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Natural Product Chemistry, Part 132 [1]: Synthesis and Oxidative Cyclisation of 1,3-Dihydroxy-10-methyl-4-(3-methylbut-2-enyl)-9(10*H*)-acridinone (Glycocitrine-II)

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Summary. Reaction of 1,3-dihydroxy-10-methyl-9(10*H*)-acridinone (**1**) and 1-bromo-3-methylbut-2-ene (mol. ratio 1 : 1) in tetrahydrofuran at 20°C in the presence of alumina gave prenylacridinones **2** (glycocitrine-II) and **8** and the diprenylacridinone **9**; with an excess of 1-bromo-3-methylbut-2-ene, the prenyldihydropyranoacridinones **12** and **13** were formed. Oxidation of glycocitrine-II (**2**) with *m*-chloroperbenzoic acid furnished the furanoacridinone **5** and the pyranoacridinone **6**; dehydration of the latter compound gave noracronycine (**10**).

Keywords. Acridone alkaloids; Cyclisation of furano- and pyrano-acridinones; Glycocitrine-II; Noracronycine; Prenylacridinones.

Naturstoffchemie, 132. Mitt.: Synthese und oxidative Cyclisierung von 1,3-Dihydroxy-10-methyl-4-(3-methylbut-2-enyl)-9(10*H*)-acridinon (Glycocitrin-II)

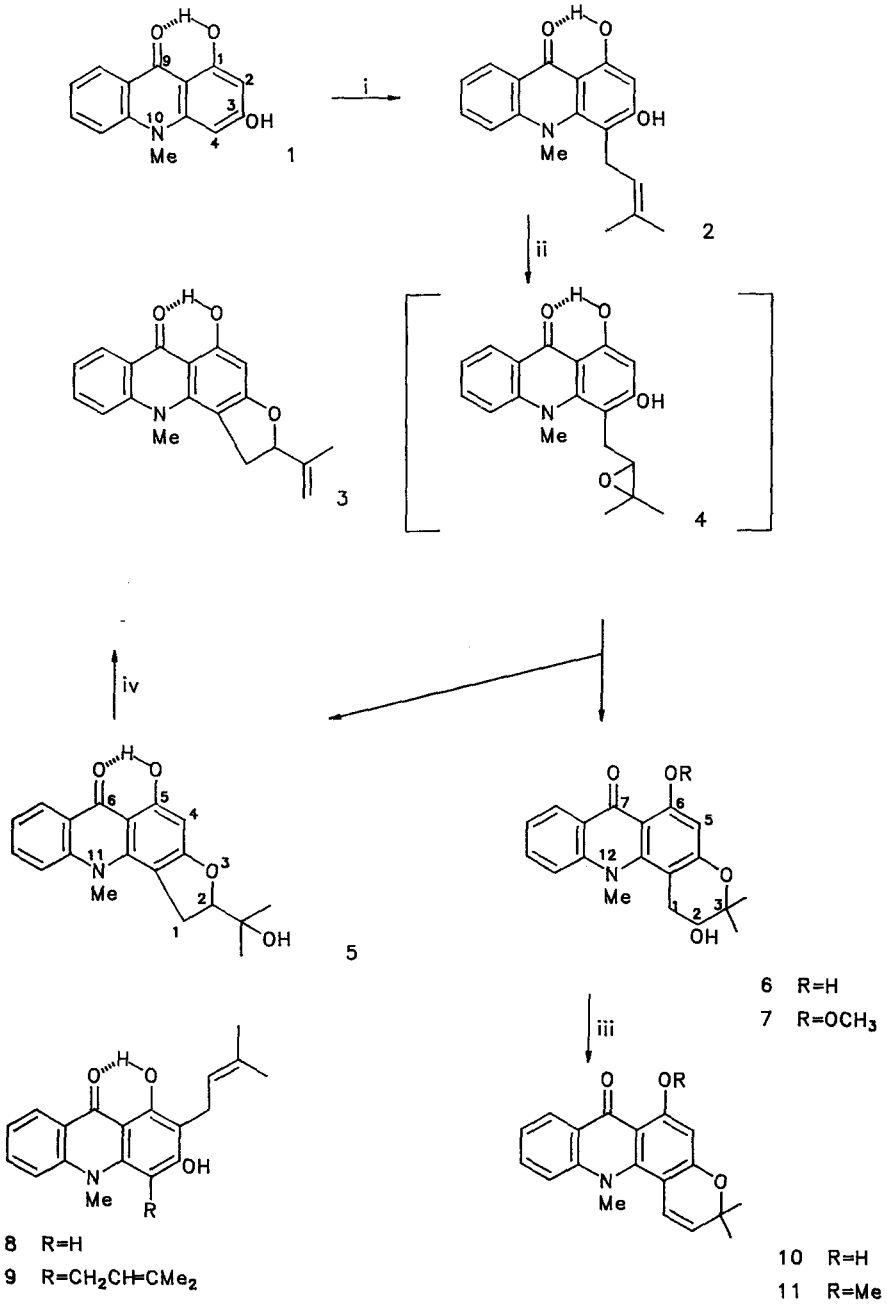
Zusammenfassung. 1,3-Dihydroxy-10-methyl-9(10*H*)-acridinon (**1**) reagierte mit 1-Brom-3-methylbut-2-en (Mol.-Verhältnis 1 : 1) in Tetrahydrofuran bei 20 °C in Gegenwart von Aluminiumoxid zu den Prenylacridinonen **2** (Glycocitrin-II) und **8** sowie dem Diprenylacridinon **9**. Bei Überschuß von 1-Brom-3-methylbut-2-en entstanden die Prenyldihydropyranoacridinone **12** und **13**. Die Oxidation von Glycocitrin-II (**2**) mit *m*-Perchlorbenzoesäure liefert das Furanoacridinon **5** und das Pyranoacridinon **6**. Die Dehydrierung von letzterem ergab Noracronycin (**10**).

