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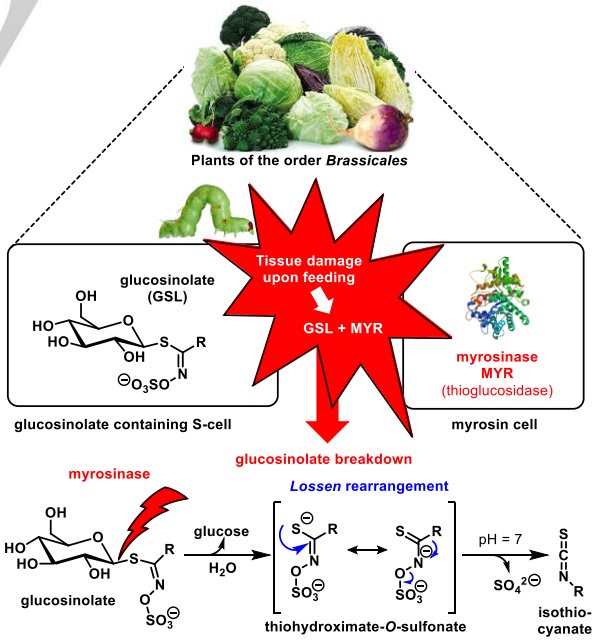
COMMUNICATION

Synthesis and biochemical evaluation of an artificial, fluorescent glucosinolate (GSL)

Carina Patrizia Glindemann,[a] Anita Backenköhler,[b] Matthias Strieker,[b] Ute Wittstock,[b] and Philipp Klahn*[a]

Abstract: The synthesis of the first example of a fluorescent glucosinolate-BODIPY conjugate (**GSL-BODIPY**) based on an azide containing artificial GSL precursor (**GSL-N_3**) is reported. The biochemical evaluation of the novel artificial GSLs revealed that the compounds are converted to the corresponding isothiocyanates in the presence of myrosinase. Furthermore, myrosinase-catalyzed hydrolysis in the presence of plant specifier proteins yielded the expected alternative products, namely nitriles. The easy assembly of the fluorescent **GSL-BODIPY** conjugate via click chemistry from **GSL-N_3** holds potential for the application as fluorescence labeling tool for the investigation of GSL-associated processes.

Glucosinolates (GSLs) are secondary metabolites produced by plants of the order Brassicales including several agricultural crops of the Brassicaceae such as cauliflower, radish, white and black mustard, broccoli or rocket. They are part of the myrosinase-GSL defense system that protects against herbivores (Scheme 1).[1–4] Chemically, GSLs are thioglycosidic thiohydroximate-*O*-sulfonates with variable, amino acid-derived side chains, which are stored in the vacuole of so-called S-cells by the producing plants.[5] Adjacent myrosin cells contain the enzyme myrosinase in vacuole-derived myrosin bodies[6,7]. Myrosinases (thioglucoside glucohydrolases, EC 3.2.1.147) hydrolyze the anomeric thioglycosidic bond of GSLs upon tissue damage under release of glucose and a thiohydroximate-*O*-sulfonate aglycone.[4] The aglycone undergoes a *Lossen* rearrangement to form a corresponding isothiocyanante, which acts as toxic or deterrent defense compound.[2–4] Interestingly, myrosinases have also been identified in certain insects.[8–10] Many plants of the Brassicaceae possess specifier proteins as additional components of the myrosinase-GSL system[11–13] In the presence of these proteins, the aglycone is converted to less reactive alternative products such as nitriles,[14,15] thiocyanates[16,17] or epithionitriles[18] whose function is not well understood. Structurally different specifier proteins are used by some specialist herbivores such as *Pieris rapae* to overcome the myrosinase-GSL defense of their host plants.[19]
Besides their roles in plant defense, glucosinolates are thought to provide health benefits to humans due to a variety of bioactivities of the isothiocyanates, e.g. chemoprotective,[1,2,4,20–22] and antibacterial effects.[1,2,4,23]. The bioactivities are related to the reaction of isothiocyanates with biological nucleophiles such as amino- and sulfhydryl moieties of enzymes.[24] While humans possess no thioglucosidases in their enzyme portfolio, it has been shown that several bacteria of the gut microbiome possess thioglucosidase activity enabling them to degrade GSLs and release isothiocyanates.[1,25]
In the context of studies on GSL metabolism and transport in plants, herbivores, bacteria or humans, artificial fluorescent GSLs, which release isothiocyanates as nucleophile-reactive fluorophores in the presence of thioglucosidases can serve as valuable tools in fluorescence imaging. Additionally, such compounds could be utilized for the fluorescence detection of thioglucosidase-producing bacteria. Due to their interesting biological activities natural GSLs have been targeted by several total syntheses.[26–32] Additionally, the syntheses of several artificial GSLs bearing non-natural[31–33] or isotopically labelled[34–38] aglycones and glucose units as well as α-anomeric GSLs[39,40] have been reported. Very recently, *Tatibouët* and co-workers reported a mannoside-GSL glycoconjugate as labeling probe for lectins.[41] Herein, we report the synthesis and biochemical evaluation of the first[42] artificial, fluorescent GSL as molecular tool for fluorescence imaging of GSL-associated biological processes.



