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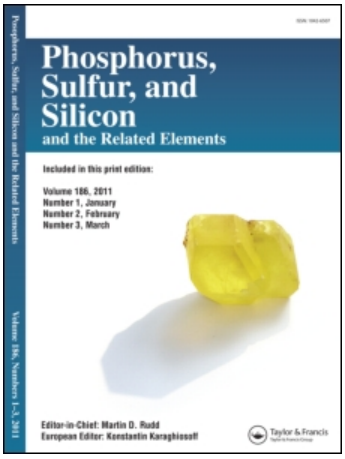

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
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Sugar Thiochemistry. First Synthesis of 1,5-Dithio-D-Glucopyranose and Related Thia-Analogs of Glucosinolates

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To cite this Article Joseph, Benoit and Rollin, Patrick(1993) 'Sugar Thiochemistry. First Synthesis of 1,5-Dithio-D-Glucopyranose and Related Thia-Analogs of Glucosinolates', Phosphorus, Sulfur, and Silicon and the Related Elements, 74: 1, 467 — 468
To link to this Article: DOI: 10.1080/10426509308038167
URL: http://dx.doi.org/10.1080/10426509308038167

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Phosphorus, Sulfur, and Silicon, 1993, Vol. 74, pp. 467–468 © 1993 Gordon and Breach Science Publishers S.A.
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SUGAR THIOCHEMISTRY. FIRST SYNTHESIS OF 1,5-DITHIO-D-GLUCOPYRANOSE AND RELATED THIA-ANALOGS OF GLUCOSINOLATES.

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Abstract A synthesis of the first representative of a new class of dithiosugars, 2,3,4,6-tetra-O-acetyl-1,5-dithio-β-D-glucopyranose **3** was devised, then applied to the elaboration of the first thia-analogs of glucosinolates.

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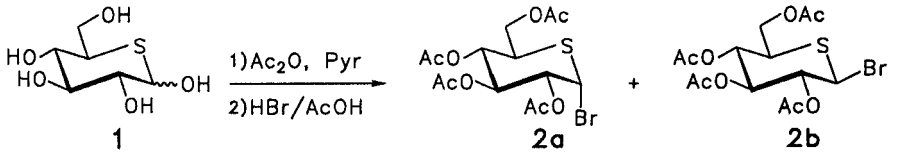
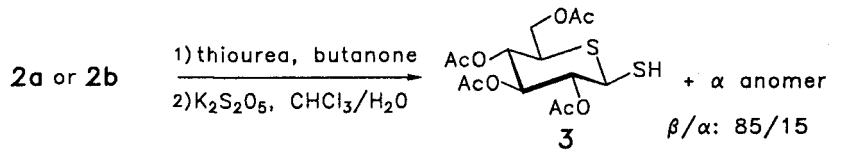
Glucosinolates are a structurally homogeneous class of more than 100 compounds - mostly encountered in the *Cruciferae* family - which display marked physiological activity through hydrolysis by myrosinase (thioglucoside glucohydrolase EC 3.2.3.1) and subsequent transformations of the enzymatically released aglucones[1].

Thorough study of the action of myrosinase requires structurally-modified substrates such as alpha-glucosinolates[2] or "non-gluco" glycosinolates[3]. We now report a synthetic pathway to thia-analogs of natural and artificial glucosinolates.

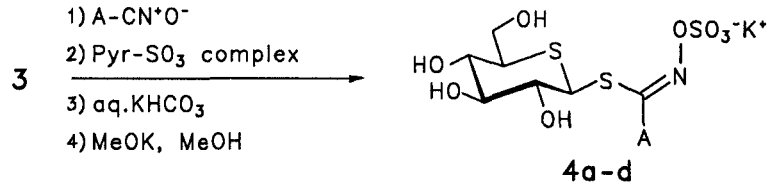
Anomeric activation of 5-thio-D-glucopyranose **1**[4] to the corresponding 1-α- and 1-β-bromo derivatives[5] **2a** and **2b** allows the smooth conversion of the monothiosugar into 2,3,4,6-tetra-O-acetyl-1,5-dithio-β-D-glucopyranose **3**[6] according to a modified Cerny methodology[7] (*ca.* 35% overall yield).





