

# Diesters of Mixed Carboxylic Acids of the Adamantane Series: Synthesis, Physicochemical Properties, and Thermo-Oxidative Stability

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**Abstract**—The synthesis of a series of 5,7-R-3-carboxy-1-adamantylacetic acid diesters has been performed and their physicochemical and thermo-oxidative properties have been studied. The properties of these diesters have been compared with those of the adipic and sebacic diesters that are currently in wide use as plasticizers and components of various lubricants.

**Keywords:** alkyladamantanes, esters, thermo-oxidative stability, thermally stable oils, plasticizers

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## INTRODUCTION

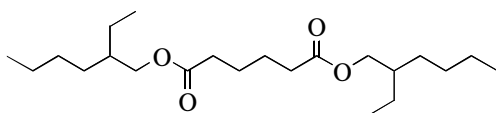
In scientific literature, various derivatives of adamantane are quite widely proposed for use as ingredients of medicaments and components of catalysts, polymer materials, and fuels and lubricants or additives for them. The lipophilicity and high thermal and thermo-oxidative stability of adamantane and its derivatives attract a great deal of attention of national and foreign researchers, as well as the possibility of increasing their availability by improving their manufacturing processes [1–14].

Esters of aliphatic and aromatic dicarboxylic and tricarboxylic acids are widely used as plasticizers in the production of cable compounds, artificial leathers, industrial rubber goods, polymer construction materials, oilcloths, film and sheet materials, and film packaging materials because they enhance significantly the options for the processing of polymers by means of changing their physical properties, as well as impart flexibility, frost resistance, and good electric and other properties to them [15]. Esters, mainly those of adipic and sebacic acids, are the base stock or components of aircraft synthetic oils, hydraulic and hydraulic brake fluids, white oils (for the textile industry), greases, and instrument oils operating in the temperature range of –60 to +175°C. Aliphatic dicarboxylic acid esters

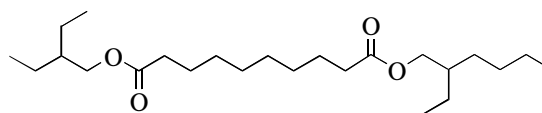
(mainly adipic and sebacic esters) possess a good viscosity–temperature dependence over a wide range of positive and negative temperatures, a low (down to minus 65–70°C) pour point, and high thermal and thermo-oxidative stability and, as such, have found application as base stock or components of lubricating oils and greases operating in the temperature range of 175 to –60°C [16].

Following the study reported in [5], we synthesized a number of diesters of 5,7-R-3-carboxy-1-adamantylacetic acids (R = H or CH<sub>3</sub>) and examined their physicochemical and thermo-oxidative properties. For comparison, most widely used aliphatic dicarboxylic diesters of a similar in structure (four and eight methylene units between the carboxylic groups), such as bis(2-ethylhexyl) adipate (DOA), and bis(2-ethylhexyl) sebacate (DOS) according to GOST (State Standard) 8728, and thermally stable dioctyl sebacate (DOSt) according to TU (Technical Specification) 6-06-11-88, were used. In the synthesis of 7-R-3-carboxy-1-adamantylacetic acid diesters, the choice of the alcohol residue size was determined by the molecular weight of the product diester, which was supposed to be close to that of DOA (370 g/mol) or DOSt (426 g/mol).

Structure of DOA



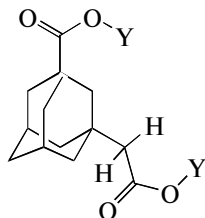
Structure of DOSt



## EXPERIMENTAL

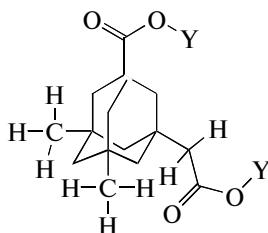
Two series of the diesters were synthesized and studied:

the 3-carboxy-1-adamantylacetic acid series



Y = C<sub>3</sub>H<sub>7</sub> (I), C<sub>4</sub>H<sub>9</sub> (II), C<sub>5</sub>H<sub>11</sub> (III), C<sub>6</sub>H<sub>13</sub> (IV)

and the 5,7-dimethyl-3-carboxy-1-adamantylacetic acid series



Y = C<sub>3</sub>H<sub>7</sub> (V), C<sub>4</sub>H<sub>9</sub> (VI), *iso*-C<sub>4</sub>H<sub>9</sub> (VII), C<sub>5</sub>H<sub>11</sub> (VIII), *iso*-C<sub>5</sub>H<sub>11</sub> (IX), C<sub>6</sub>H<sub>13</sub> (X).

**3-Carboxy-1-adamantylacetic acid** and **5,7-dimethyl-3-carboxy-1-adamantylacetic acid** were synthesized according to the procedure described in [4].

