

Pählicke,³ as described in the previous article, and are summarized in Table I.

We are indebted to Dr. A. M. Lands and Miss V. L. Nash, of the Pharmacological Laboratories, for a preliminary report on the antispasmodic activity of these compounds as included in Table I. In general, the spasmolytic activity is about the same as for the corresponding esters in the 1-naphthaleneacetic acid series. One compound, β -diethylaminoethyl methyl-1-naphthaleneglycolate, was active against acetylcholine on the isolated rabbit jejunum in a dilution greater than 1:1,000,000. As in the case of the *p*-xenyl series, it was surprising to find that the esters of glycolic acids were of the same order of activity as the esters of the corresponding acetic acids.

Experimental⁴

Methyl-1-naphthaleneglycolic Acid (I).—Methylmagnesium bromide was prepared from 15.8 g. (0.65 mole) of magnesium, 61.7 g. (0.65 mole) of methyl bromide and 300 ml. of anhydrous ether. The Grignard solution was slowly added to a cold, well-stirred solution of 60 g. (0.3 mole) of 1-naphthaleneglyoxylic acid. Throughout the addition the complex remained well suspended and, when the addition was complete, it was collected on a filter and

(3) Horenstein and Pählicke, *Ber.*, **71**, 1654 (1938).

(4) All melting points reported are uncorrected.

washed thoroughly with anhydrous ether. The dry complex was slowly added to 1 liter of 3% sulfuric acid with thorough stirring and cooling. The crystals that separated were filtered off and washed with water. The yield was 55.6 g. (85.6%); m. p. 147–148° after recrystallization from water. The product gives orange to green colors with concentrated sulfuric acid.

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 72.20; H, 5.59. Found: C, 71.82; H, 5.88.

Ethyl-1-naphthaleneglycolic Acid (II).—This compound was obtained in the manner described above from 92.6 g. (0.85 mole) of ethyl bromide, 23.2 g. (0.85 mole) of magnesium in 500 ml. of ether and 80 g. (0.4 mole) of 1-naphthaleneglyoxylic acid. The yield was 72.8 g. (78.5%); m. p. 117–118°, after recrystallization from benzene.

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 73.03; H, 6.13. Found: C, 72.60; H, 6.00.

Summary

Thirteen alkamine esters of substituted 1-naphthaleneglycolic acids were prepared by the reaction of a molecular equivalent of the appropriate acid and basic alkyl chloride. The properties of these compounds are described.

All of the esters possess antispasmodic activity although it was surprising to find that they were of the same order of activity as the esters of the corresponding acetic acids.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Fatty Acids of Corn Oil

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Corn oil is a semi-drying oil noted for its high content of linoleic acid. Its principal commercial value lies in its use as a salad oil and shortening. Additional industrial uses are as a lard substitute, in the manufacture of soft soaps, and as a paint material when used along with drying oils. In the research laboratory, corn oil is a valuable source of linoleic acid which can be isolated from the mixed acids of the oil by the debromination³ and the low temperature crystallization procedures.⁴

Comparatively few investigations have been conducted on the fatty acids of this oil. Prior to its analysis by Baughman and Jamieson⁵ in 1931, the results reported were not quantitative and were very contradictory. The following acids had been noted: palmitic, stearic, arachidic, oleic, linoleic and hypogaeic. Hehner and Mitchell⁶ in 1896 reported the absence of stearic acid. Evidence for the presence of traces of linolenic acid was presented by Frankel and Brown.^{4a}

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(3) (a) Rollett, *Z. physiol. Chem.*, **62**, 410 (1909); (b) Frankel and Brown, *THIS JOURNAL*, **65**, 415 (1943).

(4) (a) Frankel and Brown, *ibid.*, **63**, 1483 (1941); (b) Frankel, Stoneburner and Brown, *ibid.*, **65**, 259 (1943).

(5) Baughman and Jamieson, *ibid.*, **48**, 2696 (1921).

(6) Hehner and Mitchell, *Analyst*, **21**, 328 (1896).

Other than Baughman and Jamieson's analysis, the only complete investigation of the oil by modern methods is that of Longenecker in 1939.⁷ These results along with those reported in the present investigation are summarized in Table I.

TABLE I
ANALYSES OF CORN OIL FATTY ACIDS

Acid	Baughman and Jamieson, wt. %	Longenecker, mole %	Our results, wt. %
Myristic	..	1.7	0.1
Palmitic	7.8	11.0	8.1
Stearic	3.6	2.9	2.5
Arachidic	0.4
Lignoceric	0.2
Hexadecenoic	..	1.6	1.2
Oleic	46.3	48.8	30.1
Linoleic	41.7	34.0	56.3
Above C_{18}	1.7

Baughman and Jamieson used the lead salt ether procedure to separate the saturated and unsaturated acids of corn oil. They based their calculations on iodine and saponification numbers and on the bromine derivatives of the unsaturated acids. Longenecker used a modified Twitchell method to separate the acids and distilled the

(7) Longenecker, *J. Biol. Chem.*, **139**, 13 (1939).

