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BRIEF COMMUNICATIONS

New Esters of Vanillin and Vanillal with Some Alkane- and Arenecarboxylic Acids

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Abstract—Previously unknown esters were synthesized by the reaction of vanillin and vanillal with carboxylic acid chlorides.

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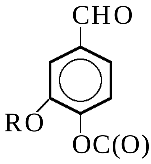
Natural plant aldehydophenols, vanillin and vanillal (**Ia**, **Ib**), are available precursors for preparing fragrance compounds and food aromatizers [1–3], medical products, and biologically active compounds [4–8]:



IIa–**IIh**, **IIIa**–**IIIv**

where **II**, R is Me, R' is (**a**) $(CH_2)_7Me$, (**b**) $(CH_2)_{14}Me$, (**c**) cyclo-C_6H_{11}, (**d**) $(CH_2)_2C_6H_5$, (**e**) $CBrCCl{=}CCl_2$, (**f**) $(CH_2)_2C(O)OMe$, (**g**) $C(CN){=}CHC_6H_5$, and (**h**) 3,5-$C_6H_3(NO_2)_2$; **III**, R is Et, R' is (**a**) $(CH_2)_4Me$, (**b**) $(CH_2)_5Me$, (**c**) $(CH_2)_6Me$, (**d**) $(CH_2)_7Me$, (**e**) $(CH_2)_8Me$, (**f**) $(CH_2)_{11}Me$, (**g**) $(CH_2)_{14}Me$, (**h**) $(CH_2)_{16}Me$, (**i**) cyclo-C_6H_{11}, (**j**) $CH_2C_6H_5$, (**k**) $(CH_2)_2C_6H_5$, (**l**) $CH_2CHMeC_6H_5$, (**m**) *trans*-$CH{=}CHC_6H_5$, (**n**) $CBrCCl{=}CCl_2$, (**o**) $CHBrCHBrC_6H_5$, (**p**) $(CH_2)_2C(O)OMe$, (**q**) $C(CN){=}CHC_6H_5$, (**r**) 2,4-$C_6H_3C_{12}$, (**s**) 2,4-$CH_2OC_6H_3C_{12}$, (**t**) 3-$C_6H_5NO_2$, (**u**) 4-$C_6H_5NO_2$, and (**v**) 3,5-$C_6H_3(NO_2)_2$.

Here we describe a convenient procedure for preparing new esters of vanillin and vanillal with a number of alkane- and arenecarboxylic acids (**IIa**–**IIh** and **IIIa**–**IIIv**).

Esters **IIa**–**IIh** and **IIIa**–**IIIv** were prepared by simpler, more convenient, and more practically feasible procedure in comparison with that described previously for similar compounds [1–3].

Esters **IIa**–**IIh** and **IIIa**–**IIIv** were synthesized by the reaction of vanillin and vanillal (**Ia**, **Ib**) with chlorides of the corresponding alkane- and arenecarboxylic acids in anhydrous benzene in the presence of pyridine. We used the stoichiometric ratio of the reactants, 1 : 1 : 1. As a result of this reaction, the initial aldehydophenols **Ia** and **Ib** were converted to the corresponding esters **IIa**–**IIh** and **IIIa**–**IIIv** with a yield of 90–96%.

Vanillin and vanillal esters **IIa**–**IIh** and **IIIa**–**IIIv** are colorless viscous liquids or crystalline substances (crystallized from a mixture of benzene and hexane) (see table). The esters do not require additional purification, distillation, or recrystallization.

The structure and composition of vanillin and vanillal esters **IIa**–**IIh** and **IIIa**–**IIIv** were confirmed by elemental analysis, cryoscopic determination of the molecular weight (see table), and ^1H NMR, IR, and UV spectra. According to the ^1H NMR data, the purity of the resulting compounds was 98 ± 1%.

In the IR spectra of vanillin and vanillal esters **IIa**–**IIh** and **IIIa**–**IIIv**, there are the following characteristic absorptions bands, ν, cm^{-1}: 3100–3000 (CHAr), 2990–2795 (CHAlk), 2740 ± 5 (CH of CHO group), 1720–1770 (C=O of ester group), 1695–1705 (C=O of CHO group), 1600–1350 (vibrations of aromatic system), 1300–1000 (C–O vibrations), and 800–600 (CHAr) [1, 3].

