

the melting points of the α -naphthylurethans of 2-methyl-5-*p*-hydroxyphenylhexane and of 2-methyl-4-*p*-hydroxyphenylhexane.

Unlike 2,2-dimethylbutanol-3, 2,2-dimethylpentanol-3 apparently forms a mixture of condensation products. The melting point of the α -naphthylurethan mixture is 114–115°. This is well below that of the α -naphthylurethan of 2,3-dimethyl-3-*p*-hydroxyphenylpentane² (124–125°) or of 2,3-dimethyl-2-*p*-hydroxyphenylpentane² (122–123°) but is quite near that of 2,2-dimethyl-3-*p*-hydroxyphenylpentane. This leads to the suggestion that the mixture is the result of the reaction of 2,2-dimethylpentene-3 with benzene and not of methyl migration.

Summary

1. The *s*-propyl, butyl, amyl, hexyl and nine of the *s*-heptyl alcohols were condensed with benzene in the presence of aluminum chloride.

2. The alkylbenzenes obtained in the condensations were converted to the corresponding *p*-hydroxy compounds through the *p*-nitro and *p*-amino derivatives. α -Naphthylurethans of the

p-hydroxy compounds were also prepared as well as acetamino derivatives of some of the alkylbenzenes.

3. A number of pure *s*-alkylbenzenes and *s*-alkylphenols were synthesized and their α -naphthylurethans prepared.

4. By comparison of the melting points of the acetamino derivatives of the alkylbenzenes with those in the literature and of the melting points of the phenols and of the α -naphthylurethans with those synthesized and with those of *t*-alkylphenols, the following facts have been established: (a) Isopropyl, *s*-butyl and pinacolyl alcohols gave the corresponding *s*-alkylbenzenes in pure form. (b) 2-Methylbutanol-3, 2-methylpentanol-3, 2-methylhexanol-3 and 3-methylhexanol-4 gave tert-alkylbenzenes. (c) The straight chain alcohols, those having a branched methyl group remote from the carbinol group, and 2,2-dimethylpentanol-3 gave mixtures of monoalkylbenzenes. (d) 3-Methylpentanol-2 and 3-methylhexanol-2 also gave mixtures consisting, probably, of the *s* and *t*-alkylbenzenes.

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[CONTRIBUTION FROM THE CHEMICAL DIVISION OF THE WOBURN DEGREASING COMPANY OF N. J.]

Solid 10,12-Octadecadienoic Acid-1. A New Conjugated Linoleic Acid Melting at 57°

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When linoleic and linolenic acids or their glycerides are treated with an excess of alcoholic potash for prolonged periods of time, a rearrangement of the double bonds into the conjugated position has been found to take place.¹ In the case of linolenic acid, a solid isomer, pseudoeleostearic acid, is formed, which was identified by Kass and Burr² as 10,12,14-octadecatrienoic acid-1. Linoleic acid, on the other hand, was found by Moore¹ (pp. 145, 147) to give rise "to a product which remains liquid at room temperature." On alcoholic-potash isomerization of maize oil containing linoleic but no linolenic acid, "no solid acids were formed" (ref. 1, p. 143).

Burr and collaborators, however, disclose an isomerization of linoleic acid to crystalline forms as a result of treatment with sodium butylate,³ and give absorption spectrum, diene number and

extinction coefficient for a solid 10,12-linoleic acid.⁴ They also describe a solid 10,12-linoleyl alcohol.⁵

As a result of extensive studies in this Laboratory⁶ a commercial conjugating process has been developed in which oils and fatty acids are isomerized with caustic soda in aqueous medium (patents pending). When oils containing a large proportion of linolenic acid, for instance linseed oil, are subjected to this process, the melting point or titer of their free fatty acids rises, indicating the formation of solid products. The fatty acids of oils containing little or no linolenic acid but a large proportion of linoleic acid experience a drop in titer.⁷ From this it appears that linoleic acid does not yield solid isomerization products to any appreciable extent under the conditions

(4) Miller and Burr, *Chem. Reviews*, **29**, 419 (1941).

