

ESTERS OF JASMORANGE OXIME

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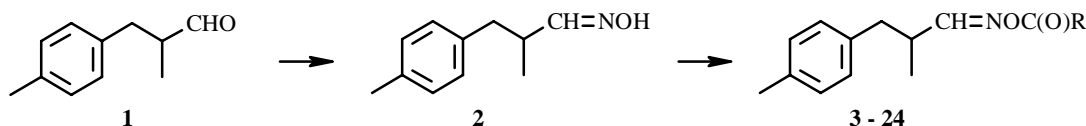
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The aldehyde jasmorange (**1**) was converted to the oxime (**2**), acylation of which by alkylcarboxylic acid anhydrides in the presence of HClO_4 or by acid chlorides in the presence of pyridine synthesized esters of jasmorange oxime **3-24** in 82-91% yields. Refluxing **3-24** in hexane converted them quantitatively into nitrile **25**.

Key words: jasmorange, oxime, carboxylic acids, anhydrides, acid chlorides, esters, nitrile, chemical modification.

The aldehyde jasmorange [2-methyl-3-(4-tolyl)propanal, **1**] has a sharp fruity-balsamic fragrance with hints of watermelon and greens and is used in perfumes and fragrances [1]. Oximes of several natural compounds act as convenient synthons for preparing fragrances and biologically active compounds based on them [2, 3].

The goal of our work was to prepare a series of new esters from jasmorange oxime (**2**). Esters of jasmorange oxime **3-24** were synthesized by reacting **2** with anhydrides of alkylcarboxylic acids in the presence of catalytic amounts of HClO_4 (**3-6**) or with alkyl- and arylcarboxylic acid chlorides in the presence of pyridine (**7-25**). The yields of **3-24** were 82-91%.



R = Me (**3**); Et (**4**); Pr (**5**); Me_2CH (**6**); $\text{Me}(\text{CH}_2)_3$ (**7**); Me_2CHCH_2 (**8**); Me_3C (**9**); $\text{Me}(\text{CH}_2)_4$ (**10**); $\text{Me}(\text{CH}_2)_5$ (**11**); $\text{Me}(\text{CH}_2)_6$ (**12**); $\text{Me}(\text{CH}_2)_7$ (**13**); $\text{Me}(\text{CH}_2)_8$ (**14**); $\text{Me}(\text{CH}_2)_{11}$ (**15**); $\text{Me}(\text{CH}_2)_{16}$ (**16**); *cyclo*- C_6H_{11} (**17**); C_6H_5 (**18**); $\text{C}_6\text{H}_5\text{CH}_2$ (**19**); $\text{C}_6\text{H}_5(\text{CH}_2)_2$ (**20**); $\text{C}_6\text{H}_5\text{CHMeCH}_2$ (**21**); *trans*- $\text{C}_6\text{H}_5\text{CH}=\text{CH}$ (**22**); MeO (**23**); EtO (**24**)

The prepared esters **3-24** are derivatives of an aldehyde and are sensitive to heating, in contrast with esters based on ketone oximes [3]. Refluxing solutions of **3-24** in hexane converted them quantitatively into 1-(4-tolyl)-2-cyanopropane (**25**) in 98-100% yield via loss of the corresponding carboxylic acids.

The structures of **2-25** were confirmed by elemental analysis; PMR, IR, and UV spectra; and cryoscopic molecular-weight determination. According to PMR spectra, the products were $98 \pm 1\%$ pure. Elemental analyses and molecular-weight determinations of all synthesized compounds agreed with those calculated.

The aromas of **2**, esters **3-24**, and nitrile **25** were assessed for organoleptic value by the Taste Council of the Accredited Monitoring Analytical Laboratory of OOO Tereza-Inter (Moscow). Table 1 lists the mean statistical taste data for the aromas of the products.

Table 1 shows that all prepared compounds are highly interesting for potential use in perfumes and food production. The hint of fresh watermelon and fruit found in most of the synthesized compounds was important and promising for modern trends in perfume development.

