Polymer Bulletin 6, 305–308 (1982)

Polymer Bulletin

Monolayers from Synthetic Glycolipids

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S U M M A R Y

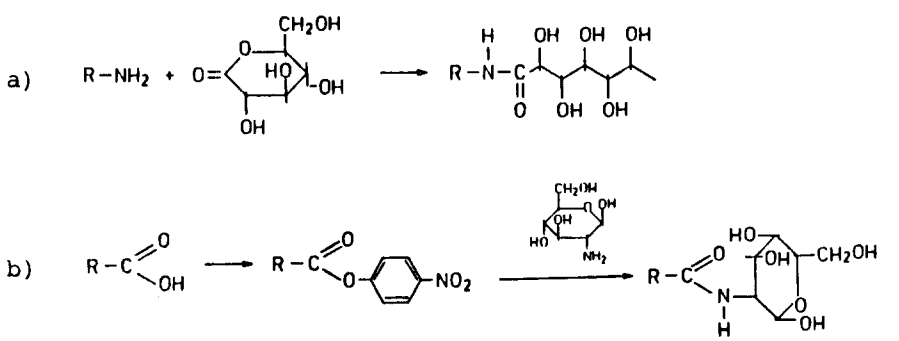
Synthetic glycolipids have been prepared by coupling of (a) aliphatic amines with lactone derivatives, or (b) fatty acids with amino derivatives of mono- and disaccharides via amide linkage. The aliphatic chain was varied with respect to the chain length and to its chemical composition (fluorination, functional end group). The influence of the glycolipid structure on the monolayer properties was investigated. Stable films are obtained with most of the products mainly due to strong interactions by hydrogen bonds in the subphase. Polymeric films may be produced by polycondensation in the subphase using particular crosslinking agents for the carbohydrate head group.

I N T R O D U C T I O N

In previous papers we have reported the grafting of aldonic acid derivatives of mono- and oligosaccharides onto di- or multifunctional carriers with aliphatic amino groups (EMMERLING and PFANNEMÜLLER 1978, 1981). Following the same procedure, glucose and maltose can be linked to monofunctional alkylamines with long aliphatic chains, thus leading to surfactants suitable as model substances for glycolipids. In this paper we will describe different ways for the synthesis of some representative products and their behaviour in monolayer formation.

R E S U L T S A N D D I S C U S S I O N

The coupling of the carbohydrate component with the aliphatic chain is performed by an amide linkage (Scheme, a).



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By varying the residue R a series of glycolipids has been obtained which differ in their chemical composition and in the length of the hydrophobic part (Table 1, 1-6). As hydrophilic head group mono- and disaccharide (3) residues were introduced.

Analogeous substances (7 and 8) have been obtained by linking fatty acids, activated as p-nitrophenyl ester, to amino group containing sugars (glucosamine, (2-aminoethyl)gluconamide), see Scheme, b. This alternative route allows the direct binding of a closed sugar ring without a preceding derivatization.

In order to study the influence of the carbohydrate residue on the film forming behaviour all products were spread on the gas-water interface of a Langmuir trough. The force-area isotherms (F/A diagrams) of the dodecylamine and dodecylgluconamide are depicted in Figure 1 (left side).

