A Simple Oleanic Acid Derivative as Potent Organogelator

Jun Hu\textsuperscript{a}, Meng Zhang\textsuperscript{a} and Yong Ju\textsuperscript{a,b,*}

\textsuperscript{a} Key Lab. of Bioorganic Phosphorus Chemistry \& Chemical Biology, Ministry of Education, Department of Chemistry, Tsinghua University, Beijing 100084, China.
\textsuperscript{b} State Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China

Email address: juyong@tsinghua.edu.cn

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Synthesis and Structure Data of 2,3-dihydroxyimino-oleanic acid (6)

Synthesis of 2, 3-dihydroxyimino-oleanic acid (6): The synthesis of 6 was carried out by the reported method. The purity of 6 was verified by NMR spectroscopy, thin-layer chromatography, mass spectroscopy and melting point (m.p. 209-213°C, ref.[1] 208-212°C). All the experimental data of the isolated products were coincident with those previously reported.  

ESI-MS(+) : m/z=499 [M+H]⁺, 1019 [2M+Na]⁺.  
HRMS(ESI): m/z [M+H]⁺ calced for C₃₀H₄₆N₂O₄: 499.3458; found: 499.3535.  

¹ H NMR (300MHz, pyridine-d₅): 5.53 (m, 1H, 12-CH), 3.39(d, 1H, 1-CH₂, J=17.19Hz), 3.34(m, 1H, 18-CH),1.10, 1.03, 1.03, 1.29, 1.38, 1.40, 1.40 (7×S, 7×3H, 23, 24, 25, 26, 27, 29, 30-CH₃).  
¹³C NMR (75MHz, pyridine-d₅): 180.00(28-C), 154.63(3-C), 152.36(2-C), 144.49(13-C), 122.12 (12-C).

1. HRMS (ESI) Spectra of 2,3-dihydroxyimino-oleanic acid (6)
2. ESI-MS Spectra of 2,3-dihydroxyimino-oleanic acid (6)
3. $^1$H NMR Spectra (pyridine-d$_5$) of 2,3-dihydroxyimino-oleanic acid (6) (300MHz)

4. $^{13}$C NMR Spectra (pyridine-d$_5$) of 2,3-dihydroxyimino-oleanic acid (6) (75MHz)
Synthesis and Structure Data of 2,3-dihydroxyimino-28-methyl oleanolate (7)

7

Synthesis of 2, 3-dihydroxyimino-28-methyl oleanolate (7): The synthesis of 7 was carried out by the reported method. The purity of 7 was verified by NMR spectroscopy, thin-layer chromatography, mass spectroscopy and melting point (m.p. 185-187°C, ref.[2] 185-188°C). All the experimental data of the isolated products were coincident with those previously reported. 2

HRMS(ESI): m/z [M+H]⁺ calc for C₃₁H₄₈N₂O₄: 513.3614; found: 513.3677.

¹H NMR (300MHz, CDCl₃): 5.31(m, 1H, 12-H), 3.61(s, 3H, 31-CO₂CH₃), 3.13(d, 1H, 1-CH₂, J=17.85Hz), 2.86(m, 1H, 18-CH), 0.75, 0.88, 0.90, 0.91, 1.12, 1.20, 1.24(7×S, 7×3H, 23, 24, 25, 26, 27, 29, 30-CH₃).

¹³C NMR (75MHz, CDCl₃): 178.74(28-C), 153.79(3-C), 153.34(2-C), 143.68(13-C), 122.23(12-C).

1. HRMS (ESI) Spectra of 2,3-dihydroxyimino-28-methyl oleanolate (7)
2. ESI-MS Spectra of 2,3-dihydroxyimino-28-methyl oleanolate (7)
3. **$^1$H NMR Spectra** (CDCl$_3$) of 2,3-dihydroxyimino-28-methyl oleanolate (7) (300MHz)

![H NMR Spectra](image)

4. **$^{13}$C NMR Spectra** (CDCl$_3$) of 2,3-dihydroxyimino-28-methyl oleanolate (7) (75MHz)

![C NMR Spectra](image)
Synthesis and Structure Data of 2,3-dione O, O-diacetyl-dioxime-oleanic acid (8)

Synthesis of 2, 3-dione O, O-diacetyl-dioxime-oleanic acid (8): 300mg (0.60 mmol) 6 and 15mg (0.12mmol) DMAP were dissolved in 10ml pyridine, then 1.33ml (12.05mmol) acetic anhydride was added slowly. After the mixture stirred for 24h at r.t, the solvent was evaporated. The residue was dissolved in dichloromethane and washed with water, saturated brine, then dried over MgSO4 and evaporated. Purification by flash chromatography (DCM: Methanol =70:1) afforded 8 as white solid (184mg, 51%).

m.p: 149-151°C.

