from 95% ethanol until a constant melting point was obtained. The yield, in general, ranged from 40–75%.

DEPARTMENT OF PHARMACOLOGY
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Preparation of Methyl 2,3,4-Triacetyl-α-D-xyloside[1]

BY ROY L. WHISTLER, K. ANN KIMMELL AND DONALD F. DURSO

During the course of work in this Laboratory it became necessary to prepare methyl 2,3,4-triacetyl-α-D-xylopyranoside in fairly large quantities. Direct preparation of this compound from D-xylose involves the preparation of pure methyl α-D-xyloside and subsequent acetylation.[2] The procedure adopted in this work was to acetylate commercially available methyl β-D-xyloside to yield the corresponding triacetate,[3] from which the desired compound was easily prepared by isomerization with boron trifluoride using the procedure of Lindberg.[4] The yield of crystalline product was 85%.

Experimental

Methyl 2,3,4-Triacetyl-β-D-xyloside.—Commercially available crystalline methyl β-D-xyloside (15.00 g.) was acetylated at 110° with sodium acetate and acetic anhydride. The acetate was isolated in the usual manner and recrystallized from 95% ethanol. The yield was 23.85 g. of material whose m.p. 114.5–115.5° and $[\alpha]^{25}\text{D}$ −61.2 (*c*, 2.42 in chloroform) agreed with the constants previously reported.[3]

Anal. Calcd. for $C_6H_9O_5(CH_3CO)_3$: acetyl, 44.49. Found: acetyl, 44.3.

Methyl 2,3,4-Triacetyl-α-D-xyloside.—The β-compound (5.00 g.) was dissolved in 150 ml. of dry chloroform and the solution saturated with BF_3. Saturation was indicated by the formation of a white gelatinous precipitate in 10 min. The flow of gas was interrupted and the reaction flask stoppered. After 24 hours, the solution was treated with two 100-ml. portions of saturated sodium bicarbonate solution followed by three 150-ml. washes with water. The chloroform solution was dried over anhydrous sodium sulfate. Upon removal of the chloroform the product crystallized spontaneously. The yield was 4.29 g. After recrystallization from 95% ethanol, m.p. was 86–87° and $[\alpha]^{25}\text{D}$ +120.1 (*c*, 1.59 in chloroform). These values agreed with those previously reported for the desired product.[2]

Anal. Calcd. for $C_6H_9O_5(CH_3CO)_3$: acetyl, 44.49. Found: acetyl, 44.4.

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[1] Paper No. 528 of the Purdue Agricultural Experiment Station.

[2] C. S. Hudson and J. K. Dale, THIS JOURNAL, **40**, 997 (1918).

[3] J. K Dale, *ibid.*, **37**, 2745 (1915).

[4] B. Lindberg, *Acta Chem. Scand.*, **2**, 426 (1948).

DEPARTMENT OF AGRICULTURAL CHEMISTRY
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RECEIVED MARCH 12, 1951

β-Amyrin from *Chimaphila umbellata*[1a]

BY F. P. VEITCH, JR., AND PEARL ADAIR WELTON[1b]

During our investigation of the plant *Chimaphila umbellata* as a possible source of steroids having an oxygen function in the 11 or 12 position, a white crystalline material was isolated in 0.25% yield. From the physical constants of this compound and its derivatives (Table I) we have concluded that it is β-amyrin, a substance not previously reported as being present in this plant.

Experimental

Four kilograms of air dry *Chimaphila umbellata* was obtained in a finely divided state by the use of a Williams crusher, rollers, and a Wiley mill. The finely ground material was treated by essentially the same process as that described by Marker[2] for the isolation of sapogenins from plant sources. Upon concentration of the final ethereal extract and addition of acetone, about 20 g. of crude crystalline material precipitated. Purification of this material was effected by recrystallization from acetone followed by formation of the acetate which could be crystallized from ethyl acetate. Saponification of the acetate followed by crystallization of the regenerated compound from ethyl alcohol gave 8.5 g. of material (0.21% yield based on the weight of air-dry plant) having the following characteristics: m.p. 200°; $[\alpha]^{20}\text{D}$ +87.7° (in $CHCl_3$).

