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研究论文

3-位长链烷基双(单)取代焦脱镁叶绿酸-a甲酯的合成

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摘要 以焦脱镁叶绿酸-a甲酯(**1**)为起始原料, 通过E环保护和3-位乙烯基的氧化反应得到卟吩醛**2**, 与长链烷基溴化镁的Grignard反应将3-位甲酰基转化为1-羟长链烷基, 选用TPAP和*N*-甲基吗啉*N*-氧化物混合氧化剂对卟吩仲醇**3**的羟基进行氧化, 生成3-位烷酰基焦脱镁叶绿酸-a衍生物**4**, 再与长链烷基溴化镁进行Grignard反应, 得到亲核加成产物卟吩叔醇**5**和还原产物**3**; 以对甲苯磺酸催化, 卟吩醇**3**和**5**在干燥苯中回流脱水, 分别给出反式结构的3-位长链烷基单或者双取代的焦脱镁叶绿酸-a甲酯衍生物**6**和**7**. 所合成的叶绿酸衍生物均经UV, IR, ^{1}H NMR及元素分析证明其结构.

关键词 叶绿素衍生物 焦脱镁叶绿酸-a甲酯 Grignard反应 光动力疗法

分类号

Synthesis of Methyl Pyropheophorbide-a Substituted with Mono(di)-long Chain Alkyl Group at 3-Position

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Abstract From methyl pyropheophorbide-a (**1**), the aldehyde chlorin **2** was obtained by the protecton of ring-E and oxidation of vinyl group at 3-position. Grignard reaction with long chain alkyl magnesium bromide converted the formyl group into the acyl group. The hydroxyl group of *sec*-alcohol chlorin **3** was oxidized by mixed oxidizing agent consisting of tetrapropylammonium perruthenate and *N*-methylmorpholine *N*-oxide to generate 3-acyl pyropheophorbide-a derivative **4**. The Grignard reaction of which with long chain alkyl magnesium bromide was carried out to yield tertiary alcohol chlorin **5** as nucleophilic adduct and chlorin **3** as reduced product. The following dehydration of alcohol chlorin **3** or **5** was performed in the dry benzene at reflux to form *trans*-form methyl pyropheophorbide-a substituted with mono- or di-long chain alkyl group at 3-position **6** or **7**, respectively. The structures of all new compounds were characterized by elemental analysis, UV, IR and ^{1}H NMR spectra.

Key words chlorophyll derivative methyl pyropheophorbide-a Grignard reaction photodynamic therapy

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