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Total Synthesis of (±)-Zearalanone[a]

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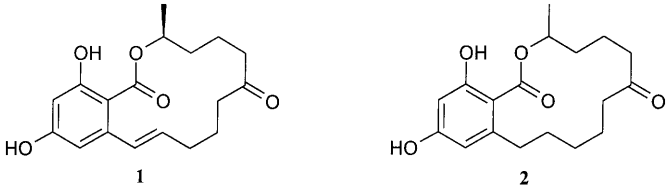
Summary. A new approach to the macrocyclic lactone zearalanone is described utilizing an alkenol and an arene trifluoromethanesulfonate as starting materials. The key step is a Pd(0)-catalyzed cross-coupling of the arene trifluoromethanesulfonate with a 9-alkyl-9-borabicyclo[3.3.1]nonane derived from the alkenol. The title compound is obtained by macrolactonization of a hydroxy acid under *Mitsunobu* conditions.

Keywords. Macrocyclic lactones; Hydroboration; Palladium-catalyzed cross-coupling; Zearalanone; Natural product.

Introduction

In 1962, *Stob et al*. [1] have isolated the β-resorcylic lactone zearalenone (**1**) from the mycelia of the fungus *Giberella zeae* (*Fusarium graminearum*). Later, numerous related macrocyclic lactones have been isolated from fungi. These lactones and their semisynthetic derivatives [2] have been shown to exhibit interesting estrogenic, anabolic, immunomodulating, and antimicrobial properties [3]. (*S*)-Zearalanone ((*S*)-**2**) has first been obtained by catalytic hydrogenation of natural **1** [2]. Later on, zearalanone (**2**) has been identified as a metabolite of the fungus *Fusarium reticulatum*. The absolute configuration of this constituent has not been determined [4]. (*R*)-Zearalanone ((*R*)-**2**) has been prepared in nine steps (2.36% overall yield) from natural (*S*)-**1** by cleavage of the lactone, inversion of the resulting chiral secondary alcohol, and relactonization [5]. An eleven-step synthesis of racemic zearalanone has been described by *Hurd et al*. [6]. Because of the poor availability



Scheme 1

[a] Dedicated to Professor Dr. *Eberhard Reimann*, Munich, on the occasion of his 65th birthday

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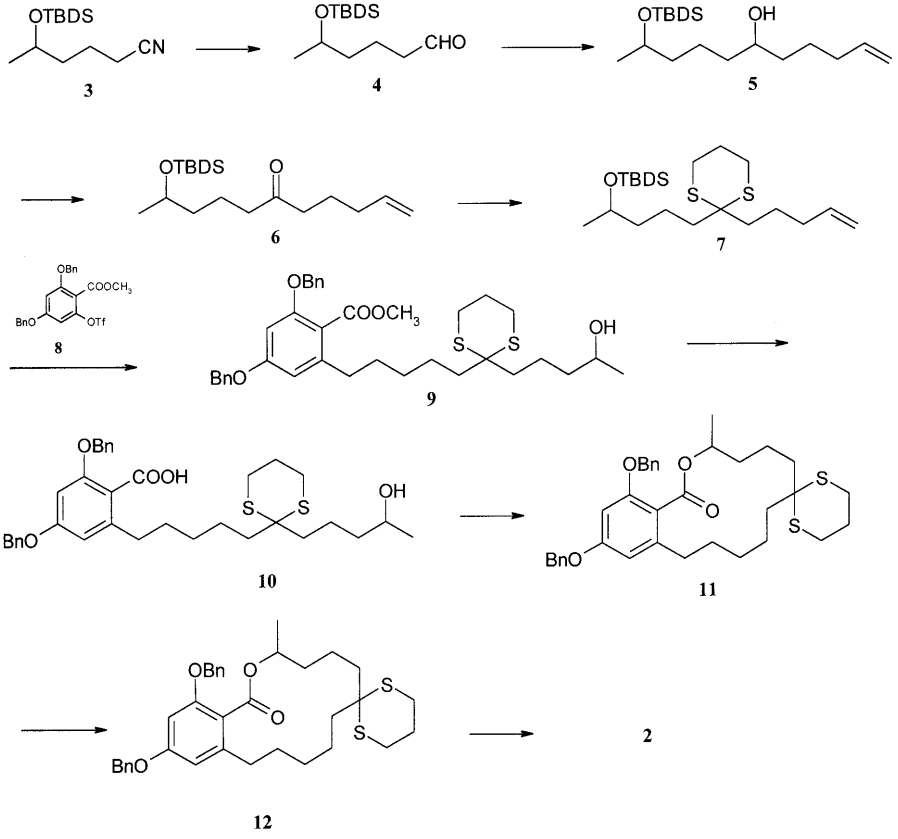
of **1** semisynthetic methods do not offer an efficient approach to zearalanone. Therefore, we worked out a new approach to (±)-zearalanone (**2**).