Anal. Calcd. for $C_{30}H_{50}O$: C, 84.43; H, 11.82. Found: C, 84.47, 84.58; H, 12.00, 12.00.

The acetate, benzoate and *p*-nitrobenzoate of this compound were prepared according to standard procedures. The physical constants of these derivatives and their analyses are summarized in Table I.

TABLE I[a]

			Analyses, %			
			Found[c]		Calculated	
Compound	M.p.,[b] °C.	$[\alpha]^{20}\text{D}$[d]	Carbon	Hydrogen	Carbon	Hydrogen
β-Amyrin	200	+87.7	84.47	12.00	84.43	11.82
Acetate	243	+80.66	82.02	11.22	82.00	11.18
Benzoate	232	.....	83.68	10.57	83.71	10.26
p-Nitrobenzoate	257	.....	...	...	...	...

[a] The values reported here are in agreement with the values reported by other workers: *cf.* L. C. King, *et al.*, THIS JOURNAL **65**, 1168 (1943); A. Vesterburg, *Ber.*, **23**, 3186 (1890); N. H. Cohen, *Rec. trav. chim.*, **28**, 391; G. L. Powers, and W. E. Powers, *Pharm. Assoc.*, **29**, 175 (1940). [b] All melting points were determined on a Fisher-Johns melting point block. [c] We are indebted to Mrs. Mary Aldridge for the micro analyses reported here. [d] All rotations are in chloroform.

Values of 411 and 443 g. were obtained by the Rast method of molecular weight determination on the isolated compound, and 423 g. by the saponification method of the acetate. β-Amyrin has a molecular weight of 426 g.

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[1] (a) Obtained from S. B. Penick, New York. (b) Taken from a thesis submitted to the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Master of Science.

[2] R. Marker, *et al.*, THIS JOURNAL, **69**, 2167 (1947).

DEPARTMENT OF CHEMISTRY
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RECEIVED MARCH 7, 1951

The Melting Point and the Heat of Sublimation of Plutonium Trifluoride[1]

BY EDGAR F. WESTRUM, JR., AND JAMES C. WALLMANN

Careful measurements by an effusion technique of the equilibrium vapor pressures over plutonium trifluoride (PuF_3) have been reported.[2a,b] The slight deviation from linearity of the log *p versus* $1/T$ plot was represented by these authors without a stated reason as two straight lines intersecting at 1169 ± 9°, which temperature was interpreted as the melting point of plutonium trifluoride.

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[1] Based on work reported in MB-IP 327, September 17, 1948, issued as Report UCRL-697 (May 19, 1950).

[2] (a) T. E. Phipps, G. W. Sears, R. L. Seifert and O. C. Simpson, *J. Chem. Phys.*, **18**, 713 (1950); (b) T. E. Phipps, G. W. Sears, R. L. Seifert, and O. C. Simpson, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 6.1a (McGraw-Hill Book Co., Inc., New York, N. Y., 1949).

The heat of fusion was reported as 7.9 ± 0.5 kcal. mole^{-1} with a heat of sublimation of 96.6 ± 0.5 kcal. mole.$^{-1}$ Inasmuch as the deviation from linearity may alternatively be accounted for by assuming a reasonable ΔC_p for the sublimation process and as the reported melting points are rather lower than would be expected from comparison with other fluorides,[3] we have undertaken a determination of the plutonium trifluoride melting point in the apparatus shown in Fig. 1. An inconclusive attempt to determine the melting point of 60 micrograms of plutonium trifluoride on a tantalum filament in purified argon yielding successive values of 1435, 1560 and 1635° has been reported by Robinson.[4] X-Ray diffraction examination indicated the formation of plutonium oxyfluoride (PuOF) in the sample. For the present work about 350 mg. of plutonium trifluoride was prepared by hydrofluorination in a platinum reactor[5] of uranium-free, spectroscopically pure plutonium dioxide. X-Ray diffraction examination and spectrochemical analyses after the measurements confirmed the purity and crystalline phase of the plutonium trifluoride and the absence of corrosion of the tantalum. The trifluoride was pelleted into an annular cylinder, placed in the tantalum crucible and a previously outgassed beryllia microfurnace. The microfurnace assembly was then placed within a bulb attached to a high vacuum apparatus. After outgassing the system, the transition temperature was then located by thermal analysis.

