tocoquinone, and the phosphoric acid catalyzes its cyclization to tocopherol. In alcoholic solution phosphoric acid also cyclizes tocoquinone provided a reducing agent is present. Such cyclization occurs in the presence of other mineral acids (7).

TABLE III

Reduction of α-Tocoquinone in the Presence of Phosphoric Acid at 75°[a] Substrate: Ethyl Esters of Lard Fatty Acids

| Time hrs. | 0 | 26 | 78 | 167 |
|---|---|---|---|---|
| α-Tocopherol formed[b], % | 0.0 | 0.04 | 0.04 | 0.07 |

[a] The initial concentration of α-tocoquinone was 0.20%; that of phosphoric acid was 0.40%.

[b] Biological assays and stability tests indicated that no substantial amounts of α-tocohydroquinone were present.

Evidence that the autoxidation of a fat may proceed in part through a dehydrogenation mechanism has been presented by Deatherage and Mattill (8) and hydrogen has been identified among the products arising from the autoxidation of fats (9, 10).

In the case of benzoquinone, some reduction to hydroquinone was detected even in the absence of phosphoric acid. The amount thus formed, determined quantitatively by the ferric chloride-dipyridyl reagent of Emmerie and Engel (6), was small (Table IV),

TABLE IV

Reduction of *p*-Quinone in the Absence[a] and Presence[b] of Phosphoric Acid at 60° Substrate: Lard

| Time, in days | 0 | 7 | 14 | 28 | 42 |
|---|---|---|---|---|---|
| Hydroquinone formed[a], % | 0 | 0.001 | 0.001 | 0.001 | 0.001 |
| Hydroquinone formed[b], % | 0 | 0.006 | 0.008 | 0.008 | 0.014 |

The initial concentration of quinone was 0.02%, and of phosphoric acid, when present, 0.10%.

but was nevertheless sufficient to account for the antioxygenic activity of the quinone. The inhibition of oxidation by certain other *p*-quinones (11) may be explained on the same basis.

When phosphoric acid was used in conjunction with benzoquinone, the amount of hydroquinone formed was several times greater than that produced in the absence of the acid. The observed powerful synergistic action of this combination (Table II) is thus not surprising. Possibly the phosphoric acid influences the hydrogen ion concentration of the fat substrate even at the low concentrations of acid employed. Nothing is known regarding the acidity of phosphoric acid in fat media but Hall and Conant (12) have demonstrated that in other non-aqueous solvents, mineral acids produce acidities ("super acid solutions") far in excess of their hydrogen ion activities in water systems.

Our results suggest that the addition of a quinone or a hydroquinone to an autoxidizing fat leads to the formation of a hydroquinone ⇄ quinone equilibrium which is shifted to the left by phosphoric acid. The tocoquinones constitute a special case of this relationship because here reversal of the reaction involves cyclization in addition to reduction.

The action of phosphoric acid is to be distinguished from that of acids such as ascorbic and tartaric, since the latter do not function synergistically with tocoquinone (3), apparently because they cannot cyclize tocohydroquinone to tocopherol.

The author is indebted to Lever Brothers Company, Cambridge, Massachusetts for a grant in support of this work.

## Summary

Phosphoric acid greatly augments the antioxygenic activity of hydroquinones and tocopherols and their corresponding quinones in autoxidizing fats. In such media, *p*-quinones are partly reduced to hydroquinones. Phosphoric acid promotes this reaction and thus enhances, in a synergistic manner, the antioxygenic activity of both quinones and hydroquinones. With tocoquinones, cyclization as well as reduction occurs, and tocopherol is thereby regenerated.

The results suggest that a hydroquinone ⇄ quinone system is set up upon the addition of either the oxidant or the reductant to an autoxidizing fat, and that the resulting equilibrium is shifted in favor of the reductant by phosphoric acid.

