under similar conditions and only 54.6 mgms. of lead to remain on the paper.


### Summary

Several methods for the preparation of tung oil monoglycerides were investigated. Products richest in both monoglyceride (78%) and triene conjugation (63% as eleostearic acid) were obtained by glycerolysis with sodium methoxide in pyridine solution. Attempts to increase the content of monoglyceride and triene conjugation by selective solvents were unsuccessful. The monoglycerides were effective in lowering the surface tension of water as well as the interfacial tension of several oils, including tung oil, against water. The tung oil monoglycerides behaved as fugitive emulsifiers and, after drying, retarded the removal of spray residue (lead arsenate) by washing with a water spray more than did other emulsifiers, such as cottonseed oil monoglycerides. The ammonium soap of tung oil fatty acids also acted as a fugitive emulsifier.



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# Glycerolysis of Coconut, Sesame, and Linseed Oils. Fractionation of the Products with Alcohol and Urea

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DIRECT ESTERIFICATIONS of raw peanut and mustard oils with excess glycerol have been studied by Mehta, Rao, Laxmikanthan, and Shah (1), who reported that the composition of the reaction product is dependent upon various factors such as temperature, time, amount and nature of the catalyst, the proportion of glycerol, and nature of oil or fat.

Choudhury and Mukherji (2) studied the interesterification of various vegetable oils with ethanol and showed that coconut oil, which has a low molecular weight and iodine value, and castor oil, which has a high hydroxyl value, interesterified most rapidly. Among the oils of nearly the same molecular weight those with lower iodine values reacted more rapidly than those possessing higher iodine values, *i.e.*, the rate of ethanolysis was inversely proportional to unsaturation. Haller (3), using an acid catalyst, also observed the same phenomenon and ascribed the behavior of coconut oil to the presence of low-molecular-weight fatty acids. Pore (4) also showed that simple saturated (stearic) triglycerides transesterified more easily with methanol than did the unsaturated (oleic) glycerides. But in contradiction to the observations of Haller, Choudhury and Mukherji, Pore found that the length of the saturated chain had no effect on the rate of methanolysis.

The reaction of glycerol with olive, coconut, and linseed oils at 220°C. in the presence of 0.1% potassium hydroxide (based on the oil) was studied by Rossi, Bottazi, and Croce (5). Although the durations of the induction periods varied, all reactions eventually proceeded at the same rate. Addition of 10 and 20% monoglycerides shortened or eliminated the induction period. The effect of chain length and unsaturation of fatty acids on the rate of glycerolysis and compositions of the products were investigated in the present work with coconut oil because of its lower molecular weight, and with linseed and sesame oils because of their varying degree of unsaturation.

Pure mono- or diglycerides are better raw materials for the manufacture of detergents, special surface-active agents, and oil-modified resins than are technical monoglycerides. Consequently an investigation was undertaken to develop relatively simple methods for the fractionation of technical monoglycerides. Feuge and Gros (6) tried to purify the commercial monoglycerides from hydrogenated cottonseed oil by distribution between hexane and methanol or ethanol. They obtained from ethanol layer monoglycerides of 80% purity in a yield of 70%. Basu-Roy-Choudhury *et al.* (7) used a low-temperature crystallization method for the purification of crude monoglycerides of olive oil and oleic acid. Crystallization from methanol at 45°C. yielded in each case a fraction containing 80–85% monoglycerides.

The principle of urea-adduct formation should also apply to the otherwise rather cumbersome separation of mono-, di-, and triglycerides. It has been cited by Holman *et al.* (8) that preliminary experiments on fractionation with urea of crude monoglycerides carried out by Roncero, Fiestas, Mazuelos, and Moreno (9) gave unsatisfactory and unexpected results. In order to study the mode of separation of mono- and diglycerides by urea, experiments were conducted in this laboratory with the technical monoglycerides of sesame oil and of lauric acid. While this work was in progress Bradley, Mueller, and Shokal (10) reported that urea forms complexes more easily with diglycerides than with monoglycerides. Contrary to this observation, Heckles and Dunlap (11) showed that urea forms adducts with monoglycerides more easily than with diglycerides. They also showed

that urea will cause separations first on the basis of unsaturation and then on the basis of degree of esterification.