Scheme 1. Myrosinase-glucosinolate (GSL) defense system of plants of the order Brassicales and GSL breakdown by myrosinase.

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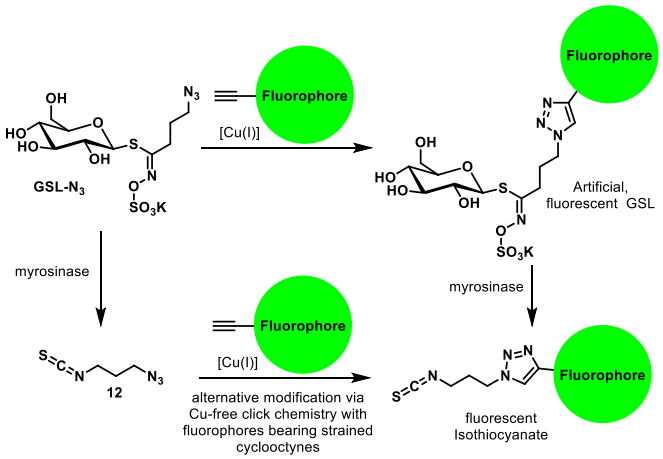
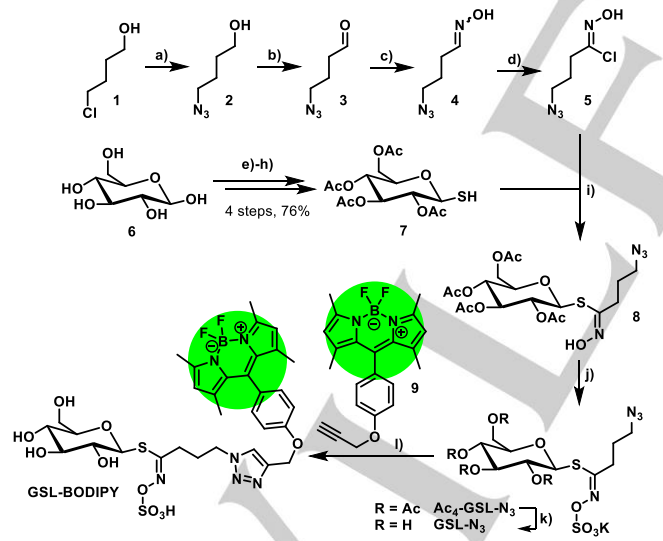


Scheme 2. Variable platform for the synthesis of artificial, fluorescent GSLs or GSL hydrolysis products via azide-alkyne click approach based on **GSL-N$_3$**.

In order to develop a variable platform for artificial, fluorescent GSLs we envisaged to generate **GSL-N$_3$** (Scheme 2) bearing an azide moiety for easy and fast attachment of different fluorophores containing terminal or strained internal alkynes via copper-mediated or copper-free azide-alkyne click chemistry, respectively.

