[18] *Clegg, K. M.:* J. Sci. Fd. Agric. **7** (1956), 40.

[19] *El-Tinay, A. H., S. B. El Hardalou* and *A. M. Nour:* J. Food Tech. **18** (1983), 1.

[20] *Singh, U., M. S. Kherdekar* and *R. Jambunathan:* J. Food Sci. **47** (1982), 510.

[21] *Abbas, I. R., J. C. Scheerens* and *J. W. Berry:* Starch/Stärke **38** (1986), 351.

[22] *Dreher, M. L., C. J. Dreher* and *J. W. Berry:* Crit. Rev. Food Sci. Nutr. **20** (1984), 47.

[23] *Ganesh Kumar, K.,* and *L. V. Venkataraman:* Nutr. Rep. Intl. **13** (1976), 115.

[24] *Geervani, P.,* and *F. Theophilus:* J. Sci. Food Agric. **32** (1981), 71.

[25] *Yound, J. L.,* and *J. E. Varner:* Arch. Biochem. Biophys. **84** (1959), 71.

[26] *Jyothi, E.,* and *P. R. Reddy:* Nutr. Rep. Intl. **23** (1981), 799.

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Kinetics of the Hydroxyethylation of Starch in Aqueous Slurries*

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Kinetic results are presented for the hydroxyethylation of potato starch with ethylene oxide. The reactions were carried out at 303.0 K in alkaline aqueous starch slurries containing sodium sulphate as swelling inhibitor. A new side reaction was discovered: the formation of hydroxyethyl hydrogen sulphate from ethylene oxide and sulphate dianions. Part of the ethylene oxide is hydrolysed to ethylene glycol. Selectivities were determined by analysis of the products hydroxyethyl starch and ethylene glycol. Since hydroxide ions are formed in the production of hydroxyethyl hydrogen sulphate, the rate of formation of this compound could be measured by the amount of acid added to keep the pH constant. The hydrolysis of ethylene oxide towards ethylene glycol can be described by two parallel reactions: a) by water, and b) catalyzed by hydroxide ions. The reaction of ethylene oxide with starch is more enhanced by alkali than the base catalyzed reaction of ethylene oxide with water to ethylene glycol, causing the selectivity of the hydroxyethylation to increase from 7 to 68% if the sodium hydroxide dose is increased from zero to 0.060 mole per mole of anhydroglucose units.

Die Kinetik der Hydroxyethylierung von Stärke in wäßrigen Suspensionen. Für die Hydroxyethylierung von Kartoffelstärke mit Ethylenoxid werden kinetische Ergebnisse mitgeteilt. Die Reaktionen wurden bei 303,0 K in alkalischen wäßrigen Stärkesuspensionen durchgeführt, die Natriumsulfat als Quellungsinhibitor enthielten. Es wurde eine neue Nebenreaktion entdeckt, und zwar die Bildung von Hydroxyethyl-hydrogensulfat aus Ethylenoxid und Sulfat-di-anionen. Ein Teil des Ethylenoxids wird zu Ethylenglykol hydrolysiert. Durch Analyse der Produkte Hydroxyethylstärke und Ethylenglykol wurden Selektivitäten bestimmt. Da bei der Herstellung von Hydroxyethyl-hydrogensulfat Hydroxid-ionen gebildet werden, konnte die Bildungsgeschwindigkeit dieser Verbindung durch die zur Konstanthaltung des pH-Wertes notwendige Säuremenge gemessen werden. Die Hydrolyse von Ethylenoxid zu Ethylenglykol kann durch zwei parallele Reaktionen beschrieben werden: a) durch Wasser und b) Katalyse durch Hydroxid-ionen. Die Reaktion von Ethylenoxid mit Stärke wird durch Alkali mehr verstärkt als die basenkatalysierte Reaktion von Ethylenoxid mit Wasser zu Ethylenglykol, wodurch die Selektivität der Hydroxyethylierung von 7 auf 68% steigt, wenn die Natriumhydroxidmenge von Null auf 0,060 Mol je Mol Anhydroglucose-Einheiten angehoben wird.