## Experimental

*Materials.*

Raw coconut oil (sapn. value 259; iodine value 7.2)

Raw linseed oil (sapn. value 192; iodine value 180.9)

Raw sesame oil (sapn. value 187; iodine value 107.7)

Refined sesame oil (sapn. value 189; iodine value 109)

Lauric acid (B.D.H. reagent; neut. value 179.2; iodine value 1.08)

Glycerol (B.D.H. reagent) 98% purity.

Commercial glycerol, 93% purity.

Lime, CaO, reagent grade, dried for six hours in oven at 600°C.

Glycerolysis was conducted in the same manner as in the previous work (1). In the case of sesame and linseed oils about 1,000 g. of the oil were reacted with glycerol (4 moles to 1 mole of oil) at temperatures of 200°C., 225°C, and 250°C. in the presence of 0.15% lime. With coconut oil the amounts of glycerol were 50, 60, and 70% of the weight of oil for the reactions at 200°, 215°, and 250°C., respectively.

The hydroxyl values of washed and unwashed samples were estimated by the pyridine-acetic anhydride method (12). The monoglyceride contents of washed samples were determined by the periodic-acid oxidation method of Pohle and Mehlenbacher (13). Compositions of washed samples in terms of mono- and diglycerides were calculated from the analytical values (1) and are shown in Tables I to VII.

## Fractionation of Mono- and Diglycerides

*Ethyl Alcohol.* A weighed amount of the washed sample was placed in a 150-ml. separating funnel and 3.8 volumes of 63% alcohol in the case of coconut-oil monoglycerides and 4 volumes of 81% alcohol in the case of linseed oil monoglycerides were added. The mixture was shaken well at intervals and allowed to settle over-night. The lower raffinate layer was then withdrawn into a 50-ml. weighed beaker. Traces of moisture and alcohol were removed under high vacuum at a temperature of 70–80°C.

The extract was placed in a round-bottom flask (250 ml.). Alcohol was distilled off at 20 to 30 cms. of Hg. pressure by heating in a water-bath. The residue was extracted with chloroform, dried over anhydrous sodium sulphate, filtered, and evaporated to dryness. Extract and raffinate fractions were then weighed.

Portions of each fraction were analyzed for monoglyceride content and hydroxyl value. In addition,

TABLE I

Reaction of Coconut Oil With Glycerol (93%)

| Temperature °C. | Time in min. | Hydroxyl values | | Glycerol in prod't | | Glycerine compn. | |
|---|---|---|---|---|---|---|---|
| | | Unwashed product | Washed product | Combined % | Dissolved % | Mono- % | Di- % |
| 200 | 0 | 10.8 | 10.0 | 0.5 | −0.04 | 1.2 | 4.5 |
| | 15 | 58.8 | 45.6 | 2.6 | 0.7 | 3.6 | 27.0 |
| | 30 | 143.1 | 76.6 | 4.4 | 4.1 | 7.6 | 39.9 |
| | 45 | 269.5 | 96.7 | 5.6 | 11.7 | 13.2 | 37.9 |
| | 60 | 426.6 | 133.0 | 7.8 | 22.5 | 20.6 | 43.5 |
| | 90 | 490.0 | 203.0 | 12.6 | 24.1 | 44.4 | 21.6 |
| | 120 | 530.0 | 243.1 | 15.0 | 25.9 | 52.8 | 27.5 |
| | 150 | 535.0 | 264.6 | 16.9 | 24.5 | 54.5 | 40.1 |
| | 180 | 535.0 | 278.3 | 18.0 | 23.4 | 58.0 | 39.9 |
| 225 | 0 | 4.0 | 5.0 | 0.3 | — | 1.0 | 0.7 |
| | 15 | 99.3 | 87.6 | 5.0 | 0.7 | 14.2 | 23.4 |
| | 30 | 262.9 | 184.4 | 11.2 | 5.5 | 35.8 | 30.1 |
| | 45 | 464.7 | 251.1 | 15.9 | 18.1 | 54.6 | 21.4 |
| | 60 | 585.5 | 290.6 | 18.9 | 28.2 | 66.6 | 13.6 |
| | 90 | 633.1 | 315.0 | 21.0 | 32.0 | 66.9 | 30.6 |
| | 120 | 633.1 | 316.9 | 20.8 | 32.0 | 67.4 | 33.8 |
| | 150 | 633.0 | 321.0 | 21.3 | 31.7 | 67.5 | 35.9 |
| | 180 | 610.0 | 317.5 | 21.0 | 29.0 | 61.6 | 51.9 |
| 250 | 0 | 12.0 | 10.0 | 0.5 | 0.1 | 1.2 | 4.5 |
| | 15 | 180.0 | 129.0 | 7.6 | 3.3 | 25.3 | 20.1 |
| | 30 | 543.7 | 271.0 | 17.4 | 25.0 | 66.0 | — |
| | 45 | 611.0 | 280.0 | 18.1 | 32.1 | 67.0 | 3.7 |
| | 60 | 639.5 | 309.0 | 20.3 | 33.4 | 66.9 | 27.5 |
| | 90 | 635.2 | 313.0 | 20.6 | 33.6 | 67.7 | 28.1 |
| | 120 | 636.0 | 310.0 | 20.4 | 34.5 | 66.7 | 29.0 |

