TABLE I

PHYSICAL AND CHEMICAL CONSTANTS OF AMARANTHUS RETROFLEXUS SEED OIL

Specific gravity (24°/4°)	0.9236
Refractive index (Abbe 25°)	1.4751
Iodine number (Hanus)	89.9
Saponification value	187.4
Unsaturated acids (basis of oil) (cor. %)	71.6
Saturated acids (basis of oil) (cor. %)	18.6
Acetyl value	14.4
Mean molecular weight saturated acids	263.0
Mean molecular weight unsaturated acids	302.0
Iodine number of unsaturated acids	122.0
Iodine number of saturated acids	22.5
Unsaponifiable matter, %	7.6
Acid value	3.9

develop a practical micro distillation unit for work at low pressure (1–4 mm.) which would have a low hold up and high efficiency.

Wyman and Barkenbus[4] have developed such a still based on the use of a spinning band in which the successful separation of the methyl esters of stearic and palmitic acids was reported. Since their column was not available in this Laboratory, another still based on a different principle was devised.

A small distilling unit constructed on the same principle as the Booth column[5] was designed. The still, one hundred centimeters over-all, was constructed from three concentric glass tubes and a glass rod. A cold finger served as the condensing unit.

Eighteen gage nichrome wire one turn per centimeter wound around a 6-mm. Pyrex rod and then inserted into a close fitting Pyrex tube served as the fractionating unit. This arrangement forced all the vapors up a spiral path between the two concentric walls.

A 30-mm. glass jacket, around which was wound nichrome wire, and an outer 50-mm. Pyrex glass tube provided the means of maintaining adiabatic conditions. The heating element was wound almost to the take off.

A thermometer was placed in the annular space between the fractionating unit and the outer jacket. The temperature of the column was controlled by means of a variable transformer (Adjustavolt) while the distillation flask was heated by means of a phosphoric acid bath.

Since no thermometer was provided at the take off, samples were removed at frequent intervals and compared by means of a refractometer.

Unsaturated Acids.—The unsaturated acids were separated by the lead salt-ether method.[3] Eight grams of methyl esters was prepared and about 3 g. then distilled at 2 mm. using the micro distillation apparatus described above. Various fractions were collected and characterized by their refractive indices.

The first and second fractions averaged 250 mg. and gave refractive indices at 25° of 1.4550 and 1.4574, respectively; next four fractions (3–6), averaging 430 mg. each, gave 1.4580 ± 0.0001, while the two remaining fractions (7–8) of 300 mg. each gave 1.4692 and 1.51; 150 mg. of material was unrecovered. The saponification equivalent of fraction 4 was 284, the iodine no. 147.1, and the percentage composition 77.1% C and 11.62% H. From the data it appears that fractions 3–6 are composed of a mixture of unsaturated acids.

The hydrogenation of fraction 5 gave a solid ester, with iodine no. of 11.7, percentage composition of 76.0 C and 12.5 H, and m. p. 37°. This agrees fairly well with corresponding data for pure methyl stearate (76.4% C, 12.8% H, and m. p. 38°) reported in literature. A further confirmation was the anilide m. p. 93° (reported 93.6°). From these data it is evident that the unsaturated fraction was composed largely of eighteen carbon atom acids, probably oleic and linoleic acids. Calculations from the iodine value (122) of the unsaturated acids indicate the presence of 46% oleic and 25% linoleic acids on the basis of the original oil.

Saturated Acids.—The mean molecular weight of the saturated fraction as obtained from the lead salt-ether separation was 263.0. This lies between the values for palmitic and stearic acids, indicating a mixture. Four and one-half grams of methyl esters was fractionally distilled at 3 mm. pressure. Various fractions were collected and characterized by their refractive indices.

