fins containing above 60% 3,3-dimethylbutene-1, above 20% 2,3-dimethylbutene-1, and below 10% of 2,3-dimethylbutene-2. Brooks, Howard and Crafton[2] obtained essentially the same results.

However, in the course of the preparation of 2,3-dimethylbutane and 2,2-dimethylbutane for the purpose of determining their *p–v–T* relations, it was found that the state of activity of the catalyst is the important factor in determining the yields of the three butenes. By employing a commercial catalyst,[3] the yields from the dehydration were 16% 3,3-dimethylbutene-1, 32% of 2,3-dimethylbutene-1, and 52% of 2,3-dimethylbutene-2. This order of percentage of yield is the reverse of those of the previous workers.

Following the procedure of Brooks, Howard and Crafton[2] *t*-butylmethylcarbinol was dehydrated by passing the vapors through a Pyrex 172-glass tube (1.5 × 100 cm.) filled with the commercial alumina. The tube was slanted slightly and the alcohol was added at a rate of 60 ml. per hour; the temperature of this electrically heated tube was maintained at 293–305°. The product, which contained none of the original alcohol, was separated from the water and was dried by contact with anhydrous sodium sulfate. A mixture of 1750 ml. of olefins was obtained from 1820 ml. of the alcohol.

Fractionation of this mixture of olefins through a 2.5 × 200 cm. Stedman packed column gave fractions with refractive indices as indicated in Fig. 1. Not including the column "hold-up," the distillation resulted in 16% of 3,3-dimethylbutene-1, 32% of 2,3-dimethylbutene-1, and 52% of 2,3-dimethylbutene-2 by volume.

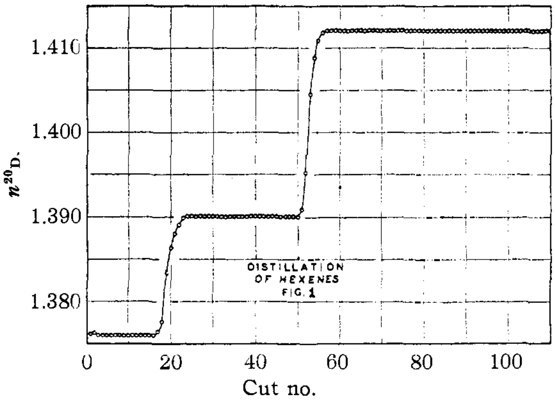

Fig. 1.—Distillation of hexenes.

The above procedure was repeated carefully, employing an ordinary Pyrex tube instead of the Pyrex-172 tube; essentially the same results were obtained.

DEPARTMENT OF CHEMISTRY
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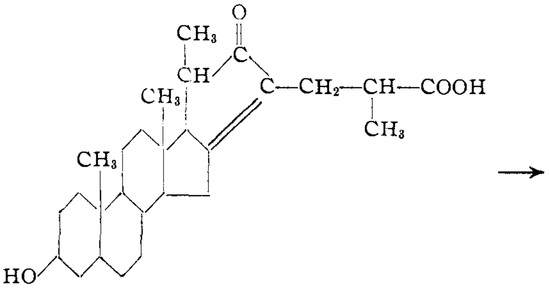
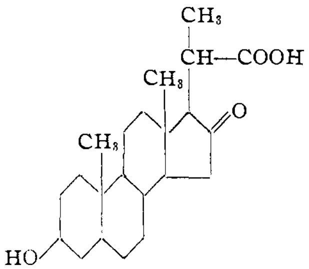
Sterols. CXXII. Sapogenins. XLIX. The Structure of the Side Chain of Sarsasapogenin. Anhydrosarsasapogenoic Acid

BY RUSSELL E. MARKER, ANTHONY C. SHABICA AND D. L. TURNER

The experimental work presented indicates that the formula for anhydrosarsasapogenoic acid is I and is not that discussed by Fieser and Jacobsen.[1] We wish to thank Parke, Davis and Company for their assistance.



I



II

Experimental Part

Ozonolysis of Anhydrosarsasapogenoic Acid.—Oxygen containing 2% ozone was passed through a solution of 1.5 g. of pure anhydrosarsasapogenoic acid in 200 cc. of chloroform at 0° for eighteen minutes. The ozonide was decomposed and the product was crystallized from ether–pentane; m. p. 283° dec. When mixed with 3(*β*)-hydroxy-16-keto-*bis-nor*-cholanic acid (II), m. p. 285° dec., there was no depression in melting point.

Anal. Calcd. for $C_{22}H_{34}O_4$: C, 72.9; H, 9.5; neut. equiv., 362. Found: C, 72.6; H, 9.4; neut. equiv., 367.

Reduction with sodium in absolute alcohol gave a product which was crystallized from ether–pentane; m. p. 200–202°. It was a lactone, and when mixed with sarsasapogenin lactone, m. p. 200–202°, there was no depression in melting point.

Anal. Calcd. for $C_{22}H_{34}O_3$: C, 76.25; H, 9.9. Found: C, 76.2; H, 10.0.

When refluxed with acetic anhydride it gave a lactone acetate, m. p. 182–184°, which gave no depression in melting point when mixed with an authentic sample of sarsasapogenin lactone acetate.

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(2) Brooks, Howard and Crafton, *J. Research Natl. Bur. Standards*, **24**, 33 (1940).

(3) "Hydralo," J. T. Baker Chemical Co., Lot No. 6340.

