SUPPLEMENTARY MATERIAL

Chemistry of α -mangostin. Studies on the semisynthesis of minor xanthenes from *Garcinia mangostana*

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α -Mangostin is the major prenylated xanthone from *G. mangostana* and it has been used also in recent times as starting material for the semisynthetic preparation of various biologically active derivatives. Its structure is characterized by the presence of few functional groups amenable of chemical manipulations, but they are present in the molecule in multiple instance (three phenolic hydroxyl groups, two prenyl chains, two unsubstituted aromatic carbons). This study represents a first approach to the systematic investigation of the reactivity of α -mangostin and describes the semisynthesis of some minor xanthenes isolated from *G. mangostana*.

Keywords: α -mangostin; *Garcinia mangostana*; semisynthesis; acid-catalyzed cyclization; oxidative cyclization.

Experimental

1 General

Mangosteen extract (Mangosteen P. E., α -mangostin 40%, Guilin Layn Natural Ingredients Corp, Guangxi, China) was kindly supplied by Variati (Concorezzo, Italy).

All reagents were purchased from Sigma-Aldrich or VWR International and were of commercial quality. They were used as received without further purification.

Solvents were dried by standard methods prior to use.

Analytical TLC were performed on Silica gel 60 F₂₅₄ precoated aluminium sheets (Merck, Darmstadt, Germany). Components were detected by inspection under UV lamp (254 nm) and by spraying with Cerium IV sulfate-Ammonium phosphomolybdate solution, followed by heating to 150 °C ca.

Silica gel 60, 40-63 mesh (Merck, Darmstadt, Germany) was used for flash-column chromatography.

¹H and ¹³C NMR spectra were acquired at 400.13 and 100.61 MHz, respectively, in CDCl₃ or in DMSO-d₆ on a Bruker Advance 400 spectrometer (Bruker, Karlsruhe, Germany) interfaced with a Silicon Graphics workstation equipped with xwinnmr software package or a workstation running Windows operating system and equipped with TopSpin software package. Chemical shifts are given in ppm (δ) and are referenced to solvent signals as internal standards (δ_{H} CDCl₃ 7.26 ppm, δ_{C} CDCl₃ 77.16 ppm; δ_{H} DMSO 2.50 ppm, δ_{C} DMSO 39.52 ppm). ¹³C signal multiplicities were based on APT (Attached Proton Test) experiments. Attributions were made on the basis of H-H COSY (Correlated Spectroscopy); HSQC (Heteronuclear Single Quantum Correlation) and HMBC (Heteronuclear Multiple-Bond Correlation) experiments. Spectra analyses were carried out with iNMR Reader software (www.inmr.net) on an Apple computer. Electrospray ionization mass spectra (ESI-MS) were recorded on a ThermoFinnigan LCQ Advantage spectrometer (Hemel Hempstead, Hertfordshire, U. K.).

2 Extraction and purification of α -mangostin

A commercial preparation of mangosteen (100 g, nominal content in α -mangostin 40%) was extracted by means of a Soxhlet apparatus using in succession hexane (1 L, 8 h extraction time), ethyl acetate (1 L, 16 h extraction time) and methanol (1 L, 8 h extraction time). Solvents were removed under reduced pressure affording the corresponding extracts, respectively GMM01 (5.2 g), GMM02 (55.0 g), GMM03 (28.9 g) and a solid residue GMMR (10.1 g).

Flash-column chromatography of the ethyl acetate fraction GMM02 (5 g) using ethyl acetate/hexane 20 : 80 as the eluent, afforded five fractions on the basis of TLC

analysis. Among these, the most abundant contained a single product with R_f 0.15.

Fractions were collected and the solvent was removed under reduced pressure to give a yellow solid (3.26 g), which was reprecipitated from hexane.

α -mangostin (**1**): yellow, amorphous solid, 3.04 g.