Introduction

The synthesis and biosynthesis of hemiterpenoid quinoline alkaloids and coumarins and related compounds such as rotenone has been studied extensively. In the acridone alkaloid group, however, the corresponding hemiterpenoid derivatives including prenylacridones, isopropyldihydrofuroacridones and dimethylpyranoacridones have received less attention, with the exception of numerous syntheses

† (the late)

of the antitumor alkaloid acronycine [2]. The biosynthesis of acronycine (**11**) and of the isopropenyldihydrofuroacridone rutacridone (**3**) probably occurs by conversion of 1,3-dihydroxy-10-methyl-9(10*H*)-acridinone (**1**) into its 4-(3-methylbut-2-enyl) derivative (**2**) (glycocitrine-II) followed by oxidative cyclisation, and we decided to explore this route by biomimetic syntheses (Scheme 1).



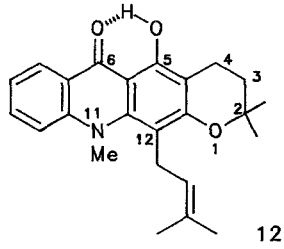
reagents: i, $BrCH_2CH{=}CMe_2$ (mol ratio 1:1);
ii, $m\text{-}ClC_6H_4CO_3H$
iii, conc. H_2SO_4;
iv, Ph_3POCl_2

Scheme 1

Results and Discussion

Glüsenkamp and Büchi [3] described the C-prenylation of phenols by reaction with 1-bromo-3-methylbut-2-ene at ambient temperature in a two-phase system containing alumina; in order to avoid O-prenylation, we applied these conditions to the prenylation of 1,3-dihydroxy-10-methyl-9(10*H*)-acridinone (**1**). When an equimolecular quantity of 1-bromo-3-methylbut-2-ene was used, three products were obtained. The required 4-(3-methylbut-2-enyl)-acridinone (**2**) had m.p. 169–170 °C, close to that, m.p. 168–169 °C, given for the alkaloid glycocitrine-II isolated from *Glycosmis citrifolia* [4] and from *Citrus grandis* [5]. The ^{1}H NMR and ^{13}C NMR spectral data and the mass spectrum are also in excellent agreement with those reported for the alkaloid. A compound derived from an O-(dimethylpropynyl)acridone was also assigned [6] structure **2**, but since it had m.p. 263–264 °C and a different ^{1}H NMR spectrum to that of glycocitrine-II, the rearrangement produce clearly has some other constitution. Our second prenylation product was isomeric with glycocitrine-II and was shown to be the 2-(3-methylbut-2-enyl) derivative **8** on the basis of its ^{1}H NMR and ^{13}C NMR spectra; the δ_c signals at 33.8 ppm (N-*Me*) and at 21.0 ppm (CH_2) are characteristic of 10-methylacridones substituted by a prenyl group at C-2 rather than at C-4 [2, 7, 8]. The third product was separated from compounds **2** and **8** and from the unchanged acridone **1** by virtue of its insolubility in aqueous alkali and was shown to be the 2,4-diprenyl derivative **9** by mass spectrometry and by nmr spectroscopy; in this case the presence of a 3-methylbut-2-enyl group at C-4 resulted in a ^{13}C NMR signal for the N-methyl group at 44.3 ppm and resonance at 21.7 and 27.4 ppm were attributable to methylene groups of the 2- and 4-prenyl substituents, respectively. Although compound **9** was insoluble in base, the proton of the hydroxy group at C-3 (δ_H 6.4 ppm) was exchanged with D_2O.

