of the residue from petroleum ether–benzene gave 1.4 g. of long white needles, m.p. 155–156°.

Anal. Calcd. for $C_9H_{12}ClN_3O$: N, 19.66. Found: N, 20.07.

2-Amino-4,6-dimethyl-5-α-chloroacetamidopyrimidine (IX) was prepared from 1.0 g. of 2,5-diamino-4,6-dimethylpyrimidine[2] (VII) and 0.82 g. of chloroacetyl chloride in 6 ml. of acetic acid and the product precipitated by the addition of a sodium acetate solution.

Recrystallization from water gave 1.4 g. of long white needles, m.p. 226–227°.

Anal. Calcd. for $C_8H_{11}ClN_4O$: C, 44.76; H, 5.17. Found: C, 44.88; H, 5.30.

2,4,6-Trimethyl-5-α-diethylaminoacetamidopyrimidine (II). A solution of 1.0 g. of 2,4,6-trimethyl-5-α-chloroacetamidopyrimidine (VIII) and 2 ml. of diethylamine in ethanol was refluxed for 5 hr. and then the solvent removed *in vacuo*. The product was extracted with benzene and precipitated by the addition of petroleum ether. Recrystallization from petroleum ether gave 0.9 g. of white crystals, m.p. 156–157°.

Anal. Calcd. for $C_{13}H_{22}N_4O$: N, 22.38. Found: N, 22.39.

2-Amino-4,6-dimethyl-5-α-diethylaminoacetamidopyrimidine (III). A solution of 1.0 g. of 2-amino-4,6-dimethyl-5-α-chloroacetamidopyrimidine (IX) and 1.2 g. of diethylamine in 40 ml. of ethanol was refluxed for 5 hr. after which the solvent was evaporated and the product precipitated by the addition of dilute alkali. Recrystallization from water gave white prisms (80% yield), m.p. 209–210°.

Anal. Calcd. for $C_{12}H_{21}N_5O$: C, 57.34; H, 8.42. Found: C, 57.53; H, 8.56.

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Synthesis of Vitamin A *p*-Phenylsulfonylbenzoate[1]

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Although numerous vitamin A derivatives have been reported in the literature[3,4,5] only a small number of these have been successfully used in the isolation and purification of small quantities of vitamin A from biological materials. For our degradation studies with biologically synthesized labeled vitamin A it is desirable to have a crystalline derivative of vitamin A which can be purified by crystallization and which contains the vitamin A molecule essentially intact. It is also necessary to have a derivative which will yield upon oxidation and steam distillation only the desired acidic degradation of products of vitamin A (*e.g.*, acetic acid and carbon dioxide). Examination of various vitamin A derivatives indicated that the ester form would satisfy the first requirement. However, none of the known ester derivatives appeared entirely suitable.

As most organic sulfones are crystalline solids and are easily crystallized, *p*-phenylsulfonylbenzoic acid was selected for investigation. The acid chloride of the above acid reacted with vitamin A to yield a white, crystalline solid. The ultraviolet spectrum of this compound exhibited the characteristic peak for vitamin A at 325 mμ and a second peak at 246 mμ indicating the presence of a sulfone group. The infrared spectra showed a strong absorption peak at 5.81 μ, which is characteristic of the ester linkage. Determination of the vitamin A component of the ester by the Carr-Price reaction[6] indicated that 51% (theoretical 51.5%) of the molecule was vitamin A. Furthermore, the experimental molecular weight of the ester was in agreement with the calculated molecular weight. Using this derivative it has been possible to isolate successfully and purify vitamin A from a 1:1 mixture of cholesterol and vitamin A.

EXPERIMENTAL

Melting points are uncorrected. *p*-Tolyl phenyl sulfone, *p*-phenylsulfonylbenzoic acid and *p*-phenylsulfonylbenzoyl chloride were prepared according to the procedure of Newell.[7]

Vitamin A p-phenylsulfonylbenzoate. *p*-Phenylsulfonylbenzoyl chloride (500 mg., 1.78 mmoles) was added to 30 ml. of dichloromethane in a two-necked flask equipped with reflux condenser and inlet tube for nitrogen. Dry pyridine (0.5 ml.) was added to the solution followed by 100 mg. (0.35 mmole) of vitamin A. The solution was mixed and heated at 52° for 5 hr. under nitrogen. The solution was evaporated to dryness under nitrogen and extracted three times with a mixture of petroleum ether (b.p. 37°) and dichloromethane (10/3, v./v.). The combined extracts were washed with 50 ml. of 1% sodium bicarbonate solution, 100 ml. of water, and dried over anhydrous sodium sulfate. The solution was taken to dryness under nitrogen and the solid extracted four times with 60 ml. of boiling petroleum ether (b.p. 37°). The extracts were combined in an Erlenmeyer flask, flushed with nitrogen, stoppered, and cooled to 0° for 16 hr. The resulting white crystals of vitamin A *p*-phenylsulfonylbenzoate (80% yield) after one recrystallization from petroleum ether (b.p. 37°) melted at 80–82°.

Anal. Calcd. for $C_{33}H_{38}SO_4$; C, 74.7; H, 7.2; mol. wt., 530. Found: C, 74.3; H, 6.9; mol. wt., 535; $E^{1\%}_{1\,cm}$ = 985 (325 mμ. petroleum ether).

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(2) From the Master's thesis of C. K. Payne, West Virginia University Medical Center, Morgantown, W. Va.

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