(5) Kass and Burr, *THIS JOURNAL*, **62**, 1796 (1940).

(6) Woburn Bulletins No. 121 and 123, Woburn Degreasing Company of N. J., Harrison, N. J.

(7) Titer of linseed fatty acids: 18° before, 23.1° after isomerization; of soybean fatty acids: 22° before, 12.5° after isomerization.

(1) Moore, *Biochem. J.*, **31**, 138–154 (1938).

(2) Kass and Burr, *THIS JOURNAL*, **61**, 3294 (1939).

(3) Kass, Miller and Burr, *ibid.*, **61**, 482 (1939).

of the commercial process. In order to verify this, the fatty acids of walnut oil were freed from the bulk of their solid constituents by storing and pressing at 0–3°. When the resulting liquid fraction was isomerized, the conjugated fatty acid product was liquid at room temperature and remained liquid on renewed cold storage at 0–3°.

In contrast herewith, it was found that a sample of dehydrated castor oil ("isoline"), the fatty acids of which remain liquid at 3°, produces a fatty acid mixture upon isomerization which sets to a semi-solid mass at 3°, and from which a considerable quantity of a solid acid separates even at room temperatures. The fatty acids of dehydrated castor oil have previously been found to contain 26% or less of 9,11-linoleic acid, the remainder being largely non-conjugated, *i. e.*, 9,12-linoleic acid.⁸

The diene value of dehydrated castor oil increases considerably during the caustic treatment, and the solid fatty acid formed, m. p. 57°, methyl ester m. p. 25°, is conjugated as shown by its analysis. It is found to be not identical with Mangold's⁹ solid 9,11-linoleic acid. Another solid conjugated linoleic acid, m. p. 56°, which was obtained by Smit¹⁰ by the debromination of tetrabromostearic acid, m. p. 124° and believed to be also a 9,11-isomer, was not available; but no bromide melting at 124° was formed by the new acid.

Oxidation with permanganate, both in alkaline and neutral solution, served to characterize the new acid as 10,12-octadecadienoic acid-1 and it may, therefore, be concluded that it resulted from the isomerization of the 9,12-linoleic acid present in dehydrated castor oil. Since other oils containing 9,12-linoleic acid, such as soybean or walnut, do not yield a solid fatty acid under similar treatment, it may be further concluded that the linoleic acid present in dehydrated castor oil, or at least a portion of it, is not identical with ordinary linoleic acid but a stereoisomer thereof.

Only one of the four theoretically possible 10,12-linoleic acids has in the past been identified. It was found by Böeseken and collaborators^{11,12} in

(8) Priest and von Mikusch, *Ind. Eng. Chem.*, **32**, 1314 (1940); Priest and von Mikusch, Chapter on dehydrated castor oil in "Protective and Decorative Coatings, etc.," J. J. Mattiello, Editor, 1st ed. vol. 1, page 128, John Wiley and Sons, New York, N. Y., 1941.

(9) Mangold, *Monatsh.*, **15**, 309 (1894).

(10) Smit, *Rec. trav. chim.*, **49**, 539 (1930).

(11) Böeseken, Smit, Hoogland and van der Broek, *ibid.*, **46**, 623 (1927).

(12) Böeseken and van Krimpen, *Koninkl. Akad. Wetensch. Amsterdam, wisk. natk. Afz.*, **37**, 66–8; *Chem. Zentr.*, **99**, 1, 2704 (1928); Böeseken, van Krimpen and Blanken, *Rec. trav. chim.*, **49**, 247 (1930).

the products of partial hydrogenation of both alpha- and beta-eleostearic acids and their esters and had a melting point of 28.5°. The melting point of the 10,12-linoleic acid referred to by Burr, *et al.*,^{2–5} has not been reported.

Experimental

The fatty acid product obtained from the commercial isomerization of dehydrated castor oil ("isoline") with caustic soda in an aqueous medium was refrigerated at 3° for forty-eight hours. Repeated filtration and pressing on a suction funnel yielded a dry cake weighing more than 20% of the original total fatty acids.

