

**CHEM****BIO**CHEM

## Supporting Information

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# CHEM **BIO** CHEM

## Supporting Information

for

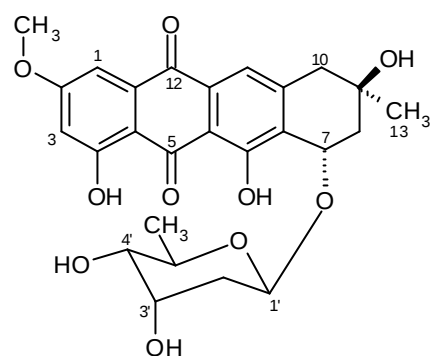
### Glycosylated Dderivatives of Steffimycin: Insights on the Role of the Sugar Moiety for the Biological Activity

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## Compound 10

$\beta$ -D-Digitoxosyl-8-demethoxy-10-deoxysteffimycin (**10**)

HR-FAB ( $m/z$  500.1672, calcd. for  $C_{26}H_{28}O_{10}$ , 500.1682).



**Table S1.**  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}$  (100 MHz) NMR data of **10** in  $[\text{D}_6]\text{acetone}$ .

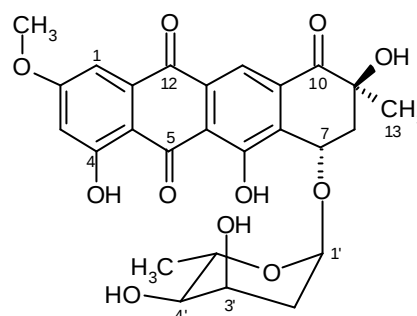
| Position   | $^1\text{H}$ (Int., mult., $J$ [Hz]) | $^{13}\text{C}$ |
|------------|--------------------------------------|-----------------|
| 1          | 7.27 (1H, d, 2.5)                    | 108.1           |
| 2          | -                                    | 166.9           |
| 2-OMe      | 3.99 (3H, s)                         | 56.1            |
| 3          | 6.79 (1H, d, 2.5)                    | 106.4           |
| 4          | -                                    | 165.6           |
| 4-OH       | 12.69 (1H, br s)                     | -               |
| 4a         | -                                    | 116.2           |
| 5          | -                                    | 196.1           |
| 5a         | -                                    | 120.4           |
| 6          | -                                    | 162.2           |
| 6-OH       | 12.23 (1H, br s)                     | -               |
| 6a         | -                                    | 129.1           |
| 7          | 5.11 (1H, t, 5.4, 4.0)               | 69.5            |
| 8A         | 2.00 (1H, dd, 12.5, 4.0)             | 44.3            |
| 8B         | 1.56 (1H, dd, 12.5, 5.4)             | -               |
| 9          | -                                    | 68.2            |
| 10A        | 3.04 (1H, d, 16.6)                   | 44.8            |
| 10B        | 2.86 (1H, d, 16.6)                   | -               |
| 10a        | -                                    | 147.5           |
| 11         | 7.48 (1H, s)                         | 113.5           |
| 11a        | -                                    | 138.1           |
| 12         | -                                    | 187.2           |
| 12a        | -                                    | 133.2           |
| 13         | 1.36 (3H, s)                         | 28.2            |
| Sugar part |                                      |                 |
| 1'         | 5.27 (1H, dd, 9.3, 3.0)              | 100.3           |
| 2'ax       | 2.17 (1H, ddd, 13.0, 3.0, 3.0)       | 38.5            |
| 2'eq       | 2.70 1H, ddd, 13.0, 3.0, 3.0)        | -               |
| 3'         | 3.14 (1H, ddd, 3.8, 3.0, 3.0)        | 72.1            |
| 4'         | 3.08 (1H, dd, 9.6, 3.8)              | 73.3            |
| 5'         | 3.78 (1H, dq, 9.6, 6.9)              | 68.4            |
| 6'         | 1.26 (3H, d, 6.9)                    | 18.2            |

**Compound 13**

$\alpha$ -L-Digitoxosyl-8-demethoxy-steffimycin (**13**)

HR-FAB ( $m/z$  514.1464, calcd. for

$C_{26}H_{26}O_{11}$ , 514.1475).