1 Introduction

Low-substituted hydroxyethyl starch is an important starch derivative. Chemically, it differs from native starch in the conversion of part of the hydroxyl groups into -O-(2-hydroxyethyl) groups. The Molar Substitution (MS) is conveniently expressed as the number of moles of C_2H_4O substituted per mole of anhydroglucose units (AGU, $C_6H_{10}O_5$) of the polymer ($M_{AGU} = 162$ kg/kmol). Low-substituted hydroxyethyl starch with an MS lower than 0.1 is usually produced by reaction of starch with ethylene oxide at temperatures below 50°C in aqueous slurries of starch granules in the presence of a swelling inhibiting salt; the reaction is catalyzed by hydroxide ions [1−3]. Under these conditions, only part of the ethylene oxide reacts with starch, since also side reactions occur: ethylene oxide reacts with water towards ethylene glycol by both an uncatalyzed reaction and a reaction catalyzed by OH⁻-ions. Besides also reaction with salts can occur [4, 5].

To develop optimal process conditions for commercial scale production, the kinetics of both the main and side reactions should be known. Therefore, we investigated the kinetics of the reactions of ethylene oxide in aqueous slurries, existing of potato starch granules and water, in the presence of sodium sulphate and sodium hydroxide.

1.1 Reactions

If NaOH is added to an aqueous slurry of starch granules, most of it is absorbed by the starch phase. In the granules, part of the hydroxide ions reacts with the phosphate groups bounded to potato starch, according to:

$$R-OPO_3H^- + OH^- \rightarrow R-OPO_3^{2-} + H_2O \qquad (1)$$
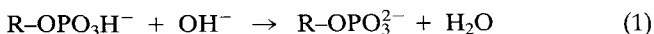
Here, R denotes the starch chain. If R = glucose, as in the case of glucose-1-phosphate, the pK at 303 K is 6.51 [12].

The amount of phosphate groups in potato starch is approximately 0.004 mole per mole anhydroglucose units (AGU) [9]. At pH-values higher than 10 the main part of the absorbed
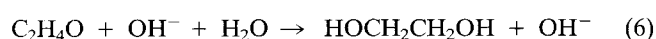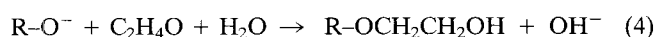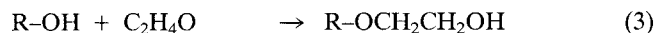
hydroxide ions reacts with the slightly acidic hydroxyl groups of starch, according to:

$$R-OH + OH^- \rightarrow R-O^- + H_2O \qquad (2)$$
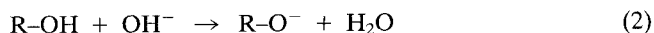
The pK of the anhydroglucose unit in amylose, the unbranched polymer of glucose, is approximately 12.7 in aqueous solution at 298 K, depending on the amylose concentration [10].

Ethylene oxide is completely soluble in the aqueous phase of the slurries in the concentration range used in the experiments. The dissolved ethylene oxide penetrates, like other small organic solutes, into the granules. It will be distributed between the starch and the water phase. Reactions with starch can only occur in the granules, whilst reactions with water are possible in both phases. This leads to the following reaction scheme:

$$R-OH + C_2H_4O \rightarrow R-OCH_2CH_2OH \qquad (3)$$
$$R-O^- + C_2H_4O + H_2O \rightarrow R-OCH_2CH_2OH + OH^- \qquad (4)$$
$$C_2H_4O + H_2O \rightarrow HOCH_2CH_2OH \qquad (5)$$
$$C_2H_4O + OH^- + H_2O \rightarrow HOCH_2CH_2OH + OH^- \qquad (6)$$

Reactions (3) and (4) yield hydroxyethyl groups, reactions (5) and (6) produce ethylene glycol.

It is likely that most hydroxyl anions will originate from ROH-groups and not from $ROCH_2CH_2OH$, because ROH is present in excess and the hydroxyl group of $ROCH_2CH_2OH$ is not expected to be much more acidic than ROH. This is confirmed by the observation that most of the hydroxyethyl groups of starch do not react further with ethylene oxide as long as the MS is low [11]. Another consecutive reaction, the importance of which depends on the relative amounts of ethylene glycol and water, is the formation of diethylene glycol by reaction of ethylene oxide with ethylene glycol:

