It seems to us probable that the compound here described is identical with a substance prepared by Heller[12] from the condensation of a keto acid obtained from phthalic anhydride and β-chloronaphthalene. Heller regarded his product as 2′-chloro-2,3-benzanthraquinone because it yielded an anthraquinone-dicarboxylic acid on oxidation. The oxidation product was analyzed, but not identified, and from the description given it might be either the 1,2- or the 2,3-isomer. His chloro compound, however, gave the vat test, which is good evidence that it was a derivative of 1,2-benzanthraquinone. His compound melted at the same temperature as ours (233–234°), hence, considering the structure of his starting material, it is probable that the two compounds are identical.[13]

Summary

Phthaloylnaphthol and a number of methylated derivatives of phthaloylnaphthalene rearrange readily under the influence of sulfuric acid to give 1,2-benzanthraquinones. The structures of the resulting compounds were established by preparing the quinones in a different way, and in the course of this work a careful study was made of the Friedel and Crafts reaction of phthalic anhydride with the methylated naphthalenes. Though the chief product is formed by substitution in an α-position ortho or para to an alkyl group, some reaction occurs at α-positions not so activated, and in one case at an unreactive β-position. The last two types of keto acids yield 1,2-benzanthraquinones on treatment with sulfuric acid, whereas all of the acids react under the influence of aluminum chloride to give mixtures which often contain both benzanthraquinones and phthaloylnaphthalenes. The reaction in some cases involves not only a wandering of the ketonic group, as pointed out in an earlier paper, but a methyl migration.

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[12] Heller, *Ber.*, **45**, 665 (1912); **46**, 1497 (1913).

[13] Compare Scholl and Neuberger, *Monatsh.*, **33**, 511 (1912).

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Lycopodiumoleic Acid[1]

BY J. L. RIEBSOMER AND JOHN R. JOHNSON

In an investigation of the spores of *Lycopodium clavatum* Langer[2] reported the presence of approximately 50% of a fatty oil, which he found to consist largely (80–87%) of the glyceride of an acid of the oleic series, $C_{16}H_{30}O_2$. This acid he named lycopodiumoleic acid and from his chemical studies formulated it as α-decyl-β-isopropylacrylic acid (I). In a contemporaneous paper, Bukowski[3] reported the glyceride of oleic acid as the main component (80%) of lycopodium oil and, in addition to small amounts

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[1] This paper is abstracted from a thesis submitted by J. L. Riebsomer to the Graduate Faculty of Cornell University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1932.

[2] Langer, *Arch. pharm.*, **227**, 241, 289, 625 (1889).

[3] Bukowski, Dissertation, Warsaw; *cf. Chem. Z.*, **13**, 174 (1889).

of palmitic and stearic acids, a quantity of 2% of a dihydroxystearic acid, m. p. 90–92°. Subsequently, Rathje[4] reported the presence of 81% of a sixteen carbon atom acid, $C_{16}H_{30}O_2$, in essential agreement with the finding of Langer, and observed the presence of a dihydroxystearic acid melting at 140–141°. The uncertainty of these statements concerning the acids from lycopodium oil and the doubtful validity of the structural formula assigned to lycopodiumoleic acid, led us to undertake this investigation.

Separation of the lead salts of the fatty acids by the method of Farnsteiner[5] showed the presence of a large proportion of unsaturated acids (*ca.* 80% of the original oil, or 90% of the total acids) in essential agreement with the statements of earlier workers. Fractional distillation of the methyl esters demonstrated the presence of two principal unsaturated acids, which were shown by ozonolysis to be 9,10-palmitoleic acid (II) and ordinary oleic acid. The unsaturated acids were estimated to contain approximately 35% of palmitoleic acid and 60% of oleic acid. In addition to a small quantity of linoleic acid (identified as the tetrabromide) there is present, in traces, at least one other unsaturated acid. This acid was detected in the oleic acid fraction by the identification of 1,9-nonanedicarboxylic acid as a product of ozonolysis. The latter might have arisen from an isomer of oleic acid (III) or from cetoleic acid (IV). Since palmitoleic and cetoleic acids are frequently associated in animal oils,[6] it is not improbable that the latter acid may be present in this oil although the other product of ozonolysis (undecanoic acid) was not detected.

