geranic acid (23), *cis* α-ionone (6), and *l*-α-phellandrene (19) also absorb in this region. On the other hand, certain steroids with cyclic double bonds in positions other than 2- or 3- lack such absorption (12). Although absorption in this region is not limited to compounds with cyclohexene structures, the band at 660 cm.$^{-1}$ in the spectrum of NAFD may indicate the presence of a double bond in a six-membered ring.

The infrared spectrum (Fig. 2E) of the material obtained from NAFD by bromination and dehydrohalogenation with collidine possesses a band at 747 cm.$^{-1}$ (13.4 μ) that is characteristic of *o*-disubstituted benzene derivatives. A small band at 1597 cm.$^{-1}$ (6.26 μ) and a shoulder at 1480 cm.$^{-1}$ (6.76 μ) are also present; bands of variable intensity in these regions are characteristic of aromatic compounds (2). In the ultraviolet (Fig. 1B) absorption due to aromatic compounds is probably obscured by the strong absorption of conjugated double bonds at 235 mμ. The evidence for an *o*-disubstituted benzene derivative further indicates that at least one compound with an unsaturated six-membered ring structure is present in NAFD.

Direct evidence for the presence of such material is provided by the isolation of phthalic anhydride from the product of the aromatization and oxidation of NAFD. The low yield of phthalic anhydride may indicate that only a small part of the NAFD has the unsaturated six-membered ring structure, or it may indicate that large losses occurred in one or more of the reactions involved. The reasons for the difference in the yields obtained by methods I and II are not apparent. It is possible that method I gives optimal results only when applied to conjugated cyclohexadienes; the lack of significant absorption above 255 mμ in the ultraviolet spectrum of NAFD probably indicates that NAFD contains little or no conjugated cyclohexadiene (25).

Since N-bromosuccinimide is a free radical reagent, the possibility that a free-radical-induced cyclization gave rise to the cyclic precursor of phthalic anhydride during the bromination step cannot be excluded. A mechanism whereby a cyclization of this type might occur has been outlined by Bloomfield (3) in explaining the action of N-bromosuccinimide on rubber. Bloomfield did not isolate any of the proposed cyclic material. If such a cyclization had occurred in the aromatization of NAFD, a higher yield of phthalic anhydride might have been expected from those experiments (aromatization and oxidation, Method I) in which two treatments with N-bromosuccinimide were employed than from those in which N-bromosuccinimide was used only once (aromatization and oxidation, Method II). Higher yields were in fact obtained by Method II.

Summary

The monomeric, non-urea-adduct-forming material from the ethanolysis of heated linseed oil exhibits an infrared absorption band at 660 cm.$^{-1}$ (15.2 μ). This absorption is not present in the spectrum of the esters of unheated linseed oil acids or in that of the adduct-forming esters prepared from heated linseed oil. The monomeric, non-urea-adduct-forming material, on aromatization and oxidation, yielded about 1% of phthalic anhydride, thus providing chemical evidence for the existence in this material of a compound containing an unsaturated six-membered ring.

Acknowledgement

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Extraction of Corn Oil by Three Petroleum Solvents

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Recovery of 99% of the oil in wet-milled corn germs is being obtained industrially by prepressing, followed by extraction with commercial hexane (4). The possibility of direct extraction without prepressing deserves consideration. It also appears desirable to consider the possibility of more efficient extraction by petroleum solvents other than the hexane fraction. In the current work, extraction rates were determined in the laboratory using three petroleum fractions: hexane, heptane, and iso-heptane.

Rate-Extractions

Apparatus. The rate-extraction apparatus employed was a batch, co-current type of laboratory column extractor shown in Figure 1. The equipment was somewhat modified from that shown by Arnold, Sweeney,