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TABLE 1. Organoleptic Assessment of Aromas of 2-25

Compound	Odor
2	Light, fruity-berry, hints of pear, cherry, and jasmine
3	Fruity-flowery, hints of watermelon, cherry, and lilac on a powdery background
4	Fruity, fresh, hints of watermelon, banana, and pineapple on an anise background
5	Fruity, heavy, hint of butter on a cheesy background
6	Oily-spicy, hints of melted butter, cheese, and cumin
7	Fruity-spicy with a hint of cream
8	Fruity-berry, hints of pineapple and strawberry
9	Berry-flowery, hints of gardenia, rose, and strawberry on a cosmetic background
10	Berry-fruity, hints of ripe apple, watermelon, sea buckthorn, and cranberry
11	Berry-fruity on a flowery background, hints of currant, forest berry, green apple, and geranium
12	Berry-fruity on a wine-spice background with a hint of anise-watermelon
13	Berry-spicy with a hint of sour wine
14	Weak, berry, hints of red wine and raspberry with a hint of metallic powder
15	Weak with a light aroma of watermelon seeds
16	Weak, flowery-fruity with a hint of woody iris
17	Fruity, aldehyde, watermelon-pear with a hint of wine
18	Fruity, spicy, watermelon with a hint of balsam
19	Fruity-honey, watermelon with a hint of myrrh and civet
20	Sweet, spicy with a chemical background
21	Fruity-spicy, hints of anise and honey on a cucumber background
22	Watermelon-spicy, hints of ozone and balsam
23	Flowery-fruity, hint of cyclamen, watermelon, and anise
24	Flowery-watermelon with a hint of milk and cheese
25	Woody-fruity with a spicy hint of benzoic resin and cinnamon on a sweet honey background

EXPERIMENTAL

IR spectra in thin layers or KBr were recorded on a Protege-460 IR-Fourier spectrophotometer (Nicolet); UV spectra in MeOH ($1 \cdot 10^{-4}$ M solutions), on a Specord UV-Vis instrument. PMR spectra in CDCl_3 (5% solutions) were obtained on a BS-587A spectrometer (100 MHz, Tesla). Chemical shifts were determined relative to TMS internal standard. Molecular weights were determined cryoscopically in benzene. Column chromatography used silica gel L 5/40 μm with hexane eluent.

Jasmorange Oxime (2). Jasmorange (**1**, 0.21 mol), hydroxylamine hydrochloride (0.27 mol), sodium bicarbonate (0.28 mol), and ethanol (75 mL, 96%) were refluxed for 1 h. The reaction mixture was poured into a beaker with water (300 mL), cooled to 5°C , and left for 10-12 h. The resulting crystalline precipitate was filtered on a porous glass filter, washed with a small quantity of water, and dried in air to afford **2**, 95% yield, mp $33\text{-}34^\circ\text{C}$, $\text{C}_{11}\text{H}_{15}\text{NO}$.

IR spectrum (ν , cm^{-1}): 3264 (OH); 3094, 3075, 3020, 3004 (=CH and CH_{Ar}); 2966, 2923, 2872 (CH_{Alk}); 1640 (C=N); 1515, 1455, 1377 (Ar); 959, 943 (N-O); 860, 840, 803, 750, 720 (CH_{Ar}). UV spectrum (λ_{max} , nm, ϵ): 216 (5000). PMR spectrum (δ , ppm): 1.06 (m, CH_3), 2.35 (s, CH_3), 2.50-2.95 (m, CH_2 and CH), 6.95-7.20 (m, C_6H_4), 7.39 (d, HC=N).

Jasmorange Oxime Esters 3-6 (General Method). Jasmorange oxime (**2**, 0.01 mol) and the appropriate acid anhydride (0.011 mol) were dissolved in hexane (30 mL), treated with HClO_4 (47%, one drop), shaken, left at $20\text{-}23^\circ\text{C}$ for 24-36 h, and diluted with water. The product was extracted with hexane. The organic layer was separated, washed with water and NaHCO_3 solution (5%), and dried over CaCl_2 . Solvent was removed at reduced (30-45 mm Hg) pressure keeping the temperature below $25\text{-}30^\circ\text{C}$. The product was purified by column chromatography over silica gel with elution by hexane.

