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Construction of a Homonaphthazarin Skeleton and Synthesis of Hydroquinone-annelated Cycloheptatriene Derivatives

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1,4-Dihydroxy-7,8-dihydro-5*H*-benzo[*a*]cycloheptene-5,9(6*H*)-dione (**7**) was synthesised from hydroquinone and glutaric acid chloride via an acylation reaction. The reaction of dione (**7**) with bromine followed by treatment with NEt_3 gave homonaphthazarin **8** as well as the brominated derivatives **9** and **10**. Reduction of 1,4-dimethoxy-7,8-dihydro-5*H*-benzo[*a*]cycloheptene-5,9(6*H*)-dione (**16**) with $LiAlH_4$ gave 2 isomeric alcohols, **17** and **18**. Reaction of these alcohols with $SOCl_2$ followed by HCl elimination with NEt_3 afforded dimethoxybenzocycloheptatriene **19** as the sole product. For the synthesis of the isomeric cycloheptatriene **20**, the double bond in **19** was isomerised with KO*t*−Bu.

Key Words: Naphthazarin, homonaphthazarin, benzocycloheptatriene, acylation, bromination.

Introduction

A large number of natural products containing 1,4-naphthoquinone moiety have been isolated and characterised[1]. Such compounds have been found in a variety of organisms including lichens, fungi, echinoids and high plants. An interesting sub-group of naphthoquinones is the 5,8-dihydroxy-1,4-naphthoquinone **1**, known as naphthazarin[2], which shows very interesting biological and pharmacological activities[3]. Recently, a number of naturally occurring naphthoquinones have been isolated from various species of the family *Boraginaceae*. In particular, alkannin **2** and shikonin **3** (2 enantiomeric dyes extracted from *Alkanna tinctoria* and *Lithospermum erythrorhizon*, respectively), seem to have peculiar biological properties.[4] The antimicrobial compound, 2-isopropenylnaphthazarin-2,3-epoxide **4**,[5,6] which is actually a homonaphthazarin derivative, was isolated from the hairy roots of *Sesamum indicum*.

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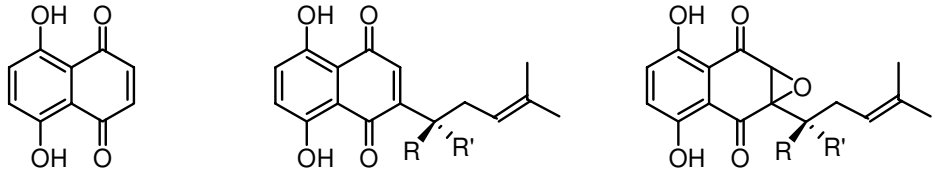
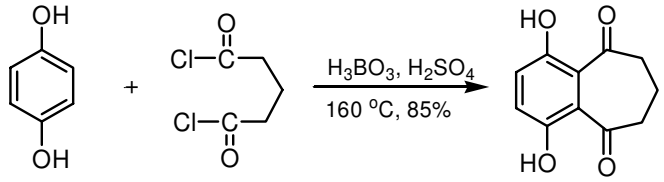


Naphthazarin (**1**) Alkannin (**2**) R = H; R' = OH
Shikonin (**3**) R = OH; R' = H **4**

In this paper we describe the synthesis of some homonaphthazarin derivatives and their conversion to benzannelated cycloheptatriene derivatives starting from the diketone **7**.

Results and Discussion

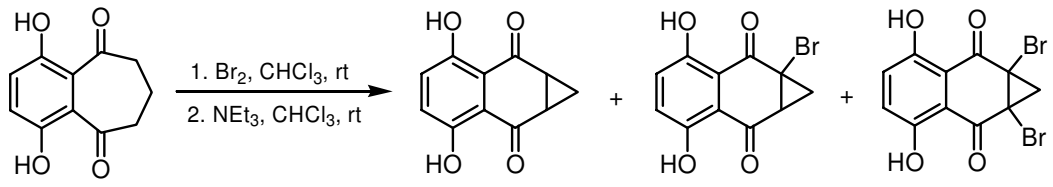
The synthesis of the diketone **7** was first reported by Thomson et al.[7]. They reacted hydroquinone (**5**) with glutaric acid in fused aluminium chloride–sodium chloride and obtained the title compound in 33% yield.[7,8] This procedure was modified to give an increased yield. Hydroquinone (**5**) was reacted with glutaric acid chloride (**6**) at 135 °C and later at 160 °C in the presence of boric acid and sulphuric acid to give the diketone **7** in 85% yield (Scheme 1). The physical properties of **7** are completely in agreement with those reported in the literature.[7]