The first five fractions collected, averaging about 400 mg. apiece, gave a refractive index at 45° of 1.4311 ± 0.0001 and a saponification equivalent of 271 ± 1, which agrees accurately with the properties of methyl palmitate. A further confirmation was the percentage composition, namely, 75.6 C and 12.5 H, of fraction 2 and its melting point, 29°, which agrees almost exactly with the corresponding data reported for methyl palmitate (75.6% C, 12.6% H, and 29°). The anilide of the fourth fraction melted at 87°, while the reported value for the anilide of palmitic acid is 87.5°. Three additional fractions were collected, giving refractive indices of 1.4353, 1.4376 and 1.4407, respectively, which agrees very closely with the properties and refractive index of methyl stearate. The saponification equivalents were, respectively, 278, 278, 292 and 296, the latter figure agreeing excellently with the saponification equivalent of pure methyl stearate. The percentage composition (76.3 C and 12.3 H) and the melting point, 34–36°, agreed closely with the values reported in the literature, namely, 76.4 C, 12.8 H and 38°. From these data it appears that the saturated fraction consists principally of palmitic acid with a small percentage of stearic acid. Calculations on the basis of the saponification equivalent gave a value of 16.9% palmitic and 1.7% stearic acids in the original oil.

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RECEIVED MAY 20, 1941

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[4] F. W. Wyman and C. Barkenbus, *Ind. Eng. Chem., Anal. Ed.*, **12**, 658 (1940).

[5] H. S. Booth and A. R. Bozarth, *Ind. Eng. Chem.*, **29**, 470 (1937).

The Vapor Phase Catalytic Conversion of Tertiary Butylmethylcarbinol

BY E. A. KELSO, GEORGE WASH, J. T. HORECZY, BILLIE SHIVE WITH W. A. FELSING

Cramer and Glasebrook[1] reported that the vapor phase dehydration of *t*-butylmethylcarbinol over activated alumina yielded a mixture of ole-

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[1] Cramer and Glasebrook, THIS JOURNAL, **61**, 230 (1939).

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.

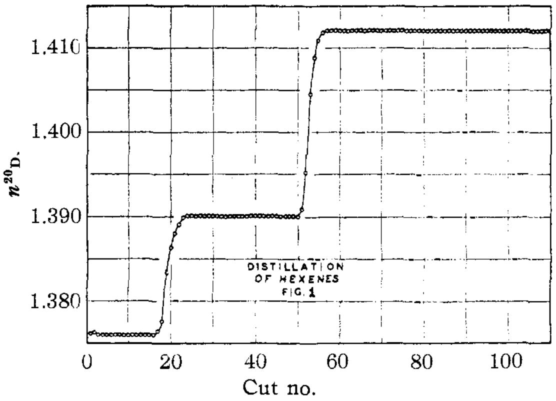

Fig. 1.—Distillation of hexenes.

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

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RECEIVED MAY 26, 1941

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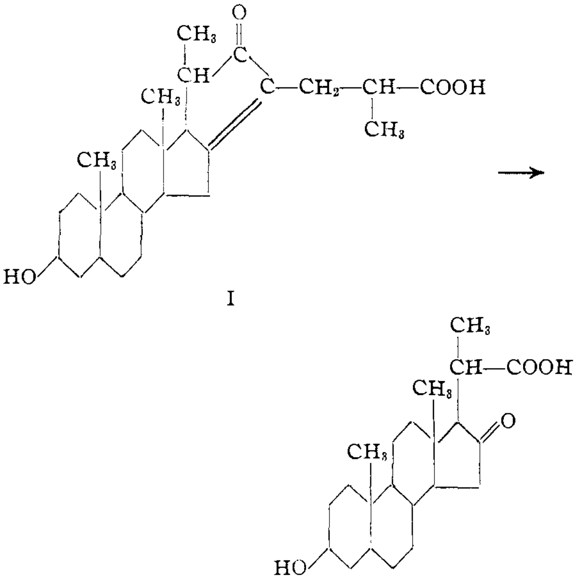
[2] Brooks, Howard and Crafton, *J. Research Natl. Bur. Standards*, **24**, 33 (1940).

[3] "Hydralo," J. T. Baker Chemical Co., Lot No. 6340.

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



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II

and is not that discussed by Fieser and Jacobsen.[1] We wish to thank Parke, Davis and Company for their assistance.

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