Therefore, the chloro oxime **5** as activated precursor for the aglycone was synthesized from commercially available 4-chlorobutanol (**1**) in 4 steps as shown in Scheme 3. First the nucleophilic substitution of the chlorine atom by sodium azide at 70°C in DMF gave azido alcohol **2** in 89% yield.



a) NaN_3, (DMF), 70°C, 24 h, 89%, **b)** IBX, (DMSO), 23°C, 12 h, 80%, **c)** H_2NOH HCl, NaOAc, ($MeCN:H_2O$/3:1), 23°C, 3h, 95%, E:Z/1:1 **d)** NCS, (DMF), 23°C, 1h, quant., **e)** Ac_2O, DMAP, (Py), 48°C, 22 h, 97%, **f)** HBr (33% in HOAc), (CH_2Cl_2), 23°C, 2h, 78%, **g)** KSAc, (DMF), 23°C, 4 h, 91%, **h)** DTT, $NaHCO_3$, (DMF), 23°C, 2 h, 98%, **i)** **5** (1.4 eq), Et_3N, (THF), 23°C, 16 h, 57%, **j)** SO_3Py, Py, (CH_2Cl_2), 60°C, 4 h, then $KHCO_3$ aq., 23°C, 30 min, 88%, **k)** NH_3 in MeOH, (MeOH), 23°C, 24 h, quant., **l)** **9** (1.0 eq), $CuSO_4$, TBTA, NaAsc, ($DMSO:MeOH:H_2O:THF$/2:1:1:1), 23°C, 2h, 87%.

Scheme 3. Synthesis of **GSL-N$_3$** and **GSL-BODIPY**.

Oxidation in the presence of IBX led to the formation of the azido aldehyde **3** in 80% yield. By treatment of **3** with hydroxylamine hydrochloride in the presence of sodium acetate the hydroxylamine 4 was obtained in 97% yield in a 1:1-mixture of *E*- and *Z*-isomers. This mixture was converted to the chloro oxime **5** in the presence of *N*-chloro succinimide in DMF in quantitative yield giving exclusively the *Z*-isomer, which was directly used in the next step without any further purification. In parallel, 1-thio-β-D-glucopyranose (**7**) was prepared from glucose (**6**) in 4 steps adapted from literature known procedures.[28,43] Coupling of 1-thio-β-D-glucopyranose (**7**) and the chloro oxime **5** in the presence of triethylamine in THF led to the formation of the GSL precursor **8** in 57% yield. The treatment of **8** with an excess of sulfur trioxide pyridine complex in the presence of pyridine in dichloromethane at 60°C led to the formation of the corresponding thiohydroximate-*O*-sulfonate, which was converted into its potassium salt **Ac$_4$-GSL-N$_3$** in the presence of aqueous potassium hydrogen carbonate solution. Finally, after deacetylation in the presence of methanolic ammonia solution the desired artificial GSL **GSL-N$_3$** was obtained in quantitative yield. To demonstrate the loading with alkyne-tagged fluorophores, we attached the BODIPY fluorophore **9** (λ_{Ex} = 480 nm, λ_{Em} = 535 nm) by copper(I)-mediated azide-alkyne click chemistry obtaining artificial, fluorescent **GSL-BODIPY** in 87% yield.

With **GSL-N$_3$** and **GSL-BODIPY** in hand, we next investigated if these artificial GSLs are still accepted as substrates by plant myrosinases. We incubated **GSL-N$_3$** with myrosinase (purified from seeds of *Sinapis alba* (Brassicaceae)) in MES buffer at 22°C for 10, 40 and 120 min. After addition of benzonitrile as an internal standard, the aqueous samples were extracted with dichloromethane and analyzed by GC-MS. As shown in Figure 1, **GSL-N$_3$** was hydrolyzed in the presence of myrosinase leading to the formation of the corresponding isothiocyanate **10** identified by its molecular mass ion 142 m/z (See SI, Figure S1, A). Detectable amounts of isothiocyanate **10** were formed already after 10 min (Figure 1 B). In the absence of myrosinase no formation of **10** was observed (Figure 1 A). Substrate conversion followed Michaelis-Menten kinetics with a K_m of 888 ± 143 µM and a K_{cat} of 37.9 s^{-1} (Figure 2), i.e. values within the range determined with natural GSLs.[44,45]

