Application of Urea Complexes in the Purification of Fatty Acids, Esters, and Alcohols. I. Oleic Acid From Inedible Animal Fats[1]

DANIEL SWERN and WINFRED E. PARKER, Eastern Regional Research Laboratory,[2] Philadelphia, Pennsylvania

THE remarkable discovery reported by Bengen in 1940 (2) that urea forms well-defined and easily handled crystalline complexes with a wide variety of straight chain compounds but generally not with branched or cyclic compounds has prompted many investigators to study the use of urea complexes in a variety of separation problems, mainly in the petroleum and fat fields (1, 3, 5, 6, 7, 9, 10, 11, 13, 17, 19, 20). Noteworthy contributions in the field of separation of fatty acids and derivatives are the papers of Schlenk and Holman (13) and Newey, *et al.* (11). The former investigators (13) studied the preparation of urea complexes from many pure fatty acids and pointed out, among other things, that saturated and unsaturated fatty acids (or methyl esters) could be separated at room temperature, taking advantage of the preferential formation of urea complexes by the saturated components of a mixture. These authors, besides demonstrating that enrichment of saturated and unsaturated acids could be readily achieved, also isolated fairly pure methyl oleate and methyl linoleate from olive oil and corn oil, respectively. Newey, *et al.* (11), took advantage of preferential urea complex formation from the saturated and monounsaturated components of mixtures and prepared concentrates (filtrates) of polyunsaturated components from soybean oil fatty acids, methyl esters and nitriles, corn oil fatty acids and methyl esters, and linseed oil methyl esters and alcohols. Newey, *et al.* (11), did not report the preparation of purified fatty acids or derivatives.

The main objects of the present study were, first, to investigate the isolation of purified oleic acid (oleic acid content > 90%) from certain animal fat sources, such as inedible tallow, grease, and red oil, and, second to employ the most efficient laboratory techniques involving urea complexes to obtain data regarding the maximum yield and purity of oleic acid which could be obtained.

To limit the scope of our study no attempt was made in this work to employ procedures which had been suggested for pilot plant or large-scale commercial use of urea complexes; nor was any study conducted on the recoverability and reuse of urea or methanol. We believed that it was essential to determine the maximum efficiency of separation possible under the best laboratory conditions with which we were familiar. If, under these so-called "ideal" conditions, the separations were poor, the commercial utilization of urea complexes for preparing purified oleic acid from animal fats would, in all probability, be impractical. On the other hand, if the separations and yields were good, then the procedures would hold some promise for large-scale utilization, provided that the usual production, development, and recovery problems could be worked out.

[1] Presented at the Spring Meeting of the American Oil Chemists' Society held in Houston, Tex., April 28-30, 1952.

[2] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

Although the most acceptable research grades of oleic acid are prepared from certain vegetable oils, such as olive oil, commercial oleic acid, either red oil or low-linoleic oleic acid, is obtained mainly from inedible animal fats. Oleic acid containing small quantities of polyunsaturated acids can be prepared from inedible animal fats (or red oil) by low-temperature crystallization at −50 to −70° (16), by preferential polymerization of the polyunsaturated acids (8), or by selective hydrogenation of the polyunsaturated acids (14, 18).

Low-linoleic oleic acid prepared from inedible animal fats often contains as much as 25% of trans-octadecenoic acids and 3-5% of polyunsaturated acids. Although it is frequently assumed that the high content of trans acids does not interfere with chemical reactions, this may not be a sound assumption, and it would be desirable to prepare from inedible animal fats a low-linoleic oleic acid which is also low in trans isomers. Since beef fat has recently been shown to contain as much as 10% of trans-octadecenoic acids (15), in all probability oleic acid prepared from the usual animal fat sources will invariably contain some trans isomers. Since the urea complex technique does not involve reaction with the double bond system, there is no increase in the content of trans isomers as a result of a purification involving urea complex formation.

Low temperature crystallization of oleic acid effectively separates the polyunsaturates, but such a procedure is not commercially feasible at present. In view of the preferential formation of urea complexes at room temperature from saturated and monounsaturated fatty acids, it should be possible to separate these readily from the polyunsaturated acids provided that there is a sufficiently great difference in the complex-forming ability of the saturates and monounsaturates compared to the polyunsaturates, and insufficient urea to form complexes with all the complex-formers is employed.