Results and Discussion

The known *TBDS* ether **3** [7] was prepared from commercially available 5-oxo-hexanenitrile by reduction with sodium borohydride to give racemic 5-hydroxy-hexanenitrile and subsequent protection of the secondary alcohol under standard conditions [7]. A first attempt to convert nitrile **3** to ketone **6** by reaction with pent-4-enyl magnesium bromide resulted in a very poor yield. Thus, **3** was reduced to aldehyde **4** with *DIBAH* [8]. This was reacted with pent-4-enyl magnesium bromide to alcohol **5** (racemic mixture of diastereomers), which in turn was oxidized to the racemic ketone **6** under *Swern* conditions [9]. For further transformations it was necessary to protect the keto group and to deprotect the hydroxy group of **6**. This could be accomplished in one single operation by dithioacetalization of the carbonyl group with 1,3-propanedithiol/BF_3 [10]. In the course of this transformation the *TBDS* protective group of the secondary alcohol was completely removed to give the hydroxy dithiane **7**.

Connection of the aliphatic part of **2** with the aromatic part was performed in a manner already successfully employed in the total syntheses of the related natural



Scheme 2

products lasiodiplodin [11], curvulin, lunularine, and lunularic acid [12]. In this method, a terminal olefin is converted to a terminal organoborane by addition of 9-borabicylononane [13]. The resulting B-alkyl-*BBN*-derivative can be subjected to a palladium-catalyzed cross-coupling reaction with an arene triflate to give the corresponding alkyl arene. For this purpose we needed the arene triflate **8** which was conveniently prepared from methyl 2,4,6-trihydroxybenzoate by O,O-dibenzylation and subsequent esterification with trifluoromethanesulfonic anhydride [14]. Thus, hydroxy olefine **7** was treated with two equivalents of *BBN*. One equivalent of the borane was consumed by reaction with the hydroxy group, whereas the second equivalent added to the olefine to give a terminal B-alkyl-*BBN*-derivative. This product was, without further purification, reacted with the triflate **8**, $Pd(PPh_3)_4$, and K_2CO_3 to give, after aqueous workup, the coupling product **9**.

Alkaline hydrolysis of ester **9** gave the hydroxy acid **10** which could be lactonized under *Mitsunobu* conditions [15] to the macrocyclic lactone **11**. Hydrolysis of the thioacetal group with HgO/BF_3 [16] gave O,O-dibenzylzearalanone (**12**). Finally, the two benzyl protective groups were removed by hydrogenolysis with palladium catalyst. The spectroscopic data of the product (±)-zearalanone (**2**) were in full accordance with those published for the natural product [3]. The overall yield of our total synthesis of **2** comprising eight steps starting from known aldehyde **4** was 1.2%.

Experimental

General

Elemental analyses were performed on a Carlo Erba CHNO Elemental Analyser. The obtained values agreed favourably with the calculated ones. FTIR spectra were recorded on a Pye-Unicam PU-9800 spectrometer. NMR spectra were recorded in $CDCl_3$ with *TMS* as internal standard on a Bruker AM 400 NMR spectrometer (400.1 MHz for ^1H, 100.5 MHz for ^{13}C). Mass spectra were recorded on a Finnigan MAT-8430 spectrometer. Flash column chromatography (FCC) was carried out on Merck Kieselgel 60 (230–400 mesh). Tetrahydrofuran (*THF*) was freshly distilled from sodium benzophenone ketyl prior to use.

