

diethyl ether, ethyl acetate, iso-octane, hexane and glacial acetic acid (10:5:35:50:1). The spots were visualized by spraying the plates with 50% aqueous H₂SO₄ saturated with potassium dichromate and charring. The procedure of Hartman (3) was employed for the cleavage of the isopropylidene glycerol ester and the isolation of α -monopalmitin. α -Monoglycerides of lauric, palmitic, stearic, oleic and linoleic acid were prepared using this method (Table I). The α -monoglyceride of linoleic acid darkened somewhat during preparation, but was easily decolorized with the aid of activated carbon.

We were unable to prepare α -monoglycerides (as the isopropylidene derivatives) in the time periods suggested by Hartman (3). In order to obtain complete reaction of the fatty acids employed here, considerably longer periods of time were required when chloroform was used as the solvent. Benzene proved to be superior to chloroform as a carrier solvent. The removal of the

water formed during the reaction is most efficiently accomplished by the use of an adsorbent such as anhydrous magnesium sulfate.

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Stabilization of Linoleic Acid by Arginine and Lysine Against Oxidation¹

THE REACTION of fatty acid anions with protein materials has long been known and since amino acids have proved to be at least potential antioxidants, we are prompted to report the stability of linoleic acid salts of amino acids toward oxidation by air.

The results illustrated in Tables I and II, clearly indicate that the linoleic acid salts with the basic amino acids have unusual stability toward oxidation. Triethanolamine also showed a stabilizing effect. The basic nitrogen compounds appear to stabilize the unsaturated site of linoleic acid and eliminate oxidative rancidity as evidenced by the fact that the iodine value and apparent linoleic acid content remained almost unchanged.

While it is recognized that linoleate content by spectral analysis may not be an accurate measure of the amt of unchanged linoleate in an oxidized linoleate, the gross decreases in the control compared to the very slight changes in the linoleate salts is certainly an indication of autoxidation stabilization in the salts. The oxidized controls were grossly rancid, while the linoleate salts were essentially non-rancid. Also, the linoleate salt of arginine, which showed no stability by analyses, was quite rancid.

The mechanism of stabilization of the unsaturated sites of the linoleic acid by basic amino acids is not fully understood. However, we speculate that these basic nitrogen compounds may either form a complex or may act as free radical chain terminators or oxygen scavengers. It is thought that C-11 (the α -methylene group) of linoleate tends to form free radicals in the presence of oxygen. This leads to the formation of hydroperoxides which undergo secondary reactions causing rancidity. The failure of basic amino acids to stabilize linolenic acid (in contrast to the linoleate) indicates that salt-complex formation is more important than free radical termination. Perhaps the free amino group of the basic amino acid forms a salt with the carboxylic acid group of the fatty acid and the α -

TABLE I
Room Temp Storage Tests

	Iodine value after exposure, days ^a		
	0	16	49
Safflower fatty acid.....	149	133.3	102.1
L-Arginine safflate.....	92.1	94.1	93.1
L-Lysine safflate.....	90.6	87.2	87.3
L-Lysine linoleate.....	116.8	113.9	114.2
Linolenic acid.....	268.9	142.0 (14 days)	
Arginine linolenate.....	161.7	83.3 (14 days)	

^a Evidence of gross loss of linoleate in the linoleic acid control and very little loss in the linoleate salts was also obtained by spectral measurements of diene content.

TABLE II
Storage Test of Salts at 60C, Hot Air Circulated Oven^a

	Iodine value after exposure, days					
	0	10	25	53	54	103
Safflower fatty acid.....	149	115.4	113.8	89.1
Linolenic acid.....	181	97.1	67.4	60
Arginine safflate.....	92.1	92.8	90.6	86.4
Lysine safflate.....	90.6	92.9	93.1	93.6	92.1
Lysine linoleate.....	116.8	114.8	114.5	114.8	113.3

^a In this series, spectral determination of diene content indicated gross loss of linoleate in the control acids and very little loss in the salts.

amino carboxylic acid portion of the basic amino acid is then in a favorable position to affect the double bonds or the doubly activated α -methylene group at C-11 in a manner which stabilizes it to attack by oxygen or free radicals.

The fact that *linolenic* salts of basic amino acids are *not* stable may be explained by the presence of two active methylenes and only one available α -amino carboxylic acid group.

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