NOTIZEN

Hydroxyamino Sugar Derivatives: New Glycolipid Analogs

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Glycolipid Analogs, Hydroxyamino Sugars, Non-Ionic Detergents, Reductive Alkylation

Synthetic glycolipid analogs are very useful as nonionic detergents for solubilization of membrane proteins [1]. Although a large number of such detergents were described, very few ones fully satisfy the desirable properties needed for such compounds [2].

Our continuous interest in hydroxyaminosugars [3] lead us to the preparation of some new glycolipid analogs bearing a hydroxylamine moiety [4]. We report hereinafter the preparation of some of these molecules.

Reduction ($NaBH_4$, 5 eq.) of the nitrone **1** [5] in ethyl alcohol gave the hydroxyamino derivative **2** in acceptable yields (65%). Acetylation of **2** with a large excess of acetic anhydride in pyridine yielded **3** (95%) which gave upon oxidation with *m*-chloroperbenzoic acid (1 eq.) in cold chloroform (4 °C) the epoxyde **4** in 96% yield (Fig. 1). Acidic hydrolysis (1 N HCl, MeOH 1:1) of **2** and **3** failed to give any pure compound. The prepared citronellal derivatives **2, 3** and **4** are stable thick liquids bearing a pleasant light lemon smell.

Another pathway to glycolipid analogs, involving the hydroxyaminosugar **5** [6] as a starting material was also explored (Fig. 2). Such a cyclopen-

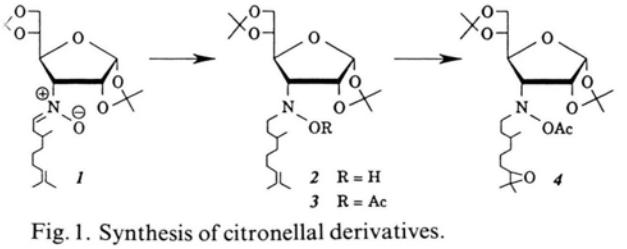

Fig. 1. Synthesis of citronellal derivatives.

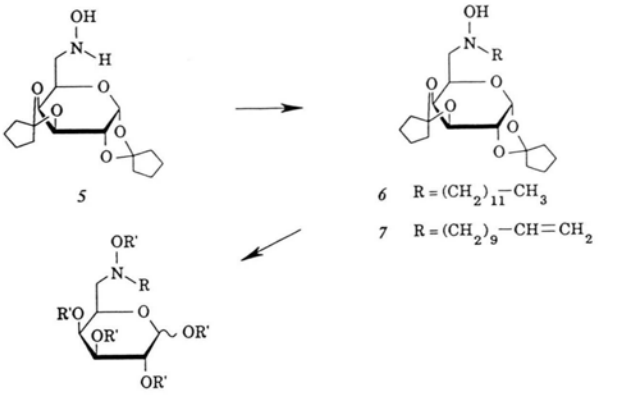

Fig. 2. Synthesis of dodecanaldehyde and undecenaldehyde derivatives.

Table I. Microanalytical data of newly synthesized compounds.

Nr.	Formula	Mol.weight	Calcd [%]	Found
2	$C_{22}H_{39}N_1O_6$	413.56	C 63.90 H 9.51 N 3.39	C 64.01 H 9.72 N 3.27
3	$C_{24}H_{41}N_1O_7$	455.60	C 63.27 H 9.07 N 3.07	C 63.16 H 9.01 N 3.18
4	$C_{24}H_{41}N_1O_8$	471.60	C 61.13 H 8.76 N 2.97	C 60.94 H 8.57 N 3.00
6	$C_{28}H_{49}N_1O_6$	495.71	C 67.85 H 9.96 N 2.83	C 67.69 H 9.93 N 3.00
7	$C_{27}H_{45}N_1O_6$	479.66	C 67.61 H 9.46 N 2.92	C 67.58 H 9.36 N 3.12
8	$C_{18}H_{37}N_1O_6$	363.50	C 59.48 H 10.26 N 3.85	C 59.44 H 10.27 N 3.89
10	$C_{28}H_{47}N_1O_{11}$	573.69	C 58.62 H 8.26 N 2.44	C 58.55 H 8.34 N 2.55
11	$C_{27}H_{42}N_1O_{11}$	556.64	C 58.16 H 7.77 N 2.51	C 58.44 H 7.73 N 2.71

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tylidene derivative is more sensitive to acidic hydrolysis than its isopropylidene counterpart [7]. Reductive alkylation ($NaBH_4$, 5 eq.) in ethyl alcohol of the galactose derivative **5** with dodecanaldehyde (3 eq.) gave the N-dodecyl hydroxyaminosugar **6** in 60% overall yields. **6** was then cleaved (1 N HCl, MeOH 1:1) into the unprotected **8** (55%) and acetylated (Ac_2O, pyridine) into the peracetyl glycolipid analog **10** (90%).

The same general procedures, applied to **5** and undecenaldehyde (3 eq.), gave the N-undecenyl hydroxyaminosugar **7** (55%), then the unprotected **9** which was directly acetylated into the peracetyl glycolipid analog **11** (50% from **7**).

All the newly synthetized compounds **2, 3, 4, 6, 7, 8, 9, 10** and **11** showed UV, IR, PMR and SM spectra in accordance with their structure [8]. Elementary analysis data [9] are presented in Table I.

Application of the above synthetic route to nucleoside derivatives is presently in progress in our laboratory.

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[8] For the general experimental methods see reference [6]. Details are available from the author (G. Z.-L.).
[9] We are grateful to Dr. H. Eder for performing the microanalyses.