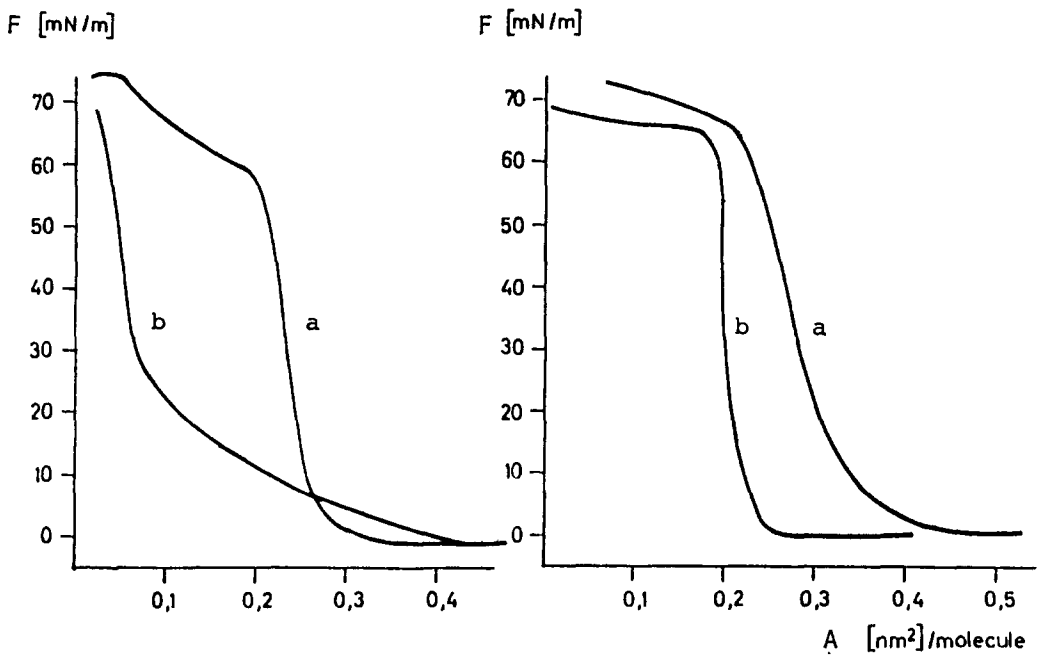

Figure 1: F/A Diagrams of dodecylgluconamide (a) and dodecylamine (b) (left side) and of octadecylgluconamide (a) and octadecylamine (b) (right side)

While film forming properties are known to be absent with dodecylamine (ADAMS 1930) the gluconamide derivative is able to form a stable solid-analogeous phase despite of its considerably larger hydrophilic head group. This sudden rise of film stability indicates a strong interaction between the glycolipids by hydrogen bonds as a result of a well ordered orientation in the monolayer. The influence of the sugar residue on the area required per molecule is clearly demonstrated

TABLE 1. Monolayer properties of synthetic glycolipids

Product	Aliphatic chain (R)	Sugar component	Monolayer properties [a]		
			Area per molecule (nm^2) [b]	Range of stability (^oC)	Loss of area at 20 nN/m and 20°C
	a) Amines				
1	$CH_3-(CH_2)_{11}-$	Gluconamide	0,23	1-10°	60% (after 3 hrs)
2	$CH_3-(CH_2)_{17}-$	Gluconamide	0,25	1-30°	0% (after 24 hrs)
3	$CH_3-(CH_2)_{17}-$	Maltobionamide	0,35	1°	100% (after 1 hr)
4	$Br-(CH_2)_{12}-$	Gluconamide	0,22	1°	100% (after 30 min)
5	$Br-(CH_2)_{20}-$	Gluconamide	0,25	1-25°	0% (after 24 hrs)
6	$CF_3-(CF_2)_{11}-(CH_2)_2-$	Gluconamide	0,30	1-20°	10% (after 24 hrs)
	b) Carbonic acids				
7	$CH_3-(CH_2)_{18}-C-$ (O)	2-Desoxi-2-aminoglucose	c	c	0% (after 24 hrs)
8	$CH_3-(CH_2)_{18}-C-$ (O)	(2-Aminoethyl) gluconamide	c	c	0% (after 24 hrs)

[a] Products 1-6 were spread from solution in chloroform/methanol 2:1; products 7 and 8 from solution in chloroform/N-methylpyrrolidone 1:1.

[b] Average between A_o (beginning of curve rise) and A_c (collapse pressure).

[c] The product was not completely soluble. Therefore exact data of the area per molecule can not be given.

in the curves measured for octadecylamine and the corresponding sugar derivative (Figure 1, right side), which both form stable monolayers.

The effect of stabilization by hydrogen bonds is confirmed by the temperature dependence of the F/A diagrams. With both dodecyl derivatives (1 and 4) monolayers are formed only at low temperatures (10° and 1° C respectively); the area per molecule is in the same range as that of the octadecylgluconamide. With further rise in temperature the stability rapidly decreases leading to an increasing reduction of the area. Monolayers obtained with octadecyl- and eicosyl derivatives (2 and 5) are stable over the whole range of temperature studied (1-30° C) and give identical F/A diagrams. - An intermediate behaviour is observed with the perfluorinated product (6): In spite of the relatively short carbon chain, the F/A diagrams showed only a small temperature dependence; this indicates that the fluor atoms contribute to a remarkable increase in surfactivity. - Octadecylmaltobionamide (3) has a rather large head group (comprising 12 C atoms) as compared to the length of the tail group (18 methylene groups); nevertheless monolayers with the expected area per molecule are formed at 1° C. In this case an additional liquid-analogue phase is observed.

For all monolayers long-time stability was determined at constant pressure (20 nN/m) at 20° C. Film areas of the glycolipids with longer aliphatic chains (2, 5, 7, 8) remained constant over 24 hours. Even the fluorinated product (6) gave only a 10% loss of area within this period. The other substances showed lower stability due to the shorter aliphatic chain.

The type of surfactants presented above allows a crosslinking reaction in the subphase at the numerous hydroxyl groups of the sugars with e.g. epichlorohydrin or divinylsulfone. This is an additional way for the synthesis of polymeric films which have been obtained so far only by polymerization in the hydrophobic part (diacetylene derivatives) (TIEKE et al. 1976).

The procedures for the synthesis of the various glycolipids and for the crosslinking of the monolayers by polycondensation or polyaddition will be reported separately.

A C K N O W L E D G E M E N T

This work was supported by the Bundesministerium für Forschung und Technologie.

R E F E R E N C E S

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Received December 15, accepted December 21, 1981
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