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Synthesis of 2(3)-8(9)-Bisanhydrolactarorufin A

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Abstract: The title compound **8** was synthesized from the furan **1** and dimethyl acetylene dicarboxylate (**2**).

Lactaranes isolated from fungi are interesting target molecules, because various biological activities of this class of compounds were reported.[1,2] In previous communications we described a new approach to the lactarane skeleton starting from the furan **1** and maleic anhydride.[3,4]

Now we report on the application of our pathway for the synthesis of the title compound **8**. 2(3)-8(9)-Bisanhydrolactarorufin A (**8**)[5] was isolated from *Lactarius vellereus* by Daniewski et al. in 1990/1991.[6]

The hydroazulene **3** was prepared by Diels-Alder reaction of the furan **1** with dimethyl acetylene dicarboxylate (**2**) and a subsequent selective oxidation of the tetralkyl substituted double bond of the resulting oxanorbornadiene with ruthenium tetroxide to give a diketo ester. The diketo ester undergoes a highly regioselective aldol condensation with methanesulfonic acid for steric reasons. By this procedure **3** was obtained in a total yield of 31% on a 10 g scale starting from **1** (See Experimental).

In principle the above procedure follows our earlier approach.[3] However the change from maleic anhydride to **2** as dienophile was necessary. All attempts to cleave the ether bridge between C-4 and C-7 of similar hydroazulenones having a (C-5)-(C-6) single bond failed so far.[7] The method of Guindon et al.[8] proved to be compatible with the more reactive compound **3**. Treatment of **3** with dimethyl boron bromide/triethylamine gave the tropone **4** in 41% yield.

Fortunately the (C-6)-(C-7) double bond of **4** could be hydrogenated preferentially with 10% Pd/C catalyst in ethyl acetate under carefully controlled conditions[9] to furnish **5** in 53% yield. Finally the lactarane skeleton was completed by methylenation of **5** with the Nysted reagent[10] in a temperature range between -78°C and room temp. The diester **6** was converted to the anhydride **7** in the usual way. Reduction of the crude compound **7** with a suspension of sodium borohydride in THF furnished after acidic working up and purification by column

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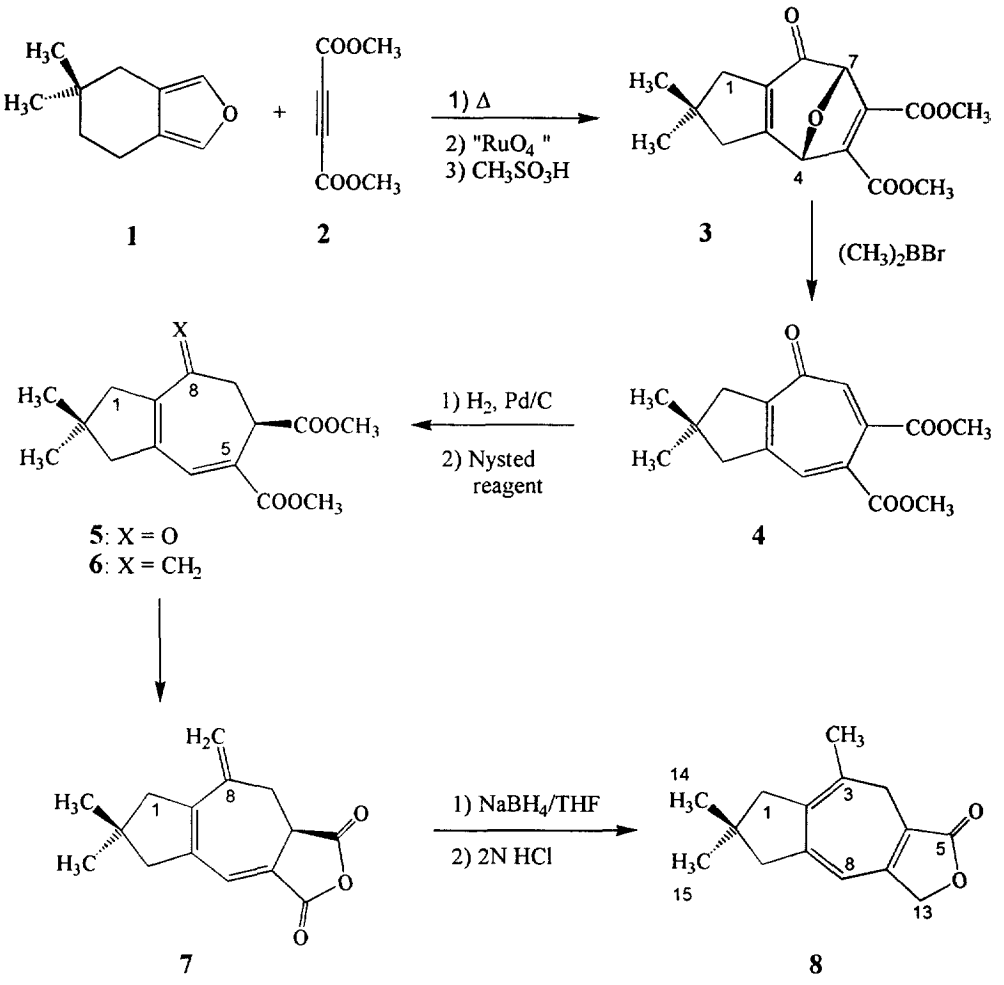
chromatography the crystalline target compound **8** in 24% yield over the last steps as the only identified product.



