ANALYSIS OF CALCIUM SALTS OF FATTY ACID-LACTIC ACID CONDENSATES[1]

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ABSTRACT

Calcium salts of fatty acid-lactic acid condensates, which are used as dough conditioner, have been analyzed. After removal of the calcium by ion exchange, the fatty acids and fatty acid-lactic acid condensates are extracted with diethyl ether and converted into their methyl esters. These esters can be analyzed by temperature-programmed gas-liquid chromatography. All samples investigated contained fatty acid-lactic acid condensates with six lactoyl groups.

Calcium salts of fatty acid-lactic acid condensates can be prepared by heating fatty acids and lactic acid at 150°–200°C. at reduced pressure. The free carboxyl groups are then converted into the calcium salts by partial neutralization with calcium oxide. The molecular structure of the product (1) obtained is $[RCO(OCHCH_3CO)_nO]_2$ Ca in which the average value of n varies between 1 and 3.

These products are used as dough conditioner (2,3) and are marketed in the USA by C. J. Patterson & Co. under the name of "Verv-Ca." Since 1963 the use of these products has been allowed by the Food and Drug Administration (4) (maximum amount: 0.5% calculated on the flour). The specification given by the FDA is: acid value 82–103, ester value 140–188, calcium content 4.2–4.4%, lactic acid content 32–35%.

These values, however, do not give any indication of the composition of the fatty acid-lactic acid condensates present in the dough conditioner. Therefore, in this paper methods are described for analyzing these products in detail.

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With deep regret we announce the sudden death of Mr. G. Jurriens during the preparation of this manuscript.

Materials and Methods

Two samples of Verv-Ca (V-I and V-II), supplied by the manufacturers, were analyzed. For comparison, two more samples of dough conditioner were prepared by us, by the method described in U.S. Patent 2,733,252 (1), and likewise investigated. In the sequel these samples are referred to as A-I and A-II.

The acid and saponification values were determined according to AOCS standard procedures (5). From these data the ester value was calculated. The calcium content was determined by charring the sample and extracting the residue with dilute hydrochloric acid. Finally the calcium in this solution was determined as calcium carbonate by precipitation with oxalic acid followed by filtration and flame photometry.

Total Content of Lactic Acid and Fatty Acid. The calcium salts are converted into their acid form by stirring 1 g. of the sample with 2 ml. ion exchanger (Bio-Rad AG 50 W-x8, hydrogen form, washed acid-free with water) in 100 ml. 80% ethanol at 50°C. After 5 min. the ion exchanger is filtered over a Büchner funnel and washed with 80% ethanol. The bulk of the ethanol is removed from the filtrate, with a Rotavapor.

The water layer is saponified with 20 ml. 0.5*N* alcoholic alkali and transferred to a separatory funnel with 20 ml. water. After acidification with 25 ml. 0.5*N* hydrochloric acid, the mass is extracted twice with light petroleum (b.p. 40°–60°C.). The light petroleum is washed with water which is afterward added to the water layer. The lactic acid content in the water layer is determined by titration with 0.1*N* NaOH. To determine the total fatty acid content in the light petroleum the solvent was evaporated, the fatty acids were taken up in neutralized ethanol (indicator phenolphthalein), and the solution was titrated with 0.1*N* NaOH.

A blank determination is carried out by titrating a mixture of 20 ml. 0.5*N* alcoholic alkali and 25 ml. 0.5*N* hydrochloric acid with 0.1*N* NaOH. The total lactic acid content is given by:

$$(S_1 - B)/W \times 0.1 \times 90 \times 100\%$$

and the total fatty acid content by

$$(S_2/W) \times 0.1 \times M \times 100\%$$

where:

S_1 and S_2 = ml. 0.1*N* NaOH used for the lactic acid and fatty acids respectively;

B = ml. 0.1*N* NaOH used for the blank;

W = weight of dough conditioner in mg.;

M = average molar weight of fatty acids.