The following compounds were prepared by this method.

2-Methyl-3-(4-tolyl)-propanal-O-acetyloxime (3). Yield 89%, d_{20}^{20} 1.0637, n_D^{20} 1.5120. $\text{C}_{13}\text{H}_{17}\text{NO}_2$. IR spectrum (ν , cm^{-1}): 3090, 3040, 3021, 3004 (=CH and CH_{Ar}); 2980, 2925, 2878, 2862 (CH_{Alk}); 1763 (C=O); 1631 (C=N); 1516, 1456, 1370 (Ar); 1244, 1208 (C-O); 875, 845, 803, 765, 745 (CH_{Ar}). UV spectrum (λ_{max} , nm, ϵ): 216 (5000). PMR spectrum (δ , ppm): 1.32 (m, CH_3), 2.35 (s, CH_3 and CH_3), 2.60-3.00 (m, CH_2 and CH), 6.95-7.20 (m, C_6H_4), 7.58 (d, HC=N).

2-Methyl-3-(4-tolyl)-propanal-O-propionyloxime (4). Yield 88%, d_{20}^{20} 1.0470, n_D^{20} 1.5105. $C_{14}H_{19}NO_2$. IR spectrum (ν , cm^{-1}): 3090, 3040, 3021, 3003 (=CH and CH_{Ar}); 2979, 2939, 2925, 2879, 2870 (CH_{Alk}); 1766 (C=O); 1631 (C=N); 1515, 1460, 1380 (Ar); 1145, 1070 (C–O); 865, 804, 745 (CH_{Ar}). UV spectrum (λ_{max} , nm, ϵ): 216 (5000). PMR spectrum (δ , ppm): 1.05-1.40 (m, CH_3 and CH_3), 2.31 (s, CH_3), 2.10-3.05 (m, CH_2 , CH_2 and CH), 6.95-7.15 (m, C_6H_4), 7.58 (d, HC=N).

2-Methyl-3-(4-tolyl)-propanal-O-butyryloxime (5). Yield 87%, d_{20}^{20} 0.9771, n_D^{20} 1.5115. $C_{15}H_{21}NO_2$. IR spectrum (ν , cm^{-1}): 3090, 3040, 3020, 3003 (=CH and CH_{Ar}); 2967, 2933, 2875 (CH_{Alk}); 1766 (C=O); 1631 (C=N); 1515, 1458, 1380 (Ar); 1149, 1080 (C–O); 850, 803, 754 (CH_{Ar}). UV spectrum (λ_{max} , nm, ϵ): 216 (5000). PMR spectrum (δ , ppm): 0.85-1.30 (m, CH_3 and CH_3), 1.77 (q, CH_2), 2.32 (s, CH_3), 2.15-3.08 (m, CH_2 , CH_2 and CH), 6.90-7.15 (m, C_6H_4), 7.58 (d, HC=N).

2-Methyl-3-(4-tolyl)-propanal-O-isobutyryloxime (6). Yield 90%, d_{20}^{20} 1.0630, n_D^{20} 1.5080. $C_{15}H_{21}NO_2$. IR spectrum (ν , cm^{-1}): 3090, 3040, 3020, 3003 (=CH and CH_{Ar}); 2975, 2933, 2876 (CH_{Alk}); 1764 (C=O); 1631 (C=N); 1516, 1458, 1385 (Ar); 1121, 1098 (C–O); 854, 830, 802, 757 (CH_{Ar}). UV spectrum (λ_{max} , nm, ϵ): 216 (5000).

PMR spectrum (δ , ppm): 1.12 (m, CH_3), 1.20 [d, (CH_3)₂C], 2.30 (s, CH_3), 2.45-3.05 (m, CH_2 , CH and CH), 6.90-7.15 (m, C_6H_4), 7.58 (d, HC=N).