The melting point, the UV, ^{1}H and ^{13}C NMR spectra of **8** were identical with those reported by Daniewski et al.[6,11] The HMBC spectrum of **8** with a correlation between the protons on C-4 and the carbonyl group on C-5[5] furnishes an additional structural proof for this compound.

The preferential reduction of the conjugated carbonyl group of **7** is somewhat surprising. Bailey and Johnson[12] reported an opposite course in the case of the analogous reaction of homophthalic anhydride. It could be possible that the formation of a boron enolate of **7** prevents the non-conjugated carbonyl group from further attack.

The reduction of **7** with sodium borodeuteride lead to a derivative of **8** that was dideuterated in the methylene group of the lactone ring. Hereby an attack of the hydride on the *exo* methylene group is excluded. We assume that the working up with hydrochloric acid causes the isomerization of the double bonds to give **8**.

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer Paragon 1000 FTIR-spectrometer. UV spectra were obtained on a Zeiss DMR 10-spectrometer. ^1H / ^{13}C NMR spectra (reference: TMS int) were taken in $CDCl_3$ on a Bruker AC 200 P, a Bruker AM 300 and a Bruker DRX 500, respectively. The assignment of signals marked as $^{*,**,***)}$ is arbitrary. EI (70 eV) and CI (^{t}BuH) mass spectra were obtained on a Finnigan-MAT 8230 spectrometer. Column chromatography was performed on Baker Silicagel 30-60 μm and analytical TLC on Macherey-Nagel SIL G/UV_{254} plates. Melting points were determined on a Büchi 510 apparatus and are uncorrected. Elemental analyses were made by the Mikroanalytisches Laboratorium Ilse Beetz, D-96301 Kronach.

Dimethyl (1R, 4S*)-1,4-Epoxy-1,4,5,6,7,8-hexahydro-6,6-dimethylnaphthalene-2,3-dicarboxylate*

A soln of dimethyl acetylene dicarboxylate (**2**) (14.2 mL, 127 mmol) and furan **1**[3] (16.7 g, 111 mmol) in toluene (350 mL) was heated to reflux for 2 h. The solvent was removed under reduced pressure, the residue was filtered through neutral Al_2O_3 (activity 2 - 3) with Et_2O. The solvent was evaporated to give the Diels-Alder adduct (39.7 g) as a yellow oil which was used in the next step without purification.

