

TABLE IV  
Comparison of Experimental Analyses for Fatty Acids with Values Based on the Random Pattern of Distribution

Acid	9 Double bonds		8 Double bonds		7 Double bonds			6 Double bonds		5 Double bonds		4 Double bonds	
	Theory	Exp. 1	Theory	Exp. 1	Theory	Exp. 1	Exp. 2	Theory	Exp. 2	Theory	Exp. 2	Theory	Exp. 2
Saturates.....	....	....	....	-2.5	....	2.8	11.3	12.7	15.0	9.1	10.4	24.5	14.8
Oleic.....	....	4.4	....	7.3	28.6	26.2	21.5	20.5	21.0	45.5	51.4	41.2	52.0
Linoleic.....	....	-0.6	33.3	28.9	10.0	11.3	11.1	21.9	24.4	16.0	12.7	11.9	16.0
Linolenic.....	100.0	98.4	66.7	66.3	61.4	59.5	55.9	45.0	39.6	29.5	25.5	22.6	17.2

under random pattern. However the incomplete resolution of glyceride types do not justify the attempt to make quantitative calculations of glyceride compositions from the fat acid data, such as was done in Table III. In Table IV are included the spectroiodine value data for fatty acid composition averaged for the regions of the curve corresponding to 7, 6, 5, and 4 double bond glycerides. Also included are the values calculated from the random distribution pattern data of Table II. Agreement for these fractions of the theoretical and experimental data (within the limits of experimental error) supports the random distribution hypothesis for this sample of linseed oil.

Another manner of representing glyceride composition data and of comparing theoretical glyceride patterns with experimental data is shown in Figure 4. It consists of calculating iodine value for combinations of high iodine value and low iodine value fractions and plotting this averaged and weighted iodine value against the percentage which that fraction represents of the whole oil. It is apparent that the combined experimental data of Figures 1 and 2

follow closely the limits imposed by the random pattern but exceed the limits imposed by the strict even distribution pattern. In fact, the deviation of the experimental data from the random pattern lines appears to be wholly accounted for by the fact that the summed and averaged iodine values for the fractions recovered is 176 rather than 183.5 determined on the whole oil.

Evidence for the generalization that linseed oil is randomly constructed is to be found in the counter-current-distribution data on the expressed sample of linseed oil. From this oil of iodine value 184.1, 19.6% of trilinolenin was isolated. Consideration of the freshness of this oil sample, the low temperature of the process for expressing the oil, and the slow rate of the uncatalyzed interesterification reaction at room temperature leads to the conclusion that the random distribution pattern found in the data of Figures 1 and 2 are not an artifact but describe the structure of linseed oil glycerides in the natural and native state.

### Summary

Linseed oil has been fractionated in a 200-tube countercurrent-distribution apparatus. Iodine values of fractions ranged from 51 to 261. As determined by the weight distribution curve, iodine values and spectrophotometric analyses, 18.2% trilinolenin, 12.3% linoleo-dilinolenin, and 19.5% oleo-dilinolenin combined with 4.1% dilinoleo-linolenin were isolated. Based upon this type of data and upon several methods of analysis and collation of the data, it is concluded that linseed oil glycerides follow essentially the random pattern of distribution.

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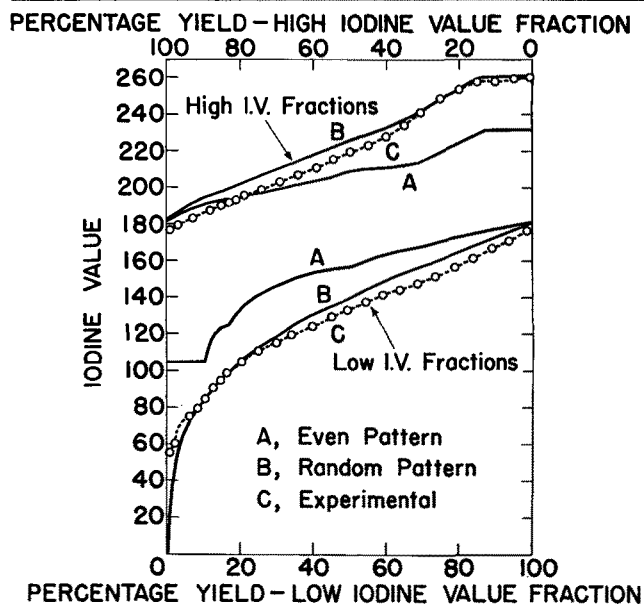


Fig. 4. Iodine value—percent yield representation for A. Even pattern; B. Random pattern; C. Counter-distribution data of Figures 1 and 2.

## Letter to the Editor

September 5, 1955.