$$(CH_3)_2CH—CH{=}C(n\text{-}C_{10}H_{21})—CO_2H \qquad \textbf{(I)}$$

$$CH_3—(CH_2)_5—CH{=}CH—(CH_2)_7—CO_2H \qquad (II)$$

$$CH_3—(CH_2)_5—CH{=}CH—(CH_2)_9—CO_2H \qquad (III)$$

$$CH_3—(CH_2)_9—CH{=}CH—(CH_2)_9—CO_2H \qquad (IV)$$

The less soluble lead salts contained mainly palmitic acid, with traces of high molecular weight saturated acids. Inconclusive evidence was obtained for the presence of erucic acid in small amounts. A dihydroxystearic acid (m. p. 93–93.5°) was isolated and identified as 9,10-dihydroxystearic acid, by oxidation to 9,10-diketostearic acid.

Experimental

Extraction of the Oil.—Commercial lycopodium powder[7] was ground intimately with an equal weight of fine sand. This procedure is necessary to rupture the outer protective coating of the spores and to allow permeation by the solvent. The ground mixture was extracted with chloroform in a continuous extraction apparatus for thirty-six to forty-eight hours. After removal of the solvent (completed by heating on a steam-bath under reduced pressure) there remained a fluid oil, slightly green in color.

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(4) Rathje, *Arch. pharm.*, **246**, 692 (1908).

(5) Farnsteiner, *Z. Untersuch. Nahr. Genussm.*, **2**, 1 (1899).

(6) Toyama, *J. Soc. Chem. Ind. Japan*, **30**, 597, 603 (1927); *Chem. Abstracts*, **23**, 575 (1928).

(7) This material was purchased from the Fuller–Morrison Co., Chicago.

Small scale extraction gave a yield of 46–47% of oil; in large scale extractions the yield fell to 35–37%.

Upon standing for a short while a small quantity of solid matter settled out. This was separated by centrifuging and the clear oil was decanted. The following constants were determined: d_4^{20} 0.9286, n_D^{20} 1.4730; iodine number (Hanus) 90.9; saponification equivalent 288.

Separation of the Unsaturated Acids.—The fatty oil was saponified in alcoholic solution with potassium hydroxide, and the fatty acids were converted to the lead salts by treatment of the faintly acid solution with aqueous lead acetate. The lead salts were separated according to the general procedure of Farnsteiner.[5] The dry lead salts from each 100-g. sample of the oil were divided into four equal portions, and each portion was treated with 1250 cc. of boiling benzene. A small quantity of lead salts remained undissolved and this was removed by rapid filtration of the hot solution. After washing with hot benzene this material was set aside (Lead Salts "A"). The filtrate was allowed to cool slowly to room temperature and was then cooled at 8–10° for two hours. The precipitated lead salts were filtered rapidly with suction, redissolved in 675 cc. of hot benzene, and allowed to crystallize as before. This process was repeated once more, using 675 cc. of benzene, and the final precipitate was set aside (Lead Salts "B").

The combined filtrates containing the lead salts of the unsaturated acids were shaken with an equal volume of 10–12% hydrochloric acid. After washing the benzene solution of the free acids with water, the solvent was removed. The last traces of benzene were eliminated by warming under reduced pressure in a stream of hydrogen. From 300 g. of the oil there was obtained 230 g. (77%) of unsaturated acids, mean mol. wt. 283, iodine number (Hanus) 97. Rathje reported the presence of 81% of a liquid unsaturated acid having an iodine number of 98.7. For further examination the unsaturated acids were converted to the methyl esters by warming with absolute methyl alcohol in the presence of 5% of concd. sulfuric acid. From 440 g. of acids there was obtained 394 g. of methyl esters; b. p. 140–185° at 4 mm., iodine number 93.5. Since this material was obviously a mixture of esters, a large sample was fractionated twice, under a pressure of 3 mm., through an efficient electrically heated column. From 187 g. of the esters, the following fractions were obtained: I, 148–156°, 3 g.; II, 156–159°, 44.5 g.; III, 159–176°, 23 g.; IV, 176–179°, 75 g.; V, 179–181°, 10.5 g.; residue, 15 g. From these data it was concluded that the esters comprised mainly two individuals, fractions II and IV. Fraction I was apparently methyl myristate, arising from the solubility of lead myristate in benzene; Langer and Rathje have reported the isolation of small quantities of myristic acid from this oil. Fraction III was obviously an intermediate fraction containing II and IV. Fraction V was very likely essentially the same as fraction IV. Further investigation (by ozonolysis) was restricted to fractions II and IV.

