

Structure revision of medermycin/lactoquinomycin A and of related C-8 glycosylated naphthoquinones

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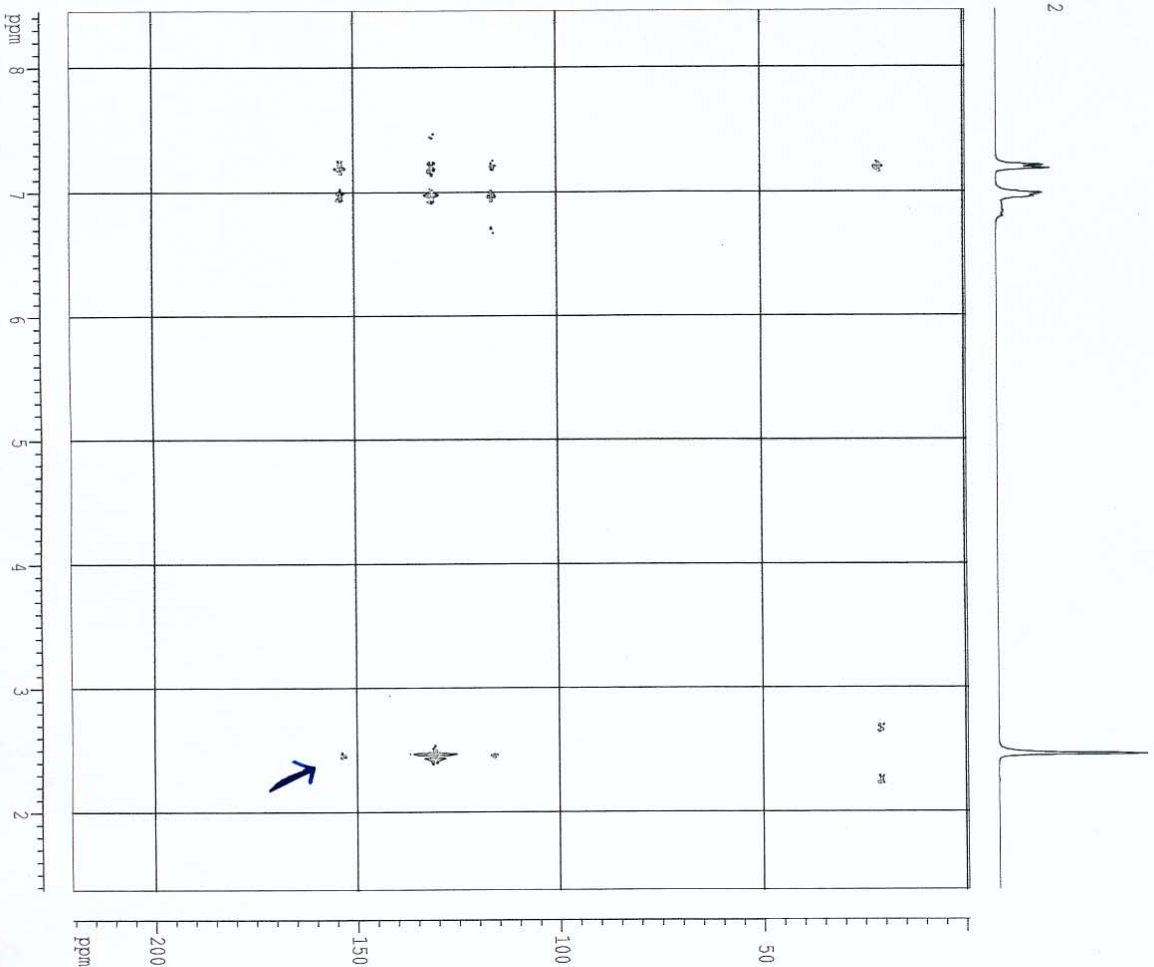
4-Bromo-3-hydroxy-benzaldehyde **3**.