When the dihydroxyacridone **1** was treated with an excess of 1-bromo-3-methylbut-2-ene, the new products **12** and **13** were obtained. The presence of a dimethyldihydropyran ring in compound **12** was apparent from the ^{1}H NMR spectrum, which showed spin-spin coupled triplets at δ 2.77 (2H, *Ar*CH_2CH_2-) and at 1.84 ppm (2H, *Ar*CH_2CH_2-) and resonances in the ^{13}C NMR spectrum for these methylene groups at δ 31.8 and 16.2 ppm, respectively; a methylene carbon signal at δ_c 27.0 ppm indicates that a prenyl moiety is located at C-4 and that there is a linear arrangement of the four rings.



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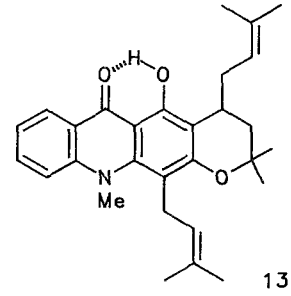

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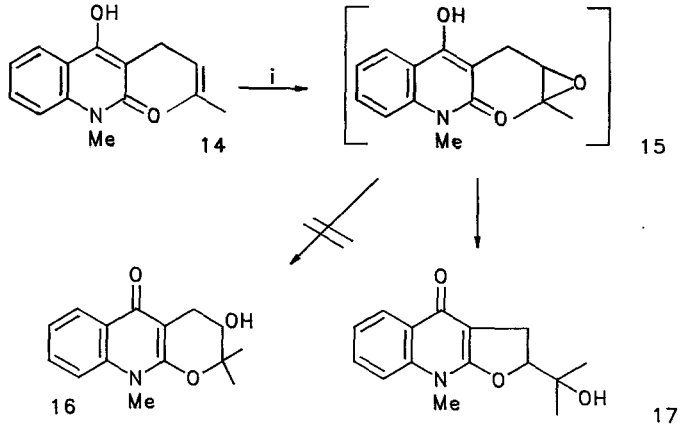
In the mass spectrum of compound **13**, the molecular ion peak at *m*/e 445 (100%) showed that three prenyl units had been introduced into acridone **1**. Although the ^{1}H and ^{13}C NMR spectra of compounds **12** and **13** were similar, it was apparent that compound **13** contained a prenyl group substituted at a sp^3 carbon

of a dihydropyran ring. Thus, in the high frequency (360 MHz) ^{1}H NMR spectrum, the resonance at δ 2.93 ppm is assigned to a methine group at C-4 and appears as a multiplet because of spin-spin coupling to the methylene group of the adjacent prenyl unit (δ 2.29 ppm) and to the methylene group at C-3, δ 1.81 ppm. The presence of dihydropyran rings in compounds **12** and **13**, which presumably arise from cyclisation of a 3-methylbut-2-enyl group at C-2 of the acridone ring, c.f. compound **9**, was unexpected in the non-acidic medium of the reaction mixture. Introduction of the third prenyl group as in compound **13** seems more likely to have occurred with the diprenyl derivative **9** rather than after formation of the dihydropyran ring in compound **12**, since the methylene protons of the C-2 prenyl group of **9** are probably more acidic than those at C-4 in the pyran **12**.



