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SELECTIVITY AND KINETICS OF INTERESTERIFICATION REACTION OF GLUCOSE PENTAACETATE WITH FATTY ACID METHYL ESTERS

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Acetylated glucose fatty esters (AGFEs) were prepared by a solvent-free interesterification reaction of glucose pentaacetate (GPA) and mixed fatty acid methyl ester (FAME) of palm oil (PO)-based fatty acids. The relative selectivity of fatty acyl groups towards the GPA ring and the kinetics of the interesterification process were studied. The selectivity studies have shown that the longer chain fatty acyl groups were preferred in the interesterification process involving GPA and FAMEs. In the C_6 to C_{10} fatty acids group, C_{10} was the most favoured, while $C_{18:1}$ had the highest selectivity in the C_{12} to $C_{18:2}$ group. The results also showed that the reactions involving oleic-FAME and C_{6-10}-FAME proceeded via zero-order kinetics with respect to GPA.

Keywords:

Palm oil, acetylated glucose fatty ester, kinetic, interesterification reaction.

INTRODUCTION

Sugar-based esters of fatty acids are nonionic surfactants and are widely used in cosmetic, pharmaceutical, detergent and food industries. They are non-toxic, biodegradable and have multi-functional properties. We have recently synthesized AGFEs of PO-based fatty acids, oleic acid and a mixture of C_{6-10} fatty acids by a solvent-free interesterification reaction (Obaje *et al.*, 1999; Dzulkefly *et al.*, 2000a). This method avoided the use of toxic solvents such as pyridine, dimethylformamide or dimethylsulfoxide during reaction and processing (Weiss *et al.*, 1972). The two main products isolated and identified were mono- and di-substituted AGFEs. Their yields and properties were also reported (Dzulkefly *et al.*, 2000b). This paper reports the kinetics of the reaction and the relative selectivity of the fatty acyl groups in the interesterification reaction between GPA and FAME of PO origin.

MATERIALS AND METHOD

Materials

FAMEs of PO, palm kernel oil (PKO) and a mixture of C_{6-10} fatty acids were obtained from a local oleochemical company. FAMEs of oleic acid and α-D-GPA (99% purity) were purchased from Fluka Biochemika (Switzerland). Silica gel 60 (particle size 0.063-0.200 mm; 70-230 mesh ASTM) and all the solvents used (analytical grade) were obtained from E. Merck (Germany).

Synthesis of AGFEs

AGFEs were synthesized according to the method previously described (Obaje *et al.*, 1999; Dzulkefly *et al.*, 2000a). Briefly, a reaction mixture of GPA, FAME (mole ratio of 1:3) and a Na-metal catalyst (0.12 g) were heated at

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85 °C - 90°C for about 6 hr at 20 mmHg. The products, mono- and di-substituted AGFEs, were separated and purified by column chromatography using a 40 x 2 cm column packed with silica gel 60 (particle size 0.063-0.200 mm; 70-230 mesh ASTM), and eluted with 20% ethanol in hexane (v/v) and 10% ethyl acetate in hexane (v/v), respectively. The products were analysed with TLC, FT-IR and the structures were confirmed by ^{1}H and ^{13}C NMR spectrometry. The optimal catalyst loading, mole ratio, temperature and pressure were determined.

