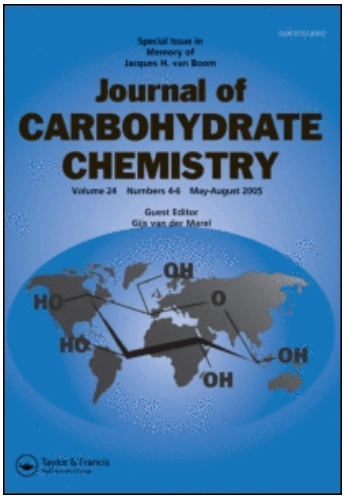

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NEW ANELLATION REACTIONS OF PYRANOSE DERIVATIVES*

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ABSTRACT

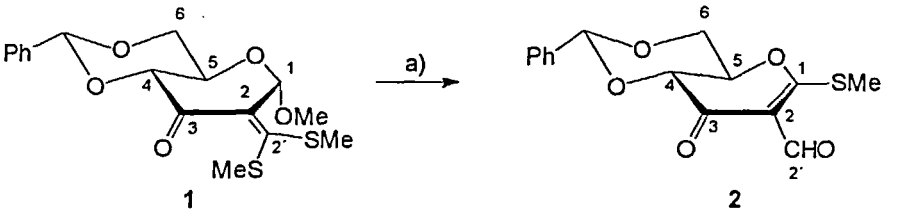
The push-pull-activated pyranosidulose **2** reacted with acetylacetone and methyl acetoacetate to afford the anellated pyranosides **3** and **4**, respectively. Treatment of the ulose **2** with acetoacetamide and malononitrile, respectively, furnished the fused pyridones **5** and **6**. Benzo-anellated pyranosides **7** were obtained by reaction of pyranosidulose **2** with dialkyl 3-oxoglutarates.

INTRODUCTION

There are different biologically active compounds in the nature containing a pyranose as an anellated ring.[1] Pharmacological studies have shown the varied antibiotic and cancerostatic effects of such substances. Representatives of these substances are the herbicidins and analogues. Therefore, the synthesis of similar systems with potentially biological activity has attracted increasing attention.[1,2]

Recently, we described the synthesis of methyl 4,6-*O*-benzylidene-2-deoxy-2-formyl-1-thio-D-*erythro*-hex-1-enopyranosid-3-ulose **2**[3] by an unusual intramolecular rearrangement of methyl 4,6-*O*-benzylidene-2-[bis(methylthio)methylene]-2-deoxy-α-D-*erythro*-hexopyranosid-3-ulose **1** (Scheme 1).[4]

* Dedicated to Professor Dr. *Günther Oehme* on the occasion of his 60th birthday.



1 2

Reagents: a) THF/H_2O (H_3O^+), 55 °C

Scheme 1

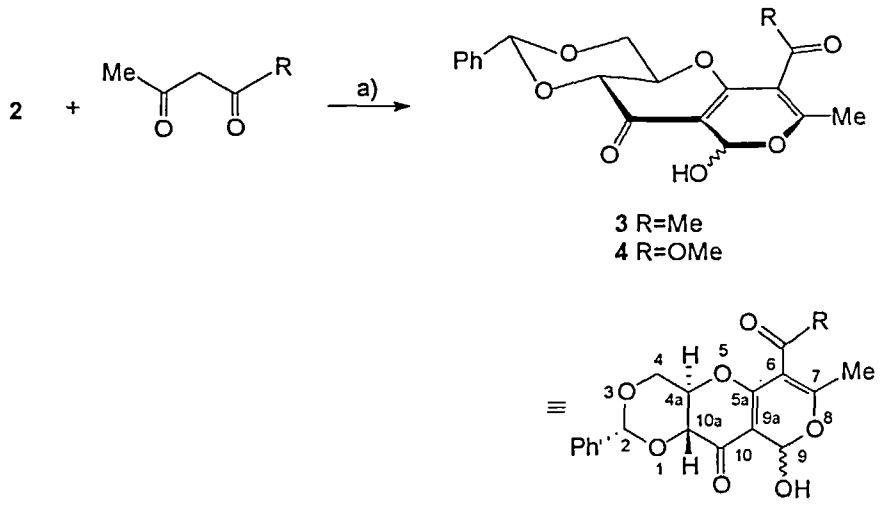
The pyranosidulose **2** contains a structural unit which corresponds to a push-pull-activated α-oxoketene dithioacetal like compound **1** and, therefore, it can be regarded as an α,α'-dioxoketene *O,S*-acetal. Nucleophilic substitution reactions at the donor substituted carbon atom (C-1) and the carbonyl atom (C-2') are typical for such systems because of their electronic properties.[5] Treatment of push-pull-activated sugar derivatives with dinucleophilic reagents is expected to result in new bicyclic compounds.[6]

