A New Method for the Synthesis of Stipitatic Acid Isomers: Photooxygenation of Ethyl 6*H*-Cyclohepta[*d*][1,3]dioxole-6-carboxylate

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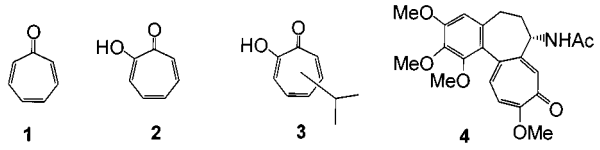
Photooxygenation of the cycloheptatriene derivative **9** gave the bicyclic endoperoxide **14**. Cleavage of the peroxide linkage in **14** with thiourea resulted in the formation of **16**. Treatment of the endoperoxide **14** with a catalytic amount of triethylamine provided a new isomer of stipitatic acid **11**, and **16**. Pyrolysis or the CoTPP (TPP = tetraphenylporphyrin) catalyzed reaction of **14** resulted in the formation of *iso*-stipitatic acid **10**, and **18**.

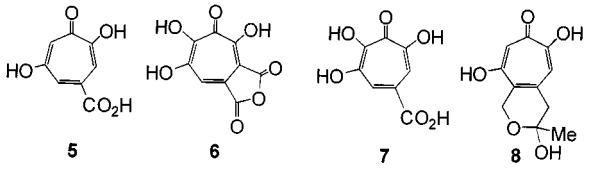
Introduction

A large number and variety of tropone (**1**) and tropolone (**2**) derivatives are found in nature.[1−4] The first naturally occurring monocyclic tropolones, Thujapliscins (isopropyl-substituted tropolones) **3** were isolated from *Cupressaceae*.[5,6] Tropone and tropolone derivatives have drawn considerable interest because of their biological activities. Perhaps the most impressive cases are those of the fungicidal activity of tropolones of *Thuja* trees, which effectively preserve their wood,[7] and the antimitotic activity of colchicine (**4**) and some of its derivatives.[8]



1 **2** **3** **4**

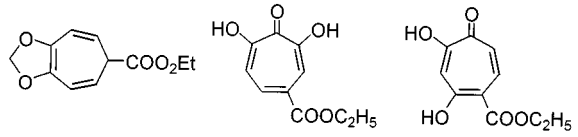
Another class of tropolone derivatives have been found in nature as secondary vegetable metabolites.[9] They include stipitatic (**5**),[10] puberulonic (**6**)[10] and puberulic acids (**7**),[11] as well as spedonin (**8**).[12]



5 **6** **7** **8**

Despite the considerable theoretical, biological and synthetic interest in troponoids, development of general and flexible synthetic routes to these compounds remains a challenging problem. Although the tropones can be oxidized to the tropolones, this approach suffers from problem of regiochemical control when the substituted tropones are used as starting materials.[1,3] A number of syntheses of these tropolone derivatives have been developed. Johnson et al.[10] reported the first synthesis of stipitatic acid **5** and puberulic acid **7**. More recently, Banwell et al.[13] have developed a ten-step synthetic method for **5** and **7** in a fully regiocontrolled manner using *cis*-1,2-dihydrocathechol as the starting material.

In connection with the development of a new synthetic strategy to tropolones, we have studied the applicability of bicyclic endoperoxides. In this present work, we describe the photooxygenation reaction of ethyl 6*H*-cyclohepta[*d*][1,-3]dioxole-6-carboxylate (**9**) and a short and efficient synthesis for the *iso*-stipitatic acid esters **10** and a new isomer of stipitatic acid **11**.