For further information on *Acrocomia Totai* (the Mbocaya palm) which K. S. Markley has reported so correctly in the July, 1955 edition of the Journal, I would like to add my experience with these products in Paraguay, where I worked under contract during the years 1939 and 1940 for one of the largest local factories and where I had the opportunity of processing thousands of tons of this seed.

The reader may be interested to know that the nature of the "pulp" is such that, contrary to ex-

pectations, processing in continuous presses of the Anderson and Rosedown type was more effective and gave a higher yield without the addition of hull than with it. When the hull was used, with or without ground mixtures, a lower yield was obtained and the oil was redder and contained more free fatty acid. At the second pressing, by either the continuous or hydraulic process, the residual oil in the cakes was never under 8%. The "kernel" was very easily handled, and notwithstanding its high oil content (sometimes up to 65%) the oil content in the cake after

the second pressing was only 4 to 5% even though we had no "super-duo" at our disposal.

The pulp oil was used for the manufacture of soap. Kernel oil was mostly refined as edible oils. (This statement is contrary to those reported by Dr. Markley and refers to the period prior to 1952.) The two oils had the following physical and chemical properties which coincide with those mentioned by Dr. Markley.

	Pulp Oil	Kernel Oil
Specific gravity.....	0.9235	0.9235
Free fatty acids		
% oleic.....	38.7	....
% lauric.....	....	0.72
Saponification value.....	199.9	243.5
Unsaponifiable matter, %.....	0.27	0.31
Iodine value.....	63.9	27.2
Reichert-Meissl value.....	2.58	7.6
Refractive index, 40°C.....	1.4583	1.4523
Polenske value.....	0.65	14.0

The average industrial yields may be summarized as follows. Freshly harvested fruit lost about 9% in weight during the first few weeks of bulk storage. Yields from processing then were (as percentage of fresh weight of seed):

	Total Fraction	Oil	Cake
Hull (epicarp).....	18	.....	.....
Pulp (mesocarp).....	28	4.97	20.18
Shell (endocarp) plus kernel.....	54	.....	.....
Kernel.....	10.9	6.04	3.99

I hope that these data may be of interest.

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## ABSTRACTS . . . . . R. A. Reiners, Editor

### • Oils and Fats

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**Synthesis of branched-chain or  $\omega$ -phenyl fatty acids by desulfurization of thiophene derivatives.** M. Sy, Ng. Ph. Buu-Hoi, and Ng. Dat-Xuong. *Comp. rend.* 239, 1224-6(1954). Thiophenecarboxylic acids treated with Raney nickel in an alkaline medium give branched-chain or  $\omega$ -phenyl fatty acids of biochemical interest. The compounds synthesized are: 9,9-dimethylcapric acid, 2,5-dimethyl-3-thiophenebutyric acid,  $n$ -C<sub>11</sub>H<sub>21</sub>CHBuCOOH, Ph(CH<sub>2</sub>)<sub>8</sub>COOH, Ph(CH<sub>2</sub>)<sub>6</sub>COOH, and Ph(CH<sub>2</sub>)<sub>5</sub>COOH. (*C. A.* 49, 13211)

**Component fatty acids and unsaponifiables in shark liver oil.** G. G. Kamath and N. G. Magar (Dept. of Biochem., Inst. of Science, Bombay). *Jour. Indian Chem. Soc.* 32, 455-62(1955). Waghbeer and Khada mushi liver oil were studied for their component fatty acids by low temperature separations, methyl ester fractionation and alkali isomerization. The nature of the two oils studied is different: in Waghbeer liver oil, C<sub>20</sub> and C<sub>22</sub> acids predominate over the C<sub>16</sub> and C<sub>18</sub> acids, whereas in Khada mushi liver oil, C<sub>18</sub> acids constitute the major portion. The unsaponifiables of the two oils were studied chromatographically and spectrophotometrically. Cholesterol and vitamin A are present in both of these samples. Presence of kitol is also confirmed.

**Antioxidant properties of spices in oil-in-water emulsions.** J. R. Chipault, G. R. Mizuno and W. O. Lundberg (The Hormel Inst., Univ. of Minn., Austin, Minn.). *Food Research* 20, 443-8 (1955). The antioxidant properties of 32 spices have been studied in a simple oil-in-water emulsion system. All spices protected the emulsion against oxygen absorption. In most cases the spices were more effective in the emulsion than in plain lard or baked pie crusts, but the order of effectiveness was different for the different substrates. Cloves were extremely effective in preventing oxidation of the emulsions. Other spices with antioxidant indexes greater than 5.0 were allspice, cardamon, cassia, cinnamon, ginger, mace, nutmeg, oregano, black pepper, white pepper, rosemary, sage, savory, thyme and turmeric.