TABLE II

Reaction of Sesame Oil With Glycerol (93%)

| Temperature °C. | Time in min. | Hydroxyl values | | Glycerol in prod't | | Glyceride compn. | |
|---|---|---|---|---|---|---|---|
| | | Unwashed product | Washed product | Combined % | Dissolved % | Mono- % | Di- % |
| 200 | 180 | 35.0 | 34.0 | — | — | 9.3 | 6.2 |
| | 240 | 63.0 | 46.9 | — | — | 13.6 | 5.6 |
| 225 | 0 | 15.0 | 7.3 | 0.4 | 0.4 | 2.1 | 0.5 |
| | 30 | 27.5 | 24.8 | 1.4 | 0.2 | 6.1 | 6.6 |
| | 60 | 60.0 | 55.0 | 3.1 | 0.3 | 16.1 | 5.6 |
| | 90 | 186.0 | 124.4 | 7.3 | 4.0 | 36.9 | 11.2 |
| | 120 | 310.0 | 166.1 | 10.0 | 10.4 | 50.5 | 10.7 |
| | 150 | 358.0 | 198.8 | 12.2 | 12.1 | 54.3 | 34.2 |
| | 180 | 360.0 | 202.6 | 12.4 | 12.0 | 52.9 | 43.2 |
| | 210 | 365.0 | 206.0 | 12.7 | 12.2 | 54.0 | 43.2 |
| 250 | 0 | 15.8 | 10.3 | 0.57 | 0.3 | 2.6 | 2.3 |
| | 15 | 57.8 | 48.9 | 2.75 | 0.5 | 11.5 | 16.9 |
| | 30 | 132.0 | 99.2 | 5.7 | 2.0 | 25.1 | 24.0 |
| | 45 | 233.0 | 145.4 | 8.6 | 6.0 | 38.5 | 29.4 |
| | 60 | 339.0 | 189.5 | 11.5 | 11.2 | 53.4 | 27.0 |
| | 90 | 393.0 | 234.0 | 14.6 | 12.7 | 64.6 | 37.9 |
| | 120 | 442.0 | 233.5 | 14.6 | 17.2 | 63.1 | 42.8 |
| | 150 | 445.0 | 233.4 | 14.6 | 17.5 | 64.6 | 37.8 |
| | 180 | 443.0 | 236.8 | 14.8 | 17.1 | 63.2 | 46.7 |

TABLE III

Reaction of Alkali-Refined Sesame Oil With Glycerol (93%)

| Temperature °C. | Time in min. | Hydroxyl value | | Glyceride composition | |
|---|---|---|---|---|---|
| | | Unwashed product | Washed product | Mono- % | Di- % |
| 200 | 60 | 17.0 | 14.9 | 4.1 | 2.4 |
| | 120 | 36.5 | 29.0 | 7.9 | 5.0 |
| | 180 | 69.0 | 54.5 | 12.9 | 16.3 |
| | 240 | 100.9 | 75.8 | 17.0 | 26.0 |
| 225 | 0 | — | — | 2.0 | — |
| | 30 | — | — | 8.5 | — |
| | 60 | — | — | 18.1 | — |
| | 90 | — | — | 37.1 | — |
| | 120 | — | — | 49.0 | — |
| | 150 | — | — | 55.5 | — |
| | 180 | — | — | 58.0 | — |
| | 210 | — | — | 57.5 | — |

TABLE IV

Sesame Oil With Glycerol (93%) Temperature 200°C.

| Time in mins. | % Monoglycerides | |
|---|---|---|
| | (a) | (b) |
| 0 | 1.2 | 1.3 |
| 30 | — | 7.3 |
| 60 | 7.2 | 25.3 |
| 90 | — | 40.6 |
| 120 | 22.0 | 46.0 |
| 180 | 46.0 | 48.0 |
| 240* | 48.5 | 48.5 |

(a) 0.21% catalyst (metal basis) on the wt. of glycerol.
(b) 0.35% catalyst (metal basis) on the wt. of glycerol.
* H.V. of final unwashed sample 290 therefore miscibility of glycerol 18.8.