5 **6** **7**

Scheme 1

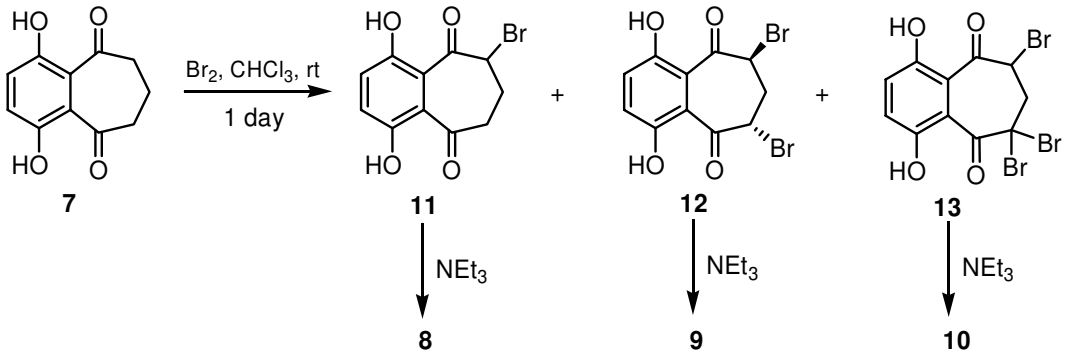
We reinvestigated the bromination reaction of **7**[9] with bromine in order to see whether the bromides formed can be transformed into the corresponding cycloheptatriene and/or tropone derivatives. A solution of diketone **7** in chloroform was treated with 2 equiv. bromine in $CHCl_3$ and the resulting solution was stirred for 1 day. The purification and analysis of products arising from this reaction were complicated because of the great tendency of the products to undergo hydrolysis during column chromatography. Therefore, the resulting mixture was submitted without isolation to NEt_3-induced elimination. The column chromatography of the mixture allowed us to separate 3 products, **8-10**, beside the starting material, **7** (Scheme 2).



7 **8** 41.5% **9** 30.2% **10** 3.7%

Scheme 2

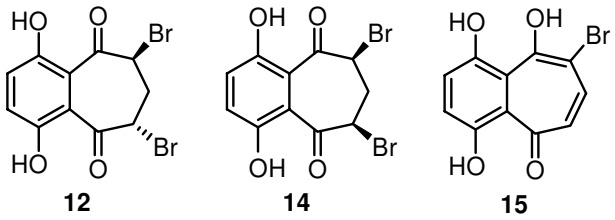
The structures were confirmed by ^{1}H and ^{13}C NMR spectral data as well as by elemental analysis. Compounds **8-10** are homonaphthazarin derivatives. Sorrie and Thomson[9] carried out the bromination reaction of **7** in acetic acid and they obtained the homonaphthazarin derivatives **9** and **10**. They did not report the formation of the homonaphthazarin **8**. Contrary to their results, we found that homonaphthazarin **8** was formed as the major product in 41.5% yield. Later, Garden and Thomson[10] reported the formation of **8** from the reaction of dibromide **12** with sodium iodide and sodium thiosulphate in acetone.



Scheme 3

We assume that the bromination of **7** first forms the brominated products **11-13**, which can be easily transformed into the corresponding naphthazarin derivatives upon treatment with NEt_3 by intramolecular substitution reactions (Scheme 3).