Two recrystallizations from petroleum ether gave snow-white crystals, m. p. 55–56°, which, with Wijs solution, showed the color of free iodine characteristic for conjugated double bonds,¹³ Wijs I. V., 130; diene value, –88.5 (Ellis-Jones).

Two recrystallizations of the purified product from ether, in which it is less soluble at low temperatures than stearic acid, and two from 95% alcohol yielded crystals melting at 56.3–57.7° (cor.), which became tacky when left exposed to air, showing sensitivity to oxidation. The final crop formed a clear solution in a little warm petroleum ether but, in ample excess, this solvent precipitated a white cloud indicating the presence of oxidized fatty acids. The dilute solution was, therefore, filtered with charcoal and cold stored. Before each of the following determinations, a sample of the resulting acid suspension in petroleum ether was removed, filtered, and dried under carbon dioxide; properties, melting point 55.7–57.5° (cor.); partial iodine value (modified Wijs, 2 min. on ice)¹⁴ 89.91, 89.80 (calcd. 90.52); total iodine value (Woburn Method, 0.32 *N* iodine bromide solution, 1 hr., 20°)¹⁵ 186.7 (calcd. 181.0); acid value 199.6 (calcd., 200.06); from this: mol. wt. 281.1 (calcd. 280.436); refractive index, n_D^{20} 1.4689; n_D^{70} 1.4656¹⁶; density by pycnometer, d_4^{20} , 0.86857; molar refraction (Lorenz-Lorentz) 89.36,¹⁶ calcd. (acc. to Eisenlohr) 85.93, exaltation, +3.43.¹⁷

The white lead soap, precipitated quantitatively from the hot aqueous potassium soap solution, was practically insoluble in cold benzene (6°), but 100 ml. of boiling benzene dissolved approximately 3 g. After one crystalliza-

(13) Böeseken and Gelber, *ibid.*, **46**, 162 (1927).

(14) von Mikusch, *Oil and Soap*, **15**, 186 (1938).

(15) von Mikusch and Frazier, *Ind. Eng. Chem., Anal. Ed.*, **13**, 782 (1941). Data on the determination of total and partial iodine values and diene values, by difference of the two, are being prepared for publication by von Mikusch and Frazier.

(16) The author is indebted to H. E. Riley for determining the refractive indices listed, and suggesting improvements in the preparation of the manuscript. Mr. Riley also points out in a private communication that the specific refraction of the new acid is 0.31853, compared to a value of 0.31772 for 9,11-linoleic acid calculated from the data cited by Smit and Böeseken.

(17) Böeseken, *et al.*,¹¹ report a molar refraction of 88.9 for 9,11-linoleic acid, m. p. 52.2°, but from this value incorrectly derive an exaltation of +3.4, although Smit (ref. 10, p. 545) correctly states the calculated molar refraction to be 85.9, showing an exaltation of +3.0. If the values for n_D^{20} 1.4624 and sp. gr. at 77° 0.8659 as reported identically by Böeseken, *et al.*, and Smit¹⁰ are used together with the calculated molecular weight for octadecadienoic acid using 1941 atomic weights, m. wt. 280.4, a molar refraction of 89.1 results giving an exaltation of +3.2. This is seen to be close to the present value for the 10,12-isomer.

tion from boiling benzene, the lead soap melted indistinctly at 115°.

Mangold's acid was prepared in the usual manner by the dry distillation of ricinelaic acid.^{9,11} The yield after one recrystallization from 95% alcohol was 17.4%, m. p. 52°. A mixture of this with the new acid melted at 48 to 51°, or lower than either acid alone.