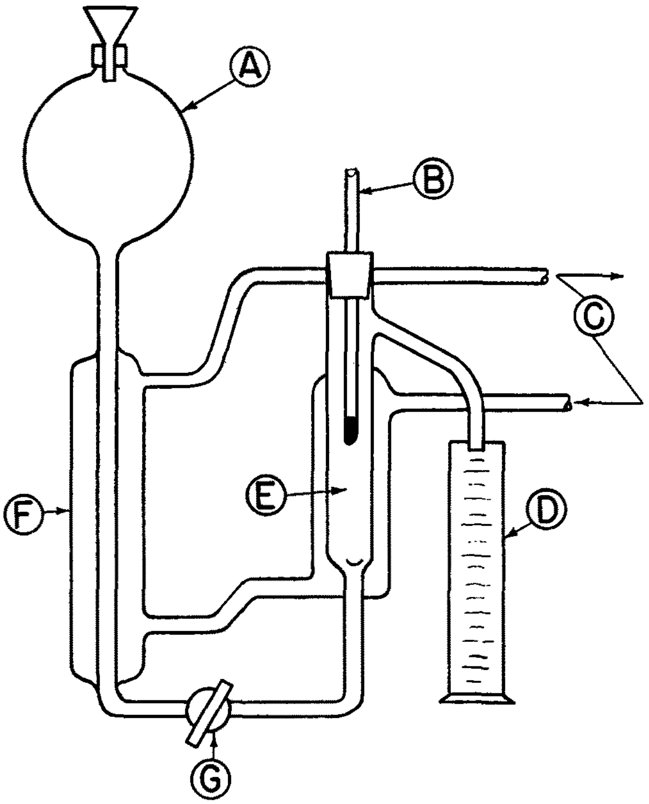

FIG. 1. Rate-extraction apparatus

A. Solvent reservoir
B. Thermometer
C. Water circulation for temperature control
D. Graduate for miscella
E. Extraction chamber
F. Water jacket
G. Solvent control stopcock

and Russell (2) to include temperature control by a recirculating hot-water bath and was basically quite similar to the laboratory column extractor of Reiners, Sniegowski, and Baldwin (3). The latter have published results on rates of corn oil extraction, using pre-heated hexane in their larger column extractor.

Procedure. Accurately weighed dry samples of flaked corn germ of approximately 10.0 g. each were extracted in all runs by heated fresh solvent at a controlled solvent rate of 10 ml. per minute. The corn germ from the wet-milling process was provided by Clinton Foods Inc., Clinton, Ia., and was flaked between smooth rolls after the addition of approximately 5% moisture and heating to about 160°F. To obtain uniform flakes all of the germ used in the rate-extraction studies was flaked at the beginning of the work and kept in an air-tight container until extracted. The rate-extraction studies were carried out over a four-month period.

Samples of the effluent miscella obtained at constant temperature and solvent flow-rate were collected for each 10-min. interval of a two-hour extraction time. These were evaporated to give the weight of oil extracted for each time increment. The sum of the weights over the two-hour extraction period was added to the weight of residual oil in the extracted flakes obtained by a Soxhlet extraction. In the absence of an official A.O.C.S. method for residual oil in corn germ (3), the Soxhlet extraction, used satisfactorily in this laboratory on other fat determinations, was used.

Results. Several rate extractions were carried out at decreasing flake thicknesses, using hexane at 150° F. as the solvent. The percentage of residual oil remaining in the extracted flakes decreased with the decrease in flake thickness. The optimum flake thickness for extraction appeared to be in the range 0.010 to 0.012 in. since at lower thickness the corn germs would disintegrate in flaking, yielding an excessive quantity of fines. For all subsequent rate-extractions flakes of average thickness of 0.011 in. were used.

Similar rate-extractions were conducted, using commercial n-hexane, n-heptane, or iso-heptane fractions. The temperature in each run was maintained constant by a re-circulating hot-water bath. Various extraction temperatures up to the lower limit of the boiling point range for each solvent were used. The hexane was Skellysolve B, with a normal boiling point range of 147°–161°F. Both the normal and iso-heptanes employed were supplied by the American Mineral Spirits Company. The n-heptane showed a boiling range from 203°–229°F. while the iso-heptane had a boiling range from 187°–220°F.

Typical time-residual oil extraction curves for the three solvents at 150°F. are shown in Figure 2. This temperature was the highest practical for hexane without the development of excessive vapor pressure. The relatively rapid extraction during the first 10 min., probably the result of washing the oil from the surface of the flakes, is typical of rate-extraction curves in general. The results indicate that hexane extracts at about the same rate as iso-heptane but at a higher rate than normal heptane.

