4. As a result of these determinations it has been established that in menhaden oil the highest unsaturation to be expected in the C_{14} series is 2 double bonds, in the C_{16} series, 3 double bonds, in the C_{18}, 4, in the C_{20}, 5 and in the C_{22}, 6.

5. In natural products, acids of higher unsaturation than indicated above are not likely to be found.

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[CONTRIBUTION FROM THE LABORATORY OF FOODS AND SANITATION, UNIVERSITY OF WISCONSIN]

MONACETIN[1]

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An attempt at experimental verification of the statement[2] that a water-soluble mixture of monacetin and diacetin is obtained when glycerol is esterified in the presence of sulfuric acid and sodium acetate has resulted in the development of a modification of that method to the end that the stage of esterification is confined to the formation of monacetin. Previously published statements on the preparation of the acetins are contradictory,[3-10] but Geitel[11] claims to have isolated all three of them, by means of solvent extraction and fractional distillation, from a reaction mixture which contained only glycerol and acetic acid, and Guédras[12] is reported to have obtained monacetin with the aid of casein as catalyst. By the substitution of phosphoric acid or its anhydride for sulfuric acid, we have been able to prepare in one operation practically pure monacetin, the experimental development of which is here outlined.

Experimental Part

Esterification in the Presence of Sulfuric Acid.—A mixture consisting of 180 g. of glycerol, 1080 g. of glacial acetic acid and 1.8 g. of sulfuric acid (66° Bé.) was heated for one and a half hours at 110°. About 10

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[1] This paper was constructed from a thesis submitted by Peter P. T. Sah to the Faculty of the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Master of Science, August 8, 1924.

[2] G. J. Esselen, Jr., U. S. Pat. 1,378,099, June 5, 1921.

[3] Berthelot, *Ann.*, **88**, 310 (1853).

[4] Würtz, *Ann.*, **102**, 339 (1857).

[5] Hübner and Müller, *Z. Chem.*, [II] **6**, 343 (1870); *Chem. Zentr.*, **41**, 450 (1870).

[6] Schmidt, *Ann.*, **200**, 99 (1879).

[7] Markownikoff, *Ber.*, **13**, 1842 (1880).

[8] Kabloukoff, *Bull. soc. chim.*, [II] **34**, 347 (1880).

[9] Böttinger, *Ann.*, **263**, 359 (1891).

[10] Seelig, *Ber.*, **24**, 3466 (1891).

[11] Geitel, *J. prakt. Chem.*, **163**, 417 (1897).

[12] Guédras, *Chem.-Ztg.*, **29**, 523 (1905).

g. of crystallized sodium acetate was then added to the mixture, which was allowed to stand for an hour with occasional agitation, and then filtered. The filtrate was concentrated by distillation until a boiling point of 125° was indicated. From this point it was distilled under a reduced pressure of 40 mm., the fraction boiling between 155° and 185° being redistilled and then filtered through decolorizing carbon; b. p., 175–177° (corr.) (40 mm.).

The product, which was colorless, practically odorless and of a characteristic taste, was soluble in water, ether, benzene, chloroform and carbon tetrachloride. It consisted in the main of diacetin, containing as impurities the mono and tri esters; ester no., 657; calcd. for diacetin, 637.

Esterification in the Presence of Zinc Chloride.—The conditions outlined above were duplicated except that zinc chloride was substituted for the sulfuric acid. The absence of any free acid made unnecessary the addition of sodium acetate, nor was there any need for filtration.

The product was soluble in water, ether and chloroform but isoluble in benzene and in carbon tetrachloride. It was a mixture of mono- and diacetin in almost equal amounts; ester no., 534.

Esterification in the Presence of Phosphoric Acid or Phosphorus Pentoxide.—Preliminary trials, in which phosphoric rather than sulfuric acid served as catalyst, indicated that the reaction could be controlled toward the direction of forming only monacetin. It is immaterial whether one uses the anhydride or the acid itself, although the stronger dehydrating property of the pentoxide recommends its use.

A mixture consisting of 500 g. of glycerol, 300 g. of glacial acetic acid and 2 g. of phosphorus pentoxide was refluxed at 170° for two hours. This operation was followed by the addition of 10 g. of sodium acetate, the removal by filtration of the sodium phosphate and the concentration of the filtrate by vacuum distillation. The fraction boiling at 150–200° was redistilled at the same pressure, 60 mm., that portion coming over at 189–191° (corr.) being collected. After filtration through decolorizing carbon, it was distilled again. The product was insoluble in ether and in benzene.

The following constants were noted: d_4^{25}, 1.19846; n_{25}, 1.4481; b. p., 189–191° (60 mm.); ester no., 418; calcd. for monacetin, 418.3.

Conversion of Diacetin and Triacetin into Monacetin.—It is stated[13] that triacetin can be transformed into monacetin by heating it with an equal volume of glycerol at 200°. This reaction does not yield the mono ester exclusively because some diacetin is also formed. It has been found that by the use of phosphoric acid as catalyst the reaction is controlled to the extent that no diacetin is formed.

One hundred cc. of the ether-soluble product obtained from the sulfuric

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[13] Knoll and Co., Ger. pat. 122,145, Nov. 17, 1900.

acid esterification procedure (mostly diacetin) was treated with 110 cc. of glycerol and 5 cc. of phosphoric acid. The technique of the preceding experiment was followed with the result that a practically quantitative yield of monacetin was obtained.

Repetition of the experiment in which triacetin, made by the interaction of glycerol and an excess of acetic anhydride, was heated with twice its volume of glycerol under the conditions outlined above led to the same results.

Conclusions

Esterification of glycerol proceeds in three stages, but a mixture of acetins containing representatives of each type of ester is obtained when the reaction is uncontrolled in so far as a catalyst is concerned. Under definite weight relationships as to reactants, the presence of sulfuric acid favors the formation of diacetin while zinc chloride tends to aid in the production of a mixture of the mono and di esters. Monacetin in practically quantitative yield is formed when molar quantities of acetic acid and glycerol are made to react in the presence of phosphoric acid or its anhydride. The formation of monacetin can also be accomplished from the other direction in that both diacetin and triacetin, when heated with an excess of glycerol, may be converted into the mono ester in the presence of phosphoric acid.

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NORMAL VALEROLACTONE

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n-Valerolactone has been known for many years, yet there is a conspicuous gap in the literature on some of its simpler physical constants. Its structure was proved by Messerschmidt[1] and by Wolff.[2] The former made it by boiling the addition compound of allylacetic and hydrobromic acids with water. The latter, by means of sodium amalgam, reduced levulinic acid to γ-hydroxyvaleric acid[3] from which he then removed the elements of a molecule of water. Since levulinic acid is a substance which can be made from cheap raw materials with no undue difficulties, the latter procedure is preferred, but the use of sodium amalgam as reducing agent in this instance cannot be recommended for not only is its reaction velocity

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[1] Messerschmidt, *Ann.*, **208**, 96 (1881).

[2] Wolff, *Ann.*, **208**, 104 (1881).

[3] Sabatier has effected the same results with hydrogen at 250° in the presence of nickel as catalyst [*Ann. chim. phys.*, [8] **16**, 70 (1909)] and Tafel and Emmert have done it electrolytically from an alkaline solution [*Z. Elektrochem.*, **17**, 569 (1911)].