Equilibrium constant data for complex formation, obtained recently by Redlich, *et al.* (12), and unpublished work from this laboratory coupled with information on the known composition of inedible animal fats and red oil, have indicated that the complete separation of saturated fatty acids from monounsaturated fatty acids by preferential urea complex formation, although theoretically possible, would be inefficient and impractical. On the other hand, the simultaneous precipitation of saturated and monounsaturated fatty acids, as urea complexes, leaving the polyunsaturates in the non-complex-forming filtrate, should be feasible. Further thought on this problem has indicated that, because of the advisability of reducing the quantity of urea as much as possible, wherever saturated acids can be separated from the other components of the mixture by solvent crystallization at or above 0°C., this technique would be preferred over precipitation as urea complexes. The reasons for making this last assertion are: a) satu-

rated acids can be cleanly separated from the mixed acids of inedible animal fats by crystallization from aqueous methanol at 0°; and b) there seems to be little point in employing the much larger quantities of urea needed to precipitate the bulk of the saturated acids with the monounsaturated acids as urea complexes and then subsequently having to separate the saturated acids from the monounsaturated acids by solvent crystallization anyway.

With the establishment of this rationale the procedure followed in preparing purified oleic acid from the mixed fatty acids of inedible animal fats consisted in a) precipitation of the bulk of the saturated fatty acids from 90% methanol: 10% water mixtures at 0°C.; b) addition of sufficient urea to the filtrate to combine with unprecipitated saturated acids and oleic acid; and c) filtration at room temperature. The final filtrate was a concentrate of polyunsaturated fatty acids (iodine number 105-136). Addition of water to the mixed urea complex (precipitate) fraction dissolved the urea and yielded an oleic acid concentrate containing 80-85% oleic acid, 12-18% saturated acids, mainly palmitic and shorter-chain saturated acids, and a maximum of 3% (usually 1-2%) of polyunsaturated acids. Straight-run distillation removed residual color, if still present, from the oleic acid concentrate, and fractional distillation yielded oleic acid concentrates containing as much as 95% oleic acid. Yields of oleic acid however based on the oleic acid content of the starting materials, were lower than those obtained by low-temperature crystallization procedures. At present we believe that the separation of saturated from monounsaturated acids is best conducted by solvent crystallization, but separation of polyunsaturated from monounsaturated acids is more convenient, although somewhat less efficient, by use of urea complexes.

Schlenk and Holman (13) employed a purification procedure involving the successive stepwise addition of urea to mixed methyl esters. In view of the earlier discussion we prefer a single dose technique for the simultaneous precipitation of oleic acid plus any saturated acids not precipitated in an earlier crystallization step.

Advantages in using urea in the separation of oleic acid from inedible animal fat sources are: a) all separations are made at room temperature (20-25°C.), whereas the conventional procedures require crystallization of oleic acid at or below —50°C.; b) the urea technique can be readily coupled with modern separation processes for fractionating the fatty acids from inedible animal fat sources merely by dissolving urea in the aqueous methanol filtrate from the separation of the saturated fatty acids; c) darkly-colored impurities are concentrated in the non-complex (filtrate) fraction; d) no highly specialized apparatus or techniques are required; and e) solvents and chemicals required are inexpensive, readily available, and presumably, readily recovered. Disadvantages are: a) large quantities of urea are required; b) after filtration of the complexes, they must be decomposed and the fatty acids recovered; c) large volumes of solids must be handled (urea complexes contain only about 25% fatty acids); d) yields are lower than those from solvent crystallization processes; and e) "recrystallization" of urea complexes does not completely free them from polyunsaturated acids whereas, in fractional crystallization procedures for preparing purified oleic acid, the content of polyunsaturated acids can be reduced to less than 1% (often less than 0.2%) by a single recrystallization of the once-crystallized oleic acid. The reason for the failure to free urea complexes from residual polyunsaturated acids by "recrystallization" has not yet been explained.

The use of aqueous urea—methyl isobutyl ketone systems, employed with such success recently in petroleum separations (1)—may offer serious problems in separations of fatty acids owing to soap and subsequent emulsion formation because of reaction of fatty acids with ammonium carbonate obtained by hydrolysis of urea. With the aqueous methanol systems employed in this study no difficulty was experienced with emulsions.

A point of interest is that the urea separation technique is least satisfactory with the lowest grades of inedible animal fatty acids and most satisfactory with the best grades. Ordinary fractional crystallization procedures show similar behavior; the best yields are obtained from the highest quality materials.