TABLE V

Reaction of Sesame Oil With Glycerol (93%) at 225°C.[a]

| Time in min. | Hydroxyl value | | Glycerol in prod't | | Glyceride Compn. | |
|---|---|---|---|---|---|---|
| | Unwashed product | Washed product | Combined % | Dissolved % | Mono- % | Di- % |
| 0 | 16.0 | 8.2 | 0.5 | 0.4 | 2.1 | 2.0 |
| 15 | 339.0 | 203.0 | 12.5 | 10.3 | 52.8 | 46.8 |
| 30 | 344.0 | 205.4 | 12.7 | 10.5 | 53.0 | 48.8 |
| 45 | 343.3 | 208.0 | 12.8 | 10.3 | 52.9 | 52.4 |
| 60 | 344.0 | 211.8 | 13.1 | 10.1 | 54.0 | 52.4 |

[a] Catalyst 0.35 per cent (metal basis) on weight of oil.

TABLE VI

Reaction of Linseed Oil With Glycerol (93%)

| Temperature °C. | Time in min. | Hydroxyl values | | Glycerol in prod't | | Glycerine compn. | |
|---|---|---|---|---|---|---|---|
| | | Unwashed product | Washed product | Combined % | Dissolved % | Mono- % | Di- % |
| 200 | 0 | 21.0 | 19.4 | 1.0 | 0.1 | 2.6 | 12.2 |
| | 30 | 39.0 | 23.0 | 1.3 | 0.9 | 4.1 | 10.9 |
| | 90 | 60.0 | 36.0 | 2.0 | 1.4 | 9.0 | 8.1 |
| | 120 | 99.0 | 42.0 | 2.4 | 3.3 | 10.1 | 10.5 |
| | 150 | 166.0 | 58.0 | 3.2 | 6.8 | 13.6 | 16.1 |
| | 180 | 307.0 | 166.0 | 10.0 | 10.1 | 42.9 | 32.3 |
| | 210 | 320.0 | 197.0 | 12.0 | 9.2 | 54.9 | 24.5 |
| 225 | 0 | 27.0 | 25.2 | 1.4 | 0.1 | 5.0 | 10.3 |
| | 30 | 32.0 | 26.0 | 1.5 | 0.3 | 5.7 | 8.6 |
| | 60 | 36.0 | 31.0 | 1.8 | 0.2 | 7.0 | 9.7 |
| | 90 | 50.0 | 45.0 | 2.6 | 0.2 | 7.6 | 23.0 |
| | 120 | 78.0 | 65.0 | 3.7 | 0.9 | 12.8 | 27.0 |
| | 150 | 128.0 | 109.0 | 6.3 | 1.2 | 24.7 | 40.6 |
| | 180 | 241.0 | 180.0 | 10.9 | 4.3 | 47.4 | 32.4 |
| | 210 | 370.0 | 210.0 | 12.9 | 12.5 | 59.2 | 24.3 |
| | 240 | 372.0 | 214.0 | 13.2 | 12.3 | 61.0 | 22.6 |
| 250 | 0 | 28.0 | 13.0 | 0.7 | 0.9 | 4.0 | 0.7 |
| | 15 | 48.0 | 35.0 | 1.9 | 0.8 | 8.9 | 7.3 |
| | 30 | 73.0 | 54.0 | 3.1 | 1.1 | 14.9 | 6.1 |
| | 45 | 121.0 | 96.0 | 5.5 | 1.6 | 26.0 | 14.6 |
| | 60 | 316.0 | 185.0 | 11.3 | 9.6 | 53.1 | 17.6 |
| | 90 | 425.0 | 238.0 | 14.9 | 15.4 | 63.0 | 40.9 |
| | 120 | 428.0 | 246.0 | 15.5 | 15.0 | 65.5 | 41.3 |
| | 150 | 423.0 | 245.0 | 15.5 | 14.6 | 61.9 | 52.6 |
| | 180 | 424.0 | 244.0 | 15.4 | 14.8 | 56.0 | 72.1 |

