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ORIGINAL PAPER

Improved synthesis and low-temperature performance of a series of saturated α-branched fatty acids

Yang Jiang[1] · Wenjing Hu[1] · Jian Xu[1] · Jiusheng Li[1]

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Abstract Five saturated α-branched fatty acids, also known as Guerbet acids, including α-propylhexyl acid (**G_1**), α-butylhexyl acid (**G_2**), α-propyloctyl acid (**G_3**), α-butyloctyl acid (**G_4**), and α-hexyloctyl acid (**G_5**), were synthesized in high yields by four-step reaction. Colorless, almost odorless, and oily products were obtained with high purity, whose structures were confirmed by GC, $^{1}H/^{13}C$ NMR, and ESI–MS characterization. **G_1**, **G_3**, and **G_4** had pour points lower than −60 °C, while **G_2** and **G_5** showed higher pour points (−42 °C and 6 °C, respectively) because of their molecular symmetry. Considering the low-temperature properties, **G_1**, **G_3**, **G_4**, and even **G_2** held great potential applications in the lubricant and oilfield.

Keywords Saturated α-branched fatty acids · Guerbet acids · Low-temperature performance · Pour point

Introduction

Low-temperature property is an important parameter to measure the performance of lubricant. The ideal lubricant should have a continuous, stable viscosity. Specifically speaking, the viscosity of lubricant should be big enough at high temperature to maintain the integrity of the lubricant film, aiming to prevent contact friction. On the other hand, the low-temperature fluidity needs to be excellent to ensure that the lubricant can quickly attach to the lubricating parts and reduce the mechanical wear. Due to their outstanding behavior at low temperature, saturated α-branched fatty acids (SBFAs) have much broader applications than their linear homologues in the lubricant industry (Haßelberg and Behr 2016). Saturated linear fatty acids with more than ten carbons are typically solid at room temperature, usually not suitable to be used as lubricants due to their non-operability and formula incompatibility at low temperature.

Unsaturated long-chain acids, such as oleic acid, although possessing lower melting point, are often thermo-oxidatively unstable due to their unsaturated carbon–carbon bonds. Tremendous work has thus been carried out to seek oxidatively stable "oily" acids, i.e., saturated branched fatty acids. Currently, these acids have been obtained by a few industrial processes including the synthesis from petro- and oleo-chemical feedstock. By employing Guerbet reaction, Guerbet alcohols were produced branched in α-position with two approximately equal-length side chains, which were then oxidized to branched fatty acids (Guerbet acids). Alkenes or alcohols can also be transformed to branched fatty acids through oxo synthesis (Neweck and Grafahrend 2012; Kent 2012) or Koch synthesis (Kinsman et al. 1989; Keenan et al. 2007). Methyl-branched chain fatty acids (isostearic acid) were obtained as by-products in the clay-catalyzed dimerization process of unsaturated acid from tall oil (fatty acid isomerization) (Denotter 1970a, b). Ngo's group (2007, 2011, 2012, 2013) has recently optimized the reaction selectivity for isostearic acid. The α-branched fatty acids could be prepared by alkylation of dimethyl malonate and the appropriate alkyl bromides using strong base NaH, and the yield of the decarboxylation in the literature was 46–78% (Erdmann et al. 2015). Another method was by synthesis from aromatic azides, which were particularly prone to explosion. The yield of the final product was around 50% (Cassani et al. 2004).

✉ Jiusheng Li
lijs@sari.ac.cn

[1] Laboratory of Advanced Lubricating Materials, Shanghai Advanced Research Institute, CAS, Shanghai, China

The existing branched fatty acid products, derived from either petro- or oleo-chemical industry, are mixtures of different acids/esters/alcohols with unsatisfactory SBFA content. Some linear acids are also formed in such petro- or oleo-chemical processes and cannot be removed completely from the final products. The accompanying linear acids, to a large extent, influence their performance and application in lubricant field.