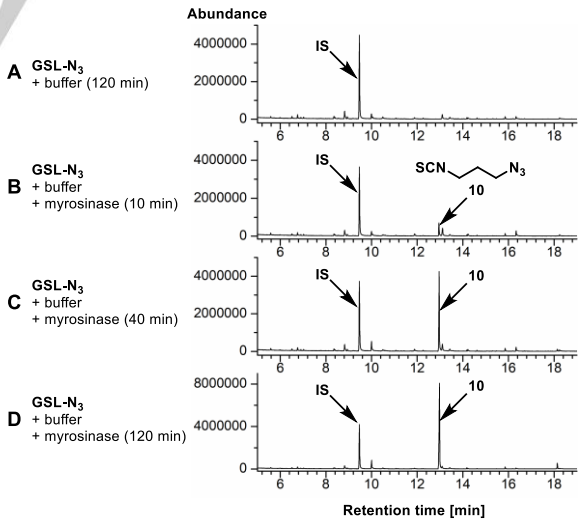


Figure 1. Isothiocyanate formation upon hydrolysis of **GSL-N$_3$** by myrosinase. **GSL-N$_3$** (2 mM) was incubated in 50 mM MES buffer (pH 6) in the absence (A) or presence (B-D) of purified myrosinase from *S. alba* at 22°C. Samples were extracted with CH_2Cl_2 after 10 min (B), 40 min (C), or 120 min (A, D), and extracts were analyzed by GC-MS. Total ion chromatograms (TIC) are shown. **IS**: internal standard (benzonitrile). Peak identities were confirmed by high-resolution mass spectrometry (See SI, Figures S1 A-B).

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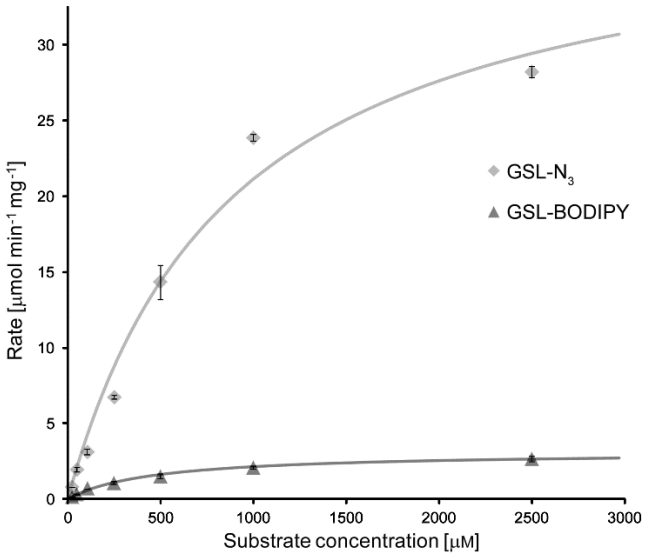

Figure 2. Myrosinase kinetics with artificial glucosinolates as substrates. **GSL-N_3** or **GSL-BODIPY** (25-2500 µM) was incubated with purified myrosinase from *S. alba* in 50 mM Tris HCl (pH 7.5) at 25°C. Substrate conversion and product formation were monitored by HPLC. Non-linear regression was applied using the Michaelis-Menten equation. Means ± SD are shown (N=3).