(±)-Zearalanone (**2**; $C_{18}H_{24}O_5$)

To 0.08 g **12** (0.2 mmol) dissolved under N_2 in 1 cm^3 ethyl acetate and 10 cm^3 methanol, 20 mg Pd/C (10%) were added, and the mixture was hydrogenated at atmospheric pressure for 4 h. After filtration the organic solvent was evaporated, and the residue was purified by FCC (hexane:ethyl acetate = 4:1) to give 28 mg (55%) of **2** as a white solid.

M.p.: 211°C (Ref. [3a]: 208°C); MS (70 eV): m/z (%) = 320 (100, M^+), 302 (62), 251 (58), 163 (88), 125 (66), 112 (56); IR (KBr): ν = 3447, 1793, 1693, 1465, 1210, 1148, 849, 801, 727 cm^{-1}; ^1H NMR ($CDCl_3$, δ, 400 MHz): 1.34 (d, J = 6.2 Hz, 3H, CH_3), 1.35–2.10 (m, 16H, $8CH_2$), 5.20 (m, 1H, CH), 6.25 (d, J = 2.5 Hz, 1H, aromat. CH), 6.30 (d, J = 2.5 Hz, 1H, aromat. CH), 9.15 (s, 1H, OH), 12.01 (s, 1H, OH) ppm; ^{13}C NMR ($CDCl_3$, δ, 100 MHz): 23.19 (CH_3), 23.20 (CH_2), 23.24 (CH_2), 28.21 (CH_2), 32.32 (CH_2), 35.73 (CH_2), 36.70 (CH_2), 38.25 (CH_2), 44.38 (CH_2), 64.72 (CH), 101.97 (aromat. CH), 104.69 (quart. C), 111.94 (aromat. CH), 149.39 (quart. C), 163.41 (quart. C), 166.91 (quart. C), 172.50 (COO), 211.38 (C=O) ppm.

(±)-2-tert.-Butyldimethylsilyloxy-10-undecen-6-ol (**5**; $C_{17}H_{36}O_2Si$; mixture of diastereomers)

Magnesium (310 mg, 13 mmol) and one crystal of I_2 were suspended in 5 cm^3 anhydrous diethyl ether, and a solution of 0.97 g 1-bromopent-4-ene (6.5 mmol) in 5 cm^3 diethyl ether was added dropwise. The mixture was refluxed for 1 h. Then, 830 mg (3.8 mmol) **4** were dissolved in 5 cm^3 diethyl ether, and the solution of the *Grignard* reagent was added dropwise at room temperature. After 1 h the reaction was quenched with saturated NH_4Cl solution. The organic layer was separated, and the aqueous phase was extracted with diethyl ether (2 × 15 cm^3). The combined organic layers were dried over Na_2SO_4, and the solvent was evaporated. The residue was purified by FCC (hexane:ethyl acetate = 20:1) to give 615 mg (54%) of **5** as a colourless liquid.

MS (CI, NH_3): m/z (%) = 301 (100, $M^+ + 1$), 283 (4), 169 (20), 151 (6), 109 (4); IR (NaCl/film): ν = 3359, 3077, 2930, 2858, 1641, 1462, 1374, 1254, 1135, 910, 835, 774 cm^{-1}; ^{1}H NMR ($CDCl_3$, δ, 400 MHz): −0.04 (s, 6H, $2CH_3$), 0.84 (s, 9H, $3CH_3$), 1.07 (d, J = 6.1 Hz, 3H, CH_3), 1.20–1.54 (m, 10H, $5CH_2$), 2.02–2.04 (m, 2H, CH_2), 3.50–3.60 (m, 1H, CH), 3.74 (tq, J = 5.7 Hz, J = 5.9 Hz, 1H, CH), 4.90 (m, 1H, CH_2=), 4.96 (ddd, J = 1.8 Hz, J = 17.2 Hz, J = 1.8 Hz, 1H, CH_2=), 5.76 (ddd, J = 6.7 Hz, J = 10.3 Hz, J = 17.2 Hz, 1H, -CH=) ppm; ^{13}C NMR ($CDCl_3$, δ, 100 MHz): −4.8 (CH_3), −4.5 (CH_3), 18.06 (quart. C), 21.64 (CH_2), 21.8 (CH_2), 23.68 (CH_3), 23.74 (CH_3), 24.82 (CH_2), 24.82 (CH_2), 24.84 (CH_2), 25.84 ($3CH_3$), 33.67 (CH_2), 36.74 (CH_2), 37.41 (CH_2), 37.50 (CH_2), 39.55 (CH_2), 39.61 (CH_2), 68.45 (CH), 68.51 (CH), 71.62 (CH), 71.64 (CH), 114.49 (H_2C=), 138.65 (=CH-) ppm.

