p. 142–143°.[5] Extraction of this mother liquor with ether recovered 6 g. of the straw-yellow oil, the major portion of which crystallized. Dried on a clay plate, the crystalline material had the correct melting point (m. p. 183–185°) and neutral equivalent (neut. equiv. 62) for succinic acid.

Hydrogenation.—Five grams of olefin mixture (distilled with alcohol, washed with water to remove the alcohol and then fractionated, 30% II) was dissolved in 25 cc. of alcohol and 2–3 g. of Raney nickel added. Hydrogenation at three atmospheres pressure was complete in three or four hours. The product had the following properties: b. p. 101–101.5°; $n^{20}D$ 1.4230; d^{20}_4 0.7712; $M^{20}D$ (found) 32.36; $M^{20}D$ (calcd.) 32.34.

1-Methyl-1-cyclohexene (II).—This compound was obtained by dehydration of 1-methyl-1-cyclohexanol prepared from cyclohexanone and methylmagnesium chloride. Its properties agreed with those reported in the literature: b. p. 110–110.5°; $n^{20}D$ 1.4500; d^{20}_4 0.8103; $M^{20}D$ (found) 31.84; $M^{20}D$ (calcd.) 31.87.

(5) Wallach, *Ann.*, **329**, 371 (1903).

Oxidation.—Oxidation of 0.7 g. of this olefin (II) with permanganate as above yielded 0.6–0.7 g. (50%) of the semicarbazone of ε-ketoheptanoic acid, m. p. 142–143°.

Hydrogenation.—Hydrogen added readily to this olefin (II) using Adams catalyst in alcohol at three atmospheres pressure. The product had the same properties as the methylcyclohexane prepared from III: b. p. 101.5–102°; $n^{20}D$ 1.4234; d^{20}_4 0.7711; $M^{20}D$ (found) 32.35; $M^{20}D$ (calcd.) 32.34.

Summary

The dehydration of *trans*-2-methylcyclohexanol with phosphoric anhydride yielded a mixture of 1-methyl-1-cyclohexene and 3-methyl-1-cyclohexene. The methylcyclohexane obtained by hydrogenation of this olefin mixture was found to be identical in every respect with other authentic samples of this hydrocarbon.

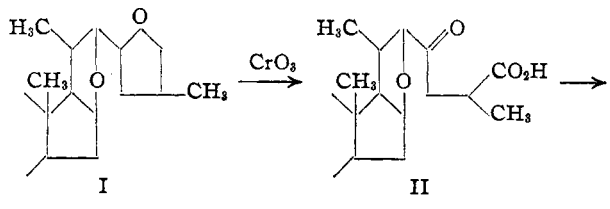
URBANA, ILLINOIS RECEIVED MAY 26, 1939

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Sarsasapogenin. IV. Further Observations Concerning Sarsasapogenoic Acid and Related Compounds

BY LOUIS F. FIESER, EDWARD M. FRY[1] AND R. NORMAN JONES[2]

From the work of Jacobsen in this Laboratory[3] it was concluded that anhydrosarsasapogenoic acid has the partial structure III and that its formation from sarsasapogenin by oxidation to sarsasapogenoic acid and treatment of the latter with alcoholic alkali is most plausibly interpreted by regarding these substances as having the structures I and II, first tentatively suggested by Tschesche and Hagedorn.[4] The structure III for the anhydro compound was based upon the results of oxidation and reduction experiments and upon spectrographic evidence[5] of the presence of an α,β-unsaturated carbonyl system. The spectrographic evidence has now been extended by a determination of the ultraviolet absorption spectrum of the methyl ester acetate of anhydrosarsasapogenoic acid in absolute alcohol[5] (curve 1, Fig. 1). This and the other determinations reported were made by one of us (R. N. J.) by a technique which will be described in a future paper (measurements at room temperature, slit width 0.12 mm.). Both the principal and the secondary absorption bands at 243 mμ (log ε = 4.13) and 303 mμ (log ε = 1.86) correspond in position and intensity with those characteristic of α,β-unsaturated ketones,[6] in conformity with formula III. The dibasic acid $C_{27}H_{40}O_7$[3b] resulting from the permanganate oxidation of anhydrosarsasapogenoic acid was regarded as having two carbonyl groups. The absorption spectrum of the dimethyl ester of this acid (curve 2, Fig. 1) definitely has carbonyl characteristics and lacks the original feature of conjugation, but it is hardly possible from the spectrographic evidence to distinguish between a monoketo and diketo carboxylic acid.