¹H NMR (400.14 MHz, DMSO-d₆): δ 13.73 (1H, s, 1-OH), 10.89 (2H, broad s, 3-OH and 6-OH), 6.79 (1H, s, H-5), 6.34 (1H, s, H-4), 5.17 (1H, m, H-12), 5.16 (1H, m, H-17), 4.01 (2H, broad d, *J* = 6.5 Hz, H-16), 3.70 (3H, s, 7-OMe), 3.21 (2H, broad d, *J* = 7.0 Hz, H-11), 1.77 (3H, s, H-19), 1.73 (3H, s, H-15), 1.62 (6H, s, H-14 and H-20).

¹³C NMR (100.61 MHz, DMSO-d₆): δ 181.3 (C-9); 162.3 (C-3); 159.9 (C-1); 157.0 (C-6); 154.6 (C-10a); 154.1 (C-4a); 143.3 (C-7); 136.3 (C-8); 130.4, 130.3 (C-13, C-18); 123.7 (C-17); 122.4 (C-12); 109.8 (C-8a); 109.6 (C-2); 101.8 (C-5); 101.8 (C-9a); 92.3 (C-4); 60.1 (OMe); 25.7 (C-16); 25.6, 25.5 (C-14 and C-19); 21.0 (C-11); 18.0 (C-15); 17.7 (C-20).

3 Acetylation and alkylation reactions of hydroxyl groups of α -mangostin

3.1 Synthesis of 3,6-di-*O*-acetyl- α -mangostin (**4**) and 6-*O*-acetyl- α -mangostin (**5**)

α -Mangostin (**1**, 205 mg, 0.5 mmol) was dissolved in dichloromethane (10 mL) and the solution was cooled to 0 °C. Triethylamine (280 μ L, 2 mmol) was then added, followed after 5 min by acetic anhydride (57 μ L, 0.6 mmol). The mixture was stirred at 0 °C for 2 h, diluted with ethyl acetate (15 mL) and washed in succession with 1M HCl (2 $\times$ 10 mL), saturated sodium hydrogen carbonate (2 $\times$ 10 mL) and saturated sodium chloride (2 $\times$ 10 mL). The organic layer was dried (sodium sulfate) and the solvent was evaporated under reduced pressure to give a yellow, oily solid (200 mg). Flash-column chromatography of the residue (silica gel, ethyl acetate/hexane 15 : 85) afforded three fractions: 3,6-di-*O*-acetyl- α -mangostin (**4**, yellow solid, 75 mg, 30% yield), 6-*O*-acetyl-

α -mangostin (**5**, yellow solid, 75 mg, 33% yield); unreacted α -mangostin (**1**, yellow solid, 30 mg, 15%).

3,6-di-*O*-acetyl- α -mangostin (**4**): ^1H and ^{13}C NMR as reported by Ren et al. (2011) and Sudta et al. (2013).

ESI-MS (+): m/z 517.4 ($\text{M}+\text{Na}$) $^+$; ESI-MS (-): m/z 493.4 ($\text{M}-\text{H}$) $^-$.

6-*O*-acetyl- α -mangostin (**5**): ^1H and ^{13}C NMR as reported by Ren et al. (2011) and Sudta et al. (2013).

ESI-MS (-): m/z 451.3 ($\text{M}-\text{H}$) $^-$.

3.2 Synthesis of 3,6-di-*O*-acetyl- α -mangostin (4) and 3-*O*-acetyl- α -mangostin (6)

α -Mangostin (**1**, 205 mg, 0.5 mmol) was dissolved in dichloromethane (10 mL) and acetylimidazole (55 mg, 0.5 mmol) was added at room temperature. After 6 hours, additional acetylimidazole (55 mg, 0.5 mmol) was added and the reaction was allowed to proceed overnight. The mixture was then diluted with ethyl acetate (15 mL) and washed in succession with 1M HCl (2×10 mL), saturated sodium hydrogen carbonate (2×10 mL) and saturated sodium chloride (2×10 mL). The organic layer was dried (sodium sulfate) and the solvent was evaporated under reduced pressure to give a yellow, oily solid (210 mg). Flash-column chromatography of the residue (silica gel, ethyl acetate/hexane 15 : 85) afforded three fractions: 3,6-*O*-diacetyl- α -mangostin (**4**, yellow solid, 20 mg, 8% yield); 3-*O*-acetyl- α -mangostin (**6**, yellow solid, 100 mg, 44% yield); unreacted α -mangostin (**1**, yellow solid, 40 mg, 20 %).