REFERENCES

1. Olcott and Mattill, J. Am. Chem. Soc., *58*, 2204 (1936).
2. Olcott, Oil & Soap, *28*, 77 (1941).
3. Golumbic and Mattill, J. Am. Chem. Soc., *63*, 1279 (1941).
4. Calkins and Mattill, Proc. Fed. Am. Soc. Exp. Biol., *1*, 104 (1942).
5. Golumbic, J. Am. Chem. Soc., *63*, 1142 (1941).
6. Emmerie and Engel, Rec. Trav. Chim., *57*, 1351 (1938).
7. John, Dietzel, and Emte, Z. Physiol. Chem., *257*, 173 (1939).
8. Deatherage and Mattill, Ind. Eng. Chem., *31*, 1425 (1939).
9. French, Olcott, and Mattill, Ind. Eng. Chem., *27*, 724 (1935).
10. Andrews, Oil & Soap, *12*, 104 (1935).
11. Golumbic, J. Am. Chem. Soc., *63*, 1163 (1941).
12. Hall and Conant, J. Am. Chem. Soc., *49*, 3047 (1927).

# The Processing of Tung Fruit for Oil*

R. S. McKINNEY and N. J. HALBROOK

Agricultural Chemical Research Division, Bureau of Agricultural Chemistry and Engineering, U. S. Department of Agriculture

The personnel of the U. S. Tung Oil Laboratory at Gainesville, Florida, have been considering for some time the possibility and advisability of hulling the tung fruit on the farm. The hull, which constitutes about 50% of the tung fruit, has no value for oil production. The oil comes only from the kernel, but a part of the shell is mixed with the ground kernels to prepare the meal from which tung oil is pressed at the mill.

Hulling the fruit on the farm would not only decrease by 50 per cent the weight of material hauled to the mill, but would leave the hulls on the farm where they could be used as a mulch. The hulls could also be used for their fertilizer value since they contain about 0.70 per cent nitrogen, 0.20 per cent phosphoric acid, and 3.1 per cent potash.

Because of the wide variation in size, and in the hardness of air-dried tung fruit, it has been impossible to remove the hulls with the present type of huller without damaging a considerable proportion of the seeds and kernels. It was believed, from experience with other oil-bearing seeds, that unless the damaged or abraded kernels are pressed almost immediately there would be a marked rise in the free-fatty acid content of the expressed oil, as well as a marked

* Agr. Chem. Res. Div. Contribution No. 83.

oxidation of the oil in the damaged kernels. However, studies made to determine the effect on the tung oil in the kernels of physical damage to seed or kernels gave results quite contrary to expectations. They indicated that the damaged kernels can be kept for several weeks with only a very slight increase in fatty acid and with no appreciable oxidation of the oil. Hulling on the farm, therefore, would not ordinarily result in serious deterioration of the oil. However, hulling of air-dried tung fruit on the farm would necessitate the use of screening and aspiration equipment there to clean the seeds.

It has been suggested that the tung fruit be gathered, whenever it is possible to do so, with a minimum amount of labor and that the gathered fruit be hulled at once. The removal of the moist hull is desirable because it would undoubtedly facilitate the removal of moisture from the tung seed and kernels.

