for the 20-g. sample r = −0.96. Although there is a slight decrease in the correlation coefficient from a 20-g. to a 10-g. sample, it is not significant and a 10-g. sample would appear suitable for routine determinations.

Since the moisture content of the seed will affect the observed weight for a given number of seeds and consequently the density of these seeds, the moisture contents must be considered in the density determination. The effect of seed moisture content on the correlation between oil content and seed density was determined by measuring the volume of a dried 10-g. sample from each of the 10 varieties. The correlation coefficient was r = −0.96, which is the same as that of the undried seeds. This indicates that, as long as the seed samples are of equivalent moisture content, a reliable correlation between the two variables exists. If seed samples are stored in a constant environment for four or five days, their moisture contents will all be very close (3). Thus, in determining the density, it is necessary to allow the seed to equilibrate for this period before measurements are taken. Alternatively one may first dry the seeds in an oven and, on removal, allow them to equilibrate with the atmospheric moisture. By this procedure, along with the use of a check sample, the comparative oil contents of different varieties of flax can be estimated.

The use of seed density as a measure of an absolute oil content is more involved. Before one can say that a seed sample with a given density has a certain oil content, several factors must be considered, the most important of which is moisture content. Since the moisture content will affect the seed weight and seed volume, one must know the regression equation for oil content on seed density with seed samples of varying moisture contents. The difference between the regression lines obtained with moisture-free seed and with seed containing 5.4% moisture is shown in Fig. 2. The regression line for the moisture-free acid was drawn from the regression equation $\hat{Y} = 194.06 - 136.10X$. It seems likely that a family of regression lines could be determined for different seed moisture contents. Such data would allow the determination of oil content by reference to the particular regression equation corresponding to the moisture content of the seed. In this case a periodic check of the moisture content of seed samples would be necessary to determine the proper regression equation to be used. In addition to moisture content, the maturity of the seed when harvested, and possibly other factors, may affect the density of the seed. The nature of these effects and the determination of regression lines for varying moisture contents will constitute further work in this area. The most significant feature of this method is that a comparative estimate of oil content can be obtained in a few minutes. In addition, the sample is neither destroyed nor harmed in any way and may be used for other analytical tests or for breeding purposes.

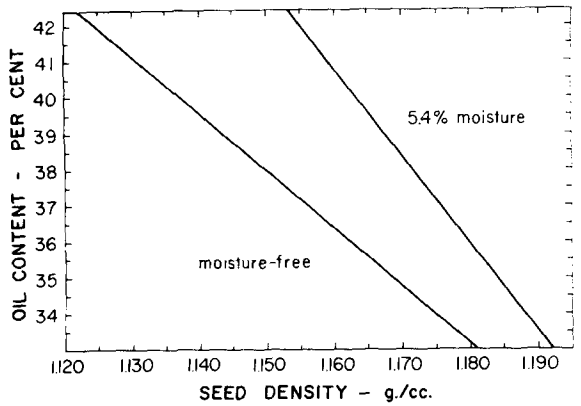

FIG. 2. Regression lines for moisture-free flaxseed and flaxseed containing 5.4% moisture.

Studies of the correlation between seed density and oil content in other oilseeds are presently being investigated with the use of the air pycnometer.

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REFERENCES

1. Hunt, W. H., Neustadt, M. H., Hart, J. R., Zeleny, L., J. Am. Oil Chemists' Soc., *29*, 258–261 (1952).
2. Comstock, V. E., Culbertson, J. O., Agron. J., *50*, 113–114 (1958).
3. Comstock, V. E., private communication.

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Search for New Industrial Oils. VI. Seed Oils of the Genus *Lesquerella*[1]

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Fatty acid composition of seed oil from 14 species of the genus *Lesquerella* has been determined by gas-liquid chromatography. All but two species contain hydroxyeicosenoic acid in amounts ranging from 45 to 74%. The remaining two species contain about 50% C_{18} hydroxy acids, but none of the C_{20} hydroxy acid.

FOLLOWING THE DISCOVERY that oils from seeds of *Lesquerella lindheimerii* and *L. lasiocarpa* contain large amounts of hydroxyeicosenoic acid (4, 5), special attention was given (a) to the determination of the structure of this new hydroxy acid (lesquerolic) and (b) to the collection by the U. S. Department of Agriculture's Crops Research Division of seeds from related species in the genus in order to ascertain whether this unique compound is characteristic of all available members. The structure was shown to be 14-hydroxy-*cis*-11-eicosenoic acid (5). In 1960, samples of 14 species were collected from the wild for analysis. This paper reports the composition of these previously uninvestigated oils.