The preparation of α-branched fatty acids from malonic acids, previously described by Browning et al. (1930), was a classical method. In the literature, various allyl alkyl acetic acids were prepared and tested for bactericidal action to *B. Leprae*. In this paper, we improved this synthesis process; both yield and purity of the products were greatly raised. We hope that through this research we can develop the industrial applications. Two alkyl groups, either same or different, were introduced to the α-carbon of malonic ester. The length of the backbone and the side chain of these SBFAs can thus be controlled by careful selection of alkyl chains. Five SBFAs, α-propylhexyl acid (**G_1**), α-butylhexyl acid (**G_2**), α-propyloctyl acid (**G_3**), α-butyloctyl acid (**G_4**), and α-hexyloctyl acid (**G_5**), were synthesized in high yields by four-step reaction sequences, and their low-temperature behavior was presented. Some physical properties, including pour points, acid values, and kinematic viscosities, were also characterized.

Experimental

Materials and instruments

Dimethyl malonate (99%), 1-bromopropane (98%), 1-bromobutane (99%), 1-bromohexane (99%), sodium methanolate (AR), *N*,*N*-dimethylformamide (99%), sulfuric acid (95–98%), and sodium hydroxide (99%) were obtained from Tansoole, an internet shopping platform of chemicals and materials. All of the chemicals were used without further purification. GC analysis of five SBFA products was carried out on Agilent 7890B equipped with an FID detector. A HP DB-1HT capillary column (30 m × 250 μm × 0.1 μm) was used, and H_2 was used as carrier gas with an average linear velocity of 55.7 cm/s. The oven temperature raising profile was: initial temperature 50 °C, hold 2 min; ramp 15 °C/min to 350 °C, hold 10 min. ^{1}H and ^{13}C NMR spectra were recorded at 25 °C on a Bruker Avance 500 spectrometer in $CDCl_3$ or DMSO-d_6 with TMS as reference. Mass spectra were obtained on Bruker Esquire 6000 (ESI), and the scan was set from 120 to 1200 *m*/*z*.

Chemicals

General procedure

Alkylation (two steps) To a solution of dimethyl malonate (**1**, 100 g, 0.758 mol) in DMF (500 mL), sodium methanolate (45.0 g, 0.833 mol) was added slowly under a N_2 atmosphere. The reaction mixture was kept at room temperature for 30 min. Alkyl bromide (R_1Br, 0.758 mol, R_1 represents the first substituent group) was added dropwise, and the reaction mixture was heated to 100 °C and kept for 1 h. Cooled to room temperature, another portion of sodium methanolate (45 g, 0.833 mol) was added slowly to the mixture and stirred for 30 min. To it was added alkyl bromide (R_2Br, 0.833 mol, R_2 represents the second substituent group) dropwise. The reaction mixture was heated to 100 °C and kept for 1 h. After salt was filtered, solvent and the unreacted alkyl bromide were removed under reduced pressure. The filtrate was crude product of dialkyl dimethylmalonate **2**, which was used directly in the next step.

