- *Letter to the Editor*

The Quantitative Separation of Mono- and Dibasic Acids Produced in the Oxidative Breakdown of Unsaturated Fatty Acids

Dear Sir: Dibasic acids isolated from the azelaoglycerides giving water-insoluble magnesium salts derived from a number of C_{16}–C_{18} acid vegetable fats showed mean molecular weights of 188 to 204, the values differed for fats from different biological sources (Kartha, JAOCS *42,* 351, 1965; Kartha and Narayanan, Ind. J. Chem. *3,* 188, 1965). This has posed a new problem in fat chemistry, namely, determination of the distribution of the site of the first double bond (FDBS) in fats from different Biological sources. The success of this depends on the availability of methods for quantitative breakdown of double bonds without producing any over-oxidation (Stein, JAOCS *38,* 636, 1961; *42,* 326, 1965) and for quantitative separation of the dibasic acids corresponding to the first double bond from other products of oxidation. Acetic acid-acetone-permanganate oxidation (Kartha, JAOCS *30,* 280, 1953) has been shown to be appropriate for the initial breakdown of the fats as it does not produce any chain degradation of saturated higher fatty acids (Kartha and Sethi, J. Sci. Ind. Res. *15B,* 103, 1953; Kartha and Narayanan, Ind. J. Agric. Sci. *27,* 73, 1957). If the fat is oxidized by this procedure and the products of oxidation are taken up in diethyl ether and washed well with water, all the lower dibasic acids produced from polyethenoid acids are quantitatively removed. Hydrolysis of the residue then gives a mixture of dibasic acids corresponding to the site of the first double bond along with the lower monobasic acids produced during the oxidation and the higher saturated acids originally present in the fats.

The quantitative separation of mono- and dibasic acids produced by the oxidative breakdown of unsaturated fatty acids has been effected almost exclusively by crystallization from or trituration with petroleum ether. However with one exception (Lemieux and von Rudloff, Can. J. Chem. *33,* 1701, 1955; von Rudloff, JAOCS *33,* 126, 1956; von Rudloff, Can. J. Chem. *34,* 1413, 1956) all other investigators have reported isolation of dibasic acids only to the extent of 80% to 90% of theory for all mono-ethenoid acids (Armstrong and Hilditch, J. Soc. Chem. Ind. *44,* 43T, 1925; Jones and Stolp, JAOCS *35,* 71, 1958; Boelhower, Gerckens, Lie and Waterman, JAOCS *30,* 59, 1953). In our laboratory when specimens of castor oil, sesame oil and peanut oil of known saturated acid contents (2%, 15.5% and 19% respectively) were oxidized and submitted to the above outlined procedure, the recovery of petrol insoluble dibasic acids amounted to only 83% to 86% of theory on the basis of unsaturated acids oxidized.

It was suspected that the less than theoretical recovery of dibasic acids might be due to inefficiency of separation procedures. To ascertain this, known mixtures of mono- and dibasic acids were separated by crystallization from petroleum ether (separation by trituration gives the same results). C_{10} and lower dibasic acids are completely insoluble in petroleum ether bp 40–60 or 60–80 C at or below 30 C, but when known mixtures of mono- and dibasic acids, in about equal proportions by weight, were submitted to the separation, the recovery of the dibasic acids was only 85% to 92% of theory. The lowest recovery took place when stearic acid was used as monobasic acid and the highest when caproic acid was used. Obviously the system petroleum ether-monobasic acid has some dibasic acid solubility at low temperatures (20–30 C) while the pure solvent has none.

Some of the dibasic acids held in the filtered petroleum ether-monobasic acid solution by intersolubility or co-solvency effects can be recovered by shaking the solution with water and evaporating off the water on a water bath. C_8 and higher monobasic acids are practically insoluble in water in presence of petroleum ether, and C_6 and lower monobasic acids dissolved in the water are removed by evaporation on the water bath. Three extraction at a solvent ratio of 1:2(petrol-water) are usually necessary to effect quantitative recovery in case of C_{10} and lower dibasic acids. C_{12} and higher dibasic acids are appreciably soluble in petroleum ether solution even at 15–30 C and they are also comparatively insoluble in cold water. Hence, when such acids are present in appreciable quantities, quantitative separation of mono- and dibasic acids is not possible at all with petroleum ether.

The present studies show that structural results based on data obtained by the earlier petroleum ether separations are liable to a larger extent of error than hitherto realized. Homologs present in smaller proportions may have escaped detection altogether, and their proportions, even when detected, may be very much different from those originally produced. It is also likely that in cases where this separation has isolated more than about 90% of theory of petroleum ether insoluble dibasic acids (Lemieux and von Rudloff, loc. cit.) the apparent yield might have been increased by accumulation of nonvolatile poly hydroxy or oxido derivatives, or both, due to incomplete scission. In instances where the petrol-insoluble dibasic acids have amounted to 98–99% of theory (Lemieux and von Rudloff, loc. cit.) a good proportion, at least 10–15%, may be only polyhydroxy or oxido acids, and this would correspond to maximum chain scission of 90–94% only, besides production of much partially oxidized materials. When such techniques are used for breakdown of fats prior to analysis for glyceride structure the results should be evaluated in the light of the limitations discussed above.

A. R. S. Kartha
Division of Chemistry, Indian
Agricultural Research Institute
New Delhi, India

[Received September 12, 1967]