**3-Carboxy-1-adamantylacetic acid di-*n*-propyl ester (I).** A mixture of 32.8 g (0.137 mol) of 3-carboxy-1-adamantylacetic acid, 33 g (0.549 mol, 41 mL) of *n*-propanol, and 3 g (0.018 mol) of *p*-toluenesulfonic acid in 120 mL of toluene was refluxed with a Dean-Stark trap for 10 h. After the release of a sufficient amount of water, the mixture was diluted with 100 mL of toluene, washed successively with a 15% NaHCO<sub>3</sub> aqueous solution to pH 7 and water, and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated and the residue was purified by vacuum distillation. During the distillation, the fraction with bp 133–138°C (0.05 torr) was collected. The weight of the distilled product was 36.5 g (83%).  $n_D^{20}$  1.4830. IR,  $\nu$ , cm<sup>-1</sup>: 1728(C=O). <sup>1</sup>H NMR,  $\delta$ , ppm: 0.89–0.93 (t, 6H, CH<sub>3</sub>,  $J$  = 7.36 Hz), 1.56–1.62 (m, (10H, CH<sub>2</sub>Ad), 1.72–1.73 (m, 4H, CH<sub>2</sub>Ad, CH<sub>2</sub>), 1.74–1.83 (m, 2H, CH<sub>2</sub>), 2.05–2.07 (m, 2H, CHAd), 2.09 s (2H, CH<sub>2</sub>), 3.96–3.98 (m, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR,  $\delta$ , ppm: 10.49 (CH<sub>3</sub>), 10.61 (CH<sub>3</sub>), 22.09 (CH<sub>2</sub>), 28.38 (CH), 32.98 (C), 35.67 (CH<sub>2</sub>), 38.19 (CH<sub>2</sub>), 41.33 (CH<sub>2</sub>), 41.51 (C), 43.51 (CH<sub>2</sub>), 48.49 (CH<sub>2</sub>), 65.79 (CH<sub>2</sub>), 171.62 (C), 177.30 (C). Mass spectrum,  $m/z$  ( $I_{rel}$ , %): 322 (2) [M]<sup>+</sup>, 281 (60), 239 (43), 235 (87), 221 (33), 193 (62), 179 (38), 147

(40), 133 (100), 91 (86), 43 (69). Found, %: C 71.80, H 9.42. Calculated for C<sub>19</sub>H<sub>30</sub>O<sub>4</sub>, %: C 70.74, H 9.38.  $M$  322.44.

**3-Carboxy-1-adamantylacetic acid di-*n*-butyl ester (II)** was prepared similar to di-*n*-propyl ester I from 32 g (0.134 mol) of 3-carboxy-1-adamantylacetic acid and 40 g (0.541 mol, 50 mL) of *n*-butanol. The yield 33.5 g (71%), bp 140–148°C (0.026 torr),  $n_D^{20}$  1.4813. IR,  $\nu$ , cm<sup>-1</sup>: 1728 (C=O). <sup>1</sup>H NMR,  $\delta$ , ppm: 0.91–0.93 (t, 6H, CH<sub>3</sub>,  $J$  = 6.88 Hz), 1.34–1.38 (m, 4H, CH<sub>2</sub>Ad), 1.56–1.59 (m, 10H, CH<sub>2</sub>Ad, CH<sub>2</sub>), 1.72–1.74 (m, 2H, CH<sub>2</sub>), 1.75–1.81 (m, 4H, CH<sub>2</sub>), 2.07–2.08 (m, 2H, CH), 2.1 (s, 2H, CH<sub>2</sub>), 4.02–4.04 (m, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR,  $\delta$ , ppm: 13.79 (CH<sub>3</sub>), 13.84 (CH<sub>3</sub>), 19.25 (CH<sub>2</sub>), 19.30 (CH<sub>2</sub>), 28.39 (CH), 30.77 (CH<sub>2</sub>), 33.01 (C), 35.67 (CH<sub>2</sub>), 38.20 (CH<sub>2</sub>), 41.33 (CH<sub>2</sub>), 41.58 (C), 43.53 (CH<sub>2</sub>), 48.52 (CH<sub>2</sub>), 64.04 (CH<sub>2</sub>), 64.14 (CH<sub>2</sub>), 171.67 (C), 177.35 (C). Mass spectrum,  $m/z$  ( $I_{rel}$ , %): 350 (<1) [M]<sup>+</sup>, 295 (65), 249 (55), 239 (100), 235 (25), 193 (89), 179 (50), 147 (37), 133 (98), 91 (75), 57 (38). Found, %: C 72.00; H 9.83. Calculated for C<sub>21</sub>H<sub>34</sub>O<sub>4</sub>, %: C 71.96; H 9.78.  $M$  350.49.

**3-Carboxy-1-adamantylacetic acid di-*n*-pentyl ester (III)** was prepared similar to di-*n*-propyl ester I from 29.59 g (0.124 mol) of 3-carboxy-1-adamantylacetic acid and 44 g (0.5 mol, 54 mL) of *n*-pentanol. The yield 38.1 g (81%), bp 157–163°C (0.038 torr),  $n_D^{20}$  1.4798. IR,  $\nu$ , cm<sup>-1</sup>: 1728 (C=O). <sup>1</sup>H NMR,  $\delta$ , ppm: 0.87–0.91 (t, 6H, CH<sub>3</sub>,  $J$  = 5.96 Hz), 1.25–1.34 (m, 8H, CH<sub>2</sub>Ad, CH<sub>2</sub>), 1.53–1.64 (m, 10H, CH<sub>2</sub>Ad, CH<sub>2</sub>), 1.72–1.74 (m, 2H, CH<sub>2</sub>), 1.75–1.84 (m, 4H, CH<sub>2</sub>), 2.07–2.08 (m, 2H, CH), 2.1 (s, 2H, CH<sub>2</sub>), 3.99–4.02 (m, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR,  $\delta$ , ppm: 14.07 (CH<sub>3</sub>), 22.38 (CH<sub>2</sub>), 28.14 (CH<sub>2</sub>), 28.22 (CH<sub>2</sub>), 28.44 (CH), 33.00 (C), 35.67 (CH<sub>2</sub>), 38.19 (CH<sub>2</sub>), 41.31 (CH<sub>2</sub>), 41.57 (C), 43.55 (CH<sub>2</sub>), 48.51 (CH<sub>2</sub>), 64.30 (CH<sub>2</sub>), 64.42 (CH<sub>2</sub>), 171.65 (C), 177.32 (C). Mass spectrum,  $m/z$  ( $I_{rel}$ , %): 378 (<1) [M]<sup>+</sup>, 263 (28), 239 (96), 193 (65), 179 (38), 147 (25), 133 (73), 91 (53), 55 (30). Found, %: C 73.03; H 10.17. Calculated for C<sub>23</sub>H<sub>38</sub>O<sub>4</sub>, %: C 72.98; H 10.12.  $M$  378.54.