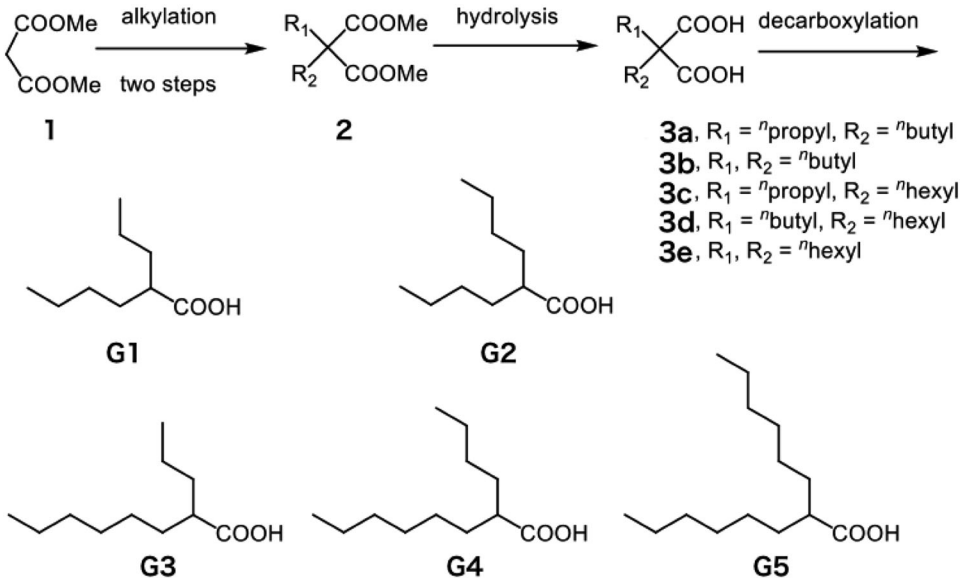
Hydrolysis To crude product **2**, were added an aqueous solution of sodium hydroxide (4 mol/L, 121 g, 3.032 mol) and 100 mL of ethanol. The mixture was heated and refluxed overnight. The reaction was cooled to room temperature and neutralized and acidified to pH 1.8–1.9 by sulfuric acid (4 mol/L). The mixture was transferred to a wide-mouth beaker and stayed for a few hours. The organic layer was turned to solid on the top of the aqueous layer. The crude product (dialkylmalonic acid) was dried and recrystallized with petroleum ether to yield a white solid. Five malonic acids, propylbutylmalonic acid (**3a**), dibutylmalonic acid (**3b**), propylhexylmalonic acid (**3c**), butylhexylmalonic acid (**3d**), and dihexylmalonic acid (**3e**), were synthesized, as shown in Scheme 1.

Decarboxylation The above-obtained disubstituted malonic acids were heated to 150–160 °C under N_2 atmosphere, and CO_2 was released. The reaction was finished until no bubbling formed. The final products were clear, colorless, and odorless oils, and no further post-treatment was needed.

3a. A white solid (three steps, 67%). ^{1}H NMR (500 MHz, DMSO, ppm): $\delta = 12.53$ (COOH, s, 2H), 1.73–1.67 (CH_2, m, 4H), 1.30–1.23 (CH_2, m, 2H), 1.16–1.05 (CH_2, m, 4H), 0.88–0.84 (CH_3, m, 6H). ^{13}C NMR (125 MHz, DMSO, ppm): $\delta = 173.6$, 57.0, 34.4, 31.9, 26.3, 23.0, 17.5, 14.8, 14.3. MS (ESI): *m*/*z* (%) calcd for $C_{10}H_{18}O_4$: 203.2 $[M + H]^+$, 225.2 $[M + Na]^+$.

3b. A white solid (three steps, 72%). ^{1}H NMR (500 MHz, DMSO, ppm): $\delta = 12.6$ (COOH, s, 2H), 1.71 (CH_2, dd, $J_1 = 10.0$ Hz, $J_2 = 5.0$ Hz, 4H), 1.31-1.24

Scheme 1 Synthetic route of the five saturated branched fatty acids



(CH_2, m, 4H), 1.11–1.05 (CH_2, m, 4H), 0.86 (CH_3, t, $J = 5.0$ Hz, 6H). ^{13}C NMR (125 MHz, DMSO, ppm): $\delta = 173.6$, 56.9, 31.8, 26.3, 23.0, 14.3. MS (ESI): *m/z* (%) calcd for $C_{11}H_{20}O_4$: 217.3 $[M + H]^+$, 239.1 $[M + Na]^+$.

3c. A white solid (three steps, 68%). ^{1}H NMR (500 MHz, DMSO, ppm): $\delta = 12.6$ (COOH, s, 2H), 1.73–1.67 (CH_2, m, 4H), 1.28–1.24 (CH_2, m, 6H), 1.16–1.10 (CH_2, m, 4H), 0.88–0.84 (CH_3, m, 6H). ^{13}C NMR (125 MHz, DMSO, ppm): $\delta = 173.6$, 57.0, 34.4, 32.1, 31.5, 29.5, 24.0, 22.5, 17.5, 14.8, 14.3. MS (ESI): *m/z* (%) calcd for $C_{12}H_{22}O_4$: 231.0 $[M + H]^+$, 253.1 $[M + Na]^+$.