Dimethyl (3R,10S*)-3,10-Epoxy-6,6-dimethyl-4,9-dioxo-cyclodec-1-ene-1,2-dicarboxylate*

$NaIO_4$ (65.9 g, 308 mmol), $RuCl_3 \cdot H_2O$ (630 mg) and H_2O (380 mL) were added to a stirred soln of the crude Diels-Alder adduct (39.7 g, <111 mmol) in CH_3CN (230 mL) and CCl_4 (260 mL) in turn. After stirring at room temp for 17 h, the mixture was diluted with CH_2Cl_2 (200 mL). The precipitate was filtered off. The organic layer was separated and the aqueous one was extracted with CH_2Cl_2 (3x200 mL). The combined organic extracts were dried with Na_2SO_4 and concentrated under reduced pressure. The residue was filtered through silicagel (0.2 - 0.5 mm) with CH_2Cl_2 to yield crude diketo ester (26.7 g) as a yellow oil which was used for the aldol condensation without further purification. An analytical sample was obtained by crystallization from Et_2O / pentane. Mp 91 - 92°C; IR (KBr): ν = 1740 cm^{-1} (ester C=O), 1728 (ester C=O), 1710 (ketone C=O), 1704 (ketone C=O), 1654 (C=C); UV (CH_3CN): λ_{max} (lgε) = 259 nm (3.19); ^1H NMR (200 MHz, $CDCl_3$): δ = 1.00 ppm (s, 3 H, 6 - CH_3), 1.03 (s, 3 H, 6 - CH_3), 1.44 (ddd, ^2J = 15.3 Hz, $^3J_{7,8}$ = 6.6 Hz, $^3J_{7,8}$ = 4.9 Hz, 1 H, 7 - *H*), 1.77 (dddd, ^2J = 15.3 Hz, $^3J_{7,8}$ = 9.5 Hz, $^3J_{7,8}$ = 5.9 Hz, $^4J_{7,5}$ = 1.0 Hz, 1 H, 7 - *H*), 2.06, (dd, ^2J = 11.3 Hz, $^4J_{5,7}$ = 1.0 Hz, 1 H, 5 - *H*), 2.34 (ddd, ^2J = 13.0 Hz, $^3J_{8,7}$ = 9.5 Hz, $^3J_{8,7}$ = 6.6 Hz, 1 H, 8 - *H*), 2.90 (ddd, ^2J = 13.0 Hz, $^3J_{8,7}$ = 5.9 Hz, $^3J_{8,7}$ = 4,9 Hz, 1 H, 8 - *H*), 3.22 (d, ^2J = 11.3 Hz, 1 H, 5 - *H*), 3,82 (s, $COOCH_3$), 3.86 (s, $COOCH_3$), 5.44 (d, $^4J_{3,10}$ = 3.08 Hz, 1 H, 3 - *H*), 5.53 (d, $^4J_{10,3}$ = 3.08 Hz, 1 H, 10 - *H*); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 27.56 ppm (q, 6 - CH_3), 29.21 (q, 6 - CH_3), 34.88 (t, *C* - 7), 36.16 (t, *C* - 8), 36.39 (s, *C* - 6), 48.06 (t, *C* - 5), 52.81 (2 q, 2 $COOCH_3$), 91.90 (d, *C* - 10)*, 92.61 (s, *C* - 3)*, 136.07 (s, *C* - 1)**, 136.23 (s, *C* - 2)**, 161.24 (s, $COOCH_3$), 161.80 (s, $COOCH_3$), 206.66 (s, *C* - 4), 207.72 (s, *C* - 9); MS (CI): *m/z* (%) = 325 (M^+ + 1, 100), 293 (M^+ + 1 - CH_4O, 2); Anal calcd for $C_{16}H_{20}O_7$ (324.33), C 59.25, H 6.22; found C 59.31, H 6.23.

