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Characterization of alkyl polyglycosides by both reversed-phase and normal-phase modes of high-performance liquid chromatography

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Abstract

Alkyl polyglycosides today represent the most important sugar surfactant. Nonionic sugar surfactants produced via different synthetic routes are mixtures of alkyl homologues, oligomers, anomers and isomers. Alkyl homologues and oligomers of alkyl mono- and diglucosides were separated by reversed-phase high-performance liquid chromatography (HPLC) with methanol–water as the mobile phase using a gradient elution. The gradient was optimized in respect to a simultaneous separation of alkyl glycosides according to their alkyl chain length and alkyl polyoxyethylene glucosides with regard to their length of the polyoxyethylene spacer. The separation of alkyl glycosides into α- and β-anomers was carried out by normal-phase HPLC with isooctane–ethyl acetate (60:40, v/v)–2-propanol in the gradient mode. Light scattering detection was used. Matrix-assisted laser desorption ionization time-of-flight mass spectra of alkyl glucosides and dodecyl glucosides with oxyethylene spacer groups are presented. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Alkyl polyglycosides; Glycosides; Surfactants

1. Introduction

Alkyl polyglycosides (APGs) represent a nonionic surfactant class produced on a large scale. They are being used in a wide range of technical and consumer products, such as detergents, cleaning agents, cosmetic products and pesticide formulations, because of their excellent behavior at interfaces [1–8]. However, alkyl polyglycoside surfactants produced on an industrial scale are mixtures of alkyl homologues, oligomers (with respect to the hydrophilic sugar moiety), anomers (α- and β-anomeric forms with respect to the bonding nature between the sugar and the alkyl chain) and isomers (furanosides and pyranosides). Their properties strongly depend on these structure and bonding parameters. Besides, their amphiphilic properties can be influenced by introducing oxyethylene spacer groups between the polar and non-polar molecule parts [9].

The surfactants are made via different synthesis routes. The Koenigs–Knorr reaction (see Ref. [10]) yields mainly β-anomers, whereas mixtures of α- and β-anomers are obtained from acidic catalyzed glycosidation according to the early investigated glucosidation reaction by Fischer and co-workers [11,12]. The analytical characterization of these type

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of surfactants is a prerequisite for their applications and environmental control. There is a lack of suitable simple high-performance liquid chromatography (HPLC) methods in this field.

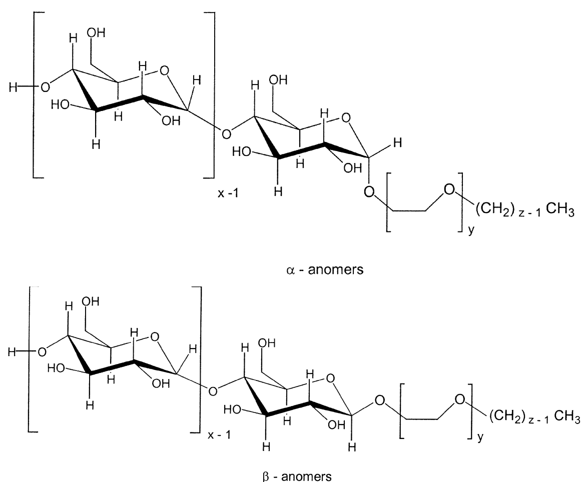
A considerable number of papers on the separation of saccharides using different HPLC column types has been published. Less information is given in the literature about the separation of alkyl polyglycosides. Reversed-phase liquid chromatography (RPLC) has proven to be reliable in routine analysis for the determination of residual fatty alcohols in alkyl polyglycosides [1]. Alkyl polyglycosides and sugar fatty acid esters are separated according to their alkyl chain length using reversed-phase isocratic or gradient HPLC [13–18]. Isocratic LC analysis combining the effect of two phases (porous graphitic carbon and NH_2 packings) permits control over the alkyl glycosides [19]. Chiral phase columns were evaluated to separate carbohydrate anomers in isocratic or gradient modes [20–22].

The aim of this contribution is the description of gradient HPLC methods for the analysis of alkyl polyglycosides. Commercial APGs are characterized by using different synthesized model compounds. The goal is to establish procedures for the complete separation of all relevant components. Therefore, reversed-phase as well as normal-phase HPLC was used for the separation with regard to the alkyl chain, the nature of the hydrophilic sugar head (mono/diglucosides), the bonding nature between the non-polar hydrophobic and polar hydrophilic molecule parts (a/β-anomers) and to the oxyethylene spacer groups between them.

Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-ToF-MS) has proved to be a suitable method for the analysis of alkyl polyglycosides [23,24]. The major advantage of this mass spectrometric method is that the ionisation of molecules is carried out without fragmentation. Therefore, in connection with the effect of the ethylene oxide (EO) spacer group, the structure of alkyl polyoxyethylene glucosides with a different number of spacer groups are systematically investigated by determination of the absolute molecular mass. These compounds can be used as references to identify high molecular mass components as mass ions in multi-component mixtures of APGs.

2. Experimental

Structures of compounds discussed are represented by the general formulae:



where x = number of saccaride units (1–2), y = oxyethylene spacer groups (0–4) and z = alkyl chain length (C_8, C_9, C_{10}, C_{11}, C_{12}, C_{14}, C_{16}, C_{18}).

