.65 q (2H, $CH_2C{=}O$), 4.13 q (2H, CH_2O), 7.16 q, 7.45 m (3H, C_6H_3), 9.91 s (1H, CHO)	3115, 3080, 3055, 2985, 2942, 2890, 2875, 2840, 2795, 2740, 1760, 1697, 1601, 1589, 1508, 1480, 1465, 1435, 1401, 1380, 1353, 1353, 1324, 1288, 1264, 1206, 1161, 1140, 1115, 1075, 1040, 1007, 973, 890, 872, 826, 800, 784, 585	205 (8000), 224 (14 000), 261 (8000), 310 (3000)
IIId	1.03 t (3H, Me), 1.42 t (3H, $MeCH_2O$), 1.64 m (2H, CH_2), 2.52 t (2H, CH_2), 4.12 q (2H, $MeCH_2O$), 7.17 d, 7.44 m (3H, C_6H_3), 9.92 s (1H, CHO)	3114, 3077, 3055, 2983, 2941, 2890, 2875, 2843, 2795, 2740, 1761, 1698, 1600, 1589, 1506, 1480, 1465, 1440, 1400, 1381, 1353, 1325, 1288, 1264, 1206, 1160, 1140, 1113, 1075, 1040, 1006, 973, 890, 872, 826, 800, 784, 585	206 (8000), 223 (15 000), 261 (8000), 310 (3000)
IIIe	1.27 d (6H, Me_2C), 1.38 t (3H, Me), 2.78 m (1H, CH), 4.08 q (2H, CH_2), 7.10 d, 7.40 m (3H, C_6H_3), 9.91 s (1H, CHO)	3120, 3080, 3055, 2990, 2975, 2939, 2895, 2880, 2842, 2790, 2740, 1752, 1697, 1600, 1586, 1508, 1420, 1435, 1400, 1385, 1320, 1288, 1262, 1160, 1117, 1099, 1033, 974, 916, 870, 821, 800, 785, 751, 655, 580	204 (8000), 223 (14 000), 261 (7000), 310 (3000)
IIIf	1.00 t (3H, Me), 1.20–1.90 m [4H, $(CH_2)_2$], 1.42 t (3H, $MeCH_2O$), 2.61 t (2H, $CH_2C{=}O$), 4.12 q (2H, $MeCH_2O$), 7.16 d, 7.43 m (3H, C_6H_3), 9.92 s (1H, CHO)	3110, 3076, 3055, 2984, 2941, 2891, 2875, 2845, 2795, 2740, 1763, 1698, 1602, 1589, 1506, 1480, 1465, 1441, 1402, 1381, 353, 1325, 1288, 1264, 1206, 1161, 1140, 1113, 1075, 1040, 1006, 975, 890, 873, 826, 801, 784, 584	205 (8000), 223 (15 000), 261 (8000), 310 (3000)
IIIg	1.08 d (6H, Me_2C), 1.40 t (3H, $MeCH_2O$), 1.40–2.85 m (3H, CH and CH_2), 4.11 q (2H, $MeCH_2O$), 7.12 d, 7.42 m (3H, C_6H_3), 9.91 s (1H, CHO)	3118, 3070, 3050, 3020, 2963, 2936, 2874, 2834, 2785, 2737, 1764, 1699, 1600, 1503, 1467, 1434, 1391, 1370, 1321, 1280, 1272, 1180, 1150, 1119, 1092, 1041, 973, 915, 897, 869, 830, 786, 744, 730, 650, 580	206 (7000), 224 (15 000), 261 (8000), 310 (3000)

Table 3. Results of organoleptic assessment of the smell of esters **IIa**–**IIg** and **IIIa**–**IIIg**

Ester	Smell
IIa	Vanilla, wood, with powder tint
IIb	Vanilla-wood, with clove-spicy tint
IIc	Vanilla, honey
IId	Cream-milk, vanilla
IIe	Chocolate-vanilla, cream
IIf	Vanilla-rum, with cream tint
IIg	Vanilla-rum, with fruit tint
IIIa	Wood, vanilla, with spicy tint
IIIb	Vanilla-flower, with honey tint
IIIc	Vanilla-honey, with wood tint
IIId	Cream-vanilla, with baked milk tint
IIIe	Vanilla-cream, with white chocolate tint
IIIf	Vanilla-rum, with cream chocolate tint
IIIg	Vanilla-fruit, with cream-clove tint

Vanillin and vanillal formates IIa and IIIa. A 0.12-mol portion of 99% formic acid was added to a solution of 0.1 mol of **Ia** or **Ib** and 0.1 mol of dicyclohexylcarbodiimide in 500 ml of absolute benzene. The mixture was stirred and kept at 20–23°C for 24–36 h. The dicyclohexylurea precipitate was filtered off and washed with 100 ml of benzene; the filtrate was washed with water and saturated aqueous $NaHCO_3$. The benzene solution was dried over $CaCl_2$, the solvent was distilled off, and the residue was recrystallized from methanol.

Vanillin and vanillal alkanoates IIb–IIm and IIIb–IIIg. A 0.25-mol portion of anhydrous pyridine was added to a solution of 0.2 mol of vanillin **Ia** or vanillal **Ib** in 500 ml of anhydrous CH_2Cl_2, and 0.2 mol of appropriate alkanecarboxylic acid chloride was added in small portions, with stirring by shaking the reaction flask. The mixture was refluxed for 1 h, the solvent was distilled off by heating on a water bath, and the residue was dissolved in 500 ml of benzene, washed three times with water and three times with 5% aqueous $NaHCO_3$, and dried over $CaCl_2$. The solvent was distilled off, and the residue was distilled in a vacuum (**IId**, **IIf**–**IIj**, **IIId**, **IIIf**, **IIIg**) or recrystallized from benzene–hexane (**IIb**, **IIc**, **IIe**, **IIm**, **IIIb**, **IIIc**, **IIIe**). In the case of **IIk** and **IIl**, the residue was a noncrystallizing greasy substance.

The solvents CH_2Cl_2 and C_6H_6 distilled from the reaction mixture can be reused after distillation from P_2O_5 on a Vigreux column.

Vanillin and vanillal alkanoates IIb–**IIg and IIIb**–**IIIg.** A 1-mol portion of appropriate alkanecarboxylic acid anhydride was added in small portions with vigorous stirring to a solution of 1 mol of vanillin **Ia** or vanillal **Ib** in 1.1 l of 1 N aqueous KOH. The mixture was stirred for 3–5 h and allowed to stand for 10–15 h at 20–23°C. Compounds **IIb**–**IIg** and **IIIb**–**IIIg** were isolated by filtration or decanting, washed with water, and dried in air.

CONCLUSION

A procedure was developed for preparing vanillin and vanillal alkanoates in 70–96% yield. These compounds are of interest as components of flavor food additives with popular chocolate, caramel, and milk-cream smells.

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