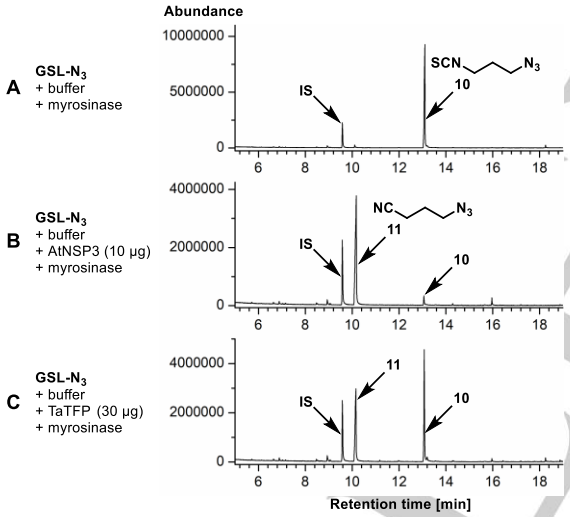

Figure 3. Nitrile formation upon hydrolysis of **GSL-N_3** by myrosinase in the presence of specifier proteins. **GSL-N_3** (2 mM) was incubated with purified myrosinase from *S. alba* in 50 mM MES buffer (pH 6) in the absence (A) or presence of AtNSP3 (10 µg; B) or TaTFP (30 µg; C) at 22°C for 120 min. Samples were extracted with CH_2Cl_2, and extracts were analyzed by GC-MS. Total ion chromatograms (TIC) are shown. **IS**: internal standard (benzonitrile). Peak identities were confirmed by high-resolution mass spectrometry (See SI, Figures S1 A-B).

Next, we tested if **GSL-N_3** hydrolysis can be diverted to nitrile formation by purified plant specifier proteins heterologously expressed in *Escherichia coli*. The incubation of **GSL-N_3** with myrosinase and 10 µg nitrile-specifier protein from *Arabidopsis thaliana* (Brassicaceae; AtNSP3) led to the formation of the corresponding nitrile **11** (Figure 3 B), identified by its molecular mass ion 110 m/z (See SI, Figure S1, B), indicating that GSL-N_3 aglycone can serve as substrate for specifier proteins. In the presence of 30 µg AtNSP3, the corresponding isothiocyanate **10** was no longer formed in favour of nitrile **11** (See SI, Figure S2). Thiocyanate-forming protein from *Thlaspi arvense* (Brassicaceae; TaTFP) was also able to promote nitrile formation upon hydrolysis of **GSL-N_3** yielding **11**. In this case, 30 µg TaTFP were not sufficient to prevent formation of **10**. This has also been observed for conversion of its natural substrate, allylglucosinolate aglycone.[46] Considering that both, **10** and **11,** present an azide function readily available for click chemistry, makes **GSL-N_3** an attractive probe for the investigation of GSL degradation and metabolism in plants.

The results of the hydrolysis experiments with **GSL-BODIPY** in the presence of myrosinase were less straight forward as initial GC-MS analyses failed to identify the expected BODIPY-isothiocyanate **12** within dichloromethane extracts of the reaction mixture. However, the LC-MS-based analysis of the fluorescent aqueous layers (See SI, Figure S3) led to the identification of the desired isothiocyanate **12** by its molecular mass ion 543 m/z (ESI, [M[**12**]+Na]$^+$, Figure 4 and SI, Figure S4 A). To further substantiate our finding, we treated **12** purified from the aqueous layer with aqueous ammonia solution and were able to identify the expected thiourea product **14** with a molecular mass of 560 m/z (ESI, [M[**14**]+Na]$^+$, see SI, Figure S4, C).