Model compounds of alkyl glucopyranosides (alkyl = C_8, C_{10}, C_{12}, C_{14}, C_{18}) and octadecyl maltoside were sythesized from the corresponding alcohols and sugars via the well studied Koenigs–Knorr reaction and several modifications, yielding mainly β-anomers. Dodecyl polyoxyethylene glucosides are available from glucosidation of the EO adducts of dodecanol $C_{12}H_{25}(OC_2H_4)_nOH$ where n = 1, 2, 3, 4.

The crude products were purified by preparative liquid chromatography to remove excess dodecanol as well as glucose and oligosaccharides. It was carried out on a Büchi MP 680 liquid chromatograph equipped with a pump B-688 (160 ml min^{-1}), a gradient former B-687, a fraction collector and a Polar monitor. A Kronlab Bio-Cart (120×20 mm I.D.) column packed with 18 g of 15-μm silica (YMC Europe, Schermbeck, Germany) was used. The column could be loaded with up to 2 g of crude product. By collecting 10-ml fractions with an ethyl acetate–methanol gradient program (0–100% methanol, flow-rate = 10 ml min^{-1}) all impurities could be separated and sufficiently pure products were obtained.

Octyl α/β-glucopyranosides and dodecyl β-glucopyranoside were obtained from Sigma–Aldrich (St. Louis, MO, USA), nonyl β-glucopyranoside, decyl β-maltoside and undecyl β-maltoside from Glycon Biochemicals (Luckenwalde, Germany), dodecyl β-maltoside from ICN Biochemicals (OH, USA). Dodecyl α-glucopyranoside was prepared by the Fischer reaction in the presence of tetradecyl benzenesulfonate and fractionated crystallization of the raw material. The eluents methanol, isooctane, ethyl acetate and 2-propanol (Promochem, HPLC-grade, YMC Europe) were used as received. The water used was prepared in a three stage Millipore-Q Milli-Q 185 purification system.

Investigations were carried out on a Jasco liquid chromatograph (Tokyo, Japan) equipped with two PU-987 HPLC pumps, an AS-950 autosampler, a CO-200 Peltier column thermostat, a Sedex 55 evaporative light scattering detector ERC (Alfortville, France) and a Borwin data system, version 1.2160. The column for the reversed-phase mode (150×4.6 mm I.D.) was packed with C_{18}-silica (YMC-Pack Pro C_{18}, 120 Å mean pore diameter, 5 μm mean particle diameter, YMC Europe). The normal-phase columns (250×4.6 mm I.D.) were packed with silica (YMC-Pack SIL-AP, 200 Å mean pore diameter, 5 μm mean particle diameter, YMC Europe) and with poly(vinyl alcohol) (YMC-Pack PVA-SIL NP, 120 Å mean pore diameter, 5 μm mean particle diameter, YMC Europe).

Solutions of the samples (5–10 mg ml^{-1}) were injected into the chromatographic system with an automatic sampler. Chromatographic separations were carried out at 25°C. The flow-rate was 1 ml min^{-1}. Because of the absence of chromophoric groups in the sugar derivatives, an evaporative light scattering detection (LSD) was used (temperature: 50°C, inert gas N_2: 2 bar).

For MALDI-Tof-MS a Reflex III time-of-flight mass spectrometer (Bruker, Germany), working in the reflectron mode, was used. The spectrometer was equipped with a nitrogen laser (337 nm, 3 ns). A micro-channel plate detector was used to detect the ions, which were accelerated through 20 kV. The laser irradiance was slightly above threshold. Typically, 100–200 transients were recorded. 2,5-Dihydroxybenzoic acid (Sigma–Aldrich) was used as the matrix compound. Matrix solutions at a concentration of 10 mg ml^{-1} in tetrahydrofuran (THF) were prepared and pre-mixed (1:1, v/v) with solutions of alkyl glucosides (alkyl = C_8, C_9, C_{10}, C_{12}, C_{16}, C_{18}) and dodecyl-EO-glucosides (EO = 2, 3, 4) at a concentration of 10 mg ml^{-1} in 2-propanol–water (1:1, v/v). Sample spots were prepared by dropping 1–2 μl of the matrix-sample solution onto the MALDI target. After evaporation of the solvent the target was inserted into the mass spectrometer.

3. Results and discussion

Methods were developed for the qualitative analysis of alkyl glycosides from different sources. Procedures were established for the complete separation of all relevant components. Therefore, reversed-phase as well as normal-phase HPLC was used for the detection and determination of these mixtures. Alkyl mono- and diglucosides were separated according to the chain length by reversed-phase chromatography. The Pro C_{18} reversed-phase material that was used is produced from a newly developed generation of ultrapure silica with minimal metal traces. It achieves excellent baseline separations with symmetric peaks and allows for the discrimination of closely related compounds.

The elution with a methanol (A)–water (B) gradient was optimized such that the sugars and alkyl glycosides are separated from the products with an EO-oligomer spacer. The gradient was initially held constant at 70% A for 5 min, then progressed within 23 min to 100% A and held constant for another 2 min. Finally, the eluent composition was reset to the starting conditions within 2 min and held for 3 min until equilibration. The flow-rate was 1 ml min^{-1} and the volume of the injection loop was 4–20 μl (gradient program 1).

