6-HYDROXYALKYLAMINO-6-DEOXY-CYCLODEXTRINS:
TOWARDS DENDRIMERIC HOST-MOLECULES

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ABSTRACT

6-Perhydroxyalkylamino-6-perdeoxy-β-cyclodextrins have been synthesised by treating
6-perbromo-6-perdeoxy-cyclodextrins with hydroxyalkylamines. The products (1, 2) are
precursors of dendrimeric cyclodextrins in which the cavity provides access for the
guest to interact with the branches. A fluorescence study has demonstrated the effects of
the branches on binding of anilinonaphthalene sulfonate probes. The hosts show
selectivity towards guests, and pH-dependence of binding, consistent with polar
interaction between guest sulfonate anions and the protonated amino groups of the
dendrimeric structure.

1. INTRODUCTION

Dendrimers [1] are highly-branched macromolecules which have potential as hosts
because of the spaces between the branch stems. Such structures, if grafted onto
cyclodextrins, might be expected to modulate the cyclodextrin’s host properties, and in
turn, the cyclodextrin might act as a channel to the dendrimer core. As a development of
our studies on branched cyclodextrins [2], we have synthesised the heptakis(6-
hydroxyalkylamino-6-deoxy)-β-cyclodextrins 1 and 2, and evaluated the effects of the
branched structures on their ability to bind naphthalene sulfonate probes.

2. MATERIALS AND METHODS

2.1 Syntheses

The heptakis(6-hydroxyethylamino-6-deoxy)-β-cyclodextrins 1 and 2 were prepared from heptakis(6-bromo-6-deoxy)-β-cyclodextrin [3] by dissolving the latter at 65° in ethanolamine (15 molar equivalents) (for 1), or in diethanolamine (for 2), and heating at the same temperature for 48 hours. The reagent/solvent was removed under vacuum, and the residue was dissolved in hot methanol and precipitated by addition of this solution to stirred acetone. The precipitate was collected by gravity filtration, then dissolved in water, and the solution was treated with basic ion-exchange resin. Lyophilisation yielded 1, [α]D+110° (c 0.1, water), or 2, [α]D+109° (c 0.1, water) (60-65%).

Persubstitution was confirmed by elemental analysis and by the simple NMR spectra, although the 1H-spectrum of the more highly branched 2 showed fl uxional broadening:

(1) 81H (500 MHz, D2O) 5.10 (d, 1H, J1,2 4Hz, H-1), 3.98-3.93 (m, 2H, H-3, H-5), 3.73-3.63 (m, 3H, CH2O, H-2), 3.51 (t, 1H, J3,4=J4,5=9Hz, H-4), 3.02 (dd, 1H, J5,6a = 2Hz, J6a,6b 13Hz, H-6a), 2.88 (dd, 1H, J5,6b = 7.5 Hz, H-6b), 2.7 (m, 2H, NCH2);
813C (68 MHz, D2O) 101.5 (C-1), 82.7 (C-4), 72.6 (C-3), 71.8 (C-2), 70.1 (C-5), 59.7 (CH2O), 50.0 (NCH2), 48.8 (C-6); (2) 81H (270 MHz, D2O) 5.25 (d, 1H, J1,2 2Hz, H-1), 3.98-3.94 (m, 2H, H-3, H-5), 3.6-3.52 (m, 4H, CH2O, H-2, H-4), 2.97-2.73 (m, H-6a, H-6b, NCH2); 813C (68 MHz, CHCl3) 99.2 (C-1), 79.7 (C-4), 72.9 (C-3), 71.8 (C-2), 70.4 (C-5), 59.0 (CH2O), 56.4 (NCH2), 55.7 (C-6).