The genus *Lesquerella*, of the family Cruciferae, is native chiefly to the arid parts of western North America from east central Mexico to Alberta and Saskatchewan. Representatives also occur in limited areas of South America, Alabama, Kentucky, and

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[2] A laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

TABLE I

Composition and Characteristics of *Lesquerella* Seed and Derived Oils

Lesquerella species	Seed analysis			Oil analysis		Composition of methyl esters										
	Wt./1,000	Oil	Protein ($N \times 6.25$)	Iodine value (Wijs)	Refractive index n_D^{40}	C_{14} sat'd.	C_{16} sat'd.	C_{18} monoene	C_{18} diene	C_{18} sat'd.	C_{18} monoene	C_{19} diene	C_{18} triene	C_{20} sat'd.	C_{20} monoene	C_{18} unsat'd. hydroxy	C_{20} unsat'd. hydroxy
	g.	% *DB*	% *DB*			%	%	%	%	%	%	%	%	%	%	%	%
L. angustifolia[a]	2.6	26	25	89	1.4717	....	2	1	....	0.9	14	8	2	....	0.4	5	65
L. argyraea	0.6	26	24	96	1.4714	....	2	1	....	2	20	6	5	....	1	0.7	61
L. argyraea	0.6	27	20	99	1.4732	....	2	0.5	....	2	14	9	4	....	0.4	0.8	67
L. densipila[b]	0.8	24	21	....	....	....	6	1	0.3	3	22	3	11	2	0.7	50	....
L. engelmannii	1.5	11	21	....	1.4714	Trace	3	2	....	2	33	10	9	....	0.7	0.6	50
L. engelmannii	1.8	21	21	104	1.4726	....	1	1	....	2	15	8	10	....	0.7	2	60
L. engelmannii	2.1	20	21	103	1.4726	....	1	1	....	2	17	8	8	....	0.8	2	60
L. fendleri	0.5	20	21	109	1.4719	....	2	1	....	2	16	7	14	0.4	0.9	Trace	57
L. fendleri	0.5	28	22	105	1.4712	....	2	0.7	....	2	17	7	11	....	0.1	Trace	60
L. fendleri	0.4	23	21	106	1.4707	....	1	0.8	....	2	14	7	11	....	1	0.9	62
L. globosa[c]	0.8	39	24	93	1.4716	....	2	0.7	....	0.6	10	9	4	....	....	7	66
L. gordonii	0.5	29	23	95	1.4716	....	2	1	....	2	22	5	7	Trace	0.5	0.7	61
L. gordonii	0.6	36	23	98	1.4720	Trace	2	1	....	1	17	4	6	Trace	1	1	66
L. gracilis	0.7	33	24	87	1.4712	....	1	0.4	....	1	11	4	3	Trace	1	6	72
L. grandiflora	1.0	37	19	87	1.4702	Trace	2	1	0.6	2	24	7	1	....	0.6	0.9	62
L. grandiflora[d]	0.8	27	21	99	1.4698	Trace	2	2	....	4	29	8	2	....	....	2	52
L. lasiocarpa[e]	1.4	29	19	86	1.4685	Trace	2	1	1	4	28	9	2	0.4	2	3	45
L. lasiocarpa	0.5	30	22	84	1.4693	....	2	1	....	4	29	6	2	....	2	1	52
L. lescurii[f]	0.8	28	21	....	....	....	7	2	0.4	4	25	3	13	....	....	44	....
L. lindheimeri	1.4	26	21	86	1.4701	0.1	2	1	....	2	12	6	2	0.4	1	1	72
L. lindheimeri	0.9	21	....	....	1.4715	Trace	2	0.4	....	1	12	6	2	....	2	0.5	74
L. ovalifolia	1.4	24	24	....	....	....	2	0.9	....	2	14	6	11	....	0.6	1	62
L. pinetorum[g]	1.0	27	22	101	1.4711	0.1	2	2	....	0.9	19	10	8	....	0.9	Trace	57

[a] Contains 2% C_{22} monoene.
[b] Contains 1% C_{16} hydroxy monoene.
[c] Contains 1% C_{22} sat'd.
[d] Immature seed.
[e] Contains 3% C_{20} diene.
[f] Contains 2% C_{18} hydroxy monoene.
[g] Contains 0.1% C_{12} sat'd.

Tennessee. Out of approximately 50 species in the genus, about one-third are annuals. So far as is known, none of the lesquerellas has ever been cultivated.