The sugar derivatives are retained exclusively by hydrophobic interactions with the stationary phase. The retention, selectivity and peak symmetry is shown in Fig. 1. It shows the separation of alkyl glycosides according to the chain length of the hydrophobic molecule part, the hydrophilic sugar moiety (glucoside–maltoside) and oxyethylene

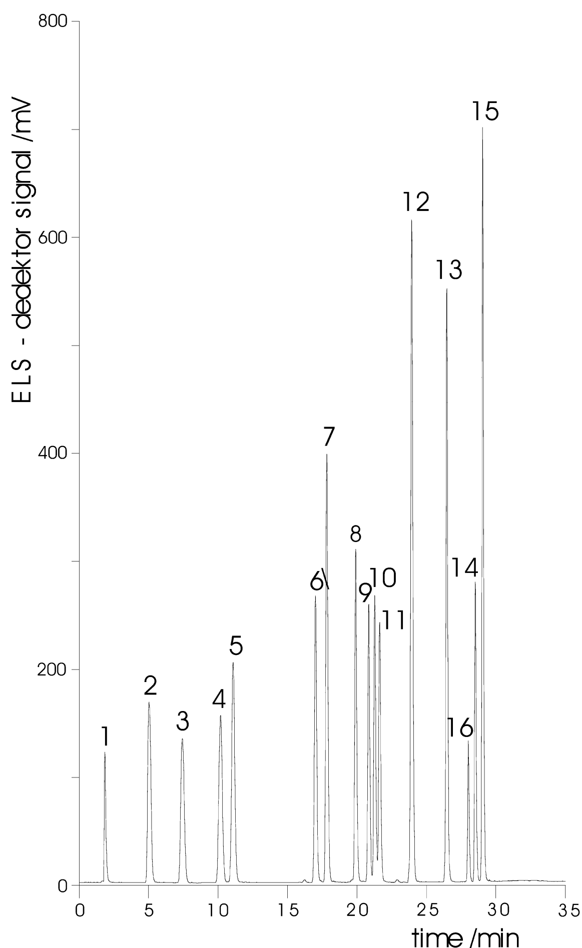


Fig. 1. Reversed-phase HPLC of glycosidation products with gradient elution. Gradient program 1, LSD, gain: 8, loop volume: 20 μl, injected quantity: 100 μg, compounds mixed in equal parts. 1: Glucose and/or maltose; 2: C_8-glucoside; 3: C_9-glucoside; 4: C_{10}-maltoside; 5: C_{10}-glucoside; 6: C_{12}-maltoside; 7: C_{12}-glucoside; 8: C_{12}-EO_1-glucoside; 9: C_{12}-EO_2-glucoside; 10: C_{12}-EO_3-glucoside; 11: C_{12}-EO_4-glucoside; 12: C_{12}-$EO_{1+2+3+4}$; 13: C_{16}-glucoside; 14: C_{18}-maltoside; 15: C_{18}-glucoside; 16: impurity.

spacer groups. The alkyl maltosides elute prior to the alkyl glycosides.

The stronger retention of the products with the oxyethylene spacer groups (C_{12}, peaks 9, 10, 11) in the reversed-phase in comparison to the corresponding alkyl glucoside without the spacer groups (C_{12}, peak 7) is a remarkable result according to the former description of the influence of EO spacer groups in different alkyl glycosides [9], showing an increased hydrophobicity from a distinct number of EO groups. Although oligoethylene oxides are water soluble substances, owing to the special chemical features of the oxyethylene group, the effect of the polyether chain cannot unambiguously be described as hydrophilic or hydrophobic. In the compounds $C_m(OC_2H_4)_nOH$, the hydrophilicity increases with increasing EO chain length. In such compounds, having in addition a polar hydrophilic head group, all the three groups of the molecule contribute to the adsorption behavior at the surfaces. As result the molecule turns out to be more hydrophobic with oxyethylene spacer groups [25,26]. It is evident that additional EO groups in amphiphiles (as spacer groups between the hydrophilic and hydrophobic molecule part) lead to a stronger adsorption both at the alkylated silica surface and at the fluid air–water interface.

Fig. 2 represents the RPLC separation of commercial and glycosidation products. The chromatograms A and B show commercial alkyl glycosides with different alkyl chain lengths (A: C_8, C_{10}; B: C_{12}, C_{14}). Chromatogram C represents a self made model alkyl glucoside (C_{12}). The retention is dominated by hydrophobic interactions of the alkyl chain. The base line separation allows a quantitative determination of the dodecylmaltoside apart from the dodecylglucoside.

However, under the HPLC conditions proposed, the separation of α- and β-anomers in alkyl glycosides was achieved by using chiral phases. There is still a need for a simple and suitable LC method, which will permit the determination of the anomer distribution. The chromatographic method should be more convenient and could be advantageously employed in laboratories where only conventional HPLC systems are available.