Dimethyl (4R,7R*)-4,7-Epoxy-1,2,3,4,7,8-hexahydro-2,2-dimethyl-8-oxo-azulene-5,6-dicarboxylate (3)*

$MeSO_3H$ (0.6 mL) was added to a soln of the crude diketo ester (26.7 g, <82.3 mmol) in toluene (350 mL), and the mixture was refluxed under azeotropic removal of water for 3 h. The solution was then cooled to room temp, neutralized with solid $NaHCO_3$ and dried with Na_2SO_4. The toluene was removed under reduced pressure. Purification by silicagel column chromatography furnished a yellow oil (R_f = 0.35). Recrystallization from Et_2O / pentane yielded **3** (10.5 g, 31% over the last 3 steps) as yellow needles. Mp 71 - 72°C; IR (KBr): ν = 1735 cm^{-1} (ester C=O), 1717 (ester C=O), 1693 (ketone C=O), 1651 (C=C); UV (CH_3CN): λ_{max} (lgε) = 226 nm (4.11), 302

(3.11); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.10 ppm (s, 3 H, 2 -C*H*$_3$), 1.14 (s, 3 H, 2 - C*H*$_3$), 2.26 (dtd, ^2J = 16.2 Hz, $^5J_{1,3}$ = 2.3 Hz, $^5J_{1,4}$ = 0.7 Hz, 1 H, 1 - *H*), 2.32 (dtd, ^2J = 16.2 Hz, $^5J_{1,3}$ = 2.3 Hz, $^5J_{1,4}$ = 1.1 Hz, 1 H, 1 - *H*), 2.56 (td, $^5J_{3,1}$ = 2.3 Hz, ^5J = 0.5 Hz, 2 H, 3 - *H*$_2$), 3.83 (s, 3 H, COOC*H*$_3$), 3.86 (s, 3 H, COOC*H*$_3$), 5.19 (s, 1 H, 7 - *H*), 5.35 (dd, $^5J_{4,1}$ = 1.1 Hz, $^5J_{4,1}$ = 0.7 Hz, 1 H, 4 - *H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.29 ppm (q, 2 - *C*H$_3$), 29.52 (q, 2 - *C*H$_3$), 38.36 (s, *C* - 2), 43.34 (t, *C* - 3), 48.79 (t, *C* - 1), 52.64 (2 q, 2 COOCH$_3$), 81.98 (d, *C* - 4), 88.84 (d, *C* - 7), 131.57 (s, *C* - 8a), 140.78 (s, *C* - 6)*, 146.83 (s, *C* - 5)*, 161,74 (s, *C*OOCH$_3$), 162.56 (s, *C*OOCH$_3$), 163.57 (s, *C* - 3a), 189.95 (s, *C* - 8); MS (CI): *m/z* (%) = 307 (M^+ + 1, 100), 275 (M^+ + 1 - CH_4O, 19); Anal calcd for $C_{16}H_{18}O_6$ (306.32), C 62.74, H 5.92; found C 62.78, H 5.88.

Dimethyl 1,2,3,8-Tetrahydro-2,2-dimethyl-8-oxo-azulene-dicarboxylate (4)

Et_3N (0.26 mL) and a soln of $(CH_3)_2BBr$[8] (11.7 g, 96.9 mmol) in CH_2Cl_2 (50 mL) were added to a soln of **3** (10.6 g, 34.6 mmol) in CH_2Cl_2 (200 mL) at 0°C under the exclusion of light. The mixture was warmed to room temp and stirred for 3 h. It was poured into sat. aq. $NaHCO_3$ (500 mL). The organic layer was separated and the aqueous one was extracted with CH_2Cl_2 (3x100 mL). The combined extracts were washed with H_2O, dried with Na_2SO_4 and concentrated under reduced pressure. Purification by silicagel column chromatography with Et_2O / pentane (1 : 1) furnished **4** (4.0 g, 41%, R_f = 0.18) as a yellow oil. IR (film): ν = 1738 cm^{-1} (ester C=O), 1698 (ketone C=O), 1620 (C=C), 1590 (C=C); UV (CH_3CN): λ_{max} (lgε) = 221 nm (4.01), 248 (4.02), 316 (3.62); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.16 ppm (s, 6 H, 2 - C*H*$_3$), 2.85 (td, $^5J_{3,1}$ = 1.7 Hz, *J* = 0.5 Hz, 2 H, 3 - *H*$_2$), 2.89 (td, $^5J_{1,3}$ = 1.7 Hz, *J* = 0.6 Hz, 2 H, 1 - *H*$_2$), 3.85 (s, 3 H, COOC*H*$_3$), 3.87 (s, 3 H, COOC*H*$_3$), 7.32 (d, *J* = 0.6 Hz, 1 H, 4 - *H*), 7.59 (dd, *J* = 1.4 und 0.7 Hz, 1 H, 7 - *H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.78 ppm (2 q, 2 2 -C*H*$_3$), 36.97 (s, *C* - 2), 49.73 (t, *C* - 1)*, 53.03 (q, COO*C*H$_3$), 53.16 (q, COO*C*H$_3$), 53.85 (t, *C* - 3)*, 133.54 (s, *C* - 8a), 136.33 (d, *C* - 4)**, 137.57 (s, *C* - 5)***, 140.47 (d, *C* - 7)**, 148.11 (s, *C* - 6)***, 157.14 (s, *C* - 3a), 167.38 (s, *C*OOCH$_3$), 168.51 (s, *C*OOCH$_3$), 183.57 (s, *C* - 8); MS (CI): *m/z* (%) = 291 (M^+ + 1, 100), 259 (M^+ + 1 - CH_4O, 20).