Some years ago the Bureau of Chemistry and Soils, now the Bureau of Agricultural Chemistry and Engineering, found that the hulling of "English" walnuts is facilitated by a treatment with ethylene gas mixed with air in a concentration of 1 to 1000. This same treatment was recently applied experimentally to newly ripened tung fruits. The fruits were placed in an air-tight compartment and ethylene gas in sufficient quantity to yield an ethylene-air concentration of 1 to 1000 was passed into the compartment which was then sealed for 12 hours. While in the air-tight compartment the fruits showed a pronounced tendency to heat, and after 12 hours it was necessary to draw cooled air through them for 2 hours to remove the heat. Five of such intermittent 12-hour periods of treatment with ethylene were required to loosen the hulls sufficiently. The best hulling results were obtained when the treated fruits were passed through a walnut huller operated at 39 r.p.m. However, it was necessary to feed the fruits slowly to obtain fairly satisfactory hulling. Even then a perfect separation was not obtained; the hulled fruit consisted of 73.2% seed and 21.8% hull material, while 5% of the seed fell through the bars with the loosened hull material. Without doubt, these seeds may be recovered from the hull material almost completely. Less promising results were obtained when the newly ripened fruits were placed in the air-tight compartment without ethylene for a similar period and when the newly ripened fruits were subjected to the action of ethylene gas in a concentration of 1 to 2000 for a similar period. Neither steaming of the air-dried tung fruits nor a preliminary soaking in water was as effective as the treatment with ethylene-air mixture (1:1000) for loosening the hulls so they could be removed with the walnut huller.

In connection with the hulling of tung fruit, it may be of interest to know that the moisture content of hulled tung seed was reduced from 33 to 15 per cent by drying for 2 hours at 100° C. and that the hull material was found to contain about 20 per cent of tannin. The hull material is now being tested to determine the quality of the tannin that can be extracted from it.

One year ago a progress report on "Dehydration of Tung Fruit" was made by the U. S. Tung Oil Laboratory to the American Tung Oil Association. Since that time, further investigations have been made on the drying of tung fruit, together with a study of factors influencing the yield of tung oil at the mill.

It was pointed out in last year's report that ventilated barns probably offer the cheapest way of completing the drying of tung fruit. In the past year several tung fruit producers have built barns similar to those described in the 1941 report and have found them fairly satisfactory for drying their tung fruit. Our studies of such barns were continued during the past year. About the last of January, samples of tung fruit were drawn from various parts of the mass in one of these large barns located in the Gainesville area. At that time it was found that there was wide variation in the moisture content of the different samples and that the fruit still contained too much moisture for processing, unless the tung-oil mill had available an efficient meal drier. The moisture content varied from 32 per cent for fruit from the center of the mass half way down, to 17 per cent for fruit from the top of the mass at the west end of the barn. Undoubtedly the fruit in this barn would reach a uniform moisture content of about 13 per cent if left in the barn for a sufficient length of time. It has been found that fruit of this moisture content will yield a tung meal containing about 7 per cent of moisture, which will be reduced to about 4 per cent in passing through the tempering bin at the tung mill. Such dried meal can be efficiently processed in the expeller press, yielding a press cake containing 4 to 5 per cent oil, which is considered good extraction practice.

In studies of the processing of tung fruit at the mill, it was found that the oil yields were invariably lower than those calculated from analysis of samples, even when an allowance was made for the oil remaining in the tung press cake. At first it was considered likely that this difference between calculated and actual oil yields was due to oxidation of some oil and retention of this oxidized oil in the press cake during the expression process. Such oxidized oil, being insoluble in ordinary oil solvents would not be easily determined in the press cake. Although recent investigation has not entirely eliminated this possibility, it has shown that there are several other factors which are at least partly responsible for the tung oil mills getting less than the theoretical yield of oil. One of the most important factors is the frequent difference between the condition of the tung fruit received at the laboratory for analysis and that of the tung fruit received at the tung oil mill for processing. The laboratory sample usually consists of well dried, clean fruits and contains no culls. On the other hand, the fruit received at the tung oil mill may contain several per cent of dirt, several per cent of culls, and perhaps 5 per cent more moisture than in the laboratory sample, or even more moisture if the fruit has been exposed to rain while being hauled from the grove to the mill. The dirt, culls, and higher moisture content of tung fruit delivered at the mill might make the oil yield per ton 27 pounds less than expected from analysis of the sample or 293 pounds instead of 320 pounds per ton.

