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Tetraphenylporphyrins Monosubstituted with Glycerol Diester Units Synthesis and Characterization

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Summary. A novel 1-monoglyceryl ether of 5-(4-hydroxyphenyl)-10,15,20-tritolylporphyrin and related diacid esters with very high solubility in hydrophobic solvents were synthesized.

Keywords. Tetraphenylporphyrine; Glycerol ethers; Tetraphenylporphyrineglycerol; 1,2-Diacylglycerols.

Glycerindiester-monosubstituierte Tetraphenylporphyrine. Synthese und Charakterisierung

Zusammenfassung. Es wurde ein neuer 1-Monoglycerylether von 5-(4-Hydroxyphenyl)-10,15,20-tritolylporphyrin und verwandte Disäuren-ester mit hoher Löslichkeit in hydrophoben Lösungsmitteln synthetisiert.

Introduction

Great interest in the chemistry of porphyrins and their biological activity has been demonstrated in many papers. A lot of porphyrins, containing units arising from nature have been obtained as synthetic model compounds for biological interactions. For example, the porphyrin-adenine derivatives were obtained as synthetic model compounds for basic investigations on interactions between nucleic acid and hematoporphyrin [1] and the carotenoid porphyrin-quinone derivatives as synthetic model for the electrical photoconduction properties on both sides of bilayer lipid membranes [2]. Furthermore, porphyrins substituted with monosaccharides [3], with nucleoside units uridine or adenosine [4], or with a steroid unit [5] have been reported in the literature.

This communication describes for the first time the synthesis of derivatives of tetraphenyl porphyrin with a glycerol unit substituted to one phenyl fragment in *para*-position by ether-linkage and their diacid esters. These compounds are precursors for porphinatometal derivatives which increase the compatibility with hydrocarbons and lipids.

Results and Discussion

The monoglyceryl-porphine ether was prepared by a conventional method with the use of isopropylidene glycerol tosylate as intermediate in the way shown in the formula scheme.

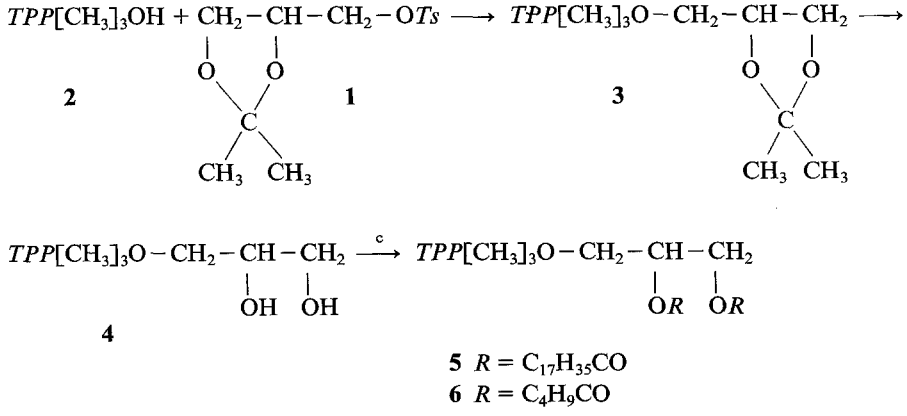
Tosyl glyceride **1**, porphyrine **2** and sodium hydride were mixed in *DMF* at room temperature for 20 hours. The crude product **3** was chromatographed on silica using chloroform as eluent. Isopropylidene derivative **3** was hydrolyzed with HCl in methanol to give the porphyrin glycerol ether **4**. Acylation of the glycerol hydroxy groups using stearoyl chloride or valeryl chloride in benzene in the presence of pyridine yielded the desired mono-acid diesters of glycerol ether, **5** and **6**, which were purified on silica by column chromatography using methylene chloride as eluent. The yields were ca. 10% based on **2**.

All porphyrins **2**–**6** exhibited high solubility in CH_2Cl_2 and $CHCl_3$, but only **3** and the diester derivatives were soluble in hydrophobic solvents like petroleum ether, hexane or decane. The products had different properties in the steps reactions, changing from hydrophilic to hydrophobic and vice versa. Therefore the synthetic way could be followed conveniently by TLC.

