increasing with each crystallization. By far the most rapid method of obtaining perfectly pure *o*-acid is by way of its methyl ester.

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MENTHOL AND PHENYLHYDRAZINE DERIVATIVES OF THE HIGHER FATTY ACIDS.

BY D. H. BRAUNS.

Received May 1, 1920.

The separation of the higher fatty acids, or their determination when several are present together is a matter of very considerable difficulty. In the hope of securing a simple and reliable method of separation or determination of these acids, the preparation and properties of their menthyl esters and their phenylhydrazids have been studied. Although in neither case was the hope of a quantitative identification realized, the compounds are of sufficient interest to merit description.

The menthol esters of lauric, myristic, palmitic, stearic, and arachidic acids were prepared by heating the acid chlorides with menthol. The acid chlorides were obtained by the action of phosphorus pentachloride and thionyl chloride on the fatty acids. It was found that the reaction with thionyl chloride was not only more nearly quantitative but also yielded a product freer from impurities. However, since even the thionyl chloride did not give a quantitative yield of the acid chlorides, it was not possible to utilize the optical rotation of these methyl esters for the estimation of the above mentioned acids in mixtures when only 2 of them were present.

The phenylhydrazine derivatives of several of these fatty acids were prepared by heating the acids with an excess of phenylhydrazine. Derivatives of palmitic, stearic, and arachidic acids were prepared and their solubilities in alcohol, which was found to be the most suitable solvent from which to crystallize them, was studied. It was found that they were only slightly soluble in cold alcohol and that with the increase of the molecular weight the solubility decreased, as was to be expected. However, there was not enough difference in their respective solubilities to enable the compounds to be utilized in the separation of these acids from each other by fractional crystallization.

Experimental Part.

Menthyl Laurate, $C_{22}H_{42}O_2$.—Equal weights of pure lauric acid and phosphorus pentachloride were heated on the steam bath. When the reaction was completed, the phosphorus oxychloride was removed by heating the mixture under 15 mm. pressure to 150°. Then the pressure was reduced to 5 mm. and the acid chloride was distilled. The lauric acid chloride was heated with an excess of menthol until the evolution of hydrochloric acid ceased. The reaction product was dissolved in ether, washed with dil. sodium hydroxide solution and water, and dried over potassium carbonate. The menthyl laurate was further purified by fractional distillation under diminished pressure. From 10 g. of lauric acid, 6.3 g. or a 37% yield of the pure ester, was obtained. Menthyl laurate is a liquid at ordinary temperatures; d_4^{20} 0.8915; $[\alpha]_D^{20} = -46.07$; $[M]_D^{20} = -155.9$. Analysis by combustion gave the following results.

Subs., 0.1866; CO_2, 0.5341; H_2O, 0.2077.

Calc. for $C_{22}H_{42}O_2$: C, 78.03; H, 12.51. Found: C, 78.06; H, 12.45.

Menthyl Myristate, $C_{24}H_{46}O_2$.—This compound was prepared in the same manner as the corresponding lauric acid derivative. A second preparation was made from myristic acid chloride which was obtained by the action of thionyl chloride on myristic acid according to F. P. Hilditch.[1] This method of obtaining the acid chlorides was found to be much more satisfactory than the customary procedure with phosphorus pentachloride. Although Hilditch described this compound as melting at 32°, it was impossible to obtain a melting point above 21–22° in spite of repeated purification by fractional distillation under diminished pressure. Ten g. of myristic acid gave 7 g. of pure ester which is equivalent to a yield of 48%; d_4^{20}, 0.882; $[\alpha]_D^{20} = -42.33$; $[M]_D^{20} = -155.1$.

Subs., 0.2097; CO_2, 0.6055; H_2O, 0.2370.

Calc. for $C_{24}H_{46}O_2$: C, 78.61; H, 12.66. Found: C, 78.76; H, 12.65.

Menthyl Palmitate, $C_{26}H_{50}O_2$.—This compound was obtained in the same manner as described above, except that it could not be distilled under diminished pressure, but had to be purified by repeated crystallization from absolute alcohol. The purified derivative was found to melt at 32°. It is very soluble in alcohol. It separates from alcohol in the form of illy defined soft crystals; d_4^{20} 0.8848; $[\alpha]_D^{20} = -39.10$; $[M]_D^{20} = -154.2$. It should be observed that the melted compound was employed in determining the specific rotation.

Subs., 0.1653; CO_2, 0.4821; H_2O, 0.1895.

Calc. for $C_{26}H_{50}O_2$: C, 79.11; H, 12.73. Found: C, 79.53; H, 12.73.

Menthyl Stearate, $C_{28}H_{54}O_2$.—This substance was prepared and purified in the same manner as the palmitic ester. Three preparations were made, starting each time with 10 g. of stearic acid for making the acid chloride. The ester was found to melt at 38° to 39°, which is in agreement with that found by E. Beckman.[2] This compound, which is very soluble in alcohol, separates in aggregates of very small crystals not well defined. Ten g. of the acid gave 3 g. of pure ester, which is a

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[1] Hilditch, *J. Chem. Soc.*, 101, 192 (1912).

[2] *J. prakt. Chem.*, [2] 55, 17 (1847).

yield of 20%; d_4^{45} 0.8665; $[\alpha]_D^{45} = -36.60$; $[M]_D^{45} = -154.6$. Analysis gave the following results.

Subs., 0.2483; CO_2, 0.7238; H_2O, 0.2839.
Calc. for $C_{28}H_{54}O_2$: C, 79.54; H, 12.88. Found: C, 79.50; H, 12.73.