reagents: i, m-$ClC_6H_4CO_3H$

Scheme 2

Oxidative cyclisation of 4-hydroxy-1-methyl-3-prenylquinolin-2-ones **14** with peroxy acids gives dihydrofuroquinolin-4-ones **17** exclusively, apparently by spontaneous cyclisation of intermediate epoxides **15** (Scheme 2) [9, 10]. In the absence of an N-methyl group, however, 4-methoxy-3-prenylquinolin-2-ones give a mixture of isomeric (hydroxyisopropyl)dihydrofuroquinolines and hydroxydimethyldihydropyranoquinolines [11]. Application of the reaction to the dihydroxy-N-methylprenylacridinone **2** also gave two isomers **5** and **6**, presumably via epoxide **4** (Scheme 1). The structure of the pyranoacridinone **6**, which was the principal product, was established by its ^{1}H NMR spectrum, which showed resonances at δ 3.18 and 3.01 (2H, 2 × dd, J = 5, 16 Hz, CH_2) and at 3.74 ppm (C**H**−OH), and by the ^{13}C NMR spectrum; similar ^{1}H NMR data were reported for the 6-methoxy analogue **7** which was prepared recently from acronycine (**11**) [12]. The structure of the pyrano-acridinone **6** was further confirmed by dehydration with concentrated sulphuric acid to give noracronycine (**10**). In the ^{1}H NMR spectrum of the furanoacridinone **5** resonances for the methylene and methine groups occurred at δ 3.77 and 4.71 ppm, respectively; in the case of the quinolinone derivatives **16** and **17** the corresponding protons also resonated at lower fields in the furano isomer **17**.

The reluctance of the quinolinone epoxide **15** to form pyranoderivatives was attributed to unfavourable non-bonded interactions between the N-methyl group and the terminal $=CMe_2$ group in the transition state [10]. Since this restraint is not present in the N-methylacridinone epoxide **4**, a mixture of furano- and pyrano-derivatives is formed as in the case of epoxides of 4-methoxy-3-prenyl-2-quinolinones.

Experimental

^{1}H NMR spectra were determined with Perkin-Elmer R 12 (60 MHz) and R 32 (90 MHz) spectrometers, ^{13}C NMR spectra with a JEOL FX-90 Q or WH 360 spectrometer (tetramethylsilane as an internal standard), mass spectra with a MS 902 instrument, and IR spectra with a Perkin-Elmer 457 spectrometer.

Reaction of 1,3-Dihydroxy-10-methyl-9 (10H)-acridinone (**1**) *with 1-Bromo-3-methyl-2-ene*

(*a*) The acridinone **1** (241 mg, 1.0 mmol) in tetrahydrofuran (30 ml) was added to a slurry of neutral alumina containing 15% calcium sulphate (10 g) in ether. The solvent was evaporated, 1-bromo-3-methylbut-2-ene (150 mg, 1.0 mmol) was added, the mixture was stirred for 14 h, filtered and the solid washed with ethyl acetate containing 1% acetic acid. The combined organic solution was evaporated and the residue was extracted with toluene. The toluene solution was extracted with *N* sodium hydroxide and evaporated; chromatography of the residue on silica and elution with methylene chloride followed by methylene chloride-methanol (98 : 2) and then preparative tlc on silica (methylene chloride-methanol 98 : 2) gave:

1,3-Dihydroxy-10-methyl-2,4-bis(3-methyl-2-enyl)-9 (10H)-acridinone (**9**) (22.5 mg), m.p. 142–143 °C (yellow needles from hexane). IR (film): 3400, 1610 (C=O). ^{1}H NMR ($CDCl_3$, 60 MHz): δ (ppm) = 14.95 (1H, s, 1-OH, exchanged with D_2O), 8.4 (1H, dd, J = 2, 8 Hz, 8-H), 7.85–7.10 (3H, m, 5-H, 6-H and 7-H), 6.4 (1H, s, 3-OH, exchanged with D_2O), 5.40 (2H, m, 2 × CH=), 3.80 (3H, s, N*Me*), 3.50 (4H, d, 2 × CH_2) and 1.85 (12H, s, 2 × CMe_2). ^{13}C NMR ($CDCl_3$, 22.5 MHz): δ (ppm) = 181.6 (C-9), 161.8, 160.3 (C-1, C-3), 145.7, 145.6 (C-4a, C-5a), 135.1, 134.7 (2 × **C***Me*$_2$), 133.7 (C-7), 126.2 (C-8), 123.3 (2 × CH=), 121.9 (C-8a), 121.3 (C-7), 116.3 (C-5), 107.8, 107.2 (C-4, C-9a), 104.3 (C-2), 44.2 (N*Me*), 27.4 (CH_2 at C-4), 25.8 (2 × =C*Me*), 21.7 (CH_2 at C-2), 18.2, 18.0 (2 × =C*Me*). MS: *m*/e (%) = 377.1969 (M^+, 100; $C_{24}H_{27}NO_3$ requires 377.1994), 362 (8), 334 (51), 322 (64), 306 (29), 278 (39), 266 (69), 254 (21), 252 (15). Neutralisation of the aqueous layer and extraction with ethyl acetate gave a fraction which on chromatography on silica and elution with methylene chloride-methanol (98 : 2) and then preparative tlc on silica using the same solvent furnished first:

