Anal. Calcd. for $C_{25}H_{38}O_3(COOH)_2 \cdot CH_3COOH$: C, 64.91; H, 8.26; neut. equiv., 178.7. Found: C, 65.89; H, 8.53; neut. equiv., 176.1.

The solutions from the above determinations of neutralization equivalent were evaporated to a small volume on the steam-bath, diluted to 25 cc. with water, filtered and acidified with 0.05 *N* hydrochloric acid. The precipitate was filtered on a hardened paper and washed with hot water until free of chlorides. After drying it melted at 234–236° and analysis showed it to be free of acetic acid.

Anal. Calcd. for $C_{25}H_{38}O_3(COOH)_2$: C, 68.05; H, 8.46; neut. equiv., 238.3. Found: C, 68.03; H, 8.30; neut. equiv., 240.5.

In order to determine whether this dibasic acid was derived from the diketone, 3.5 g. of pure diketone was covered with 35 cc. of acetic acid and treated with 28 g. of the oxidizing mixture of Kiliani and Merck. After fifty-two hours the product was filtered and washed, and amounted to 0.8 g. The filtrate was diluted to 1 liter and filtered. The light green precipitate was dissolved in 15 cc. of hot glacial acetic acid and poured into 500 cc. of water. The precipitate after drying weighed 0.5 g. The total product of 1.3 g. was dissolved in benzene, extracted with sodium carbonate solution and the extract acidified. After filtering, washing and drying, the acid fraction weighed 0.3 g. and melted at 210–215°. After recrystallization from acetic acid it melted at 235–237° with decomposition and did not depress the melting point of the acid obtained by the direct oxidation of chlorogenin.

Dimethyl Ester of Ketodibasic Acid.—A solution of diazomethane in ether was added in excess to 0.3 g. of the dibasic acid containing acetic acid of crystallization. On evaporation of the ether an oil remained which soon solidified. It was soluble in methyl alcohol and acetone and only slightly soluble in petroleum ether, but crystallized well from 60–70° ligroin. After two crystallizations it melted at 158–159°; $[\alpha]^{22}_{D} - 39.1$, $[\alpha]^{22}_{546.1} - 46.5$. These rotations were microdeterminations which are not as accurate as the macro determinations made on the diketone and ketodibasic acid. Titration showed the product to contain no free carboxyl groups.

Anal. Calcd. for $C_{25}H_{38}O_3(COOCH_3)_2$: C, 69.02; H, 8.78; sap. equiv., 252.2. Found: C, 68.76; H, 8.55; sap. equiv., 256.5.

The acid recovered from the determinations of saponification equivalent did not depress the melting point of the original ketodibasic acid.

Summary

A tentative structural formula for chlorogenin is proposed which is based on the products of oxidation with dichromic acid.

STANFORD UNIVERSITY, CALIF. RECEIVED APRIL 5, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTH CAROLINA]

Identification of Alcohols by 3-Nitrophthalic Anhydride[1]

BY G. M. DICKINSON, LEO H. CROSSON AND J. E. COPENHAVER

The use of 3-nitrophthalic anhydride as a reagent for the identification of alcohols was suggested by Nicolet and Sachs,[2] who prepared esters from this acid with nine of the lower alcohols. Ashdown and Monier[3] gave an extensive discussion of the use of this reagent at the Atlanta Meeting of the American Chemical Society in 1930. There has been much study of the higher alcohols within the last few years and it was thought that an extension of this series would be of interest.

The general procedure of the above workers was followed for the preparation of the acid anhydride reagent and the lower esters, but it was found that certain modifications were necessary for the higher derivatives. Their work and that of others showed that the 2-mono-alkyl esters were the principal product and that the 3-mono-alkyl esters were eliminated by crystallization.

Esters of the lower, less expensive alcohols were prepared by heating 3 g. of 3-nitrophthalic anhydride with approximately 2.5 g. of the alcohol and refluxed in a 50-cc. Erlenmeyer flask for one hour. The same quantities were used up to nonyl alcohol but with the increase in the boiling point of the alcohols, they were heated to 100° for two hours to ensure better esterification. From *n*-decyl to *n*-octadecyl, 3 g. of 3-nitrophthalic anhydride and one of alcohol were dissolved in purified toluene and refluxed for three hours.