All compounds **2**–**6** were identified by means of their mass spectra, visible spectra and ^{1}H-NMR spectra.

In the mass spectra (LSIMS technique) the prominent ions correspond to the protonated compound **4** at *m/z* 747, the diprotonated compound **5** at *m/z* 1 280 and the protonated compound **6** at *m/z* 915. The electronic absorption spectrum of the linked porphyrin glycerol derivative **4** shows, in the visible region, the characteristic porphyrin pattern of four Q bands (654, 598, 559, and 522 nm) in addition to the Soret band absorption (423 nm). All bands in the spectra of compounds **3**, **5**, and **6** are very similar to the spectrum of **4**.

The absorption spectra of the metallated porphyrins **2**–**6** are characteristic for metallated tetratolylporphyrin. The ^{1}H-NMR spectra of the new compounds measured in $CDCl_3$ show the presence of the expected protons, in agreement with the



TPP[CH_3]$_3$OH = 5-(4-Hydroxyphenyl)-10,15,20-tritolylporphyrine

a: NaH, *DMF*; b: HCl, *Me*OH; c: *R*COCl, C_6H_6, r.t.

proposed structures. The highly shielded protons on the porphyrin nitrogen atoms in **4** appear at −2.77. The pyrrole β-hydrogen protons are magnetically non-equivalent (centered at 8.85 ppm). The tolyl ring protons are visible as an AA'BB' system at 8.09 and 7.54 ppm (J = 7.8 Hz) and the corresponding methyl groups are at 2.69 ppm. Two other complex signals, centered at 4.29 and 3.95 ppm, were assigned to the protons of the glycidyl group. The hydroxy protons are observed clearly at 1.55 ppm. The spectrum of compound **5** shows bands centered at 1.25, 2.28, and 3.30 ppm, corresponding to the protons of the heptadecan chain (0.95, 1.44, 1.66, and 2.43 for **6**, protons of the butyl chain). Additional ^{1}H-NMR date for **3**, **5**, and **6** are presented in experimental section.

In summary, we have developed a synthetic route to the ether linked porphyrin-glycerol compounds. These compounds and their metallated derivatives may allow to prepare new functionalized materials important for material science.

Experimental Part

All reagents were used without further purification. Column chromatography was performed on silica gel Kieselgel 100 − 70 − 230 mesh (Merck). The ^{1}H-NMR spectra were recorded on a Varian VXR 300 spectrometer, chemical shifts in δ/ppm ($CDCl_3$/*TMS*). Electronic spectra were recorded on a Specord UV-VIS (Carl Zeiss-Jena) spectrophotometer in CH_2Cl_2 solutions. Mass spectrometry was performed on a LSIMS(+) model AMD 604 (AMD Intectra) spectrometer (NBA matrix).

Starting Materials

D,L-1,2-Isopropylideneglycerol [6], *D,L*-2,3-isopropylideneglycerol tosylate [7], and 5-(4-hydroxyphenyl)-10,15,20-tritolylporphyrine [8] were prepared by procedures described earlier.

D,L-1,2-O-Isopropylidene-3-O-(5-p-phenylene-10,15,20-tritolylporphyrin)glycerol (**3**)

A suspension containing sodium hydride 0.12 g (5 mmol), 1.34 g (2 mmol) of **2** and 0.58 g (2.5 mmol) of **1** in N,N-dimethylformamide (80 ml) was stirred at room temperature for 20 h. Then the mixture was diluted with water (200 ml) and extracted five times with hot benzene (tot. 500 ml). The extracts were washed with water, dried with anh. $MgSO_4$ and evaporated under reduced pressure. The product was purified by chromatography on a silica gel column using chloroform as eluent to give in the first fraction the product **3**, and in the second fraction unreacted **2**. Yield 1.1 g (70%). MS (m/z): 787 ($M+H^+$). UV (CH_2Cl_2): λ_{max} 424, 523, 559, 599, 657; **3**-Zn derivative: 425.5, 563, 604 nm. ^{1}H-NMR (δ): 8.85 (bs, 8 H, β-pyrrole), 8.07 and 7.49 (dd, 12 H, J = 7.8 Hz, tolyl), 8.09 and 7.21 (dd, 4 H, J = 8.4 Hz, phenylene), 4.60 (q, 1 H, C−H glycerol), 4.26 − 3.99 (m, 4 H, CH_2 glycerol), 2.65 (s, 9 H, CH_3), 1.54 (s, 3 H, CH_3), 1.46 (s, 3 H, CH_3), −2.73 (s, 2 H, NH).