Jasmorange Oxime Esters 7-24 (General Method). Jasmorange oxime (**2**, 0.01 mol) was dissolved in hexane (50 mL), treated with absolute pyridine (0.01 mol), cooled to 15°C, stirred by carefully shaking, and treated with the appropriate acid chloride (0.01 mol). The mixture was left at 20-23°C for 24-36 h and diluted with water. The product was extracted with hexane. The organic layer was separated, washed with water and $NaHCO_3$ solution (5%), and dried over $CaCl_2$. Solvent was removed at reduced (30-45 mm Hg) pressure keeping the temperature below 25-30°C. The product was purified by column chromatography over silica gel with elution by hexane.

The following compounds were prepared by this method.

2-Methyl-3-(4-tolyl)-propanal-O-valeryloxime (7). Yield 88%, d_{20}^{20} 1.0334, n_D^{20} 1.5100. $C_{16}H_{23}NO_2$. IR spectrum (ν , cm^{-1}): 3090, 3040, 3020, 3003 (=CH and CH_{Ar}); 2961, 2931, 2873 (CH_{Alk}); 1765 (C=O); 1631 (C=N); 1516, 1457, 1379 (Ar); 1148, 1092 (C–O); 877, 855, 802, 754 (CH_{Ar}). UV spectrum (λ_{max} , nm, ϵ): 216 (5000). PMR spectrum (δ , ppm): 0.89 (t, CH_3), 1.12 (m, CH_3), 1.20-1.80 [m, (CH_2)₂], 2.32 (s, CH_3), 2.00-3.02 (m, CH_2 , CH_2 and CH), 6.90-7.20 (m, C_6H_4), 7.58 (d, HC=N).

2-Methyl-3-(4-tolyl)-propanal-O-isovaleryloxime (8). Yield 89%, d_{20}^{20} 1.1073, n_D^{20} 1.5075. $C_{16}H_{23}NO_2$. IR spectrum (ν , cm^{-1}): 3090, 3040, 3020, 3003 (=CH and CH_{Ar}); 2962, 2931, 2873 (CH_{Alk}); 1765 (C=O); 1631 (C=N); 1516, 1457, 1379 (Ar); 1154, 1090 (C–O); 876, 855, 802, 754 (CH_{Ar}). UV spectrum (λ_{max} , nm, ϵ): 216 (5000). PMR spectrum (δ , ppm): 0.92 [d, (CH_3)₂C], 1.12 (m, CH_3), 1.20-1.40 (m, CH_2), 2.32 (s, CH_3), 1.90-3.05 (m, CH_2 , CH and CH), 6.90-7.15 (m, C_6H_4), 7.58 (d, HC=N).

2-Methyl-3-(4-tolyl)-propanal-O-pivalyloxime (9). Yield 86%, d_{20}^{20} 0.9121, n_D^{20} 1.4960. $C_{16}H_{23}NO_2$. IR spectrum (ν , cm^{-1}): 3090, 3040, 3021, 3003 (=CH and CH_{Ar}); 2976, 2932, 2875 (CH_{Alk}); 1754 (C=O); 1631 (C=N); 1516, 1457, 1379 (Ar); 1150, 1111 (C–O); 876, 855, 802, 755 (CH_{Ar}). UV spectrum (λ_{max} , nm, ϵ): 216 (5000). PMR spectrum (δ , ppm): 1.10 (m, CH_3), 1.28 [s, (CH_3)₃C], 2.34 (s, CH_3), 2.55-3.02 (m, CH_2 and CH), 6.90-7.15 (m, C_6H_4), 7.60 (d, HC=N).

