19. Inveastigation And Nanopartical Synthesis of 2-S-Hepta-O-Benzoyl- B -D-Maltosyl-1-Aryl-5-Tetra-O-Acetyl- B -D-Glucosyl-2-Isothiobiurets

Ashish G. Sarap
Department of Chemistry, Shri R. L. T. College of Science, Akola.
P. T. Agrawal
Department of Chemistry, Shri R. L. T. College of Science, Akola.

Abstract

Nanoparticles-based chemical reaction are emerging as alternative to bulk material based chemical reaction Due to their various advantages such as partials are converted into nano dimension enhance chemical activities and photochemical stability and ease of introduction of multifunctionality. In this work we propose 2-S-hepta-O-benzoyl-β-D-maltosyl-1-aryl-5-tetra-O-acetyl- β -D-glucosyl-2-isothiobiurets have been synthesized for the first time by the interaction of S-hepta-O-benzoyl- β -D-maltosyl-1-aryl-isothiocarbamides and tetra-O-acetyl- β -D-glucosyl isocyanate. All the synthesized compounds were characterized on the basis of elemental analysis and XRD studies. The polarimetric study of the title compounds has been carried out.

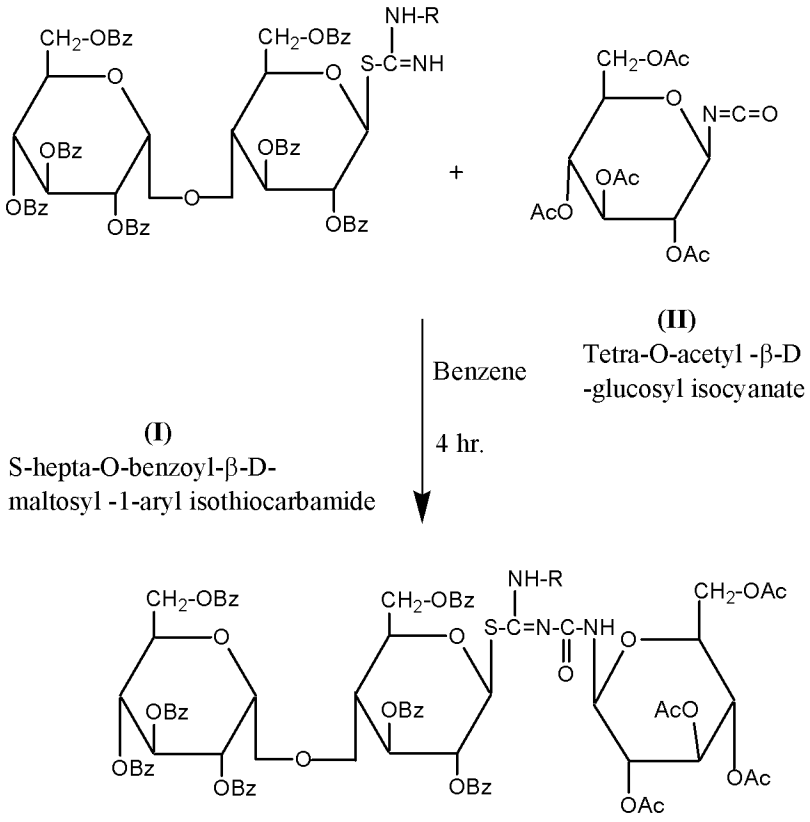
Introduction

Carbohydrates comprise more than 80% of biomass, making them the most abundant class of biopolymers on earth. They mainly serve energy storage and structural functions. Recently, the regulatory role of carbohydrates in several biological processes has become evident [1]. Despite the challenges, carbohydrates remain an exciting substrate for biomaterial applications, due to their biological relevance and tendency to form supramolecular networks.

Here, we review the recent progress in the field of carbohydrate-based nanomaterials. There have been several reports of S-glucosylated isothiobiurets with possible microbial activity [2]. S-tetra-O-benzoyl-D-glucopyranosyl-1-aryl isothiocarbamides and phenyl isocyanate [3] interacted to create these isothiobiurets. The synthesis of N and S-linked bis lactosyl isothiobiurets has also recently been conducted in our lab. This involves the interaction of hepta-O-acetyl-† β -D-lactosyl isocyanate[4] with S-hepta-O-acetyl-β -D-lactosyl-1-aryl-isothiocarbamides. It has also been shown recently that a number of lactosyl isothiocarbamides and lactosyl isocyanate generate matching lactosyl monothio and dithiobiurets [5-6]

In synthetic carbohydrate chemistry, glycosyl isocyanates such as isothiocyanate[7] and glycocynate play a crucial role. Glycosyl isocyanate has been used to create a wide range of chemicals, including galactosyl amino derivatives, glycosyl isocyanide, and other heterocycles [8].However, there is no information available on the synthesis of isothiobiurets with a β-glucosyl substituent. It was rather intriguing to synthesise some novel Nglucosylated thioamides based on the information obtained from the work done on Nglucosylated isomonothio and dithiobiurets[9–10].