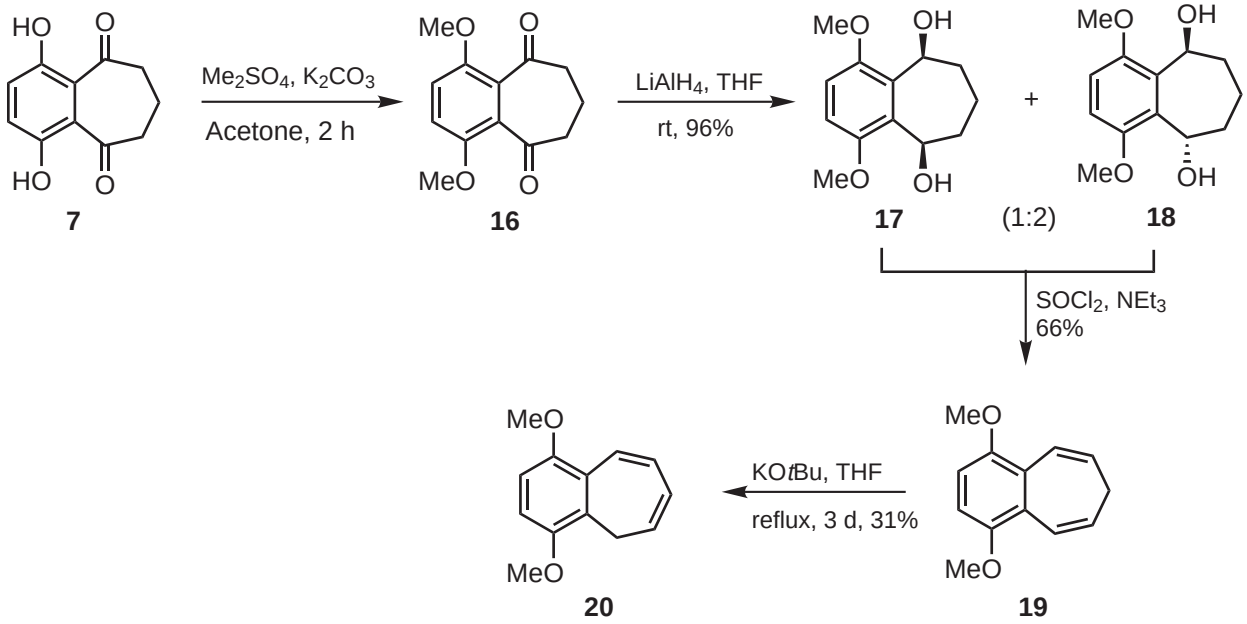
To establish the formation mechanism of these products, we tried to isolate at least one of the formed intermediates, **11-13**, of this bromination reaction. Bromination of **7** was carried out in $CHCl_3$ as described above and the resulting solution was stirred at room temperature for 3 days and dibromide **12**[10] was formed as the sole product.



The exact configuration of bromine atoms in **12** was determined on the basis of the NMR spectral data. The ^{1}H and ^{13}C NMR studies of the dibromide **12** showed the formation of a highly symmetrical compound. The ^{13}C NMR spectrum consisted of 6 distinct carbon resonances indicating high symmetry in the molecule. This could be in agreement with 2 possible diastereomeric structures, **12** and **14**. The ^{1}H NMR spectrum shows 2 sets of signals in the sp^3-region. The methine protons as well as the methylenic protons appear as a triplet at 4.97 ppm (J=7.3 Hz) and at 3.17 ppm (J=7.3 Hz), respectively. In the case of *cis*-configurated bromine atoms, the methylenic protons would give rise to the formation of an AB system, which was not the case. Therefore, the structure **14** was excluded. Treatment of **12** with NEt_3 afforded **9** in 80% yield. No products having benzotropolone derivatives such as **15** were observed.

For the synthesis of benzocycloheptatriene derivatives, the 7-membered ring in **7** should be transformed into a cycloheptatriene unit. First of all, it was necessary to maintain the phenolic hydroxyl groups

in **7** as their methyl ethers. The dimethylether **16** was prepared by refluxing **7** with dimethyl sulphate-acetone-potassium carbonate. Reduction of dimethylether **16** with lithium aluminium hydride in tetrahydrofuran (rt, 20 h) furnished a mixture of separable diols, **17** and **18**, in a ratio of 1:2 where the *cis*-isomer was separated by fractional crystallisation of a mixture (Scheme 4).



Scheme 4

The *cis*-configuration of hydroxyl groups in **17** was unambiguously assigned on the basis of its ^{1}H NMR spectrum. The methylenic protons (H_7) resonate as an AB system, which can only be in agreement with the *cis*-orientation of the alcohol groups. In the case of the *trans*-orientation of alcohol functionalities as in the isomer **18**, the methylenic protons are equal and resonate as a quintet. Reaction of a mixture consisting of isomeric alcohols **17** and **18** with $SOCl_2$ followed by elimination in the presence of NEt_3 afforded dimethoxybenzocycloheptatriene **19** in 66% yield as the sole product. The 7-line ^{13}C NMR spectrum of **19** showed the presence of a symmetrical structure. Furthermore, ^{1}H NMR data also supported the proposed structure. For the formation of the isomeric cycloheptatriene derivative **20**, symmetrical cycloheptatriene **19** was reacted with KO*t*−Bu in refluxing tetrahydrofuran for 3 days to give **20**. The spectral data of **20** were in agreement with the expected cycloheptatriene derivative **20**. The driving force for the double bond isomerisation is the formation of the thermodynamically more stable isomer **20**. AM1 calculations show that isomer **20** is approximately 1.06 kcal/mol more stable than isomer **19**.