Experimental

Separation of Simulated Animal Fatty Acids. Preliminary separation experiments were conducted on a model mixture of pure fatty acids designed to simulate the fatty acid composition of some typical inedible tallows and greases. The following model mixture was employed:

Myristic acid	3%
Palmitic acid	30
Stearic acid	15
Oleic acid	45
Linoleic acid	7

The experiment to be described was the most satisfactory from the standpoint of ease of handling and separation of products. Twenty grams of the above-described fatty acid mixture was dissolved in 100 ml. of a 90% methanol: 10% water mixture. The solution was cooled to 0°, and the glistening, well-formed crystals were filtered, yielding 8.4 g. of solid fatty acids, m.p. 54-5°, and iodine number 1.7. These corresponded to a typical triple-pressed stearic acid.

Forty-five grams of urea was dissolved in the filtrate with heating, and the solution was allowed to cool to room temperature. The long, hard crystals of urea complex (33 g.) were filtered off and air-dried. Addition of warm water to the complex yielded 8.2 g. of colorless liquid, iodine number 73 (composition: 78% oleic acid, 20% saturated acids, 2% linoleic acid). The yield of oleic acid precipitated as urea complex was 70%.

The filtrate from the precipitation of urea complex was evaporated nearly to dryness, warm water was added to the crystalline residue to dissolve urea, and the oily phase was separated by ether extraction. Evaporation of the ether yielded 3.4 g. of pale-yellow oil, iodine number 121 [composition (4): 48% linoleic acid, 37% oleic acid, 15% saturated acids].

Separation of Commercial Prime Tallow Fatty Acids. These had been straight-run distilled (commercially) and had the following composition: 53.2% octadecenoic acids (mainly oleic acid), 40.7% saturated acids, 6.1% polyunsaturated acids. One thousand grams were crystallized from 4,000 ml. of 90% methanol at 0°, yielding 429 g. of saturated fatty acids, iodine number 4.2, as the precipitate.

To the filtrate 2,550 g. of urea (5 g. of urea per g. of oleic acid plus unprecipitated saturated acids) were dissolved at the boiling point, and the solution was cooled to room temperature and filtered, yielding 1,960 g. of urea complexes, iodine number 22. Warm water was added to these, yielding 495 g. of pale-yellow liquid fatty acids, iodine number 79 (composition: 83% octadecenoic acids, 15% saturated acids, 2% polyunsaturated acids). The yield of octadecenoic acids recovered to this point was 77%. Fractional distillation yielded 259 g. of purified oleic acid, iodine number 85.1 and n_D^{30} 1.4563 (composition: 90% octadecenoic acids, 7.7% saturated acids, 2.3% polyunsaturated acids). The yield of octadecenoic acids was 45%. The lower fractions from this distillation weighed 198 g. and had an iodine number of 62.

The filtrate from the urea complex precipitation step was evaporated nearly to dryness, warm water was added, and the oily layer was extracted with petroleum naphtha (hexane fraction). Evaporation of the solvent under vacuum in a nitrogen atmosphere yielded 87 g. of brown liquid, iodine number 131.

Separation of Commercial Brown Grease Fatty Acids. These were darkly colored and had the following composition: 48.1% octadecenoic acids (mainly oleic acid), 48.0% saturated acids, 3.9% polyunsaturated acids. As described under Separation of Prime Tallow Fatty Acids, 543 g. of saturated acids were obtained by crystallization of 1,000 g. of Brown Grease Fatty Acids from 90% methanol at 0°.

Addition of 2,100 g. of urea to the filtrate yielded 1,514 g. of urea complexes from which 358 g. of liquid fatty acids, iodine number 68, were obtained as described. Straight-run distillation yielded 341 g. of straw-yellow acids, iodine number 65.3 (composition: 69% octadecenoic acids, 29% saturated acids, 2% polyunsaturated acids). Fractional distillation yielded only 145 g. of straw-yellow liquid acids, b.p. 201-205°/3.5-4.0 mm. and iodine number 81.8 (composition: 87% octadecenoic acids, 11% saturated acids, 2% polyunsaturated acids). The yield of oleic acid was only 26%. The lower fraction from the distillation weighed 196 g. and had an iodine number of 53.

The polyunsaturated acid fraction, isolated from the urea complex filtrate, weighed 94 g. and had an iodine number of only 105.

Separation of Commercial Hydrolyzed Inedible Tallow. These fatty acids were obtained directly from a commercial Twitchell hydrolysis operation, and they were dark brown and foul smelling. Mineral acid was removed by three hot water washes, but the fatty acids were not distilled.