I II III

The spectrum of the acetate of sarsasapogenoic acid (curve 2, Fig. 2) is characterized by the ap-

(1) Du Pont Research Fellow.
(2) Commonwealth Fund Fellow.
(3) Fieser and Jacobsen, THIS JOURNAL, **60**, (a) 28, (b) 2753, (c) 2761 (1938).
(4) Tschesche and Hagedorn, *Ber.*, **68**, 1412, 2247 (1935).
(5) Fieser and Jones, THIS JOURNAL, **61**, 532 (1939).
(6) For example, see Mohler, *Helv. Chim. Acta*, **20**, 289 (1937).

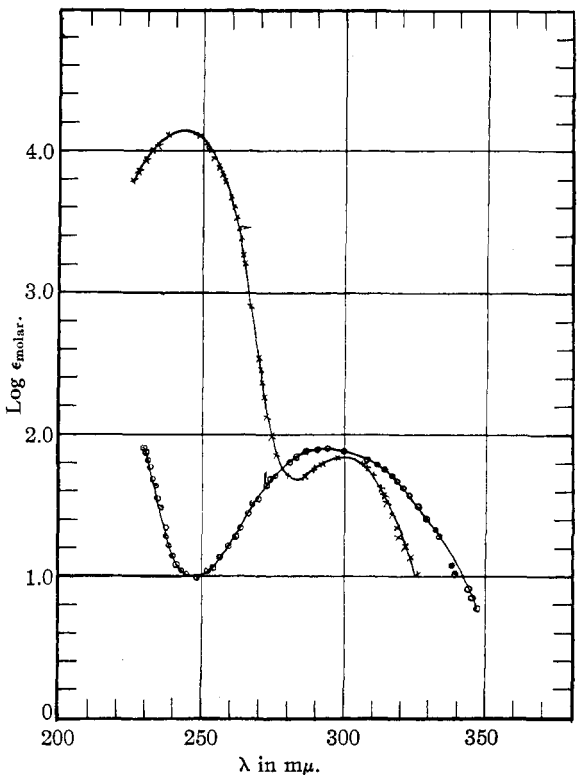


Fig. 1.—Curve 1 (crosses), anhydrosarsasapogenoic acid methyl ester acetate in absolute alcohol; curve 2 (circles), dimethyl ester of dibasic acid $C_{27}H_{40}O_7$ in absolute alcohol.

pearance of a low intensity band at 281 mμ (log ε = 1.92), which is indicative of the presence of a non-conjugated carbonyl group, as in formula II. A determination made with a sample of chlorogenoic acid diacetate monohydrate[7] kindly supplied by Professor C. R. Noller gave a practically identical result (maximum at 286 mμ, log ε = 1.91; solvent, 95% alcohol). A similar absorption curve (curve 1, Fig. 2) was found for the acidic oxidation product obtained[3c] from desoxysarsasapogenin and previously regarded as an unsaturated, conjugated diketo acid in the form of a hydrate, $C_{27}H_{40}O_4 \cdot H_2O$. Reëxamination of the acid has provided indications that it is indeed a hydrate, but the spectrum shows that it lacks conjugation. The similarity to the above sapogenoic acid suggests that the substance in question may be a mono-carbonyl compound of the same type, namely, desoxysarsasapogenoic acid. The analyses reported[3c] for the acid agree satisfactorily with the revised formula $C_{27}H_{42}O_4 \cdot H_2O$, and the results for the unhydrated methyl ester and monoxime accord better with the new formulation than with that originally proposed. The apparent presence of an active hydrogen atom in the ester[3c] may be due to enolization or other change. Another acid which appears to be of the same type has been obtained by the oxidation of sarsasapogenone with chromic acid. Analyses of the acid and its methyl ester point to the formula $C_{27}H_{40}O_5$ of dehydrosarsasapogenoic acid, and this designation is supported by the sensitivity of the compound to alkali.

