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단신

PCDA가 부착된 새로운 탄수화물 유도체 합성에 관한 연구

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Synthesis of New PCDA-Carbohydrate Derivatives

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주제어: 글루코즈-PCDA-아마이드, 갈락토즈-PCDA-아마이드, 다이아세틸렌 보호기제거, 바이오센서

Keywords: Glucose-PCDA amide, Galactose-PCDA amide, Diacetylene, Deprotection, Biosensor

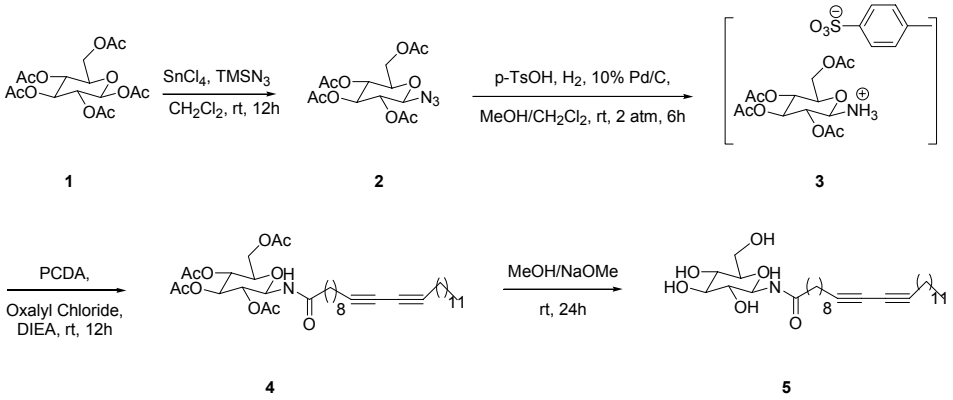
INTRODUCTION

Carbohydrates constitute a large and diverse class of compounds present in varied materials and have major roles in applications in chemistry, biology, material science and related fields. In the context of biological systems, in particular, carbohydrate research has emerged as the "new frontier" for elucidating fundamental biochemical processes and for identifying new pharmaceutical substances.

Polyacetylene based sensor systems are unique because of blue to red color transitions due to their polymerized diacetylene unit.[1-10] It is well known that the spacially aligned monomeric diacetylene moieties undergo photo polymerization process *via* a 1,4-addition mechanism and form conjugated chains that give the molecule a significant color change.[11] Due to this unique color change, efforts have been devoted to develop efficient sensor systems based on the polyacetylenes.[12,13] Our plan is devising PCDA (10,12-pentacosadynoic acid) biosensor, which is tagging carbohydrates with PCDA dye.

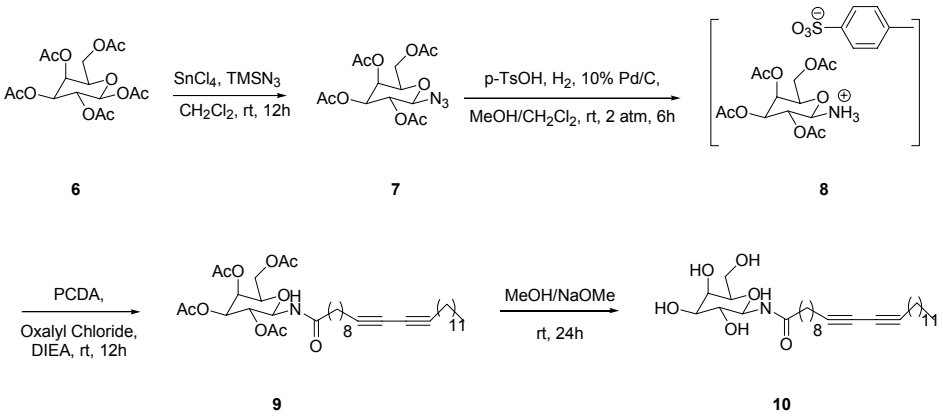
RESULTS AND DISCUSSION

Commercially available β-D-glucose pentaacetate (**1**) was transformed into corresponding β-azide **2** by the known method.[14] β-D-glucose pentaacetate azide (**2**) was reduced with *p*-toluenesulfonic acid to get carbohydrate p-TSA ammonium salt **3** in good yield. The crude 10,12-pentacosadynoyl chloride which was inturn prepared from the PCDA and oxalyl chloride was react with compound **3** to get the glucose acetate derivative **4** with PCDA tail.[15] The compound **4** has undergone deprotection reaction with methanol



1 **2** **3** **4** **5**

***Scheme* 1**



Scheme 2

and sodium methoxide to get the carbohydrate-PCDA amide **5** with 55% yield (*Scheme* 1).

Similarly, Galactose-PCDA amide **10** was synthesized by the deprotection of galactose pentaacetate-PCDA amide[15] **9** with 45% yield (*Scheme* 2).

Herewith we have prepared precursors of dye labeled carbohydrate ligands which will be tested as a new biosensor. Further studies of biosensing living cell systems such as Concanavalin A[16] or tumour cells are now on going and will be discussed soon.

EXPERIMENT

General procedure for the preparation of β-D-glucose-PCDA amide 5 and β-D-galactose-PCDA amide 10.

Compound (**4** and **9**) (each 0.07 mmol) was taken in a schlenk flask and added 1.6 mL of MeOH and 0.6 mL of NaOMe under nitrogen atmosphere. The reaction mixture was kept for stirring at room temperature. After 24 h, Amberlist IR-120 resin was added at the pH range 5 to 6. The resin was removed by aspiration and MeOH was evaporated under reduced pressure and dried. The crude compound was subjected to short column chromatography (Dichloromethane/Methanol 3:1) to get the products **5** and **10** respectively.

Spectral data.

β-D-Glucose-PCDA amide 5: Purple solid (yield 55%), m.p., 41 - 43 ^{o}C; IR (KBr) cm^{-1}: 3251, 2921, 2850, 1672, 1534, 1219, 1021; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.00 (d, J = 9.8 Hz, 1H), 4.09 (dd, J = 10.1, 9.6 Hz, 1H), 4.28 (t, J = 9.8 Hz, 1H), 4.11 (dd, J = 12.3, 4.1 Hz, 1H), 3.95 (dd, J = 12.4, 1.5 Hz, 1H), 3.50 (m, 1H), 2.17 (t, J = 7.2 Hz, 3H), 1.90-1.30 (m, 36H), 0.95 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.3, 78.2, 77.6, 77.3, 73.0, 62,4, 36.8, 32.4, 30.1, 29.9, 29.7, 29.1, 28.9, 28.8, 28.8, 28.7, 28.7, 28.3, 28.3, 28.2, 28.1, 28.0, 28.0, 24.5, 19.8, 14.5.

β-D-Galactose-PCDA amide 10: Colorless oil (yield 45%); IR (KBr) cm^{-1}: 3263, 2925, 2835, 1700, 1533, 1277; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.37 (d, J = 9.5 Hz, 1H), 5.45 (d, J = 2.4 Hz, 1H), 5.28 (t, J = 9.2 Hz, 1H), 5.13 (m, 1H), 4.08 (m, 3H), 2.22 (t, J = 7.0 Hz, 3H), 2.16 (m, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.00 (s, 3H), 1.7-1.2 (m, 36H), 0.89 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.8, 79.9, 77.7, 77.3, 73.4, 62,2, 37.1, 32.4, 30.1, 29.8, 29.7, 29.0, 28.9, 28.8, 28.8, 28.8, 2876, 284, 28.3, 28.2, 28.1, 28.0, 28.0, 24.4, 20.0, 14.9.

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