TABLE II
 FRACTION ANALYSIS OF CORN OIL ESTERS

Fraction	C Series	B. p., °C. 0.5 mm.	Weight, g.	I. no.	SCN. no.	Mol. weight	Carbon series, g.			
							C ₁₄	C ₁₆	C ₁₈	C ₂₀ etc.
1	14-16	126	2.7	10.84	11.12	267.0	0.3	2.4
2	16	126-131	3.6	5.69	2.05	271.7	...	3.6
3	16	131-135	39.4	13.36	9.67	269.0	...	39.4
4	16-18	135-144	22.0	89.28	56.52	282.9	...	10.8	11.2	..
5	18	144-146	106.3	131.90	81.96	296.0	106.3	..
6	18	146	155.8	139.27	86.88	296.4	155.8	..
7	18	146-147	148.6	141.21	88.83	297.4	148.6	..
8	18	147	113.1 ^a	137.64	88.05	294.4	113.1	..
Res.	20-24		10.7 ^a	101.13	...	359.3	10.7
Total			602.2		Total		0.3	56.2	535.0	10.7
					Weight per cent.		0.1	9.3 ^b	88.9 ^c	1.7

^a Hold-up, 3.2 g.; 1.2 g. to fract. 8 and 2.0 g. to residue. ^b From the iodine numbers, this material is 8.1% palmitate and 1.2% hexadecenoate. ^c From thiocyanometric calculations, 2.5% stearate, 30.1% oleate and 56.3% lineoleate.

methyl esters of the resulting saturated and unsaturated acids through an efficient 60-cm. fractionating column. The composition of the fatty acids was calculated from the analyses of the two series of fractions. In our work we have distilled the esters of the oil, without previous separation into saturated and unsaturated acids, through an electrically heated and glass helices packed column and have calculated the composition of the several fractions from iodine number, molecular weights, and thiocyanometric equations. The C₁₆ fraction was also studied by the low temperature crystallization procedure developed in this Laboratory. Our results differ from previous analyses mainly in finding a substantially larger content of linoleic acid, and a correspondingly lower content of oleic acid.

Experimental

An authentic specimen of corn oil, supplied to us through the courtesy of the Corn Products Company, Argo, Illinois, was converted into methyl esters by the usual procedure. The iodine number of the original oil was 127.1 and of the esters, 126.0; the molecular weight of the esters was 292.7. The esters, 602.2 g., were distilled through an efficient column into eight fractions, 3.2 g. of hold-up and 8.7 g. of residue (Table II). Fractions 2 and 3 were calculated as C₁₆ main fractions. Fraction 1 was calculated into C₁₄ and C₁₆ and fraction 4 into C₁₆ and C₁₈ components on the basis of molecular weights; the constants of these latter two components were assumed to be those of fractions 3 and 5, respectively. The hold-up was arbitrarily assigned, 1.2 g. to fraction 8 and 2.0 g. to the residue. Fractions 5-8 were calculated as stearate, oleate and lineoleate by the thiocyanometric equations of Cramer and Brown.⁸ The iodine numbers of fractions 1-3 and of the C₁₆ component of fraction 4 were used in the estimation of hexadecenoate. The results of the fractionation and of the several calculations are shown in Table II.

As noted previously, the iodine numbers of fractions 1-3 were assumed to be due to methyl hexadecenoate. It was subsequently found, however, that small amounts of linoleate had been carried over into fraction 3. The acids of this fraction (30 g.) were twice crystallized from about 700 cc. acetone at -23° to yield 26.5 g. of pure palmitic

acid (I No. 0.05; mol. wt. 255.2; m. p. 63.5-63.7°) and 3.0 g. filtrate acids; I No. 140.5. These filtrate acids were shown to contain about 50% linoleic acid on the basis of a tetrabromide number of 48.1; m. p. bromides 112.5-113.4°. This amount of linoleic acid in fraction 3 would raise the reported value in Table I for this acid about 0.3% and would lower the value for hexadecenoate about 0.5%.

With respect to the acids above C₁₈, the residue esters in Table II showed a molecular weight about equal to that for the C₂₂ series. However, we did not extract the unsaponifiable from this material, and, consequently, hesitate to report these acids (1.7%) as a mixture of C₂₀, C₂₂ and C₂₄ acids as indicated by the molecular weight. Also, the iodine number of this residue (101.1) is clearly an average of more than one double bond. The thiocyanogen number (59.7) allows a rough calculation of about 50% dienolic acids in this mixture. However, due to the possible presence of unsaponifiable in this residue, we do not rely on this thiocyanogen number or on results obtained from even approximate thiocyanometric calculations. We did not investigate this fraction further.

Thiocyanometric calculations of the original corn oil esters show them to contain the following acids: saturated, 11.5 (11.5); monoethenoic, 31.1 (32.2); linoleic (dienic) 57.4 (56.3)%. Values in parentheses were calculated from the data in Table I, assigning 0.8% and 0.9%, respectively, to the saturated and monoethenoic values in order to account for the 1.7% acids above C₁₈. We feel that these two sets of values show excellent agreement and that they further confirm the value of the thiocyanometric method.

A recent report from this Laboratory,⁹ describing the properties of the naturally occurring octadecenoic acids, included the oleic acid of corn oil which was shown to be ordinary oleic acid, with no evidence of the presence of isomers. Likewise, in previous work from this Laboratory on the linoleic acid of corn oil,⁸ no evidence was found of the presence of other isomeric octadecadienoic acids.

Summary

An authentic specimen of corn oil has been subjected to the ester fractionation procedure for determination of the composition of its fatty acids. The results have been compared with those previously reported by Baughman and Jamieson and by Longenecker. The acids of this specimen of oil were shown to contain over 56% linoleic acid.

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(8) Cramer and Brown, *J. Biol. Chem.*, **151**, 427 (1943).

(9) Millican and Brown, *ibid.*, **154**, 437 (1944).