In this paper we want to report substitution reactions of the ulopyranose **2** with *C*-nucleophiles and *C,C'*-dinucleophiles resulting in heterocyclic and carbocyclic anellated uloses.

RESULTS AND DISCUSSION

In situ generated carbanions of 1,3-dicarbonyl compounds are useful reagents for cyclization reactions.[7] Treatment of ulopyranose **2** with acetylacetone and potassium carbonate in *N,N'*-dimethylformamide resulted in the formation of a mixture of the diastereomers **3a, b** (Scheme 2). In the ^{13}C NMR spectrum of **3a, b** doubled peaks for all carbon atoms were observed.

The formation of compounds **3**, certainly, was caused by substitution of the methylthio group through the anion of acetylacetone. Enolization of a carbonyl group of the acetylacetone unit followed by an attack on C-2' of ulopyranose **2** led to the anellated pyranosides **3**. In the ^1H NMR spectrum of **3** the signals for H-9 of the isomers were found at δ 6.19 and δ 6.28 ppm, respectively; the signal at δ 7.73 ppm, which



Reagents: a) K_2CO_3, 18-C-6, DMF

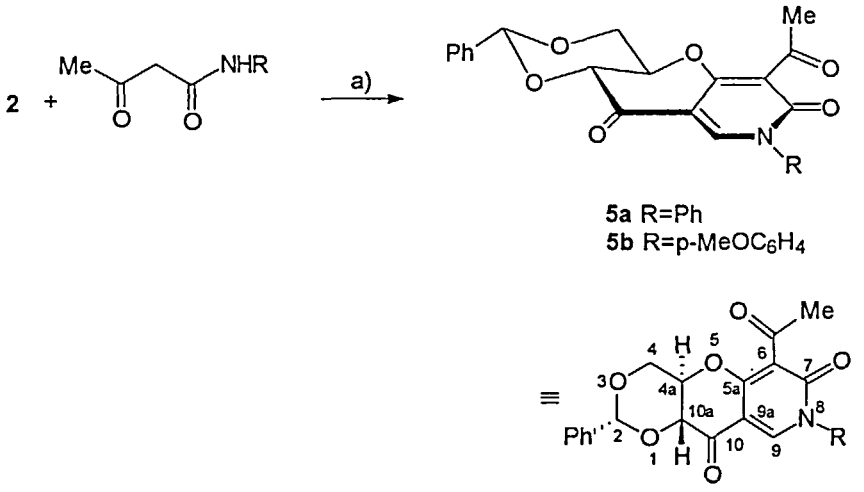
Scheme 2

disappeared by treatment with D_2O, was assigned to the OH-proton. The ratio of diastereomers is 3:1.

Analogous structures and ratio of stereoisomers were found for the compounds **4a, b** resulting from the reaction of ulopyranose **2** with methyl acetoacetate (Scheme 2). The addition of crown ether to the reaction mixture accelerated the reaction. The configuration at C-9 could not be determined since a NOESY spectrum of compounds **3** did not give reliable information about it.