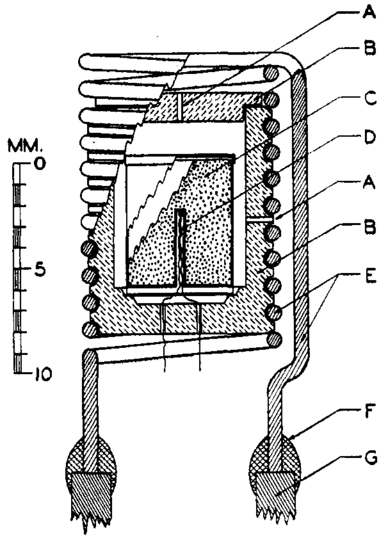

Fig. 1.—PuF_3 melting point apparatus: (A) optical pyrometric sighting ports, (B) beryllia furnace block and cover, (C) PuF_3 pellet in a covered tantalum crucible with entrant thermocouple well, (D) thermocouple, (E) 0.6 mm. diam. tungsten wire heating coil, (F) platinum weld, (G) 2 mm. diam. tungsten electrodes.

Continuous potential curves of the platinum *versus* platinum plus 10% rhodium thermocouple were automatically traced on a Leeds and Northrup Speedomax recorder checked against a Rubicon Type B potentiometer. These curves were essentially interpolations over ten to thirty degree ranges, the limits of which were established by direct optical pyrometer observation of the tantalum crucible at temperature equilibrium. Since essentially "black body" conditions obtain for the tantalum crucible, no emissivity correction is involved. Both optical pyrometers were calibrated against a standard lamp and also against the melting point of palladium in the present apparatus upon substitution of a beryllia liner. Direct observation of the fusion and solidification points with the optical pyrometer were found to agree with the thermocouple values and with each other regardless of the sign or magnitude of the thermal head. Corrections were applied for the transmissivity of the Pyrex window and after many transitions a compensation amounting to several degrees was required to correct for the sublimed film of plutonium trifluoride on the window. Repeated transitions were observed under various thermal heads both in high vacuum and under 10^{-2} atm. of argon, fusion temperature (11 observations): 1426 ± 2°; solidification temperature (13 observations): 1425 ± 3° the uncertainties indicated are average deviations. The plutonium trifluoride had fused, and no thermal effect was detected near the temperature previously interpreted as the melting point.[1] We believe that a phase transition with a molar enthalpy change greater than two kilocalories would have been apparent.

By use of the Gaussian criterion for closeness of fit, a three constant equation fitted by weighted least squares indicated as good agreement with the vapor pressure data reported by Phipps, *et al.*,[2] as did their two similarly fitted linear equations previously reported.

The ΔC_p of sublimation corresponding to this equation was -32 cal. mole^{-1} deg.$^{-1}$. A least squares treatment with an assumed value of $\Delta C_p = -15$ cal. mole^{-1} deg.$^{-1}$ and two arbitrary constants also fits the data well and yielded the equation

$$\log_{10} P_{\text{mm}} = -24{,}917T^{-1} - 7.5513 \log T + 38.920$$

valid from 1200 to 1660°K. for the dissociation pressure and a value of 89 kcal. mole^{-1} for the heat of sublimation of 1400°.

The experimental work was performed under the auspices of the U. S. Atomic Energy Commission at the University of California Radiation Laboratory.

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[3] L. Brewer, L. Bromley, P. W. Gilles and N. L. Lofgren, *ibid.*, Paper No. 6.40.

[4] H. P. Robinson, Manhattan Project Metallurgical Laboratory Report CN-2159 (Oct., 1944).

[5] E. F. Westrum, Jr., and LeRoy Eyring, THIS JOURNAL, **73**, 3399 (1951).

The Condensation of Ethyl Acetoacetate to Isodehydroacetic Acid and Ethyl Ester

BY RICHARD H. WILEY AND NEWTON R. SMITH[1]

The sulfuric acid catalyzed condensation of ethyl acetoacetate to a mixture of isodehydroacetic acid

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[1] The authors are indebted to the Research Corporation for a grant in support of this research.