Dimethyl (6R)-1,2,3,6,7,8-Hexahydro-2,2-dimethyl-8-oxo-azulene-5,6-dicarboxylate (5)*

Pd / C-catalyst (10% Pd, 1.93 g) was added to a soln of **4** (3.99 g, 13.7 mmol) in EtOAc. The reaction mixture was hydrogenated for 4 h until 308 mL H_2 were used up. The catalyst was filtered off, and the solvent was removed under reduced pressure. The residue was chromatographed on silicagel with Et_2O / pentane (1 : 1) to give **5** (2.13 g, 53%, R_f = 0.25) as a yellow oil. IR (film): ν = 1738 cm^{-1} (ester C=O), 1714 (ketone C=O), 1659 (C=C), 1631 (C=C); UV (CH_3CN): λ_{max} (lgε) = 215 nm (4.15), 312 (4.06); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.04 ppm (s, 3 H, 2 - C*H*$_3$), 1.12 (s, 3 H, 2 - C*H*$_3$), 2.46 - 2.67 (m, 4 H, C*H*$_2$), 2.76 (dd, ^2J = 17.1 Hz, $^3J_{7,6}$ = 2.7 Hz, 1 H, 7 - *H*), 3.19 (dd, ^2J = 17.1 Hz, $^3J_{7,6}$ = 5.9 Hz, 1 H, 7 - *H*), 3.64 (s, 3 H, COOC*H*$_3$), 3.85 (s, 3 H, COOC*H*$_3$), 4.29 (dd, $^3J_{6,7}$ = 5.9 Hz, $^3J_{6,7}$ = 2.7 Hz, 1 H, 6 - *H*), 7.21 (m, 1 H, 4 - *H*); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 28.67 (q, 2 - *C*H$_3$), 28.88 (q, 2 - *C*H$_3$), 36.27 (s, *C* - 2), 38.46 (d, *C* - 6), 43.58 (t, *C* - 3)*, 47.86 (t, *C* - 1)*, 52.53 (q, COOCH$_3$), 52.74 (q, COOCH$_3$), 53.70 (t, *C* - 7), 134.78 (d, *C* - 4), 134.98 (s, *C* - 8a), 143.35 (s, *C* - 5), 146.49 (s, *C* - 3a), 166.69 (s, *C*OOCH$_3$), 170.78 (s, *C*OOCH$_3$), 195.58 (s, *C* - 8); MS (CI): *m/z* (%) = 293 (M^+ + 1, 100), 261 (M^+ + 1 - CH_4O, 18); Anal calcd for $C_{16}H_{20}O_5$ (292.33), C 65.74, H 6.89; found C 65.63, H 7.00.