Detailed determination of α- and β-anomers is only possible with a more polar phase. Consequently, normal-phase HPLC was used for separation of alkyl glucosides into α- and β-anomers. The separation was carried out by gradient elution on a silica phase (column: YMC SIL AP, 250×4.6 mm I.D.). The mobile phase A consisted of isooctane–ethyl acetate (60:40, v/v) and mobile phase B of 2-propanol. Eluent A was decreased from 100 to 30% within 10 min. A was further reduced to 0% within 2 min and kept constant for another 6 min. Finally, the eluent

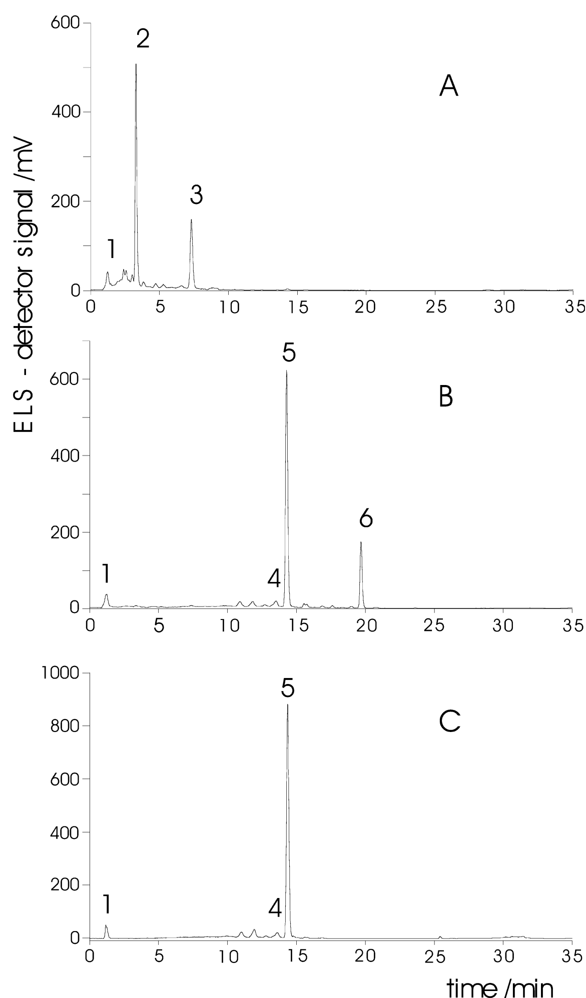


Fig. 2. RPLC of commercial alkyl polyglycosides and a synthesis product, gradient program 1, LSD, gain: 8. (A) APG 200, loop volume: 5 μl, injected quantity: 50 μg; (B) APG 600, loop volume: 5 μl, injected quantity: 50 μg; (C) synthesis product; loop volume: 4 μl, injected quantity: 40 μg. 1: Glucose; 2: C_8-glucoside; 3: C_{10}-glucoside; 4: C_{12}-maltoside; 5: C_{12}-glucoside; 6: C_{14}-glucoside.

composition was reset to the starting conditions within 3 min and held at equilibration for 2 min. The flow-rate was 1 ml min^{-1} and the volume of the injection loop was 4–16 μl (gradient program 2).

In Fig. 3, the separation of alkyl glycosides into α- and β-anomers is presented. The base line separation allows the quantitative determination of the dodecyl maltoside beside the dodecyl glucoside (Fig. 2).

Fig. 4 shows the nature of bonding of the alkyl

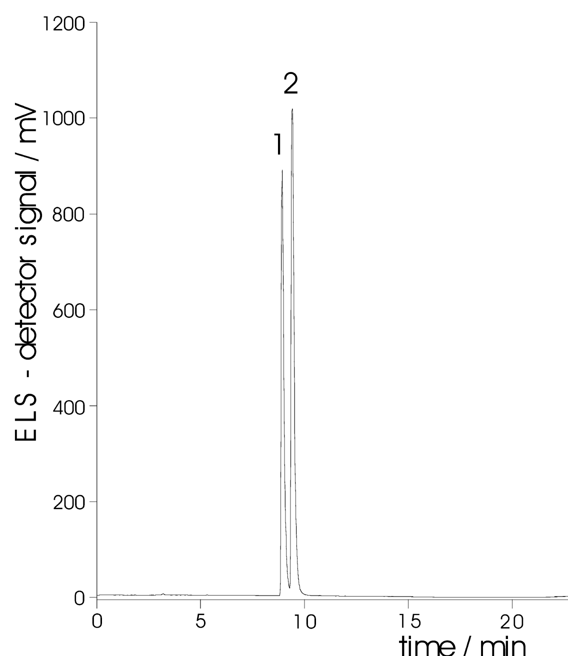


Fig. 3. Normal-phase separation of α/β-anomers on silica, gradient program 2, LSD, gain: 8, loop volume: 4 μl, injected quantity: 20 μg (1:1). 1: C_8-β-Glucoside; 2: C_8-α-glucoside.

chain in the commercial products APG 600 (A) and APG 220 (B) from Henkel and the glucosidation product of dodecanol. Retention on this polar phase is dominated by the bonding structure of the sugar molecule, not by the alkyl chain length. The retention is nearly independent of the alkyl chain length. By addition of C_8-β-glucoside to APG 220 in Fig. 4C the anomers are identified.

In addition, normal-phase HPLC was used for the separation of alkyl-EO-glucosides according to the EO spacer groups. Fig. 5 shows the influence of the EO spacer groups, which are bound between the fatty alcohol and sugar. Fig. 5A (the elution of the defined EO adducts of dodecanol) and Fig. 5B (that of the mixture of these EO adducts with the glycosidation products) show that the polar sugar surfactants are more strongly retarded than the amphiphiles $C_{12}EO_{2-4}$. By mean of preparative LC, defined EO adducts could be refined and rechromatographed.