**Table S2.**  $^1H$  NMR (400 MHz) and  $^{13}C$  NMR Data (100 MHz) of **13** in  $[D_6]$ acetone.

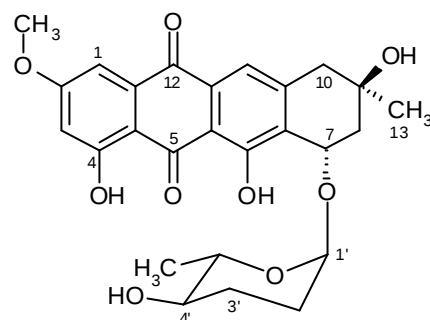
| Position   | $^1H$ (Int., mult., J [Hz])        | $^{13}C$ |
|------------|------------------------------------|----------|
| 1          | 7.26 (1H, d, 2.6)                  | 108.1    |
| 2          | -                                  | 167.0    |
| 2-OMe      | 3.99 (3H, s)                       | 61.2     |
| 3          | 6.79 (1H, d, 2.6)                  | 105.6    |
| 4          | -                                  | 163.7    |
| 4-OH       | 12.80 (1H, br s)                   | -        |
| 4a         | -                                  | N.O.     |
| 5          | -                                  | 196.2    |
| 5a         | -                                  | 122.7    |
| 6          | -                                  | 161.2    |
| 6-OH       | 12.23 (1H, br s)                   | -        |
| 6a         | -                                  | N.O.     |
| 7          | 5.01 (1H, t, 6.4, 4.7)             | 70.1     |
| 8A         | 2.08 (1H, dd, 12.3, 4.7)           | 48.9     |
| 8B         | 1.92 (1H, dd, 12.3, 6.4)           | -        |
| 9          | -                                  | 72.5     |
| 10         | -                                  | 199.2    |
| 10a        | -                                  | 146.2    |
| 11         | 7.49 (1H, s)                       | 113.3    |
| 11a        | -                                  | N.O.     |
| 12         | -                                  | 187.8    |
| 12a        | -                                  | N.O.     |
| 13         | 1.40 (3H, s)                       | 28.2     |
| Sugar part |                                    |          |
| 1'         | 5.27 (1H, d, 3.5)                  | 98.4     |
| 2'ax       | 2.20 (1H, ddd, 13.0, 3.5, 3.5)     | 40.9     |
| 2'eq       | 2.29 (1H, ddd, 13.0, 3.0, 1.1)     | -        |
| 3'         | 3.14 (1H, ddd, 6.5, 3.5, 3.0, 3.0) | 76.2     |
| 3'-OH      | 3.35 (1H, d, 6.5)                  | -        |
| 4'         | 3.09 (1H, ddd, 9.5, 7.0, 3.0)      | 78.3     |
| 4'-OH      | 3.27 (1H, d, 7.0)                  | -        |
| 5'         | 3.83 (1H, dq, 9.5, 6.2)            | 73.4     |
| 6'         | 1.26 (3H, d, 6.2)                  | 22.6     |

N.O. = not observed due to miniscule amounts of the compound

## Compound 16

$\alpha$ -L-Amicetosyl-8-demethoxy-10-deoxysteffi-  
mycin (**16**)

HR-FAB ( $m/z$  484.1735, calcd. for  $C_{26}H_{28}O_9$ ,  
484.1733).



**Table S3.**  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}$  (100 MHz) NMR data of **16** in  $[\text{D}_6]\text{acetone}$ .