TABLE VII

Reaction of Linseed Oil With Glycerol (98%) (Temp. 225°C.)

| Time in min. | Hydroxyl value | | Glycerol in product | | Glyceride compn. | |
|---|---|---|---|---|---|---|
| | Unwashed product | Washed product | Combined % | Dissolved % | Mono- % | Di- % |
| 0 | 27 | 26 | 1.4 | .0 | 4.9 | 11.4 |
| 30 | 36 | 30 | 1.6 | .3 | 5.3 | 14.4 |
| 60 | 58 | 49 | 2.7 | .4 | 7.4 | 27.9 |
| 90 | 68 | 58 | 3.2 | .5 | 11.0 | 25.2 |
| 120 | 84 | 74 | 4.2 | .5 | 18.0 | 18.3 |
| 150 | 169 | 140 | 8.3 | 1.8 | 32.8 | 39.3 |
| 180 | 290 | 174 | 10.5 | 8.3 | 47.6 | 27.4 |
| 210 | 371 | 210 | 12.9 | 12.5 | 59.5 | 23.2 |
| 240 | 370 | 212 | 13.1 | 12.3 | 59.3 | 24.2 |

the saponification value of the coconut-oil monoglyceride fractions and the iodine values of the linseed-oil monoglyceride fractions were determined. The analytical values and the composition of the extracts of linseed oil samples were calculated from the experimental values of the original samples and raffinates. Results are shown in Tables VIII and IX.

*Urea, Experiment 1.* For the fractionation studies with urea two technical monoglycerides were used. One had been produced from sesame oil and the other

TABLE VIII

Fractionation of Crude–Coconut-Oil Monoglycerides With 63.8% Ethyl Alcohol

| Sample No. | 1 | 2 | 3 |
|---|---|---|---|
| Weight (g.) | 15.8 | 17.9 | 20.1 |
| Extract | — | — | — |
| Yield % | 51.8 | 25.9 | 24.9 |
| Saponification value | — | — | — |
| Original | 235 | 247 | 253 |
| Extract | 230 | 227 | 237 |
| Raffinate | 239 | 255 | 259 |
| Hydroxyl value | — | — | — |
| Original | 203 | 133 | 96.8 |
| Extract | 287 | 294 | 208.0 |
| Raffinate | 130 | 70.4 | 49.0 |
| Glyceride composition, % | — | — | — |
| Original | — | — | — |
| Mono- | 44.5 | 20.6 | 13.2 |
| Di- | 21.6 | 43.5 | 37.9 |
| Tri- | 35.5 | 35.9 | 48.9 |
| Extract | — | — | — |
| Mono- | 60.0 | 62.0 | 40.4 |
| Di- | 40.5 | 39.7 | 39.9 |
| Tri- | nil | nil | 19.6 |
| Raffinate | — | — | — |
| Mono- | 22.0 | 7.0 | 3.6 |
| Di- | 36.2 | 36.7 | 29.6 |
| Tri- | 41.8 | 56.3 | 66.6 |

TABLE IX

Fractionation of Crude Linseed Oil Monoglycerides With 81% Ethyl Alcohol

| Sample No. | 1 | 2 | 3 |
|---|---|---|---|
| Weight (g.) | 12.1 | 15.9 | 13.2 |
| Extract | — | — | — |
| Yield % | 33.6 | 31.3 | 23.5 |
| Iodine value | — | — | — |
| Original | 167.0 | 170.1 | 173.6 |
| Extract | 153.0 | 161.8 | 166.2 |
| Raffinate | 174.0 | 174.0 | 175.8 |
| Hydroxyl value | — | — | — |
| Original | 140.0 | 109.0 | 74.0 |
| Extract | 277.8 | 195.7 | 148.9 |
| Raffinate | 70.0 | 69.4 | 51.0 |
| Glyceride composition, % | — | — | — |
| Original | — | — | — |
| Mono- | 32.8 | 24.7 | 18.0 |
| Di- | 39.3 | 40.6 | 18.3 |
| Tri- | 27.9 | 34.7 | 63.7 |
| Extract | — | — | — |
| Mono- | 81.0 | 52.7 | 40.8 |
| Di- | 21.9 | 30.7 | 20.8 |
| Tri- | nil | 16.5 | 38.3 |
| Raffinate | — | — | — |
| Mono- | 8.3 | 11.9 | 10.1 |
| Di- | 47.7 | 34.5 | 20.6 |
| Tri- | 42.9 | 53.6 | 69.2 |