To 4-bromo-3-hydroxy-benzylalcohol (2.42 g - prepared according to Canceill, J.; Collet, A. *New J. Chem.* **1986**, *10*, 17-23) in dichloromethane (25 mL) was added in 4 portions over 24 hours, activemanganese dioxide (11 g) , which allowed the reaction to be complete. The reaction mixture was poured onto Celite, which was rinsed abundantly with dichloromethane then methanol. Evaporation of the volatile left pure aldehyde **3** (2.0 g - 83 %) ; m.p. = 132-4 °C (dichloromethane/pentane). <sup>1</sup>H-NMR (300 MHz, acetone-d<sub>6</sub>) δ : 7.0 (dd, J= 8.6, 3.0 Hz, 1H) ; 7.3 (d, J=3.0 Hz, 1H) ; 7.5 (d, J= 8.6 Hz, 1H) ; 9.1 (OH), 10.2 (CHO, 1H). <sup>13</sup>C-NMR (75 MHz, acetone-d<sub>6</sub>) δ : 116.7 (C-2), 116.9, 124.7 and 135.8 (C-3, -4, -6) ; 135.8 (C-1) ; 159.1 (C-5) ; 192.8 (CHO).

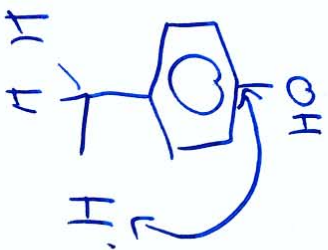
2-Bromo-5-hydroxy-benzaldehyde **4**.

Meta-hydroxybenzaldehyde (50 g) was dissolved (some warming is necessary) in glacial acetic acid (200 mL) then cooled at 15 °C (internal temperature). To the stirred solution, bromine (26 mL) was added dropwise while keeping temperature under 20 °C. After overnight stirring at room temperature, the volatiles were removed in vacuum without heating; the residue was co-evaporated three times with cyclohexane and taken up in warm chloroform. Upon cooling 2-bromo-5-hydroxy-benzaldehyde **4** (m.p. 130 °C) was obtained in two crops (47 g - 57%). <sup>1</sup>H-NMR (300 MHz, acetone-d<sub>6</sub>) δ : 7.3 (dd, J= 8.1, 1.6 Hz, 1H) ; 7.5 (d, J= 1.6 Hz, 1H) ; 7.7 (d, J=8.1 Hz, 1H) ; 9.3 ((OH), 9.7 s (CHO), 1H). <sup>13</sup>C-NMR (75 MHz, acetone-d<sub>6</sub>) δ : 118.1 (C-4), 116.4, 123.4, 135.0 (C-2, -3, -6) ; 138.4 (C-1) ; 155.8 (C-5) ; 192.2 (CHO).