Treatment of **2** with acetoacetamides provided the substituted 1,3-dioxino-[4′,5′:5,6]pyrano[3,2-c]pyridine-7,10-diones **5a** and **5b** (Scheme 3). Therefore, a subsequent nucleophilic attack of the amide nitrogen atom on C-2' should have taken place to realize the condensation reaction. In the NOESY spectrum of compound **5a** correlations between H-9 and the ortho-protons of phenyl at N-8 were found, thus excluding an alternative nucleophilic attack of the amide nitrogen on C-1 of ulose **2**.

The reaction of the ulopyranose **2** with malononitrile or cyanoacetamide in the presence of potassium carbonate in *N,N'*-dimethylformamide provided the pyridone **6**, which is another type of pyridone as **5**. Compound **6** was isolated while reprocessing as a monohydrate. Generally, the two tautomeric structures **6a** and **6b** can be formulated



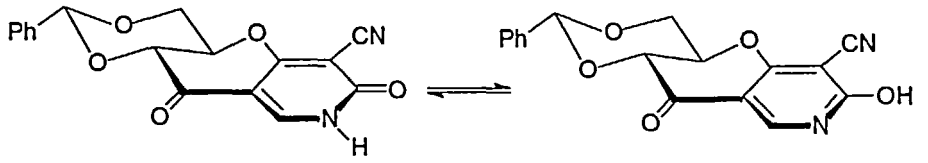
Reagents: a) K_2CO_3, DMF

Scheme 3

(Scheme 4). The NMR spectra showed the existence of only one compound in solution. The ^1H NMR spectrum displayed a signal at δ 13 ppm which disappeared by treatment with D_2O. In the ^{13}C NMR spectrum the C-9 signal was found at δ 145.1 ppm which is comparable with that for compound **5a** (δ 148.1 ppm). In addition, the IR spectrum showed typical absorptions for the free and associated NH group of lactams at 3415 and 3558 cm^{-1}.[8] The carbonyl band of the lactam at $\tilde{\nu}$ 1657.5 cm^{-1} was found in the same range as for the amide groups of the compounds **5a** and **5b**. These data show the amide structure **6a** to be favored.

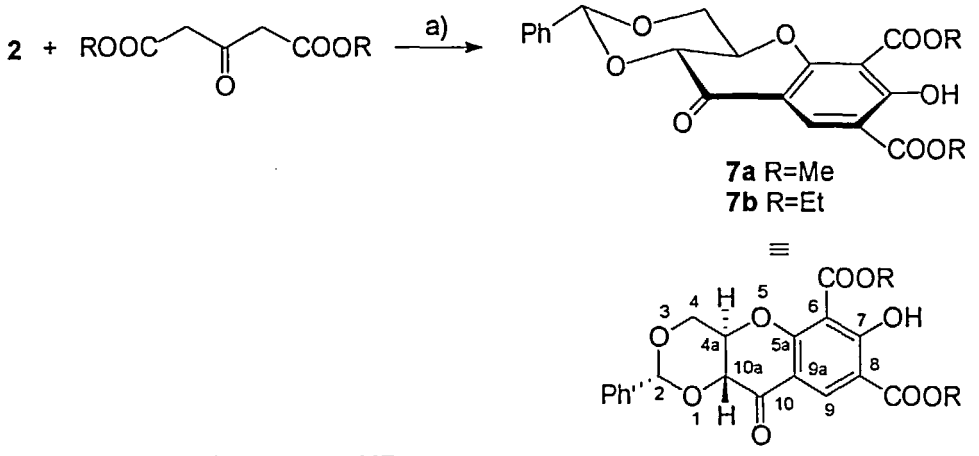
Benzo-anellated pyranoses **7a,b** were prepared by similar reactions of **2** with dialkyl 3-oxoglutarates. They can be regarded as *C,C'*-dinucleophiles (Scheme 5).