PVA-SIL is an alternative to the silica phase in normal-phase chromatography. It is a unique stationary phase possessing a monomolecular coating of polymerized PVA. The PVA covers completely the

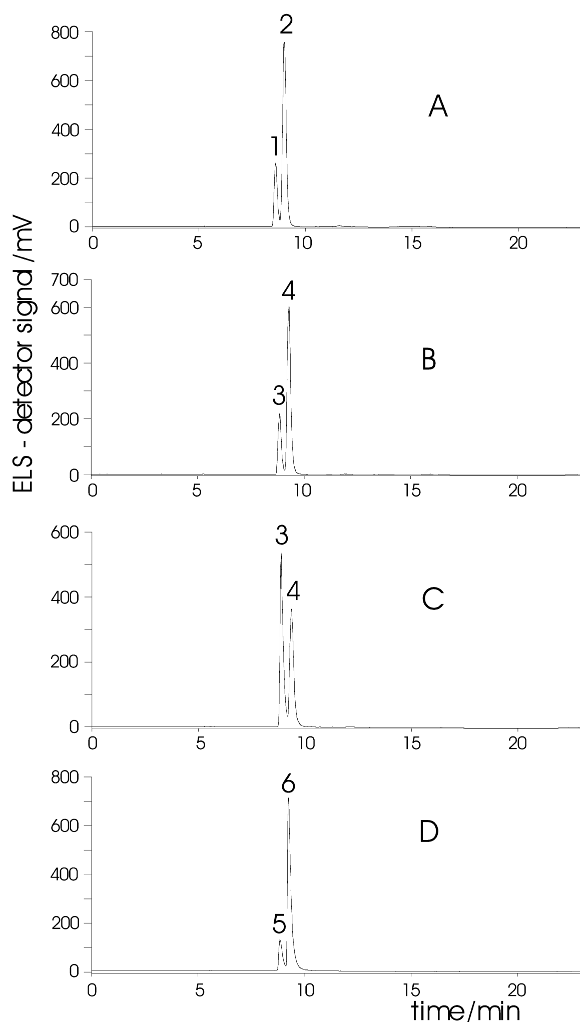


Fig. 4. Normal-phase chromatography of commercial and synthesis products, gradient program 2, LSD, gain: 8. (A) APG 600, loop volume: 5 μl, injected quantity: 50 μg; 1: C_{12}/C_{14}-β-glucoside, 2: C_{12}/C_{14}-α-glucoside. (B) APG 200, loop volume: 5 μl, injected quantity: 50 μg; 3: C_8/C_{10}-β-glucoside, 4: C_8/C_{10}-α-glucoside. (C) APG 200+C_8-β-glucoside (1:1); loop volume: 5 μl, injected quantity: 50 μ. (D) Lewis-acid catalyzed glucosidation product of dodecanol after purification by middle pressure liquid chromatography (MPLC), loop volume: 5 μl, injected quantity: 50 μg; 5: C_{12}-β-glucoside, 6: C_{12}-α-glucoside.

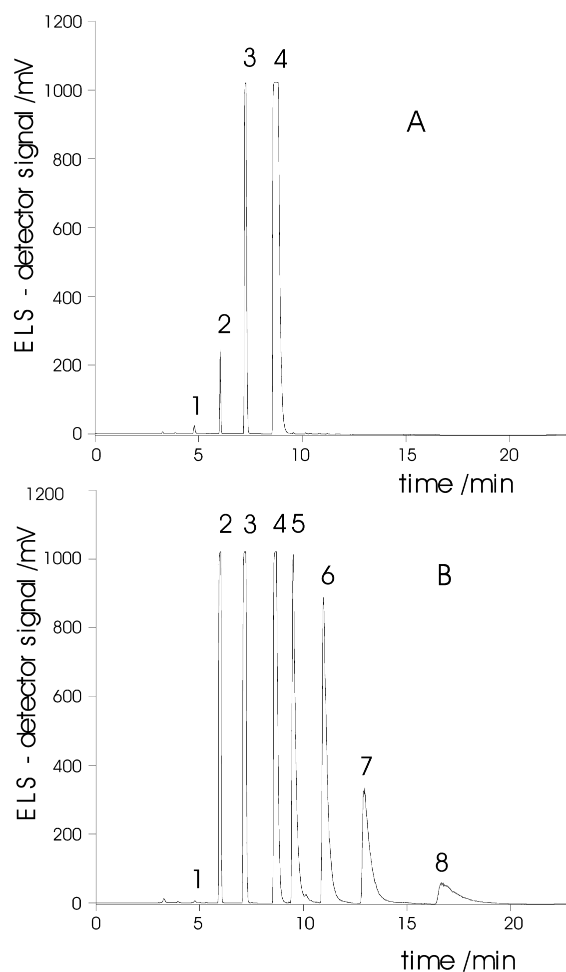


Fig. 5. Normal-phase chromatography of defined EO adducts of dodecanol and dodecyl polyoxyethylene glucosides, gradient program 2, LSD, gain: 8. (A) EO adducts of dodecanol (four compounds mixed in equal parts), loop volume: 6 μl, injected quantity: 60 μg. (B) Mixture of A and dodecyl polyoxyethylene glucosides (eight compounds mixed in equal parts), loop volume: 16 μl, injected quantity: 160 μg. 1: C_{12}-EO_1; 2: C_{12}-EO_2; 3: C_{12}-EO_3; 4: C_{12}-EO_4; 5: C_{12}-EO_1-glucoside; 6: C_{12}-EO_2-glucoside; 7: C_{12}-EO_3-glucoside; 8: C_{12}-EO_4-glucoside.

surface of the 5-μm spherical silica support including the internal surface of the 120-Å pores. This polymer coating isolates the silica against aggressive, high pH buffers and solvents. This polar bonded phase provides a variety of selectivity options for normal-phase applications. Fig. 6A shows the separation of defined EO adducts of dodecanol and dodecyl-polyoxyethylene glucosides on this stationary phase. Fig. 6B shows the separation in dependence of the nature of the sugar head (mono/di-glucoside).