Reaction Scheme



(III)
2-S-hepta-O-benzoyl-β-D-maltosyl -1aryl-5-tetra-O-acetyl-β-D-glucosyl -2-isothiobiurets

Where, R = a) phenyl, b) o-Cl-phenyl, c) m-Cl-phenyl, d) p-Cl-phenyl, e) o-tolyl, f) m-tolyl, g) p-tolyl

Ac = $COCH_3$

Bz = COC_6H_5

Result and Discussion

Nanoparticals A sub-classification of ultrafine particle with lengths in two or three dimensions greater than 0.001 micrometer (1 nanometer) and smaller than about 0.1 micrometer (100 nanometers) and which may or may not exhibit a size-related intensive property. This term is a subject of controversy regarding the size range and the presence of a size-related property. Current usage emphasizes size and not properties in the definition. The length scale may be a hydrodynamic diameter or a geometric length appropriate to the intended use of the nanoparticle. The European community has discussed the topic and issued a document Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR) that offers a more complex approach. Chemistry of sugar isothiocyanate with special reference to their utility as intermediate in the synthesis of nitrogen and sulphur containing open chain and cyclic compounds has been investigated by earlier workers. It appeared quite interesting to prepare nanoparticals of carbohydrate related compounds, by the extension of already known methods and to investigate the chemistry of these new related compounds with reference to their synthetic application, towards medicinal chemistry.

The interaction of other S-hepta-O-benzoyl- β -D-maltosyl-1-aryl isothiocarbamides and Tetra-O-acetyl- β -D-glucosyl isocyanate was carried out the related 2-S-hepta-O-benzoyl- β -D-maltosyl-1-aryl-5-tetra-O-acetyl- β -D-glucosyl-2-isothiobiurets.

Experimental

1. Preparation of S-hepta-O-benzoyl- β -D-maltosyl-1-aryl isothiocarbamides

The isopropanolic suspension of hepta-O-benzoyl-α-D-maltosyl bromide (0.001 M, 11.3 g in 30 ml) was mixed with suspension of Phenyl thiocarbamide (0.001 M, 1.5 g in 10 ml). This mixture was warmed over water bath at 70°C until the clear solution was obtained. The clear solution was kept at room temperature for 18 hr. It was then mixed with water (100 ml). When small quantity of semi-solid mass was separated. The semi-solid mass was then triturated with petroleum ether was converted into solid. It was identified as unreacted phenyl thiocarbamide. The aqueous solution when rendered basic with ammonia a sticky mass was separated out which was not solidified on standing for several hours. The sticky mass was failed to afford a solid when triturated several times with petroleum ether (60-80°). The sticky mass was purified by ethanol-water and solid was obtained, m.p. 156-158°C

2. Synthesis of 2-S-hepta-O-benzoyl- β -D-maltosyl-1-phenyl-5-tetra-O-acetyl- β -D-glucosyl-2-isothiobiuret

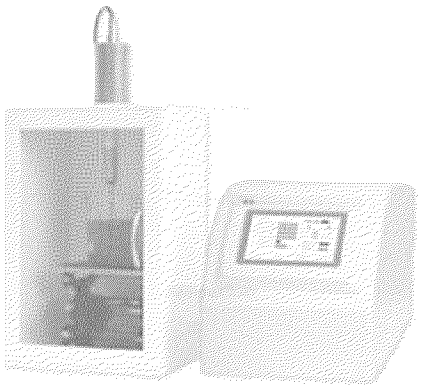
Benzene solution of tetra-O-acetyl- β -D-glucosyl isocyanate (0.005 M, 1.9 g in 20 ml) was added to benzene solution of S-hepta-O-benzoyl- β -D-maltosyl-1-phenyl isothiocarbamide

(0.005 M, 6.0 g in 10 ml) and reaction mixture was refluxed over boiling water bath for 4 hr. Afterwards, solvent benzene was removed by distillation and resultant syrupy mass was triturated several times with petroleum ether, a granular solid was obtained, crystallized from ethanol-water, m.p. 135-137°C. [Found: C, 63.05; H, 4.60; N, 2.55; S, 2.10, $C_{83}H_{75}O_{27}N_3S$ requires; C, 63.15, H, 4.75; N, 2.66, S, 2.02%].