(±)-10-(tert.-Butyldimethylsilyloxy)-1-undecen-6-one (**6**; $C_{17}H_{34}O_2Si$)

A solution of 0.20 cm^3 oxalyl chloride (2.0 mmol) in 1 cm^3 CH_2Cl_2 was added dropwise to a solution of 0.40 cm^3 *DMSO* (5.6 mmol) in 1 cm^3 CH_2Cl_2 under N_2 at −70°C. After 30 min, a solution of 500 mg (1.7 mmol) **5** in 1 cm^3 CH_2Cl_2 was added, and the resulting mixture was stirred for 30 min. Then 1 cm^3 of triethylamine was added, and the reaction was allowed to warm up to room temperature. After addition of 5 cm^3 H_2O the organic layer was separated, the aqueous phase was extracted with CH_2Cl_2 (2 × 5 cm^3), and the combined organic layers were dried over Na_2SO_4. The solvent was evaporated, and the residue was purified by FCC (hexane:ethyl acetate = 20:1) to give 360 mg (72%) of **6** as a colourless oil.

MS (CI, NH_3): m/z (%) = 299 ($M^+ + 1$, 58), 265 (46), 202 (35), 197 (50), 167 (100); IR (NaCl/film): ν = 2953, 2929, 2904, 2857, 1715, 1641, 1471, 1462, 1410, 1374, 1254, 1215, 1137, 1005, 836, 775 cm^{-1}; ^{1}H NMR ($CDCl_3$, δ, 400 MHz): −0.04 (s, 6H, $2CH_3$), 0.88 (s, 9H, $3CH_3$), 1.12 (d, J = 6.0 Hz, 3H, CH_3), 1.21–1.66 (m, 6H, $3CH_2$), 2.00 (dt, J = 7.0 Hz, J = 6.9 Hz, 2H, CH_2), 2.34 (t, J = 7.4 Hz, 2H, CH_2), 2.35 (t, J = 7.4 Hz, 2H, CH_2), 3.74 (tq, J = 6.0 Hz, J = 6.0 Hz, 1H, CH), 4.93 (m, 2H, H_2C=), 5.71 (ddt, J = 6.9 Hz, J = 10.3 Hz, J = 17.0 Hz, 1H, =CH-) ppm; ^{13}C NMR ($CDCl_3$, δ, 100 MHz): −4.73 (CH_3), −4.38 (CH_3), 20.16 (CH_2), 18.10 (quart. C), 22.80 (CH_2), 23.75 (CH_3), 25.90 ($3CH_3$), 33.14 (CH_2), 39.13 (CH_2), 41.76 (CH_2), 42.90 (CH_2), 68.34 (CHOH), 115.17 (CH_2=), 137.98 (CH=), 210.79 (C=O) ppm.

(±)-2-(4-Hydroxypentyl)-2-(4-pentenyl)-1,3-dithiane (**7**; $C_{14}H_{26}OS_2$)

To 360 mg (1.5 mmol) **6** dissolved in 5 cm^3 MeOH at 0°C, 2 cm^3 $BF_3 \cdot Et_2O$ and 0.75 cm^3 (19 mmol) 1,3-propanedithiol were added. The mixture was allowed to warm up to room temperature with stirring, and the solvent was evaporated. The residue was purified by FCC (hexane:ethyl acetate = 5:1) to give 160 mg (39%) of **7** as a pale yellow oil.

