drops of water. A drop of the reagent was then allowed to flow into the test sample (magnification, 100 ×).

Discussion.—The distillation is employed to remove substances which may interfere with the analysis. It also serves to concentrate the acids present. Incidentally, too large an excess of acetic acid is conveniently and simultaneously frozen out.

If only the sodium salts of the acids involved comprise the test substance, the distillation may be dispensed with if one can be sure of at least 0.15 mg. of propionate in the test drop.

The method also may be used to identify either acetates or butyrates when they are present alone. As little as 0.15 mg. present in the test drop permits positive identification.

Formates tend to interfere with the analysis when the concentration is equal to or greater than either of the other anions. When smaller amounts are present, however, propionates may be identified although the crystal structure is slightly altered. Hence, if formates are indicated in a test solution (by the reduction of silver nitrate or mercuric chloride), it is advisable to destroy or otherwise remove them.

Attempts were made to employ other cations for the detection of the ions discussed under similar conditions. Thus, silver, bismuth, antimony, and lead salts of the acids were studied. Also, various cobaltammine complexes were tried. However, none of these were found to be completely suitable.

Acknowledgment.—The authors wish to express their thanks to Dr. W. Schmidt for permission to publish this paper. Thanks are also due to Mr. W. Pera for technical advice on photomicrography and to W. A. Hynes and L. K. Yanowski for supplying samples of the cobaltammine complexes.

AGFA ANSCO CORPORATION
BINGHAMTON, NEW YORK RECEIVED MAY 11, 1939

Saponins and Sapogenins. XIV. The So-called Pyridazine Derivatives of Steroid Diones

BY C. R. NOLLER

The fact that the diketone obtained by the oxidation of chlorogenin[1] has been found to react with hydrazine to give a product the analysis of which checks that of a pyridazine derivative, has led Marker and Rohrmann[2] to postulate that the carbonyl groups of the diketone and hence the hydroxyl groups of chlorogenin occupy the 3,6-positions of the sterol nucleus. Several factors have led us to believe that this is not a likely structure for chlorogenin. Since tigogenin on oxidation gives gitogenic acid, one would expect chlorogenin, if it had the 3,6-formulation, to give digitogenic acid, which is not the case. Moreover, if oxidation opened ring I between C-3 and C-4, a β-keto acid would be formed or if ring I opened between C-2 and C-3 but the nuclear configuration were different, one would expect the ketodibasic acid to be isomerized readily by alkali since digitogenic acid readily is converted to digitoic acid, but the ketodibasic acid was recovered unchanged after alkaline saponification of the dimethyl ester. The opening of ring II between C-6 and C-7 on oxidation would not be expected since in the further oxidation of digitogenic acid ring II is opened between C-5 and C-6 to give a ketotribasic acid, oxydigitogenic acid. Finally the surface film of digitogenin appears to be unlike that of chlorogenin since the former contracts rapidly under pressure giving a solid condensed film which is partially collapsed[3] whereas chlorogenin gives a gaseous film which does not collapse until the pressure reaches 18 dynes per centimeter and which remains mobile even up to 32 dynes per centimeter.[4]

Because of the possibility of polymolecular condensation,[5] we have determined the molecular weight of the condensation product formed from hydrazine and the diketone from chlorogenin and have obtained values of 1410, 1980 and 2770 for three different preparations compared with a calculated value of 425 for a monomolecular pyridazine derivative. It is evident that the formation of condensation products with hydrazine does not prove that the hydroxyl groups of chlorogenin are in the 3,6-positions although the fact that the condensation products are polymolecular does not exclude these positions.

Since molecular weight determinations have not been reported for similar compounds from other steroid diones,[6] it seemed desirable to determine the molecular weight of a typical so-called pyridazine derivative such as that from choles-

(1) Noller, THIS JOURNAL, **59**, 1092 (1937).

(2) Marker and Rohrmann, *ibid.*, **61**, 946 (1939).

(3) Askew, Farmer and Kon, *J. Chem. Soc.*, 1399 (1936).

(4) Noller, THIS JOURNAL, **60**, 1629 (1938).

(5) Zimmerman and Lochte, *ibid.*, **60**, 2456 (1938).

(6) Windaus, *Ber.*, **39**, 2256 (1906); Fernholz, *Ann.*, **508**, 217 (1934); Windaus, Inhoffen and Reichel, *ibid.*, **510**, 259 (1934); Coffey, Heilbron and Spring, *J. Chem. Soc.*, 738 (1936).

tane-3,6-dione. A single preparation gave a value of 3000 compared with 396 for a monomolecular product. It is surprising that the fact has been overlooked that reaction with hydrazine cannot, in the absence of molecular weight determinations, be considered as proof or confirmatory evidence for the 1,4-diketone grouping since Fernholz[6] points out that a pyridazine from a 3,6-dione is possible stereochemically only if one of the double bonds is outside of the heterocycle. Moreover, Marker and Wittle[7] have objected to a deduction of others[8] based on "pyridazine" formation on the grounds that the pyridazine in question was probably a linear polymer.

