

4. Lewkowitsch—The Chemistry and Technology of Oils, Fats and Waxes, Sixth Edition, London 1923, Vol. III, p. 55.
 5. Hefter—Technologie der Fette und Oele, Berlin, 1906, Vol. I, p. 686.
 6. U. S. Patent No. 11,239, 1854.
 7. Cochrane of Everett, Mass.; see Fritsch—Fabrication et Raffinage des Huiles Vegetables, Paris 1914, p. 719, 4th Edition.

8. See Hefter—Tech. der Fette und Oele, 1906, Vol. I, p. 685.
 9. Chmic. Gazette 1854, p. 283.
 10. Jacobson, Chem. Tech. Repert. 1872, p. 39.
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 19. English Patent No. 24,714, December 24, 1895.
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THE SEED OIL OF THE HACKBERRY

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THE hackberry, or sugar-berry*, is the fruit of *Celtis occidentalis* L., a tree which bears a superficial resemblance to the elm and, like it, is one of the Ulmaceae. This tree attains its best development in the deep alluvial soils of the river bottoms, but thrives on gravelly and stony upland sites, especially limestone outcrops. It is widely scattered, its range extending from southern Quebec to eastern Washington and Oregon, southward to Florida and westward to eastern Texas, New Mexico and Nevada. A smaller, more dainty edition of this genus is the southern hackberry (*C. mississippiensis*, Bosc.) whose habitat is the south central states and Mexico. The fruit of the species in question is a cherry-like, slightly ovoid drupe whose color, at first an ocher-yellow, eventually becomes a purple black. It matures in autumn and persists into winter. The nutlet or pit is oblong-oval, thick-walled and light brown in color. From data obtained in this Laboratory (1) it appears that the shell constitutes three-fourths of the weight of the pit; that the latter contains 37 per cent mineral matter and 11.33 per cent (petrolic) ether extract and the "meat" itself 43.15 per cent of fatty matter. That its popular name should reflect the chief saccharine characteristic of the fruit whose pleasant taste suggests the flavor of figs is not surprising in view of the fact that reducing sugars account for approximately one-third of its composition (2).

If the seed oil of *C. occidentalis* L., or that of any other species of this genus, has ever been subjected to critical study, then this fact escaped notice during the course of the survey of the literature which was made preliminary to the inception of an investigation, the results

*This term is used in its popular sense. What is called here a berry is, botanically, a drupe.

of which are herein recorded. Some work, however, has been done on the fruit and the pit itself. Over eighty years ago Payen (3) reported on his studies of the pit of *C. cordata*, a species name which is probably here synonymous with *C. occidentalis*. The outstanding fact resulting from his researches is the preponderance of the element calcium which, he observed, exists here as the carbonate. More recently Yanovsky and associates (2) examined the whole fruit. They confirmed the findings of Payen in respect to the high calcium carbonate content of the pits, extended the analysis to include its other inorganic constituents and investigated the nature of the organic acids of the pulp.

This investigation was carried out for the purpose of determining whether the genetic relationships existing among the Ulmaceae might be reflected in chemical similarities in composition of the seed oils of two of its genera, *Ulmus* and *Celtis*.

The unusual composition of the seed oil of the elm, *Ulmus americana* L., reference to which has already been made in this Journal (4), raised the hope that equally interesting facts might be brought to light in this instance also.

The fruit from whose pit the fatty oil was extracted† was collected during the months of October to December, 1935, on the campus of the University of Wisconsin and on private property in a suburb of the city lying over a limestone outcrop. Extraction of the oil was made with purified petroleum ether (b.p. 60-70°) by a two-step operation: a preliminary extraction of the cracked whole pit followed by re-extraction of the comminuted partially de-fatted residue. Removal of the solvent under reduced pressure in the presence of carbon dioxide and filtration gave an oil, 12 yellow in color, whose physical and

chemical characteristics were found to be as follows (Table I):

TABLE I
Analytical Constants of Hackberry Seed Oil

| | |
|----------------------------------|--------|
| Specific gravity 25°/25° | 0.9204 |
| Refractive index 25° | 1.4794 |
| Iodine number (Wij's) | 150.0 |
| Thiocyanogen number | 81.97 |
| Saponification number | 191.1 |
| Reichert-Meissl number | 0.0 |
| Polenske number | 0.3 |
| Hydroxyl number | 4.9 |
| Soluble acids (per cent butyric) | 0.08 |
| Insoluble acids (per cent corr.) | 91.97 |
| Unsaponifiable matter (per cent) | 1.35 |

†Grateful acknowledgment is made to the NYA for supplying the labor necessary in the collection of the fruit and the subsequent recovery of the pits of which approximately 5 kgs. were obtained.

The presence of both low and medium molecular weight fatty acids in any noticeable amounts seems to be contra-indicated by the low order of magnitude of Reichert Meissl and Polenske numbers, a view which is supported by a normal saponification value. Hydroxyacids, likewise, are not conspicuous. On the other hand, the ratio between thiocyanogen and iodine numbers furnish a clew to the probable presence of not only oleic acid but at least one other of a higher degree of unsaturation, such as linoleic, a fact which was subsequently demonstrated.