The fatty acids are converted into methyl esters with diazomethane and analyzed gas-chromatographically. Apparatus: Carlo Elba model C, column 180 × 0.4 cm. Polyethylene glycol adipate (3%) on Diatoport S (80- to 100-mesh). Column temperature 175°C., temperature injection port and detector 200°C.

Content of Lactic Acid and Lactic Acid Condensates. After conversion of the calcium salts into acids and removal of the ethanol, the water layer is extracted with ether. The water layer is now divided into two equal portions in which the amount of acid is determined before and after saponification. Assuming that only lactic acid and lactoyl-lactic acid are present, the percentages of these components can be calculated by means of the following equations:

$$\text{lactoyl-lactic acid content} = (B-S_3-S_4)/\tfrac{1}{2}W \times 162 \times 0.1 \times 100\%$$

$$\text{free lactic acid content} = (2\,S_3+S_4-B)/\tfrac{1}{2}W \times 90 \times 0.1 \times 100\%$$

where:

S_3 = ml. 0.1*N* NaOH used before saponification;

S_4 = ml. 0.1*N* NaOH used after saponification;

B = ml. 0.1*N* NaOH used by the blank after saponification;

W = weight of dough conditioner in mg.

Analysis of Ether-Soluble Acids. The ether-soluble acids (fatty acids and fatty acid-lactic acid condensates) are converted into methyl esters with diazomethane and subsequently analyzed by means of temperature-programmed gas-liquid chromatography (GLC). The apparatus used was an F&M model 400 equipped with flame ionization detector; column length 2 m.; internal diam. 2 mm.; packed with 2% SE-30 (General Electric) on Diatoport S (80- to 100-mesh); temperature of the injection port 210°C., detector 300°C. During the analysis the flow rate of the carrier gas (nitrogen) was maintained at 20 ml./min. Programming was started 5 min. after injection at 170°C. at 2.5°C./min. and stopped at 295°C.

Results and Discussion

The conversion of the dough conditioner into the acid form by means of an ion exchanger can be completed within 5 min. This was checked by drawing samples after 1 and 5 min. and investigating them for the presence of calcium lactate by paper chromatography (see Fig. 1).

To ascertain whether hydrolysis of the fatty acid-lactic acid condensate occurs during the treatment with the ion exchanger, the amount of water-soluble acids was determined after 10 and 40 min.

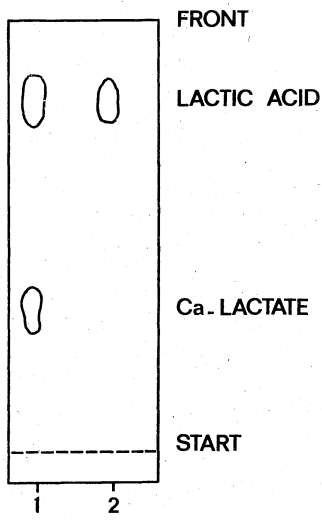

Fig. 1. Paper chromatography of dough conditioner (samples A) after conversion into its acid form by ion exchange. Paper: Whatman No. 1 (5 × 23 cm.) washed with water-pyridine-glacial acetic acid (80–15–5). Eluant: isopropyl alcohol-pyridine-glacial acetic acid-water (8–8–1–4). Detection: solution of 100 mg. brom-cresol purple in 100 ml. ethanol-acetone (10/90 v./v.) with 3 drops of 28% ammonia. 1) After ion exchange for 1 min. 2) After ion exchange for 5 min.

The amounts found were 0.91 and 1.01 meq. per g. of sample respectively, showing that hardly any hydrolysis had occurred.

In Table I some characteristic values and the percentages of the

TABLE I
ANALYTICAL DATA OF THE SAMPLES

	VERV-I	VERV-II	A-I	A-II
Acid value	92.5	85.7	100.0	...[a]
Ester value	198.1	151.8	150.8	...[a]
Calcium (wt. %)	4.0	4.2	3.1	1.1
Total fatty acid (wt. %)	72.0	65.3	66.7	65.7
Total lactic acid (wt. %)	20.5	32.0	27.9	33.3
Free lactic acid (wt. %)	6.2	9.3	5.7	6.1
Polymeric lactic acid (wt. %)	3.8	0.4	1.4	3.3

[a] Not determined.

main components are given, and in Table II, the fatty acid composition of the samples.