**3-Carboxy-1-adamantylacetic acid di-*n*-hexyl ester (IV)** was prepared similar to di-*n*-propyl ester I from 27.55 g (0.115 mol) of 3-carboxy-1-adamantylacetic acid and 47.23 g (0.462 mol, 58 mL) of *n*-hexanol. Yield 37.1 g (79%), bp 192–198°C (0.021 torr),  $n_D^{20}$  1.4782. IR,  $\nu$ , cm<sup>-1</sup>: 1728 (C=O). <sup>1</sup>H NMR,  $\delta$ , ppm: 0.85–0.88 (t, 6H, CH<sub>3</sub>,  $J$  = 5.92 Hz), 1.27–1.32 (m, 12H, CH<sub>2</sub>Ad, CH<sub>2</sub>), 1.56–1.59 (m, 10H, CH<sub>2</sub>Ad, CH<sub>2</sub>), 1.72–1.74 (m, 2H, CH<sub>2</sub>), 1.75–1.81 (m, 4H, CH<sub>2</sub>), 2.07–2.08 (m, 2H, CH), 2.10 (s, 2H, CH<sub>2</sub>), 4.01–4.03 (m, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR,  $\delta$ , ppm: 14.10 (CH<sub>3</sub>), 22.62 (CH<sub>2</sub>), 25.64 (CH<sub>2</sub>), 25.72 (CH<sub>2</sub>), 28.40

(CH), 28.64 (CH<sub>2</sub>), 28.70 (CH<sub>2</sub>), 33.00 (C), 31.49 (CH<sub>2</sub>), 35.67 (CH<sub>2</sub>), 38.20 (CH<sub>2</sub>), 41.31 (CH<sub>2</sub>), 41.57 (C), 43.57 (CH<sub>2</sub>), 48.52 (CH<sub>2</sub>), 64.33 (CH<sub>2</sub>), 64.43 (CH<sub>2</sub>), 171.65 (C), 177.32 (C). Mass spectrum,  $m/z$  ( $I_{rel}$ , %): 406 (<1) [M]<sup>+</sup>, 325 (80), 279 (40), 239 (100), 193 (52), 179 (20), 133 (50), 91 (10), 43 (19). Found, %: C 73.89; H 10.43. Calculated for C<sub>25</sub>H<sub>42</sub>O<sub>4</sub>, %: C 73.85; H 10.41. *M* 406.59.

**5,7-Dimethyl-3-carboxy-1-adamantylacetic acid di-*n*-propyl ester (V)** was prepared similar to di-*n*-propyl ester *I* from 35.75 g (0.134 mol) of 5,7-dimethyl-of 3-carboxy-1-adamantyl acetic acid and 32 g (0.537 mol, 40 mL) of *n*-propanol. Yield 38 g (81%), bp 148–152°C (0.23 torr),  $n_D^{20}$  1.4785. IR,  $\nu$ , cm<sup>-1</sup>: 1728 (C=O). <sup>1</sup>H NMR,  $\delta$ , ppm: 0.84 (s, 6H, CH<sub>3</sub>), 0.90–0.92 (t, 6H, CH<sub>3</sub>,  $J$  = 5.96 Hz), 1.07–1.09 (m, 2H, CH<sub>2</sub>Ad), 1.21–1.23 (m, 4H, CH<sub>2</sub>Ad), 1.44–1.47 (m, 4H, CH<sub>2</sub>), 1.58–1.61 (m, 6H, CH<sub>2</sub>Ad, CH<sub>2</sub>), 2.13 (s, 2H, CH<sub>2</sub>), 3.97–3.99 (m, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR,  $\delta$ , ppm: 10.52 (CH<sub>3</sub>), 10.61 (CH<sub>3</sub>), 22.08 (CH<sub>2</sub>), 30.08 (CH<sub>3</sub>), 31.66 (C), 34.61 (C), 42.35 (CH<sub>2</sub>), 43.34 (C), 44.39 (CH<sub>2</sub>), 47.71 (CH<sub>2</sub>), 47.83 (CH<sub>2</sub>), 49.98 (CH<sub>2</sub>), 65.81 (CH<sub>2</sub>), 65.89 (CH<sub>2</sub>), 171.66 (C), 177.15 (C). Mass spectrum,  $m/z$  ( $I_{rel}$ , %): 350 (<1) [M]<sup>+</sup>, 321 (65), 275 (100), 247 (35), 233 (90), 191 (25), 145 (36), 105 (22), 91 (18), 43 (19). Found, %: C 72.02; H 9.80. C<sub>21</sub>H<sub>34</sub>O<sub>4</sub>. Calculated for, %: C 71.96; H 9.78. *M* 350.49.