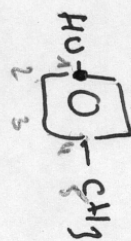
GHMBC 10013 u 14 2



CH 144



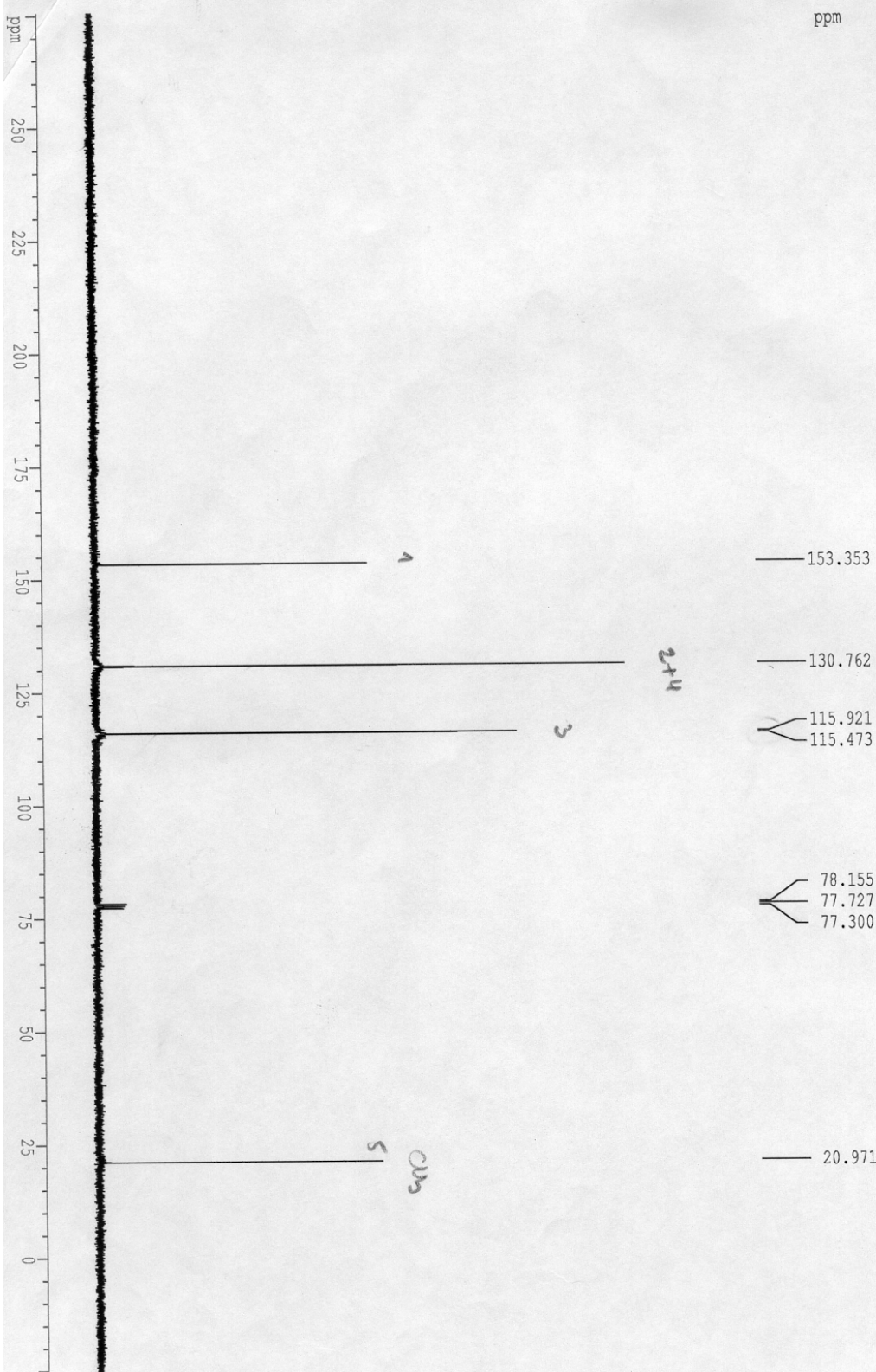
arrow  
shows  
[J] correlation  
GHMBC



C13R00

75 MHz / CDCl<sub>3</sub>

CH 144.1

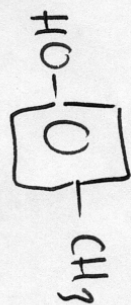


$^{13}\text{C}$  75 MHz

H-undecoupled

CH<sub>3</sub> 44.5

ppm



- 155.295
- 155.171
- 155.046
- 133.485
- 133.404
- 132.512
- 132.425
- 132.341
- 132.253
- 132.167
- 131.409
- 131.375
- 130.724
- 119.509
- 118.679
- 118.631
- 116.566

- 79.840
- 79.415
- 78.991

- 34.156
- 32.012
- 25.240
- 25.182
- 25.125
- 23.567
- 23.510
- 23.452
- 21.895
- 21.838
- 21.780
- 20.223
- 20.165
- 20.108