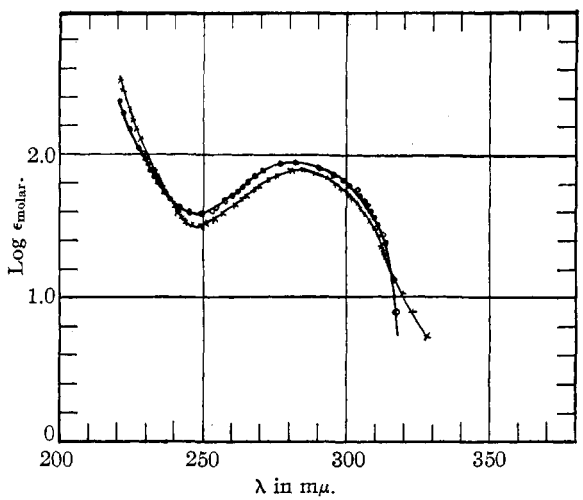
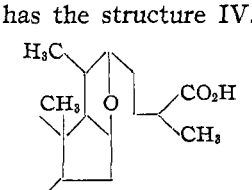


Fig. 2.—Curve 1 (crosses), desoxysarsasapogenoic acid ($C_{27}H_{42}O_4 \cdot H_2O$) in absolute alcohol; curve 2 (circles), sarsasapogenoic acid acetate in absolute alcohol.

Spectrographic examination was also made of the "anhydrotetrahydrosarsasapogenoic acid"[3b] resulting from the slow and irregular catalytic hydrogenation of the sapogenoic acid. The formula of a γ-keto acid, previously considered as a possibility, is definitely eliminated by the present observation that the substance shows no selective absorption in the ultraviolet region. Since this is true also of sarsasapogenin, the reduction product probably contains one of the original oxidic linkages and has the structure IV. On this interpretation the reaction consists in the reduction of the carbonyl group of II to a methylene group, which would account for the slow and irregular absorption of hydrogen. The same formula has been ascribed by Marker and Rohrmann[8] to an



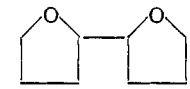
IV

(7) McMillan and Noller, THIS JOURNAL, **60**, 1630 (1938).

(8) Marker and Rohrmann, *ibid.*, **61**, 846 (1939).

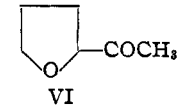
acid (sarsasapogentic acid) obtained by hydrogenating sarsasapogenin in an acidic medium and oxidizing the resulting crude 3-acetate dihydride. Their acid is stated to melt at "187°" ("189°" is given in the theoretical discussion) and to form a crystalline methyl ester. Our acid, like certain other compounds of the series, melts over a characteristically long range (174–184°, corr.) and gives a liquid methyl ester, isolated as the crystalline acetate and benzoate.

Marker and Rohrmann[8] found that sarsasapogenin not only can be hydrogenated in acid solution, but also can be reduced by the Clemmensen method, and brominated in the presence of hydrogen bromide. These workers also noted that the sapogenin acetate is attacked by selenium dioxide in acetic acid–benzene, but no reaction product was isolated.[9] They considered these observations to indicate the presence of a spiro ketone acetal grouping in the side chain and suggested that formula I should be modified by transposing the terminal oxidic linkage from C_{23} to C_{22}. This formulation seems contrary to the evidence from our oxidation experiments, particularly since it provides no rational interpretation of the formation and properties of anhydrosarsasapogenoic acid (III). On the other hand, the newly observed transformations at least can be formulated on the basis of the side chain structure I postulated by Tschesche and Hagedorn. It is a more subtle problem to decide whether such a formulation is justifiable. The most distinctive feature of the hydrogenation, reduction, and halogenation reactions is that they proceed only in acidic media, and their occurrence, therefore, may well be dependent upon the same structural features which are responsible for the well-known sensitivity of the sapogenin side chain to cleavage[10,3a] and isomerization[3a,8] by mineral acids. The susceptibility to attack by acids is, to be sure, a matter of degree, for while the side chain is subject both to fission by hydrochloric–acetic acid[10,3a] and to reductive cleavage in the Clemmensen reaction,[8] conditions have been found under which the carbonyl group of sarsasapogenone can be reduced by the Clemmensen method without disturbance of the oxidic side chain.[3c,11] Furthermore, no alteration of the genin occurs during its liberation from the glycoside by acid hydrolysis.[10] There is little basis for deciding from known analogy if a substance having the oxidic structure I should show acid sensitivity of just the degree found in the natural product; on the keto acetal formulation the persistence of the oxide ring structure in the Clemmensen reduction of sarsasapogenone would seem to require explanation. Marker and Rohrmann[8] observed that under the conditions employed for the acid-specific reactions of the sapogenin, tetrahydrofurfuryl acetate is resistant to hydrogenation, bromination, and oxidation with selenium dioxide, and they considered this an argument against formula I. The monocyclic acetate did not seem to us an adequate model, and we consequently investigated octahydro-α,α'-difuryl (V). This compound is attacked readily by acids.