The product was soluble in ethanol, acetone, chloroform and benzene while insoluble in water and petroleum ether. It charred on heating with conc. sulphuric acid. It was found non-desulphurisable when boiled with alkaline plumbite solution. The product was optically active and its specific rotation was found to be $[\alpha]_D^{30}$ = -152° (c, 0.90 in chloroform). The purity of the product was checked by TLC, Rf Value 0.90 ($CHCl_3$: EtOAc, 3:2).

3. Preparation of Nanoparticles of 2-S-hepta-O-benzoyl- β -D-maltosyl-1-phenyl-5-tetra-O-acetyl- β -D-glucosyl-2-isothiobiuret

Take about 1 gm of 2-S-hepta-O-benzoyl- β -D-maltosyl-1-phenyl-5-tetra-O-acetyl- β -D-glucosyl-2-isothiobiuret and dissolve it completely in the 50ml of solvent in 250 ml beaker. Now put this beaker in sonicator. The highly penetrating acoustic waves are passed through mixture, which create high pressure bubbles in the beaker due to which breakdown of the bulk material is takes place and desired sized nanoparticles are formed. The size determination of nanoparticlesis done by the X-ray diffraction studies



Characterization of Nanoparticles

1. Characterization using UV-Spectrophotometer: Single Beam UV-Spectrophotometer with software BI/CI/SP/SB-S-03 of Bio Era make. The UV-Visible Spectroscopy reveals the formation of Nanoparticles Characterization of Nanoparticles was done using visible Spectrophotometer by using model by showing different absorption those from bulk material. 2. Size determination of 2-S-hepta-O-benzoyl- β -D-maltosyl-1-phenyl-5-tetra-O-acetyl- β -D-glucosyl-2-isothiobiuret. Nanoparticles by X-ray Diffraction studies: From the X-ray diffraction

it comes to know that size of nano 2-S-hepta-O-benzoyl- β -D-maltosyl-1-phenyl-5-tetra-O-acetyl- β -D-glucosyl-2-isothiobiuret is 74.2 nm. **(by Scherrer Equation Method).**

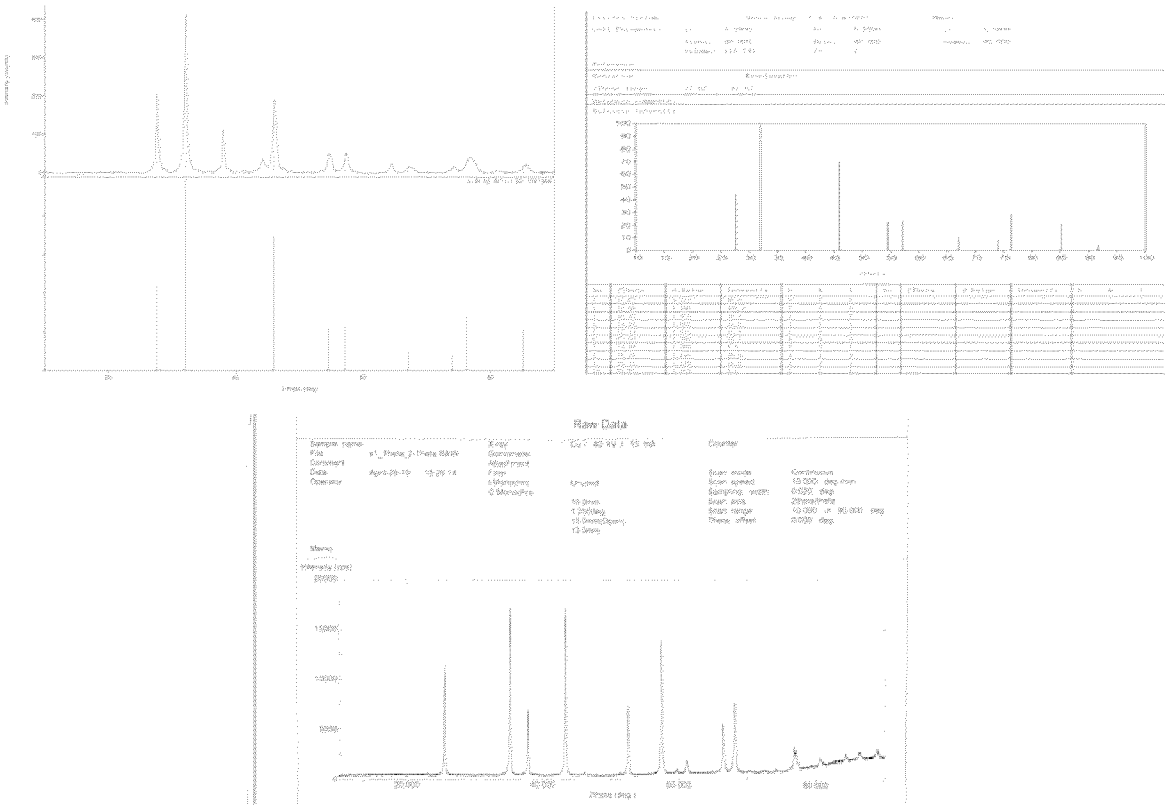


Table No1:- Characterization data of synthesis of 2-S-hepta-O-benzoyl- β -D-maltosyl-1-phenyl-5-tetra-O-acetyl- β -D-glucosyl-2-isothiobiuret