Selectivity Studies

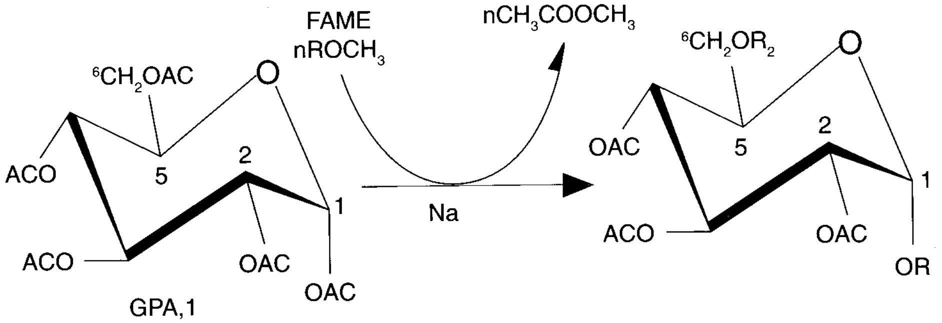
The profile of fatty acids substituted on the AGFE was studied by alcoholysis (using methanol) of the AGFE, and analysing the released FAMEs by GC-MS. Alcoholysis (or transesterification) of AGFE was performed according to the method described by Akoh and Swanson (1988). AGFE (1.0 g) was dissolved in 10.0 ml methanol, followed by addition of 0.5 ml methanolic NaOH solution (1.0 M) and vortexed vigorously for 2 min at room temperature. After neutralization with HCl (2.0 M), the released FAME was extracted with pentane (2.0 ml), dried over anhydrous Na_2SO_4 and analysed by GC-MS. Thin layer chromatography (TLC) was used to establish the completion of transesterification. GC-MS analysis (using a HP 1909B-112 gas chromatograph) was performed using an Ultra-2 capillary column (25 m length x 0.32 mm diameter x 0.52 µm film thickness) which was operated at initial temperature 100 °C (2 min), final temperature 200 °C (10 min) and ramp rate 5 °C min^{-1}. About 1 µl sample was injected at a split ratio of 50:1. Helium was used as carrier gas and the scan mass was between 50 to 550 amu. Identification of the fatty acyl groups was done by comparing the ion fragmentation patterns with that in the library resource. The percentages of the individual components were calculated from their peak areas. The percentage compositions of FAMEs from AGFEs and the corresponding reactant FAMEs were then compared peak by peak to determine their selectivity.

Kinetic Studies

Methyl acetate released as co-product during the interesterification reaction between FAME and GPA as previously described (Dzulkefly *et al.*, 2000b) was used in the kinetic studies. The amounts of methyl acetate-condensate, trapped by a cold trap, were measured quantitatively with time. The reactions involving $C_{6\text{-}10}$-FAME and oleic-FAME were selected for the purpose of the study. An ice-cold trap, fitted with a preweighted 10 ml graduated tube was connected in series to the reaction vessel, before the liquid nitrogen cold trap. The amount of methyl acetate collected in the tube was recorded at intervals. No condensate was observed in the liquid nitrogen cold trap. The amount (in moles) of methyl acetate, generated with time, was then fitted into the 1st-order (equation 6), 2nd-order (equation 7) and zero-order (equation 8) kinetic equations. The equation that gave the best fitted plot was adjudged the rate equation.

RESULTS AND DISCUSSION

Figure 1 shows the interesterification reaction of GPA and PO FAME.



GPA,1

Products
2. PKO-m; R_1 = palm kernel fatty acyl moiety; R_2 = Ac.
3. PKO-d; $R_1 = R_2$ = palm kernel fatty acyl moiety.
4. PO-m; R_1 = palm fatty acyl moiety; R_2 = Ac.
5. $C_{6\text{-}10}$-d; $R_1 = R_2 = -CO-(CH_2)_{4\text{-}8}-CH_3$.
6. Oleic-m; $R_1 = -CO-(CH_2)_7-CH{=}CH-(CH_2)_7CH_3$; R_2 = Ac.

Figure 1. Interesterification reaction of GPA with FAME and products.

Interesterification of GPA with FAMEs of PO, PKO, a mixture of C_{6-10} and oleic acids gave either one or two main products, *i.e.* mono- and/or di-substituted AGFEs (Dzulkefly *et al.*, 2000b). The mono-substituted product was identified as 1-O-fatty acyl-1,2,3,4-tetraacetyl-α-D-glucopyranose and the di-substituted was identified as 1,6-O-di-fatty acyl-2,3,4-triacetyl-α-D-glucopyranose (Dzulkefly *et al.*, 2000a). These results indicated that two positions were preferred for substitution of fatty acyl groups on the GPA ring, *i.e.* at positions C-1 and C-6. *Table 1* gives a summary of the starting materials and reaction products. The optimum reaction conditions were found to be at a reaction temperature of 80 °C-88°C, pressure of 20 -25 mmHg, mole ratio of 1 GPA: 3 FAME, catalyst load of 0.5% w/w, and reaction time of 4 - 6 hr.