3-*O*-acetyl- α -mangostin (**6**): ^1H and ^{13}C NMR as reported by Ren et al. (2011).

ESI-MS (-): m/z 451.5 ($\text{M}-\text{H}$) $^-$.

3.3 Synthesis of 3,6-di-*O*-acetyl- α -mangostin (**4**)

α -Mangostin (**1**, 205 mg, 0.5 mmol) was dissolved in toluene (20 mL) at room temperature. Triethylamine (280 μ L, 2 mmol) was then added, followed after 5 min by acetic anhydride (142 μ L, 2.2 mmol). The mixture was stirred at room temperature for 2 h, diluted with ethyl acetate (15 mL) and washed with 1M HCl (2×10 mL), saturated sodium hydrogen carbonate (2×10 mL) and saturated sodium chloride (2×10 mL). The organic layer was dried (sodium sulfate) and the solvent was evaporated under reduced pressure to give the title compound **4** as a yellow, chromatographically homogeneous solid (246 mg, 99% yield).

3.4 Synthesis of 6-*O*-benzoyl- α -mangostin (**7**) and 3,6-di-*O*-benzoyl- α -mangostin (**8**)

α -Mangostin (**1**, 205 mg, 0.5 mmol) was dissolved in dichloromethane (10 mL) and the solution was cooled to 0 °C. Triethylamine (280 μ L, 2.0 mmol) was then added, followed after 5 min by a solution of benzoyl chloride (70 μ L, 0.6 mmol) in dichloromethane (3 mL) added dropwise over 10 min. The mixture was stirred at 0 °C for 2 h, diluted with ethyl acetate (15 mL) and washed in succession with 1M HCl (2×10 mL), saturated sodium hydrogen carbonate (2×10 mL) and saturated sodium chloride (2×10 mL). The organic layer was dried (sodium sulfate) and the solvent was evaporated under reduced pressure to give a yellow, oily solid (255 mg). Flash-column chromatography of the residue (silica gel, ethyl acetate/hexane 10 : 90) afforded three fractions: 3,6-di-*O*-benzoyl- α -mangostin (**8**, yellow solid, 110 mg, 36% yield); 6-*O*-benzoyl- α -mangostin (**7**, yellow solid, 100 mg, 39% yield); unreacted α -mangostin (**1**, yellow solid, 20 mg, 10%).

3,6-di-*O*-benzoyl- α -mangostin (**8**): ^1H NMR and ^{13}C NMR as reported by Sudta et al. (2013).

ESI-MS (-): m/z 617.2 (M-H) $^-$.

6-*O*-benzoyl- α -mangostin (**7**): ^1H NMR and ^{13}C NMR as reported by Sudta et al. (2013).

ESI-MS (-): m/z 513.3 (M-H) $^-$.

3.5 Synthesis of 6-*O*-methyl- α -mangostin (**9**) and 3,6-di-*O*-methyl- α -mangostin (**10**)

α -Mangostin (**1**, 205 mg, 0.5 mmol) was dissolved in DMF (15 mL) and solid sodium hydrogen carbonate (378 mg, 4.5 mmol) was then added in one portion, followed after 30 min by methyl iodide (560 μ L, 9.0 mmol). The mixture was stirred at room temperature for 24 h, diluted with ethyl acetate (15 mL) and washed in succession with 1M HCl (2 $\times$ 10 mL, CAUTION: gas evolution), saturated sodium hydrogen carbonate (2 $\times$ 10 mL) and saturated sodium chloride (2 $\times$ 10 mL). The organic layer was dried (sodium sulfate) and the solvent was evaporated under reduced pressure to give a dark-yellow oil (249 mg). Flash-column chromatography of the residue (silica gel, ethyl acetate/hexane 10 : 90) afforded three fractions: 3,6-di-*O*-methyl- α -mangostin (**10**, yellow solid, 64 mg, 29% yield); 6-*O*-methyl- α -mangostin (**9**, yellow solid, 129 mg, 51% yield); unreacted α -mangostin (**1**, yellow solid, 39 mg, 19%).