In analogy with previously described procedures[8], nucleophilic addition of **3** on miscellaneous *in situ* generated nitrile oxides afforded with good yields (70-85%)

protected 1,5-dithio-β-D-glucopyranosyl (*Z*)-thiohydroximates[9]. O-Sulfation of the hydroxyimino moiety followed by selective deprotection of the thiosugar unit yielded thia-analogs of artificial (**4a**) and natural (**4b-d**) glucosinolates[10].



4a-d

A = **a** phenyl **c** 2-phenylethyl
b benzyl **d** indol-3-ylmethyl

Further investigation of the reactivity scope of **3** and related dithiosugars is currently under way in our Laboratory.

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3) B. Joseph & P. Rollin unpublished results.
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6) Selected data for **3**: mp 128°C (from MeOH), $[\alpha]_D$ +11° (*c 1.0*, $CHCl_3$), ^{1}H-NMR ($CDCl_3$): δ (ppm) 1.91 (d, $J_{SH,1}$ 10.7 Hz, SH), 2.00, 2.02, 2.08 (3s, 12H, OAc), 3.31 (m, 1H, H-5), 4.12 (dd, 1H, $J_{5,6b}$ 3.1 Hz, H-6b), 4.23 (dd, 1H, $J_{5,6a}$ 5.5 Hz, $J_{6a,6b}$ 12.2 Hz, H-6a), 3.82 (ft, 1H, $J_{1,2}$ 10.3 Hz, H-1), 5.02 (ft, 1H, $J_{3,4}$ 9.9 Hz, H-3), 5.09 (ft, 1H, $J_{2,3}$ 9.9 Hz, H-2), 5.28 (ft, 1H, $J_{4,5}$ 9.9 Hz, H-4). ^{13}C-NMR ($CDCl_3$): δ (ppm) 41.0 (C-1), 45.2 (C-2), 60.9 (C-6), 71.7 (C-3), 74.1 (C-2), 76.5 (C-4). MS(CI, NH_3): m/z = 398 $(M + NH_4)^+$.
7) J. Stanek, M. Sindlerova & M. Cerny, Coll. Czech. Chem. Comm., 30, 297 (1965).
8) M.C. Viaud & P. Rollin, Tetrahedron Lett., 31, 1417 (1990) and references cited.
9) All new compounds were characterized by optical rotation, 300 MHz ^{1}H-NMR and high resolution mass spectrometry.
10) Selected data for **4d**: amorphous solid, $[\alpha]_D$ -3° (*c 1.0*, $CHCl_3$), ^{1}H-NMR (D_2O): δ (ppm) 2.37 (m, 1H, H-5), 2.97 (ft, 1H, $J_{3,4}$ 9.1 Hz, H-3), 3.42 (ft, 1H, $J_{4,5}$ 9.5 Hz, H-4), 3.50 (ft, 1H, $J_{2,3}$ 9.5 Hz, H-2), 3.69 (dd, 1H, $J_{5,6b}$ 3.3 Hz, H-6b), 3.75 (dd, 1H, $J_{5,6a}$ 5.1 Hz, $J_{6a,6b}$ 12.1 Hz, H-6a), 4.20 (d, 1H, $J_{1,2}$ 10.4 Hz, H-1), 4.25 and 4.45 (2d, 2H, J_{gem} 16.1 Hz, H-8b and H-8a), 7.24 (ft, 1H, $J_{5i,6i}$ 7.1 Hz, H-5i), 7.31 (ft, 1H, H-6i), 7.41 (s, 1H, H-2i), 7.57 (d, 1H, $J_{7i,6i}$ 7.9 Hz, H-7i), 7.81 (d, 1H, $J_{4i,5i}$ 7.9 Hz, H-4i). Hi refers throughout to the indole moiety.