In conclusion, dione (**7**) was synthesised from the reaction of glutaric acid chloride with hydroquinone in the presence of H_2SO_4 and H_3BO_3 at high temperature in high yield. The reaction of **7** with bromine followed by treatment with NEt_3 provided the homonaphthazarin derivatives **8-10**. The reduction of carbonyl groups in **16** with $LiAlH_4$ gave isomeric alcohols **17** and **18**. Reaction of a mixture of alcohols **17** and **18** with $SOCl_2$ followed by NEt_3-induced elimination opened up the possibility of synthesising dimethoxybenzocycloheptatriene derivatives such as **19** and **20**. Further functionalisation of the cycloheptatriene units would allow the synthesis of interesting tropone and tropolone derivatives.[11]

Experimental

All chemicals and solvents are commercially available and were used after distillation or treatment with drying agents. M.p.: Thomas-Hoover cap. Melting apparatus. Melting points are uncorrected. IR spectra were obtained from solutions in 0.1 mm cells with a Perkin-Elmer spectrophotometer. The ^{1}H and ^{13}C NMR spectra were recorded on a 200 (50)-MHz Varian spectrometer; δ in ppm, with Me_4Si as the internal standard. Mass spectra were determined on a VG ZabSpec, range 1000 EI. All column chromatography was performed on silica gel (60-mesh, Merck).

Synthesis of 1,4-dihydroxy-7,8-dihydro-5*H*-benzo[*a*]cycloheptene-5,9(6*H*)-dione (7): In a 1-L 2-necked flask, fitted with a dropping funnel and reflux condenser, were placed hydroquinone **5** (30 g, 272 mmol), boric acid (H_3BO_3, 16.86 g, 272 mmol) and sulphuric acid (H_2SO_4, 200 mL). To the resulting solution was added glutaric acid chloride **6** (46 g, 272 mmol) at 135 °C dropwise over 30 min and the temperature was raised to 160 °C. After 30 min additional stirring the mixture was cooled to room temperature, and it was poured into water (500 mL) and then extracted with $CHCl_3$ (3 x 200 mL). The combined organic extracts were washed and dried (Na_2SO_4) and evaporated. The product, **7** (22 g, 85%), was obtained as the sole product and crystallised from $CHCl_3$/hexane to give pale yellow crystals. M.p. 146-148 °C (Lit. m.p. 149 °C[7,8]); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 11.49 (s, OH, 2H), 7.12 (s, aromatic, 2H), 2.89 (t, J= 7.5 Hz, methylenic, 4H), 2.16 (qui., J= 7.5 Hz, methylenic, 2H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 206.3 (CO), 156.9 (C-OH), 129.3 (CH), 120.1 (CH), 43.9 (CH_2), 21.2 (CH_2); MS, m/z,: 208.0/207.0/205.9 (2/10/100), 179.9/178.9/177.9 (2/8/80), 160.9/159.9 (3/17), 149.9 (20), 136.9 (8), 129.1/120.9 (8/42), 107.9 (12). Anal. Calcd for $C_{11}H_{10}O_4$: C, 64.07; H, 4.89. Found: C, 64.24; H, 4.61.

Synthesis of homonaphthazarin derivatives 8-10: To a stirred solution of dione **7** (670 mg, 3.25 mmol) in $CHCl_3$ (40 mL) was added a solution (10 mL) of Br_2 (1.0 g, 5.56 mmol) in one portion at room temperature. After stirring for 1 day, the solvent and excess Br_2 were removed by evaporation. The residue was dissolved in $CHCl_3$ (40 mL) and cooled to 0 °C, and then a solution of NEt_3 (1.0 g) in 5 mL was added dropwise over 5 min. After stirring for 30 min, the cold bath was removed and the mixture was stirred at room temperature for 20 h. The reaction mixture was poured into a cold solution of 10% HCl (100 mL, 0 °C) and it was stirred for 5 min. After separation of the organic phase, the water phase was extracted with $CHCl_3$ (2 x 30 mL). The combined organic extracts were washed with water (50 mL), dried ($CaCl_2$), and then the solvent was evaporated. The residue was submitted to column chromatography (silica gel, 50 g), eluting with ethyl acetate/hexane (5:95). The unreacted starting material, **7** (41 mg, 0.2 mmol, 6.2%), was separated as the first fraction followed by dibromide **10** (42 mg, 0.12 mmol, 3.7%), monobromide **9** (276 mg, 0.98 mmol, 30.2%) and **8** (275 mg, 1.35 mmol, 41.5%). On the other hand, dibromide **10** was also separated from a mixture consisting of **9** and **10** by crystallisation from methanol.