For application of the separation in synthesis control and preparative column purification, the dependence of the k' values was measured for

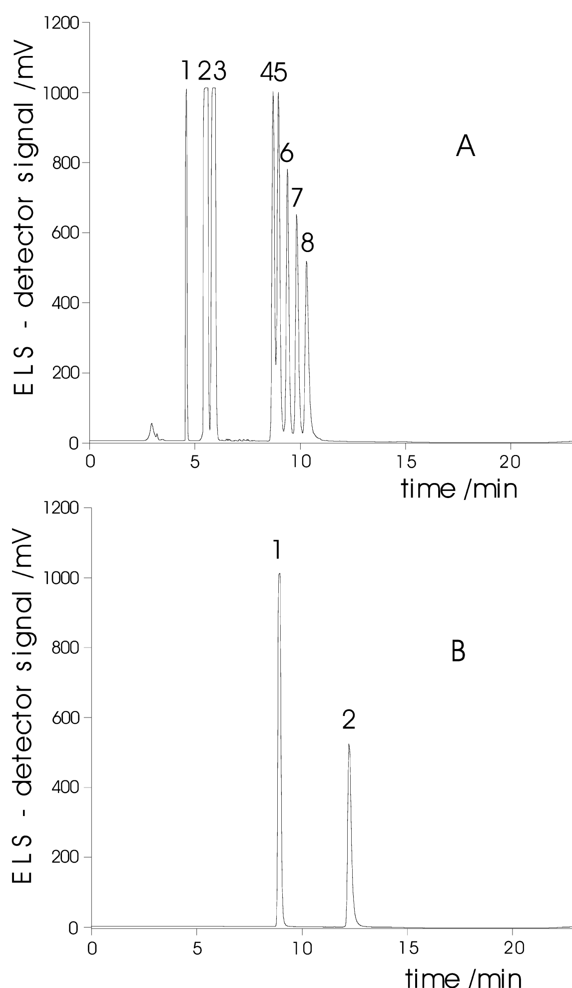


Fig. 6. Separation on a PVA-SIL stationary phase, gradient program 2, LSD, gain: 8. (A) Mixture of EO adducts of dodecanol and dodecyl oxyethylene glucosides (eight compounds mixed in equal parts), loop volume: 10 μl, injected quantity: 100 μg; 1: C_{12}-EO_2, 2: C_{12}-EO_3, 3: C_{12}-EO_4, 4: C_{12}-glucoside, 5: C_{12}-EO_1-glucoside, 6: C_{12}-EO_2-glucoside, 7: C_{12}-EO_3-glucoside, 8: C_{12}-EO_4-glucoside. (B) 1: Decyl glucoside, 2: decyl maltoside, loop volume: 5 μl, injected quantity: 25 μg (1:1).

different mixtures of the mobile phases, reversed-phase as well as normal-phase (Figs. 7 and 8). The hold-up time (t_0) for different mixtures of the mobile phase was measured using uracil. By means of this dependence from the k'-values, the optimal composition of the mobile phase can be selected with respect to the chain length range of the alkyl glucoside mixture to be analyzed.

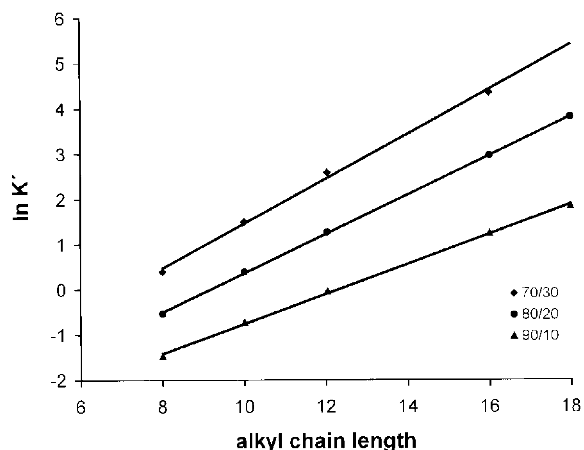


Fig. 7. Optimization of the isocratic reversed-phase separation of alkyl glucosides with methanol–water: ♦ = 70:30, ● = 80:20, ▲ = 90:10 (v/v).