Several years ago, both the millers and the producers of tung fruits suggested that a considerable quantity of tung oil was probably being lost at the mill during the dehulling process. As a matter of fact, it is standard practice at tung oil mills to periodically take a sample of tung hulls and to determine the per cent of broken kernels present. In order to learn the effect of such losses on tung oil yields, various tung mills were inspected and numerous samples were taken

during the milling process. Samples of whole tung fruits, dehulled tung fruits, and tung hulls, and also samples of meal going in and coming out of the tempering bin, press-cake, and filter-cake were taken and analyzed.

For the analysis of tung hulls, the whole sample was weighed and then divided into fine, medium and coarse hull material. The broken pieces of kernel were removed from the medium hull portion by hand. Each component of the hulls was then weighed and analyzed for oil and moisture content. In analyzing tung hulls for oil content it is necessary to make a correction for the naturally-present ether-soluble non-oil constituents which usually amount to about 0.60 per cent in commercial hull material.

It was found that there was wide variation in the loss of tung oil during the dehulling process, both at different tung oil mills and at the same tung oil mill when processing different lots of tung fruits. In every case the loss of oil in hulling was due, not only to the visible pieces of broken kernels found in the tung hulls, but also to the presence of appreciable quantities of tung oil in the fine and medium, and sometimes in the coarse, hull material. This latter loss of oil was at times considerably higher than that due to the visible pieces of kernels in the hulls. The fine hull material was usually richer in oil content than the other hull components. On one occasion the fine hull material (which may represent from 8 to 27 per cent of the hulls) contained 7.6 per cent tung oil. It can be readily seen that the loss of oil in this portion of the hulls may be appreciable. At first it was considered likely that the presence of oil in the fine hull material was due to absorption of free oil from the very oily kernel. However, a microscopic examination of this material by Mr. George L. Keenan of the Food and Drug Administration showed that this was not the case. Mr. Keenan isolated fine kernel particles, which were readily friable and very oily. The number of such particles was small in comparison with those of white skin and brown shell particles present, but these other substances contained no oil. Obviously then, the oil in the fine hull material is chiefly due to the presence of fine particles broken from the tung kernels in the dehulling process and aspirated away from the dehulled tung fruit together with the hull material.

The very interesting observation was made that the oil content of the hull material, and particularly of the fine hull material increased as the moisture content of the tung fruit decreased. However, this is not surprising because it is well known and easily demonstrated that the moist tung kernels are pliable, while dried tung kernels are brittle, and that the brittleness of the tung kernels increases with increasing dryness. The highest and the lowest losses of tung oil in hulling were found to occur at the same mill. The highest loss of oil, 3.13% on weight of hulls, occurred when the mill was processing tung fruit containing 12.9% moisture. In this instance there was twice as much oil in the medium and fine hull material as in all the pieces of kernels picked from the hull sample by hand. The lowest loss of oil, 0.63% on weight of hulls, occurred when the mill was processing tung fruit containing 15.4% moisture. The oil was about evenly distributed between the pieces of tung kernels removed from the tung hulls and the medium and fine portions of hull material.

From the results of this study it seems that the appreciable loss of oil in the hulling process may be prevented by processing the tung fruit while the kernels are moist and pliable. Unfortunately, if this is done, the miller may find that the dehulled tung fruits are too high in moisture content for efficient expression of oil. The rather obvious solution of this problem is the installation of adequate tung meal drying equipment at the tung oil mill. At two mills where such equipment had been installed it was found that the moist tung meal could be dried to such an extent that efficient expression of oil was possible. It was also found at one of these mills that the loss of oil in the hulls was appreciably lower if the tung fruit was dehulled while the kernels were still moist and pliable.

With regard to the application of drying processes to tung meal, the results of our studies have indicated that high temperatures should be avoided. The temperature of the tung meal should never rise above 205° F. Although a higher temperature does not injure the tung oil in the meal, it affects the non-oil constituents of the meal in such a manner that the physical character of the meal is unfavorable to good oil expression. When the meal is overheated the miller has difficulty in handling it properly and finds that excessive amounts of oil foots and filter cake are produced.