3,6-Dihydroxy-1a,7a-dihydro-1H-cyclopropa[b]naphthalene-2,7-dione (8). M.p. 172-174 °C (Lit. m.p. 173 °C[10]), pale yellow crystals from $CHCl_3$; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 11.96 (s, OH, 2H), 7.23 (s, aromatic, 2H), 2.69 (dd, J= 9.1, 5.2 Hz, cyclopropane, 2H), 1.90 (dt, J= 9.1, 5.2 Hz, cyclopropane, 1H), 1.55 (q, J= 5.2 Hz, cyclopropane, 1H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 200.6 (CO), 158.1 (C-OH), 130.4 (CH), 113.1 (C), 29.8 (CH), 21.9 (CH_2).

1a-Bromo-3,6-dihydroxy-1a,7a-dihydro-1H-cyclopropa[b]naphthalene-2,7-dione (9): M.p. 132-134 °C (lit. m.p. 135 °C[9]), pale yellow needles from $CHCl_3$; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 11.81 (s,

OH, 1H), 11.75 (s, OH, 1H), 7.26 (s, aromatic, 2H), 3.12 (dd, J= 10.1, 6.2 Hz, *exo*-cyclopropane, 1H), 2.31 (dd, J= 10.1, 6.2 Hz, cyclopropane, 1H), 2.03 (t, J= 6.2, Hz, *endo*-cyclopropane, 1H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 198.0 (CO), 194.5 (CO), 158.8 (C-OH), 158.4 (C-OH), 131.3 (CH), 130.9 (CH), 112.7 (C), 111.2 (C), 39.9, 36.6, 32.1; m/z (EI) 284/282 (34/40), 267 (10), 204/203 (14/100), 176/175 (10/90), 146 (34), 119 (22), 108 (16), 91 (42).

1a,7a-Dibromo-3,6-dihydroxy-1a,7a-dihydro-1H-cyclopropan[b]naphthalene-2,7-dion (**10**): M.p. 174-176 °C (lit. m.p. 174 °C[9]), pale yellow crystals from $CHCl_3$; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 11.78 (s, OH, 2H), 7.32 (s, aromatic, 2H), 2.54 (d, A part of AB system, J= 7.8 Hz, cyclopropane, 1H), 2.41 (d, B part of AB system, J= 7.8 Hz, cyclopropane, 1H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 192.5 (CO), 159.2 (C-OH), 132.0 (CH), 110.1 (C), 47.4 (C), 41.0 (CH_2); m/z: 364/362/360 (20/38/19), 322 (7), 284/283/282/281 (19/99/19/100), 255 (37), 246 (14), 209 (8), 202 (48), 174 (22), 146 (19), 118.0 (11).

Synthesis of 6,8-dibromo-1,4-dihydroxy-7,8-dihydro-5*H*-benzo[*a*]cycloheptene-5,9(6*H*)-dione (12): To a stirred solution of diol **7** (532 mg, 2.58 mmol) in $CHCl_3$ (15 mL) was added a solution of Br_2 (1.0 g, 5.56 mmol) in 10 mL of chloroform in one portion at room temperature. After stirring for 3 days, the solvent and excess Br_2 were removed by evaporation. The residue was filtered through a short silica gel column (5 g silica gel), eluting with $CHCl_3$ to give dibromide **12** (520 mg, 1.43 mmol) in 55% yield, which was crystallised from $CHCl_3$. M.p. 177-179 °C (lit. m.p. 180 °C[10]) pale yellow crystals from $CHCl_3$; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 11.31 (s, OH, 2H), 7.26 (s, aromatic, 2H), 4.97 (t, J= 7.3 Hz, CH-Br, 2H), 3.17 (t, J= 7.3 Hz, methylenic, 2H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 197.7 (CO), 158.3 (C-OH), 130.9 (CH), 116.1 (C), 52.3 (CH), 42.6 (CH_2); m/z 366/364/362 (5/10/4), 283/281 (84/100), 255/253 (44/48), 207 (56), 201.9 (68), 173.5 (28), 146.0 (40), 118.0 (38), 89.0 (46).