9 **10** **11**

Results and Discussion

The cycloaddition of carbenes to aromatic compounds is an important method for the construction of seven-membered rings and its application to alkoxybenzenes followed by photooxygenation should become a facile method for the synthesis of tropolones. Thus, the $Rh_2(OAc)_4$-catalyzed cycloaddition reaction of 1,3-benzodioxole (**12**) with ethyl diazoacetate affords the cycloheptatriene derivatives **9** and **13** (Scheme 1).[14]

Our synthetic sequence was based on the introduction of the other oxygen functionalities by photooxygenation of the formed cycloheptatriene derivative **9**. Singlet oxygen serves as an important preparative tool for the synthesis of oxy-functionalized organic compounds.[15] For that reason, we investigated the tetraphenylporphyrin-sensitized photooxy-

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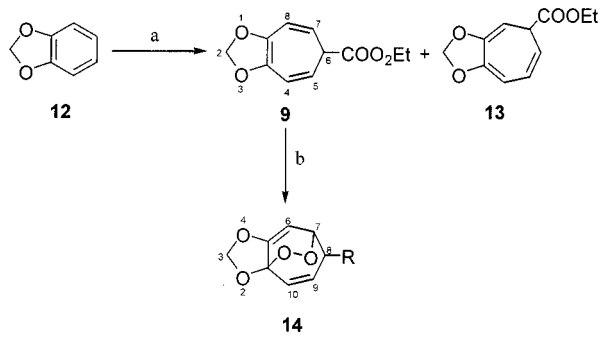
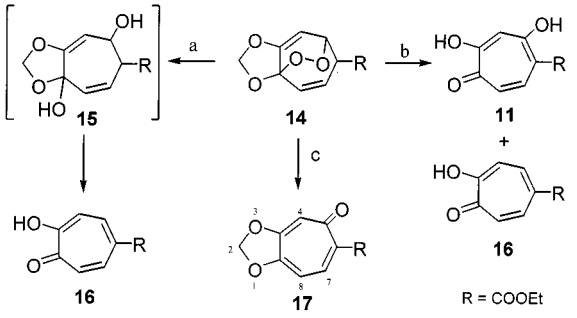


Scheme 1. Reaction of 1,3-benzodioxole **12** with ethyl diazoacetate and photooxygenation: a) N_2CHCO_2Et (EDA), $Rh_2(OAc)_4$, room temp., 40% based on EDA; b) tetraphenylporphyrin, O_2, *hν*, CCl_4, 90%

genation of the cycloheptatriene **9** at room temperature and obtained the bicyclic endoperoxide **14** in 90% yield (Scheme 1). The structural assignments were determined from the ^1H and ^{13}C NMR spectra.

The sensitized photooxygenation of electron-rich olefins constitutes an effective means of preparing 1,2-dioxetanes by [2+2] cycloaddition. During the photooxygenation reaction of **9** we also expected some amount of dioxetane. However, a careful inspection of the reaction mixture did not reveal the formation of any such products.

We therefore turned our attention to the rearrangement reactions of the endoperoxide **14**. It is well established that thiourea reduces oxygen−oxygen bonds to give a diol.[16] When the reduction of endoperoxide **14** with thiourea in methanol was carried out, the tropolone **16** was isolated in 57% yield as the sole product after chromatography and

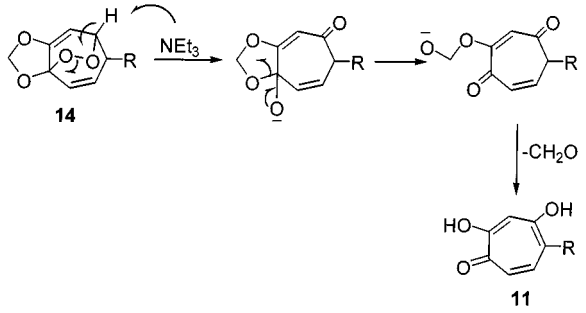


Scheme 2. Some transformations of endoperoxide **14**: a) $(H_2N)_2C=S$, MeOH, room. temp., 50%; b) NEt_3, $CHCl_3$, **11** 57%, **16** 26%; c) SiO_2, $CHCl_3$, room. temp., 25%

crystallization (Scheme 2). The structural assignment of **16** was performed predominantly from its 200 MHz ^1H NMR and 50 MHz ^{13}C NMR spectra. The olefinic protons, as required by the molecule symmetry, resonate as an AX system at δ = 8.17 and 6.83 (J = 12.0 Hz). The ^{13}C NMR spectrum consisting of five sp^2 carbon and two sp^3 (ethyl group) signals is completely in agreement with the proposed structure. For the formation of the symmetric tropolone **16** we assume that the initially formed diol **15** undergoes a ring-opening reaction followed by H_2O elimination to give the tropolone **16** (Scheme 2).

