The Oxidation of 9:10 Diketostearic Acid by Peracetic Acid (Baeyer and Villiger Reaction)

ABSTRACT

Diketostearic acid 9:10 is readily and speedily oxidized by peracetic acid, at low temperatures to high yields of azaleic acid and nonanoic acids.

Diketostearic acid 9:10 (Stearoxylic acid) was prepared from stearolic acid by the method of Khan and Newman (1). Stearolic acid, 5.6 g, (prepared from oleic acid by bromination at 0 C in petrol ether solution followed by dehydrobomination with methanolic potassium hydroxide) was dissolved in a solution of 1.5 g KOH in 100 cc water and diluted to 3 liters. Sodium bicarbonate, 1 g, was added and the pH adjusted to ca. 7.5 by the passage of CO_2 gas until the mixture was only very faintly pink to phenolphthalein. A solution of 6.3 g potassium permanganate in 300 cc water was added all at once and the mixture was maintained at 25 C for 60 min. Then the excess permanganate was removed by passage of SO_2 gas until colorless. The product was filtered off, washed with water and recrystallized from 80 cc of 95% ethanol. Pale lemon crystals were obtained, mp = 84-85 C, neutralizing equivalent = 310. (Diketostearic acid requires mp = 85 C, neutralizing equivalent = 312.)

Oxidation of Diketostearic Acid With Peracetic Acid

Diketostearic acid (3.12 g, 0.01 mole) was dissolved in 40 cc glacial acetic acid by warming gently to ca. 40 C. Then 10 cc 30% hydrogen peroxide (100 vol) was added. This caused the precipitation of the diketo-acid, giving the mixture the consistency of a thick slurry. After 5 min the mixture became clear and homogeneous, and after a further 20 min the last traces of the yellow color due to the diketo-acid had disappeared. The reaction was evidently more or less complete, but the mixture was allowed to stand for a further 18 hr at 28 C. It was then diluted with 300 cc^3 water and extracted three times with petroleum ether (3 x 100 cc^3) to remove the monobasic acid scission product. On removal of the solvent, 1.502 g of product was obtained, mp = 12.5 C., neutralizing equivalent = 160, n_D^{20} = 1.4310. (Nonanoic acid requires mp = 12.5 C, neutralizing equivalent = 158, n_D^{20} = 1.43057.) Yield was 95.05%.

The extracted aqueous solution was further extracted with four successive quantities of ether. On removal of the solvent, 1.740 g residue was obtained. This was recrystallized from water, when the final product had mp = 106.5 C, neutralizing equivalent = 94. This corresponds to azaleic acid. Yield was 92.55%.

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Rapid Methods for Determination of Free Fatty Acids Contents in Fatty Oils

ABSTRACT

Rapid qualitative and quantitative methods for determining the free fatty acid (FFA) contents in common oils and fats are reported. Qualitative method is based on the type of color developed in the presence of BDH indicators (Universal and "678") when a known excess of alkali is added to an alcoholic solution of oil or fat. By this method, low (0.0-0.25), medium (0.26-0.99) and high (1.0 and above) FFA levels in fatty oils may be distinguished. Quantitative method is a simplified modification of the usual procedure of determining the FFA contents of oils and fats by titration against standard alkali solution in the presence of BDH Universal or "678" indicator. The results of the rapid methods agree well with those of the standard AOCS method.

TABLE I

Colors and Free Fatty Acid (FFA) Contents

Range	FFA level	Color developed
With BDH Universal indicator		
Low	0.0-0.25	Indigo to blue
Medium	0.26-0.99	Green to yellowish green
High	Over 1.0	Yellow, orange, buff or chocolate
With BDH "678" indicator		
Low	0.0-0.25	Violet or indigo
Medium	0.26-0.99	Light blue to light green
High	Over 1.0	Yellow to orange yellow

Fatty oils may contain low or high FFA. Raw oils might look like alkali-refined oils. Tests have been developed to rapidly (a) distinguish between low and high FFA content oils and (b) determine the FFA contents in such oils.

