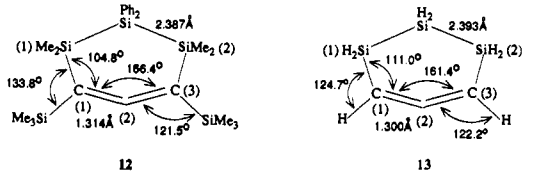

Figure 3. Experimentally (12) and theoretically (13) determined structures of trisilacyclohexa-1,2-dienes.

The X-ray structure of 7[9] is shown in Figure 1. Planes defined by the ring silicons and allene carbons (Si(1)C(1)C(2) and Si(2)C(3)C(2)) yield a dihedral angle of 80.1°.[6] The allene unit is bent from linearity to 174.1°.

As cyclohexa-1,2-diene 8 is a liquid, it was necessary to prepare a crystalline derivative (Scheme II). Trisilane 11[10] was quantitatively dichlorinated in CCl_4, and the resulting 1,3-dichlorosilane was condensed with dianion 2 to afford trisilacyclohexa-1,2-diene 12 in 67% yield as white crystalline needles after purification by GC.

The crystal structure of 12 was solved by direct methods,[11] and the molecular structure is shown in Figure 2. The allene unit is bent to 166.4°, and the dihedral angle, as defined by the Si(1)C(1)C(2) and Si(2)C(3)C(2) planes, is a remarkable 64.6°. Thus, twisting in the trisilacyclohexa-1,2-diene ring is even greater than the previous record of 72.4° measured in octasila[4.4]betweenallene,[12] where only twisting is allowed in fusing an allene simultaneously into two seven-membered rings since the allene must remain linear. Also of interest is the fact that there is considerable rehybridization[6] of the terminal allenic carbons, as evidenced by, for example, the Si(1)C(1)$SiMe_3$ angle of 133.8°, which allows the internal Si—C═C bond angles to reduce to ca. 105° to accommodate a 6-membered ring (Figure 3).

The structure of trisilacyclohexa-1,2-diene 13 was optimized with the 6-31G(d)[13] basis set at the SCF level and verified as a minimum. The calculated and experimental structures (Figure 3) are in reasonable agreement. The dihedral angle is predicted to be 56.2°, significantly smaller than the observed value of 64.6°, and the C═C═C bond angle is calculated to be 161.4°, about 5° less than the experimental value. These two properties are certainly related and are expected to be sensitive to variance in substituents. To assess the possible effect of the ring twisting on the reliability of a single configuration description of the wave function, a TCSCF/6-31G(d) calculation was performed on the ring. The mixing of electron density into the LUMO from the HOMO is essentially 0 (i.e., no diradical character), and thus a single configuration description is valid. The 0 K enthalpy for the MP2[14]/6-31G(d) isodesmic reaction,[15]

$$13 + 2SiH_4 + 2CH_4 \rightarrow 2CH_3SiH_3 + SiH_3SiH_2SiH_3 + H_2C{=}C{=}CH_2$$

is predicted to be 6.3 kcal/mol. This prediction of a stable ring may be compared with our earlier prediction of 18.0 kcal/mol stabilization energy for tetrasilacyclohexyne.[4]

Acknowledgment. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-ENG-82. This work was supported by the Director for Energy Research, Office of Basic Energy Sciences. Mark S. Gordon acknowledges the support of the National Science Foundation, Grant No. CHE-8911911.

(9) Crystal data for 7 at −50 °C; a = 10.256(1) Å, b = 27.667(6) Å, c = 11.051(4) Å, β = 117.14(2)°, V = 2790(2) Å^3, monoclinic with space group $P2_1/c$, Z = 4, ρ = 0.99 g cm^{-3}. The structure was solved by direct methods, R = 0.037 and R_w = 0.055 for 3817 reflections with $F_o^2 > 2.5\sigma F_o^2$. A complete description is available as supplementary material.

(10) Prepared in 27% yield by lithium-induced coupling of 3 equiv of HMe_2SiCl and 1 equiv of Ph_2SiCl_2. The literature procedure employs HPh_2SiCl and affords a 10% yield of 11: Gerval, P.; Frainnet, E.; Lain, G.; Moulines, F. *Bull. Soc. Chim. Fr.* **1974**, *7-8*(2), 1548.

(11) 12: mp 85–87 °C; ^{13}C NMR (less phenyls) δ 207.57 (1 C), 64.14 (2 C), 1.03 (2 C), 0.62 (6 C), 0.06 (2 C); ^{29}Si NMR δ 18.15, −4.69, −5.85; IR (neat film) 1846 cm^{-1}. Crystal data at −60 °C: a = 8.492(2) Å, b = 13.590(3) Å, c = 13.623(3) Å, α = 88.60(2)°, β = 75.94(2)°, γ = 77.53(2), V = 1488.8(4) Å^3, triclinic with space group $P\bar{1}$, Z = 2, ρ = 1.073 g cm^{-3}. The structure was solved by direct methods, R = 0.036 and R_w = 0.053 for 3500 reflections with $F_o^2 > 2.0\sigma F_o^2$. A complete description is available as supplementary material.