Sr. No.	S-hepta-O-benzoyl- β -D-maltosyl-1-aryl isothiocarbamides	2-S-hepta-O-benzoyl- β -D-maltosyl-1-phenyl-5-tetra-O-acetyl- β -D-glucosyl-2-isothiobiuret	M.P. (^{0}C)	% yield	Optical Rotation $[\alpha]_D^{32}$	R_f value
1	O-toludine	2-S-hepta-O-benzoyl- β -D-maltosyl-1-O-toludine-5-tetra-O-acetyl- β -D-glucosyl-2-isothiobiuret	130-135°	65	$[\alpha]_D^{30}$ = -51.2° (c, 0.373 in chloroform).	0.83
2	o-Cl-aniline	2-S-hepta-O-benzoyl- β -D-maltosyl-1- o-Cl-aniline-5-tetra-O-acetyl- β -D-glucosyl-2-isothiobiuret	98-102°C	86	$[\alpha]_D^{30}$ = - 52.3° (c, 0.386 in chloroform).	0.90
3	Phenyl	2-S-hepta-O-benzoyl- β -D-maltosyl-1-phenyl-5-tetra-O-acetyl- β -D-glucosyl-2-isothiobiuret	135-137°C	78	$[\alpha]_D^{30}$ = -152° (c, 0.333 in chloroform).	0.90

References

1. S. K. Bhagat and S. P. Deshmukh, synthesis and antimicrobial studies of new 2-stetra-o-acetyl-β-d-glucopyranosyl-1-aryl-5-hepta-o-acetyl-β-d-maltosyl-2-isothiobiurets Asian J. Chem, 15(2), 981-986, (2003)
2. A. S. Dandale, D. V. Mangte and S. P. Deshmukh Synthesis of *N*- and *S*-bis-protected lactosyl isothiobiurets Carbohydr. Res., 342, 753 (2007)
3. D.V. Mangte and S. P. Deshmukh Indian. Synthesis of S-hepta-O-acetyl lactosyl-1,5-disubstituted-2-isothiobiurets and 1,5-disubstituted-2,4-isodithiobiurets J. Chem., 45(B), 1285-1287 (2006)
4. A. Varki; R. Cummings; J. Esko; H. Freeze; P. Stanley; G. Hart; P.H. Seeberger.. Essentials of glycobiology (3rd ed.). Cold Spring Harbor, N.Y.: Cold Spring Harbor Laboratory Press. (2017)
5. Abdullah, T. A., Ibrahim, N. J., & Warsi, M. H.. Chondroitin sulfate-chitosan nanoparticles for ocular delivery of bromfenac sodium: Improved permeation, retention, and penetration. International journal of pharmaceutical investigation, 6(2), 96(2016).
6. Abedini, F., Ebrahimi, M., Roozbehani, A. H., Domb, A. J., & Hosseinkhani, H.. Overview on natural hydrophilic polysaccharide polymers in drug delivery. Polymers for Advanced Technologies, 29(10), 2564-2573 (2018).
7. Agarwal, T., Narayana, S. G. H., Pal, K., Pramanik, K., Giri, S., & Banerjee, I.. Calcium alginatecarboxymethyl cellulose beads for colon-targeted drug delivery. International journal of biological macromolecules, 75, 409-417 (2015).
8. Ai, S., Zhen, S., Liu, Z., Sun, F., He, X., Chu, F., . . . Wang, J.. An iRGD peptide conjugated heparin nanocarrier for gastric cancer therapy. RSC Advances, 8(52), 30012-30020 (2018).
9. Al-Rashida, M., Haider, A., Kortz, U., Joshi, S. A., & Iqbal, J.. Development and in vitro anticancer evaluation of self-assembled supramolecular pH responsive hydrogels of carboxymethyl chitosan and polyoxometalate. ChemistrySelect, 3(5), 1472-1479 (2018).
10. Alinejad, Y., Adoungotchodo, A., Hui, E., Zehtabi, F., & Lerouge, S.. An injectable chitosan/chondroitin sulfate hydrogel with tunable mechanical properties for cell therapy/tissue engineering. International journal of biological macromolecules, 113, 132-141 (2018).