2-Methyl-3-(4-tolyl)-propanal-O-caproyloxime (10). Yield 91%, d_{20}^{20} 1.0088, n_D^{20} 1.5070. $C_{17}H_{25}NO_2$. IR spectrum (ν , cm^{-1}): 3090, 3040, 3020, 3003 (=CH and CH_{Ar}); 2958, 2930, 2872, 2861 (CH_{Alk}); 1766 (C=O); 1631 (C=N); 1516, 1458, 1379 (Ar); 1149, 1093 (C–O); 871, 855, 803, 755 (CH_{Ar}). UV spectrum (λ_{max} , nm, ϵ): 216 (5000). PMR spectrum (δ , ppm): 0.90 (t, CH_3), 1.12 (m, CH_3), 1.15-1.90 [m, (CH_2)₃], 2.32 (s, CH_3), 2.10-3.00 (m, CH_2 , CH_2 and CH), 6.90-7.20 (m, C_6H_4), 7.58 (d, HC=N).

2-Methyl-3-(4-tolyl)-propanal-O-enanthyloxime (11). Yield 92%, d_{20}^{20} 0.9936, n_D^{20} 1.5065. $C_{18}H_{27}NO_2$. IR spectrum (ν , cm^{-1}): 3090, 3040, 3020, 3003 (=CH and CH_{Ar}); 2957, 2930, 2872, 2859 (CH_{Alk}); 1766 (C=O); 1631 (C=N); 1516, 1458, 1379 (Ar); 1149, 1096 (C–O); 871, 855, 803, 755 (CH_{Ar}). UV spectrum (λ_{max} , nm, ϵ): 216 (5000). PMR spectrum (δ , ppm): 0.91 (t, CH_3), 1.12 (m, CH_3), 1.10-1.90 [m, (CH_2)₄], 2.32 (s, CH_3), 2.10-3.00 (m, CH_2 , CH_2 and CH), 6.90-7.20 (m, C_6H_4), 7.58 (d, HC=N).

2-Methyl-3-(4-tolyl)-propanal-O-caprylyloxime (12). Yield 88%, d_{20}^{20} 0.9820, n_D^{20} 1.4980. $C_{19}H_{29}NO_2$. IR spectrum (ν , cm^{-1}): 3090, 3040, 3020, 3003 (=CH and CH_{Ar}); 2956, 2928, 2870, 2857 (CH_{Alk}); 1766 (C=O); 1631 (C=N); 1516, 1458, 1378 (Ar); 1142, 1096 (C–O); 877, 855, 802, 754 (CH_{Ar}). UV spectrum (λ_{max} , nm, ϵ): 216 (5000). PMR spectrum (δ , ppm): 0.89 (t, CH_3), 1.13 (m, CH_3), 1.08-1.90 [m, (CH_2)₅], 2.32 (s, CH_3), 2.10-3.05 (m, CH_2 , CH_2 and CH), 6.90-7.20 (m, C_6H_4), 7.58 (d, HC=N).

2-Methyl-3-(4-tolyl)-propanal-O-pelargonyloxime (13). Yield 90%, d_{20}^{20} 0.9750, n_D^{20} 1.4850. $C_{20}H_{31}NO_2$. IR spectrum (ν , cm^{-1}): 3090, 3040, 3020, 3002 (=CH and CH_{Ar}); 2955, 2926, 2870, 2856 (CH_{Alk}); 1766 (C=O); 1631 (C=N); 1516, 1458, 1378 (Ar); 1143, 1099 (C–O); 880, 855, 802, 754 (CH_{Ar}). UV spectrum (λ_{max} , nm, ϵ): 216 (5000). PMR spectrum (δ , ppm): 0.89 (t, CH_3), 1.13 (m, CH_3), 1.02-1.90 [m, (CH_2)₆], 2.32 (s, CH_3), 2.08-3.05 (m, CH_2 , CH_2 and CH), 6.90-7.20 (m, C_6H_4), 7.58 (d, HC=N).