(12) Petrich, S. A.; Pang, Y.; Young, V. G., Jr.; Barton, T. J. *J. Am. Chem. Soc.* In press.

(13) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *16*, 217. Gordon, M. S. *Chem. Phys.* **1980**, *76*, 163.

(14) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem.* **1976**, *10*, 1.

(15) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796.

A New Type of Galactosyltransferase Reaction: Transfer of Galactose to the Anomeric Position of *N*-Acetylkanosamine

Yoshihiro Nishida, Torsten Wiemann, Volker Sinnwell, and Joachim Thiem*

Department of Organic Chemistry
University of Hamburg, Martin-Luther-King Platz 6
D-2000 Hamburg 13, Germany

Received September 2, 1992

Galactosyltransferase from bovine milk (GalT, EC 2.4.1.22) catalyzes the transfer of galactose from UDP-galactose to the OH-4 position of glucose and *N*-acetylglucosamine (GlcNAc). Flexibility of this enzyme allows the transfer of 2-deoxygalactose,[1,2] glucose,[3a] or glucosamine[3b] from corresponding UDP-hexose analogs. Many glucose or GlcNAc derivatives have been tested as acceptors,[4,5] and the structure requirement for the substrate has also been proposed.[6,7] In this communication, we report a quite new type of GalT reaction which involves the regio-mistaken transfer of galactose.

As a part of our synthetic work toward C-3 modified lactose derivatives by chemical and enzymatic means,[8] we have tested GalT reactions with a variety of C-3 modified methyl β-D-glucosides and glucoses in which OH-3 was replaced by H, F, OMe, N_3, or NHAc. The enzymic assay[9] showed that Glc3NAc was the best substrate among them. The relative initial rate at 20 mM was about 3% of the glucose reaction. In order to check the utility of this reaction, Glc3NAc (80 mg, 0.36 mmol)[10,11] and UDP-glucose (205 mg, 0.36 mmol) were reacted in the presence of UDP-glucose epimerase (EC 5.1.3.2, 5 units), GalT (2 units),[12]

(1) Thiem, J.; Wiemann, T. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1163.
(2) Thiem, J.; Wiemann, T. *Synthesis* **1992**, 141.
(3) (a) Berliner, L. J.; Robinson, R. D. *Biochemistry* **1982**, *21*, 6340. (b) Palcic, M. M.; Hindsgaul, O. *Glycobiology* **1991**, *1*, 205.
(4) (a) Schanbacher, F. L.; Ebner, K. E. *J. Biol. Chem.* **1970**, *245*, 5057. (b) Morrison, J. F.; Ebner, K. E. *J. Biol. Chem.* **1971**, *246*, 3985. (c) Khatra, B. S.; Herries, D. G.; Brew, K. *Eur. J. Biochem.* **1974**, *44*, 537. (d) Bushway, A. A.; Keena, T. W. *Biochem. Biophys. Res. Commun.* **1978**, *81*, 305. (e) Sinha, S. K.; Brew, K. *Carbohydr. Res.* **1980**, *81*, 239. (f) White, M. D.; Ward, S.; Kuhn, N. J. *Int. J. Biochem.* **1982**, *14*, 449. (g) Palcic, M. M.; Srivastava, O. P.; Hindsgaul, O. *Carbohydr. Res.* **1987**, *159*, 315. (h) Wong, C. H.; Ichikawa, Y.; Krach, T.; Gautheron, C.; Dumas, D.; Look, G. *J. Am. Chem. Soc.* **1991**, *113*, 8137.
(5) (a) Nunez, H. A.; Barker, R. *Biochemistry* **1980**, *19*, 495. For a review, see: (b) Toone, E. J.; Simon, E. S.; Bednarski, M. D.; Whitesides, G. M. *Tetrahedron* **1989**, *45*, 5365. For recent papers, see: (c) Palcic, M. M.; Venot, A. P.; Ratcliffe, R. M.; Hindsgaul, O. *Carbohydr. Res.* **1989**, *190*, 1. (d) Auge, C.; Gautheron, C.; Pora, H. *Carbohydr. Res.* **1989**, *193*, 288. (e) Thiem, J.; Wiemann, T. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 80.
(6) Berliner, L. J.; Davis, M. E.; Ebner, K. E.; Beyer, T. A.; Bell, E. *Mol. Cell Biochem.* **1984**, *62*, 37.
(7) Wong, C. H.; Lie, K.-K.-C.; Kajihara, T.; Shen, L.; Zhong, Z.; Dumas, D. P.; Liu, J. L. C.; Ichikawa, Y.; Shen, G. J. *Pure Appl. Chem.* **1992**, *64*, 1197.
(8) Partly reported in Nishida, Y.; Thiem, J. XVI International Carbohydrate Symposium, July 5–10, 1992, Paris.
(9) Fitzgerald, D. K.; Colvin, B.; Marval, R.; Ebner, K. E. *Anal. Biochem.* **1970**, *36*, 43.
(10) 3-Acetamido-3-deoxy-D-glucose was prepared by hydrogenation of 3-azido-3-deoxy-D-glucose[11] with $Pd(OH)_2$ followed by N-acetylation with acetic anhydride in methanol and identified by NMR spectroscopy (cf. supplementary material).
(11) Faghih, R.; Escribano, F. C.; Castillon, S.; Garcia, J.; Lukacs, G.; Olesker, A.; Thang, T. T. *J. Org. Chem.* **1986**, *51*, 4558.