Ozonolysis of the Methyl Esters. (a) Fraction II.—A solution of 44.5 g. of the esters in 100% acetic acid was treated with ozonized oxygen from a generator of the type described by Henne.[8] When ozonation was complete the solution was treated with 40 g. of 30% hydrogen peroxide and refluxed gently until a negative test for hydrogen peroxide was obtained with starch–iodide paper (15–20 hours). The water present was removed by distillation with benzene, and the latter was eliminated by direct distillation at atmospheric pressure. The acetic acid was removed practically completely, by distillation under reduced pressure (35 mm.) until the temperature of the bath attained 100°. The residue was esterified with methyl alcohol in the usual manner and the resulting esters were fractionated under reduced pressure.

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[8] Henne, THIS JOURNAL, **51**, 2676 (1929).

Fraction	B. p., °C.	Pressure, mm.	Weight, g.	Components (see below)
II A	60–65	15	12.0	Methyl heptoate
II B	65–127	3	3.7	(Intermediate)
II C	127–131	3	15.6	Methyl azelate
II D	131–133	3	3.0	(Intermediate)
II E	125–145	1.5	5.0	(Intermediate)
II F	145–170	1.5	3.4	Methyl palmitate
II X	Residue		2.0	
Total recovery of methyl esters			44.7	

Fraction II A.—The refractive index and density of this fraction were compared with those of authentic methyl heptoate: d_4^{20} 0.876, n_D^{20} 1.4120; methyl heptoate, d_4^{20} 0.880, n_D^{20} 1.4114. The ester was hydrolyzed and the resulting acid was identified as *n*-heptoic acid: b. p. 116–118° at 15 mm., neut. equiv., 129.7 (calcd. 130.1); anilide, m. p. 62.5–63°, mixed m. p. with known *n*-heptanilide (m. p. 62.5–63°), 62.5–63°.

Fraction II C.—The refractive index and density of this fraction were compared with those of authentic dimethyl azelate: d_4^{20} 1.008, n_D^{20} 1.4350; dimethyl azelate, d_4^{20} 1.005, n_D^{20} 1.436. The ester was hydrolyzed and the resulting acid was identified as azelaic acid: neut. equiv. 94.5 (calcd. 94.1), m. p. 106.5° (unchanged by admixture with known azelaic acid, m. p. 106.5°).

Fraction II F.—The ester was hydrolyzed and the acid was recrystallized from acetone; m. p. 62°. A mixed melting point with known palmitic acid (m. p. 62°) showed no depression. The occurrence of a small quantity of palmitic acid in this fraction arises from the solubility of lead palmitate in benzene. Palmitic acid has previously been reported by Bukowski[3] and Rathje.[4]

The occurrence of *n*-heptoic and azelaic acids as products of ozonolysis establishes the constitution of the original unsaturated acid as 9,10-hexadecenoic acid (9,10-palmitoleic acid).

(b) **Fraction IV.**—Forty grams of this fraction was subjected to ozonolysis according to the procedure described above, and the methyl esters of the oxidation products were fractionated under reduced pressure.

Fraction	B. p., °C.	Pressure, mm.	Weight, g.	Components (see below)
IV A	55–95	15–16	5.9	Methyl heptoate (+ caproate?)
IV B	95–98.5	15–16	4.7	Methyl pelargonate
IV C	102–125	3	6.0	(Intermediate)
IV D	126–130	3	7.6	Methyl azelate
IV E	131–141	3	6.0	(Intermediate)
IV F	141–142	3	0.5	Methyl nonane-1,9-dicarboxylate
IV G	175–185	3	4.0	(Unreacted original ester)
IV X	Residue		4.5	
Total recovery of methyl esters			39.2 g.	