A COLOC spectrum of **7b** did not allow the assignment of all signals for the quarternary C-atoms. However, a ^{13}C-labeling of position 1 in the ulopyranose **2**[9] should give C-C coupled signals of the adjacent C-atoms. Treatment of the labeled compound **2** with diethyl 3-oxoglutarate provided compound **7b** with the ^{13}C-labeling in position 5a. The intense carbon resonance for C-5a was found in the ^{13}C NMR spectrum at δ 161.2 ppm. Thus, the signal at δ 164.5 ppm was assigned to C-7. But, the spectrum did not



6a **6b**

Scheme 4



Reagents: a) K_2CO_3, $N(Et)_3$, DMF

Scheme 5

show any coupling between C-5a and C-6 or C-9a making a correct assignment of the resonances in the range 108.9–113.1 ppm impossible. The signal for the OH proton was observed at about δ 12 ppm. The down-field shift characterized the proton as involved in an intramolecular hydrogen bond to the adjacent alkoxycarbonyl groups.

EXPERIMENTAL

General methods. Melting points were determined with a Boëtius melting point apparatus and were corrected. Specific rotations were measured using a Polar LμP (IBZ Messtechnik). Infrared spectra were recorded on a Nicolet 205 FT-IR spectrometer. ^1H NMR (250.1 MHz and 300.1 MHz, respectively) and ^{13}C NMR (62.9 MHz and 75.5

MHz, respectively) were obtained with Bruker instruments AC 250 and ARX 300, respectively. ^1H and ^{13}C chemical shifts (δ) are given in ppm. The calibration of spectra was made by means of solvent peaks ($CDCl_3$: $\delta^1H = 7.25$, $\delta^{13}C = 77.0$; DMSO-d_6: $\delta^1H = 2.50$, $\delta^{13}C = 39.7$). Mass spectra were recorded on an AMD 402/3 spectrometer. For column chromatography Merck Silica gel 60 (63-200 mesh) was used. TLC was performed on silica gel 60 GF_{254} (Merck) and visualized with UV light (λ = 254 nm) and/or by heating after alcoholic sulphuric acid treatment. Elemental analyses were carried out with a Leco CHNS-932.

[2*R*-(2α,4aα,9α/β,10aβ]-6-Acetyl-4,4a,10,10a-tetrahydro-9-hydroxy-7-methyl-2-phenyl-9H-pyrano[3′,4′:5,6]pyrano[3,2-d][1,3]dioxin-10-one (3a,b). A mixture of **2** (306 mg, 1.0 mmol) and acetylacetone (110 mg, 1.1 mmol) in 10 mL anhydrous DMF was treated with K_2CO_3 (200 mg) and stirred at room temperature for 18 h. Then the mixture was diluted with cold water (100 mL) and saturated aqueous $NaHSO_4$ solution (5 mL), and extracted with chloroform (4 × 25 mL). The combined organic layers were washed with water (4 × 20 mL), dried with Na_2SO_4, and the solvent was evaporated. The crude solid was recrystallized from acetone/diethyl ether to give 82 mg of **3a,b** (23%) as a 3:1 diastereomeric mixture, colorless needles: mp 180-183 °C (dec.); R_f = 0.10 (toluene/ethyl acetate, 4:1); ^1H NMR (250.1 MHz, DMSO-d_6) δ 2.19 (s, 3H, 7-CH_3), 2.36 (s, 3H, CH_3CO), 4.05-4.20 (m, 1H, H-4ax), 4.42-4.83 (m, 3H, H-4eq, H-4a, H-10a), 5.74 (s, 1H, H-2), 6.19 (s, 0.75H, H-9, **3a**), 6.28 (s, 0.25H, H-9, **3b**), 7.36-7.50 (m, 5H, Ph), 7.73 (bs, 1H, OH). ^{13}C NMR (75.5 MHz, DMSO-d_6) δ 20.4 (7-CH_3), 30.8 (CH_3CO, **3b**), 32.4 (CH_3CO, **3a**), 66.9 (C-4), 72.2 (C-4a, **3a**), 73.5 (C-4a, **3b**), 75.5 (C-10a, **3b**), 76.1 (C-10a, **3a**), 90.6 (C-9, **3b**), 91.1 (C-9, **3a**), 100.2 (C-9a), 101.0 (C-2), 110.2 (C-6, **3b**), 110.6 (C-6, **3a**), 126.5 (o-Ph), 128.3 (m-Ph), 129.4 (p-Ph), 137.1 (i-Ph), 161.0 (C-5a, **3b**), 161.7 (C-5a, **3a**), 168.6 (C-7, **3b**), 169.5 (C-7, **3a**), 184.7 (C-10, **3a**), 185.2 (C-10, **3b**), 196.4 (CH_3CO, **3b**), 196.8 (CH_3CO, **3a**). MS (CI, isobutane): *m/z* 359 $(M+H)^+$.