We noticed that the endoperoxide **14** partly rearranged to the troponoid **17** during column chromatography on silica gel. For that reason, compound **14** was treated with silica gel in $CHCl_3$. After 30 min. the rearrangement was complete and, the tropone derivative **17** was isolated in 25% yield from the reaction mixture. It was characterized by its 200 MHz ^1H NMR spectrum (Scheme 2). The vicinal olefinic protons (H_7 and H_8) of **17** resonate as an AX system. The part A of the AX system appears at δ = 7.21 as a doublet (J = 9.6 Hz) and the part X at δ = 6.71, again as a doublet, whereas the olefinic proton H_4 resonates at δ = 6.70 as a singlet. The eleven-line ^{13}C NMR spectrum of **17** supports the suggested unsymmetrical structure. The silica gel presumably acts as an acid to promote the rearrangement.

The base-catalyzed decomposition of unsaturated bicyclic peroxides is a general type of elimination reaction.[16,17] The application of this reaction to the endoperoxide **14** should open up an entry to the synthesis of new hydroxytropolone derivatives. Thus, treatment of the endoperoxide **14** with a catalytic amount of triethylamine at 0 °C provided a new isomeric stipitatic acid **11** and the tropolone **16** (Scheme 2). For this conversion of **14** to **11** we propose the mechanism depicted in Scheme 3. Abstraction of the bridgehead proton by the amine catalyst with concomitant cleavage of the O−O bond, followed by formaldehyde elimination, should generate the unsaturated keto alkoxide, which could then afford the substituted tropolone **11** via a diketone intermediate.

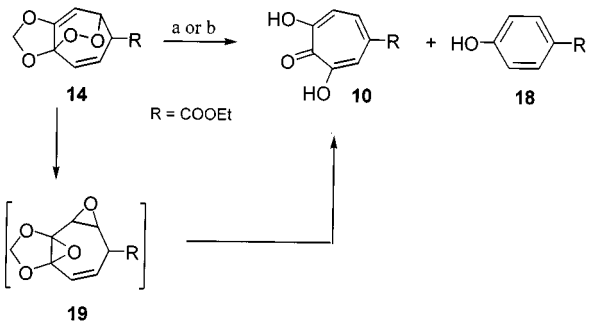


Scheme 3. Base-catalyzed formation mechanism of **11**

To our surprise, the symmetrical tropolone **16** was also formed as the minor product in the base-catalyzed reaction of endoperoxide **14**. Triethylamine acts here as a reducing reagent and reduces the peroxide linkage in **14** to give **15**, which is then transformed into **16**. During our research we have encountered similar cases where triethylamine reduces peroxide bonds.[18]

Next, we investigated the cobalt *meso*-tetraphenylporphyrin-catalyzed (CoTPP) rearrangement of the bicyclic endoperoxide **14**. Foote et al.[19] and our group[20] have reported that CoTPP promotes the catalytic rearrangement of endoperoxides to bis-epoxides. Thus, the endoperoxide **14** was treated with a catalytic amount of CoTPP at low temperature. Chromatography of the reaction mixture provided the *iso*-stipitatic acid ester **10** and compound **18** in yields of 60 and 6%, respectively (Scheme 4). The thermolysis of **14** also

gave the same products **10** and **18** in 46 and 7% yields, respectively. We assume that *iso*-stipitatic acid **10** is formed by the ring opening of the initially formed bis-epoxide **19** under the given reaction conditions.



Scheme 4. Reaction of the endoperoxide **14** a) with CoTPP, CH_2Cl_2, 0 C°; b) CCl_4, 6 h, reflux

In summary, we have developed an efficient three- or four-step synthesis of tropolone derivatives and shown the applicability of the photooxygenation reaction. This method provides sufficient flexibility to allow the incorporation of a variety substituents into the tropolone rings.

Experimental Section

General: All solvents were dried and distilled by standard procedures. Melting points were determined using a capillary melting point apparatus (Thomas−Hoover) and are uncorrected. IR: Perkin−Elmer 377 Infrared recording spectrophotometer. − NMR: Varian Gemini 200 at 200 MHz (^{1}H). Data are reported in δ units with TMS as internal standard. All column chromatography was performed on silica gel (60-mesh, Merck). All substances reported in this paper are in their racemic form.