The only hydroxylated vegetable oil available at present in rather large commercial quantities is castor oil. The industrial importance attained by this oil in numerous applications, including protective coatings, plastics, and synthetic intermediates, suggests that additional hydroxylated acids may extend the range of usefulness of this type of compound and find immediate usage in industry. For example, cleavage reactions should provide intermediates not readily available from castor oil or other sources.

The analyses of 23 samples in 14 species are presented in Table I.

Experimental

Seed samples were obtained, prepared, and analyzed as described in Parts I and V of this series (2, 3). Methyl esters for gas chromatography were prepared by methanolysis, using HCl as catalyst, in yields ranging from 91 to 97%. In addition to qualitative infrared examination of the oils, two were examined in the near infrared to indicate the positional relationship between the hydroxyl group and the double bond.

Results and Discussion

All samples of *Lesquerella* oil analyzed contain large amounts of hydroxy acids. On the basis of retention characteristics by gas chromatographic analysis, conveniently expressed as equivalent chain lengths (ECL) (4), 12 of the 14 species contain lesquerolic acid (45–74%) such as isolated from seed oil of *L. lasiocarpa* and characterized by Smith *et al.* (5). These 12 species also contain a hydroxyoctadecenoic acid in amounts ranging from a trace up to 7%.

The remaining two species, *L. densipila* and *L. lescurii,* contain approximately 50% of material indicated by the Apiezon L column to be a hydroxyoctadecenoic acid but revealed by the LAC-2-R 446 column to be two components. Absorption in the near infrared at 2.761 and 2.788 μ reveals that the hydroxyl in the oil from *L. densipila* is *beta* to a double bond like that in the hydroxyeicosenoic acid from *L. lasiocarpa* (5) and in ricinoleic acid (6). Structural studies of these two components are under way. The component present in greater amount (about 35%) has ECL different from those of ricinoleic acid but approximating those expected for a hydroxyoctadecadienoic acid; the other component (12–15%) has ECL like those of ricinoleic acid.

Oils from *L. densipila* and *L. lescurii* contain none of the C_{20} hydroxy acid common to the majority of species examined, but contain small amounts of a compound with retention characteristics like those of a hydroxyhexadecenoic acid. Oil from *L. densipila* contains small amounts of arachidic and eicosenoic acids.

Differences other than those noted with regard to hydroxy acids are minor. Oils from *L. densipila* and *L. lescurii* contain definitely more palmitic acid (6 and 7%) than oils from the other Lesquerella species (1 and 2%). *L. densipila, L. lescurii,* and both accessions of *L. grandiflora* contain oil with a small amount of an acid with ECL like hexadecadienoic acid, a component rare in vegetable oils but recently reported in oil from *Asclepias syriaca* by Chisholm and Hopkins (1).

The variation in linolenic acid content from 1 to 14% may influence the selection of species for certain uses.

Variations in oil content from 11% (possibly not fully mature) to 39% and in hydroxy acid content from 45% to 74% suggest that the development or selection of plant types suitable for present production and harvesting methods is feasible.

Acknowledgments

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REFERENCES

1. Chisholm, Mary J., and Hopkins, C. Y., Can. J. Chem., *38*, 805–812 (1960).
2. Earle, F. R., Melvin, E. H., Mason, L. H., VanEtten, C. H., Wolff, I. A., and Jones, Q., J. Am. Oil Chemists' Soc., *36*, 304–307 (1959).
3. Mikolajczak, K. L., Miwa, T. K., Earle, F. R., Wolff, I. A., and Jones, Q., J. Am. Oil Chemists' Soc., *38*, 000–000 (1961).
4. Miwa, T. K., Mikolajczak, K. L., Earle, F. R., and Wolff, I. A., Anal. Chem., *32*, 1739–1742 (1960).
5. Smith, C. R., Jr., Wilson, T. L., Miwa, T. K., Zobel, H., Lohmar, R. L., and Wolff, I. A., J. Org. Chem., *26*, 2903 (1961).
6. Personal communication from Dr. L. J. Morris, Hormel Institute, Austin, Minnesota.

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The Oxyethylation of 9, 10-Octadecanediols and 9, 10-Dihydroxystearonitrile. Nonionic Soaps[1]

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The alkali-catalyzed reaction of ethylene oxide with the *meso*- and *dl*-forms of 9,10-octadecanediol and with *threo*-9,10-dihydroxystearonitrile was carried out in an apparatus that was equipped with automatic controls for temperature and pressure.

The earlier consumption found for the *dl*-form compared to the *meso* is attributed to intramolecular hydrogen bonding. A characteristic constant for the distribution of products is calculated.