Methyl [2*R*-(2α,4aα,9α/β,10aβ]-4,4a,10,10a-Tetrahydro-9-hydroxy-7-methyl-10-oxo-2-phenyl-9H-pyrano[3′,4′: 5,6]pyrano[3,2-d] [1,3]dioxine-6-carboxylate (4a,b). K_2CO_3 (200 mg) and 18-crown-6 (100 mg) were added to a mixture of **2** (306 mg, 1.0 mmol) and methyl acetoacetate (128 mg, 1.1 mmol) in 10 mL anhydrous

DMF. The mixture was stirred at room temperature for 7 h and the products were isolated as described above for **3a,b**. Recrystallization from acetone/diethyl ether gave 150 mg (40%) of **4a,b** as a 3:1 diastereomeric mixture, colorless needles: mp 104-107 °C (dec.); R_f = 0.11 (toluene/acetone, 5:1); ^{1}H NMR (250.1 MHz, DMSO-d_6) δ 2.22 (s, 3H, 7-CH_3), 3.75 (s, 3H, $COOCH_3$), 4.00-4.08 (m, 1H, H-4ax), 4.30-4.80 (m, 3H, H-4eq, H-4a, H-10a), 5.75 (s, 1H, H-2), 6.21 (s, 0.75H, H-9, **4a**), 6.30 (s, 0.25H, H-9, **4b**), 7.31-7.50 (m, 5H, Ph), 7.64 (bs, 0.25H, OH, **4b**), 7.74 (bs, 0.75H, OH, **4a**). ^{13}C NMR (62.9 MHz, DMSO-d_6) δ 20.4 (7-CH_3), 52.2 ($COOCH_3$), 67.0 (C-4), 72.3 (C-4a, **4a**), 73.5 (C-4a, **4b**), 75.6 (C-10a, **4b**), 76.1 (C-10a, **4a**), 90.8 (C-9, **4b**), 91.0 (C-9, **4a**), 100.1 (C-9a), 101.0 (C-2), 102.6 (C-6), 126.5 (o-Ph), 128.3 (m-Ph), 129.4 (p-Ph), 137.1 (i-Ph), 160.7 (C-5a, **4b**), 161.3 (C-5a, **4a**), 164.4 ($COOCH_3$), 168.5 (C-7, **4b**), 169.1 (C-7, **4a**), 184.8 (C-10, **4a**), 185.2 (C-10, **4b**). MS (CI, isobutane): *m/z* 375 $(M+H)^+$.