$$C_2H_4O + HOCH_2CH_2OH \rightarrow HOCH_2CH_2OCH_2CH_2OH \qquad (7)$$
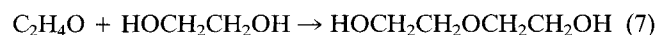
Under the conditions of our experiments the amounts of diethylene glycol formed were negligible, however. It is well-known that ethylene oxide reacts with the anions of several salts [4]. To the best knowledge of the authors, the reaction of ethylene oxide with sulphate di-anions has not yet been reported before in the open literature. However, analogous to the reaction of Cl^--ions with ethylene oxide a reaction with sulphate di-anions may be proposed. In water, this reaction generates hydroxide ions according to:

$$C_2H_4O + SO_4^{2-} + H_2O \rightarrow {}^-OSO_3CH_2CH_2OH + OH^- \qquad (8)$$
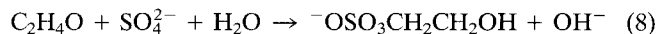
Due to this this reaction the pH of the slurry will increase and as a consequence also the concentration of the reactive RO^--groups on the starch chains. The production of hydroxide ions allowes the determination of the rate of this reaction by recording the amount of acid that must be added in order to keep the pH constant.

2 Experimental

Kinetic measurements

The kinetics of the hydroxyethylation of potato starch was studied batchwise at 303.0 K on stirred aqueous slurries of starch granules. In all runs the water-dry starch ratio was 3.85:1 by weight. To prevent gelatinization of the starch, sodium sulphate was added. When a constant pH was obtained after addition of a desired amount of 1.00 N sodium hydroxide, the reaction was started by addition of a certain amount of a 2.5 kmol/m^3 aqueous solution of ethylene oxide. The reaction of ethylene oxide with sulphate anions produces hydroxide ions, thus increasing the pH of the slurry. To maintain a constant pH, diluted sulphuric acid was added by a pH-controlled motor-driven buret and recorded versus time. In this way the rate of formation of hydroxide-ions could be determined.

At regular times samples were taken and centrifuged for 60 seconds in a preheated, closed tube in order to separate the phases at the reactor temperature and to prevent loss of ethylene oxide by evaporation. Gaschromatographic analysis of the liquid phase was carried out with a Packard Becker 428 gas-liquid chromatograph equipped with a glass column (length 0.25 m, internal diameter 3 mm), packed with Porapak PS. Isopropyl alcohol was added to the sample as an internal standard. After 60 s at 55°C, the oven temperature was increased with 2°C per 3 s up to 150°C. The retention times of ethylene oxide, isopropyl alcohol, ethylene glycol, and diethylene glycol were 45, 120, 225, and 460 s, respectively. The amount of ethylene glycol formed was measured at the end of a run, by filtrating 0.020 kg of slurry on a glass filter, and washing the cake three times during at least 300 s with 10 cm^3 of fresh water. Then the collected filtrate was analysed by the gaschromatographic analysis as described above. The molar substitution of the starch at the end of an experiment was determined according to *Morgan* as adjusted by *Lortz* [18].

3 Results and Discussion

A series of experiments was carried out at 303.0 K at identical concentrations of Na_2SO_4 and at several NaOH concentrations. The experimental conditions are summarized in Table 1. The final conversion of ethylene oxide was always at least 90%. It appeared that in all runs the concentration of ethylene oxide in the water phase decreased exponentially, which means that the rates of all occurring reactions are proportional to the concentration of ethylene oxide.

Table 1.
Experimental Conditions of Hydroxyethylation of Aqueous Slurries of Starch Granules.

Temperature	303.0 K
Weight of dry starch	0.324 kg (= 2 mol)
Total amount of water	1.250 kg
Amount of Na_2SO_4	0.120 kg (= 0.845 mol)
Amount of ethylene oxide (initial)	± 0.01 kg (= 0.227 mol)
Slurry density	1150 kg/m^3
Liquid phase density	1080 kg/m^3
Volume of slurry	$1.47 * 10^{-3}$ m^3

As an example, in Figure 1 the decrease of the concentration of ethylene oxide in the water phase is shown on a semi-logarithmic scale for the case that the number of moles of NaOH added per mole of AGU (N_{NaOH}) is 0.040. The slope of the logarithmic plot = $-k_{obs}$. This slope is a measure of the overall reaction rate. After $(\ln 2)/k_{obs}$ s, the amount of ethylene oxide in the slurry is 50% of its initial value. That means that the degree of substitution has reached $100 - 50 = 50\%$ of its final value. After another period $(\ln 2)/k_{obs}$, only 25% of the initial amount of ethylene oxide has not reacted, and so on. The k_{obs} of all experiments is shown in Table 2, together with the other measured parameters. No diethylene glycol was found during these experiments.