2-Methyl-3-(4-tolyl)-propanal-O-capryloxime (12). Yield 92%, d_{20}^{20} 0.9916, n_D^{20} 1.4970. $C_{21}H_{33}NO_2$. IR spectrum (ν , cm^{-1}): 3090, 3040, 3020, 3002 (=CH and CH_{Ar}); 2955, 2926, 2870, 2855 (CH_{Alk}); 1767 (C=O); 1631 (C=N); 1516, 1458, 1378 (Ar); 1141, 1101 (C–O); 878, 855, 802, 754 (CH_{Ar}). UV spectrum (λ_{max} , nm, ϵ): 216 (5000). PMR spectrum (δ , ppm): 0.89 (t, CH_3), 1.13 (m, CH_3), 1.00-1.88 [m, (CH_2)₇], 2.33 (s, CH_3), 2.08-3.04 (m, CH_2 , CH_2 and CH), 6.90-7.18 (m, C_6H_4), 7.58 (d, HC=N).

2-Methyl-3-(4-tolyl)-propanal-O-tridecanoyloxime (15). Yield 86%, d_{20}^{20} 0.9845, n_D^{20} 1.4860. $C_{24}H_{39}NO_2$. IR spectrum (ν , cm^{-1}): 3090, 3040, 3020, 3002 (=CH and CH_{Ar}); 2953, 2924, 2852 (CH_{Alk}); 1767 (C=O); 1631 (C=N); 1516, 1459, 1378 (Ar); 1140, 1104 (C–O); 876, 850, 804, 745, 720 (CH_{Ar}). UV spectrum (λ_{max} , nm, ϵ): 216 (5000). PMR spectrum (δ , ppm): 0.88 (t, CH_3), 1.12 (m, CH_3), 1.00-1.90 [m, (CH_2)₁₀], 2.32 (s, CH_3), 2.06-3.04 (m, CH_2 , CH_2 and CH), 6.90-7.20 (m, C_6H_4), 7.58 (d, HC=N).

2-Methyl-3-(4-tolyl)-propanal-O-stearyloxime (16). Yield 89%, mp 37-38°C. $C_{29}H_{49}NO_2$. IR spectrum (ν , cm^{-1}): 3090, 3040, 3020, 3002 (=CH and CH_{Ar}); 2954, 2918, 2850 (CH_{Alk}); 1752 (C=O); 1631 (C=N); 1516, 1459, 1378 (Ar); 1472 (CH_2); 1145, 1102 (C–O); 876, 845, 802, 750, 720 (CH_{Ar}). UV spectrum (λ_{max} , nm, ϵ): 216 (5000). PMR spectrum (δ , ppm): 0.88 (t, CH_3), 1.12 (m, CH_3), 1.00-1.92 [m, (CH_2)₁₅], 2.32 (s, CH_3), 2.06-3.04 (m, CH_2 , CH_2 and CH), 6.90-7.20 (m, C_6H_4), 7.58 (d, HC=N).

2-Methyl-3-(4-tolyl)-propanal-O-cyclohexanemethanoyloxime (17). Yield 89%, d_{20}^{20} 1.1037, n_D^{20} 1.5245. $C_{18}H_{25}NO_2$. IR spectrum (ν , cm^{-1}): 3090, 3040, 3020, 3002 (=CH and CH_{Ar}); 2931, 2856 (CH_{Alk}); 1762 (C=O); 1631 (C=N); 1515, 1451, 1379 (Ar); 1151, 1107 (C–O); 876, 848, 803, 755, 720 (CH_{Ar}). UV spectrum (λ_{max} , nm, ϵ): 216 (5000). PMR spectrum (δ , ppm): 0.80-2.10 (m, C_6H_{11}), 1.12 (m, CH_3), 2.33 (s, CH_3), 2.45-3.10 (m, CH_2 and CH), 6.90-7.22 (m, C_6H_4), 7.61 (d, HC=N).

2-Methyl-3-(4-tolyl)-propanal-O-benzoyloxime (18). Yield 84%, d_{20}^{20} 1.0845, n_D^{20} 1.5185. $C_{18}H_{19}NO_2$. IR spectrum (ν , cm^{-1}): 3090, 3070, 3045, 3033, 3020, 3004 (=CH and CH_{Ar}); 2981, 2935, 2926, 2876, 2856 (CH_{Alk}); 1720 (C=O); 1631 (C=N); 1516, 1479, 1454, 1380 (Ar); 1276, 1110 (C–O); 855, 817, 792, 775, 755, 730, 715, 682 (CH_{Ar}). UV spectrum (λ_{max} , nm, ϵ): 207 (15,000), 218 (13,000), 250 (8000). PMR spectrum (δ , ppm): 1.20 (m, CH_3), 2.36 (s, CH_3), 2.60-3.05 (m, CH_2 and CH), 7.00-8.15 (m, C_6H_5 and C_6H_4), 7.60 (d, HC=N).