[2*R*-(2α,4aα,10aβ)]-6-Acetyl-4,4a,7,8,10,10a-hexahydro-2,8-diphenyl-1,3-dioxino[4′,5′:5,6]pyrano[3,2-c]pyridine-7,10-dione (5a). **2** (306 mg, 1.0 mmol) and acetoacetanilide (209 mg, 1.1 mmol) were dissolved in anhydrous DMF (10 mL). After addition of K_2CO_3 (200 mg) the reaction mixture was stirred at room temperature for 22 h. Then cold water (100 mL) and saturated aqueous $NaHSO_4$ solution (5 mL) were added and the mixture was stirred for further 10 min. The colorless precipitate was collected, washed with water (2×15 mL) and recrystallized from acetone to give **5a** as colorless needles (102 mg, 24%): mp >266 °C (dec.); R_f = 0.34 (toluene/acetone, 5:1); $[\alpha]_D^{20.5}$ +175.0° (*c* 1.0, chloroform); IR (KBr): $\tilde{\nu}$ = 1712.2 cm^{-1} (C=O), 1693.4 (CH_3C=O), 1661.3 (N–C=O). ^{1}H NMR (250.1 MHz, $CDCl_3$) δ 2.55 (s, 3H, CH_3CO), 4.11 (dd, $J_{4ax,4eq}$= 10.2 Hz, $J_{4ax,4a}$= 9.3 Hz, 1H, H-4ax), 4.47-4.65 (m, 3H, H-4eq, H-4a, H-10a), 5.65 (s, 1H, H-2), 7.32-7.57 (m, 10 H, 2,8-Ph), 8.38 (s, 1H, H-9). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 31.5 (CH_3CO), 68.1 (C-4), 71.4 (C-4a), 78.0 (C-10a), 102.4 (C-2), 106.3 (C-9a), 114.8 (C-6), 126.3, 126.4, 128.4, 129.6, 129.7, 135.9, 138.8, 143.8 (2-Ph, 8-Ph), 148.1 (C-9), 160.0 (C-5a), 162.4 (C-7), 184.0 (C-10), 197.5 (CH_3CO). MS (70 eV): *m/z* 417 $(M)^+$.

Anal. Calcd for $C_{24}H_{19}NO_6$ (417.42): C, 69.06 I, 4.59; N, 3.36; Found: C, 69.05; H, 4.50; N, 3.44.

[2*R*-(2α,4aα,10aβ)]-6-Acetyl-4,4a,7,8,10,10a-hexahydro-8-(p-methoxyphenyl)-2-phenyl-1,3-dioxino[4′,5′:5,6]pyrano[3,2-c]pyridine-7,10-dione (5b). K_2CO_3 (200 mg) was added to a solution of **2** (306 mg, 1.0 mmol) and acetoacetanisidide (244 mg, 1.1 mmol) in anhydrous DMF (10 mL). The mixture was stirred at room temperature for 7 h and the product was isolated as described for **5a**. Recrystallization from chloroform gave **5b** as colorless needles (127 mg, 27%): mp >283 °C (dec.); R_f = 0.31 (toluene/acetone, 5:1); $[\alpha]_D^{20.5}$ +127.0° (*c* 1.0, chloroform); IR (KBr): $\tilde{\nu}$ = 1715.9 cm^{-1} (C=O), 1693.2 (CH_3C=O), 1663.1 (N–C=O). ^1H NMR (250.1 MHz, $CDCl_3$) δ 2.55 (s, 3H, CH_3CO), 3.85 (s, 3H, OCH_3), 4.10 (dd, $J_{4ax,4eq}$= 11.0 Hz, $J_{4ax,4a}$= 9.5 Hz, 1H, H-4ax), 4.46-4.66 (m, 3H, H-4eq, H-4a, H-10a), 5.65 (s, 1H, H-2), 6.97-7.03 (m, 2 H, 8-C_6H_4), 7.23-7.29 (m, 2 H, 8-C_6H_4), 7.35-7.55 (m, 5H, 2-Ph), 8.37 (s, 1H, H-9). MS (CI, isobutane): *m/z* 448 $(M+H)^+$.

Anal. Calcd for $C_{25}H_{21}NO_7$ (447.45): C, 67.11; H, 4.73; N, 3.13; Found: C, 66.70; H, 4.76; N, 3.16.