MS (70 eV): m/z (%) = 274 (50, M^+), 205 (48), 199 (65), 187 (100), 167 (86), 145 (84), 106 (90); IR (NaCl/film): ν = 3399, 3392, 3075, 2935, 2909, 2865, 1640, 1456, 1422, 1273, 1131, 993, 909 cm^{-1}; ^{1}H NMR ($CDCl_3$, δ, 400 MHz): 1.20 (d, J = 6.1 Hz, 3H, CH_3), 1.24–1.97 (m, 12H, $6CH_2$), 2.08 (dt, J = 6.9 Hz, J = 7.2 Hz, 2H, CH_2), 2.80 (dd, J = 3.6 Hz, J = 3.9 Hz, 4H, $2CH_2$), 3.83 (tq, J = 6.2 Hz, J = 6.1 Hz, 1H, CH), 4.98 (ddt, J = 1.8 Hz, J = 17.1 Hz, J = 1.7 Hz, 1H, HC=), 5.04

(ddt, $J = 1.0$ Hz, $J = 1.9$ Hz, 10.1 Hz, 1H, HC=), 5.80 (ddt, $J = 6.6$ Hz, $J = 10.1$ Hz, $J = 17.1$ Hz, 1H, -CH=) ppm; ^{13}C NMR ($CDCl_3$, δ, 100 MHz): 20.46 (CH_2), 23.39 (CH_2), 23.58 (CH_3), 25.49 (CH_2), 26.02 (CH_2), 26.02 (CH_2), 33.71 (CH_2), 37.59 (CH_2), 38.23 (CH_2), 39.33 (CH_2), 67.85 (CH), 114.90 (quart. C), 115.03 (CH_2=), 138.32 (CH=) ppm.

(±)-Methyl 2,4-bis-(benzyloxy)-6-(5-(2-(4-hydroxypentyl)-1,3-dithian-2-yl)-pentyl)-benzoate (**9**; $C_{36}H_{46}O_5S_2$)

An oven-dried flask equipped with a reflux condenser and a septum inlet was flushed with N_2 and charged with a solution of 13.0 cm^3 (6.5 mmol) 0.5 *M BBN* in *THF*; then, 0.84 g (3.1 mmol) **7** were added at 0°C. The mixture was warmed up slowly to room temperature and stirred for further 4–6 h to give a solution of the B-alkyl-*BBN* derivative.

To the above solution, 4 cm^3 dioxane, 5 cm^3 H_2O, 1.1 g (5.2 mmol) powdered K_3PO_4, 100 mg (0.09 mmol) $Pd(PPh_3)_4$, and 1.45 g (2.9 mmol) aryl triflate **8** [14] were added. The mixture was heated at 95°C for 16 h, extracted with diethyl ether, and the organic layer was concentrated *in vacuo*. The residue was purified by FCC (hexane:ethyl acetate = 1:1) to give 1.06 g (55%) of **9** as a pale yellow oil.

MS (70 eV): m/z (%) = 622 (8, M^+), 620 (26), 604 (44), 497 (58), 311 (100), 181 (70); IR (NaCl/film): $\nu = 3488$, 3474, 3459, 2932, 2863, 1725, 1601, 1454, 1432, 1376, 1272, 1160, 1098, 737, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, δ, 400 MHz): 1.17 (d, $J = 6.3$ Hz, 3H, CH_3), 1.19–1.69 (m, 10H, 5CH_2), 1.82–1.92 (m, 6H, 3CH_2), 2.57 (t, $J = 7.8$ Hz, 2H, CH_2), 2.77 (t, $J = 5.6$ Hz, 4H, 2CH_2), 3.79 (m, 1H, CH), 3.85 (s, 3H, OCH_3), 5.01 (s, 2H, CH_2O), 5.02 (s, 2H, CH_2O), 6.43 (s, 2H, aromat. CH), 7.27–7.40 (m, 10H, aromat. CH) ppm; ^{13}C NMR ($CDCl_3$, δ, 100 MHz): 20.48 (CH_2), 23.55 (CH_3), 23.82 (CH_2), 25.47 (CH_2), 25.96 (CH_2), 26.21 (CH_2), 29.44 (CH_2), 30.83 (CH_2), 33.70 (CH_2), 38.11 (CH_2), 38.14 (CH_2), 39.25 (CH_2), 52.04 (OCH_3), 67.68 (CHOH), 70.05 (CH_2O), 70.37 (CH_2O), 98.45 (aromat. CH), 107.34 (aromat. CH), 107.34 (aromat. CH), 116.95 (quart. C), 126.85 (aromat. CH), 127.50 (aromat. CH), 127.74 (aromat. CH), 128.07 (aromat. CH), 128.43 (aromat. CH), 128.58 (aromat. CH), 136.51 (quart. C), 136.69 (quart. C), 142.82 (quart. C), 157.06 (quart. C), 160.38 (quart. C), 168.79 (C=O) ppm.