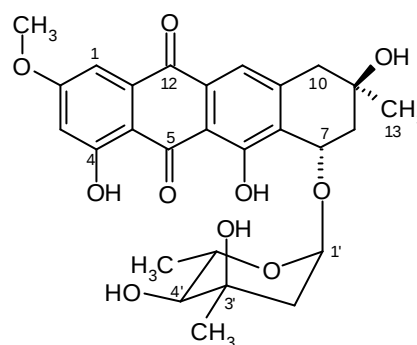
| Position   | $^1\text{H}$ (Int., mult., $J$ [Hz])  | $^{13}\text{C}$ |
|------------|---------------------------------------|-----------------|
| 1          | 7.25 (1H, d, 2.5)                     | 108.1           |
| 2          | -                                     | 167.1           |
| 2-OMe      | 3.98 (3H, s)                          | 56.8            |
| 3          | 6.78 (1H, d, 2.53)                    | 106.4           |
| 4          | -                                     | 165.6           |
| 4-OH       | 12.73 (1H, br s)                      | -               |
| 4a         | -                                     | 116.1           |
| 5          | -                                     | 193.8           |
| 5a         | -                                     | 120.4           |
| 6          | -                                     | 162.9           |
| 6-OH       | 12.22 (1H, br s)                      | -               |
| 6a         | -                                     | 131.2           |
| 7          | 5.03 (1H, t, 5.7, 3.2)                | 69.4            |
| 8A         | 2.26 (1H, dd, 12.1, 3.2)              | 43.8            |
| 8B         | 2.18 (1H, dd, 12.1, 5.7)              | -               |
| 9          | -                                     | 68.8            |
| 10A        | 3.07 (1H, d, 17.3)                    | 44.9            |
| 10B        | 2.88 (1H, d, 17.3)                    | -               |
| 10a        | -                                     | 147.1           |
| 11         | 7.47 (1H, s)                          | 113.6           |
| 11a        | -                                     | 138.2           |
| 12         | -                                     | 187.1           |
| 12a        | -                                     | 132.6           |
| 13         | 1.43 (3H, s)                          | 28.4            |
| Sugar part |                                       |                 |
| 1'         | 5.19 (1H, br d, 2.7)                  | 99.4            |
| 2'ax       | 1.79 (1H, m, compl.)                  | 30.0            |
| 2'eq       | 1.68 (1H, m, compl.)                  | -               |
| 3'ax       | 1.72 (1H, m, compl.)                  | 27.9            |
| 3'eq       | 1.60 (1H, dddd, 11.0, 4.2, 4.2, 4.2)  | -               |
| 4'         | 3.15 (1H, dddd, 11.0, 11.0, 4.2, 4.2) | 72.4            |
| 4'-OH      | 4.95 (1H, d, 4.2)                     | -               |
| 5'         | 3.75 (1H, dq, 6.2, 4.2)               | 70.4            |
| 6'         | 1.19 (3H, d, 6.2)                     | 17.8            |

**Compound 17**

$\alpha$ -L-Mycarosyl-8-demethoxy-10-deoxysteffermycin (**17**)

HR-FAB (  $m/z$  514.1848, calcd. for

$C_{27}H_{30}O_{10}$ , 514.1839).



**Table S4.**  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}$  (100 MHz) NMR data of **17** in  $[\text{D}_6]\text{acetone}$ .

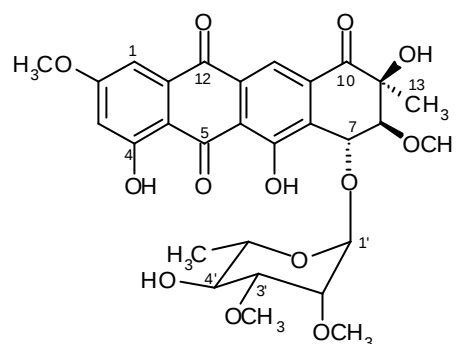
| Position | $^1\text{H}$ (Int., mult., $J$ [Hz]) | $^{13}\text{C}$ |
|----------|--------------------------------------|-----------------|
| 1        | 7.25 (1H, d, 2.5)                    | 108.2           |
| 2        | -                                    | 166.9           |
| 2-OMe    | 4.01 (3H, s)                         | 56.4            |
| 3        | 6.79 (1H, d, 2.5)                    | 106.4           |
| 4        | -                                    | 165.5           |
| 4-OH     | 12.77 (1H, br s)                     | -               |
| 4a       | -                                    | 110.3           |
| 5        | -                                    | 191.2           |
| 5a       | -                                    | 120.6           |
| 6        | -                                    | 162.2           |
| 6-OH     | 12.21 (1H, br s)                     | -               |
| 6a       | -                                    | 132.2           |
| 7        | 5.01 (1H, t, 6.7, 5.3)               | 68.9            |
| 8A       | 2.13 (1H, dd, 12.1, 6.7)             | 43.1            |
| 8B       | 1.95 (1H, dd, 12.1, 5.3)             | -               |
| 9        | -                                    | 68.4            |
| 10A      | 3.31 (1H, d, 17.1)                   | 44.9            |
| 10B      | 2.82 (1H, d, 17.1)                   | -               |
| 10a      | -                                    | 146.9           |
| 11       | 7.48 (1H, s)                         | 113.7           |
| 11a      | -                                    | 135.5           |
| 12       | -                                    | 181.1           |
| 12a      | -                                    | 132.3           |