In Fig. 9, the MALDI mass spectra of the alkyl glucosides are presented. Since the ionization in the MALDI-MS process is characterized by addition of a cation (preferably sodium and/or potassium ions), one has to expect different molecule peaks resulting from different cation adducts. Thus, as shown in Fig. 9, the main peak is characterized by the addition of one sodium adduct. A second peak differing by +16 Da can be assigned to the potassium adduct. Additional peaks can be seen in the mass region between 300 and 400 Da. In that region, especially matrix adducts as well as low-molecular impurities can

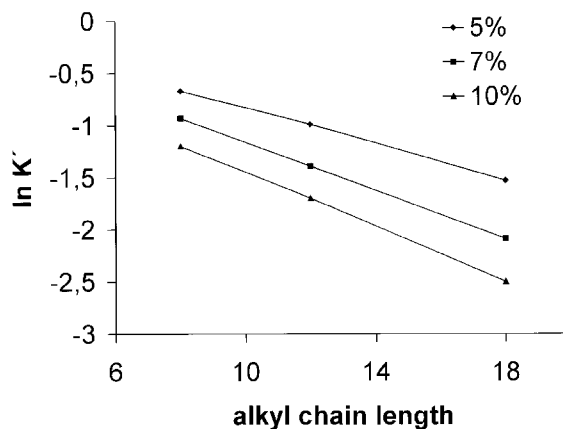


Fig. 8. Optimization of the isocratic normal-phase separation of alkyl glucosides with isooctane–ethyl acetate (60:40, v/v)–2-propanol, 2-propanol: 5, 7, 10%.

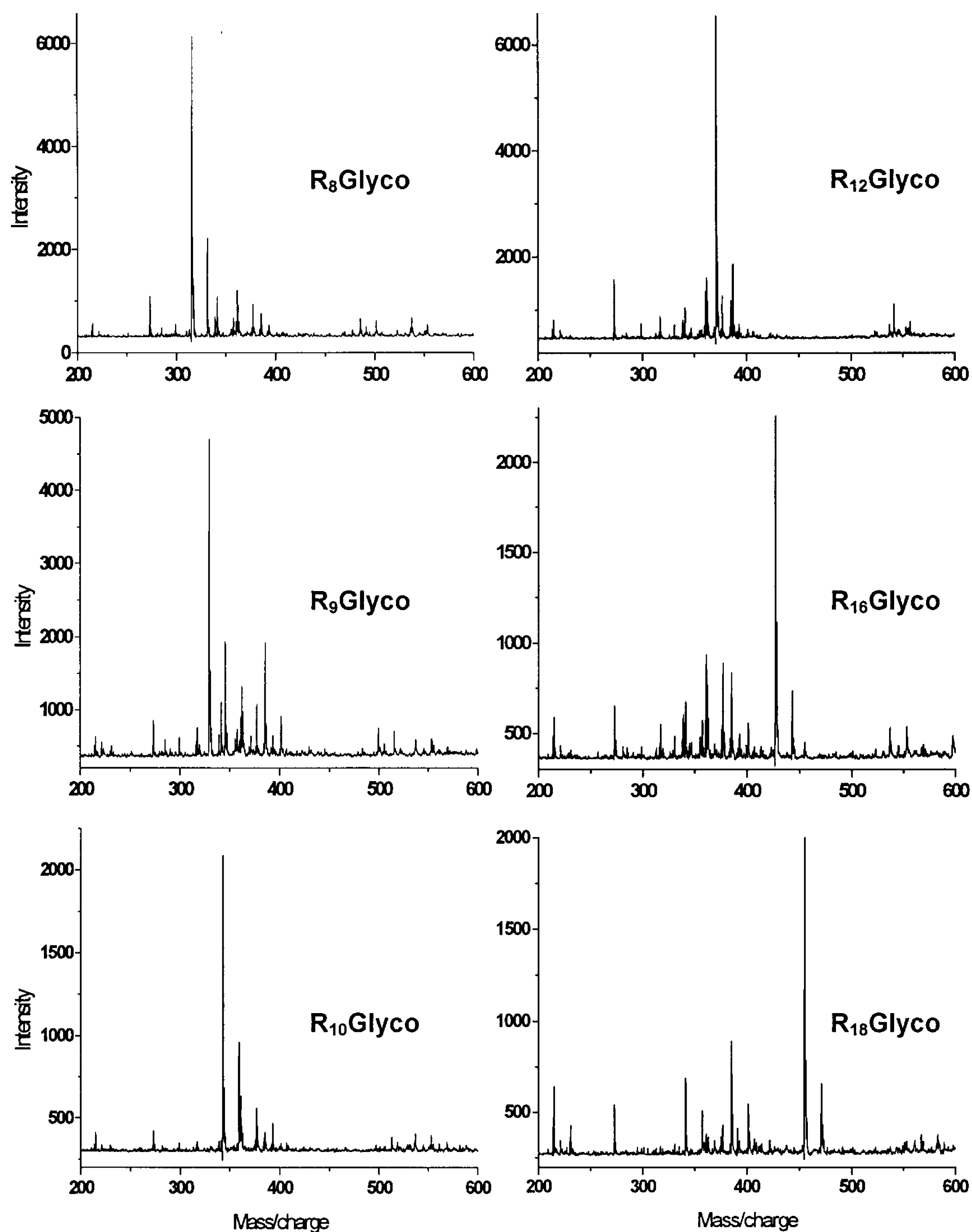


Fig. 9. MALDI mass spectra of alkyl glucosides. Alkyl = C_8, C_9, C_{10}, C_{12}, C_{16}, C_{18}.