V

Acetolysis of sarsasapogenin can be accomplished by short heating at 90° with equal volumes of acetic acid and concentrated hydrochloric acid, and under the same conditions V is converted largely into a higher boiling liquid which appears to be a chlorohydrin formed by cleavage of one of the oxide rings. Octahydro-α,α'-difuryl also slowly absorbs a full mole of bromine in acetic–hydrobromic acid solution and is attacked by chromic acid at 60°. The freshly purified material did not undergo hydrogenation under conditions similar to those employed by Marker and Rohrmann[8] and was inert to selenium dioxide, although on standing in the air the material rapidly became contaminated with an impurity which is oxidized by this reagent. Since the nature of the selenium dioxide reaction on the sapogenin is unknown and occurrence or absence of hydrogenation dependent upon the nature of the catalyst as well as the presence of acids, the similarities between octahydro-α,α'-difuryl and sarsasapogenin seem more striking than the differences. We also examined α-acetotetrahydrofuran (VI) as a possible model



VI

for sarsasapogenoic acid, formulated as in II, and found that, like this acid, the simpler compound

(9) We have observed that sarsasapogenin, or its acetate, is oxidized rapidly by lead tetraacetate in acetic acid or acetic anhydride solution at temperatures from 60 to 100°. With either one or two moles of oxidizing agent considerable starting material was recovered and the remainder was non-crystalline.

(10) Jacobs and Simpson, *J. Biol. Chem.*, **105**, 501 (1934).

(11) Marker and Rohrmann, THIS JOURNAL, **61**, 1284 (1939).

is sensitive to alcoholic alkali and rapidly undergoes alteration.

From these observations we conclude that on present evidence the Tschesche–Hagedorn formulation provides the most satisfactory expression of the known properties of the sapogenins.

Experimental Part[12]

Preparation of Desoxysarsasapogenin.—Results obtained by the procedure[3c] previously given for the Clemmensen reduction of sarsasapogenone were somewhat irregular. After several trials it was found that the reduction proceeds better when the proportion of benzene (to methanol) is decreased, and that with very brisk refluxing the time can be greatly decreased. The identification of the product is somewhat uncertain because the melting point is close to that of the starting material and because mixtures of the two substances show no depression. There is little difference in the optical rotations of the compounds, the value found for desoxysarsasapogenin being $\alpha^{24}D$ −59.6° (1.5% in benzene), while that for sarsasapogenone was $\alpha^{27}D$ −45° (1.2% in benzene). A convenient method of separation and identification was found in the removal of the ketone as the oxime. The following procedure is believed to provide a reliable method of obtaining the pure desoxy compound, and the yield is considerably better than by the previously reported process[3c] or by reduction with unamalgamated zinc in alcohol according to Marker and Rohrmann.[11]

