

The Alkylation of Linseed Oil

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The structures of linoleic and linolenic acids which are present in linseed oil, have been indicated as having the $=CHCH_2CH=$ grouping.^{1,2,3} It occurred to the authors that the CH_2- portion of the grouping might be active enough to show the reactions of active methylene groups, as shown by such compounds as cyclopentadiene, malonic ester and others.

The first evidence of reaction which it is desired to report at this time is a reaction analogous to that of malonic ester. For this purpose an alkali-refined neutral linseed oil was converted to the mixed methyl esters directly by alcohol interchange. An excess of absolute methanol, containing hydrogen chloride was added to dry linseed oil and refluxed until the reaction was complete. The mixed methyl esters after purification were distilled at 200° under 6 mm. pressure.

Approximately 0.1 mole of these mixed methyl esters was treated with 0.1 mole of sodium ethoxide dissolved in excess absolute ethanol, and refluxed at 60° for about ten minutes. To the cooled mixture in the flask, 0.13 mole of ethyl iodide was added gradually, with thorough shaking. This reaction mixture after heating at 90° on the water-bath for forty minutes, was allowed to stand overnight. The excess ethanol and ethyl iodide were distilled and the remaining solution filtered. The filtrate was dissolved in ether, washed with brine, then water, and dried. After removal of the ether, the major portion distilled at 205° and 14 mm. pressure, as a very pale, highly mobile liquid. This procedure was followed closely on two other runs. All of the samples were kept under nitrogen to prevent oxida-

tion. The analytical data are given in the tabulation.

With an average of 1.1 active CH_2- groups, condensation with 1.1 ethyl groups should be expected, forming an ethylated methyl ester of the mixed acids. The fair agreement of the determined iodine number with the calculated value (an approximation) is evidence of reaction. The lower values for refractive index are also evidence of reaction. Furthermore, it was believed that if alkylation had occurred, the alkylated esters should give a negative fulvene reaction whereas unalkylated ester should be positive. This actually was the case. Again, confirmation of the fulvene test was obtained by oxidation tests, where a dark red color was produced in the original methyl ester but no appreciable darkening in the alkylated methyl ester. The oxidation presumes the formation of a $-CO-$ group, according to Scheiber.⁴ The oxidized portion should in turn condense with unoxidized oil to give the fulvene color reaction.

This study is being continued on pure methyl linoleate and pure methyl linolenate.

(4) J. Scheiber, *Farbe u. Lack.*, 477 (1929); 585 (1929).

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The Oxidation of Amino Acids by Hydrogen Peroxide in Formic Acid

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It has been shown¹ that the action of hydrogen peroxide on casein dissolved in formic acid causes a selective oxidation of its tryptophan, methionine and (partly) cystine units. As regards the effect of other acid oxidizing agents on the natural amino acids Williams and Woods² stated that of 16 samples tested only cystine, tyrosine and tryptophan were oxidized by iodic acid (at 100°), and Nicolet and Shinn³ showed that periodic acid selectively attacks tryptophan, methionine and cystine, as well as the α -hydroxy amino acids. Since, however, according to the same authors the latter type of compound seemed to be protected against the oxidation by acylation or by peptide formation through the amino group, and since our own observations¹ on the action of performic acid (the product of interaction of hydrogen peroxide and formic acid), which showed

	Iodine No. (Wijs)		Refractive index
	Determined	Theoretical ^a	
Linseed oil	192.0	...	1.4811
Mixed methyl esters	186.0	...	1.4632
Alkylated esters			
A	170.9	167.0	1.4616
B	178.1		1.4619
C	183.1		1.4613
Av.	177.4		1.4616

^a The theoretical iodine number was calculated on the assumption that linseed oil contains 60% linoleic acid, with one active CH_2- group and 25% linolenic acid, with two active CH_2- groups.

- (1) Erdmann, Bedford and Raspe, *Ber.*, **42**, 1334 (1909).
 (2) Goldsobet, *Chem. Ztg.*, **30**, 825 (1906).
 (3) Hilditch and Vidyarthi, *Proc. Roy. Soc. (London)*, **A122**, 563 (1929).

- (1) Toennies, *J. Biol. Chem.*, **145**, 667 (1942).
 (2) Williams and Woods, *THIS JOURNAL*, **59**, 1408 (1937).
 (3) Nicolet and Shinn, *ibid.*, **51**, 1615 (1929).