Fraction IV A.—This fraction was found to contain methyl heptoate and a small quantity of a lower-boiling ester. After refractionation 1.4 g. of the latter was obtained; b. p. 55–58° (15 mm.). This material was obviously a mixture for it distilled at 155–165° under 745 mm. Since methyl caproate boils at 150°, and methyl heptoate at 173°, it was inferred that these two esters were present. The corresponding fraction (from a quantity of 214 g. of unsaturated acids) from another ozonolysis, was hydrolyzed and the acids were carefully dried and fractionated. The neutralization equivalent of the most volatile fraction (1 g.) was 118 (calcd. for caproic acid, 116). The quantity of the lower-boiling material was not sufficient for further fractionation and identification. It is possible that caproic acid may have arisen from ozonolysis of traces of an hydroxylated acid containing the system $n\text{-}C_5H_{11}—CHOH—CH{=}CH—R$ or $n\text{-}C_5H_{11}—CHOH—CH_2—CH{=}CH—R$.

Fraction IV B.—This fraction was identified as methyl pelargonate; n^{20}_{D} 1.4315 (reported n^{20}_{D} 1.433). The ester was hydrolyzed and the resulting acid was examined: b. p. 108–110° at 2 mm., d^{20}_{4} 0.904, neut. equiv., 157 (calcd. 158.1); anilide, m. p. 57°, mixed m. p. with known *n*-nonoic anilide (m. p. 57°), 57°.

Fraction IV D.—This ester was hydrolyzed and gave azelaic acid, m. p. 106–106.5°; mixed m. p. with pure azelaic acid (m. p. 106–106.5°) showed no depression.

Fraction IV F.—Hydrolysis of this fraction gave a solid acid, which was crystallized once from benzene and once from ethyl acetate; m. p. 107–109°. A mixed m. p. with azelaic acid (m. p. 106.5°) showed a marked depression. A larger specimen of this acid (from 214 g. of unsaturated acids) after exhaustive purification melted at 110–110.5°, and further purification did not raise the melting point; neut. equiv., 108.4 (calcd. for $COOH—(CH_2)_9—COOH$, 108.1). Since these data suggested nonane-1,9-dicarboxylic acid, an authentic specimen of the latter was prepared synthetically by the method of Chuit.[9] The synthetic specimen melted at 109–110°, and a mixed melting point with the unknown acid was 109.5–110°. The occurrence of heptoic and nonane-1,9-dicarboxylic acids in practically equivalent quantities in the products of ozonolysis of fraction IV suggests the presence of a small quantity of an isomeric oleic acid (11,12-octadecenoic acid), $CH_3—(CH_2)_5—CH{=}CH—(CH_2)_9—COOH$, in this fraction. On the other hand, since heptoic acid may be expected from traces of palmitoleic and linoleic acids, it is possible that this acid arose from the presence of a small quantity of cetoleic acid ($CH_3—(CH_2)_9—CH{=}CH—(CH_2)_9—COOH$), and the other fragment of ozonolysis (undecylic acid) escaped detection. We are not inclined to reject the latter suggestion merely because of the observation that cetoleic acid has thus far only been isolated from marine animal oils.[6]

Detection of Linoleic Acid.—A sample of the unsaturated acids dissolved in petroleum ether, on treatment with bromine at −5°, gave a small quantity of an insoluble tetrabromide. The latter after recrystallization from petroleum ether melted at 112.5–113.5° (linoleic tetrabromide, m. p. 113–114°). From 2.80 g. of the unsaturated acids there was obtained 0.053 g. of recrystallized bromide, corresponding to 0.88% of linoleic acid. Since this is not a quantitative method, it is likely that a somewhat larger quantity of linoleic acid was actually present in the unsaturated acids.