[2*R*-(2α,4aα,10aβ)] -4,4a,7,8,10,10a-Hexahydro-7,10-dioxo-2-phenyl-1,3-dioxino-[4′,5′:5,6]pyrano[3,2-c]pyridine-6-carbonitrile (6). *Method A:* **2** (306 mg, 1.0 mmol) and malononitrile (73 mg, 1.1 mmol) were dissolved in anhydrous DMF (10 mL) and treated with K_2CO_3 (200 mg). The reaction mixture was stirred at 0 °C (3–4 h) until the starting material had been used up as indicated by TLC (toluene/acetone, 1:1). After addition of cold water (100 mL) the resulting precipitate was filtered off, washed with water (2×15 mL) and recrystallized from acetone to yield **6** as colorless plates (146 mg, 45%).

Method B: A mixture of **2** (306 mg, 1.0 mmol) and acetoacetamide (93 mg, 1.1 mmol) in 10 mL anhydrous DMF was treated with K_2CO_3 (200 mg) and 18-crown-6 (100 mg) and stirred at room temperature for 15 h. Then the mixture was diluted with cold water (100 mL) and a saturated aqueous $NaHSO_4$ solution (5 mL). The product **6** was isolated as described in method A. The crude solid was recrystallized from acetone to give colorless plates (50 mg, 15%): mp 240–242 °C (dec.); R_f = 0.49 (toluene/acetone, 1:1); $[\alpha]_D^{20.5}$ +117.5° (*c* 1.0, DMF); IR (KBr): $\tilde{\nu}$ 3415.2 cm^{-1}, 3558.4 (NH), 2231.1 (CN), 1725.7 (C=O), 1656.4 (HN–C=O). ^1H NMR (300.1 MHz, DMF-d_7) δ 4.29 (dd, $J_{4ax,4eq}$ = 10.2

Hz, $J_{4ax,4a}$ = 10.0 Hz, 1H, H-4ax), 4.68 (dd, $J_{4eq,4a}$ = 5.2 Hz, 1H, H-4eq), 4.94 (ddd, $J_{4a,10a}$ = 11.5 Hz, 1H, H-4a), 5.12 (d, 1H, H-10a), 5.93 (s, 1H, H-2), 7.43-7.50 (m, 3H, m-Ph, p-Ph), 7.54-7.60 (m, 2H, o-Ph), 8.54 (s, 1H, H-9), 13.00 (bs, 1H, NH). ^{13}C NMR (75.5 MHz, DMF-d_7) δ 67.9 (C-4), 72.9 (C-4a), 77.6 (C-10a), 86.8 (C-6), 102.0 (C-2), 106.6 (C-9a), 113.5, (CN), 126.9 (o-Ph), 128.8 (m-Ph), 129.9 (p-Ph), 137.8 (i-Ph), 145.1 (C-9), 161.9 (C-5a), 171.5 (C-7), 184.1 (C-10). MS (70 eV): *m/z* 324 $(M)^+$.

Anal. Calcd for $C_{17}H_{14}N_2O_6$ ($C_{17}H_{12}N_2O_5 + H_2O$, 342.25): C, 59.64; H, 4.12; N, 8.18; Found: C, 59.76; H, 4.15; N, 8.25.