In 1940-41 consideration was given to the possibility of drying tung fruit by artificial means in order to allow the tung milling industry to dry and process the tung fruit at once, instead of waiting for several months or longer for the fruit to dry naturally. After trying almost every conceivable method of drying, it appeared that artificial drying was hardly feasible because of its higher cost in comparison with that of natural drying. This past year consideration was given to the possibility of drying the tung fruit sufficiently for hulling purposes and then drying the resulting tung meal, if necessary, to the point where efficient oil expression would be possible. In this study six tons of moist tung fruits were dried in a tray-type drier at the Florida Agricultural Experiment Station. In this drier, air was heated to the desired temperature by means of a gas furnace (using butane gas) and suitable fans were used to keep the air circulating; the draft to the outside was arranged so that it could be varied according to the moisture content of the drying material. It was understood that a temperature of 210° F. could be obtained in this drier, and previous laboratory tests indicated that at this temperature the tung fruit containing 40% moisture could be dried sufficiently for hulling purposes in 5 hours. However, it was found that a temperature of only 135° F. could be obtained and that 18 hours' exposure to this temperature was necessary to dry the moist fruit sufficiently for hulling purposes. The tung fruits were placed in burlap sacks and some of the partly filled sacks were placed on shelves; others were placed on the floor of the drier. It was found that uneven drying occurred in the sacks; the outer fruits became dryer than was desired before the inside fruits were sufficiently dried. Also, the fruits in the bags on the floor of the drier did not dry as rapidly as those on the shelves and therefore it was necessary to dry the fruits on the floor for an extra period of time. Notwithstanding these rather unfavorable factors and the high cost of shelf drying with butane gas, it was found that, as a result of drying, enough extra tung

oil was recovered in the milling process to pay several times over for the drying process. The drying cost was calculated as $2.25 per ton. The extra oil obtained per ton of tung fruits amounted to 17.8 pounds, which, at 35 cents per pound, was worth $6.24. This leaves a balance of $3.99 extra profit per ton of tung fruit processed, which would soon pay for the drying equipment. It should be noted that a tray-type dryer of a different design than the above has been used for the drying of tung fruit broken into segments with satisfactory results.

At the time this study was made it was believed that the tung hulls could not be separated from the rest of the fruit if they contained more than 20% moisture. However, since that time one of the tung oil mills has successfully hulled moist tung fruit, the hulls of which probably contained 40 per cent moisture; no difficulty was encountered in obtaining a good separation.

In conclusion, it might be well to point out that, so far as we know, every tung oil mill now located in the South is making a real effort to obtain maximum tung oil yields. This objective is not easy to attain. At times, the fruits processed may be too wet, or too dry, or too old, for maximum tung oil yields. However, it is our hope that, as we learn more about the influence of various factors on the yield of tung oil at the mill, the benefits resulting from this knowledge will be passed on to the tung fruit producers in the form of increased returns from higher tung oil yields on their crops of tung fruits.

# Abstracts

## Oils and Fats

Edited by
M. M. PISKUR and SARAH HICKS

THE COMPOSITION OF THE DEPOT FATS OF AQUATIC ANIMALS. J. A. Lovern. Dept. Sci. & Ind. Research. Food Invest. Sp. Rpt. No. 51, 72 pp. (1942). The fat of most aquatic animals is derived mainly from ingested fat, and this accounts for the generally similar type of fat found throughout the whole range of species studied. It also accounts for the differences between the fats of freshwater and marine forms. Superimposed on this general type are various modifications which are more or less restricted to groups of closely related species, and the development of these specific types is closely bound up with the evolutionary history of the animals in question. The modifications themselves have been brought about by the selective operation of one or two processes, which function to widely varying extents and along different lines in different species. In some animals one or more of these mechanisms may not be in evidence at all. By means of a reversible hydrogenation/dehydrogenation process, fatty acids of the same number of carbon atoms, whether saturated, monoethylenic or polyethylenic, are interconvertible. Fatty acids may be converted into aliphatic alcs. and triglycerides into alkoxy-diglycerides. There may also be a selective production of fully-saturated glycerides. By processes of synthesis or degradation, fatty acids may be converted into derivatives of longer or shorter chain length. The mobiliation of depot fat is largely nonselective, but in some cases there may be a slight tendency to preferential mobilization of small molecules or of the more unsaturated constituents.