A mixture of 2 g. of sarsasapogenone, 20 g. of zinc (treated with 2 g. of mercuric chloride), 75 cc. of methanol, 75 cc. of benzene, and 20 cc. of 6 *N* hydrochloric acid was refluxed very vigorously on the steam-bath for six and one-half hours, adding 5-cc. portions of concentrated hydrochloric acid after the second and fourth hours. After dilution with water and separation, the aqueous layer was extracted with ether and the extracts combined with the benzene layer and concentrated to the point of crystallization. The crystalline material obtained in successive crops was freed of adhering oil by washing with cold alcohol, giving 1.51 g. of crude desoxysarsasapogenin. This was suspended with 1.5 g. of hydroxylamine hydrochloride in 5 cc. of pyridine and 10 cc. of alcohol and the mixture was refluxed for two hours. The desoxy compound did not dissolve to any noticeable extent, and after cooling the suspension the solid was collected and washed with water and alcohol, giving 1.3 g. (68%) of satisfactory desoxysarsasapogenin, m. p. 213–217°. The mother liquor afforded 0.13 g. of crude material, m. p. about 130°, which probably is sarsasapogenone oxime.

Desoxysarsasapogenoic Acid.—The oxidation of desoxysarsasapogenin (5 g.) was conducted essentially as before[3c] (in 450 cc. of solvent, adding 4.6 g. of chromic anhydride in 15 cc. of water) but at a lower temperature (45–50°) and for a longer time (eight hours). After filtering from 0.15 g. of starting material the acidic fraction was worked up as described, giving after crystallization from dilute acetone 1.41 g. (26%) of product. This melted at 109–114° to a jelly-like mass which became clear at 121°; $\alpha^{24}D$ −112° (0.65% in alcohol). None of the high melting acid[3c] was observed.

The reported analyses[3c] are to be compared with the percentages calculated for the revised formula $C_{27}H_{42}O_4 \cdot H_2O$: C, 72.28; H, 9.89; ester ($C_{28}H_{44}O_4$): C, 75.63; H, 9.97; oxime ($C_{27}H_{43}O_4N$): C, 72.77; H, 9.73; N, 3.14.

When the acid was heated in a bath at 200° a gas was evolved and a condensate formed on the cool portion of the tube and then evaporated. After adding ether (moist) to the oil remaining on cooling, the material crystallized and was identified as the starting material (hydrate). Contrary to the previous observations,[3c] the acid slowly decolorizes permanganate even in the cold, giving largely non-crystalline material. The compound undergoes alteration in alkaline solution even in the cold and the change could be followed by observing the optical rotation, but no crystalline product was isolated. The alkali-modified material absorbed hydrogen in an acidic medium in the presence of Adams catalyst. No hydrogenation was observed with desoxysarsasapogenoic acid itself, although the methyl ester absorbed somewhat less than one mole of gas, giving unchanged ester and an oil.

Dehydrosarsasapogenoic Acid.—A solution of 5 g. of sarsasapogenone in 390 cc. of glacial acetic acid was stirred at room temperature (30°) and treated with a solution of 4.2 g. of chromic anhydride in 75 cc. of 80% acetic acid. At the beginning this was added at the slow rate at which the reagent was consumed, but after half of the oxidant had been added (eight hours) the remainder was introduced rapidly and stirring was continued for fourteen hours longer at 33°. After dilution with water the cloudy reaction mixture was extracted with ether and the washed solution was extracted with 1 *N* alkali. Fine needles of a sodium salt separated at this point, but as the material was not easily filtered the alkaline suspension was acidified and the product taken into ether. After evaporation of the solvent the oily residue gave a crystalline salt when treated with 1 *N* sodium hydroxide solution. This was collected and washed with 1 *N* alkali, and when a solution of the salt in water was acidified there was obtained 1.28 g. of fairly pure, crystalline dehydrosarsasapogenoic acid. The alkaline mother liquor remaining after removal of the crystalline sodium salt gave on acidification 2 g. of a crusty, non-crystalline acid mixture. No satisfactory acid, ester, or semicarbazone was isolated. The neutral fraction (1 g.) from the oxidation yielded unidentified material crystallizing in plates, m. p. 202–209°. Oxidations at temperatures up to 75° gave lower yields of the crystalline sodium salt.