|                    |                          |       |
|--------------------|--------------------------|-------|
| 13                 | 1.45 (3H, s)             | 28.5  |
| Sugar part         |                          |       |
| 1'                 | 5.39 (1H, d, 3.9)        | 100.8 |
| 2'ax               | 2.15 (1H, dd, 15.0, 3.9) | 35.1  |
| 2'eq               | 2.26 1H, dd, 15.0, 1.1)  | -     |
| 3'                 | -                        | 72.5  |
| 3'-CH <sub>3</sub> | 1.20 (3H, s)             | 27.3  |
| 4'                 | 3.09 (1H, d, 9.7)        | 78.6  |
| 5'                 | 3.81 (1H, dq, 9.7, 6.8)  | 76.6  |
| 6'                 | 1.28 (3H, d, 6.8)        | 17.8  |

### Compound 18

3'-O-methylsteffimycin (**18**)

HR-FAB (*m/z* 588.1863, calcd. for C<sub>29</sub>H<sub>32</sub>O<sub>13</sub>, 588.1843).



**Table S5.** <sup>1</sup>H (400 MHz) and <sup>13</sup>C (100 MHz) NMR data of **18** in [D<sub>6</sub>]acetone.

| Position           | <sup>1</sup> H (Int., mult., <i>J</i> [Hz]) |
|--------------------|---------------------------------------------|
| 1                  | 7.35 (1H, d, 2.8)                           |
| 2                  | -                                           |
| 2-OMe              | 4.05 (3H, s)                                |
| 3                  | 6.88 (1H, d, 2.8)                           |
| 4                  | -                                           |
| 4-OH               | 12.78 (1H, br s)                            |
| 4a                 | -                                           |
| 5                  | -                                           |
| 5a                 | -                                           |
| 6                  | -                                           |
| 6-OH               | 12.20 (1H, br s)                            |
| 6a                 | -                                           |
| 7                  | 5.23 (1H, d, 2.3)                           |
| 8                  | 4.61 (1H, br d)                             |
| 8-OCH <sub>3</sub> | 3.40 (3H, s)                                |
| 9                  | -                                           |
| 10                 | -                                           |

|            |                         |
|------------|-------------------------|
| 10a        | -                       |
| 11         | 8.2 (1H, s)             |
| 11a        | -                       |
| 12         | -                       |
| 12a        | -                       |
| 13         | 1.51 (3H, s)            |
| Sugar part |                         |
| 1'         | 5.61 (1H, d, 1.5)       |
| 2'         | 3.26 (1H, dd, 3.2, 1.5) |
| 2'-OMe     | 3.50 (3H, s)            |
| 3'         | 3.65 (1H, dd, 9.7, 3.2) |
| 3'-OMe     | 3.54 (3H, s)            |
| 4'         | 3.32 (1H, dd, 9.7, 9.2) |
| 5'         | 3.78 (1H, dq, 9.7, 6.2) |
| 6'         | 1.37 (3H, d, 6.2)       |

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