Saturated Acids.—The lead salts of the saturated acids (Lead Salts, "B") were heated with aqueous hydrochloric acid in the presence of benzene, and the acids were isolated in the usual way. The crude saturated acids amounted to 5–6% of the weight of the original oil. Without further purification the acids showed a mean molecular weight of 283 and an iodine number of 52. To identify the unsaturated material, 25 g. of the acids was esterified with methyl alcohol and the esters were subjected to ozonolysis. After ozonolysis and repeated esterification, the methyl esters were fractionated under reduced pressure. The small quantities of material available did not permit a positive identification of the fragments of ozonation (pelargonic and brassylic acids), but suggested the presence of a small quantity of erucic acid. The specimen of dibasic acid obtained melted at 105–106°; mixed m. p. with azelaic acid (m. p. 106–106.5°), 89–94°, mixed m. p. with brassylic acid (m. p. 108–110°), 106–107°. The principal saturated acid in this fraction was proved to be palmitic acid, m. p. 62°. The higher-boiling methyl esters gave an acid fraction melting at 69–70°, which was not stearic acid. A mixed melting point with known stearic acid (m. p. 69–70°) was 63–65°. The quantity of this acid was too small for further work.

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[9] Chuit, *Helv. Chim. Acta*, **9**, 264 (1926).

Dihydroxystearic Acids.—The lead salts insoluble in hot benzene (Lead Salts, "A") were converted to the free acids in the usual way. From 400 g. of the original oil there resulted 9.3 g. (2.4%) of the crude brownish acids, not quite entirely soluble in hot ether. After repeated crystallizations from ether there was obtained 2.7 g. of a white solid, m. p. 93–93.5°. Further crystallizations from ether or benzene did not change the melting point; neut. equiv., 316.8 (calcd. for a dihydroxystearic acid, 316.3). To avoid complications arising from stereoisomerism of the dihydroxystearic acids, a specimen was oxidized to the corresponding diketostearic acid. From 0.4 g. of the unknown acid there was obtained by oxidation with chromic acid, a pale yellow crystalline diketostearic acid, m. p. 83–84°. A mixed m. p. of this acid with an authentic specimen of 9,10-diketostearic acid, m. p. 83–84° (prepared by a similar oxidation of known 9,10-dihydroxystearic acid, from oleic acid), showed no depression. From these data the acid melting at 93–93.5° is shown to be a mixture of stereoisomeric 9,10-dihydroxystearic acids.

An examination of the mother liquors from the dihydroxystearic acids led to the separation of a small fraction (1.3 g.) which was insoluble in cold petroleum ether. Crystallization from acetone gave four fractions: (a) m. p. 77–80°, (b) 72–75°, (c) 62–74°, (d) 62–72°. The highest fractions may be a mixture of higher saturated fatty acids (C_{20}–C_{24}). The portion which was soluble in cold petroleum ether (5 g.) was deeply colored; attempts to obtain definite information concerning its composition were unsuccessful.

Summary

The fatty acids of lycopodium oil have been found to consist mainly of oleic acid (*ca.* 55–60%) and 9,10-palmitoleic acid (*ca.* 30–35%). The lycopodiumoleic acid of Langer was apparently a mixture of these acids. Palmitic, linoleic and 9,10-dihydroxystearic acids were also identified.

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Thermal Decomposition of Dibutylmercury

BY F. E. FREY AND H. J. HEPP

In 1929 Paneth and Hofeditz[1] reported that the vapors of lead tetramethyl, passed rapidly through a heated tube, acquired the property of removing a lead mirror. The activity was thought to be due to the presence of free methyl radicals. In other investigations[2,3,4,5] additional evidence has been obtained that these active molecules are free alkyl radicals. Rice has proposed a detailed mechanism[6] for the decomposition of paraffins through the intermediate formation of free alkyl radicals. The removal from the paraffin molecule of any one of the hydrogen atoms is

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(1) Paneth and Hofeditz, *Ber.*, **62**, 1335 (1929).

(2) Paneth and Lautsch, *ibid.*, **64**, 2702 (1931).

(3) Simons, McNamee and Hurd, *J. Phys. Chem.*, **36**, 939 (1932).

(4) Rice, Johnston and Evering, THIS JOURNAL, **54**, 3529 (1932). A bibliography of previous work in this field is given.

(5) Meinert, *ibid.*, **55**, 979 (1933).

(6) Rice, *ibid.*, **53**, 1959 (1931).