Reaction of dibromide 12 with NEt_3: A solution of **12** (500 mg, 1.37 mmol) in $CHCl_3$ (20 mL) was cooled to 0 °C, and then a solution of NEt_3 (415 mg) in 5 mL of $CHCl_3$ was added dropwise over 8 min. The ^{1}H NMR spectral studies indicated the formation of **9** (290 mg, 1.10 mmol, 80%) as the sole product.

1,4-Dimethoxy-7,8-dihydro-5*H*-benzo[*a*]cycloheptene-5,9(6*H*)-dione (16) was synthesised as described in the literature.[7] Colourless crystals (86%) from $CHCl_3$/ether, m.p. 137-139 °C, (lit. m.p. 148 °C[7]). ^{1}H-NMR (200 MHz, $CDCl_3$) δ 6.98 (s, aromatic, 2H), 3.77 (s, methoxide, 6H), 2.72 (t, J= 6.2 Hz, methylenic, 4H), 2.02 (qui, J= 6.2 Hz, methylenic, 2H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 204.3 (CO), 151.9 (C-OMe), 130.3 (CH), 117.6 (C), 59.1 (OMe), 45.2 (CH_2), 21.0 (CH_2); m/z: 236/235/233 (2/14/100), 208/207/206/205 (1/10/42/16), 177 (62), 163 (14), 148 (12), 135/134/131 (20/12/8), 105 (8), 85/83/82 (14/16/10).

Reduction of 16 with $LiAlH_4$: To a stirred solution of **16** (4.3 g, 18.4 mmol) in dry tetrahydrofuran (40 mL) was added $LiAlH_4$ (2.5 g, 65.79 mmol) in portions over 30 min at 0 °C. After stirring at the same temperature for 1 h, the cold bath was removed and the mixture was stirred at room temperature for 20 h, cooled to 0 °C, and hydrolysed by the addition of methanol and water (1:1). After the removal of inorganic salts by filtration, the solution was filtered through a short silica gel (5 g) column, eluting with methanol/THF (1:1). The solvent was evaporated and a mixture (96% , 4.2 g, 17.66 mmol) of alcohols **17** and **18** was obtained in a ratio of 1:2. Fractional crystallisation afforded *cis*-alcohol **17** (177 mg, 0.74 mmol) as white crystals.

5*S*(*R*),9*R*(*S*)-1,4-dimethoxy-6,7,8,9-tetrahydro-5*H*-benzo[*a*]cycloheptene-5,9-diol (17): M.p. 180-182 °C from methanol, ^{1}H-NMR (200 MHz, CD_3OD) δ 6.90 (s, aromatic, 2H), 5.64 (bd, C<u>H</u>-OH, J= 6.9 Hz, 2H), 4.9 (s, -OH, 2H), 3.77 (s, methoxide, 6H), 2.61-2.41 (qt, A part of AB system, J =13.8 and 3.2 Hz, methylenic, 1H), 2.22-2.10 (m, methylenic, 2H), 1.71-1.61 (m, methylenic, 3H), 2.69 (dd, B part of AB system, J =13.8 and 2.7 Hz, methylenic 1H); ^{13}C-NMR (50 MHz, CD_3OD) δ 154.3 (C-OMe), 136.9 (C), 115.5 (CH), 67.4 (CH-OH), 59.3 (OMe), 36.7 (CH_2), 20.8 (CH_2); υ_{max} (KBr) 3316, 3247, 3185, 3116, 3085, 2954, 2923, 2838, 1596, 1442, 1265, 1211, 1064, 948, 910, 802, 717, 663 cm^{-1}.

5*R*(*S*),9*R*(*S*)-1,4-Dimethoxy-6,7,8,9-tetrahydro-5H-benzocycloheptene-5,9-diol (18): The NMR data for **18** were extracted from a mixture of **17** and **18** where the isomer **18** was enriched. ^{1}H-NMR (200 MHz, $CDCl_3$) δ 6.78 (s, aromatic, 2H), 5.50 (d, C<u>H</u>-OH, J= 5.1 Hz, 2H), 3.80 (s, OCH_3, 6H), 2.95 (m, OH, 2H), 2.19-1.57 (m, methylenic, 4H), 2.07 (qui. J= 6.9 Hz, methylenic, 2H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 154.1 (C-OMe), 134.5 (C), 113.0 (CH), 69.3 (CH-OH), 58.4 (OMe), 33.8 (CH_2), 21.1 (CH_2).