**5,7-Dimethyl-3-carboxy-1-adamantyl acetic acid di-*n*-butyl ester (VI)** was prepared similar to the di-*n*-propyl ester (I) from 31.3 g (0.118 mol) of 5,7-dimethyl-of 3-carboxy-1-adamantylacetic acid and 26.0 g (0.351 mol, 32 mL) of *n*-butanol. Yield 35.8 g (81%), bp 159–162°C (0.21 torr),  $n_D^{20}$  1.4774. IR,  $\nu$ , cm<sup>-1</sup>: 1730 (C=O). <sup>1</sup>H NMR,  $\delta$ , ppm: 0.85 (s, 6H, CH<sub>3</sub>), 0.89–0.93 (t, 6H, CH<sub>3</sub>,  $J$  = 7.32 Hz), 1.08–1.10 (m, 2H, CH<sub>2</sub>Ad), 1.22–1.24 (m, 4H, CH<sub>2</sub>Ad), 1.32–1.40 (m, 4H, CH<sub>2</sub>Ad, CH<sub>2</sub>), 1.45–1.47 (s, 4H, CH<sub>2</sub>), 1.57–1.60 (m, 6H, CH<sub>2</sub>Ad, CH<sub>2</sub>), 2.13 (s, 2H, CH<sub>2</sub>), 4.01–4.04 (m, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR,  $\delta$ , ppm: 13.76 (CH<sub>3</sub>), 13.84 (CH<sub>3</sub>), 19.28 (CH<sub>2</sub>), 30.08 (CH<sub>3</sub>), 30.75 (CH<sub>2</sub>), 31.67 (C), 34.62 (C), 42.38 (CH<sub>2</sub>), 43.32 (C), 44.38 (CH<sub>2</sub>), 47.70 (CH<sub>2</sub>), 47.85 (CH<sub>2</sub>), 49.98 (CH<sub>2</sub>), 64.04 (CH<sub>2</sub>), 64.22 (CH<sub>2</sub>), 171.70 (C), 177.19 (C). Mass spectrum,  $m/z$  ( $I_{rel}$ , %): 378 (<1) [M]<sup>+</sup>, 323 (38), 277 (48), 267 (47), 221 (26), 161 (71), 119 (100), 105 (32), 91 (29), 57 (42). Found, %: C 73.03; H 10.15. Calculated for C<sub>23</sub>H<sub>38</sub>O<sub>4</sub>, %: C 72.98; H 10.12. *M* 378.54.

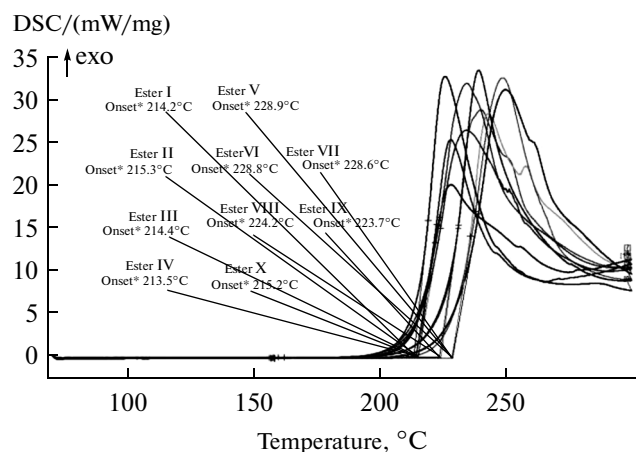
**5,7-Dimethyl-3-carboxy-1-adamantylacetic acid diisobutyl ester (VII)** was prepared similar to di-*n*-propyl ester *I* from 35 g (0.13 mol) of 5,7-dimethyl-of 3-carboxy-1-adamantylacetic acid and 48.0 g (0.648 mol, 60 mL) of isobutanol. Yield 43 g (87%), bp 150–152°C (0.04 torr),  $n_D^{20}$  1.4745. IR,  $\nu$ , cm<sup>-1</sup>: 1730 (C=O). <sup>1</sup>H NMR,  $\delta$ , ppm: 0.85 (s, 6H, CH<sub>3</sub>),