Dimethyl (6R)-1,2,3,6,7,8-Hexahydro-2,2-dimethyl-8-methylene-azulene-5,6-dicarboxylate (6)*

At first a soln of **5** (631 mg, 2.16 mmol) in THF (10 mL) and afterwards titanium tetrachloride (0.24 mL, 2.16 mmol) were added to a suspension of the Nysted reagent[10] (11.29 g, 4.96 mmol) in THF (20 mL) at -78°C. The mixture was stirred for 3 h. During this time the bath slowly warmed to room temp and the yellow suspension

turned black. The reaction mixture was quenched by water (40 mL) and diluted with Et_2O (40 mL). The organic layer was separated and the aqueous one was extracted with Et_2O (4x20 mL). The combined organic layers were extracted with H_2O and brine and were then dried with Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silicagel column chromatography with Et_2O / pentane (1 : 2) to furnish **6** (370 mg, 59%, R_f = 0.39) as a light yellow oil. IR (film): ν = 1740 cm^{-1} (ester C=O), 1708 (ester C=O); UV (CH_3CN): λ_{max} (lgε) = 216 nm (2.88), 313 (3.78); ^1H NMR (200 MHz, $CDCl_3$): δ = 1.09 ppm (s, 6H, 2 - CH_3), 2.22 - 2.70 (m, 5 H, CH_2, 7 - *H*), 3.01 (dd, ^2J = 14.29 Hz, $^3J_{7,6}$ = 6.0 Hz, 1 H, 7 - *H*), 3.61 (s, 3 H, $COOCH_3$), 3.77 (s, 3 H, $COOCH_3$), 4.27 (dd, $^3J_{6,7}$ = 6.0 Hz, $^3J_{6,7}$ = 2.4 Hz, 1 H, 6 - *H*), 5.01 - 5.10 (m, 2 H, $=CH_2$), 7.23 (s, 1 H, 4 - *H*); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 29.07 ppm (q, 2 - CH_3), 29.25 (q, 2 - CH_3), 35.51 (t, *C* - 7), 36.49 (s, *C* - 2), 43.34 (d, *C* - 6), 50.76 (t, *C* - 3)*, 52.09 (q, $COOCH_3$), 52.20 (s, $COOCH_3$), 53.70 (t, *C* - 1)*, 118.47 (t, $=CH_2$), 129.75 (s, *C* - 8a), 133.08 (s, *C* - 5)**, 136.17 (d, *C* - 4), 141.49 (s, *C* - 3a)**, 145.38 (s, *C* - 8), 167.83 (s, $COOCH_3$), 171.92 (s, $COOCH_3$); MS (CI): *m/z* (%) = 291 (M^+ + 1, 100), 259 (M^+ + 1 - CH_4O, 44).

(6R)-1,2,3,6,7,8-Hexahydro-2,2-dimethyl-8-methylene-5,6-dicarboxylic acid anhydride (7)*

A soln of NaOH (580 mg, 14.50 mmol) in H_2O (12.0 mL) was added to a soln of **6** (1.05 g, 3.62 mmol) in MeOH (30 mL). The colour of the reaction mixture turned red. After heating to reflux for 2 h the yellow mixture was extracted with Et_2O (3x20 mL) and the solvent of the combined organic layers was removed in vacuo. The residue was diluted with Et_2O (40 mL), dried with Na_2SO_4 and concentrated under reduced pressure. Acetic anhydride (15 mL) was added to the yellow solid and the soln was heated at 80°C for 0.5 h. The mixture was cooled to room temp and the acetic anhydride was removed under reduced pressure. The crude product **7** (0.93 g) was used without further purification. An analytical sample was obtained by crystallization from Et_2O / pentane. Mp 98 - 99°C; IR (KBr): ν = 1833 (anhydride C=O), 1762 (anhydride C=O), 1654 (C=C); ^1H NMR (300 MHz, $CDCl_3$): δ = 1.11 ppm (s, 3 H, 2 - CH_3), 1.14 (s, 3 H, 2 - CH_3), 2.47 - 2.60 (m, 4 H, CH_2), 2.73 (ddt, ^2J = 16.8 Hz, ^4J = 1.8 und 1.7 Hz, 1 H, 1 - *H*), 3.16 (ddd, ^2J = 14.1 Hz, $^3J_{7,6}$ = 2.1 Hz, ^5J = 0.6 Hz, 1 H, 7 - *H*), 3.61 - 3.67 (m, 1 H, 6 - *H*), 5.27 - 5.33 (m, 2 H, $=CH_2$), 7.14 - 7.15 (m, 1 H, 4 - *H*); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 29.12 ppm (q, 2 - CH_3), 29.20 (q, 2 - CH_3), 34.63 (t, *C* - 7), 36.31 (s, *C* - 2), 44.45 (d, *C* - 6), 51.14 (t, *C* - 1)*, 52.97 (t, *C* - 3)*, 121.90 (t, $=CH_2$), 125.84 (s, *C* - 8a)**, 133.25 (s, *C* - 5)**, 134.79 (d, *C* - 4), 140.57 (s, *C* - 3a)**, 148.24 (s, *C* - 8), 164.04 (s, 5 - *C*O), 171.06 (s, 6 - *C*O); the structure was established by a COSY-experiment; MS (CI): *m/z* (%) = 245 (M^+ + 1, 100), 217 (M^+ + 1 - CO, 4); Anal calcd for $C_{15}H_{16}O_3$ (244.29), C 73.75, H 6.60; found C 73.76, H 6.67.