TABLE II

Efficacy of Rapid Methods of Determining Free Fatty Acids (FFA) of Oils[a]

Sample no.	FFA by standard AOCS method	FFA by rapid methods	
		BDH indicator	Phenolphthalein indicator
		BDH Universal	
1	0.637	0.599	0.599
2	0.952	0.839	0.863
3	1.09	0.911	0.935
4	1.37	1.39	1.39
5	2.70	2.78	2.92
6	5.83	5.99	5.85
		BDH "678"	
7	1.40	1.50	1.55
8	1.90	1.70	1.75
9	2.56	2.20	2.25

[a]Peanut oil and cottonseed oil were used in the experiments. For samples 1-3, 0.017 N alkali was used. For samples 4-6, 0.09877 N alkali was used. For samples 7-9, 0.03546 N alkali was used.

QUALITATIVE METHOD

The qualitative method distinguishes fatty oils having low FFA contents from those having high FFA contents. The principle of the test is that the nature of visible color that is developed when a known excess amount of alkali is added to fatty oils in ethyl alcohol with BDH Universal or "678" indicators depends upon the FFA contents of the oils. The principle is the same as that of determining the acidity of transformer oils reported by Nanda (1) who used sodium carbonate. In the present method sodium hydroxide is used instead of sodium carbonate, which was found not suitable for fats which possess wider and higher range of acidity than the transformer oils for which Nanda's work was developed. The reagents employed are: neutral ethyl alcohol, standard sodium hydroxide solution (0.0085 N) (strength of the alkali may vary slightly on either side of this value but should be clearly around this figure) and BDH universal or BDH "678" indicator with dropper of 1 mm diameter. The apparatus used are: test tubes, 16 mm x 125 mm; pipette 5 ml capacity, graduated in 0.1 ml; 1 ml pipette; semimicro burette, 5 or 10 ml capacity, graduated in 0.05 or 0.10 ml; and test tube stand.

The test is conducted as follows: Take 1.1 ml oil-fat sample into a clean and dry test tube using 5 ml pipette and shake the tube. Add 1 ml standard sodium hydroxide solution using the pipette and shake the tube. Add five drops of BDH Universal indicator or BDH "678" indicator with the dropper and shake. Observe the resulting color in the alcohol layer. Depending on the acidity of the oil sample, different colors develop.

Table I gives the range of free fatty acids in the oil and the color developed.

The method was tested on oils from peanut, sesame seed, safflower, cotton seed, ajowan, rice bran, tea seed, orange seed, muskmelon, watermelon and tobacco seed oil.

QUANTITATIVE METHOD

In the quantitative method the principle is the same as that of estimating FFA of oils and fats by titration against alkali using suitable indicators.

The reagents employed are: neutral ethyl alcohol; standard sodium hydroxide solution (For low and medium FFA oils, as determined by the quantitative method, 0.02 N solution may be used, and in the work 0.017 N solution was used. For high FFA oils, decinormal solution may be used. In the work, solutions of 0.0988 N and 0.03546 N were actually used); and BDH Universal indicator, BDH "678" indicator, or phenolphthalein indicator. The apparatus used are the same as those in the qualitative method. The quantitative test is carried out as follows: Take 1.1 ml oil-fat sample in a test tube by means of 5 ml pipette. Add 1 ml neutral ethyl alcohol using 1 ml pipette and shake the test tube. Add three drops of BDH Universal, "678" indicator or phenolphthalein, and shake the test tube. Into this mixture, run sodium hydroxide solution from burette shaking the test tube, until a sky blue color, in the case of BDH Universal indicator, is obtained as an end point. The test tube can be placed in the stand during addition of alkali. The color also corresponds to Sky Blue given in the Indian Standard IS: 5-1961 Colors for Ready-Mixed Paints (Second revision). In the case of BDH "678" indicator, the color corresponds to Light Admiralty Grey as given in the above standard. With phenolphthalein indicator, the end point is the familiar pink color.

The FFA content as oleic acid is calculated by the formula: V x N x 28.8, where V is the milliliters of alkali used up and N is the normality of the alkali solution. Table II gives the efficacy of the rapid method as compared to the standard method (AOCS Method Ca 5a-40).

The methods described above are applicable to common oils and fats and take about 2-5 min to perform. They do not require weighing, heat or electricity. They are simple and inexpensive. The results compare favorably with those of standard method.

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