Because all reaction rates are proportional to the concentration of ethylene oxide, this concentration has no influence on the selectivity S.
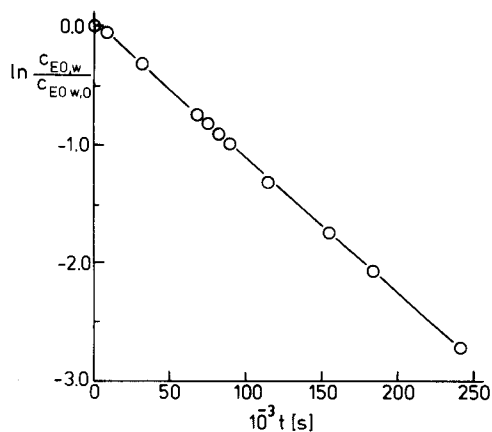
Fig. 1. Exponential decrease of the ethylene oxide concentration in the water phase; $N_{NaOH} = 0.040$ kmol/kmol AGU, 0.324 kg potato starch, 1.250 kg distilled water, 0.120 kg sodium sulphate; $T = 303$ K.

Fig. 2. Observed pseudo-first order reaction rate constant at 303 K as a function of the amount of added sodium hydroxide.

Table 2.
Kinetic Data, Selectivities and Final Degree of Substitution of Hydroxyethylation of Starch in Aqueous Slurry Phase Experiments at 303 K as a Function of N_{NaOH}, Number of kmoles of NaOH per kmole Anhydroglucose Unit.

Exp. nr.	N_{NaOH} (kmol/kmol AGU)	$10^5 k_{obs}$ (s^{-1})	S_{HES} —	S_{EG} —	S_{HHS} —	$MS^{a)}$ —
1	0.00	0.32	0.07	0.59	0.28	0.009
2	0.0075	0.35	0.22	0.60	0.21	0.021
3	0.015	0.57	0.42	0.30	0.114	0.045
4	0.025	0.74	0.51	0.31	$-^{b)}$	0.046
5	0.0325	0.86	0.54	0.29	0.048	0.047
6	0.040	1.17	0.53	0.20	0.078	0.045
7	0.060	1.54	0.68	0.14	0.030	0.070
8	0.075	1.94	0.62	0.17	$-^{b)}$	0.124

a) final MS
b) not measured.

Fig. 3. Effect of NaOH on the selectivities S_{HES}, S_{EG}, and S_{HHS}.

S_X is defined as $\dfrac{\text{moles of ethylene oxide in product X}}{\text{total moles of ethylene oxide reacted}}$ (9)

with X one of the products hydroxyethyl starch (HES), ethylene glycol (EG), or hydroxyethyl hydrogen sulphate (HHS), respectively. Using Eq 9, S_X is equal to the rate of formation of X relative to the overall reaction rate, so S times k_{obs} is a measure of the rate of formation of X.