The ratio of the different components obtained by temperature-programmed GLC of the ether-soluble acids (Fig. 2) was determined by triangulation. The peak area is corrected by means of the response factors calculated according to Ongkiehong (6,7). It then increases by

TABLE II
FATTY ACID COMPOSITION OF THE SAMPLES (WT. %)

FATTY ACIDS	VERV-I	VERV-II	A-I	A-II
14:0	trace	trace	1.5	1.5
16:0	1.5	6.0	43.0	46.5
16:1	0.5	trace	6.5	1.5
17:0	trace	trace	1.5	1.5
18:0	74.5	93.5	38.5	46.5
18:1	21.5		9.0	2.0
20:0	1.5	0.5	0.5	

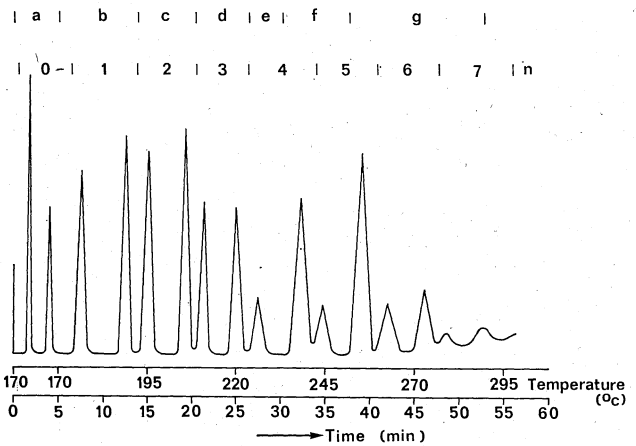

Fig. 2. GLC analysis of methyl esters of fatty acid-lactic acid condensates of samples A-II: n = number of lactoyl groups; heating rate 2.5°C./min. Attenuation: a = 100 × 64; b = 100 × 32; c = 100 × 16; d = 100 × 8; e = 100 × 4; f = 100 × 2; g = 10 × 4.

12%. The average response factor determined for the methyl esters of Verv-II is 1.10.

The theoretical correction factors are given in Table III.

TABLE III
THEORETICAL RESPONSE FACTORS FOR FATTY ACID-LACTIC ACID CONDENSATES

	THEORETICAL RESPONSE FACTOR
Fatty acid (C_{18})	1.00
Fatty acid + lactoyl group	1.10
Fatty acid + two lactoyl groups	1.19
Fatty acid + three lactoyl groups	1.27
Fatty acid + four lactoyl groups	1.33
Fatty acid + five lactoyl groups	1.38
Fatty acid + six lactoyl groups	1.42

The results of the GLC analyses are given in Table IV. The com-

TABLE IV
COMPOSITION (WT. %) OF THE ETHER-SOLUBLE ACIDS DETERMINED BY GAS-LIQUID CHROMATOGRAPHY

SAMPLE	CHAIN-LENGTH OF FATTY ACID	NUMBER OF LACTOYL GROUPS						
		0	1	2	3	4	5	6
Verv-I	16	2	1.0	0.5				
	18	32.5	35.5	16.5	7.0	3.0	1.0	0.5
Verv-II	16	3.0	3.0					trace
	18	24.0	40.0	19.0	7.5	3.0	0.5	trace
A-I	16	17.0	18.0	8.5	3.0	1.0	0.5	trace
	18	22.0	18.5	7.5	2.5	1.0	0.5	trace
A-II	16	14.5	23.5	9.5	3.0	1.0	0.5	trace
	18	14.0	21.0	8.0	2.5	1.0	0.5	trace

pounds were identified on the basis of their retention times. From the occurrence in the samples of Verv of fatty acid-lactic acid condensates with three and more lactoyl groups, it can be concluded that these products were not prepared by polymerization of stearoyl chloride and lactic acid polymerized at low temperature (< 100°C.), as described in the patent (8).

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