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## HIGHER FATTY ACID ESTERS OF LACTIC ACID

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Direct esterification of fatty acids with lactic acid was carried out by solventless technique to give products containing essentially monoesters by activating the hydroxy group of lactic acid with the help of an alkali metal catalyst under specialized conditions. After finding a safe and convenient method fatty acid upto C<sub>18</sub> have been esterified with lactic acid. Characteristic of these compounds were evaluated by thin layer chromatography, melting point, ash contents and nuclear magnetic resonance. Ash contents of the compounds have been determined so as to observe the side reaction of the catalyst.

**Key words:** Fatty acid esters, Lactic acid, Glycerides.

### Introduction

History of esters originates from fatty acid esters of sucrose but very few references on synthesis of fatty acid esters of lactic acid are available in literature and most of them are on the use and analysis of acyl-lactylates which shows that these esters cover the field of synthesis upto 2 carbons of acetic anhydride with fatty acids.

Among fatty acid lactic acid esters, the application of only acyl-lactylate in cosmetics and toiletries has been reported [1]. However, it is open to question whether higher or lower acylates are being considered for the same purpose. Bruesch-weiler [2] analysed various non-ionic surfactants which include fatty acid glycerides themselves and esterified with HOAC, citric, lactic, tartaric and diacetyltartaric and fatty acid esters with sorbitan, polyglycol and sugars being used in foods and cosmetics. However, it neither depicts any method of preparation nor the type of fatty acid esterified. These appear to be acyl- derivative of acetic anhydride because there is a hint about diacetyl-tartaric acid that 2 carbons have been employed.

Data from Franzkec *et al.* [3] research on the use of acyl- lactylate as a food emulsifier covered preparations and analyses of acyllactylate but lacked the information about the number of carbon acylated. The present study have been undertaken with a view to developing a convenient and safe method for the preparation of fatty acid esters similar to carbohydrate material without affiliating solvent system.

The present method of ester synthesis is devoid of initial preparation of methyl or propylene glycol esters of fatty acids or chlorides and then breaking of these esters into fatty acid for reaction with lactic acid under high vacuum and temperature and solvent distillation during reaction. The product purification is achieved by obtaining the product at the surface of the water. It results in increasing the efficacy of the product.

### Experimental

**Procedure.** Lactic acid mono-esters of caprylic, lauric, myristic, Oleic, palmitic and stearic acids were prepared by reacting equimolar ratios and by activating hydrogen of the hydroxyl group of lactic acid with 31 gram atoms of potassium to one mole of lactic acid under specialized conditions. These conditions are : temperature was maintained upto 110° for 7 hr under anhydrous conditions with constant stirring using 2 gm anhydrous sodium sulphate so as to take the water of reaction under acidic conditions.

After completion of reaction several freezing and thawing of the compounds were performed so as to give negative energy for stabilization of ester bond. Lactic acid has acted both for solute and solubilizer.

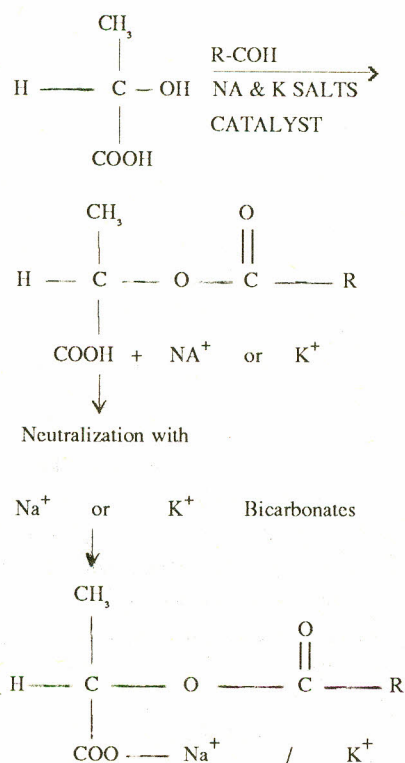
**Analysis.** Thin layer chromatograph plates 20 x 20 cm were prepared using silica gel 60 and activated by heating at 110° for 1 hr. Lactic acid esters were applied in butanol or chloroform solution with the help of a capillary tube (being used for paper chromatography).