(±)-2,4-Bis-(benzyloxy)-6-(5-(2-(4-hydroxypentyl)-1,3-dithian-2-yl)-pentyl)-benzoic acid (**10**; $C_{35}H_{44}O_5S_2$)

Methyl ester **9** (1.06 g, 1.7 mmol) was dissolved in 30 cm^3 EtOH and 30 cm^3 aqueous 8 *M* KOH. The solution was refluxed for 30 h, 60 cm^3 4 *M* HCl were added, and the solution was extracted with diethyl ether. The organic layer was evaporated to give 980 mg (95%) of **10** as a yellow oil.

MS (70 eV): m/z (%) = 608 (0.2, M^+), 457 (2), 367 (3), 106 (62), 91 (100); IR (NaCl/film): $\nu = 2932$, 2863, 1713, 1602, 1497, 1454, 1376, 1320, 1279, 1162, 1112, 908, 831 cm^{-1}; ^{1}H NMR ($CDCl_3$, δ, 400 MHz): 1.17 (d, $J = 8.1$ Hz, 3H, CH_3), 1.20–2.01 (m, 14H, 7CH_2), 2.57–2.82 (m, 4H, 2CH_2S), 3.83 (m, 1H, CH), 5.00 (s, 2H, CH_2O), 5.05 (s, 2H, CH_2O), 6.44 (d, $J = 2.1$ Hz, 1H, aromat. CH), 6.45 (d, $J = 2.1$ Hz, 1H, aromat. CH), 7.20–7.85 (m, 10H, aromat. CH) ppm; ^{13}C NMR ($CDCl_3$, δ, 100 MHz): 20.32 (CH_2), 23.37 (CH_3), 23.43 (CH_2), 25.55 (CH_2), 25.96 (CH_2S), 29.14 (CH_2), 30.62 (CH_2), 33.73 (CH_2), 37.87 (CH_2), 37.96 (CH_2), 38.98 (CH_2), 68.04 (CHO), 70.07 (CH_2O), 70.76 (CH_2O), 98.56 (aromat. CH), 107.99 (aromat. CH), 115.99 (quart. C), 127.09 (aromat. CH), 127.52 (aromat. CH), 127.91 (aromat. CH), 128.12 (aromat. CH), 128.54 (aromat. CH), 128.61 (aromat. CH), 136.30 (quart. C), 136.42 (quart. C), 144.32 (quart. C), 157.36 (quart. C), 160.56 (quart. C), 170.21 (COOH) ppm.

(±)-14,16-Bis-(benzyloxy)-3,4,5,6,7,8,9,10,11,12-decahydro-3-methyl-7,7-trimethylenedithiobenzoxacyclotetradecin-1-one (**11**; $C_{35}H_{42}O_4S_2$)

0.50 g (0.8 mmol) PPh_3 were dissolved in 290 cm^3 toluene under N_2. 0.4 cm^3 (2.6 mmol) diethyl azodicarboxylate (*DEAD*) were added to the solution, and the mixture was stirred for 20 min. Over a

period of 6 h, one half of a solution of 500 mg (0.8 mmol) **10** in 10 cm^3 *THF*:toluene = 1:4 was added with a syringe pump. After stirring for additional 10 h, 0.35 g (1.3 mmol) PPh_3 and 0.2 cm^3 (1.3 mmol) *DEAD* were added; the rest of the solution of the hydroxy acid was added over 6 h. After stirring for further 10 h the organic solvent was evaporated, and the residue was purified by FCC (hexane:ethyl acetate = 20:3) to give 200 mg (42%) of **11** as a white solid.