2(3)-8(9)-Bisanhydrolactarorufin A (8)[5]

A soln of crude **8** (925 mmol, <3.63 mmol) in THF (18 mL) was added to a suspension of $NaBH_4$ (300 mg, 7.93 mmol) in THF (20 mL) during a period of 10 min at 0°C . The reaction mixture was stirred 30 min at 0°C and then 60 min at room temp. It was quenched by 2 N HCl (15 mL) and extracted with Et_2O (4x20 mL). The solvent of the combined organic layers was removed in vacuo. The residue was diluted with Et_2O (20 mL), dried with Na_2SO_4 and concentrated under reduced pressure. Purification by silicagel column chromatography with Et_2O / pentane (1 : 2) furnished **8** (197 mg, 24% over the last two steps, R_f = 0.22) as a yellow solid. Recrystallization from Et_2O / pentane yielded **8** as light yellow crystals. Mp 104 - 105°C; IR (KBr): ν = 1728 cm^{-1} (lactone C=O), 1639 (C=C); UV (EtOH): λ_{max} (lgε) = 229 nm (4.24), 275 (3.33), 335 (3.58); ^1H NMR (500 MHz, $CDCl_3$):[5] δ = 1.05 ppm (s, 6 H, 14 - H_3, 15 - H_3), 1.92 (s, 3 H, 12 - H_3), 2.31 (s, 2 H, 1 - H_2), 2.45 (d, *J* = 1.3 Hz, 2 H, 10 - H_2), 2.92 (s, 2 H, 4 - H_2), 4.74 (s, 2 H, 13 - H_2), 6.15 (s, 1 H, 8 - *H*); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 23.20 ppm (q, *C* - 12), 28.33 (2 q, *C* - 14, *C* - 15), 29.30 (t, *C* - 4), 36.83 (s, *C* - 11), 47.25 (t, *C* - 10), 51.27

(t, *C* - 1), 69.59 (t, *C* - 13), 113.78 (d, *C* - 8), 114.73 (s, *C* - 9), 130.00 (s, *C* - 7),136.98 (s, *C* - 2), 153.98 (s, *C* - 3), 155.76 (s, *C* - 6), 174.18 (s, *C* - 5); the structure was established by a HMBC experiment; MS (70 eV): *m/z* (%) = 230 (M^+, 34), 215 (M^+ - CH_3, 100), 201 (6), 187 (M^+ - CO_2, 15), 171 (20), 156 (10), 141 (15), 128 (20), 115 (21), 91 (14), 77 (12); Anal calcd for $C_{15}H_{18}O_2$ (230.31), C 78.23, H 7.88; found C 78.28, H 7.98; the above spectroscopic data are identical with the data of ref.[6]

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5. The numbering of the lactarane skeleton according to ref. 1 and 6 is used for **8**. **3** - **7** are numbered as hydroazulenes.
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