1,3-Dihydroxy-10-methyl-2-(3-methylbut-2-enyl)-9(10H)-acridinone (**8**) (17 mg), m.p. 242–244 °C (yellow needles from methylene chloride). IR (KBr): 3450, 1630 (C=O). ^{1}H NMR (*d_6-DMSO*, 360 MHz): δ (ppm) = 15.07 (1H, s, 1-OH), 8.28 (1H, dd, J = 1.3, 8.5 Hz; 8-H), 7.78 (2H, m, 5-H, 6-H), 7.30 (1H, m, 7-H), 6.47 (1H, s, 4-H), 5.21 (1H, t, J = 7 Hz; CH=), 3.75 (3H, s, N*Me*), 3.24 (2H, d, J = 7Hz; CH_2) and 1.75, 1.62 (6H, 2 × s, CMe_2). ^{13}C NMR (*d_6-DMSO*, 90 MHz): δ (ppm) = 179.3 (C-9), 162.8, 161.6 (C-1, C-3), 142.6, 141.8 (C-4a, C-5a), 134.0 (C-6), 130.2 (**C***Me*$_2$), 125.7 (C-8), 122.8 (CH=), 121.1 (C-7), 119.9 (C-8a), 115.6 (C-5), 107.7 (C-9a), 103.7 (C-2), 90.4 (C-4), 33.8 (N*Me*), 25.5 (C*Me*), 21.0 (CH_2) and 17.7 (C*Me*). MS: *m*/e (%) = 309.1362 (M^+, 100; $C_{19}H_{19}NO_3$ requires 309.1365), 294 (36), 292 (18), 266 (100), 255 (20), 254 (100), 241 (22) and then:

1,3-Dihydroxy-10-methyl-4-(3-methylbut-2-enyl)-9-(10H)-acridinone (**2**) (glycocitrine-II) (29.5 mg), m.p. 169–170 °C (orange prisms from methylene chloride–light petroleum) Lit. [4], 168–169 °C. IR (film): 3400, 1610 (C=O). ^{1}H NMR ($CDCl_3$-*d_6-Me_2CO*, 60 MHz): δ (ppm) = 14.7 (1H, s, 1-OH),

8.34 (1H, d, J = 8 Hz; 8-H), 7.9–7.1 (3H, m, 5-H, 6-H and 7-H), 6.38 (1H, s, 2-H), 5.47 (1H, m, CH=), 3.90 (3H, s, N*Me*), 3.52 (2H, d, J = 7 Hz; CH_2) and 1.77 (6H, s, C*Me*$_2$). ^{13}C NMR ($CDCl_3$-d_6-*Me*$_2$CO, 22.5 MHz): δ (ppm) = 181.6 (C-9), 163.9, 163.3 (C-1, C-3), 147.5, 146.1 (C-4a, C-5a), 133.8 (C-6), 132.1 (**C***Me*$_2$), 126.0 (C-8), 124.5 (CH=), 121.5 (C-7, C-8a), 116.6 (C-5), 106.7, 105.5 (C-4, C-9a), 97.3 (C-2), 43.9 (N*Me*), 27.1 (CH_2), 25.7 (C*Me*) and 18.1 (C*Me*). MS: *m*/e (%) = 309.1366 (M^+, 72; $C_{19}H_{19}NO_3$ requires 309.1365), 294 (50), 266 (16), 264 (16), 254 (26), 252 (52), 241 (100).