D,L-1,2-O-(5-p-phenylene-10,15,20-tritolylporphyrin)glycerol (**4**)

The protective isopropylidene group of compound **3** was removed with hydrochloric acid in methanol. To the stirred suspension of 0.79 g (1 mmol) of **3** in methanol (200 ml) 1 ml of conc. HCl was added. The green solution was allowed to stand at room temperature for two days, and than methanol was removed by evaporation under reduced pressure. The crude product was dissolved in chloroform, washed with aqueous saturated sodium bicarbonate and water and dried with anhydrous $MgSO_4$. The chloroform was partially removed and the residue was put on top of silica gel column. This column was washed with chloroform to remove traces of unreacted **3**. The fraction of **4** was eluted with chloroform : methanol = 10 : 1 (v/v). After rotatory evaporation, 0.6 g (76%) of product was

obtained. The product was used for the following reaction without further purification. MS (*m/z*): 747 ($M+H^+$). UV (CH_2Cl_2): λ_{max} 424, 522, 559, 598, 654; **4**-Zn derivative: 428, 564, 605 nm. ^{1}H-NMR (δ): 8.85 (m, 8 H, β-pyrrole), 8.09 and 7.54 (dd, 12 H, $J=7.8$ Hz, tolyl), 8.13 and 7.28 (dd, 4 H, $J=8.4$ Hz), 4.29 (m, 3 H, glycerol), 3.95 (m, 2 H, glycerol), 2.69 (s, 9 H, CH_3), 1.55 (bs, 2 H, OH), −2.77 (bs, 2 H, NH).

D,L-1-O-(5-p-phenylene-10,15,20-tritolylporphyrin)-2,3-distearoylglycerol (**5**)

Compound **4** (0.37 g, 0.5 mmol) was dissolved in dichloromethane (5 ml). Stearoyl chloride (0.45 g, 1.5 mmol) and two ml of pyridine were added. This mixture was allowed to stand at room temperature for 24 h. The solution was diluted with dichloromethane and washed with water (5−6 times) and dried with anhydrous $MgSO_4$. After evaporation of the solvent under reduced pressure, the residue was purified by chromatography on silica gel column using chloroform as eluent to give the product **5**. Yield 0.12 g (ca. 20%). MS (*m/z*): 1 280 ($M+2H^+$). UV (CH_2 Cl_2): λ_{max} 423, 522, 559, 597, 655; **5**-Zn derivative: 428, 557, 604 nm. ^{1}H-NMR (δ): 8.84 (m, 8 H, β-pyrrole), 8.09 and 7.55 (dd, 12 H, $J=7.8$ Hz, tolyl), 8.12 and 7.32 (dd, 4 H, $J=$ca. 9 Hz, phenylene), 4.40 and 3.70 (ms, 5 H, glycerol), 3.30, 2.28, and 1.25 (ms, 70 H), −2.78 (bs, 2 H, NH).

D,L-1-O-(5-p-phenylene-10,15,20-tritolylporphyrin)-2,3-divalerylglycerol (**6**)

Compound **6** was prepared from **4** and valeryl chloride by a similar procedure to that describe above. Yield ca. 30%. MS (*m/z*): 915 ($M+H^+$). UV (CH_2Cl_2): λ_{max} 425, 524, 561, 600, 659 nm. ^{1}H-NMR (δ): 8.85 (m, 8 H, β-pyrrole), 8.09 and 7.56 (dd, 12 H, $J=7.8$ Hz, tolyl), 8.12 and 7.27 (dd, 4 H, $J=$ca. 9 Hz, phenylene), 5.61 (m, 1 H, CH glycerol), 4.62 (m, 2 H, CH_2 glycerol), 4.42 (d, 2 H, CH_2 glycerol), 2.70 (s, 9 H, CH_3), 2.43, 1.66, 1.44, and 0.95 (ms, 18 H), −2.77 (bs, 2 H, NH).

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