1,4-Dimethoxy-7*H*-benzo[*a*]cycloheptene (19): A mixture of diols **17** and **18** (3.48 g, 14.6 mmol) in $CHCl_3$ (40 mL) was cooled to –10 °C (NaCl/ice mixture). To the resulting solution was added dropwise a solution of $SOCl_2$ (10 mL) in $CHCl_3$ (10 mL) over 10 min. The colour of the reaction mixture slowly changed to black. After stirring for 30 min, the cold bath was removed, followed by further stirring for 1 h. Excess $SOCl_2$and $CHCl_3$ were evaporated and $CHCl_3$ (10 mL) was added. The resulting solution was cooled to –10 °C and then a solution of NEt_3 (6 mL) in $CHCl_3$ (15 mL) was added dropwise over 15 min. After stirring for 30 min, the cold bath was removed, with further stirring at room temperature for 2 days. The reaction mixture was poured into dilute HCl solution (200 g) to remove the excess NEt_3. It was extracted with $CHCl_3$ (2 x 75 mL). The combined organic layer was washed with $NaHCO_3$ (5% , 100 mL) and water (100 mL) and dried ($CaCl_2$) After evaporation of the solvent the residue was crystallised from ethanol/CHC_3 to give **19** as white crystals (1.93 g, 9.6 mmol, 66%). M.p. 104-106 °C. ^{1}H-NMR (200 MHz, $CHCl_3$) δ 6.86 (d, J = 10.1 Hz, A part of AB system, olefinic, 2H), 6.74 (s, aromatic, 2H), 5.94 (dt, J= 10.1 and 6.8 Hz, B part of AB system, olefinic, 2H), 3.87 (s, OCH_3, 6H), 2.37 (t,J= 6.8 Hz, methylenic, 2H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 153.3 (C-OMe), 130.0 (C), 129.8 (CH), 126.1 (CH), 109.7 (CH), 58.0 (OMe), 28.5 (CH_2); υ_{max} (KBr) 3016, 2939, 2838, 1596, 1450, 1326, 1257, 1072, 941, 786, 694 cm^{-1}.

1,4-Dimethoxy-5*H*-benzo[*a*]cycloheptene (20): To a stirred solution of **19** (640 mg, 3.17 mmol) in dry THF (30 mL) was added potassium *t*-butoxide (2.0 g, 13.4 mmol) at room temperature, and then the mixture was refluxed for 3 days. It was cooled to room temperature and the solvent was evaporated. After the adding of water (100 mL), the mixture was neutralised with solid NH_4Cl. The mixture was extracted with $CHCl_3$ (3 x 60 mL). The combined organic layer was dried over $CaCl_2$ and the solvent was evaporated. The isomerised cycloheptatriene **20** was obtained (195 mg, 0.97 mmol) in 31% yield. Pale yellow liquid; ^{1}H-NMR (200 MHz, $CHCl_3$) δ 7.46 (d, J = 11.7 Hz, A part of AB system, H_9, 1H), 6.90 (d, J = 8.7 Hz, A part of AB system, aromatic, 1H) 6.69 (d, J = 8.7 Hz, B part of AB system, aromatic, 1H), 6.63 (dd, J= 11.7, 5.1 Hz, B part of AB system, H_8, 1H), 6.17 (dd, J= 9.5, 5.1 Hz, A part of AB system, H_7, 1H), 5.84 (dt, J= 9.5, 6.9 Hz, B part of AB system, H_6, 2H), 3.84 (s, OCH_3, 3H), 3.83 (s, OCH_3, 3H), 3.09 (d,J= 6.9 Hz, methylenic, 1H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 152.8 (C-OMe), 151.4 (C-OMe), 131.0 (CH), 130.0 (CH), 129.6 (C), 129.3 (CH), 128.7 (CH), 128.6 (C), 113.4 (CH), 108.9 (CH), 58.5 (OMe), 57.9 (OMe), 27.5 (CH_2); υ_{max} ($CHCl_3$) 2998, 2941, 2837, 1601, 1470, 1324, 1258, 1093, 965, 797 cm^{-1}.

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