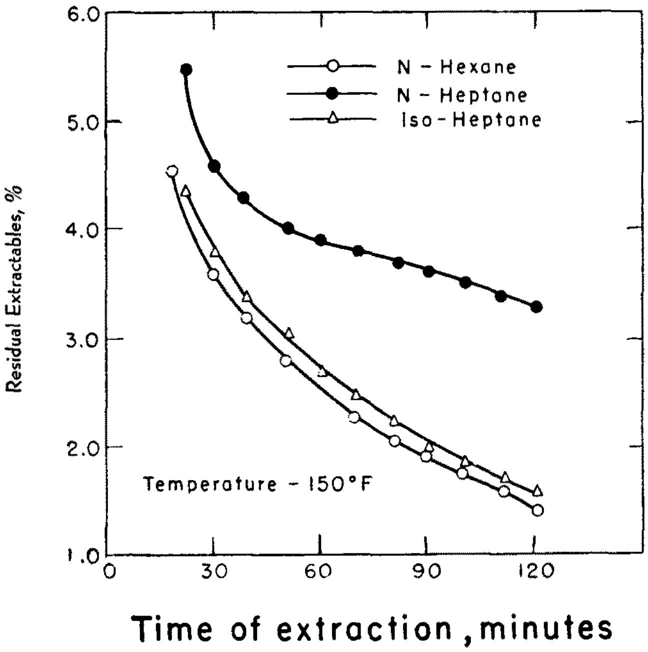

FIG. 2. Relation of residual extractables to extraction time for three solvents. Rate-extraction.

Figures 3 and 4 show the effect of progressively higher extraction temperatures on the rate of oil removal during one-half- and 2-hr. extraction times. At the higher temperatures of extraction possible with iso-heptane better rate-extraction is shown for this solvent than for hexane at its applicable lower temperature. The extraction curve for iso-heptane is a nearly direct continuation above 150°F. of the curve for hexane. Thus any better solvent action by iso-

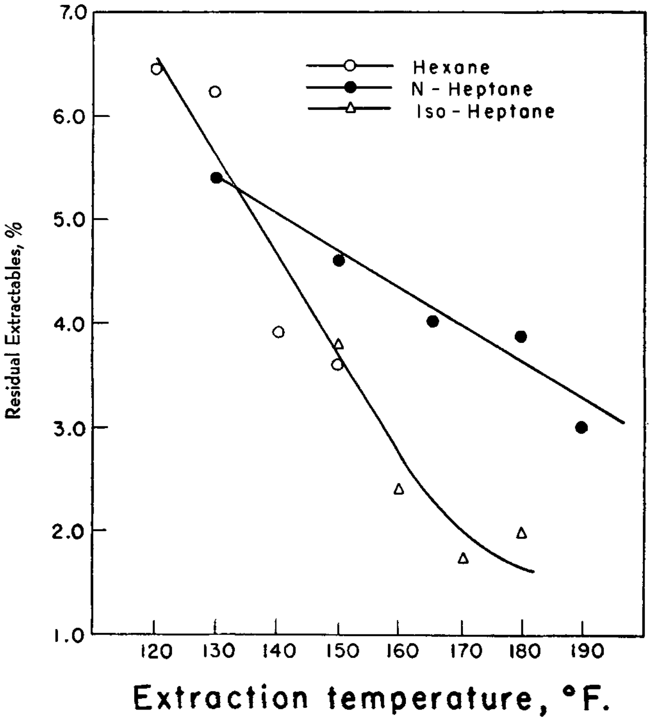

FIG. 3. Relation of residual extractables to extraction temperature. Time 30 min. Rate-extraction.

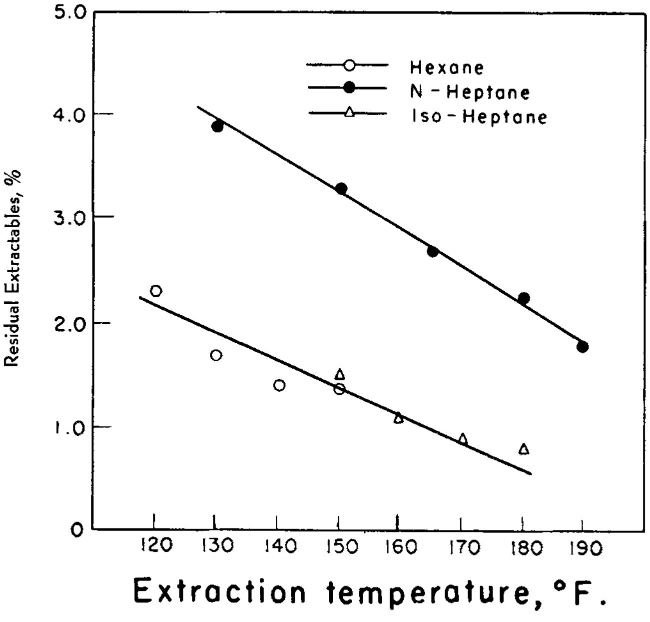

FIG. 4. Relation of residual extractables to extraction temperature. Time 2 hrs. Rate-extraction.