Identification of the unsaturated fatty acids was effected by means of their bromo-derivates as well as their oxidation products. No hexabromide derivative of linolenic acid was obtained by brominating a 2-g. sample at -10°. It is true that a voluminous precipitate was obtained at this temperature but analysis proved it to be the tetrabromo-derivate of linoleic acid. It had the same composition as that fraction which was insoluble in cold petroleum ether (m. p. 114.3; Br theoretical 53.3%, observed 53.8%). Its precipitation at this point was probably due to the unexpected solubility conditions in cold ethyl ether which had been created because of its abundance. That there are involved here the two isomeric forms of this acid seemed not improbable,

a conclusion later confirmed when identification of the unsaturated fatty acids was attempted by means of their permanganate oxidation products.

The hydroxy acids formed in the aforementioned reaction, after having been thoroughly dried, were washed with a liberal volume of ethyl ether. From the ether solution, after concentration, there crystallized a small quantity of material of neutralization equivalent 184 and melting point 130.7°. Since the corresponding values for pure dihydroxy-stearic acid are 184° and 137°, respectively, it is evident that the product was slightly contaminated notwithstanding the fact that the parent compound was obviously oleic acid. From the ether-insoluble residue, after crystallization from hydro-alcohol (30%) solution, there were obtained four fractions; of these three melted in the range 155.6°-157°, the fourth, which constituted approximately one-tenth of the whole, at 167°-169°. The melting points of the two forms of sativic acid (tetrahydroxy stearic acid) are 162°-163° and 173°. It seems not improbable,

therefore, that linoleic acid occurs in this oil in two isomeric forms.

The saturated acids were found to be composed entirely of stearic acid (neutralization equivalent 196, required for stearic acid 197). Crystallization from alcohol yielded no arachidic acid. The absence of homologues of this acid containing less than C₁₂ has already been accounted for.

Because of the elimination of the several acids, as above indicated, and for the added reason that by the lead-salt-ether procedure the content of solid fatty acids was found to be approximately 5.9 per cent and that of the liquid acids 86.4 per cent, the assumption may very well be made that the Hehner number of this oil, or 91.97, represents in this case its content of total fatty acids. Using, therefore, as a basis for calculation this value, and the iodine and thiocyanogen numbers of the total fatty acids, which were found to be 155 and 85.6, respectively, the composition of this oil in terms of its constituent fatty acids is saturated acids (stearic) 4.90 per cent, oleic acid 16.50 per cent and linoleic acid 70.40.

CONCLUSIONS

It does not follow, from this examination of the seed oil of the hackberry, that genetic relationships within the plant family here in question are reflected in the composition of the seed oil of two of its members. Elm seed oil is characterized by its large content of a low-molecular weight saturated fatty acid (capric) whereas, similarly, that of hackberry seed oil is a high-molecular unsaturated one (linoleic) which, apparently, exists here in two isomeric forms.

The relative scarcity of the tree, the low yield of oil from its fruit and the uncertainty of the crop stand in the way of a commercial exploitation of this oil. It might, however, have a nutritional interest because of its high content of linoleic acid.

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ABSTRACTS

Oils and Fats

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Research on obtaining fats by means of microorganisms with special consideration to the work by the Institute of Fermentation Industries. H. Fink, H. Haehn and W. Hoerburger. *Chem.-Ztg.* **61**, 689-693, 723-6, 744-7 (1937).

Antioxygens of fatty oils. XV. Action of carotene on the oxidation of fatty oils. XVI. Ultra-violet rays as a cause of inversion of oxidation catalysts for fatty oils. N. Nakamura. *J. Soc. Chem. Ind. Japan* **40**, Suppl. binding 203-5, 205-6 (1937).—The action of carotene on the oxidation of fatty oils varies with the kind of fatty oil in which it is dissolved and, in some cases, with the concns. of carotene added. The stability of carotene varies with the kind of oils in which it is dissolved, viz., it is most unstable in tsubaki oil, moderately stable in linseed and most stable in maize oil. Moderate unsatn. in fatty oils is considered necessary for the highest stability of carotene. (*Chem. Abs.*)

Pressure cooking contributes increased cottonseed processing profits. R. B. Taylor. *Chem. & Met. Eng.* **44**, 478-81 (1937).—Apparatus, technic and av. results of 275 test runs are described. With cooking temps. of 270° F. or higher, and proper moisture content control, it was found possible to maintain an av. "standard" (ratio of oil to NH₃ in the cake) of 55 as compared with "standards" of 65 to 70 for av.

oil mill practice. On the basis of "prime" seed (3.5% NH₃ and 18.5% oil), 10 to 15 points reduction in the "standard" is equivalent to from 6½ to 10 lb. increase in oil yield per ton of seed, a gain of 67c to \$1 per ton of oil at 10c per lb. The quality of cake and oil was uniformly equal to or better than that produced in the best mill practice.

Reducing the oil lost through deacidifying. R. Dieterle. *Seifen-Ztg.* **64**, 632-3 (1937).—A prominent problem for fat refiners is the choice of either deacidifying with dilute caustic at high temps. or concn. caustic at low temps. Coco and babassu fats, good palm fat, sesame and peanut oil and some types of whale oil are in general refined with caustic of 2 to 6° Be and at 98° C. and a caustic factor of 1.1 to 1.4 being used. The amt. of caustic used is that necessary to neutralize the free fat acids multiplied by the caustic factor. Poor quality train type oils, certain types of peanut oil and palm fat and about all types soy, rape and cottonseed oils require concd. caustic. In this case the caustic factor is 2 to 5, temp. 60-80° and concn. of caustic 10 to 20° Be.

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