2-Methyl-3-(4-tolyl)-propanal-O-phenylacetyloxime (19). Yield 87%, d_{20}^{20} 1.0838, n_D^{20} 1.5265. $C_{19}H_{21}NO_2$. IR spectrum (ν , cm^{-1}): 3090, 3070, 3045, 3033, 3020, 3004 (=CH and CH_{Ar}); 2981, 2935, 2926, 2876, 2856 (CH_{Alk}); 1720 (C=O); 1631 (C=N); 1516, 1479, 1454, 1380 (Ar); 1276, 1110 (C–O); 855, 817, 792, 775, 755, 730, 715, 682 (CH_{Ar}). UV spectrum (λ_{max} , nm, ϵ): 210 (6000), 216 (6000). PMR spectrum (δ , ppm): 1.20 (m, CH_3), 2.36 (s, CH_3), 2.60-3.05 (m, CH_2 and CH), 3.84 (s, CH_2), 7.05-7.55 (m, C_6H_5 and C_6H_5), 7.60 (d, HC=N).

2-Methyl-3-(4-tolyl)-propanal-O-(3-phenylpropionyl)oxime (20). Yield 88%, d_{20}^{20} 1.1314, n_D^{20} 1.5375. $C_{20}H_{23}NO_2$. IR spectrum (ν , cm^{-1}): 3090, 3048, 3026, 3002 (=CH and CH_{Ar}); 2978, 2925, 2872, 2860 (CH_{Alk}); 1764 (C=O); 1631 (C=N); 1601, 1516, 1498, 1454, 1379 (Ar); 1181, 1121 (C–O); 877, 855, 803, 752, 700 (CH_{Ar}). UV spectrum (λ_{max} , nm, ϵ): 212 (9000). PMR spectrum (δ , ppm): 1.30 (m, CH_3), 2.35 (s, CH_3), 2.55-3.15 [m, (CH_2)₂, CH_2 and CH], 6.90-7.35 (m, C_6H_5 and C_6H_4), 7.59 (d, HC=N).

2-Methyl-3-(4-tolyl)-propanal-O-(3-phenylbutyryl)oxime (21). Yield 90%, d_{20}^{20} 1.0650, n_D^{20} 1.5260. $C_{21}H_{25}NO_2$. IR spectrum (ν , cm^{-1}): 3090, 3049, 3024, 3003 (=CH and CH_{Ar}); 2979, 2925, 2876, 2865 (CH_{Alk}); 1764 (C=O); 1631 (C=N); 1516, 1497, 1454, 1380 (Ar); 1120 (C–O); 845, 814, 792, 770, 765, 730, 701 (CH_{Ar}). UV spectrum (λ_{max} , nm, ϵ): 213 (9000). PMR spectrum (δ , ppm): 1.30 (m, CH_3), 1.43 (d, CH_3), 2.35 (s, CH_3), 2.50-3.60 (m, $2\times CH_2$ and $2\times CH$), 6.90-7.30 (m, C_6H_5 and C_6H_4), 7.59 (d, HC=N).

2-Methyl-3-(4-tolyl)-propanal-O-(trans-cinnamyl)oxime (22). Yield 85%, d_{20}^{20} 1.1045, n_D^{20} 1.5510. $C_{20}H_{21}NO_2$. IR spectrum (ν , cm^{-1}): 3090, 3049, 3024, 3003 (=CH and CH_{Ar}); 2979, 2925, 2876, 2865 (CH_{Alk}); 1738 (C=O); 1636 (C=C); 1631 (C=N); 1516, 1497, 1454, 1380 (Ar); 1120 (C–O); 845, 814, 792, 770, 765, 730, 701 (CH_{Ar}). UV spectrum (λ_{max} , nm, ϵ): 206 (24,000), 220 (30,000), 280 (28,000). PMR spectrum (δ , ppm): 1.22 (m, CH_3), 2.36 (s, CH_3), 2.60-3.05 (m, CH_2 and CH), 6.80-7.90 (m, $CH=CH$, C_6H_5 and C_6H_4), 7.60 (d, HC=N).