Dehydrosarsasapogenoic acid crystallized from dilute alcohol in needle clusters. Water of crystallization was held tenaciously but was removed on drying for three hours at 130° and 10 mm. The substance melts at 164–165°; $\alpha^{25}D$ (air dried) −105° (1.1% in alcohol).

Anal. Calcd. for $C_{27}H_{40}O_5$: C, 72.94; H, 9.07; neut. equiv., 445. Found: C, 72.82; H, 9.12; neut. equiv., 445, 442.

The acid absorbed about 2 moles of hydrogen in acetic acid solution using Adams catalyst, giving a small amount of product, m. p. about 200°. The sapogenoic acid is attacked rapidly by alkaline permanganate and is converted into an oily reaction product on refluxing for ten

(12) Experiments by E. M. Fry. All melting points are corrected. Microanalyses by Lyon Southworth.

minutes with 1 *N* alkali. After being heated at 85° with a 1:1 mixture of acetic acid and concentrated hydrochloric acid for two hours, only about one-third of the acid could be recovered as the sodium salt, and the remainder was an oil. Sarsasapogenoic acid is also altered on similar treatment.

The **methyl ester** was obtained by esterification both with diazomethane and with methanol and hydrogen chloride. The substance crystallizes from dilute acetone in the form of rectangular plates, m. p. 125–126°; $\alpha^{27}D$ −101° (1.5% in alcohol). The analytical sample was dried at 66° and 10 mm.

Anal. Calcd. for $C_{28}H_{42}O_5$: C, 73.32; H, 9.23. Found: C, 73.16, 73.35; H, 9.61, 9.30.

Octahydro-α,α′-difuryl (V).—α,α′-Difuryl was obtained by the method of Reichstein and co-workers[13] as a colorless oil, b. p. 67° at 12 mm. Hydrogenation was tried without success in alcoholic solution in the presence of Adams catalyst or palladium charcoal, but in the same solvent with Raney nickel the reaction proceeded satisfactorily at 150° in the pressure apparatus. The octahydride distilled as a colorless liquid, b. p. 73–76° at 12.5 mm., completely soluble in water and giving a negative test for the furan nucleus. Kondo and co-workers[14] effected the hydrogenation with palladium charcoal in acetone and found the b. p. 77–80° at 13 mm.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.37; H, 9.66.

Bromination of V.—A solution of 1.03 g. of octahydro-α,α′-difuryl in 35 cc. of glacial acetic acid was treated with 2 drops of 48% hydrobromic acid and a solution of 1.15 g. of bromine in 3 cc. of glacial acetic acid was run in slowly to the solution held at 55°. The reagent was absorbed slowly and the molecular amount was consumed in the course of a day.

Oxidation and Hydrogenation Tests.—A solution of 0.05 g. of V in 90% acetic acid consumed 0.035 g. of chromic anhydride in about two hours at 60°.

On heating 2.05 g. of octahydro-α,α′-difuryl on the steam-bath with a solution of 2.7 g. of selenium dioxide in 11 cc. of acetic acid and 1 cc. of water, a red precipitate of selenium formed almost at once and did not increase in amount in the course of one hour. The excess dioxide was then neutralized with potassium acetate and the solvent removed by distillation at reduced pressure. The recovered oil distilling at 50–70° at 13 mm. was redistilled twice over sodium carbonate, giving 1.3 g. of purified octahydro-α,α′-difuryl, b. p. 75.5–76.5° at 12.5 mm.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.34; H, 10.28.

This purified and freshly distilled material was not attacked by selenium dioxide under the above conditions, but after standing for two days the same sample again gave a positive test for oxidation by this reagent. The freshly purified substance (0.6 g.) likewise absorbed no hydrogen in a mixture of alcohol (9 cc.) and concentrated hydrochloric acid (1 cc.) in the presence of Adams catalyst (50 mg.). A sample (1 g.) which had not been purified with selenium dioxide under similar conditions absorbed about 17% of the theoretical amount of hydrogen; the reaction then stopped and did not proceed further on adding fresh catalyst. The recovered material boiled at 78° (13 mm.).