0.89–0.93 (m, 12H, CH<sub>3</sub>), 1.05–1.13 (m, 2H, CH<sub>2</sub>Ad), 1.19–1.27 (m, 4H, CH<sub>2</sub>Ad), 1.45–1.48 (s, 4H, CH<sub>2</sub>Ad), 1.57–1.60 (m, 2H, CH<sub>2</sub>Ad), 1.88–1.92 (m, 2H, CH), 2.15 (s, 2H, CH<sub>2</sub>), 3.79–3.81 (m, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR,  $\delta$ , ppm: 19.19 (CH<sub>3</sub>), 19.28 (CH<sub>3</sub>), 27.73 (CH), 27.87 (CH), 30.08 (CH<sub>3</sub>), 31.67 (C), 34.62 (C), 42.43 (CH<sub>2</sub>), 43.43 (C), 44.42 (CH<sub>2</sub>), 47.75 (CH<sub>2</sub>), 47.90 (CH<sub>2</sub>), 49.98 (CH<sub>2</sub>), 70.38 (CH<sub>2</sub>), 70.48 (CH<sub>2</sub>), 171.70 (C), 177.07 (C). Mass spectrum,  $m/z$  ( $I_{rel}$ , %): 378 (<1) [M]<sup>+</sup>, 323 (54), 277 (40), 267 (100), 221 (60), 161 (55), 119 (62), 105 (30), 91 (20), 57 (44). Found, %: C 73.01; H 10.12. Calculated for C<sub>23</sub>H<sub>38</sub>O<sub>4</sub>, %: C 72.98; H 10.12. *M* 378.54.

**5,7-Dimethyl-3-carboxy-1-adamantylacetic acid di-*n*-pentyl ester (VIII)** was prepared similar to di-*n*-propyl ester *I* from 37 g (0.14 mol) of 5,7-dimethyl-of 3-carboxy-1-adamantylacetic acid and 32.4 g (0.369 mol, 40 mL) of *n*-pentanol. Yield 47.4 g (83%), bp 170–173°C (0.03 torr),  $n_D^{20}$  1.4767. IR,  $\nu$ , cm<sup>-1</sup>: 1730 (C=O). <sup>1</sup>H NMR,  $\delta$ , ppm: 0.84 (s, 6H, CH<sub>3</sub>), 0.86–0.89 (t, 6H, CH<sub>3</sub>,  $J$  = 7.08 Hz), 1.04–1.35 (m, 14H, CH<sub>2</sub>Ad, CH<sub>2</sub>), 1.43–1.45 (m, 4H, CH<sub>2</sub>), 1.57–1.64 (m, 6H, CH<sub>2</sub>, CH<sub>2</sub>Ad), 2.12 (s, 2H, CH<sub>2</sub>), 3.98–4.04 (m, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR,  $\delta$ , ppm: 14.05 (CH<sub>3</sub>), 22.36 (CH<sub>3</sub>), 28.10 (CH<sub>2</sub>), 28.26 (CH<sub>2</sub>), 28.37 (CH<sub>2</sub>), 28.43 (CH<sub>2</sub>), 30.07 (CH<sub>2</sub>), 31.66 (C), 34.62 (C), 42.40 (CH<sub>2</sub>), 43.31 (C), 44.39 (CH<sub>2</sub>), 47.70 (CH<sub>2</sub>), 47.85 (CH<sub>2</sub>), 49.99 (CH<sub>2</sub>), 64.30 (CH<sub>2</sub>), 64.45 (CH<sub>2</sub>), 171.65 (C), 177.14 (C). Mass spectrum,  $m/z$  ( $I_{rel}$ , %): 406 (<1) [M]<sup>+</sup>, 338 (74), 291 (60), 267 (100), 221 (20), 203 (26), 161 (34), 119 (8), 43 (14). Found, %: C 73.90; H 10.44. Calculated for C<sub>25</sub>H<sub>42</sub>O<sub>4</sub>, %: C 73.85; H 10.41. *M* 406.59.

**5,7-Dimethyl-3-carboxy-1-adamantylacetic acid diisoamyl ester (IX)** was prepared similar to di-*n*-propyl ester *I* from 35 g (0.13 mol) of 5,7-dimethyl-of 3-carboxy-1-adamantylacetic acid and 34.3 g (0.390 mol, 50 mL) of isoamyl alcohol. Yield 46.4 g (88%), bp 140–142°C (0.021 torr),  $n_D^{20}$  1.4755. IR,  $\nu$ , cm<sup>-1</sup>: 1728 (C=O). <sup>1</sup>H NMR,  $\delta$ , ppm: 0.82 (s, 6H, CH<sub>3</sub>), 0.86–0.87 (m, 6H, CH<sub>3</sub>), 0.88–0.89 (m, 6H, CH<sub>3</sub>), 1.18–1.24 (m, 6H, CH<sub>2</sub>Ad), 1.41–1.44 (m, 4H, CH<sub>2</sub>Ad), 1.45–1.50 (m, 4H, CH<sub>2</sub>), 1.53–1.58 (m, 2H, CH<sub>2</sub>Ad), 1.59–1.68 (m, 2H, CH), 2.09 (s, 2H, CH<sub>2</sub>), 4.02–4.05 (m, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR,  $\delta$ , ppm: 22.48 (CH<sub>3</sub>), 22.57 (CH<sub>3</sub>), 25.09 (CH), 25.17 (CH), 26.11 (CH<sub>2</sub>), 30.06 (CH<sub>3</sub>), 31.63 (C), 34.60 (C), 37.40 (CH<sub>2</sub>), 37.43 (CH<sub>2</sub>), 42.34 (CH<sub>2</sub>), 43.26 (C), 44.36 (CH<sub>2</sub>), 47.69 (CH<sub>2</sub>), 47.97 (CH<sub>2</sub>), 62.73 (CH<sub>2</sub>), 63.00 (CH<sub>2</sub>), 171.56 (C), 177.06 (C). Mass spectrum,  $m/z$  ( $I_{rel}$ , %): 406 (<1) [M]<sup>+</sup>, 338 (47), 291 (28), 267 (100), 221 (37), 207 (19), 161 (39), 119 (28), 70 (46). Found, %: C 73.84; H 10.38. Calculated for C<sub>25</sub>H<sub>42</sub>O<sub>4</sub>, %: C 73.85; H 10.41. *M* 406.59.