Ethyl 6*H*-Cyclohepta[*d*][1,3]dioxole-6-carboxylate[14] (9): A solution of ethyl diazoacetate (3.42 g, 0.03 mol) in 1,3-benzodioxole (3.66, 0.03 mmol) was added dropwise during 20 min. to a magnetically stirred solution of 1,3-benzodioxole (**12**) (14.46 g, 0.12 mol) and $Rh_2(OAc)_4{\cdot}2H_2O$ (90 mg, 0.19 mmol) at room temperature. After stirring at reaction temperature for 2 h, unchanged 1,3-benzodioxole (**12**) was removed under reduced pressure. The reaction mixture was then chromatographed on a silica gel column (40 g) and eluted with hexane/ethyl acetate (93:7) to give **9** (colorless liquid, 2.5 g, 40%, yield based on ethyl diazoacetate). − ^{1}H NMR (200 MHz, $CDCl_3$) δ = 6.33 (bd, A part of AX system, $J_{4,5} = J_{7,8}$ = 9.6 Hz, 2 H, 4-H, 8-H), 5.86 (d, A part of AX system, $J_{2,2'}$ = 1.6 Hz, 1 H, 2-H), 5.68 (d, X part of AX system, $J_{2,2'}$ = 1.6 Hz, 1 H, 2′-H), 5.15 (dd, X part of AX system, $J_{4,5} = J_{7,8}$ = 9.6, $J_{5,6} = J_{6,7}$ = 5.9 Hz, 2 H, 5-H, 7-H) 4.27 (q, 2 H, -OCH_2), 2.62 (br. t, $J_{5,6} = J_{6,7}$ = 5.9, 1 H, 6-H), 1.28 (t, 3 H, CH_3). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 174.3, 144.0, 117.4, 112.3, 100.6, 63.2, 47.32, 16.2.

Photooxygenation of Ethyl 6*H*-Cyclohepta[*d*][1,3]dioxole-6-carboxylate (9). Formation of Ethyl 2,4,11,12-Tetraoxatricyclo[5.3.2.0^{1,5}]-dodeca-5,9-diene-8-carboxylate (14): Ethyl 6*H*-cyclohepta[*d*][1,3]-dioxole-6-carboxylate (**9**) (208 mg, 1.00 mmol) and tetraphenylporphyrin (10 mg) were dissolved in 25 mL of CCl_4. The solution was then irradiated with a projection lamp (500 W) while a slow stream of dry oxygen was passed through the solution at room temperature. After a total irradiation time of 30 min., the solvent was evaporated at low temperature (10−20 °C). ^{1}H NMR analysis indicated that the endoperoxide **14** was formed quantitatively. Crystallization of the residue from CH_2Cl_2/ether gave ethyl 2,4,11,12-tetraoxatricyclo[5.3.2.0^{1,5}]dodeca-5,9-diene-8-carboxylate (**14**) as pale yellow crystals (216 mg, 90%; M.p. 90−91 °C): − IR (KBr): ν̃ = 3106, 3029, 2978, 2927, 1727, 1344, 1293, 1268, 1191, 1038, 961, 885 cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.96 (dd, A part of AB system, $J_{9,10}$ = 11.2 Hz, $J_{8,10}$ = 1.8 Hz, 1 H, 10-H), 5.88 (dd, B part of AB system, $J_{9,10}$ = 11.2 Hz, $J_{8,9}$ = 2.7 Hz, 1 H, 9-H), 5.46 (m, 1 H, 6-H), 5.44 (m, 2 H, 3-H), 5.21 (m, 1 H, 7-H), 4.14 (q, J = 7.1 Hz, 2 H, CH_2), 3.34 (m, 1 H, 8-H), 1.19 (t, J = 7.1 Hz, 3 H, CH_3). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 172.0, 158.7, 130.5, 128.3, 103.1, 100.6, 93.6, 80.1, 63.8, 54.4, 16.1. − $C_{11}H_{12}O_6$ (240.1): calcd. C 55.00, H 5.04; found C 55.01, H 5.01