from lauric acid. To a weighed sample of the monoglyceride a conical flask 3 parts (by wt.) of urea and 13.5 parts (by vol.) of methanol were added. The mixture was then heated in a water-bath until it became clear solution and was allowed to stand overnight at room temperature. The adduct was separated in a sintered glass funnel by suction filtration. The adduct was decomposed with an acidulated, hot, saturated solution of salt. The fatty portion was extracted with chloroform. After evaporation of the chloroform each fraction was weighed and analyzed for hydroxyl value, iodine value, and monoglyceride content. Results are shown in Tables X and XI.

TABLE X

Urea Fractionation of Crude–Sesame-Oil Monoglycerides

| Fraction | Fat content | Iodine value | Hydroxyl value | Glyceride composition | |
|---|---|---|---|---|---|
| | | | | Mono- % | Di- % |
| Original-A | 30.5 | 91.8 | 200.0 | 50.3 | 49.9 |
| I | 10.1 | 73.9 | 126.0 | 17.0 | 82.5 |
| II | 6.6 | 89.7 | 175.0 | 39.0 | 60.9 |
| III | 7.7 | 100.0 | 269.0 | 81.2 | 19.4 |
| Raffinate | 3.9 | 121.8 | 256.6 | 75.8 | 24.2 |
| Original-B | 13.2 | 88.0 | 99.2 | 25.1 | 24.0 |
| Adduct | 4.9 | 79.8 | 133.8 | 20.3 | 79.6 |
| Raffinate | 8.2 | 93.0 | 78.4 | 28.0 | —9.4 |
| Original-C | 15.2 | 87.0 | 145.4 | 38.5 | 29.3 |
| Adduct | 6.4 | 69.9 | 132.9 | 19.9 | 80.0 |
| Raffinate | 8.6 | 100.0 | 155.0 | 52.7 | —9.4 |
| Original-D | 11.2 | 85.0 | 189.5 | 53.4 | 27.0 |
| Adduct | 4.4 | 75.0 | 142.7 | 24.3 | 75.6 |
| Raffinate | 6.7 | 93.3 | 221.0 | 72.8 | —4.5 |
| Original-E | 16.0 | 85.0 | 233.4 | 64.6 | 37.2 |
| Adduct | 6.9 | 75.8 | 186.2 | 44.0 | 55.9 |
| Raffinate | 9.1 | 92.0 | 270.0 | 80.3 | 23.7 |
| Original-F | 14.9 | 86.5 | 236.8 | 63.2 | 46.7 |
| Adduct | 5.6 | 74.2 | 167.7 | 35.6 | 64.3 |
| Raffinate | 9.3 | 94.0 | 280.0 | 80.0 | 35.1 |

TABLE XI

Urea Fractionation of Crude Glycerol Monolaurate

| Fraction | Fat content | Hydroxyl value | Glyceride composition | |
|---|---|---|---|---|
| | | | Mono- % | Di- % |
| Original | 21.1 | 260.0 | 50.0 | 46.3 |
| I | 7.6 | 181.0 | 21.0 | 78.3 |
| II | 3.5 | 247.5 | 44.0 | 56.0 |
| III | 5.6 | 319.0 | 69.1 | 30.8 |
| Raffinate | 2.7 | 332.0 | 81.5 | — |

*Experiment 2.* To a portion of the washed product from the glycerolysis of sesame oil were added three times its weight of urea and sufficient methanol so as to moisten the mixture. The contents were mixed thoroughly with a glass rod and were allowed to stand over-night in an open beaker. Most of the alcohol evaporated. The adduct was collected on a sintered glass funnel and washed with four 20-ml. portions of chloroform to remove any adhering fatty material. Raffinate was transferred to a dry, clean, weighed beaker. The chloroform was evaporated by heating at 80°C. in the oven and the last traces of chloroform were removed under vacuum. The residue was weighed. It and the original sample were analyzed for hydroxyl values and monoglyceride contents. The values for the fatty matter in the adduct were calculated from the above values. Data are summarized in Table X.