**5,7-Dimethyl-3-carboxy-1-adamantylacetic acid di-*n*-hexyl ester (X)** was prepared similar to di-*n*-propyl ester *I* from 35 g (0.131 mol) of 5,7-dimethyl-of

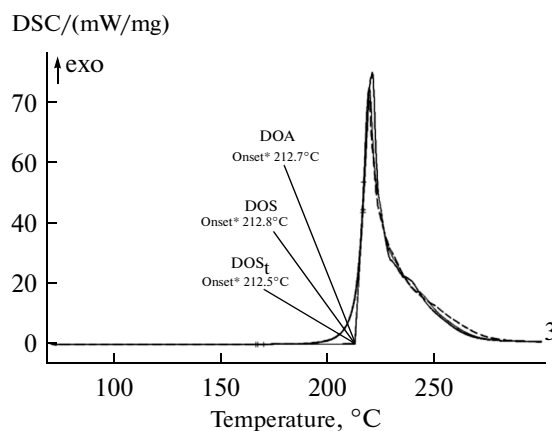


**Fig. 1.** Thermo-oxidative stability of 5,7-R-3-carboxy-1-adamantylacetic acid diesters according to ASTM E2009.

3-carboxy-1-adamantylacetic acid and 41 g (0.40 mol, 50 mL) of *n*-hexanol. Yield 43.8 g (77%), bp 205–208°C (0.046 torr),  $n_D^{20}$  1.4763. IR,  $\nu$ ,  $\text{cm}^{-1}$ : 1728 (C=O).  $^1\text{H}$  NMR,  $\delta$ , ppm: 0.84 (s, 6H,  $\text{CH}_3$ ), 0.86–0.89 (t, 6H,  $\text{CH}_3$ ,  $J = 6.88$  Hz), 1.05–1.36 (m, 18H,  $\text{CH}_2\text{Ad}$ ,  $\text{CH}_2$ ), 1.43–1.45 (m, 4H,  $\text{CH}_2$ ), 1.54–1.62 (m, 6H,  $\text{CH}_2$ ,  $\text{CH}_2\text{Ad}$ ), 2.12 (s, 2H,  $\text{CH}_2$ ), 3.98–4.03 (m, 4H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR,  $\delta$ , ppm: 14.08 ( $\text{CH}_3$ ), 22.57 ( $\text{CH}_2$ ), 22.63 ( $\text{CH}_2$ ), 25.60 ( $\text{CH}_2$ ), 25.78 ( $\text{CH}_2$ ), 28.62 ( $\text{CH}_2$ ), 28.70 ( $\text{CH}_2$ ), 30.07 ( $\text{CH}_3$ ), 31.48 ( $\text{CH}_2$ ), 31.65 (C), 34.60 (C), 42.42 ( $\text{CH}_2$ ), 43.31 (C), 44.40 ( $\text{CH}_2$ ), 47.69 ( $\text{CH}_2$ ), 47.85 ( $\text{CH}_2$ ), 49.98 ( $\text{CH}_2$ ), 64.31 ( $\text{CH}_2$ ), 64.49 ( $\text{CH}_2$ ), 171.63 (C), 177.12 (C). Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 434 (<1) [ $\text{M}]^+$ , 352 (73), 306 (61), 267 (100), 221 (24), 207 (28), 203 (22), 161 (30), 119 (8), 43 (24). Found, %: C 74.66; H 10.71. Calculated for  $\text{C}_{27}\text{H}_{46}\text{O}_4$ , %: C 74.61; H 10.67.  $M$  434.65.

The structure of the synthesized compounds and their purity was confirmed by the modern chromatographic and spectral methods (GC–MS, elemental analysis, IR and NMR spectroscopy). The mass spectra were recorded on a ThermoFinnigan DSQ combined chromatograph–mass spectrometer with the use of a BPX-5 capillary column  $30 \times 0.32$  at an ionizing electron energy of 70 eV. The elemental analysis was performed on a EuroVector 3000 EA element analyzer using L-cystine as the standard. The IR spectra were recorded on a Shimadzu IRAffinity-1 spectrometer as a thin film between KBr plates. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Jeol JNM ECX-400 spectrometer (operating at a frequency of 400 MHz) in  $\text{CDCl}_3$ .

The physicochemical properties of the synthesized diesters were studied according to GOST and ASTM procedures (kinematic viscosity at positive and negative temperatures by ASTM D7042, open cup flash



**Fig. 2.** Thermo-oxidative stability of adipic and sebacic diesters according to ASTM E2009.

point by GOST 4333, and pour point by GOST 20287).

The thermo-oxidative stability of the samples in a thin film was studied using high-pressure differential scanning calorimetry (HP-DSC) according to ASTM E2009 (test method B) on aluminum crucibles in an oxygen atmosphere (35 atm) and in the dynamic mode (heating from 70 to 300°C at a rate of 10°C/min) on a DSC 204 HP Phoenix instrument (NETZSCH-Gerätebau, Germany).