0002-7863/93/1515-2536$04.00/0

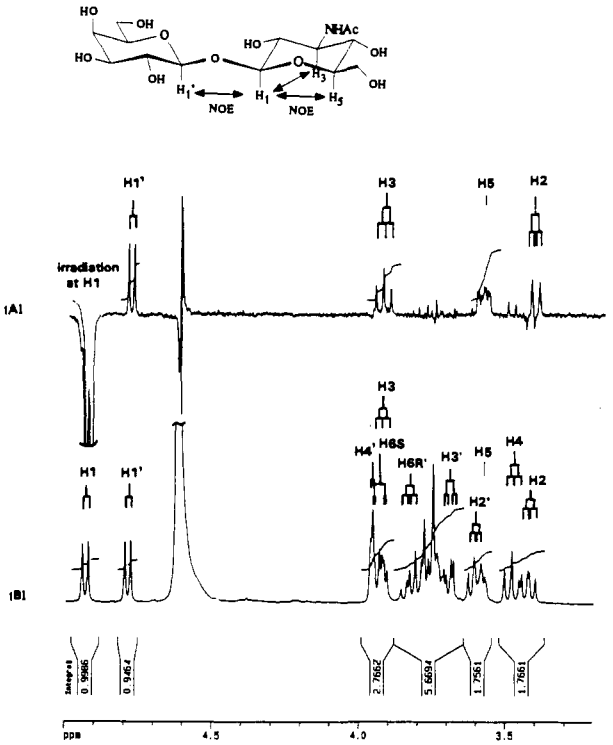

Figure 1. ^1H NMR spectrum (B) of βGal1,1βGlc3NAc in D_2O (50 °C) and NOE differential spectrum (A) with irradiation at the anomeric proton of the βGlc3NAc residue.

and α-lactalbumin (0.1 mg/mL)[13] in Tris-HCl buffer (pH 7.4, 12 mL). After 30 h at 30 °C, the product was isolated by gel filtration chromatography (Bio Gel P-2) as a hygroscopic solid (36 mg, 26% yield).

FAB-MS ($[M + 1]^+$ = 384, $[M + Na]^+$ = 406) was in agreement with the structure composed of galactose and Glc3NAc, while NMR showed a quite different feature from an expected βGal1,4-linked disaccharide. Only two β-anomeric protons were observed, and they were highly deshielded (4.93 and 4.78 ppm) compared with the β-anomeric proton at the βGal1,4-linkage of lactose or *N*-acetyllactosamine (ca. 4.5 ppm). The information allowed us to assign the structure as βGal1,1βGlc3NAc. In order to confirm it, NOE experiments were carried out (Figure 1). Consequently, ca. 7% NOE was detected between H-1 and H-1′ on either irradiation at H-1 or at H-1′. No NOE was observed between H-1′ and H-4 on irradiation at H-1′. These NOE data confirmed the structure with a β1,1-linkage in contrast to a β1,4-linkage.[14]

A control experiment in the absence of GalT did now show any disaccharide formation, which excluded a potential nonenzymatic pathway.

All of these results showed that GalT catalyzed the βGal transfer to the β-anomeric position of Glc3NAc, and this finding is the first regio-mistaken reaction of GalT.[15,16] This reaction may be simply rationalized when the substrate structure is compared with GlcNAc (Figure 2). Obviously, the stereochemistry of the β-anomer along C-1 to C-4 is superimposable to that of C-4 to C-1 of GlcNAc. This identity may allow GalT to transfer

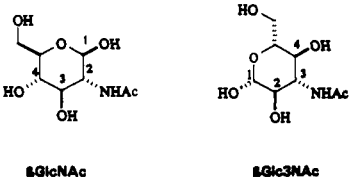

Figure 2. Stereochemical correlations between βGlcNAc and βGlc3NAc. The latter is shown from the reverse side of the ring plane.

galactose to the β-anomeric position of Glc3NAc.[17] The selective reaction of the β-anomer can be also rationalized because the stereochemistry of the α-anomer is comparable to that of GalNAc or galactose which is not accepted by GalT.