Menthyl Arachidate, $C_{30}H_{58}O_2$.—This substance was prepared from arachidic acid chloride obtained by both the phosphorus pentachloride and thionyl chloride methods. After repeated recrystallization from alcohol, a melting point of 55° was obtained. From 10 g. of acid, 3 g. of purified ester was obtained; d_4^{55} 0.8566; $[\alpha]_D^{55} = -30.63$; $[M]_D^{55} = -138.0$. Analysis gave the following results.

Subs., 0.1906, 0.2049; CO_2, 0.5639, 0.6051; H_2O, 0.2218, 0.2392.
Calc. for $C_{30}H_{58}O_2$: C, 79.92; H, 12.98. Found: C, 80.69, 80.54; H, 13.02, 13.06.

The analysis as well as the low result obtained for the rotation indicate that in spite of repeated recrystallizations from alcohol, the compound was not quite pure. This compound crystallizes in illy defined soft thin prisms.

It should be observed that all the figures given for the rotation in this paper were determined directly with the molten derivatives, while Hilditch, who previously prepared those of myristic, palmitic, and stearic acids, measured the rotations in chloroform and alcoholic solutions, with the result that he obtained slightly higher values. It is interesting to note that with the exception of the menthyl arachidate, these compounds gave an average molecular rotation of —155 which is in close agreement with the average value —157, found by L. Tchugaeff[1] for the corresponding derivatives of the lower members of this series of acids extending from acetic acid to caprylic acid.

Palmitic Phenylhydrazide, $C_{16}H_{31}O.HNNHC_6H_5$, was obtained by heating palmitic acid with an excess of phenylhydrazine until the mixture began to boil, according to the method of Strache and Iritzer,[2] who described the corresponding stearyl compound. After the reaction was completed, alcohol was added and the mixture was allowed to cool. The crystals from this solution were further purified by recrystallization from alcohol until the constant melting point 105° was obtained. A yield of 25% of the purified compound was obtained.

Subs., 0.1419; CO_2, 0.3958; H_2O, 0.1379.
Calc. for $C_{22}H_{38}N_2O$: C, 76.23; H, 11.06. Found: C, 76.07; H, 10.87.

It is readily soluble in hot 95% alcohol and sparingly soluble in cold alcohol. From alcohol it separates in aggregates of extremely small soft crystals. This compound was found to be quite soluble in chloroform and ether.

Stearic Phenylhydrazid, $C_{18}H_{35}O.HNNHC_6H_5$, was obtained by heating 2 g. of stearic acid with 1.5 cc. of phenylhydrazine to 140° for 20

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[1] Tchugaeff, *Ber.*, 31, 360 (1898).

[2] Strache and Iritzer, *Monatsh.*, 14, 37 (1893).

minutes. After cooling somewhat, alcohol was added and the solution was allowed to stand until crystallization had taken place. After 2 recrystallizations the constant melting point of 110° to 111° was obtained. It was observed that Strache and Iritzer,[1] who previously described this compound, gave the melting point 105° to 107°. When crystallized from alcohol it crystallized in well defined small, thin, rectangular prisms. It is readily soluble in hot alcohol, but sparingly soluble in cold alcohol. 100 cc. of 95% alcohol at 29° dissolved 0.076 g. A yield of 18% of the pure derivative was obtained.

Subs., 0.1315; CO_2, 0.3706; H_2O, 0.1298.

Calc. for $C_{24}H_{41}N_2O$: C, 76.93; H, 11.04. Found: C, 76.71; H, 11.05.

Arachidic Phenylhydrazid, $C_{20}H_{39}O.HNNHC_6H_5$ was obtained in the same manner as the stearyl derivative starting with 2 g. of arachidic acid and 1.5 cc. of phenylhydrazine. The highest melting point obtained by recrystallization from alcohol was 108 to 109°. From alcohol it crystallizes in small illy defined thin prisms. It was found that 100 cc. of 95% alcohol at 27° dissolved 0.050 g. while at 40° 0.0530 g. was dissolved. A yield of 29% of the pure derivative was obtained.

Subs., 0.1384; CO_2, 0.3924; H_2O, 0.1409.

Calc. for $C_{26}H_{46}N_2O$: C, 77.54; H, 11.52. Found: C, 77.33; H, 11.39.

Summary.

The menthyl esters of lauric, myristic, palmitic, stearic, and arachidic acids have been prepared and their optical rotations have been determined.

Also the phenylhydrazine derivatives of palmitic, stearic, and arachidic acids have been made and studied.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH.]

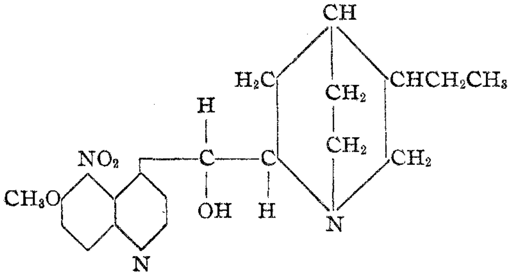
SYNTHESES IN THE CINCHONA SERIES.

IV.[2] NITRO- AND AMINO-DERIVATIVES OF THE DIHYDRO ALKALOIDS.

BY WALTER A. JACOBS AND MICHAEL HEIDELBERGER.

Received May 4, 1920.

In the preparation of 5-nitro-dihydro-quinine



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[1] *Loc. cit.*

[2] Cf. THIS JOURNAL, **41**, 817, 2090, 2131 (1919).