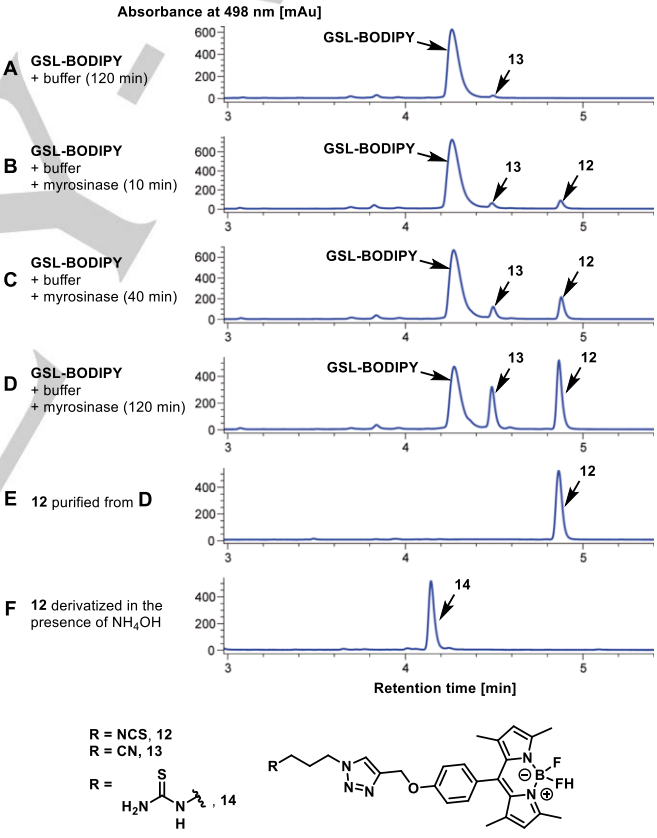

Figure 4. Isothiocyanate formation upon hydrolysis of **GSL-BODIPY** by myrosinase. **GSL-BODIPY** (2 mM) was incubated in 50 mM MES buffer (pH 6) in the absence (A) or presence (B-D) of purified myrosinase from *S. alba* at 22°C. Aliquots were taken from the reaction mixture after 10 min (B), 40 min (C), or 120 min (A, D) and analyzed by HPLC. The peak at 4.87 min from (D) was collected and analyzed by HPLC directly (E) or after reaction with NH_4OH to yield the thiourea derivative (F). Chromatograms recorded at λ= 498 nm are shown. Peak identities were confirmed by high-resolution mass spectrometry (See SI, Figures S4 A-C).

In contrast to the hydrolysis of **GSL-N$_3$** and natural GSLs, significant amounts of the corresponding nitrile **13** were also formed during hydrolysis of **GSL-BODIPY** (Figure 4, B-D) as confirmed by its molecular mass ion 511 m/z (ESI, [M[**13**]+Na]$^+$, see SI, Figure S4 B).

Product formation followed Michaelis-Menten kinetics with a K_m of 464 ± 47 µM and a K_{cat} of 2.9 s^{-1} (Figure 2), i.e. about tenfold lower efficiency than product formation from **GSL-N$_3$**, but still in the range reported with natural GSLs. When myrosinase-catalyzed hydrolysis was performed in presence of specifier protein AtNSP3 no significant amounts of the nitrile **13** were formed, instead the overall hydrolysis was slower (See SI, Figure S5). As a possible explanation, AtNSP3 might block the binding pocket of myrosinase without being able to accept the aglycone of **GSL-BODIPY** due to its size. Very small amounts of **13** were also formed in absence of myrosinase (Figure 4, A). This slow auto-degradative process is currently not fully understood.

In summary, we synthesized the first artificial, fluorescent GSL-derivative as well as an artificial, azido-functionalized GSL. We demonstrated their ability to serve as substrate for myrosinase and, in case of **GSL-N$_3$,** as substrate for specifier proteins. Therefore, we consider **GSL-N$_3$** and **GSL-BODIPY** suitable probes for tracing GSLs and their metabolism in biological systems.

Experimental Section

The Experimental Details can be found in the Supporting Information.

Author's Contributions

The research was conceived by P.K.. The manuscript was written by P.K. with contributions from U.W.. All compounds were synthesized by C.P.G., and P.K.. Biochemical evaluation of the compounds was planned by U.W., A.B., and M.S. and conducted by A.B. and M.S.. / All authors have given approval to the final version of the manuscript.

Conflict of interests

There are no conflicts of interests to declare.

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Keywords: Glucosinolates • Thioglucosidases • Isothiocyanates • Fluorescence labelling • artificial natural product derivatives

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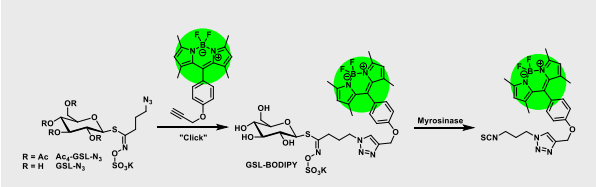

From mustard into the fluorescent marker toolbox: Synthesis and biochemical evaluation of a platform compound for the generation of artificial, fluorescent glucosinolates (GSLs).

*C. P. Glindemann, A. Backenköhler, M. Strieker, U. Wittstock, and P. Klahn**

Page No. – Page No.

Synthesis and biochemical evaluation of an artificial, fluorescent glucosinolate (GSL)