Figure 2 shows the typical ion chromatograms of FAMEs obtained from alcoholysis of C_{6-10}-d (A) and PKO-m (insert). The relative compositions of individual fatty acids are given in *Table 2*. The percentage compositions were calculated based on the normalized peak area percentages. The selectivity of components was calculated by subtracting the initial FAME (reactant) percentile from the product FAME (AGFE) percentile. A positive difference indicated a preference for a fatty acyl group by the GPA ring, and thus, higher selectivity. Results have shown that for the short chain, C_{6-10} mixed fatty acids, C_{10} was the most favoured while C_8 was the least favoured in the interesterification reaction. Within the C_{12} to $C_{18:2}$ fatty acid series, $C_{18:1}$ was the most favoured (as shown by PKO-d and PO-m, *Table 2*) and C_{12} was the least favoured in all

TABLE 1. INTERESTERIFICATION PRODUCT OF GPA WITH FAMEs

Reactant FAME	Mono-substituted AGFE (yield)	Di-substituted AGFE (yield)
PKO-FAME	PKO-m (67%)	PKO-d (21%)
PO-FAME	PO-m (86%)	-
Oleic-FAME	Oleic-m (62%)	-
C_{6-10}-FAME	-	C_{6-10}-d (91%)

Notes:
m: mono-substitution of fatty acyl at position C-1 on the GPA ring.
d: di-substitution of fatty acyl at positions C-1 and C-6 on the GPA ring.

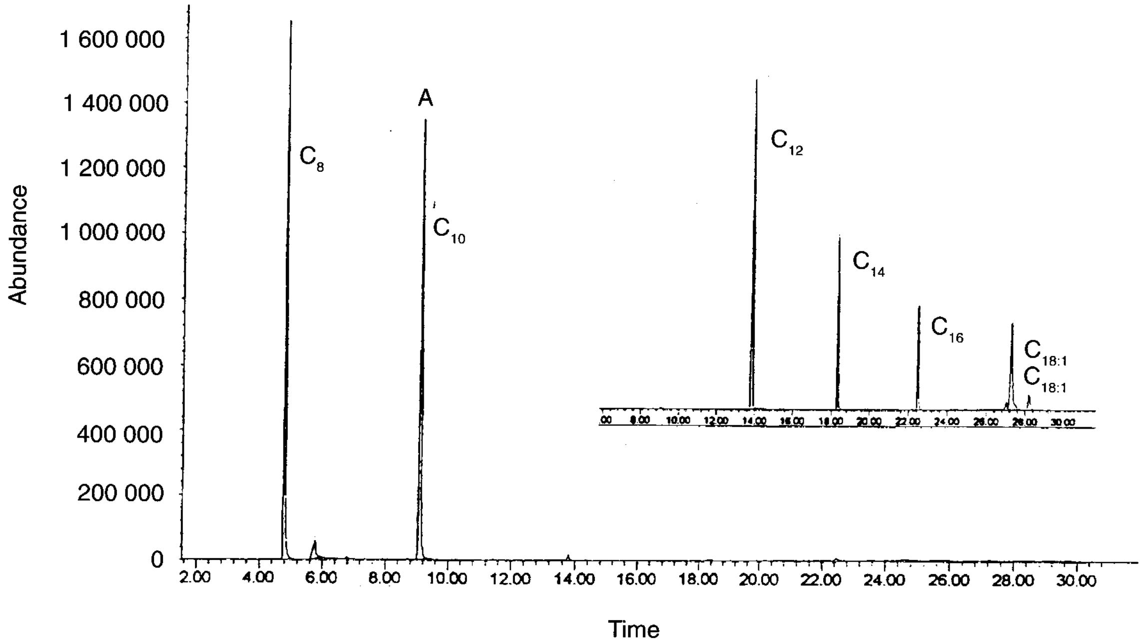


Figure 2. Total ion chromatograms (TIC) of fatty acyl groups obtained from alcoholysis of C_{6-10}-d (A) and PKO-m (insert).