heptane as compared to hexane appears to be a function of temperature rather than direct specificity of solvent action. The solvent action of normal heptane is definitely lower than that for iso-heptane at comparable temperatures. No apparent changes were observed in the oil at the higher temperatures of extraction.

Pilot Plant Extractions

Equipment. The continuous countercurrent laboratory pilot plant used for these studies has been previously described (1). Prior to starting the current work, the extractor portion was wound spirally with ¼-in. copper tubing which was supplied with steam controlled by a suitable pressure regulator. Heat losses were kept low by lagging the extractor with magnesia insulation. Extraction temperatures were varied by controlling the steam pressure and determined at 10 points along the extractor by thermocouples.

Procedure. The desired extraction times were varied by changing sprockets in the driving mechanism. The exact average flake feed-rate was determined by weighing the amount of flakes actually fed to the machine. Flakes were prepared from two new batches of germ from the same source and in the same manner as for the rate-extraction studies. The first of these batches, extracted by hexane, was stored in tight containers in a cool room about two months prior to flaking and used over a three-month period. The second, extracted by iso-heptane, was stored about one month and used over a three-week period.

The solvent was determined by a rotameter. The pilot plant was first operated until the feed rate, temperature, and miscella oil content were constant, indicating steady state operation. The oil contents of the meal samples and the feed flakes were determined in Soxhlet extraction apparatus.

Results. With hexane as the solvent the solvent-feed ratio was varied at a constant extraction temperature of 157°F. between 1.5 and 4.5. Optimum extraction results, as indicated by the residual oil content in the meal, were obtained with a ratio in the range of 2 to 3. Poorer extraction at higher rates probably resulted from some by-passing of the solvent because of higher flow rates. The solvent-feed ratio for use with both hexane and iso-heptane was set at 2.3.

The effect of extraction time on the residual extractables for both hexane at 157°F. and iso-heptane at 192°F. is shown in Figure 5. Hexane was a slightly better solvent even though used at a lower temperature.

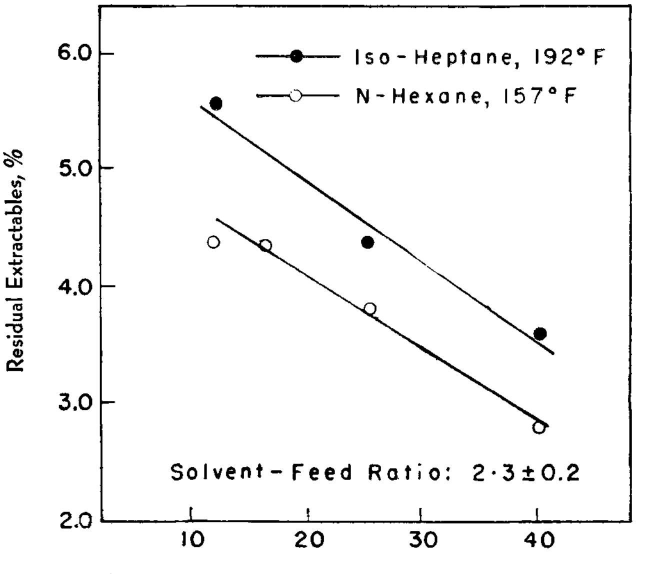

FIG. 5. Effect of extraction time on residual extractables, using hexane at 157°F. and iso-heptane at 192°F. as solvents. Pilot-plant extraction.