3d. A white solid (three steps, 71%). ^{1}H NMR (500 MHz, DMSO, ppm): $\delta = 12.6$ (COOH, s, 2H), 1.73–1.70 (CH_2, m, 4H), 1.30–1.24 (CH_2, m, 8H), 1.11–1.05 (CH_2, m, 4H), 0.87–0.84 (CH_3, m, 6H). ^{13}C NMR (125 MHz, DMSO, ppm): $\delta = 173.7$, 57.0, 32.1, 31.9, 31.5, 29.5, 26.3, 24.0, 23.0, 22.5, 14.3, 14.2. MS (ESI): *m/z* (%) calcd for $C_{13}H_{24}O_4$: 245.2 $[M + H]^+$, 267.1 $[M + Na]^+$.

3e. A white solid (three steps, 73%). ^{1}H NMR (500 MHz, DMSO, ppm): $\delta = 11.3$ (COOH, s, 2H), 1.97–1.93 (CH_2, m, 4H), 1.30 (CH_2, m, 16H), 1.11–1.08 (CH_2, m, 4H), 0.90 (CH_3, t, $J = 5.0$ Hz, 6H). ^{13}C NMR (125 MHz, DMSO, ppm): $\delta = 178.0$, 58.0, 34.4, 31.4, 29.4, 24.5, 22.6, 14.0. MS (ESI): *m/z* (%) calcd for $C_{15}H_{28}O_4$: 273.2 $[M + H]^+$, 295.1 $[M + Na]^+$.

G_1. A clear, colorless, and odorless oil (96%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): $\delta = 11.62$ (COOH, s, 1H), 2.41–2.35 (CH, m, 1H), 1.65–1.62 (CH_2, m, 2H), 1.51–1.47 (CH_2, m, 2H), 1.40–1.32 (CH_2, m, 6H), 0.95–0.90 (CH_3, m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): $\delta = 183.5$, 45.4, 34.3, 31.9, 29.5, 22.6, 20.6, 13.9, 13.8. MS (ESI): *m/z* (%) calcd for $C_9H_{18}O_2$: 159.1 $[M + H]^+$, 181.1 $[M + Na]^+$.

G_2. A clear, colorless, and odorless oil (95%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): $\delta = 11.7$ (COOH, s, 1H), 2.39–2.33 (CH, m, 1H), 1.66–1.64 (CH_2, m, 2H), 1.51–1.50 (CH_2, m, 2H), 1.33 (CH_2, m, 8H), 0.90 (CH_3, t, $J = 5.0$ Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): $\delta = 183.4$, 45.6, 31.9, 29.5, 22.6, 13. 9. MS (ESI): *m/z* (%) calcd for $C_{10}H_{20}O_2$: 173.2 $[M + H]^+$.

G_3. A clear, colorless, and odorless oil (98%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): $\delta = 11.85$ (COOH, s, 1H), 2.40–2.34 (CH, m, 1H), 1.67–1.60 (CH_2, m, 2H), 1.50–1.42 (CH_2, m, 2H), 1.41–1.29 (CH_2, m, 10H), 0.94–0.88 (CH_3, m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): $\delta = 183.5$, 45.4, 34.4, 32.2, 31.7, 29.2, 27.3, 22.6, 20.6, 14.0, 13.9. MS (ESI): *m/z* (%) calcd for $C_{11}H_{22}O_2$: 187.2 $[M + H]^+$, 209.2 $[M + Na]^+$.

G_4. A clear, colorless, and odorless oil (96%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): $\delta = 11.61$ (COOH, s, 1H), 2.39–2.33 (CH, m, 1H), 1.68–1.61 (CH_2, m, 2H), 1.52–1.48 (CH_2, m, 2H), 1.33–1.30 (CH_2, m, 12H), 0.93–0.88 (CH_3, m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): $\delta = 183.3$, 45.6, 32.2, 31.9, 31.7, 29.6, 29.2, 27.3, 22.6, 22.6, 14.0, 13.9. MS (ESI): *m/z* (%) calcd for $C_{12}H_{24}O_2$: 201.0 $[M + H]^+$.