## Discussion

Glycerolysis of linseed, coconut, and sesame oils in the presence of lime was carried out at temperature of 200°, 225°, and 250°C. In the case of coconut oil the consistency of the reaction product changed from liquid to semi-solid and then to a solid state, but in the case of linseed and sesame oils the mixtures remained semi-solid perhaps because of the lower melting points of monolinolein and monolinolenin. The reaction product from sesame oil darkened progressively. However slight bleaching was observed in almost every case. This difference may have resulted from the presence of unsaponifiables (sesamin or sesamolin) in raw sesame oil.

Results indicate that the maximum yields of monoglyceride increased directly with the increase in reaction temperatures in all cases. However, in the case of coconut oil, there was no remarkable difference between the yields at 225 and 250°C. At 250°C. the yield of monoglyceride was as high as 64–66% with all three oils. The rate of reaction with coconut oil was higher than that with linseed or sesame oils at all the three temperatures. At 250°C. with 0.15% lime as catalyst the maximum monoglyceride content for coconut oil was reached within 0.5 hr. whereas linseed and sesame oils required about 1½ to 2 hrs. This finding indicates that coconut oil is easily esterified because of the presence of intermediate weight fatty acids. Similar observations were made by Haller (3), Choudhury and Mukherji (2), and Kawai (14) while studying the interesterification reactions with methanol, ethanol, and glycerol, respectively. However Rossi, Bottazi, and Croce (5) found that linseed oil reacted more rapidly than coconut oil. They have not been able to explain this unusual behavior.

The data in Table II and VI show that at 250°C. there was no significant difference between the rates of reaction of linseed and sesame oils. At 225° sesame oil reacted more rapidly than did linseed oil, thus indicating that saturated fatty acids are more reactive than unsaturated ones. This conclusion is not in agreement with the observations of Kawai (14) but confirms those of Choudhury and Mukherjee (2) and Pore (4). At 200° sesame oil reacted very slowly, possibly because it contained sesamin or sesamolin, which causes a longer induction period. In two experiments with alkali-refined sesame oil a slight improvement in the reaction rate was noticed at 200°C., but that at 225° was almost the same as for raw sesame oil.

Use of 98% instead of 93% glycerol with linseed oil (Table VII) did not cause a marked change in the rate of reaction or in the maximum monoglyceride content at 225°. Although the rates of reaction of sesame oil at 200° and 225° were increased as the amount of catalyst was increased, the maximum monoglyceride yields were not altered. These findings indicate that the maximum yield of monoglyceride at a particular temperature is not affected by the amount of water in the glycerol or the concentration of the catalyst.

Hydroxyl values of the unwashed and washed reaction-products were determined. The total percentage of glycerol in the product was calculated from the hydroxyl value of the unwashed product. The percentage of combined glycerol was calculated from the hydroxyl value of the washed product. The difference between these two values was the amount of free glycerol dissolved in the product. Data in Table II and V show that the total amounts of glycerol retained in the products varied between 24 and 32% of the weight of sesame oil. The miscibility of glycerol with the coconut oil product was very much higher than with the products from linseed or sesame oils, possibly because the lower-molecular-weight monoglycerides formed from the coconut oil decreased the interfacial tension to a comparatively greater extent. Although the miscibility with linseed oil at 200° and 225° was slightly higher than with sesame oil, the reverse situation was found at 250° and may have resulted from the greater degree of polymer formation in the linseed oil. The analyses show that as the concentration of monoglyceride in the reaction mixture increased, the miscibility of the glycerol, *i.e.*, the amount dissolved in the product, also increased.

### *Fractionation of Technical Monoglycerides*

*Ethyl Alcohol.* As the data in Table VIII and IX show, the glycerolysis products from coconut oil and linseed oil contained, respectively, less than 45 and less than 33% of monoglycerides. These products were extracted with 63.8 and 81% alcohol, respectively. The extract in each case contained more monoglyceride than did the starting material. The iodine, hydroxyl, and saponification values indicate that the degree of esterification, rather than unsaturation, was the controlling factor in determining the purification achieved by separation with ethanol. Feuge and Gros (16) have made similar observations. The maximum concentration of monoglyceride, in the extract was 62% in the case of the coconut oil product and 81% in the case of the linseed-oil product.