1H NMR (CDCl₃, 300 MHz): 5.28(m, 1H, 12-H), 2.81(d, 1H, 1-CH₂, J=16.47Hz), 2.21, 2.10(2S, 2×3H, NOCOCH₃), 0.75, 0.88, 0.90, 0.96, 1.12, 1.22, 1.24(7S, 7×3H), 23, 24, 25, 26, 27, 29, 30-CH₃;
13C NMR(CDCl₃, 75MHz): 184.04 (28-C), 168.71, 168.64 (2C, NOCOCH₃), 165.06 (3-C), 157.67 (2-C), 144.01 (13-C), 121.70 (12-C).

1. HRMS (ESI) Spectra of 2,3-dione O, O-diacetyl-dioxime-oleanic acid (8)
2. ESI-MS Spectra of 2,3-dione O, O-diacetyl-dioxime-oleanic acid (8)
3. $^1$H NMR Spectra (CDCl$_3$) of 2,3-dione O, O-diacetyl-dioxime-oleanic acid (8) (300MHz)

4. $^{13}$H NMR Spectra (CDCl$_3$) of 2,3-dione O, O-diacetyl-dioxime-oleanic acid (8) (75MHz)
Thermodynamic Parameters of Gel 2,3-dihydroxyimino-oleanic acid (6) \(^{3,4}\)

The thermoreversible melting of a two-component gel can be expressed as:
\[
\text{Gel} \rightleftharpoons \text{liquid}
\]

For one-component gel, the equilibrium constant can be expressed as:
\[
K = [\text{Gelator}] / [\text{Gel}]
\]

Assuming unit activity of the gel and taking concentration of the solution to be equal to the dissolved concentration of the gelator, the equilibrium constant can be expressed as:
\[
K = [\text{Gelator}].
\]

The Gibbs free energy changed during gel melting can be expressed as:
\[
\Delta G^0 = -\Delta R T \ln K = \Delta H^0 - T \Delta S^0,
\]

Hence, \(\ln K = -\Delta H^0 / R (1/T) + T \Delta S^0 / R\)

The gel melting temperature (T\(_{gel}\)) increases with the concentration of the “solutes”. A plot of lnK vs 1/T allowed us to calculate the thermodynamic parameters.

**Benzene**

\[
\ln K = -4.6547 \times 10^{-1} \frac{1}{T} + 9.7907, \quad r = 0.97546
\]

\[
\Delta H^0 / R = -4654.7, \quad \Delta H^0 = 38.7 \text{kJ/mol};
\]

\[
\Delta S^0 / R = 9.7907, \quad \Delta S^0 = 81.4 \text{ J/mol/K}
\]

\[
\Delta G^0 = \Delta H^0 - T \Delta S^0 = 38.7 - 297 \times 0.0814 = 14.5 \text{kJ/mol}
\]
**Toluene**

\[
\ln K = -4.1000 \times 10^3 \frac{1}{T} + 8.4500, \quad r = 0.98104
\]

\[\Delta H^0/R = -4100.00, \quad \Delta H^0 = 34.1 \text{kJ/mol};\]

\[\Delta S^0/R = 8.45, \quad \Delta S^0 = 70.3 \text{J/mol/K}\]

\[\Delta G^0 = \Delta H^0 - T \Delta S^0 = 34.1 - 297 \times 0.0703 = 13.2 \text{kJ/mol}\]

**Chloroform**

\[
\ln K = -6.2816 \times 10^3 \frac{1}{T} + 16.544, \quad r = 0.98357
\]
ΔH°/R = −6281.6, ΔH° = 52.2 kJ/mol;
ΔS°/R = 16.544, ΔS° = 137.5 J/mol/K
ΔG° = ΔH° − TΔS° = 52.2 − 297 × 0.1375 = 11.4 kJ/mol

Table 1. Thermodynamic parameters (ΔH°, ΔS° and ΔG°) of gel 6 in various solvents at 298K

<table>
<thead>
<tr>
<th>Solvent</th>
<th>ΔH° kJ/mol</th>
<th>ΔS° J/mol/K</th>
<th>ΔG° kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>38.7</td>
<td>81.4</td>
<td>14.5</td>
</tr>
<tr>
<td>Toluene</td>
<td>34.1</td>
<td>70.3</td>
<td>13.2</td>
</tr>
<tr>
<td>Chloroform</td>
<td>52.2</td>
<td>137.5</td>
<td>11.4</td>
</tr>
</tbody>
</table>

References

2 Huneck and Siegfried, Chemische Berichte, 1965, 98, 2284-2290.