Plates were run in a conventional solvent of 1-butanol: methanol: water, using a ratio of 40:11:19, by volume respectively at a temperature of 32°. Spots were visualised with iodine. The diethyl-ether and chloroform solutions were dried and analysed for melting point, normal proton NMR and ash contents. Statistical evaluation has been performed to establish a mean variation, and standard deviation between each experiment and standard error has been calculated to know the error of experiments performed.

**Crystalization.** The ester were neutralized with a mixture of sodium and potassium bicarbonates at room temperature with constant stirring. The esters start crystalizing at the surface of the water as curd and all these impurities remain soluble in water as the pH touches to near neutral i.e. pH 5-6.5. The esters were separated and dried in an oven at 100° for 12 hr for calculation of the yield

### Results and Discussion

Two phases were observed at the start of the reaction. The reactants became homogenous after 7 hr of the reaction. The product equate well with the theory. The authors believe the following structure of compounds.



Reactants used were of analytical or technical grades.

*Evidences to support the synthesis:*  $R_f$  values of the compounds showed the formation of fast moving compounds as compared to their respective fatty acid except the oleic acid-lactic acid compound which has shown slow moving compound as compared to oleic acid which may be due to the unsaturation in oleic acid (Table 1).

Fatty acid esters formulated from lactic acid by reaction with fatty acids such as lauric, myristic, palmitic and stearic acids have been obtained in solid forms. The esters obtained in solid forms have shown an increase in melting point by 8 to 16° and crystalized

TABLE 1.  $R_f$  VALUE OF ESTERS AND THEIR FATTY ACID.

Esters	$R_f$ value	Fatty acid	$R_f$ value
Caprylic-Lactic acid	0.95	Caprylic acid	0.85
Lauric-Lactic acid	0.873	Lauric acid	0.83
Myristic-Lactic acid	0.807	Myristic acid	0.66
Palmitic-Lactic acid	0.866	Palmitic acid	0.686
Stearic-Lactic acid	0.64	Stearic acid	0.53
Oleic-Lactic acid	0.625	Oleic acid	0.73

saturated fatty acid esters have shown a melting point of 142° to 145°. The esters of caprylic and oleic acids with lactic acid were obtained in liquid forms with decrease in 16° to 5° in melting point. The melting point of these compounds have to be taken very carefully to avoid any mistake. Refractive index of these compounds were also taken as compared to their parent fatty acids so as to verify the formation of esters (Table 2).

TABLE 2. MELTING/SIPPING POINT OF FATTY ACIDS AND THEIR ESTERS.

Fatty acid	Melting/Slipping point °C	Esters	Melting/Slipping point °C
Caprylic acid	16° (R.I:1.4232)	Caprylic-Lactic acid	0 - 2° (R.I:1.4315)
Lauric acid	42° - 44°	Lauric-Lactic acid	58° - 60°
Myristic acid	55° - 57°	Myristic-Lactic acid	68° - 70°
Palmitic acid	60° - 63°	Palmitic-Lactic acid	68° - 70°
Stearic acid*	52° - 54°	Stearic-Lactic acid	60° - 62°
Oleic acid	12° - 14° (R.I:1.4617)	Oleic-Lactic acid	7° - 9° (R.I:1.4665)
Lactic acid	18°	-	-
Yield %	= 75-80		

Refractive index = R.I. ;(\*Serono): It is of low melting point made in Switzerland.

Table 3 and 4 depicts the chemical shift of normal proton (<sup>1</sup>H) in all the esters. NMR. spectra of lactic acid and only palmitic acid were taken as standards because the method of synthesis of all these esters was same.

In NMR spectra the shift in normal proton (<sup>1</sup>H) position of the fatty acid esters appears to be found from ppm, 2.2, 2.6τ, 7.8, τ 7.4 respectively. Protons of fatty acids are found from ppm 0.9τ 9.1 to ppm 3.5τ 6.4 while the protons of lactic acid are found from ppm 5.5 τ 4.5. For evaluation of NMR spectra for shift position of proton bound to carbon near a single functional group is to be found in the vicinity of ppm 3.0 τ 7.0 and in every compound the shift in proton position is found to be at ppm 2.2 τ 7.8 which depicts the formation of and ester bond because protons of a hydrocarbon in a compound ends at ppm 1.5 τ 8.5.