Methyl Ester.—Twenty-four grams of a sample of the new acid which had been recrystallized only once from petroleum ether was refluxed with twice its weight of anhydrous methyl alcohol for three and one-half hours while passing hydrogen chloride gas into the solution. Recrystallization of the product from methyl alcohol gave 12.2 g. of white scales melting at 25°; the remaining brown oil was not further investigated; (9,11-linoleic methyl ester, m. p. 29.8°, according to Böeseken, *et al.*¹¹). The bulk of the dried scales distilled at 207–208° (uncor.) at 9 mm. The distillate solidified sharply at 23–23.5°; total iodine value (Woburn, 1 hr. 20°)¹⁵ 173.4; 173.4 (calcd. 172.4); partial iodine value (mod. Wijs, 2 min., ice)¹⁴ 86.6; 86.1 (calcd. 86.2); Woburn diene value (by diff.) compare¹⁸ 87.0 (calcd. 86.2).

Bromination of the new acid in cold petroleum ether with one mole of bromine and storing of the solution at 3° for forty-eight hours did not lead to solid products. After adding a second mole of bromine and allowing to stand in diffuse daylight at room temperature for two days, the color of free bromine had disappeared and a white solid had settled out, m. p. 104–113°. Extensive fractional crystallizations from 95% alcohol resulted in two portions, melting at 149.5–150.5° and 104–105° (cor.), respectively; acid values 95.8 and 94.7 resp. (calcd. 93.5 for tetrabromide).

Mild oxidation with alkaline potassium permanganate of 15 g. of the once recrystallized acid yielded a cake of hydroxy acids from which 0.1 g. of soluble substance was extracted with petroleum ether. Extraction of the remaining cake with warm ether yielded 4.8 g. of a viscous, almost water-white liquid which did not solidify after several days at 3°; acid value 178.6 (calcd. for dihydroxystearic acid, 178.4).

The remaining hydroxy acids were extracted successively with hot chloroform and boiling alcohol. These extracts on cooling yielded 0.3 and 0.9 g., respectively, of white precipitates, identical although of different purity, melting at 177–182° and 186–189°, recrystallized, 187–188.5° (cor.); acid value 159.9 and 156.6 (calcd. for tetrahydroxy stearic acid 161.0).

Ether extraction of the aqueous solution remaining after the separation of the hydroxy acids yielded 2.5 g. of an oil which on extraction with boiling water yielded

crystals, melting after one recrystallization at 127–129.5°. They showed no depression with sebacic acid; acid value 580 (calcd. for sebacic acid 554.8). Other oxidation products, in evidence, were not further investigated.

Destructive Oxidation of Methyl Ester.—Following in general the procedure of Armstrong and Hilditch,¹⁸ 8 g. of the recrystallized and distilled methyl ester was oxidized with 75 g. of powdered potassium permanganate in 250 ml. of boiling acetone. The ether-soluble oxidation products were dry-distilled at atmospheric pressure. When the distillate, which had the odor of caproic acid, was redistilled, the two main fractions collected passed over at 193–201° and 201–205.5°, respectively, and had equivalent weights by titration of 106.1 and 110.3 (caproic acid, mol. wt., 116.2; b. p. 202°).

The residue was boiled with alcoholic potassium hydroxide, acidified with dilute sulfuric acid, and the acidified solution extracted three times with ether. After evaporation, a white solid, contaminated with a yellow oil, remained. The solid was soluble in boiling water, which on cooling yielded 1.4 g. of white crystals, m. p. after four recrystallizations from boiling water 130.5–132.5°, acid value 542, which gave no depression with genuine sebacic acid.

Summary

A new solid conjugated isomer of linoleic acid, melting at 57°, was isolated from the isomerization products obtained from dehydrated castor oil in a commercial conjugating process using aqueous alkali. It is identified as 10,12-octadecadienoic acid-1 by its oxidation products.

The exaltation of the new acid compares with that of 9,11-octadecadienoic acid-1, which has been recalculated from data listed in the literature.

Properties of the acid and some of its derivatives are given.

Since other oils containing linoleic acid do not yield the new solid isomer upon identical treatment, it is concluded that it is formed from a stereoisomer of 9,12-linoleic acid in dehydrated castor oil which is not identical with ordinary linoleic acid.

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(18) Armstrong and Hilditch, *J. Soc. Chim. Ind.*, **44**, 43T (1925)