Despite the large number of hydroxyl groups of starch they are very unreactive, however. This can be concluded from the low S_{HES} in combination with a low k_{obs} in Exp. 1, where no alkali has been added and thus no RO^--groups have been formed. This shows why an alkaline catalyst is necessary for hydroxyethylation of starch. The reactant concentrations of RO^--groups and OH^--ions both increase with increasing NaOH concentration. Thus k_{obs} should increase. This is actually the case (Figure 2). Initially k_{obs} remains more or less constant; this has to be ascribed to inactivation of the first mmoles of NaOH by the starch-bounded phosphate groups. When no alkali is added, k_{obs} is not zero, however. This is caused by the side reactions of ethylene oxide with H_2O and SO_4^{2-}.
The effect of the amount of NaOH added per mole of starch on the selectivities is shown in Figure 3. This Figure shows, that a substantial part of ethylene oxide can disappear by reaction with the swelling inhibitor, especially if no alkali is added.
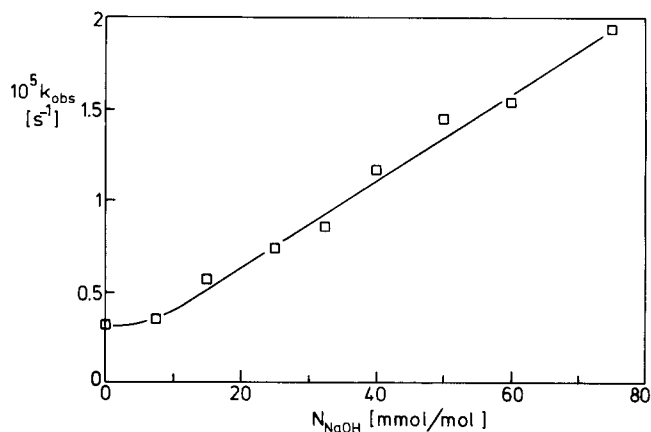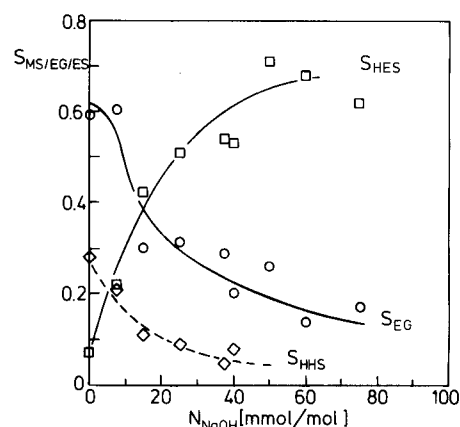
Besides, if the pH of the slurry is not controlled, a considerable amount of extra catalyst is formed, which is not always desirable. Clearly rate of the desired reaction is enhanced more by addition of alkali than the rates of the other reactions, resulting in an increase in the selectivity S_{HHS} of this reaction. However, a selectivity of 100% is not reached, the maximum value is 68%. This can be explained as follows: the uncatalyzed reactions become less important under alkaline conditions. However, the ratio between the contributions of the remaining reactions of ethylene oxide with hydroxide ions on the one side and starch hydroxyl anions on the other side is governed by the ratio of the amounts of each of these ions, respectively. From the acid base equilibrium it follows, that this ratio is constant if the concentration of starch hydroxyl groups is constant. The latter condition is fulfilled due to the excess of these groups. This leads ultimately to a situation of a maximum value in S_{HES} less than 100%. The selectivity can be improved further by decreasing the water-starch ratio, because this decreases the relative volume in which the undesired hydrolysis of ethylene oxide can take place. At this moment experiments with varying water-starch ratios are under way.

4 Conclusions

The reaction kinetics of the hydroxyethylation of starch granules in aqueous slurries at 303.0 K was studied, using sodium hydroxide as catalyst. A new reaction was observed: the reaction of ethylene oxide with sulphate di-anions, which has not been reported previously in the literature. All reactions, the formation of hydroxyethyl starch, the hydrolysis of ethylene

oxide and the formation of hydroxyethyl hydrogen sulphate, are first order in ethylene oxide, resulting in a linear dependence of the overall reaction rate on the concentration of ethylene oxide. As a consequence the selectivity to the desired hydroxyethyl starch is independent of the concentration of ethylene oxide. The reaction of ethylene oxide with undissociated ROH-groups of the starch chains is very slow, resulting in a low yield of hydroxyethyl starch when no alkali is added. By adding hydroxide the selectivity to hydroxyethyl starch may increase from 7 to maximally 68%. Because of the side reactions, the hydroxyethylation in a slurry-phase system is optimally carried out with a high starch-water ratio and a NaOH concentration as high as possible with respect to the swelling of the starch granules. Overall rate constants for these reactions are given as well as selectivities to main- and side reactions.