From 1,000 g. of fatty acids 325 g. of saturated acids, iodine number 10.2, were obtained by crystallization from 90% methanol at 0°. From 1,546 g. of urea complexes, prepared as already described, 390 g. of dark-brown liquid acids, iodine number 76.1, were isolated. Straight-run distillation yielded 298 g. of yellow-brown acids, iodine number 77.6, and a substantial tarry still residue. Fractional distillation yielded only 145 g. of oleic acid, iodine number 89.7 (composition: 95% octadecenoic acids, 3% saturated acids, 2% polyunsaturated acids), and 153 g. of lower fraction, iodine number 66. The yield of oleic acid was only 26%.

When hot water was added to the filtrate from the urea complex separation after evaporation of methanol, an emulsion was obtained which could not be completely broken by the addition of salt. The mixture was extracted with commercial hexane, the lower milky aqueous layer discarded, and the polyunsaturated acids were isolated from the solvent as already described. The polyunsaturated acid fraction weighed 38 g. and had an iodine number of 127.

Separation of Single-Distilled Commercial Oleic Acid (Red Oil). This product was a dark brown, foul-smelling liquid prepared commercially by hot pressing of single-distilled fatty acids obtained by the Twitchell hydrolysis of inedible tallow and grease. The composition of the red oil, iodine number 92, was 70% octadecenoic acids, mainly oleic, 15% saturated acids, and 15% polyunsaturated acids (12.1% diene and 2.6% triene). One thousand grams of red oil were dissolved in a boiling solution of 4,250 g. of urea (5 g. of urea per gram of oleic plus saturated acids) in 10 l. of 90% methanol. Urea complexes formed immediately on cooling. The mixture was allowed to cool to room temperature and filtered, yielding 2,727 g. of urea complexes. Addition of warm water to the complex to dissolve the urea yielded a pale-yellow insoluble oil which weighed 682 g., iodine number 73.7. Straight-run distillation yielded 630 g. of colorless liquid, iodine number 79.2 (composition: 84% octadecenoic acids, 14% saturated acids, 2% polyunsaturated acids). Yield of octadecenoic acids recovered, 76%. Fractional distillation yielded 448 g. of colorless liquid, iodine number 87.4 (composition: 91% octadecenoic acids, 6% saturated acids, 3% polyunsaturated acids). Yield of octadecenoic acids recovered 58%. The lower fraction from this distillation weighed 182 g. and had an iodine number of 59.

The filtrate from the urea complex separation was worked up in the usual way, yielding 222 g. of dark-colored, foul-smelling liquid, iodine number 132.

Separation of Double-Distilled Commercial Oleic Acid. This product [composition: 70% octadecenoic acids (59% cis, 11% trans; ratio of cis to trans, 5.4:1), 15% saturated acids, 15% polyunsaturated acids] was straw-yellow and was prepared commercially by a straight-run distillation of the single-distilled commercial oleic acid, described in the preceding section. From 1,000 g. dissolved in 10 l. of 90% methanol, 2,800 g. of urea complexes were obtained (4,250 g. of urea employed). These yielded 735 g. of colorless liquid, iodine number 79.8 [composition: 84% octadecenoic acids (71% cis, 13% trans; ratio of cis to trans, 5.5:1), 14% saturated acids, 2% polyunsaturated acids]. Yield of octadecenoic acids recovered, 88%. Fractional distillation yielded 452 g. of colorless liquid, b.p. 206°/4 and iodine number 86.7 (composition: 90% octadecenoic acids, 7% saturated acids, 3% polyunsaturated acids). Yield of octadecenoic acids recovered, 58%. The lower fraction from this distillation weighed 212 g. and had an iodine number of 62.

The filtrate from the urea complex separation was a yellow oil which weighed 244 g., iodine number 136.

Acknowledgment

The authors thank S. F. Herb for some of the analyses for polyunsaturated fatty acids, and H. B. Knight and J. E. Coleman for helpful suggestions.

Summary

Urea complex formation has been employed in the preparation of purified oleic acid (oleic acid content,

80-95%) from various grades of inedible animal fats and red oils. Since the urea complex of oleic acid forms in good yield at room temperature, low temperatures are not required in the isolation procedure. Yields of oleic acid are equal to or lower than those obtained by conventional low-temperature crystallization procedures, but the preparation of a polyunsaturate-free oleic acid is apparently not possible by urea complex formation alone. The separation of polyunsaturated acids from oleic acid by urea complex formation is more convenient than but not as efficient as by solvent crystallization, but separation of saturated acids from unsaturated acids is less convenient.