2-Methyl-3-(4-tolyl)-propanal-O-(methylcarbonate)oxime (23). Yield 90%, d_{20}^{20} 1.1037, n_D^{20} 1.5140. $C_{13}H_{17}NO_3$. IR spectrum (ν , cm^{-1}): 3090, 3040, 3021, 3003 (=CH and CH_{Ar}); 2978, 2960, 2925, 2876, 2862 (CH_{Alk}); 1778 (C=O); 1631 (C=N); 1516, 1454, 1380 (Ar); 1244 (C–O); 879, 845, 804, 780, 745 (CH_{Ar}). UV spectrum (λ_{max} , nm, ϵ): 216 (5000). PMR spectrum (δ , ppm): 1.32 (m, CH_3), 2.34 (s, CH_3), 2.55–3.00 (m, CH_2 and CH), 3.87 (s, CH_3), 6.95–7.20 (m, C_6H_4), 7.58 (d, HC=N).

2-Methyl-3-(4-tolyl)-propanal-O-(ethylcarbonate)oxime (24). Yield 91%, d_{20}^{20} 1.0948, n_D^{20} 1.5030. $C_{14}H_{19}NO_3$. IR spectrum (ν , cm^{-1}): 3090, 3040, 3019, 3002 (=CH and CH_{Ar}); 2980, 2929, 2875 (CH_{Alk}); 1775 (C=O); 1631 (C=N); 1516, 1456, 1369 (Ar); 1236 (C–O); 843, 804, 779, 755 (CH_{Ar}). UV spectrum (λ_{max} , nm, ϵ): 216 (5000) PMR spectrum (δ , ppm): 1.32 (m, CH_3), 1.40 (t, CH_3), 2.34 (s, CH_3), 2.55–3.00 (m, CH_2 and CH), 4.30 (q, CH_2), 6.95–7.16 (m, C_6H_4), 7.58 (d, HC=N).

1-(4-Tolyl)-2-cyanopropane (25). A solution of jasmorange oxime ester (**3-24**, 0.005 mol) in hexane (50 mL) was refluxed for 1 h, diluted with water, and extracted with hexane. The organic layer was separated, washed with water and $NaHCO_3$ solution (5%), and dried over $CaCl_2$. Solvent was removed at reduced (60–75 mm Hg) pressure. The product was purified by column chromatography over silica gel with elution by hexane. Yield 98–100%, d_{20}^{20} 1.0163, n_D^{20} 1.5225. $C_{11}H_{13}N$. IR spectrum (ν , cm^{-1}): 3090, 3049, 3022, 3003 (=CH and CH_{Ar}); 2979, 2925, 2877, 2865 (CH_{Alk}); 2239 (C≡N); 1516, 1455, 1380 (Ar); 855, 816, 792, 745 (CH_{Ar}). PMR spectrum (δ , ppm): 1.35 (m, CH_3), 2.35 (s, CH_3), 2.65–3.05 (m, CH_2 and CH), 7.15 (s, C_6H_4).

REFERENCES

1. S. A. Boitkevich, *865 Fragrances for Perfume and Household Chemistry* [in Russian], Pishchevaya Promyshlennost', Ufa (1994).
2. E. A. Dikumar, N. G. Kozlov, N. A. Zhukovskaya, and K. L. Moiseichuk, *Khim. Prir. Soedin.*, 154 (2002).
3. N. A. Zhukovskaya, E. A. Dikumar, K. L. Moiseichuk, and O. G. Vyglazov, *Zh. Prikl. Khim.*, **79**, 642 (2006).