Table 5 shows the estimation of ash contents and subjection of the data to statistical evaluation. Percentage of ash has been calculated so as to check the side-reaction of potassium catalyst which attacks the COOH group of lactic acid during reaction because the TLC showed a single spot. Percentages of potassium varies from 6 to 10.3 with respect to the fatty acids employed. It also depicts the verification of the product which is 75-80%. All the statistical limits fall within the range.

TABLE 3. ELUCIDATION OF CHEMICAL SHIFT OF NORMAL PROTONS ( $^1\text{H}$ ) OF VARIOUS ESTERS AS WELL AS STANDARD SAMPLES.

Lactic acid	PPM( $\delta$ )	0	1.3	1.5	2.6	3.3	3.7	4.1	4.2	5.00	5.5
	$\tau$ (TMS)	10	8.7	8.5	7.4	6.7	6.3	5.9	5.8	5.00	4.5
Palmitic-acid PP	PPM( $\delta$ )	0	0.9	1.3	1.6	2.25	2.6	3.6	—	—	—
	$\tau$ (TMS)	10	9.1	8.7	8.4	7.75	7.4	6.4	—	—	—
Caprylic-Lactic acid	PPM( $\delta$ )	0	0.9	1.3	1.5	2.2	2.6	5.9	—	—	—
	$\tau$ (TMS)	10	9.1	8.7	8.5	7.8	7.4	4.1	—	—	—
Lauric-Lactic acid	PPM( $\delta$ )	0	0.9	1.3	1.5	2.2	2.6	3.6	—	—	—
	$\tau$ (TMS)	10	9.1	8.7	8.5	7.8	7.4	6.4	—	—	—

TABLE 4. ELUCIDATION OF CHEMICAL SHIFT OF NORMAL PROTONS ( $^1\text{H}$ ) OF VARIOUS ESTERS AS WELL AS STANDARD SAMPLES.

Myristic-Lactic acid	PPM( $\delta$ )	0	0.9	1.3	2.2	2.6	3.5	—	—	—
	$\tau$ (TMS)	10	9.1	8.7	7.8	7.4	6.5	—	—	—
Palmitic-Lactic acid	PPM( $\delta$ )	0	0.9	1.3	2.2	2.5	3.5	—	—	—
	$\tau$ (TMS)	10	9.1	8.7	7.8	7.5	6.4	—	—	—
Stearic-Lactic acid	PPM( $\delta$ )	0	0.9	1.3	2.2	2.6	3.6	—	—	—
	$\tau$ (TMS)	10	9.1	8.7	7.8	7.4	6.4	—	—	—
Oleic-Lactic acid	PPM( $\delta$ )	0	0.8	1.2	1.5	1.9	2.15	2.5	2.7	2.25
	$\tau$ (TMS)	10	9.2	8.8	8.5	8.1	7.85	7.5	7.3	4.75

TABLE 5. ESTIMATION OF ASH PERCENTAGE IN ESTERS AND STATISTICAL CALCULATION ABOUT THE LIMIT OF CONFIDENCE OF EXPERIMENTS PERFORMED

Esters	% of ash in		M e a n	
	compound	Rearranging in data in sequence		
Caprylic-Lactic acid	6.00	6.00	-2.3	5.29
Lauric-Lactic acid	9.60	7.3	-1.00	1.00
Myristic-Lactic acid	8.00	8.00	-0.3	0.09
Palmitic-Lactic acid	7.30	8.6	+0.3	0.09
Stearic-Lactic acid	10.3	9.6	+1.3	1.69
Oleic-Lactic acid	8.6	10.3	+2.0	4.00
				12.16

SD = 0.58; SE = 0.24; The limit of confidence is 95%

### Conclusion

The authors found that safe and most convenient method for the preparation of hydroxy-glycerides of sugar

derivatives using metal ion as a catalyst. The reaction takes place well near acidic as well as near neutral pH. Catalyst reacts only with the COOH of lactic acid to some extent, if present, while COOH group of fatty acid do not react with the catalyst as to form potassium soap.

This process is not extendable to other organic acid other than fatty acids.

### References

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