(*b*) Reaction of acridone (**1**) (1.0 mmol) with 1-bromo-3-methylbut-2-ene (800 mg, 5.3 mmol) for 5 days as described in (*a*) above, chromatography of the product on silica (elution with hexane-ether, 10:3), and then preparative tlc on silica with toluene gave:

2,3,4,11-Tetrahydro-5-hydroxy-2,2,11-trimethyl-12-(3-methylbut-2-enyl)-6H-pyrano[3,2-b]acridin-6-one (**12**) (10 mg), m.p. 152–154 °C (orange prisms from hexane), R_f 0.33 (hexane-ether, 10:3), 0.34 (*PhMe*). IR (film): 3400, 1620 (C = O). ^{1}H NMR ($CDCl_3$, 360 MHz): δ (ppm) = 14.92 (1H, s, 5-OH), 8.33 (1H, dd, J = 7.5 Hz, 1.5 Hz; 7-H), 7.65 (1H, m, 9-H), 7.55 (1H, d, J = 8 Hz; 10-H), 7.22 (1H, m, 8-H), 5.30 (1H, t, J = 6 Hz; CH=), 3.80 (3H, s, N*Me*), 3.40 (2H, d, J = 6 Hz; CH_2 at C-12), 2.77 (2H, t, J = 7 Hz; 4-H_2), 1.84 (2H, t, J = 7 Hz; 3-H_2), 1.75, 1.72 (6H, 2 × s, C*Me*$_2$), and 1.37 (6H, s, 2-*Me*$_2$). ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) = 181.5 (C-6), 160.2, 160.1 (C-5, C-12a), 146.0, 144.9 (C-10a, C-11a), 133.4 (C-9), 130.8 (= **C***Me*$_2$), 126.0 (C-7), 124.6 (CH=), 121.5 (C-6a), 120.9 (C-8), 116.1 (C-10), 106.2, 106.1 (C-5a, C-12), 102.6 (C-4a), 75.8 (C-2), 43.8 (N*Me*), 31.8 (C-4), 27.0 (**C**H_2CH=), 26.8 (2-*Me*$_2$), 25.6 (= C*Me*), 18.0 (= C*Me*) and 16.2 (C-3). MS: *m*/e (%) = 377.1985 (M^+, 100; $C_{24}H_{27}NO_3$ requires 377.1991), 322 (14), 309 (36), 306 (25), 378 (37), 266 (25) and then:

2,3,4,11-Tetrahydro-5-hydroxy-2,2,11-trimethyl-4,12-bis(3-methylbut-2-enyl)-6H-pyrano[3,2-b]acridin-6-one (**13**) (22.1 mg) as a yellow oil, R_f 0.37 (hexane-ether, 10:3), 0.48 (*PhMe*). IR (film): 3400, 1615 (C=O). ^{1}H NMR ($CDCl_3$, 360 MHz): δ (ppm) = 14.97 (1H, s, 5-OH), 8.33 (1H, dd, J = 8.5 Hz, 1.5 Hz; 7-H), 7.65 (1H, m, 9-H), 7.35 (1H, d, J = 8.5 Hz; 10-H), 7.21 (1H, m, 8-H), 5.30 (1H, t, J = 6 Hz; CH_2CH= at C-12), 5.22 (1H, t, J = 10 Hz; CH_2CH= at C-4), 3.80 (3H, s, N*Me*), 3.40 (2H, m, CH_2 at C-12), 2.93 (1H, m, 4-H), 2.29 (2H, dd, J = 17 Hz, 10 Hz; CH_2 at C-4), 1.81 (2H, m, 3-H_2), 1.75 (3H, s, = C*Me*), 1.72 (6H, s, 2 × C*Me*), 1.61 (3H, s, = C*Me*) and 1.47, 1.21 (6H, 2 × s, 2-*Me*$_2$). ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) = 181.5 (C-6), 160.0 (C-5, C-12a), 146.0, 144.8 (C-10a, C-11a), 133.4 (C-9), 133.0, 130.8 (2 × = **C***Me*$_2$), 125.9 (C-7), 124.7 (CH_2**C**H= at C-12), 122.1 (CH_2**C**H= at C-4), 121.4 (C-6a), 120.9 (C-8), 116.1 (C-10), 106.2, 105.8 (C-5a, C-12), 103.3 (C-4a), 79.2 (C-2), 43.8 (N*Me*), 40.8 (C-4), 29.5 (C-3), 27.6 (2-*Me*), 27.0 (CH_2 at C-12), 25.7, 25.6 (2 × = C*Me*), 21.9 (CH_2 at C-4), 20.9 (2-*Me*) and 18.0, 17.7 (2 × = C*Me*). MS: *m*/e (%) = 445.2633 (M^+, 100; $C_{29}H_{35}NO_3$ requires 445.2617), 430 (131), 376 (15), 362 (15), 322 (28), 306 (32), 278 (50), 266 (48), 252 (16).