G_5. A clear, colorless, and odorless oil (94%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): $\delta = 11.20$ (COOH, s, 1H), 2.39–2.33 (CH, m, 1H), 1.65–1.64 (CH_2, m, 2H), 1.51 (CH_2, m, 2H), 1.32–1.30 (CH_2, m, 16H), 0.91–0.89 (CH_3, t, $J = 5.0$ Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): $\delta = 183.4$, 45.7, 32.2, 31.7, 29.2, 27.3, 22.6, 14.0. MS

(ESI): *m/z* (%) calcd for $C_{14}H_{28}O_2$: 229.2 $[M + H]^+$, 251.3 $[M + Na]^+$.

Results and discussion

Synthesis and structure confirmation

Scheme 1 shows the synthetic route of five saturated branched fatty acids from dimethyl malonate **1**. Using sodium methanolate as the strong base, either the same or different alkyl groups were introduced to the α-carbon of the malonate **1**. Then, the generated five disubstituted malonates **2** were hydrolyzed to the corresponding malonic acids, **3a**, **3b**, **3c**, **3d**, and **3e**, respectively. The malonic acids were finally transformed to the designed SBFAs via a decarboxylation reaction at ca 150–160 °C.

The structures of the five malonic acids and the five SBFAs were confirmed by GC, $^1H/^{13}C$ NMR, and ESI–MS characterization. As listed in Table 1, the purities of the SBFAs were very high. As the molecular weights of the SBFAs increase, from $\mathbf{G_1}$ to $\mathbf{G_5}$, the retention time turned regularly longer.

The ^1H and ^{13}C NMR spectra of the five SBFAs are shown in Figs. 1 and 2.

ESI–MS analysis further supported the formation of the ten products. All of the ten acids exhibited a peak of $[M + H]^+$, and eight of the ten compounds gave a peak of $[M + Na]^+$. Two exceptional samples, $\mathbf{G_2}$ and $\mathbf{G_4}$, had been distilled under reduced pressure, and trace of sodium salts (introduced from the hydrolysis reaction) had been removed before MS characterization. To verify it, we distilled another sample, $\mathbf{G_3}$ for ESI–MS analysis, and the $[M + Na]^+$ peak disappeared, indicating that sodium salt could be removed by distillation.

Physical properties of SBFAs

The acid values, kinematic viscosities, and pour points of SBFAs are listed in Table 2. As the molecular weights increased, from $\mathbf{G_1}$ to $\mathbf{G_5}$, their acid values decreased regularly. This is because the acids with lower molecular weight have higher acidic contents and thus larger acid values. However, their kinematic viscosities (40 or 100 °C) increased with the incremental molecular weights of SBFAs.

However, the performance of their pour points did not follow the order of their acid values and viscosity properties. It was hard to find the change pattern between the pour points and the molecular weights. $\mathbf{G_1}$, $\mathbf{G_3}$ and $\mathbf{G_4}$ had pour points lower than −60 °C, which was our measure limit. $\mathbf{G_2}$, with a molecular weight between $\mathbf{G_1}$ and $\mathbf{G_3}$, had relatively higher pour points, because of its molecular symmetry. Symmetric molecular structure resulted in the tendency to crystallize and hence a higher pour point. This phenomenon happened for $\mathbf{G_5}$ possessing extended side chains. To a large extent, $\mathbf{G_5}$ intensified the trend to precipitate as crystals and yielded a much higher pour point of 6 °C.

In general, $\mathbf{G_1}$, $\mathbf{G_3}$, $\mathbf{G_4}$ and even $\mathbf{G_2}$ had very good performance at low temperature, whose pour points were much lower than those commercially available saturated branched fatty acids, for instance Versatic™ Acid Neo 10 (Hexion)

Table 1 GC data of SBFAs

Entry	SBFA	Retention time (min)	Purity
1	$\mathbf{G_1}$	9.9	99.6%
2	$\mathbf{G_2}$	10.7	99.3%
3	$\mathbf{G_3}$	11.8	95.6%
4	$\mathbf{G_4}$	12.5	99.7%
5	$\mathbf{G_5}$	14.5	98.7%