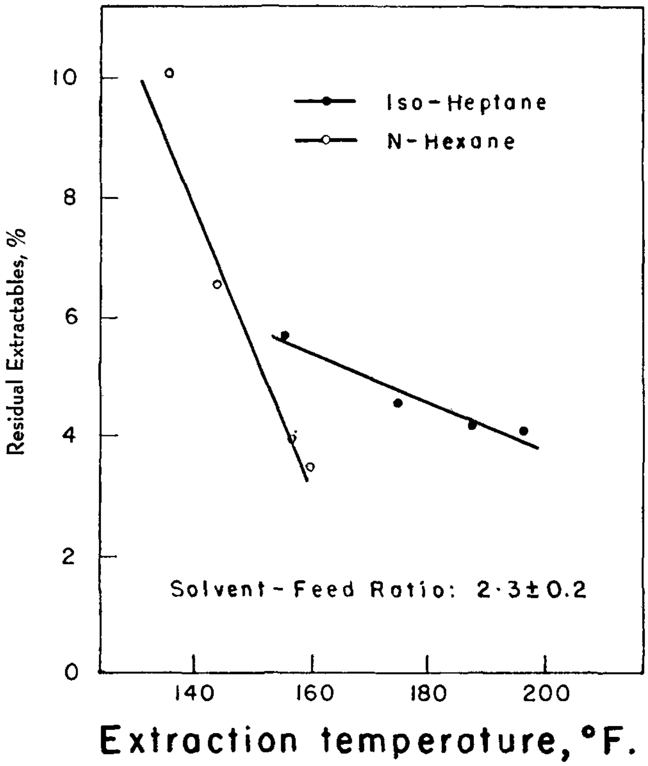

FIG. 6. Effect of temperature on residual extractables, using hexane and iso-heptane as solvents. Extraction time, 25 min. Pilot-plant extraction.

The effect of temperature in 25-min. extraction time on the residual extractables is shown in Figure 6. As would be expected, the amount of oil extracted by both solvents increased with the temperature. Here again hexane appeared to be a somewhat better solvent.

The somewhat better extraction obtained with hexane would have little significance if the two solvents were being compared at the same temperature. However, on the basis of the rate-extraction data, the iso-heptane at 192° F. should be definitely superior to hexane at 157°F. On the other hand, since the rate extraction studies and the pilot plant studies were not carried out under the same extraction conditions, close correlation between the results of the two should not be expected. Based on previous work with other materials, it was expected that the results would show a rough correlation. A possible explanation for the discrepancy is that at 157°F. the agitation caused by boiling hexane might have a beneficial effect. At the solvent-entry end of the extractor vapors from the boiling solvent rising upward with the extracted flakes might condense on them before reaching the dryer and exert an extra washing action. At the feed end vapors passing up into the incoming mass of flakes would condense on the flakes and start dissolving oil.

Summary and Conclusions

Rate-extractions of corn germ oil by heptane, iso-heptane, and hexane at the same temperature showed the latter two to be better solvents than heptane. Extraction rate increased with the temperature.

Countercurrent extraction in a continuous laboratory pilot plant showed hexane at 157°F. apparently equal to iso-heptane at 192°F. It is suggested that the boiling of the hexane at 157°F. might account for the better extraction.

It can be concluded that hexane is at least as good a solvent for the extraction of corn oil from whole germ as is iso-heptane.

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Reactions of Unsaturated Fatty Alcohols. I. Preparation and Properties of Some Vinyl Ethers[1]

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ALTHOUGH a polymer of vinyl octadecyl ether was among the first vinyl ether products offered commercially, comparatively little information is available on the preparation, properties, and polymerization of alkyl vinyl ethers having long-chain alkyl groups. Vinyl octadecyl and vinyl oleyl ethers are referred to a number of times in the patent literature, but detailed procedures and descriptions are seldom provided. So far as we have been able to determine, vinyl ethers of polyunsaturated alcohols such as linoleyl and linolenyl alcohols, or of mixed alcohols derived from unsaturated oils like soybean and linseed oils, are not mentioned in the literature. For a general discussion of the chemistry of alkyl vinyl ethers and a review of existing literature Reference 6 should be consulted.

Preparation of Vinyl Ethers

For laboratory purposes it was desired to synthesize vinyl ethers from the appropriate alcohol and acetylene at atmospheric pressure in order to avoid the hazardous operations and the complexities of technique and apparatus involved in pressure reactions with acetylene (3). Reppe has pointed out (5) that pressure is not required in vinylation of high-boiling alcohols and has described a procedure for the synthesis of vinyl octadecyl ether, using acetylene at atmospheric pressure. This procedure, which is a continuous process intended for industrial use, was not

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