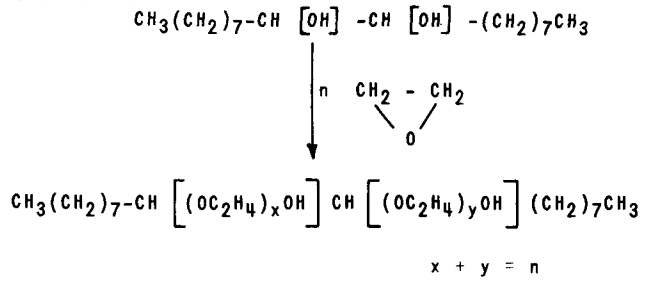
The products formed are nonionic surface-active agents with the hydrophilic portion at the middle rather than at the end of the hydrophobic chain. Properties were primarily determined by the value of n, the average number of oxyethyl groups. Optimum emulsifying properties were found at n = 4; optimum wetting at n = 12.

The oxyethylated nitriles were hydrolyzed to the corresponding "nonionic soaps," which have typical nonionic characteristics; unlike soap they are not easily precipitated by hard water or various metal ions.

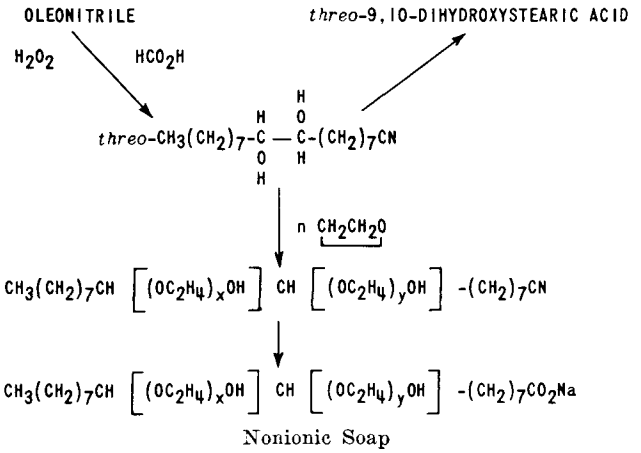
THE REACTION of ethylene oxide with mono- or dihydroxystearic acids under the usual conditions of alkaline catalysis seems to occur exclusively at the carboxyl group (1,17), and the product is a mixture of monoesters, diesters, and polyethylene glycols (6,19). This appears to be true even with the corresponding methyl esters; in each case there is practically no reaction of ethylene oxide at the secondary hydroxyl groups.

To avoid the presence of competing groups, *meso*- and *dl*-9,10-octadecanediols were used as model compounds to investigate the alkali-catalyzed reaction of ethylene oxide with fat-based secondary glycols.

The *meso*- and *dl*-9,10-octadecanediols were oxyethylated under controlled conditions (1.4 atms. pressure of ethylene oxide, 160°, 4 mole % KOH) to a selected average number, n, of oxyethyl groups (n = 4, 8, 12, 16):



threo-9,10-Dihydroxystearonitrile was oxyethylated in a similar manner (n = 4, 6, 8) and hydrolyzed to the corresponding nonionic soap:



Nonionic Soap

9,10-Octadecanediols

meso-9,10-Octadecanediol, m.p. 129.4–130.5° and *dl*-9,10-octadecanediol, m.p. 78.5–79.4°, were made from nonyloin (19). The ditosylate of the *meso*-glycol, m.p. 56.2–57.0°, was found to melt lower than the ditosylate of the *dl*-glycol, m.p. 64.6–65.6°; this is an anomalous relationship though not without parallel (14). The ditosylates were reconvertible in high yield to the original glycols by means of potassium acetate, followed by hydrolysis.

threo-9,10-Dihydroxystearonitrile

Commercial oleonitrile was redistilled; and middle fractions, b.p. 140–145°/0.05 mm., n_D^{25} 1.4564–1.4568 [reported (7) 1.4566], iodine value 96.2 (calcd. 96.3) were used for hydroxylation. Oleonitrile was treated with 98% formic acid and 30% hydrogen peroxide (12) to give the hydroxy-formate, hydrolyzed under mild conditions to *threo*-9,10-dihydroxystearonitrile, m.p. 74.7–75.7°, yield 45–50%. To prove structure a sample was hydrolyzed with 10% aqueous alcoholic

[1] Presented at the Annual Meeting, American Oil Chemists' Society, St. Louis, Mo., May 1–3, 1961.

[2] Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.