The reaction with hydrazine of the diketone, m. p. 233–235°, from chlorogenin was carried out in the usual way.[2,6] Methyl alcohol was added to a boiling solution of the product in benzene and on cooling a pale yellow oil separated which solidified on rubbing with more methyl alcohol. Solution in benzene and precipitation with methyl alcohol was repeated three times. The product, which was amorphous, was dried at 130° and 3 mm. pressure. It turned a deep yellow at 240°, light brown at 270° and was a dark brown powder at 300°.

Anal. Calcd. for $C_{27}H_{40}O_2N_2$: N, 6.59. Found: N, 7.05, 6.89. When 0.1661 g. was dissolved in 1.889 g. of benzene, the freezing point was depressed 0.16°. Calcd. mol. wt., 425; found, 2770.

The mother liquors from the above preparation were concentrated, dissolved in benzene and precipitated by methyl alcohol. This product showed the same behavior on heating and was found to contain 6.82% nitrogen. When 0.0534 g. was dissolved in 1.247 g. of benzene, the freezing point was depressed 0.11°, indicating a molecular weight of 1981.

In another preparation a product with different properties was obtained although the conditions were to all outward appearances the same. This product was crystalline but showed the same behavior on heating as the previous products.

Anal. Calcd. for $C_{27}H_{40}O_2N_2$: C, 76.38; H, 9.49; N, 6.59. Found: C, 73.73, 73.80; H, 9.62, 9.22; N, 6.49, 6.84.

This crystalline product had only limited solubility in benzene and the solubility appeared to decrease with repeated crystallizations. This solubility behavior is different from that of all previously recorded products, which appear to be characterized by ready solubility in benzene.

In order to get sufficient material into solution for a molecular weight determination, it was necessary to warm the solution but there was no evidence that the material separated before freezing of the benzene took place. A depression of 0.15° was obtained when 0.0950 g. was dissolved in 2.290 g. of benzene, indicating a molecular weight of 1410. A micro Rast determination in camphor by Mr. L. H. Goodson gave a value of 894 for the molecular weight but decomposition of the compound was evident from the brown color of the solution.

A sample of cholestanedione-3,6, m. p. 169–171°, prepared by the method of Dane and Wang,[9] after reaction with hydrazine and purification from benzene and methyl alcohol, gave an amorphous product which darkened at 190° and melted to a red-brown liquid at 210–220°. Windaus[6] reported obtaining a crystalline product which sintered at 188°.

Anal. Calcd. for $C_{27}H_{44}N_2$: N, 7.06. Found: N, 6.72.

When 0.1235 g. was dissolved in 1.750 g. of benzene the freezing point was depressed 0.12°, indicating a molecular weight of 2999.

When 0.1040 g. of the diketone from chlorogenin was dissolved in 1.845 g. of benzene the freezing point depression was 0.69°, giving a molecular weight of 417 compared with a calculated value of 428.

(7) Marker and Wittle, THIS JOURNAL, **61**, 855 (1939).

(8) Odell and Marrian, *J. Biol. Chem.*, **125**, 333 (1938).

(9) Dane and Wang, *Z. physiol. Chem.*, **245**, 86 (1937).

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Purification of *p*-Acetaminobenzenesulfonyl Chloride

BY L. H. PENCE AND H. C. WINTER

A convenient method for the purification of large quantities of *p*-acetaminobenzenesulfonyl chloride will be of interest to the many investigators engaged in the synthesis of sulfanilamide and related compounds.

The crude acid chloride obtained by the procedure described by Smiles and Stewart[1] in "Organic Syntheses" frequently may be employed in subsequent reactions without further purification; but they state that it must be used immediately after preparation, since it decomposes rapidly on standing. Once the sulfonyl chloride is purified, however, it may be kept indefinitely. According to their procedure recrystallization of the 90 g. of crude product from benzene yielded 70 g. of pure *p*-acetaminobenzenesulfonyl chloride melting at 149°. However, because of the slight solubility of the sulfonyl chloride in this solvent (2% hot and 0.5% cold), recrystallization from benzene has been reported[1] to be impractical for purifying more than a small amount at a time.

The following modification of the above procedure has been used in our laboratory and found to be much better adapted for the purification of large quantities of the compound from the standpoints of both time and convenience.

(1) Smiles and Stewart, *Org. Syntheses*, **5**, 3 (1925).