3,6-di-*O*-methyl- α -mangostin (**10**): ^1H NMR and ^{13}C NMR as reported by Sudta et al. (2013).

ESI-MS (-): m/z 437.4 (M-H) $^-$.

6-*O*-methyl- α -mangostin (**9**): ^1H NMR and ^{13}C NMR as reported by Sudta et al. (2013).

ESI-MS (-): m/z 423.1 (M-H) $^-$.

4 Oxidative cyclization reactions involving the prenyl groups of α -mangostin

4.1 Synthesis of 9-hydroxycalabaxanthone (**11**)

To a stirred solution of α -mangostin (**1**, 410 mg, 1.0 mmol) in toluene (25 mL) under a stream of nitrogen, DDQ (250 mg, 1.1 mmol) was added at room temperature and the mixture was stirred for 12 h. The reaction mixture was diluted with ethyl acetate (15 mL) and washed with saturated sodium hydrogen carbonate (2 $\times$ 15 mL) and saturated sodium chloride (2 $\times$ 15 mL). The organic layer was dried (sodium sulfate) and the solvent was evaporated under reduced pressure, affording a viscous, dark-yellow oil

(570 mg). Flash column chromatography of the residue (silica gel, ethyl acetate/hexane 20 : 80) gave a pale yellow solid (9-hydroxycalabaxanthone **11**, 286 mg, 70% yield).

¹H NMR (400.14 MHz, DMSO-d₆): δ 13.67 (1H, s, 1-OH), 11.12 (1H, s, 6-OH), 6.78 (1H, s, H-5), 6.58 (1H, d, *J* = 10.0, H-11), 6.31 (1H, s, H-4), 5.73 (1H, d, *J* = 10.0 Hz, H-12), 5.15 (1H, broad t, *J* = 6.4 Hz, H-17), 3.98 (2H, d, *J* = 6.4 Hz, H-16), 3.70 (3H, s, 7-OMe), 1.76 (3H, s, H-19 or H-20), 1.62 (3H, s, H-19 or H-20), 1.42 (6H, s, H-14 and H-15).

¹³C NMR (100.61 MHz, DMSO-d₆): δ 181.5 (C-9), 159.2 (C-1), 157.3 (C-6), 157.2 (C-3), 155.7 (C-4a), 154.7 (C-10a), 143.6 (C-7), 136.3 (C-8), 130.5 (C-18), 128.0 (C-12), 123.5 (C-17), 114.7 (C-11), 109.9 (C-8a), 103.7 (C-2), 102.9 (C-9a), 101.9 (C-5), 93.9 (C-4), 78.1 (C-13), 60.2 (C-7-OMe), 27.9 (C-14 and C-15), 25.8 (C-16), 25.6 (C-19 or C-20), 18.0 (C-19 or C-20).

ESI-MS (-): *m/z* 407.7 (M-H)⁻.

4.2 Synthesis of mangostanin (**12**)

4.2.1 Reaction of α-mangostin with *m*-chloroperbenzoic acid

α-Mangostin (**1**, 205 mg, 0.5 mmol) was dissolved in dichloromethane (12 mL) and the solution was cooled to 0 °C. A *m*-chloroperbenzoic acid (77%, 123 mg, 0.71 mmol) solution in dichloromethane (4 mL) was then added dropwise over 10 min. The reaction mixture was stirred at 0 °C for 6 h, washed with 10% sodium hydrogen sulfite solution (10 mL), 5% sodium hydrogen carbonate solution (2 × 10 mL) and saturated sodium chloride (2 × 10 mL) and dried (sodium sulfate). The solvent was evaporated under reduced pressure to give a yellow, oily solid (170 mg). Flash-column chromatography of the residue (silica gel, ethyl acetate/hexane 25 : 75) afforded unreacted α-mangostin

(**1**, yellow solid, 35 mg, 17%) and mangostanin (**11**, pale yellow solid, 50 mg, 25%).