Recrystallization of the Esters

As shown by Nicolet and Sachs, the esters from methyl to *n*-butyl were recrystallized from water without hydrolysis.

Upon the addition of water and warming, the esters above propyl separated as oils, which, up to and including *n*-hexyl, crystallized on cooling.

---

(1) This is an extract from the theses presented by Messrs. Dickinson and Crosson in partial fulfilment of the requirements for the Master of Science degree at the University of South Carolina.

(2) Nicolet and Sachs, THIS JOURNAL, **47**, 2348 (1925).

(3) Ashdown and Monier, *Ind. Eng. Chem.*, *News Ed.*, **8**, No. 6, 6 (1930).

The excess anhydride was decomposed by the water and it was separated as the acid by decantation from the insoluble esters, due to its solubility of 2.05 g. per 100 g. of water. Several solvents were tried but a 30% ethyl alcohol solution was found most satisfactory for esters from *n*-amyl to *n*-heptyl. The concentration had to be increased to 40% for octyl and nonyl. For the lower alcohols, three or four recrystallizations gave constant melting points, but for the higher esters it was necessary to repeat the treatment. Those esters prepared in toluene were separated from the solvent by vacuum distillation and the excess anhydride was removed by warming with 300–400 cc. of water. It was found that the best method to cause these to crystallize was to dissolve them in 95% alcohol, cool slowly and dilute to about 50%, taking care that none of the ester separated as an oil. This process was continued until a constant melting compound was obtained. Higher melting points were obtained by cooling the compounds in a desiccator. The yields of the lower alcohols averaged around 70% and for the higher ones from 60–65%.

Ester	M. p., (corr.), °C.	Molecular weight	
		Calcd.	Found
Methyl[a]	152.9–153.4	...	...
Ethyl	157.7–158.3	239.1	239.7
n-Propyl	144.9–145.7	...	...
Isopropyl	153.9–154.3	253.1	253.6
n-Butyl	146.8–147.0	267.1	267.5
Isobutyl	179.9–180.6	267.1	267.3
s-Butyl	130.6–131.4	...	...
n-Amyl	136.2–136.4	281.1	281.2
Isoamyl	163.2–163.4	281.1	280.7
n-Hexyl	123.9–124.4	295.1	295.2
n-Heptyl	126.9–127.2	308.2	308.5
n-Octyl	127.8–128.2	323.2	323.5
n-Nonyl	124.8–125.2	337.2	336.8
n-Decyl	122.7–122.8	351.7	351.7
n-Undecyl	123.2–123.3	365.2	366.1
n-Dodecyl	123.9–124.0	379.2	379.0
n-Tridecyl	124.0–124.2	393.3	393.8
n-Tetradecyl	123.2–123.5	407.3	407.1
n-Pentadecyl	122.4–122.6	...	...
n-Hexadecyl	121.4–122.0	...	...
n-Heptadecyl	121.0–121.8	449.3	449.4
n-Octadecyl	118.3–119.2	...	...

[a] Nicolet and Sachs reported on the following esters listed above: Methyl, 152–153°; ethyl, 156–157°; *n*-propyl, 141–142°; isopropyl, 152–153°; *n*-butyl, 146–147°; isobutyl, 182–183°; isoamyl, 165–166°.

There is not as great a difference in the melting points of the higher esters as might be desired to absolutely distinguish them from a near homolog but they are of value in checking with other methods. Mixed melting points of adjacent esters above decyl alcohol gave a lowering of 3 to 5°.

The melting points were determined in a 200-cc. round-bottomed flask with a side-tube for insertion of thermometer. Standard Anschütz thermometers, graduated in 0.1 and 0.2°, were used and the bath was stirred by a motor at such a rate to ensure uniform distribution of heat. These precautions gave corrected melting points. The melting point range was taken from the point the compound softened and began sliding down the tube to complete melting. The molecular weights were determined by titrating the esters, dissolved in 50% alcohol, against 0.1 normal sodium hydroxide.

The alcohols from methyl to butyl were carefully distilled with a standard thermometer over a 1° range. *n*-Butyl was donated by the Commercial Solvents Corporation, amyl to heptyl were purchased from Eastman Kodak Company, and for octyl to octadecyl, the authors are indebted to Dr. E. Emmet Reid of Johns Hopkins University. All alcohols above butyl were used without further purification.

COLUMBIA, S. C.

RECEIVED APRIL 28, 1937