TABLE 2. FATTY ACID PROFILES OF REACTANT AND PRODUCT FAMEs

FAME		PKO-m	PKO-d	PO-m	$C_{6/10}$-d
C_6	Reactant % comp.	_	_	_	3.0
	Product % comp.	–	–	–	0.0
	Difference in % comp.	–	–	–	-3.0
C_8	Reactang % comp.	_	_	_	58.7
	Product % comp.	_	_	_	48.8
	Difference in % comp.	_	_	_	-9.0
C_{10}	Reactant % comp.	_	_	_	46.3
	Product % comp.	_	_	_	47.7
	Difference in % comp.	_	_	_	+1.4
C_{12}	Reactant % comp.	52.4	50.4	0.6	7.8
	Product % comp.	43.4	36.7	0.0	0.0
	Difference in % comp.	-9.0	-14.7	-0.6	-7.8
C_{14}	Reactant % comp.	17.3	16.7	1.7	–
	Product % comp.	19.7	18.4	1.3	–
	Difference in % comp.	+2.4	+1.7	-0.4	–
C_{16}	Reactant % comp.	9.9	9.6	45.5	–
	Product % comp.	12.5	13.5	47.3	–
	Difference in % comp.	+2.6	+3.9	+1.8	–
C_{18}	Reactant % comp.	2.4	2.3	4.3	–
	Product % comp.	3.6	5.0	6.5	–
	Difference in % comp.	+1.2	+2.7	+2.2	–
$C_{18.1}$	Reactant % comp.	18.2	17.6	38.3	–
	Product % comp.	20.8	24.5	39.7	–
	Difference in % comp.	+2.6	+6.9	+1.4	–
$C_{18.2}$	Reactant % comp.	3.0	3.0	9.0	–
	Product % comp.	0.0	1.9	5.3	–
	Difference in % comp.	-3.0	-1.1	-3.7	–

the AGFEs produced. This shows that the longer chain fatty acyl groups are generally preferred in the solvent-less interesterification process involving GPA and PO-based FAMEs.

Kinetic Studies

Two interesterification reactions involving oleic-FAME (leading to oleic-m product) and $C_{6\text{-}10}$-FAME (leading to $C_{6\text{-}10}$-d product) were selected for the purpose of kinetic studies. In order to avoid the difficulty of monitoring the reactant concentrations during the reaction, the rate equations were derived in product concentration terms as follows:

A 1st-order rate with respect to the methyl acetate product can be written as:

$$r_M = dC_M/dt = k_1C_G \qquad (1)$$

where C_G and C_M are the molar concentrations of GPA and methyl acetate, respectively, at any time, *t*, during the reaction. The fraction conversion, $X_{G,}$ is defined as the fraction of reactant converted into the product at any time, *t*, and is given as:

$$X_G = (N_{Gi} - N_G)/N_{Gi} = N_M/N_{M\infty} = X_M \quad (2)$$

where *N* is the number of moles of the respective species indicated as subscripts. N_{Gi} represents the initial number of moles of GPA and $N_{M\infty}$ is the maximum number of moles of methyl acetate possible at optimum reaction time. But the molar concentration of *G* is:

$$C_G = N_G/V = N_{Gi}(1 - X_G)/V = C_{Gi}(1 - X_G) \quad (3)$$

Substituting $N_M/N_{M\infty}$ for X_G, equation (3) becomes:

$$C_G = C_{Gi}(1 - N_M/N_{M\infty}) \quad (4)$$

Substituting for C_G in equation (1) and integrating both sides gives:

$$\int dC_M/[C_{Gi}(N_{M\infty} - N_M)/N_{M\infty}] = k_1\int dt \quad (5)$$

Upon simplification and rearrangement, the 1st-order rate equation can be written as:

$$-\ln(N_{M\infty} - N_M)/N_{M\infty} = k_1t + C \quad (6)$$

Similarly, a 2nd-order rate equation can be written as:

$$N_M/[(N_{M\infty} - N_M)N_{M\infty}] = k_2t + C \quad (7)$$

and a zero-order rate equation is:

$$N_M = k_0t + C \quad (8)$$

The amount of methyl acetate collected in the two reactions were converted into mole numbers and fitted into the 1st-order (equation 6), 2nd-order (equation 7) and zero-order (equation 8) equations which were plotted against time (*t*). The results showed that the reactions involving oleic-FAME and $C_{6\text{-}10}$-FAME with GPA fitted best into the zero-order plot. The results from the $C_{6\text{-}10}$-FAME experiment gave the best fit on the zero-order plot with $R^2 = 0.966$, k_0 value of 0.0053 and an intercept of -0.0047 (*Figure 3*). Similarly, the results from the oleic-FAME experiment fitted best into the zero-order plot with a correlation coefficient $R^2 = 0.8963$, k_0 value of 0.0033 and an intercept of -0.0035. The 1st and 2nd-order plots for both reactions gave lower correlation coefficients (*Table 3*). These results suggested that the interesterification reaction between GPA and FAME followed zero-order kinetics with respect to GPA. This implies that the above reaction kinetics were independent of the GPA concentration. *Table 3* gives a summary of the rate constants and correlation coefficients (R^2) with respect to various rate orders.

For this reaction system, the minimum and the maximum reaction temperatures were 80°C and 92°C, respectively. Above 92°C, caramelization of the sugar moiety set in. This temperature range was too narrow and the silicon-oil bath used could not be kept at any fixed temperature for the duration of the reaction. The activation energy could not therefore be determined.

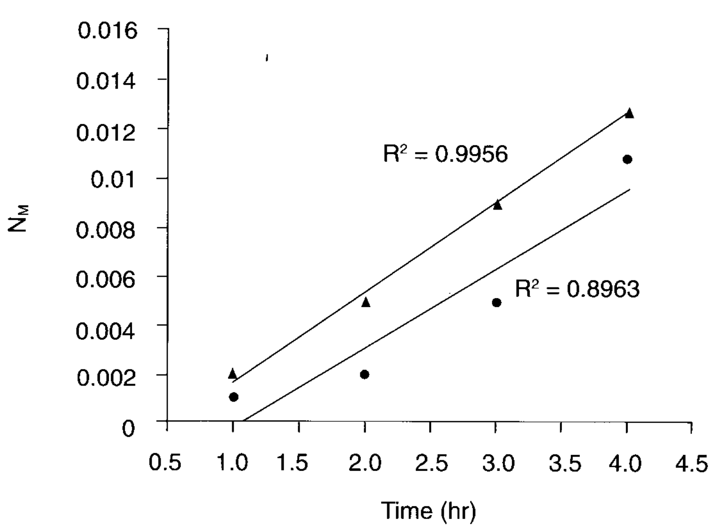


Figure 3. Zero-order plots for the interesterification reactions between GPA and oleic-FAME (•), and GPA and $C_{6\text{-}10}$-FAME (▲)

TABLE 3. RATE CONSTANTS (k_i) AND CORRELATION COEFFICIENTS (R^2) CALCULATED FOR THE ZERO-, 1st- AND 2nd-ORDER KINETICS

Reactant	Zero-order		1st-order		2nd-order	
Oleic-FAME	R^2	0.896	R^2	0.8513	R^2	0.8038
	k_0	0.0033	k_1	*-9.5564*	k_2	0.0067
C_{6-10}-FAME	R^2	0.996	R^2	0.8172	R^2	0.7099
	k_0	0.0053	k_1	-23.166	k_2	0.0299

Notes: 1st-order rate: $\ln(N_{M\infty} - N_M)/N_{M\infty}$ was plotted against *t*.
2nd-order rate: $N_M/[(N_{M\infty} - N_M)N_{M\infty}]$ was plotted against *t*.
Zero-order rate: N_M was plotted against *t*.

CONCLUSION

The solvent-free interesterification reaction provided a convenient route to the production of PO-based glucose fatty esters. This method produced non-toxic (solvent-residue-free) products, thus expanding the scope for application of products. A selectivity study showed that the long chain fatty acyl groups were preferred in the interesterification process and the reaction proceeded via zero-order kinetics with respect to GPA. The optimum reaction conditions were found to be at a reaction temperature of 80 °C-88°C, pressure of 20 - 25 mmHg, mole ratio of 1 GPA: 3 FAME, catalyst load of 0.5 % w/w, and reaction time of 4 - 6 hr.

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