In the UV spectra of vanillin and vanillal esters **IIa**–**IIh** and **IIIa**–**IIIw**, there are the following absorption peaks, λ_{max}, nm (ε): 206 (9000), 224 (15 000), 260 (8000), and 310 (3000), caused by the presence of the 4-alkanoyloxy-3-alkoxybenzaldehyde fragment

Characteristics of vanillin and vanillal esters **IIa**–**IIh** and **IIIa**–**IIIv**

Ester	Yield, %	mp, °C	Found, %		Formula	Calculated, %		*M*	
			C	H		C	H	found	calculated
IIa*	90	–	70.02	8.34	$C_{17}H_{24}O_4$	69.84	8.27	281.9	292.4
IIb	92	37–38	74.05	9.93	$C_{24}H_{38}O_4$	73.81	9.81	372.3	390.6
IIc	90	73–74	68.90	7.11	$C_{15}H_{18}O_4$	68.69	6.92	252.7	262.3
IId	93	46–47	71.94	5.75	$C_{17}H_{16}O_4$	71.82	5.67	275.5	284.3
IIe**	93	103–104	36.08	2.12	$C_{12}H_8BrCl_3O_4$	35.81	2.00	393.4	402.5
IIf	90	72–73	58.91	5.42	$C_{13}H_{14}O_6$	58.65	5.30	254.4	266.3
IIg**	94	165–166	70.58	4.35	$C_{18}H_{13}NO_4$	70.35	4.26	300.2	307.3
IIh**	96	163–164	52.17	3.10	$C_{15}H_{10}N_2O_8$	52.03	2.91	328.3	346.3
IIIa*	90	–	68.37	7.65	$C_{15}H_{20}O_4$	68.16	7.63	258.6	264.3
IIIb*	93	–	69.18	8.01	$C_{16}H_{22}O_4$	69.04	7.91	270.1	278.3
IIIc*	92	–	70.02	8.29	$C_{17}H_{24}O_4$	69.84	8.27	286.6	292.4
IIId*	92	–	70.64	8.60	$C_{18}H_{26}O_4$	70.56	8.55	299.2	306.4
IIIe*	93	–	71.45	8.95	$C_{19}H_{28}O_4$	71.22	8.81	313.0	320.4
IIIf	91	42–43	73.08	9.49	$C_{22}H_{34}O_4$	72.89	9.45	354.7	362.5
IIIg	90	35–36	74.30	10.00	$C_{25}H_{40}O_4$	74.22	9.96	395.6	404.6
IIIh	96	47–48	75.14	10.31	$C_{27}H_{44}O_4$	74.96	10.25	426.8	432.6
IIIi	92	61–62	69.75	7.42	$C_{16}H_{20}O_4$	69.55	7.29	270.0	276.3
IIIj*	91	–	71.98	5.77	$C_{17}H_{16}O_4$	71.82	5.67	277.1	284.3
IIIk	93	73–74	72.74	6.19	$C_{18}H_{18}O_4$	72.47	6.08	290.3	298.3
IIIl*	94	–	73.32	6.58	$C_{19}H_{20}O_4$	73.06	6.45	300.5	312.4
IIIm	93	107–108	73.21	5.60	$C_{18}H_{16}O_4$	72.96	5.44	288.7	296.3
IIIn**	94	84–85	37.66	2.47	$C_{13}H_{10}BrCl_3O_4$	37.49	2.42	402.9	416.5
IIIo**	94	110–111	47.50	3.59	$C_{18}H_{16}Br_2O_4$	47.40	3.54	442.3	456.1
IIIp*	92	–	60.27	5.85	$C_{14}H_{16}O_6$	60.00	5.75	271.7	280.3
IIIq**	93	127–128	71.54	4.76	$C_{19}H_{15}NO_4$	71.33	4.70	314.6	321.3
IIIr**	90	117–118	56.92	3.70	$C_{16}H_{12}Cl_2O_4$	56.66	3.57	329.8	339.2
IIIs**	91	107–108	55.68	3.95	$C_{17}H_{14}Cl_2O_5$	55.31	3.82	354.2	369.2
IIIt**	91	133–134	61.20	4.25	$C_{16}H_{13}NO_6$	60.95	4.16	303.4	315.3
IIIu**	90	155–156	61.15	4.20	$C_{16}H_{13}NO_6$	60.95	4.16	308.0	315.3
IIIv**	90	137–138	53.60	3.38	$C_{16}H_{12}N_2O_8$	53.34	3.36	348.9	360.3

* d_{20}^{20}, n_D^{20}: 0.9908, 1.5090 (**IIa**); 0.9169, 1.5090 (**IIIa**); 0.9679, 1.5070 (**IIIb**); 0.9358, 1.5065 (**IIIc**); 0.9103, 1.5060 (**IIId**); 0.9213, 1.5030 (**IIIe**); 1.2079, 1.5700 (**IIIj**); 1.0866, 1.5580 (**IIIl**); 1.1222, 1.5234 (**IIIp**).