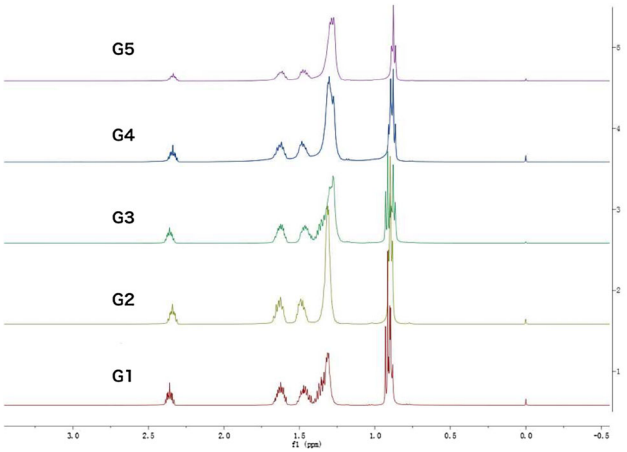


Fig. 1 ^1H NMR spectra of SBFAs in $CDCl_3$

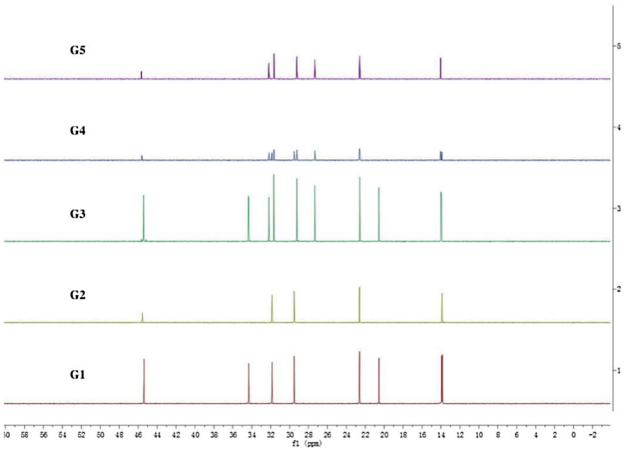


Fig. 2 ^{13}C NMR spectra of SBFAs in $CDCl_3$

Table 2 Physical properties of saturated branched fatty acids

Entry	SBFA	Molecule weight	Pour point (°C)	Acid value	Kinematic viscosity at 40 °C (mm^2/s)	Kinematic viscosity at100 °C (mm^2/s)
1	$\mathbf{G_1}$	181.1	<−60	360	6.55	1.73
2	$\mathbf{G_2}$	173.2	−42	325	9.03	2.11
3	$\mathbf{G_3}$	209.2	<−60	304	10.5	2.44
4	$\mathbf{G_4}$	201.0	<−60	275	13.2	2.82
5	$\mathbf{G_5}$	251.3	6	249	18.2	3.63

(pour point of <−30 °C) (Hexion 2015) and isostearic acid prepared by Ngo's group (pour point of 0 °C) (Ngo et al. 2007). Another important application of saturated branched fatty acids was used as water-based additives to resist hard water and antifoam in metalworking fluids. Comparing with the commercially available additives, such as octanoic acid, isocaprylic acid, and oleic acid, the reported acids possess the advantage of colorlessness and odorlessness, meaning that they can be used in higher demanding occasions.

Conclusions

A series of new saturated branched fatty acids have been designed and synthesized, which have good performance at low temperature. Four-step reaction sequences were employed, and five SBFAs were obtained in high yields. Their structures are confirmed by GC, $^1H/^{13}C$ NMR, and ESI–MS characterization. The colorless, almost odorless, and oily SBFAs products are pure enough for corresponding experimental tests. $\mathbf{G_1}$, $\mathbf{G_3}$, and $\mathbf{G_4}$ have pour points lower than −60 °C, while geometrically symmetric $\mathbf{G_2}$ and $\mathbf{G_5}$ have higher pour points (−42 and 6 °C, respectively). Considering the low-temperature properties, the benefit of these new molecules is specifically in providing an extension to the use of ester-based lubricants into regions of extreme low temperature.

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