Reaction of Ethyl 2,4,11,12-Tetraoxatricyclo[5.3.2.0^{1,5}]dodeca-5,9-diene-8-carboxylate (14) with Thiourea. Formation of Ethyl 4-Hydroxy-5-oxocyclohepta-1,3,6-triene-1-carboxylate (16): The endoperoxide **14** (185 mg, 0.77 mmol) was dissolved in 25 mL of $CHCl_3$. A solution of thiourea (60 mg, 0.79 mmol) in 5 mL of methanol was then added dropwise in 10 min. After the solution was stirred at room temperature for 2 h, the residue was filtered through silica gel (5 g) eluting with ethyl acetate/hexane (50:50) to give tropolone **16** as pale yellow crystals (85 mg, 57%; M.p. 106 °C) from CH_2Cl_2/hexane. − IR (KBr): ν̃ = 3259, 3029, 3004, 1727, 1625, 1574, 1472, 1370, 1242, 1089, 1012, 885, 782, 731 cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.28 (d, A part of AX system, $J_{2,3} = J_{6,7}$ = 12.0 Hz, 2 H, 2-H and 7-H), 7.37 (d, X part of AX system, $J_{2,3} = J_{6,7}$ = 12.0 Hz, 2 H, 3-H and 6-H), 4.36 (q, J = 7.1 Hz, 2 H, CH_2), 1.38 (t, J = 7.1 Hz, 3 H, CH_3). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 174.7, 167.9, 141.0, 131.0, 124.3, 64.1, 16.3.

Reaction of Ethyl 2,4,11,12-Tetraoxatricyclo[5.3.2.0^{1,5}]dodeca-5,9-diene-8-carboxylate (14) with NEt_3: Triethylamine (1 mL) in 3 mL of $CHCl_3$ was added dropwise during 15 min. to a solution of endoperoxide **14** (240 mg, 1.00 mmol) in 25 mL of $CHCl_3$ at −10 °C. The mixture was then stirred at −10 °C for 1 h and the solvent evaporated. The residue was submitted to column chromatography (silica gel, 50 g) eluting with ethyl acetate/$CHCl_3$ (10:90). Elution gave ethyl 2,4-dihydroxy-5-oxocyclohepta-1,3,6-triene-1-carboxylate (**11**) as the first fraction as pale yellow crystals (105 mg, 50%) after removal of the solvents. − M.p. 145−147 °C from CH_2Cl_2/hexane. − IR (KBr): ν̃ = 3208, 3004, 1702, 1676, 1651, 1625, 1523, 1472, 1421, 1293, 1217, 859, 834 cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.12 (d, part A of AX system, $J_{6,7}$ = 12.8 Hz, 1 H, 7-H), 7.06 (s, 1 H, H_3), 6.87 (d, part X of AX system, $J_{6,7}$ = 12.8 Hz, 1 H, 6-H), 4.44 (q, J = 7.2 Hz, 2 H, CH_2), 1.44 (t, J = 7.2 Hz, 3 H, CH_3). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 179.2, 175.3, 173.7, 166.7, 140.5, 122.5, 112.8, 109.7, 64.8, 16.1. − $C_{10}H_{10}O_5$ (210.2): calcd. C 57.14, H 4.80; found C 56.94, H 4.87.

The second fraction contained ethyl 4-hydroxy-5-oxocyclohepta-1,3,6-triene-1-carboxylate (**16**) (50 mg, 26%).

Reaction of Ethyl 2,4,11,12-tetraoxatricyclo[5.3.2.0^{1,5}]dodeca-5,9-diene-8-carboxylate (14) with SiO_2. Formation of Ethyl 5-Oxo-5*H*-cyclohepta[*d*][1,3]dioxole-6-carboxylate (17): A solution of endoperoxide **14** (480 mg, 2.00 mmol) in 20 mL of $CHCl_3$was loaded onto a silica gel column (40 g) prepared with hexane, and the faucet of column was closed for 30 min. After a total waiting time of 30 min., the faucet of the column was opened and elution was continued with $CHCl_3$ to give **17** as pale yellow crystals (111 mg, 25%). − M.p. 119 °C from CH_2Cl_2/hexane. − IR (KBr): ν̃ = 3412, 3029, 3004, 2978, 1727, 1651, 1580, 1516, 1446, 1401, 1311, 1247, 1170, 1106, 1029, 977, 887, 746, 566 cm^{-1}. − ^{1}H NMR (200 MHz,