¹H NMR and ¹³C NMR as reported by Nilar (2002).

ESI-MS (+): *m/z* 427.1 (M+H)⁺; 449.2 (M+Na)⁺. MS-MS: 371.3 (M-isobutylene)⁺.

4.2.2 Reaction of α-mangostin with oxone[®]

α-Mangostin (**1**, 205 mg, 0.5 mmol) was dissolved in dichloromethane (12 mL) and acetone (1 mL). Saturated aqueous sodium hydrogen carbonate (15 mL) was then added in order to set up the biphasic system. An aqueous (8 mL) solution of oxone[®] (615 mg, 1 mmol) was then added dropwise over 10 min at 5 °C to the vigorously stirred suspension. The reaction mixture was stirred for 24 h, during which time the temperature was allowed to raise to room temperature. The phases were separated and the aqueous layer was extracted with ethyl acetate (2 × 30 mL). The combined organic layers were dried (sodium sulfate) and the solvent was evaporated under reduced pressure to give an oily residue (200 mg). Flash-column chromatography (silica gel, ethyl acetate/hexane 25 : 75) afforded unreacted α-mangostin (**1**, yellow solid, 51 mg, 25%) and mangostanin (**11**, 99 mg, 46% yield).

5 Non-oxidative cyclization reactions involving the prenyl groups of α-mangostin

5.1 Reaction of α-mangostin with p-toluenesulfonic acid. Synthesis of compounds 13-16

To a cooled (0 °C) solution of α-mangostin (**1**, 300 mg, 0.73 mmol) in toluene/dichloromethane 2 : 1 (24 mL) catalytic *p*-toluenesulfonic acid (10 mg) was added. The mixture was stirred allowing to reach room temperature for 24 h. The reaction mixture was washed with saturated sodium hydrogen carbonate (20 mL) and the aqueous layer was extracted with ethyl acetate (2 × 15 mL). The combined organic

layers were washed with saturated sodium chloride (30 mL) and dried (sodium sulfate). The solvent was evaporated under reduced pressure to give a dark-yellow, oily solid (300 mg). Flash column chromatography (silica gel, ethyl acetate/hexane 25 : 75) afforded five fractions: 3-isomangostin (**14**, 80 mg, 27% yield); 1-isomangostin (**13**, 45 mg, 15% yield); unreacted α -mangostin (**1**, 45mg, 15%); 3-isomangostin hydrate (**16**, 25 mg, 9% yield) and 1-isomangostin hydrate (**15**, 40 mg, 15% yield).

3-isomangostin (**14**): ^1H NMR and ^{13}C NMR as reported by Mahabusarakam, Wiriyachitra and Taylor (1987) and Ren et al. (2011).

1-isomangostin (**13**): ^1H NMR (400.14 MHz, DMSO- d_6): δ 13.83 (1H, s, 1-OH), 6.68 (1H, s, H-5), 6.31 (1H, s, H-4), 5.17 (1H, t, $J = 12.8$ Hz, H-17), 3.94 (2H, d, $J = 6.8$ Hz, H-16), 3.68 (3H, s, H-7-OMe), 2.55 (2H, t, $J = 13.6$ Hz, H-11), 1.77 (3H, s, H-19), 1.74 (2H, t, $J = 13.6$, H-12), 1.63 (3H, s, H-20), 1.32 (6H, s, H-14 and H-15). See also Mahabusarakam, Wiriyachitra and Taylor (1987). ^{13}C NMR (100.61 MHz, DMSO- d_6): δ 176.1 (C-9), 161.1 (C-3), 157.0 (C-6), 156.4 (C-4a), 155.9 (C-1), 154.2 (C-10a), 144.1 (C-7), 137.1 (C-8), 130.7 (C-18), 125.7 (C-17), 114.4 (C-8a), 107.8 (C-9a), 105.3 (C-2), 102.3 (C-5), 93.8 (C-4), 75.8 (C-13), 61.1 (C-7-OMe), 32.0 (C-12), 27.6 (C-14 e C-15), 26.7 (C-20), 26.5 (C-16), 19.1 (C-19), 17.8 (C-11).