List of symbols:

AGU	= anhydroglucose unit $C_6H_{10}O_5$	
c_{EO}	= concentration of ethylene oxide	$(kmol/m^3)$
k_{obs}	= observed overall reaction rate constant	(s^{-1})
MS	= molar substitution, kmoles C_2H_4O bounded per kmole of anhydroglucose units	
N_{NaOH}	= number of moles NaOH per mole anhydroglucose unit	
S_{EG}	= selectivity of hydrolysis of ethylene oxide to ethylene glycol	
S_{HHS}	= selectivity of reaction with sulphate anions to hydroxyethyl hydrogen sulphate	
S_{HES}	= selectivity of reaction with starch to hydroxyethyl starch	
t	= reaction time	(s)

Bibliography

[1] *Kesler, C. C.,* and *E. T. Hjermstad,* in: "Methods in Carbohydrate Chemistry", ed. by R. L. Whistler, Vol. IV, 304, Acad. Press, New York, 1964.
[2] *Kesler, C. C.,* and *E. T. Hjermstad:* US Pat. 2,516,633 (1950).
[3] *Hjermstad, E. T.:* US Pat. 3,706,731 (1972).
[4] *Parker, R. E.,* and *N. S. Isaacs:* Chem. Rev. **59** (1959), 737.
[5] *Kesler, C. C.,* and *E. T. Hjermstad:* US Pat. 2,516,634 (1950).
[6] *Jetten, W. J., E. J. Stamhuis* and *G. E. H. Joosten:* Starch/Stärke **32** (1980), 364.
[7] *BeMiller, J. N.,* and *G. W. Pratt:* Cer. Chem. **58** (1981), 517.
[8] *Lortz, H. J.:* Anal. Chem. **28** (1956), 893.
[9] *Schoch, T. J.:* J. Am. Chem. Soc. **64** (1942), 2954.
[10] *Doppert, H. L.,* and *A. J. Staverman:* J. Polym. Sci. **4** (1966), 2367.
[11] *Merkus, H. G., J. W. Mourits, L. de Galan* and *W. A. de Jong:* Starch/Stärke **29** (1977), 406.
[12] *Ashby, J. H., H. B. Clarke, E. M. Crook* and *S. P. Datta:* Biochim. J. **59** (1955), 201.

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Solvent Extraction of Fatty Acids from Amylose Inclusion Complexes

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The extractability of palmitic and other common fatty acids from inclusion complexes with potato amylose was studied using a wide range of common lipid solvents. At ambient temperature negligible yields were obtained with light petroleum or diethyl ether, and yields were low with most other solvents except those containing methanol or water. At 100°C, methanol, ethanol and propanol and all alcohol-water mixtures gave good yields. Complexes of amylose with 1-*O*-palmitoyllysophosphatidylcholine also gave good yields when extracted with propanol-water (3:1) at 100°C. Since more rigorous conditions are required for extraction of lipids from native cereal starch granules, it seems that the barrier to lipid extraction is the structure of the granule rather than the resistance to lipid extraction of any possible inclusion complexes in the granules.

Lösungsmittelextraktion von Fettsäuren aus Amylose-Einschluß-Komplexen. Unter Verwendung vielfältiger allgemeiner Fettlösungsmittel wurde die Extrahierbarkeit von Palmitin- und anderen gewöhnlichen Fettsäuren aus Einschluß-Komplexen mit Kartoffelamylose untersucht. Bei Raumtemperatur wurden mit Leichtpetroleum oder Diethylether nur vernachlässigbare Ausbeuten erhalten, und die Ausbeuten waren gering bei den meisten anderen Lösungsmitteln außer denjenigen, die Methanol oder Wasser enthielten. Bei 100°C gaben Methanol, Ethanol und Propanol sowie alle Alkohol-Wasser-Mischungen gute Ausbeuten. Komplexe von Amylose mit 1-*O*-Palmitoyl-lysophosphatid-cholin gaben ebenfalls gute Ausbeuten, wenn mit Propanol-Wasser (3:1) bei 100°C extrahiert wurde. Da für die Extraktion von Lipiden aus nativen Getreidestärkekörnern härtere Bedingungen erforderlich sind, ist die Struktur der Körner eher die Lipidextraktion begrenzende Barriere als der Widerstand irgendwelcher möglicher Einschlußkomplexe in den Körnern gegenüber der Extraktion.

1 Introduction

The non-waxy cereal starches are unique among the major food starches in that they contain lipids roughly in proportion to their amylose content [1–13]. The lipids consist of free fatty acids (FFA) an lysophospholipids (LPL) in which 36–58% of the fatty acids are saturated and the rest are *cis*-unsaturated (linoleic and oleic with traces of linolenic) [13]. These lipids,