SUPPLEMENTARY MATERIAL

A new patchoulane-type sesquiterpenoid glycoside from the roots of

_Croton crassifolius_

Qing-Qing Yuan\textsuperscript{a,b}, Wei-Bin Song\textsuperscript{a,b}, Wen-Qiong Wang\textsuperscript{a,b} and Li-Jiang Xuan\textsuperscript{a,b}

\textsuperscript{a} State Key Laboratory of Drug Research, Shanghai Institute of Materia Medica, Chinese Academy of Sciences, 501 Haike Road, Shanghai 201203, People’s Republic of China

\textsuperscript{b} University of Chinese Academy of Sciences, No.19A Yuquan Road, Beijing 100049, People’s Republic of China

*Corresponding Author: E-mail: ljxuan@simm.ac.cn

Abstract: A new patchoulane-type sesquiterpenoid glycoside (1), together with five known sesquiterpenoids (2-6), was isolated from the roots of _Croton crassifolius_. Their structures were elucidated on the basis of spectroscopic methods. This is the first report about the sesquiterpenoid glycoside from _C. crassifolius_. All the isolated compounds 1-6 were evaluated for their cytotoxic activities against human tumour cell lines HL-60 and A549, but none showed significant activity.

Key words: _Croton crassifolius_; sesquiterpenoid glycoside; cytotoxic activity
List of content

Table S1. $^1$H (500 MHz) and $^{13}$C NMR (126 MHz) data for compound 1 (in DMSO-$d_6$, $J$ in Hz)…………………………………………………………………………………………1

Table S2. Cytotoxic activities of the isolated compounds ………………………1

Figure S1. Key COSY, HMBC and ROESY correlations of compound 1. ………1

Figure S2. HRESIMS spectrum of 1…………………………………………………………2

Figure S3. IR spectrum of 1……………………………………………………………………2

Figure S4. $^1$H NMR spectrum of 1 (in DMSO-$d_6$)………………………………3

Figure S5. $^{13}$C NMR spectrum of 1 (in DMSO-$d_6$) ………………………………3

Figure S6. $^1$H-$^1$H COSY spectrum of 1 (in DMSO-$d_6$) ………………………………4

Figure S7. HSQC spectrum of 1 (in DMSO-$d_6$) …………………………………………4

Figure S8. HMBC spectrum of 1 (in DMSO-$d_6$) …………………………………………5

Figure S9. ROESY spectrum of 1 (in DMSO-$d_6$) …………………………………………5
Table S1. $^1$H (500 MHz) and $^{13}$C NMR (126 MHz) data for compound 1 (in DMSO-$d_6$, $J$ in Hz)

| Position | $\delta_H$  | $\delta_C$  | Position | $\delta_H$  | $\delta_C$  |
|----------|-------------|-------------|----------|-------------|-------------|
| 1        | 66.5        | 25.3        | 12       | 0.76 s      | 19.2        |
| 2a       | 1.49 dd (13.2, 7.5) | 25.5 | 13       | 0.96 s      | 13.5        |
| 2b       | 1.64 dt (13.2, 9.8)  | 36.7 | 14       | 0.99 d (6.3) | 166.0       |
| 3a       | 2.51-2.61 overlapped | 124.6 | 15       | 166.2       | 73.9        |
| 3b       | 2.62-2.70 m      | 30.9 | 2'       | 2.91 dd (8.3, 8.3) | 76.6        |
| 4        | 1.91 dt (6.6, 3.2) | 47.4 | 3'       | 3.04-3.13 overlapped | 70.2        |
| 5        | 2.10-2.18 m      | 35.5 | 4'       | 3.00 dd (9.1, 9.1) | 61.3        |
| 6a       | 2.51-2.61 overlapped | 80.9 | 5'       | 3.04-3.13 overlapped | 61.3        |
| 6b       | 2.51-2.61 overlapped | 1.97 dd (10.1, 6.3) | 42.3 | 6'       | 3.64 dd (11.6, 2.1) | 3.39 dd (11.6, 6.1) |
| 7        | 1.91 dt (6.6, 3.2) | 1.97 dd (10.1, 6.3) | 42.3 | 6'       | 3.64 dd (11.6, 2.1) | 3.39 dd (11.6, 6.1) |
| 8a       | 2.03 ddd (13.4, 7.1, 3.8) | 1.97 dd (10.1, 6.3) | 42.3 | 6'       | 3.64 dd (11.6, 2.1) | 3.39 dd (11.6, 6.1) |
| 8b       | 1.73 ddd (13.4, 10.4, 2.6) | 1.97 dd (10.1, 6.3) | 42.3 | 6'       | 3.64 dd (11.6, 2.1) | 3.39 dd (11.6, 6.1) |

Table S2. Cytotoxic activities of the isolated compounds

| compound | 20(μM) Inh(%) |  |  |
|----------|---------------|---|---|
|          | HL-60         | A549 |  |
| 1        | 14.5          | 4.6 |  |
| 2        | 10.8          | 16.8 |  |
| 3        | 16.1          | 13.7 |  |
| 4        | 4.2           | 2.0  |  |
| 5        | 0.4           | 0.8  |  |
| 6        | 17.2          | 13.9 |  |
| cisplatin | 96.8          | 94.5 |  |

Figure S1. Key COSY, HMBC and ROESY correlations of compound 1.
Figure S2. HRESIMS spectrum of 1

Peak List

| m/z  | z  | Abund | Formula          | Ion            |
|------|----|-------|------------------|----------------|
| 435.1988 | 1  | 100.174 | C21 H32 Na O8     | (M+Na)+        |

Formula Calculator Element Limits

| Element | Min | Max |
|---------|-----|-----|
| C       | 3   | 60  |
| H       | 0   | 120 |
| O       | 0   | 30  |
| N       | 0   | 0   |
| S       | 0   | 0   |
| F       | 0   | 0   |
| Cl      | 0   | 0   |

Formula Calculator Results

| Formula | Best | Mass     | Tgt Mass | Diff (ppm) | Ion Species | Score |
|---------|------|----------|----------|------------|-------------|-------|
| C21 H32 O8 | TRUE | 412.2096 | 412.2097 | 0.38       | C21 H32 Na O8 | 94.5  |

Figure S3. IR spectrum of 1
Figure S4. $^1$H NMR spectrum of 1 (in DMSO-$d_6$)

Figure S5. $^{13}$C NMR spectrum of 1 (in DMSO-$d_6$)
Figure S6. $^1$H-$^1$H COSY spectrum of 1 (in DMSO-$d_6$)

Figure S7. HSQC spectrum of 1 (in DMSO-$d_6$)
Figure S8. HMBC spectrum of 1 (in DMSO-$d_6$)

Figure S9. ROESY spectrum of 1 (in DMSO-$d_6$)