** Br + Cl, %: found 46.10, calculated 46.28 (**IIe**); N, %: found 4.30, calculated 4.56 (**IIg**); N, %: found 7.90, calculated 8.09 (**IIh**); Br + Cl, %: found 44.45, calculated 44.72 (**IIIn**); Br, %: found 34.88, calculated 35.04 (**IIIo**); N, %: found 4.03, calculated 4.36 (**IIIq**); Cl, %: found 20.70, calculated 20.91 (**IIIr**); Cl, %: found 18.93, calculated 19.21 (**IIIs**); N, %: found 4.37, calculated 4.44 (**IIIt**); N, %: found 4.30, calculated 4.44 (**IIIu**); N, %: found 7.51, calculated 7.78 (**IIIv**).

[1]. In addition, the UV spectra of esters of functionality substituted and aromatic carboxylic acids (**IId**, **IIe**, **IIg**, **IIh**, **IIIj**–**IIIo**, and **IIIq**–**IIIv**) contain absorption bands typical of the corresponding fragments of these acids [3].

In the ^1H NMR spectra of vanillin derivatives **IIa**–**IIh**, the MeO group gives a singlet in the range 3.90–3.96 ppm, and in the ^1H NMR spectra of vanillal derivatives **IIIa**–**IIIv** the EtO group gives a triplet at 1.40–1.45 ppm (Me) and a quartet at 4.08–4.18 ppm (CH_2). The aromatic protons of esters **IIa**–**IIh** and **IIIa**–**IIIv** (C_6H_3) give a multiplet in the range 7.10–7.60 ppm, and the aldehyde proton of the CHO group gives a singlet in the range 9.95–10.0 ppm. The ^1H NMR spectra of compounds **IIa**–**IIh** and **IIIa**–**IIIv** contain characteristic signals of ester fragments [1, 3].

EXPERIMENTAL

The IR spectra were recorded on a Protege-460 Nicolet Fourier spectrophotometer in thin layer or in KBr. The UV spectra of 1×10^{-4} M solutions in methanol were recorded on a Specord UV-Vis spectrophotometer. The ^{1}H NMR spectra were recorded on a Tesla BS-587A spectrometer operating at 100 MHz (5% solutions in $CDCl_3$, TMS internal reference). The molecular weights were determined cryoscopically in benzene.

Carboxylic acid chlorides were synthesized by refluxing the corresponding carboxylic acids with a 1.5-fold excess of $SOCl_2$ in benzene. Freshly distilled carboxylic acid chlorides and anhydrous benzene and pyridine were used.

Vanillin and vanillal alkanoates IIa–IIh and IIIa–IIIv. To a solution of 0.02 M of vanillin or vanillal (**Ia**, **Ib**) and 0.02 mol of alkene- or arenecarboxylic acid chlorides in 50 ml of benzene, a solution of 0.02 mol of pyridine in 10 ml of benzene was added with shaking. The vessel with the reaction mixture was hermetically sealed and the mixture allowed to stay for 10–12 h at 20–23°C with intermitted careful shaking. Then it was placed in a separating funnel, thoroughly washed with water and 20% NaCl for suppression of emulsion formation, and washed 2–3 times with 5% $NaHCO_3$. The organic layer was separated and filtered through a paper filter. Benzene was removed in a vacuum, with heating of the residue above 30°C avoided. Compounds **IIb**–**IIh**, **IIIf**–**IIIi**, **IIIk**, **IIIm**–**IIIo**, and **IIIq**–**IIIv** were crystallized from a mixture of benzene and hexane.

CONCLUSIONS

(1) An improved procedure was developed for preparing vanillin and vanillal esters with a yield of 90–96%.

(2) Some of the resulting compounds may be of interest as components for perfume and food industry and can serve as accessible precursors in synthesis of biologically active substances and medicinals.

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