The DOA, DOS, and DOST diesters are produced by national manufacturers (Roshal' Plasticizer Plant, Ural Plasticizer Plant) according to GOST 8728 and TU 6-06-11-88. A batch (October 2012) of diesters from the Roshal' Plasticizer Plant was used in this study.

## RESULTS AND DISCUSSION

A number of  $\text{C}_3$ – $\text{C}_6$  dialkyl esters were synthesized from 3-carboxy-1-adamantylacetic acid and 5,7-dimethyl-3-carboxy-1-adamantylacetic acid and aliphatic alcohols (*n*-propanol, *n*-butanol, isobutanol, *n*-pentanol, isoamyl alcohol, and *n*-hexanol) in the presence of a homogeneous catalyst (*p*-toluenesulfonic acid). The reactions proceeded with good yields irrespective of the acid used and the structure of the alcohol component; the yields of diesters I–X purified by vacuum distillation were 71–88%.

The data on the physicochemical properties (kinematic viscosity at positive and negative temperatures, viscosity index, pour temperature, flash point, density, and refractive index) and thermo-oxidative stability of compounds I–X, DOA, DOS, and DOST are presented in Tables 1 and 2.

It is seen from the presented data that esters I–IV containing the adamantane moiety possess better viscosity–temperature characteristics at positive and negative temperatures as compared with the diesters of

Table 1. Physicochemical properties of 3-carboxy-1-adamantylacetic acid diesters, DOA, DOS, and DOST

Sample no.	I	II	III	IV	DOA	DOS	DOST
Y =	-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	n-C <sub>6</sub> H <sub>13</sub>	-	-	-
Empirical formula	C <sub>19</sub> H <sub>30</sub> O <sub>4</sub>	C <sub>21</sub> H <sub>34</sub> O <sub>4</sub>	C <sub>23</sub> H <sub>38</sub> O <sub>4</sub>	C <sub>25</sub> H <sub>42</sub> O <sub>4</sub>	C <sub>22</sub> H <sub>42</sub> O <sub>4</sub>	C <sub>26</sub> H <sub>50</sub> O <sub>4</sub>	C <sub>26</sub> H <sub>50</sub> O <sub>4</sub>
Mol. weight, g/mol	322	350	378	406	370	426	426
Kinematic viscosity, cSt:							
at 100°C	3.30	3.48	3.84	4.42	2.33	3.32	3.45
at 50°C	10.04	10.17	11.35	13.89	5.91	9.29	9.75
at 40°C	14.47	14.73	16.47	17.95	7.68	12.41	13.05
at -30°C	-	-	-	-	298.1	634.4	677.3
at -40°C	3333	2564	3001	3459	861.2	2799	1921
Viscosity index	94	114	127	167	121	148	148
Pour point, °C	-58	-62	-65	-64	-70	-65	-64
Flash point, °C	194	206	220	236	196	222	234
Density (20°C), kg/m <sup>3</sup>	1068	1048	1024	1006	925.8	920.4	921.2
Refractive index (20°C)	1.4830	1.4813	1.4798	1.4782	1.4469	1.4535	1.4540
Thermal oxidative stability, ASTM E 2009, OOT, °C	214.2	215.3	214.4	213.5	212.7	212.8	212.5

**Table 2.** Physicochemical properties of 5,7-dimethyl-3-carboxy-1-adamantylacetic acid diesters

Sample no.	V	VI	VII	VIII	IX	X
Y =	-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	-CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	-CH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	n-C <sub>6</sub> H <sub>13</sub>
Empirical formula	C <sub>21</sub> H <sub>34</sub> O <sub>4</sub>	C <sub>23</sub> H <sub>38</sub> O <sub>4</sub>	C <sub>23</sub> H <sub>38</sub> O <sub>4</sub>	C <sub>25</sub> H <sub>42</sub> O <sub>4</sub>	C <sub>25</sub> H <sub>42</sub> O <sub>4</sub>	C <sub>27</sub> H <sub>46</sub> O <sub>4</sub>
Mol. weight, g/mol	350	378	378	406	406	434
Kinematic viscosity, cSt:						
at 100°C	3.20	3.62	4.17	3.76	4.39	4.21
at 50°C	11.06	11.75	17.15	12.97	17.26	14.96
at 40°C	15.92	15.60	26.92	18.54	25.81	21.54
at -30°C	-	-	9318	2715	8899	3196
at -40°C	12672	9028	-	11145	47991	12748
Viscosity index	36	116	8	84	61	97
Pour point, °C	-50	-56	-40	-59	-52	-57
Flash point, °C	198	210	204	224	220	232
Density (20°C), kg/m <sup>3</sup>	1031	1012	1006	997.2	994.9	987.6
Refractive index (20°C)	1.4785	1.4774	1.4745	1.4767	1.4755	1.4763
Thermal oxidative stability, ASTM E 2009, OOT, °C	228.9	228.8	228.6	224.2	223.7	215.2

adipic and sebacic acids of a similar molecular weight. As the chain length of the alkoxy group, the viscosity index and flash point increase and the pour point is improved; however, the kinematic viscosity increases at the same time, especially at negative temperatures. Diesters **III** and **IV** are of the greatest interest with respect to the set of parameters, especially in comparison with DOSt.