Acid Cleavage of V.—A mixture of 2.21 g. of octahydro-α,α′-difuryl, 2 cc. of glacial acetic acid, and 2 cc. of concentrated hydrochloric acid was heated on the steam-bath (88°) for two hours, the solution acquiring a brown color. After evaporation at reduced pressure the remaining oil was neutralized with solid sodium carbonate and distilled, giving a fore-run of 0.98 g. of starting material, b. p. 75° (12 mm.), and a fraction (0.93 g.) boiling at 140–143° (12 mm.). This material, only grossly purified, was found to have approximately the composition of a chlorohydrin $C_8H_{15}O_2Cl$ (Calcd.: C, 53.9; H, 8.5; Cl, 19.8. Found: C, 54.9; H, 8.3; Cl, 18.6). A diester was obtained by heating 0.08 g. of the substance with 0.2 g. of 3,5-dinitrobenzoyl chloride on the steam-bath for six hours. The mixture was treated with 1 *N* sodium hydroxide at room temperature, and after the excess reagent had been destroyed the extracted oil was caused to crystallize from alcohol–ether (0.1 g.). The substance has no m. p. but decrepitates with explosive violence. It is sparingly soluble in the usual solvents and decomposes easily. For purification it was dissolved in alcohol (15 cc.) and the solution allowed to evaporate, giving hexagonal crystals. The analysis corresponds approximately to the formula of a dinitrobenzoate of the glycol corresponding to the chlorohydrin.

Anal. Calcd. for $C_{22}H_{20}O_{18}N_4$: N, 10.22. Found: N, 10.71.

The crystalline derivative (32 mg.) on hydrolysis with 0.5 *N* alkali gave 20 mg. of 3,5-dinitrobenzoic acid.

α-Acetotetrahydrofuran (VI).—The starting material, **tetrahydrofuroamide** was prepared by the hydrogenation of recrystallized commercial furoamide in alcohol at atmospheric pressure and room temperature using 10% palladium charcoal catalyst. Purified by crystallization from benzene and distillation, the substance boiled at 135–138° (10 mm.) and showed a wide range of m. p. (65–76°). The composition (C, 52.3; H, 7.2) is close to that calculated for $C_5H_9O_2N$ (C, 52.1; H, 7.8). Wienhaus and Sorge[15] give about the same b. p. but state that this was at 20 mm.; they make no mention of the range in m. p.

This amide (9.8 g.) was suspended in a Soxhlet thimble in the drip from a condenser in a flask containing the Grignard reagent prepared from 8.5 g. of magnesium, 250 cc. of ether, and excess methyl chloride. As the amide was carried into the solution on refluxing a vigorous reaction ensued with separation of a white complex. After refluxing and stirring for forty-five hours, the mixture was treated with water and 20 cc. of glacial acetic acid and extracted thoroughly with ether. The oil from the ether on first distillation afforded 5.9 g. of colorless ketone, b. p. 53–58° (10 mm.). After three further distillations the substance boiled at 52.3–54.8° (10 mm.); the analysis indicates that it probably contained some water (Calcd.: C, 63.1; H, 8.8. Found: C, 62.4; H, 8.9).

(13) Reichstein, Grüssner and Zschokke, *Helv. Chim. Acta*, **15**, 1068 (1932).

(14) Kondo, Suzuki and Takeda, *J. Pharm. Soc. Japan*, **55**, 142 (1935).

(15) Wienhaus and Sorge, *Ber.*, **46**, 1930 (1913).

For characterization the aceto compound (0.15 g.) was refluxed in alcohol (10 cc.) and acetic acid (5 drops) with 2,4-dinitrophenylhydrazine (0.2 g.). The product separating in bright yellow crystals (0.24 g.) proved to be a mixture of stereoisomers present in about equal amounts. Fractional crystallization from alcohol gave orange plates, m. p. 122–124°, and yellow needles, m. p. 135–136°, of the isomeric **2,4-dinitrophenylhydrazones.**

Anal. Calcd. for $C_{12}H_{14}O_5N_4$: C, 48.98; H, 4.79; N, 19.04. Found, plates: C, 48.92; H, 4.73; N, 18.89. Found, needles: C, 48.92; H, 4.59; N, 18.75.