Reaction of Glycocitrine-II (**2**) *with m-Chloroperbenzoic Acid*

A solution of glycocitrine-II (50 mg) and *m*-chloroperbenzoic acid (50 mg) in methylene chloride (15 ml) was kept at ambient temperature for four days, washed with aqueous sodium carbonate and evaporated. Preparative tlc of the residue on silica with methylene chloride-ethyl acetate (100:8) gave:

1,2,3,12-Tetrahydro-2,6-dihydroxy-3,3,12-trimethyl-7H-pyrano[2,3-c]acridin-7-one (**6**) (8.8 mg), m.p. 238–239 °C (yellow prisms from methylene chloride-light petroleum), R_f 0.42 (methylene chloride-ethyl acetate 7:3). IR (KBr): 3400, 1610 (C=O). ^{1}H NMR (*d*$_6$-*Me*$_2$CO, 360 MHz): δ (ppm) = 14.40 (1H, s, 6-OH), 8.26 (1H, d, J = 8 Hz; 8-H, 7.80 (1H, dd, 10-H), 7.68 (1H, d, J = 9 Hz; 11-H), 7.32 (1H, dd, 9H), 6.07 (1H, s, 5-H), 4.40 (1H, d, J = 5 Hz; 2-OH), 3.99 (3H, s, N*Me*), 3.74 (1H, m, **C**H-OH), 3.18, 3.01 (2H, 2 × dd, J = 5, 16 Hz; CH_2) and 1.45, 1.40 (6H, 2 × s, C*Me*$_2$). ^{13}C NMR (*d*$_6$-*Me*$_2$CO, 90.56 MHz): δ (ppm) = 181.6 (C-7), 163.0 (C-4a), 161.4 (C-6), 148.6 (C-12a), 146.8

(C-11a), 134.1 (C-10), 125.7 (C-8), 122.3 (C-7a), 121.9 (C-9), 117.6 (C-11), 107.5 (C-6a), 98.6 (C-12a), 98.0 (C-5), 78.0 (C-3), 69.3 (C-2), 43.6 (N*Me*), 31.9 (C-1) and 25.6, 20.2 (C*Me*$_2$). MS: *m/e* (%) = 325.1313 (M^+, 100; $C_{19}H_{19}NO_4$ requires 325.1314), 255 (11), 254 (59), 242 (13), 241 (70), 226 (17), 225 (84), 212 (13) and then:

1,11-Dihydro-5-hydroxy-2-(1-hydroxy-1-methylethyl)-11-methyl-furo[2,3-c]acridin-6(2H)-one (**5**) (3.2 mg), m.p. 238–240 °C (yellow prisms from methylene chloride), R_f 0.31 (methylene chloride-ethyl acetate, 7:3). IR (KBr): 3400, 1625 (C=O). ^{1}H NMR (d_6-*Me*$_2$CO, 360 MHz): δ (ppm) = 15.30 (1H, s, 5-OH), 8.32 (1H, d, J = 8 Hz; 7-H), 7.79 (1H, dd, 9-H), 7.67 (1H, d, J = 9 Hz; 10-H), 7.32 (1H, dd, 8-H), 6.11 (1H, s, 4-H), 4.71 (1H, t, J = 9 Hz; 2-H), 4.10 (3H, s, N*Me*), 3.82 (1H, s, C*Me*$_2$**OH**), 3.77 (2H, d, J = 9 Hz; 1-H) and 1.30, 1.27 (6H, 2 × s, C*Me*$_2$). MS: *m/e* (%) = 325.1295 (M^+, 66; $C_{19}H_{19}NO_4$ requires 325.1314), 392 (38), 267 (19), 266 (100), 265 (20).

Conversion of the Pyranoacridinone **6** *into Noracronycine* (**10**)

A solution of the pyranoacridinone **6** (5 mg) in concentrated sulphuric acid (0.5 ml) was kept at 0 °C for 30 min, added to water, neutralised with sodium carbonate and extracted with ethyl acetate to give noracronycine (**10**), which was shown by tlc to be identical with an authentic sample, R_f 0.78 (methylene chloride-ethyl acetate, 7:3) and 0.70 (toluene-ethyl acetate-formic acid, 5:4:1).

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