ESI-MS (+): m/z 433.3 ($\text{M}+\text{Na}$) $^+$; 411 ($\text{M}+\text{H}$) $^+$. MS-MS: 355 (M -isobutylene) $^+$.

3-isomangostin hydrate (**16**): ^1H NMR and ^{13}C NMR as reported by Mahabusarakam, Wiriyachitra and Taylor (1987) and Ren et al. (2011).

1-isomangostin hydrate (**15**): ^1H NMR and ^{13}C NMR as reported by Mahabusarakam, Wiriyachitra and Taylor (1987) and Ren et al. (2011).

5.2 Reaction of α -mangostin with sulfuric acid. Synthesis 1-isomangostin hydrate (**15**) and 3-isomangostin (**14**)

α -Mangostin (**1**, 410 mg, 1 mmol) was dissolved in dry toluene (20 mL) in the presence of 4 Å molecular sieves (1.0 g) under a stream of nitrogen. The mixture was warmed to 40 °C. After dissolution of the starting material, sulfuric acid (98 mg, 1.0 mmol) was

added dropwise and the mixture was stirred at 40 °C for 4 h. The formed precipitate was collected by filtration and washed with cold hexane affording a yellow, amorphous solid (269 mg, 63% yield), 1-isomangostin hydrate (**15**). The clear filtrate was diluted with ethyl acetate (10 mL) and washed with saturated sodium hydrogen carbonate (2 × 10 mL) and saturated sodium chloride (10 mL). The solvent was evaporated under reduced pressure affording a yellow oil (167 mg). Flash column chromatography of the residue gave a lemon-yellow, amorphous solid (120 mg, 29% yield), 3-isomangostin (**14**).

5.3 Reaction of α -mangostin with boron trifluoride etherate. Synthesis of 1-isomangostin (13)

α -Mangostin (**1**, 205 mg, 0.5 mmol) was dissolved in dry dichloromethane (15 mL) and the solution was cooled to 0 °C. Catalytic boron trifluoride etherate (7 mg) was added and the mixture was stirred at 0 °C for 3 h and then allowed to reach room temperature within further 11 h. The reaction mixture was washed with 1M HCl (10 mL) and water (2 × 10 mL). The combined aqueous layers were extracted with ethyl acetate (15 mL). The organic layers were combined, dried (sodium sulfate) and the solvent was removed under reduced pressure giving a dark-yellow oil, 250 mg. The residue was chromatographed (flash-column chromatography, silica gel, ethyl acetate/hexane 20 : 80) affording two main fractions of chromatographically homogeneous materials. 1-isomangostin (**13**, 70 mg, 29% yield) and 1-isomangostin hydrate (**15**, 20 mg, 9% yield).

5.4 Reaction of α -mangostin with trifluoroacetic acid. Synthesis of 18-O-trifluoroacetate-1-isomangostin hydrate (19) and 18-O-trifluoroacetate-3-isomangostin hydrate (20)

α -Mangostin (**1**, 410 mg, 1.0 mmol) was dissolved in dichloromethane (40 mL) under a

stream of nitrogen at room temperature. Trifluoroacetic acid was added (114 mg, 1.0 mmol) and the reaction was stirred at room temperature for 24 h. The mixture was diluted with ethyl acetate (20 mL) and washed with saturated sodium hydrogen carbonate (2×30 mL) and saturated sodium chloride (30 mL). The organic layer was dried (sodium sulfate) and the solvent was evaporated under reduced pressure. Dark-yellow oil, 490 mg. The residue was chromatographed (flash-column chromatography, silica gel, ethyl acetate/hexane 20 : 80) affording 18-*O*-trifluoroacetyl-3-isomangostin hydrate (**20**, yellow-green amorphous solid, 133 mg, 25% yield) and 18-*O*-trifluoroacetyl-1-isomangostin hydrate (**19**, yellow amorphous solid, 292 mg, 56% yield).