Advantages and disadvantages in using urea in the preparation of purified oleic acid are briefly discussed.

REFERENCES

1. Bailey, W. A., Jr., Bannerot, R. A., Fetterly, L. C., and Smith, A. G., Ind. Eng. Chem., *43*, 2125-2129 (1951).
2. Bengen, F., German patent application O. Z. 12438, March 18, 1940; Translation Book 319, Technical Oil Mission Reel 143, Frames 135-139.
3. Bradley, T. F., Official Digest, Federation Paint and Varnish Clubs, *No. 310*, 795-805 (1950).
4. Brice, B. A., Swain, M. L., Schaeffer, B. B., and Ault, W. C., Oil and Soap, *22*, 219-224 (1945).
5. Coleman, J. E., Knight, H. B., and Swern, D., J. Am. Chem. Soc., (in press).
6. Fetterly, L. C., U. S. Patents 2,520,715 and 2,520,716 (1950).
7. Garner, P. J., Goldsbrough, L. N., and Buyers, T. B., U. S. Patent 2,518,677 (1950).
8. Goebel, C. G., J. Am. Oil Chem. Soc., *24*, 65-68 (1947).
9. Heckles, J. S., M.S. Thesis, Franklin and Marshall College (1951).
10. Linstead, R. P., and Whalley, M., J. Chem. Soc., *1950*, 2987-2989.
11. Newey, H. A., Shokal, E. C., Mueller, A. C., Bradley, T. F., and Fetterly, L. C., Ind. Eng. Chem., *42*, 2538-2541 (1950).
12. Redlich, O., Gable, C. M., Dunlop, A. K., and Millar, R. W., J. Am. Chem. Soc., *72*, 4153-4160 (1950).
13. Schlenk, H., and Holman, R. T., Science *112*, 19-20 (1950); J. Am. Chem. Soc., *72*, 5001-5004 (1950).
14. Swern, D., and Ault, W. C., U. S. Patent 2,457,611 (1948).
15. Swern, D., Knight, H. B., and Eddy, C. R., J. Am. Oil Chem. Soc., *29*, 44-46 (1952).
16. Swern, D., Knight, H. B., and Findley, T. W., Oil and Soap *21*, 133-139 (1944).
17. Swern, D., and Port, W. S., J. Am. Chem. Soc., *74*, 1738-1739 (1952).
18. Swern, D., Scanlan, J. T., and Roe, E. T., Oil and Soap, *23*, 128-131 (1946).
19. Truter, E. V., J. Chem. Soc., *1951*, 2416-2419.
20. Zimmerschied, W. J., Dinerstein, R. A., Weitkamp, A. W., and Marschner, R. F., Ind. Eng. Chem., *42*, 1300-1306 (1950); J. Am. Chem. Soc., *71*, 2947 (1949).

[Received March 19, 1952]

ABSTRACTS . . . . . E. S. Lutton, Editor

• Oils and Fats

R. A. Reiners, Abstractor

Steam consumption under different working conditions in oil-deodorization processes. T. K. Ghose and N. C. Chakravartty (Coll. Eng. Technol., Calcutta). *Trans. Indian Inst. Chem. Engrs.* **3**, 21-31(1949-50). Information on deodorization conditions in 9 Indian factories manufacturing Vanaspati [a hydrogenated peanut oil (95%) and sesame oil (5%) mixture] is summarized. 19 references. (*Chem. Abs.* **46**, 6853)

Sesame oil in margarine and in similar fats, additions of coloring matters. S. Anselmi and Adriana Cesari (Inst. super sanita, Rome). *Ann. chim.* (Rome) **41**, 573-86 (1951); *Rend, ist super sanita* (Rome) **14**, 624-38(1951). The colored material in sesame oil was extracted with ethanol, treated with activated C, and evaporated to dryness over a water bath. The oily residue gave a characteristic red color with a furfural-HCl mixture. Fat-soluble dyes either used alone or in mixtures could be easily distinguished from the dye in sesame oil by the HCl test. (*Chem. Abs.* **46**, 6853)

Turbidity due to impurities in edible beechnut oils. H. P. Kaufmann, J. Baltes and L. Grunwald (Univ. Munster/Westf., Ger.). *Fette u. Seifen.* **53**, 531-3(1951). The turbidity was due mainly to the precipitation of myricyl lignocerate and β-sitosterol. The unsaponifiable fraction of beechnut oil may contain isophytosterol. (*Chem. Abs.* **46**, 6852)