In summary, we have discovered a new type of GalT reaction with Glc3NAc, namely, βGal1,1 transfer. It provides new insights into the study of GalT, which has long been carried out based on the βGal1,4 transfer. The extension of this reaction to other acceptor substrates is in progress in our group and will be discussed in due course.

Acknowledgment. The authors are grateful to Alexander von Humboldt Stiftung for a fellowship to Y.N. and to the Deutsche Forschungsgemeinschaft, the Bundesministerium für Forschung und Technologie, and the Fonds der Chemischen Industrie for support of this study.

Supplementary Material Available: ^1H NMR spectra of Glc3NAc and Galβ1,1βGlc3NAc and ^1H-^1H COSY and FAB-MS spectra for Galβ1,1βGlc3NAc (7 pages). Ordering information is given on any current masthead page.

(12) GalT was purchased from Sigma Chemical Company (activity: 12 units per mg of protein; contamination: 4.4% of α-lactalbumin) and used without further purification.

(13) The reaction proceeded also in the absence, but was accelerated ca. 3 times in the presence, of α-lactalbumin.

(14) The structure was further confirmed by per-*O*-acetylation. NMR gave only two β-anomeric protons for the acetylated product. Substantial deshielding due to the geminal OAc group was not observed at H-1 (shift from 4.93 to 5.12 ppm) but at H-4 (shift from 3.44 to 4.94 ppm).

(15) Another regio-mistaken reaction by fucosyltransferase was discussed by Lemieux et al.[16]

(16) Khare, D. P.; Hindsgaul, O.; Lemieux, R. U. *Carbohydr. Res.* **1985**, *136*, 285.

(17) Glc3NAc satisfies the requirement for the acceptor substrate of GalT reported by Berliner et al.[6] for both βGal1,4 and βGal1,1 transfer. The latter reaction in the present study may be explained in the same way as the reaction of *N*-acetylmannosamine.[6]

CIDNP Detection of the 1,3-Dimethyluracil Dimer Radical Anion Splitting Sensitized by 2-Methylindole

Richard R. Rustandi and Hanns Fischer*

Physikalisch-Chemisches Institut der Universität Zürich CH-8057 Zürich, Switzerland

Received December 11, 1992

UV radiation (200–300 nm) causes adjacent pyrimidines in DNA to form cis, syn dimers through (2 + 2) photocycloaddition. The enzyme DNA photolyase is capable of repairing this damage by splitting the dimers back to monomers and uses visible or near UV light (300–500 nm).[1] Its activity has been attributed to dihydroflavin ($FADH_2$)[2] and either 5,10-methenyltetrahydrofolate or a deazaflavin[3] as noncovalently bound cofactors and a tryptophan residue.[1b]

It has been proposed that the dimer splitting involves electron transfer (ET) to or from the dimer.[4] Model compound studies have shown that both pathways can operate,[5] but on the basis of chemical and thermodynamic considerations, ET to the dimer

(1) (a) Sancar, A. Photolyase. In *Advances in Electron Transfer Chemistry*; Mariano, P. S.; JAI Press: London, 1992; Vol. 2, pp 215–272. (b) Kim, S.-T.; Li, Y. F.; Sancar, A. *Proc. Natl. Acad. Sci. U.S.A.* **1992**, *89*, 900.

(2) Payne, G.; Heelis, P. F.; Rohrs, B. R.; Sancar, A. *Biochemistry* **1987**, *26*, 7121.

(3) (a) Jorns, M. S.; Wang, B.; Jordan, S. P.; Chanderkar, L. P. *Biochemistry* **1990**, *29*, 552. (b) Payne, G.; Wills, M.; Walsh, C.; Sancar, A. *Biochemistry* **1990**, *29*, 5706.

(4) Okamura, T.; Sancar, A.; Heelis, P. F.; Begley, T. P.; Hirata, Y.; Mataga, N. *J. Am. Chem. Soc.* **1991**, *113*, 3143.

(5) (a) Roth, H. D.; Lamola, A. A. *J. Am. Chem. Soc.* **1972**, *94*, 1013. (b) Rokita, S. E.; Walsh, C. T. *J. Am. Chem. Soc.* **1984**, *106*, 4589. (c) Jorns, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 3133. (d) Hélène, C.; Charlier, M. *Photochem. Photobiol.* **1977**, *25*, 429. (e) Van Camp, J. R.; Young, T.; Hartman, R. F.; Rose, S. D. *Photochem. Photobiol.* **1987**, *45*, 365.

0002-7863/93/1515-2537$04.00/0