**Production of synthetic fatty acids by oxidation of soft paraffin.** N. K. Man'kovskaya, G. B. Al'terman and G. I. Moskvina (All-Union Sci. Research Inst. Fats and Combine of Synthetic Fats, Shebekinsk). *Masloboino-Zhirovaya Prom.* 20(4), 15-18 (1955). The hydrocarbon fraction, boiling point 300-400°, produced in the manufacture of synthetic liquid fuel and containing 16-26 carbon atoms per molecule was treated with 0.1-0.2% KMnO<sub>4</sub> in 10% aqueous solution and oxidized by air in a stainless steel column first at 125° and then at 107-105° until the acid number reached 6-8 and 70 mg. of potassium hydroxide, respectively, allowed to settle, filtered, and saponified with sodium hydroxide; the unsaponifiable matter (2/3) was returned

to the original paraffin for reprocessing. The free fatty acids obtained in the soap comprised water soluble acids 18, C<sub>5</sub>-C<sub>6</sub> acids 11.2, C<sub>10</sub>-C<sub>15</sub> acids 20.8, C<sub>15</sub>-C<sub>17</sub> acids 13.5, C<sub>18</sub>-C<sub>20</sub> acids 3.5%; the residue was 11.8%. (*C. A.* 49, 13671)

**Suitable methods to work up slaughterhouse, sewage, and tannery fats.** F. Gawenda and H. Niewiadomski (Zaklad Tluszczow GIPRIS, Gdansk, Poland). *Prace Glownego Inst. Przemyslu Rolnego i Spozyczczego* 3(3), 35-9(1954). A slaughterhouse, a sewage and a tannery fat which analyzed, respectively, water 0.2, 0.1, 0.6; ash 0.43, 0.37, 0.70%; setting point 34.0, 40.0, 42.0°; acid number 33.2, 22.7, 43.2; iodine number (Hanus) 53.8, 53.2, 52.5; saponification number, 188.0, 189.5, 189.5; unsaponifiable, insoluble in ether, 1.2, 2.1, 3.2; unsaponifiable, soluble in ether, 0.3, 0.3, 0.5; nitrogen, 0.3, 0.08, 0.07%; were refined. The experiments led to the following recommendations: filter the fat with some filter aid; and acid refine (2 kg. fat is stirred at 50 r.p.m. and at 60°, add 300 g. sulfuric acid in the course of 2 hours), and steam deodorize with the fat at 180-190°, and the steam at 300-325°, for 2.5-3 hours with 0.5 kg. steam per kg. fat. The refined fat is suitable for making soap. (*C. A.* 49, 14346)

**Structure of isoacids formed in the process of hydrogenation of vegetable oils.** P. A. Artamonov. *Zhur. Priklad. Khim.* 28, 775-7(1955). The following m.p., iodine number and principal Raman lines of the isoacids isolated through mercury complexes from hydrogenated oils are given: for sunflower oil 40.2°, 86.7, 1300(0.25), 1441(0.25), 1675(0.5), 3049(1), 3128(1); cottonseed oil 40.0°, 88.0, 1304(0.25), 1440(0.25), 1670(0.25), 3130(1); soybean oil 35.2°, 87.8, 1301(0.5), 1440(0.5), 1673((0.5), 3129(2); rapeseed oil 38.4°, 72.4, 1294(0.25), 1440(0.25), 1669(0.25), 3129(1). These indicate *trans* configurations. (*C. A.* 49, 14349)

**Synergistic action of  $\alpha$ -alanine for the inhibition of fat autoxidation of phenolic antioxidants.** W. Heimann, M. Matz, B. Grünwald and H. Holland (Tech. Hochschule, Karlsruhe, Ger.). *Z. Lebensm.-Untersuch. u. Forsch.* 102, 1-6(1955). When sunflower oil containing 0.03% hydroquinone and 0.12%  $\alpha$ -alanine rancidified under ultraviolet light, pyrroacetic acid, a decomposition product of  $\alpha$ -alanine could be detected in the mixture. The reaction mechanism begins with an oxidative deamination of the amino acid to yield pyrroacetic acid and ammonia, and follows with a reduction of the oxidized phenolic antioxidant. In addition to these reactions there can occur a double decomposition between  $\alpha$ -alanine and quinones, whereby a red coloring develops. The synergistic action is limited to  $\alpha$ -amino acids, for  $\beta$ -alanine shows no synergistic effect. (*C. A.* 49, 14346)

**Chemical composition of the mesenteric fat of Pimelodius albicans.** R. R. Brenner, W. H. E. Reinke, and P. Cattaneo (Univ. Buenos Aires, Arg.). *Anales asoc. quim. argentina* 43, 67-77 (1955). The mesenteric fat of the omnivorous fresh-water fish *P. albicans*, representing 2.72% of the body weight, had the following constants: acid no. 0.20; peroxide no. 9.20; saponification no. 195.1; m.p. 31°; iodine no. 78.1;  $n_D^{20}$  1.4681; unsaponifiable matter 4.47%. The fatty acid composition of the