REPT. U. S. VEGETABLE OIL MISSION TO BRAZIL, 1942, 117pp. The report contains statistical data on exports, production and amt. available, information on equipment, transportation and labor, and recommendation for increasing supplies of oils from this source.

REAGENTS FOR THE DETERMINATION OF THE TENDENCY OF FATS TO BECOME RANCID. Ch. S. Goreglyad. *Lab. Prakt. (U.S.S.R.), Sammelband 1938*, 72 (Pub. 1939); Chem. Zentr. 1940, I, 3722—With a view of finding a cheap reagent for testing the peroxide content of fats, expts. were carried out with phenol, picric acid, quinine, pyrogallol, etc. The last was found to be useful for the purpose when used in 1% ether soln. The following method is given: 2 c.c. of the melted fat is cooled to 45°, shaken with 1 c.c. HCl (d.1.19) and treated with 8-10 drops of pyrogallol soln. If the fat is rancid, a raspberry-red ring develops after 1-8 min. When an acetone soln. of pyrogallol was used a yellow ring developed after 10-15 min. However, it was difficult to detect this ring if the fat was also yellow. *(Chem Abs.)*

A RAPID METHOD OF MEASURING THE UNSATURATION OF HYDROGENATED FATS. H. Jasperson. *J. Soc. Chem. Ind. 61*, 115-17 (1942). Reagents—0.5-1.0% $Br_2$ by volume in glacial HAc. 2½% $Hg(OAc)_2$ in glacial HAc. 10% KI in aq. 0.1N Na-thiosulfate. $CHCl_3$, starch soln. Procedure—0.3-1.0 g. fat is weighted in flask and dissolved in 15 c.c. $CHCl_3$. After addg. 20 c.c. of $Hg(OAc)_2$ soln., titrate directly with Br reagent until color is faint yellow. The concn. of reagent is detd. by adding 5-10 c.c. into 20 c.c. KI soln., adding 15 c.c. $CHCl_3$ and 20 c.c. $Hg(OAc)_2$ soln. and titrating the $I_2$ liberated.

BOILING POINTS OF N-ALKYL ACIDS. W. O. Pool and A. W. Ralston. *Ind. & Eng. Chem. 34*, 1104-5 (1942). Freezing point and boiling point curves are presented for the satd. fat acids $C_6$ to $C_{18}$.

HIGH-MOLECULAR-WEIGHT FATTY ACID DERIVATIVES. II. SULFIDES, SULFOXIDES AND SULFONES. Byron A. Hunter. *Iowa State Coll. J. Sci. 15*, 215-21 (1941). III. Carboxylic acid salts and amides of dodecylamine and octadecylamine, *ibid.*, 223-30. *(Chem. Abs.)*

REPORTS ON FAT, OILS AND WAXES. J. Fitelson. *J. Assoc. Off. Agr. Chem. 25*, 726-8 (1942). Titer test coloring matter and detn. of olive oil are discussed.

REPORT ON UNSAPONIFIABLE MATTER. G. Kirsten. *J. Assoc. Off. Agr. Chem. 25*, 728-33 (1942). Results on various oils by four different methods show that the S.P.A. method gives consistently higher results than do the other methods. Tests showed that while the S.P.A. method effected practically complete extn. of added unsaponifiable matter, the F.A.C. and modified Kerr-Sorber methods did not.