The presence of the methyl substituents in the 5- and 7-positions of the adamantane skeleton (esters **V–X**) results in a significant growth in the kinematic viscosity, especially at negative temperatures, and in pour point elevation by 5–6°C. Among the diesters of 5,7-dimethyl-3-carboxy-1-adamantylacetic acid, ester **VI** is of the greatest interest.

The introduction of the iso-branched chain alcohol into the diester structure instead of the linear alcohol (esters **VI** vs **VII** and **VIII** vs **IX**) results in a significant growth in the viscosity, pour point elevation, and decrease in the flash point. Esters **VII** and **IX** can be used in climatic regions, where the viscosity at positive temperatures is of greatest importance and the level of viscosity at negative temperatures and the pour point of not more than 40°C have acceptable values. From this point of view, ester **IX** is of greater interest.

Figures 1 and 2 show the results of the investigation of the thermo-oxidative stability (ability of compounds to resist oxidation in the absence of antioxidants) of the diesters according to ASTM E2009 as the oxidation onset temperature (OOT). The diesters of adipic and sebacic acids demonstrated similar results having an OOT of 212.5–212.7°C. Diesters of 3-carboxy-1-adamantyl acetic acid **I–IV** possess higher OOT values of 213.5–215.3°C, which is more clearly demonstrated by the height of the oxidation peak (a twofold reduction); moreover, the OOT gradual decreases with an growth in the length of the linear alkyl chain of the alcohol (esters **II–IV**). The diesters of 5,7-dimethyl-3-carboxy-1-adamantylacetic acid follow the same trend, although their OOT values are substantially higher. For example, the IOT is 228.6–228.9 or 228.6–228.9°C for esters **V–VII** or **VIII–IX**, respectively, but it is only 215.2°C for ester **X** with the longer *n*-hexyl radical. There is significant difference in IOT between the diesters containing linear and iso-branched radicals (**VI** vs **VII**, **VIII** vs **IX**).

Thus, 5,7-R-3-carboxy-1-adamantylacetic acid diesters are very promising as more thermally stable analogues of the esters DOA and DOSt for use in lubricant compositions; although 3-carboxy-1-adamantylacetic and, especially, 5,7-dimethyl-3-carboxy-1-adamantylacetic diesters exhibit higher viscosity values, they will not have so a substantial effect on the viscosity–temperature properties of the lubricant composition as a whole, since the amount of esters in such compositions most frequently varies within 5–40%.

In summary, the influence of the methyl substituents in the 5- and 7-positions of the adamantane skeleton of 5,7-R-3-carboxy-1-adamantylacetic acid

diesters and of the structure of the alcohol alkyl chain on the physicochemical and thermo-oxidation properties have been studied. The properties of the adamantane-containing esters have been compared with those of DOA, DOS, and DOSt. The possibility in principle of replacing of the aliphatic dicarboxylic diesters acids by more thermally stable 5,7-dimethyl-3-carboxy-1-adamantylacetic acid diesters with similar physicochemical properties has been shown.

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## REFERENCES

1. E. I. Bagrii, *Adamantanes: Preparations, Properties, and Use* (Nauka, Moscow, 1989) [in Russian].
2. U. M. Dzhemilev, R. I. Khusnutdinov, N. A. Shchadnina, et al., RU Patent No. 2504533; Byull. Izobret., No. 2 (2014).
3. T. Kawai and M. Kitamura, RU Patent No. 2494084; Byull. Izobret., No. 27 (2013).
4. E. A. Ivleva, D. I. Gnusarev, and Yu. N. Klimochkin, RU Patent No. 2489417; Byull. Izobret., No. 22 (2013).
5. E. I. Bagrii and G. B. Maravin, *Pet. Chem.* **53**, 418 (2013).
6. Y. Klimochkin, A. Reznikov, M. Skomorokhov, and E. Golovin, *Antiviral Res.* **86** (I), A58 (2010).
7. Y. Klimochkin, V. Osyanin, E. Golovin, et al. *Antiviral Res.* **86** (I), A59 (2010).
8. Y. Klimochkin, M. Baimuratov, E. Knyazeva, et al., *Antiviral Res.* **90** (I), A71 (2011).
9. V. A. Shibnev, P. G. Deryabin, M. P. Finogenova, et al., RU Patent No. 2524216; Byull. Izobret., No. 21 (2014).
10. I. S. Akhrem, L. V. Afanas'eva, S. V. Vitt, et al., RF Patent No. 2409 545; Byull. Izobret., No. 2 (2011).
11. I. S. Akhrem, D. V. Avetisyan, E. I. Goryunov, et al., RU Patent No. 2458911; Byull. Izobret., No. 23 (2012).
12. V. A. Sokolenko, N. M. Svirskaya, A. F. Gogotov, and D. S. Rudenko, RU Patent No. 2458904; Byull. Izobret., No. 23 (2012).
13. L. Chen, T. V. Leung, T. Tao, and K. Gao, RU Patent Application No. 2011 147476; Byull. Izobret., No. 15 (2013).
14. H. Ding, S. Elmore, L. Hexamer, et al., RU Patent Application No. 2012 145298; Byull. Izobret., No. 12 (2014).
15. H. Zweifel, R. D. Maier, and M. Schiller, *Plastics Additives Handbook* (Hanser, Munich, 2009), 6th Ed.
16. *Lubricants and Lubrication*, Ed. by T. Mang and W. Dresel, (Wiley, New York, 2007), 2nd Ed.

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