Boleko (isano) oil. I. The fat acids of the oil and their separation. H. P. Kaufmann, J. Baltes and H. Herminghaus (Univ. Munster/Westf., Ger.). *Fette u. Seifen* **53**, 537-42(1951). A new, highly unsaturated monohydroxy fat acid, $C_{18}H_{28}O_3$, for which the name isanolic acid is proposed, has been separated from Boleko *(Ongoekoa gore* or *Oklaineana)* oil. Isanolic acid has an acid no. of 190.7, hydroxyl value 191.7, n_D^{60} 1.4924, and iodine no. (Kaufmann) 166.0. Isanolic acid is the chief fat acid in Boleko oil (44%). Since its absorption spectrum closely resembles that of isanic acid, it is assumed that isanolic acid is 8-hydroxyisanic acid. Isanic acid is also present in the oil in appreciable quantity together with a small amount of linolenic acid and saturated acids. (*Chem. Abs.* **46**, 6852)

The analysis of isomerized oils. J. D. v. Mikusch (F. Thorl's Ver. Harburger Oelfabriken, Hamburg-Harburg, Ger.). *Ind. vernice* (Milan) **6**, 15-22(1952). A review with 38 references of the development of oil isomerization and of chemical and physical methods to study it. (*Chem. Abs.* **46**, 6852)

Utilization of by-products and waste products of the fatty-oil industry. I. Recovery of nickel from spent nickel catalyst. G. K. Belekar, J. G. Kane, and H. S. Shahani (Univ. Bombay). *J. Sci. Ind. Research* (India) **11B**, 28-30(1952). Five spent catalyst samples were digested with 10-50% H_2SO_4 and with various H_2SO_4-HNO_3 mixtures of 15-70% and 20-70% proportions. Higher Ni recoveries (93.2 to 98.3%) in the combined mother liquor and washings occurred from mixed acid treatment. 27 references. (*Chem. Abs.* **46**, 6852)

Use of the titers of fatty acids for the analysis of binary and tertiary mixtures. C. Paquot (Centre natl. recherches, Paris). *Bull. mens. ITERG* (Inst. tech. etudes et recherches corps gras) **6**, 174-8(1952). The titers of a series of binary and tertiary mixtures containing lauric, myristic, stearic, oleic, and linoleic acids are given on 11 charts. With these values and the acid nos. it is possible to determine the composition of tertiary mixtures of the saturated acids. The systems containing unsaturated acids, palmitic-stearic-oleic and stearic-oleic-linoleic, are determined by their titer and iodine value. (*Chem. Abs.* **46**, 6852)

Fats. CXXIX. Paper chromatography in the field of fats. 7. Identification and separation of fatty acids. H. P. Kaufmann and J. Budwig (Chem. Landes-Untersuchungsamt Nordrhein-Westfalen, Munster, Ger.). *Fette u. Seifen* **53**, 390-9 (1951). The paper chromatography of propionic, butyric, valeric, caproic, enanthic, caprylic, octenoic, pelargonic, decanoic, undecylenic, stearic, oleic, elaidic, linoleic, and erucic acids was investigated. Basic dyes, particularly Rhodamine B and Nile Blue, give characteristic reactions with these acids, particularly under ultraviolet light. By using No. 214 paper (Fa. Macherey, Nagel & Co.) and treating successively with $PhNHNH_2$, Rodamine B, and aqueous $AgNO_3$, characteristic colors are obtained. N_2H_4, toludine, and quinine react similarly to $PhNHNH_2$.

CXXX. 8. Lipid replacement in the human skin and its measurement by paper chromatography. H. P. Kaufmann, A. Szakall and J. Budwig. *Ibid.* 406-8. The lipids present in the epidermis after defatting consisted mainly of fatty acids, particularly oleic acid. An extract of the skin (not defatted) contained glycerides.

CXXXI. 9. Application to lacquer raw materials. H. P. Kaufmann, J. Budwig and C. W. Schmidt. *Ibid.* 408-12. The boiling of stand oil was investigated. By using 99% methanol as the developer, the free fat acids could be removed from the glycerides; after application of a contrasting dye the fat acid area was dependent on the increase in saponification no. of the oil. During the boiling process, the most unsaturated glycerides vanish slowly, and, parallel to the increase in viscosity of the oil, the amount of polymerized products increases. (*Chem. Abs.* **46**, 6851)