M.p.: 64°C; MS (70 eV): m/z (%) = 590 (22, M^+), 490 (24), 91 (100); IR (KBr): ν = 2934, 2862, 1715, 1602, 1497, 1455, 1378, 1268, 1162, 1097, 737, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, δ, 400 MHz): 1.12 (d, J = 6.2 Hz, 3H, CH_3), 1.17–2.0 (m, 18H, 9CH_2), 2.73 (m, 4H, 2CH_2S), 4.99 (s, 4H, 2CH_2O), 5.12 (m, 1H, CH), 6.43 (d, J = 2.1 Hz, 1H, aromat. CH), 6.46 (d, J = 2.1 Hz, 1H, aromat. CH), 7.25–7.69 (m, 10H, aromat. CH) ppm; ^{13}C NMR ($CDCl_3$, δ, 100 MHz): 18.39 (CH_2), 20.16 (CH_3), 21.18 (CH_2), 25.39 (CH_2), 25.90 (CH_2), 25.95 (CH_2), 26.72 (CH_2), 29.52 (CH_2), 31.18 (CH_2), 34.96 (CH_2), 36.31 (CH_2), 36.24 (CH_2), 69.97 (CH_2O), 70.13 (CH), 70.39 (CH_2O), 98.14 (aromat. CH), 106.67 (aromat. CH), 117.87 (quart. C), 127.45 (aromat. CH), 127.54 (aromat. CH), 127.87 (aromat. CH), 127.97 (aromat. CH), 128.29 (aromat. CH), 128.32 (quart. C), 128.51 (aromat. CH), 136.43 (quart. C), 136.61 (quart. C), 142.08 (quart. C), 156.90 (quart. C), 160.27 (quart. C), 168.14 (C=O) ppm.

(±)-14,16-Bis-(benzyloxy)-3,4,5,6,7,8,9,10,11,12-decahydro-3-methylbenzoxacyclotetradecin-1,7-dione ((±)-O,O-dibenzylzearalanone) (**12**; $C_{32}H_{36}O_5$)

To 0.38 g (0.64 mmol) **11** dissolved in 20 cm^3 *THF*:H_2O = 7:3, 480 mg (2.2 mmol) red HgO and 260 mg (1.83 mmol) $BF_3 \cdot Et_2O$ were added. The suspension was stirred for 30 min and extracted first with CH_2Cl_2 and then with ethyl acetate. The combined organic layers were dried over Na_2SO_4, and the solvent was evaporated. The residue was purified by FCC (hexane:ethyl acetate = 5:1) to give 210 mg (66%) of **12** as pale yellow crystals.

M.p.: 78°C; MS (70 eV): m/z (%) = 500 (M^+, 14), 482 (4), 424 (10), 409 (4), 272 (30), 202 (38), 91 (100); IR (KBr): ν = 2960, 1720, 1610, 1460, 1440, 1270, 1170, 1080, 960, 850, 740, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, δ, 400 MHz): 1.13 (d, J = 6.3 Hz, 3H, CH_3), 1.11–2.63 (m, 16H, 8CH_2), 4.32 (m, 1H, CH), 4.99 (d, J = 3.0 Hz, 2H, CH_2O), 5.03 (s, 2H, CH_2O), 6.42 (d, J = 2.1 Hz, 1H, aromat. CH), 6.46 (d, J = 2.1 Hz, 1H, aromat. CH), 7.07–7.43 (m, 10H, 10 aromat. CH) ppm; ^{13}C NMR ($CDCl_3$, δ, 100 MHz) 19.19 (CH_3), 19.83 (CH_2), 23.28 (CH_2), 27.67 (CH_2), 30.74 (CH_2), 33.72 (CH_2), 34.42 (CH_2), 38.74 (CH_2), 70.10 (CH_2O), 70.34 (CH), 70.51 (CH_2O), 98.32 (aromat. CH), 107.18 (aromat. CH), 117.44 (aromat. CH), 127.52 (aromat. CH), 127.56 (aromat. CH), 127.97 (aromat. CH), 128.10 (aromat. CH), 128.40 (aromat. CH), 128.62 (aromat. CH), 136.45 (quart. C), 136.59 (quart. C), 142.57 (quart. C), 157.07 (quart. C), 160.36 (quart. C), 167.96 (COO), 212.49 (C=O) ppm.

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