$CDCl_3$): δ = 7.21 (d, A part of AB system, $J_{7,8}$ = 9.6 Hz, 1 H, 7-H), 6.71 (s, 1 H, 4-H), 6.38 (d, B part of AB system, $J_{7,8}$ = 9.6 Hz, 1 H, 8-H), 5.99 (s, 2 H, 2-H), 4.29 (q, J = 7.1 Hz, 2 H, CH_2), 1.31 (t, J = 7.1 Hz, 3 H, CH_3). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 182.9, 169.9, 159.2, 158.7, 140.9, 136.0, 118.8, 106.6, 103.0, 63.5, 16.1. – $C_{11}H_{10}O_5$ (222.2): calcd. C 59.46, H 4.54; found C 59.29, H 4.42.

CoTPP-Catalyzed Reaction of Ethyl 2,4,11,12-Tetraoxatricyclo[5.3.-2.0^{1,5}]dodeca-5,9-diene-8-carboxylate (14): Cobalt-*meso*-tetraphenylporphyrin (CoTPP; 20 mg) was added in portions to a magnetically stirred solution of endoperoxide **14** (480 mg, 2.00 mmol) in 15 mL of CH_2Cl_2 at −10 °C. The mixture was then stirred for 30 min. and the solvent evaporated. ^{1}H NMR spectral analysis of the reaction mixture indicated the formation of compounds **10** and **18**. The residue was submitted to column chromatography (silica gel, 5 g) eluting with $CHCl_3$. Elution gave compound **10** as the first fraction as yellow crystals (252 mg, 60%). M.p. 105−107 °C from $CHCl_3$/hexane. – IR (KBr): $\tilde{\nu}$ = 3361, 3285, 3208, 3004, 1727, 1548, 1370, 1319, 1242, 1191, 1038, 782 cm^{-1}. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.31 (d, $J_{2,7}$ = 1.5 Hz, 1 H, 2-H), 8.12 (dd, A part of AX system, $J_{6,7}$ = 10.8 Hz, $J_{2,7}$ = 1.5 Hz, 1 H, 7-H), 7.53 (d, X part of AX system, $J_{6,7}$ = 10.8 Hz, 1 H, 6-H), 4.40 (q, J = 7.2 Hz, 2 H, CH_2), 1.41 (t, J = 7.2 Hz, 3 H, CH_3). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.9, 167.9, 163.6, 160.0, 133.8, 132.0, 122.2, 120.8, 64.4, 16.2. – $C_{10}H_{10}O_5$ (210.2): calcd. C 57.14, H 4.80; found C 57.37, H 4.69.

Further elution with ethyl acetate furnished ethyl 4-hydroxybenzoate (**18**) as pale yellow crystals (20 mg, 6%). – M.p. 109−110 °C from $CHCl_3$/hexane. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.97 (AA′ part of AA′XX′ system, 2 H, aromatic), 6.87 (XX′ part of AA′XX′ system, 2 H, aromatic), 4.35 (q, J = 7.2 Hz, 2 H, CH_2), 1.38 (t, J = 7.2 Hz, 3 H, CH_3). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 168.5, 162.7, 133.8, 125.1, 117.1, 62.7, 16.3.

Thermolysis Reaction of Ethyl 2,4,11,12-Tetraoxatricyclo[5.3.2.0^{1,5}]-dodeca-5,9-diene-8-carboxylate (14): A solution of endoperoxide **14** (480 mg, 2.00 mmol) in 25 mL of CCl_4 was refluxed for 6.5 h. After evaporation of the solvent, the residue was submitted to column chromatography (silica gel, 5 g) eluting with $CHCl_3$. Elution gave compound **10** as the first fraction (193 mg, 46%). Further elution with ethyl acetate furnished ethyl 4-hydroxybenzoate (**18**) (23 mg, 7%).

Acknowledgments

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