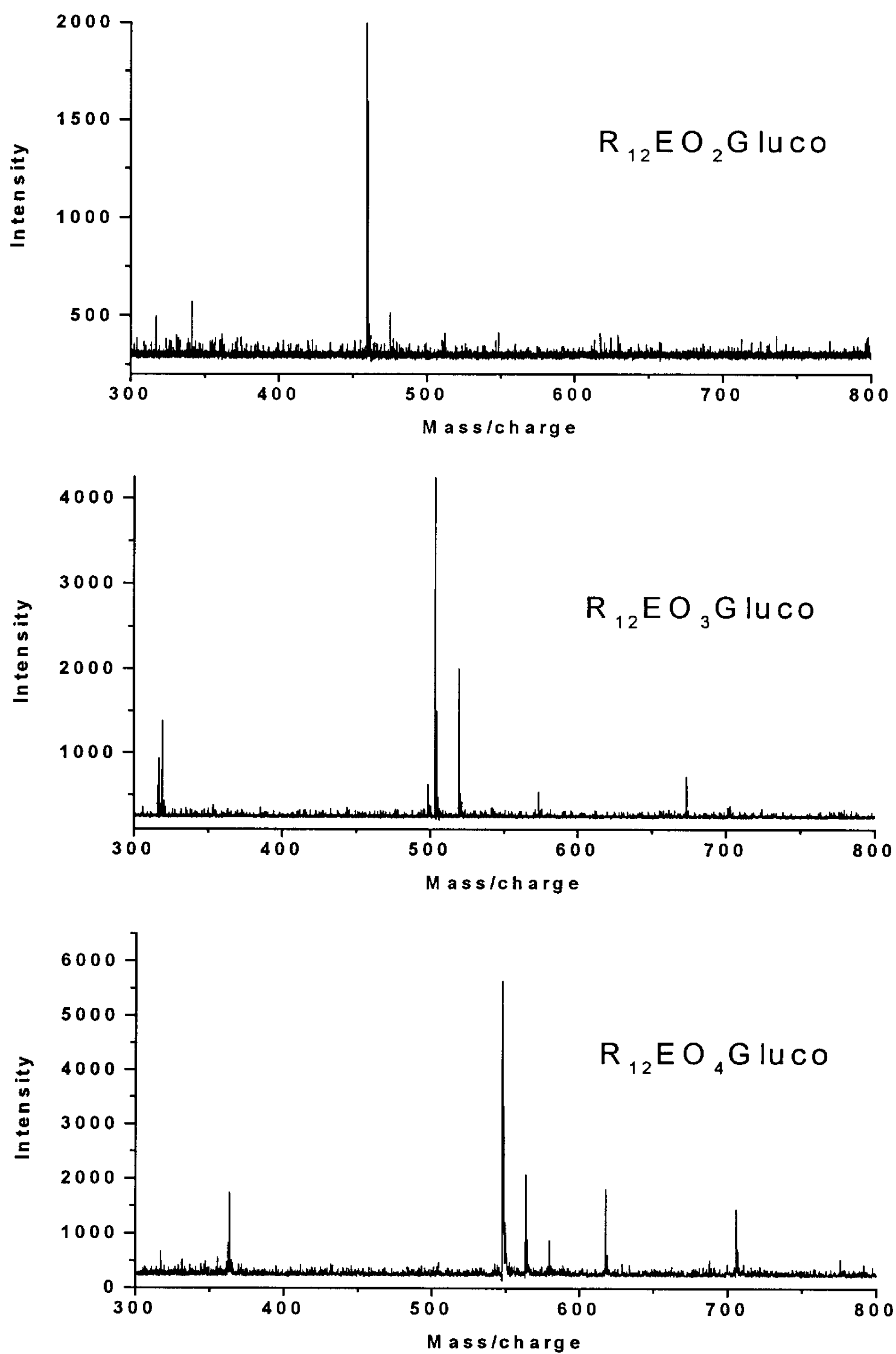


Fig. 10. MALDI mass spectra of dodecyl glucosides with oxyethylene spacer groups. EO=2, 3, 4.

often be found. The amounts of these impurities does not correspond to the peak areas obtained in HPLC. However, one has to keep in mind that MALDI-MS is not a quantitative method. Quite different ionization probabilities caused even by slight changes in the structure result in different peak intensities in MALDI-MS [27,28]. Besides these quantitative restrictions, the choice of the matrix used for MALDI-MS plays an essential role in the ionization–desorption process.

In Fig. 10 the MALDI mass spectra of dodecyl polyoxyethylene glucosides are shown. As already explained, the main peak is represented by the sodium adduct ion. The increase in the number of EO units results in a shift of this peak by 44 Da towards higher molecular masses. Simultaneously, the potassium adduct ions, different by +16 Da, could be detected again.

4. Conclusion

Alkyl polyglycosides have been characterized by both reversed-phase and normal-phase HPLC. Methods were developed for the qualitative analysis of alkyl glycosides from different sources in addition to the study their retention behavior in correlation to the different structure of synthesized model compounds and mixtures of commercial products. Procedures were established for the complete separation of all the relevant components. Separations were carried out with regard to the alkyl chain length, the nature of the hydrophilic sugar head (mono/diglucosides), the bonding nature between the non-polar hydrophobic and the polar hydrophilic molecular parts (α- and β-anomers) and the EO spacer groups between them. In connection with the effect of the EO spacer group, the structure of alkyl polyoxyethylene glucosides with different number of EO groups were investigated by determination of the absolute molecular mass using MALDI-ToF-MS.

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