*Urea.* During the urea fractionation of crude monoglycerides prepared from sesame oil (Table X) the iodine values of the successive fractions increased, also the monoglycerides content.

This shows that the separation is only partially according to the degree of unsaturation and that the diglycerides form urea inclusion compounds more easily than do monoglycerides. Heckles and Dunlap (11) interpreted their data as showing that the separation is based primarily on unsaturation and secondarily on esterification. However they depended on saponification numbers which, alone, are not sufficient for the accurate estimation of mono- and di-ester contents in the presence of triglycerides. Furthermore their

assumption that mono- and di-esters have the same adduct-forming tendency is also questionable.

Urea fractionation of crude glycerol monolaurate prepared by the method of Basu-Roy-Choudhury *et al.* (17) also supported these conclusions. The percentages of diglycerides decreased in the successive fractions and the monoglycerides showed a gradual increase (Table XI). The triglycerides appeared in the last fraction. The results obtained in this laboratory are supported by those of Roncero, Fiestas, Mazuelos, and Moreno (9) and by Bradley, Mueller, and Shokal (10).

## Summary

This study of the glycerolysis of linseed, coconut, and sesame oil at 200°C., 225°C., and 250°C. shows that coconut oil, because of its low-average-molecular weight, is esterified more easily than sesame and linseed oils. Comparison of the reactions of sesame and linseed oils indicates that saturated acids are transesterified more easily than the unsaturated ones. The amount of glycerol to be used is determined by its miscibility at the particular reaction temperature.

Results of alcohol extraction of the crude monoglycerides from linseed and coconut oil indicate that the glycerides separate on the basis of degree of esterification rather than on unsaturation.

Urea adduct fractionations of the technical monoglycerides of sesame oil and lauric acid show that diglycerides form urea adducts more easily than do monoglycerides. In this case, also, the fractionation is related to the degree of esterification rather than unsaturation.

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# International Collaboration on Glycerine Analysis

DURING the past four years collaborative analyses have been carried out among laboratories in the United Kingdom, Europe, and the United States under the auspices of the Glycerine Analysis Committee of the American Oil Chemists' Society. The first-year analyses were made by the International Acetin Method and the new A.O.C.S. Sodium Periodate Method. These analyses and previous collaborative work showed the superior accuracy of the sodium periodate method. This led to the withdrawal of the Acetin Method and the adoption of the Sodium Periodate Method as the Official Method by the A.O.C.S. and the International Union of Pure and Applied Chemistry. Since then some modifications of the sodium periodate method have been proposed. The principal modifications involve using an indicator for determining the titration endpoint in place of the electrometric endpoint, a larger sample so that the titration would be approximately 80 ml. in place of 40 ml., the use of nitrogen to protect the solution during the titration, and the use of a neutral, sodium periodate reagent in place of the acidified sodium periodate. These variations were incorporated in the Sodium Periodate Method adopted by the British. During the past year a collaborative study was undertaken to determine the relative merits of the various modification.

For this collaborative work we are indebted to the British Group, which provided a specially purified glycerol which was diluted to approximately 90% glycerol and a synthetic crude containing approximately 68% glycerol.

The glycerol content of the C. P. glycerol was based upon the specific gravity tests which are the most precise and accurate means for determining the glycerol content of such solutions. The accuracy of the various procedures and modifications were evaluated by comparing the average analyses on the C. P. glycerine with the percentage of glycerol found by the specific gravity method.

There were eight laboratories in the United Kingdom, eight in Europe, and 14 in the United States which took part in this collaborative work. The results are given in the following tables. Table I gives a comparison of the methods and modifications with respect to accuracy and precision. The individual analyses are given in Tables II, III, and IV. The statistical analysis of the collaborative data by H. P. Andrews follows the tables together with Table V summarizing his data.

## Statistical Analysis of International Collaborative Study

Two samples of glycerine, one C. P. and a made-up crude, were analyzed for percentage of glycerol in duplicate by 29 international collaborating laboratories, each using a number of variations of the A.O.C.S. and British methods. The variations involved acidified and neutral reagent, the use or omission of nitrogen with the acidified reagent, and the use of an indicator or electrometric endpoint.

Statistical analyses have been made to determine the within- and among-laboratories precision of the various modifications of the methods. The means and