(1) Fieser, *et al.*, THIS JOURNAL, **60**, 2753 (1938); **61**, 1849 (1939).

Summary.—Ozonolysis of anhydrosarsasapogenoic acid gave 3(β)-hydroxy-16-keto-*bis-nor*-cholanic acid, thus establishing structure I and eliminating the formula earlier suggested by Fieser.

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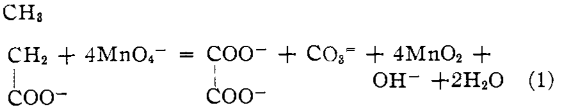
Tracer Studies with Radioactive Carbon: The Oxidation of Propionic Acid

BY P. NAHINSKY AND S. RUBEN

Using radioactive carbon,[1] C^{14}, as a tracer we have investigated the oxidation of propionic acid with (1) alkaline permanganate and (2) dichromate in acid solution. Propionate is converted to oxalate and carbonate[2] by alkaline permanganate. The reaction may be represented by the equation



$$\begin{array}{l} CH_3 \\ CH_2 + 4MnO_4^- = \underset{\displaystyle COO^-}{COO^-} + CO_3^= + 4MnO_2 + \\ | \qquad\qquad\qquad\qquad\qquad\qquad OH^- + 2H_2O \quad (1) \\ COO^- \end{array}$$

This reaction is followed by the slow oxidation of oxalate. (The ΔF^0_{298} for the oxidation of $C_2O_4^=$ by alkaline permanganate is ∼ −250 kcal.[3]) However under certain conditions (temperature of ∼100° and ∼2 *M* OH^-) the reaction rates are sufficiently different so that the oxalate/carbonate ratio is close to 1.

Employing short-lived radio-carbon, C^{11} (twenty-one minute half-life), reaction (1) was used[4] to determine the distribution of labelled carbon in the propionic acid formed from glycerol[5,6] by the propionic acid bacteria in the presence of $C^{11}O_2$. From 70 to 75% of the radiocarbon was found[4] in the oxalate fraction and 25 to 30% in the carbonate. Also in a single experiment the barium salt of the labelled propionate was thermally decarboxylated into (presumably) $(C_2H_5)_2CO$ and barium carbonate. The activity of the ketone was ∼5–7 times that found in the barium carbonate; however, this experiment was incomplete because the molal ratio of ketone/carbonate recovered was not measured. It was prematurely concluded[4] that the C* was randomly distributed in the propionic acid. Further work[7,8] has shown this conclusion to be erroneous and the C* to be present only in the carboxyl group. Thus it was considered of interest to study the mechanism of the propionate oxidation and in particular to answer the question: does the $CO_3^=$ come from the carboxyl group, the α- or β-carbon or from all positions of the propionic acid?

It is apparent that the use of labelled carbon affords a direct method of study and we have therefore synthesized propionic acid ($C_2H_5C^*$-OOH) with radiocarbon in the carboxyl group by means of the reaction between C^*O_2 and C_2H_5-MgBr. 1.58×10^{-3} mole of C^*O_2 was shaken with 6×10^{-3} mole of C_2H_5MgBr in ether for about thirty minutes at room temperature and the excess Grignard reagent hydrolyzed by careful addition of water. Excess solid silver sulfate was added to precipitate silver bromide and the propionic acid separated from this mixture by acidification with sulfuric acid and steam distillation. The propionic acid formed was subjected to a Duclaux distillation and the constants found to agree to within 1% with those obtained using reagent propionic acid. Over 90% of the C^*O_2 was converted into propionic acid. 9×10^{-4} mole of the $C_2H_5C^*OOH$ was treated with $\sim 4 \times 10^{-3}$ mole of sodium permanganate in 2 *N* sodium hydroxide at 100°. Under these conditions reaction (1) is complete within two hours The excess MnO_4^- was reduced in the cold with hydrogen peroxide and the manganese dioxide centrifuged off. The solution was acidified and the carbon dioxide swept out by a stream of nitrogen and absorbed in calcium hydroxide solution. The calcium carbonate was filtered, washed, dried, and weighed. The oxalate was precipitated as calcium oxalate in slightly acid solution. The radioactivity of these fractions was measured by means of a screen wall Geiger counter. The results are tabulated in Table I.

TABLE I

Moles $CO_3^=$ obtained	Moles[a] $C_2O_4^=$ obtained	Activity, counts/min. $CO_3^=$	Activity, counts/min. $C_2O_4^=$
9×10^{-4}	9.7×10^{-4}	45 ± 3	136 ± 3

[a] The oxalate value is high, probably due to hydrate formation.

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(1) Ruben and Kamen, *Phys. Rev.*, **57**, 549 (1940); **59**, 349 (1941).

(2) Przewalsky, *J. prakt. Chem.*, **88**, 500 (1913).

(3) *Cf.* "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," by W. M. Latimer, Prentice-Hall, Inc., New York, N. Y., 1938, p. 302.

(4) Carson, Foster, Ruben and Kamen, *Science*, **92**, 433 (1940).

(5) Carson and Ruben, *Proc. Nat. Acad. Sci.*, **26**, 422 (1940).

(6) Wood, Werkman, Hemingway and Nier, *J. Biol. Chem.*, **135**, 789 (1940).

(7) Carson, Foster, Ruben and Barker, *Proc. Nat. Acad. Sci.*, **27**, 229 (1941).

(8) Wood, Werkman, Hemingway and Nier, *Proc. Soc. Exptl. Biol. Med.*, **46**, 313 (1941).