18-*O*-trifluoroacetyl-3-isomangostin hydrate (**20**)

^1H NMR (400.14 MHz, DMSO- d_6): δ 11.12 (1H, s, 6-OH), 6.78 (1H, s, H-5), 6.27 (1H, s, H-4), 3.76 (3H, s, H-7-OMe), 3.37 (2H, t, $J = 11.2$ Hz, H-16), 2.58 (2H, t, $J = 13.2$ Hz, H-11), 2.04 (2H, t, $J = 20.4$ Hz, H-17), 1.80 (2H, t, $J = 20.4$ Hz, H-12), 1.70 (6H, s, H-19 and H-20), 1.32 (6H, s, H-14 and H-15).

^{13}C NMR (100.61 MHz, DMSO- d_6): δ 181.8 (C-9), 160.8 (C-1), 160.4 (C-4a), 157.5 (C-6), 155.2 (C-10a), 155.1 (q, $^2J_{\text{CF}} = 40$ Hz, CF_3CO), 154.5 (C-3), 143.9 (C-7), 136.8 (C-8), 117.1 (q, $^1J_{\text{CF}} = 288$ Hz, CF_3CO), 110.3 (C-8a), 104.0 (C-2), 102.5 (C-5), 102.1 (C-9a), 94.0 (C-4), 90.3 (C-18), 76.9 (C-13), 60.8 (C-7-OMe), 40.5 (C-17), 31.5 (C-12), 26.9 (C-14 e C-15), 25.9 (C-19 e C-20), 21.5 (C-16), 16.2 (C-11).

ESI-MS (+): m/z 547.0 ($\text{M}+\text{Na}$) $^+$; 525.0 ($\text{M}+\text{H}$) $^+$; 411.3 ($\text{M}-\text{CF}_3\text{COO}$) $^+$.

18-*O*-trifluoroacetyl-1-isomangostin hydrate (**19**)

^1H NMR (400.14 MHz, DMSO- d_6): δ 10.59 (2H, s, 3-OH and 6-OH), 6.69 (1H, s, H-5),

6.30 (1H, s, H-4), 3.70 (3H, s, H-7-OMe), 3.27 (2H, t, $J = 8.0$ Hz, H-16), 2.54 (2H, t, $J = 13.2$ Hz, H-11), 2.03 (2H, t, $J = 8.0$ Hz, H-17), 1.76 (2H, t, $J = 8.4$ Hz, H-12), 1.65 (6H, s, H-19 and H-20), 1.30 (6H, s, H-14 and H-15).

^{13}C NMR (100.61 MHz, DMSO- d_6): δ 174.9 (C-9), 160.0 (C-3), 155.9 (C-4a), 155.4 (C-1), 154.8 (q, $^2J_{\text{CF}} = 22$ Hz, CF_3CO), 154.7 (C-6), 153.1 (C-10a), 143.0 (C-7), 136.0 (C-8), 117.1 (q, $^1J_{\text{CF}} = 287$ Hz, CF_3CO), 113.4 (C-8a), 106.0 (C-9a), 104.2 (C-2), 101.4 (C-5), 92.6 (C-4), 90.1 (C-18), 74.6 (C-13), 60.2 (C-7-OMe), 40.1 (C-17), 30.9 (C-12), 26.4 (C-14 e C-15), 25.3 (C-19 e C-20), 20.9 (C-16), 16.8 (C-11).

ESI-MS (+): m/z 525.0 ($\text{M}+\text{H}$) $^+$; 411.2 ($\text{M}-\text{CF}_3\text{COO}$) $^+$.

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