The First Tetra(meso-aryl)porphyrin with Isobornyl Substituents

Dmitry V. Belykh, Tatiana K. Rocheva, Evgeny V. Buravlev, Irina Yu. Chukicheva, and Alexander V. Kutchin

Institute of Chemistry, Komi Scientific Centre of Ural Division of Russian Academy of Sciences, 167982 Syktyvkar, Russia

 Corresponding author E-mail: belykh-dv@mail.ru

The first example of tetra(meso-aryl)porphyrin bearing isobornyl substituents was synthesized by tetrapyrrole condensation from 4-hydroxy-3,5-diisobornylbenzaldehyde and pyrrole.

Keywords: Tetrapyrrole condensation, tetra(meso-aryl)porphyrin, isobornyl substituents, atropoisomers.

Introduction

In recent years, much attention is paid to the synthesis of hybrid antioxidants. In this respect the combination of alkyl phenol units with porphyrin macrocycle is rather promising.1-3 Introduction of several sterically hindered phenol fragments to the periphery of the porphyrin macrocycle can lead to increased antioxidant activity, due to inhibition activity of phenolic moieties in respect to free radicals, and ability of the porphyrin itself to interact with free radicals and oxygen.4-7 It is known that isobornylphenols possess membrane-protecting properties8 and can be used as bio- and technical antioxidants.9 Therefore, the synthesis of porphyrin macrocycles with such substituents is of interest for the synthesis of hybrid antioxidants. In addition, isobornylphenyls exhibit anti-inflammatory and hemorheological activity10-13 what allows to consider isobornylphenolic fragment as a potential pharmacophore group. In this regard, the introduction of these fragments to the periphery of the porphyrin macrocycle is promising in terms of obtaining new biologically active substances. Thus, the synthesis of hybrid molecules, containing porphyrin macrocycle and the fragments of terpenophenols, is of a great interest.

Here we report on the synthesis of the first tetra(meso-aryl)porphyrin with isobornyl substituents in the aromatic rings by tetrapyrrole condensation of 4-hydroxy-3,5-diisobornylbenzaldehyde with pyrrole (Scheme 1).

Experimental

IR spectra were recorded on FT-IR spectrometer in tablets with KBr. Electronic absorption spectra (UV-vis) were recorded on a Shimadzu UV-1700 spectrophotometer in 10 mm quartz cuvettes with KBr. Electronic absorption spectra (UV-vis) were recorded on a Bruker Avance II NMR spectrometer in tablets (the operating frequency of 2012 5(2) 121-124 462.0, 424.5, 418.5. m/z (MALDI): 1768.265 (MH+), calculated 1768.236. H NMR (CDCl3) δ ppm: -2.65 (2H, br s, NH), 0.92 (24H, br s, C10,10'H3), 0.99/1.00/1.02* (24H, s, C9,9'H3), 1.18 (24H, s, C8,8'H3), 1.37-2.06 (48 H, m, H3,3'), 3.00 (2H, t, H2,2'), 3.39 (8H, s, OH), 8.81/8.83/8.85/8.89* (8H, s, H5,5').

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Scheme 1.

Figure 1. $^1$H NMR spectrum of compound 3 in CDCl$_3$. 

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Results and Discussion

4-Hydroxy-3,5-diisobornylbenzaldehyde 2 was received by oxidation of methyl group in compound 1 with bromine in tert-butanol by the procedure described for the synthesis of 4-hydroxy-3,5-di-tert-butylbenzaldehyde.\textsuperscript{[14]} Tetrapyrrrole condensation with the aldehyde 2 was carried out by a procedure similar to the synthesis of tetra(meso-phenyl)porphine – in boiling propionic acid at large dilution with following slow oxidation by atmospheric oxygen.\textsuperscript{[15]} The structure of the obtained porphyrin 3 was confirmed by NMR, UV-vis and IR spectroscopy and mass spectrometry. The mass spectrum of the compound contains peak with m/z = 1768.265, corresponding to the protonated molecular ion [MH⁺]. \textsuperscript{1}H NMR spectrum of product 3 contains well resolved signals of the proton of porphyrin macrocycle (the signals corresponding to pyrrolic Hβ protons at 8.95-8.70 ppm and a broadened singlet, corresponding to the protons of the inner NH groups at -2.65 ppm), and the signals of protons in the terpenophenol groups (the singlets, corresponding to H14,16 protons at 8.08-8.09 ppm and to hydroxyl group protons at 5.23 ppm, as well as multiplets of terpene substituents in the 3.4-0.8 ppm region) (Figure 1).

The ratio of integrated intensities of signal belonging to protons of the porphyrin macrocycle and terpenophenol substituents corresponds to the expected for tetrasubstituted macrocycle. The formation of the porphyrin macrocycle was also confirmed by UV-vis spectroscopy: the electronic absorption spectrum contains the Soret band and the bands characteristic of the tetra-meso-substituted porphyrin chromophore in the visible region.

It is known, that for meso-arylporphyrins, atropoisomerism is possible in the case of hindered rotation of the aryl substituents.\textsuperscript{[16]} Very likely, the similar atropoisomerism is realized in the case of porphyrin 3, in which disobornyphenol substituents are quite large and create a difficulty in rotation around the bonds C15-Cmeso. Possible atropoisomers (A-D) of the compound 3 are schematically shown in Figure 2.

The presence of atropoisomers is confirmed by NMR spectroscopy. In the \textsuperscript{1}H NMR spectrum of compound 3 the signals corresponding to pyrrolic Hβ protons of each of the four atropoisomers are observed; a small splitting is seen also for the signals of H14, H16 and OH protons (Figure 1). In addition, a broadening of the signals of the other protons could also be due to small deviations of the spectral characteristics of different atropoisomers.

Conclusion

Thus, in this paper we propose a simple method for the synthesis of tetra(meso-aryl)porphyrin with diisobornyphenol substituents on the basis of 4-hydroxy-3,5-diisobornylbenzaldehyde by tetrapyrrrole condensation.

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Figure 2. Possible atropoisomers of the compound 3.
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References


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