Action of Alkali on α-Acetotetrahydrofuran.—The ketone (2 g.) was refluxed for two hours with 16 cc. of alcohol and 4 cc. of 10 *N* sodium hydroxide, 10 cc. of alcohol was added to the two-phase, dark red mixture and refluxing was continued for two hours. After removing the alcohol at reduced pressure the alkaline liquor was extracted with ether. Distillation gave a small fraction (0.35 g.) of colorless liquid of b. p. close to that of the starting material (61–63° at 10 mm.). The remainder was a dark red oil which did not distil to an appreciable extent up to 190° (8 mm.). In another experiment the proportion of red oil was about the same after refluxing for only one hour. This oil seemed to contain an alcoholic reaction product for there were indications of interaction with dinitrobenzoyl chloride in pyridine and with both phenyl isocyanate and α-naphthyl isocyanate; the products were obtained only as oils. There was no reaction with dinitrophenylhydrazine and the reagent was recovered unchanged.

Summary

Spectrographic evidence confirms the previous indications that anhydrosarsasapogenoic acid contains an α,β-unsaturated carbonyl group and that sarsasapogenoic is a non-conjugated carbonyl compound. Another compound of the sapogenoic acid type has been obtained by the oxidation of sarsasapogenone, and a previously described oxidation product has been recognized as desoxysarsasapogenoic acid. Anhydrotetrahydrosarsasapogenoic acid shows no selective absorption in the ultraviolet and hence does not contain a carbonyl group as previously supposed; a new formula is suggested.

Octahydro-α,α′-difuryl, examined as a possible model for the Tschesche-Hagedorn formulation of the side chain, exhibits sensitivity to acids comparable with that characteristic of the sapogenins. It is considered that this formulation accounts satisfactorily for the acid-specific reactions as well as for the oxidation results.

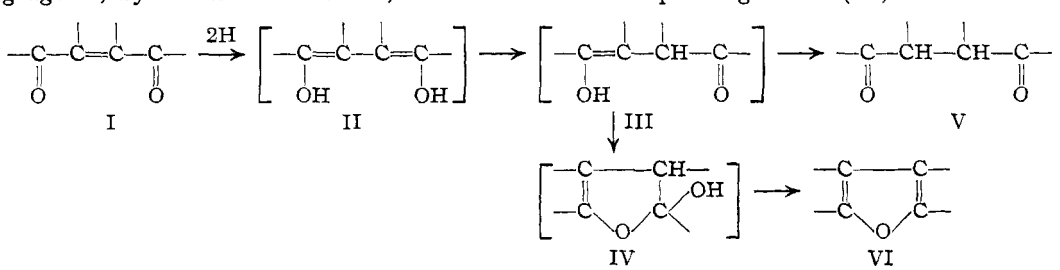
CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS RECEIVED MAY 17, 1939

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

The Mechanism of Reduction of Conjugated Systems with Terminal Carbonyl Groups. Dienols Obtained from Unsaturated 1,4-Diketones[1]

BY ROBERT E. LUTZ AND WILLIAM G. REVELEY

There is definite evidence that reductions of unsaturated 1,4-diketones by means of soluble reducing agents, by metal combinations, and even by catalytic hydrogen under certain conditions, proceed largely if not exclusively through 1,6-addition of hydrogen or its equivalent at the oxygen atoms with the formation of intermediate dienols (II) which correspond to hydroquinones formed in the reduction of quinones, but which are unstable and ketonize quickly to the saturated 1,4-diketones (V) or undergo dehydration to the corresponding furans (VI).[2]



The furans probably are not formed directly from the dienol but rather through rearrangement to the monoenol III, cyclization to IV, and finally loss of water. In support of this sequence of changes mention should be made of the formation of the furan from the monoenol produced by 1,4-

(1) This paper was presented at the Baltimore meeting of the American Chemical Society, April 4, 1939.

(2) *Cf.* (a) Conant and Lutz, THIS JOURNAL, **45**, 1047 (1923) (b) Lutz, *ibid.*, **51**, 3008 (1929); (c) Lutz and Palmer, *ibid.*, **57**, 1947 1953, 1957 (1935).