Dimethyl [2*R*-(2α,4aα,10aβ)]-4,4a,10,10a-Tetrahydro-7-hydroxy-10-oxo-2-phenyl-1,3-dioxino[5,4-b]chromene-6,8-dicarboxylate (7a). **2** (306 mg, 1.0 mmol) and dimethyl 3-oxoglutarate (192 mg, 1.1 mmol) were dissolved in 10 mL anhydrous DMF and K_2CO_3 (200 mg) and a few drops of triethylamine were added. The suspension was stirred at room temperature for about 100 h. After diluting the mixture with cold water (100 mL) and a saturated aqueous $NaHSO_4$ solution (5 mL) the resulting product was filtered off, washed with water (2×15 mL) and recrystallized from methanol to yield **7a** as colorless needles (171 mg, 40%): mp 257–259 °C (dec.); R_f = 0.60 (toluene/acetone, 5:1); $[\alpha]_D^{20.5}$ +120.0° (*c* 1.0, chloroform); ^{1}H NMR (250.1 MHz, $CDCl_3$) δ 3.95, 3.98 (2 × s, 6H, 2 × OCH_3), 4.05–4.17 (m, 1H, H-4ax), 4.50–4.68 (m, 3H, H-4eq, H-4a, H-10a), 5.65 (s, 1H, H-2), 7.34-7.42 (m, 3H, m-Ph, p-Ph), 7.50–7.58 (m, 2H, o-Ph), 8.59 (s, 1H, H-9), 11.88 (bs, 1H, OH). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 52.8, 52.9 (2 × CH_3), 68.1 (C-4), 72.3 (C-4a), 78.1 (C-10a), 102.4 (C-2), 108.8, 111.5, 113.3 (C-6, C-8, C-9a), 126.4 (o-Ph), 128.4 (m-Ph), 129.5 (p-Ph), 132.9 (C-9), 136.0 (i-Ph), 161.5 (C-5a), 163.8, 169.4 (2 × COO), 164.5 (C-7), 185.1 (C-10). MS (CI, isobutane): *m/z* 415 $(M+H)^+$.

Anal. Calcd for $C_{21}H_{18}O_9$ (414.38): C, 60.87; H, 4.38; Found: C, 60.78; H, 4.41.

Diethyl [2*R*-(2α,4aα,10aβ)]-4,4a,10,10a-Tetrahydro-7-hydroxy-10-oxo-2-phenyl-1,3-dioxino[5,4-b]chromene-6,8-dicarboxylate (7b). To a mixture of **2** (306 mg, 1.0 mmol) and diethyl 3-oxoglutarate (222 mg, 1.1 mmol) in 10 mL anhydrous DMF K_2CO_3 (200 mg) and a few drops of triethylamine were added. The mixture was used to react as described above for **7a**. Recrystallization from ethanol furnished colorless

needles of **7b** (172 mg, 39%): mp 186-190 °C (dec.); R_f = 0.40 (toluene/ethylacetate, 11:2); $[\alpha]_D^{20.5}$ +104.9° (*c* 1.0, chloroform); ^{1}H NMR (250.1 MHz, $CDCl_3$) δ 1.38, 1.42 (2 × t, 6 H, J_{CH_3,CH_2} = 7.2 Hz, 2 × $COOCH_2CH_3$), 4.03-4.14 (m, 1H, H-4ax), 4.41, 4.43 (2 × q, 4H, 2 × $COOCH_2CH_3$), 4.48-4.60 (m, 2H, H-4eq, H-4a), 4.64 (d, 1H, $J_{10a,4a}$= 11.3 Hz, H-10a), 5.63 (s, 1H, H-2), 7.25-7.38 (m, 3H, m-Ph, p-Ph), 7.50-7.53 (m, 2 H, o-Ph), 8.55 (s, 1H, H-9), 11.96 (bs, 1H, OH). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.1, 14.1 (2 × CH_3), 61.9, 62.3 (2 × $COOCH_2$), 68.0 (C-4), 72.2 (C-4a), 78.1 (C-10a), 102.3 (C-2), 109.0, 111.9, 113.2 (C-6, C-8, C-9a), 126.4 (o-Ph), 128.3 (m-Ph), 129.4 (p-Ph), 132.6 (C-9), 136.1 (i-Ph), 161.3 (C-5a), 163.3, 169.0 (2 × $COOCH_2$), 164.6 (C-7), 185.1 (C-10). MS (CI, isobutane): *m/z* 443 $(M+H)^+$.

Anal. Calcd for $C_{23}H_{22}O_9$ (442.43): C, 62.44; H, 5.01; Found: C, 62.63; H, 4.95.

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