butoxy-diaminosilane. The presumed di-*t*-butyl-di-(2-ethylaminoethyl) silicate boiled at 285° at 740 mm. and did not decompose appreciably upon being refluxed at this temperature for one hour. Variation of conditions by adding the diaminosilane to the refluxing amino alcohol and *vice versa* appeared to give no improvement in eliminating or minimizing the formation of the side-product arising presumably by ester-interchange.

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Solubility and Specific Rotation of *l*-Ascorbyl Palmitate and *l*-Ascorbyl Laurate

BY DANIEL SWERN

Renewed interest in *l*-ascorbyl palmitate,[2] resulting from its recently reported antiscorbutic activity,[3] non-toxicity[4] and commercial availability[5] has prompted us to determine its solubility at 25° in some typical organic solvents, water, and cottonseed and peanut oils. For purposes of comparison, we also determined the solubility of *l*-ascorbyl laurate[2] in the two vegetable oils. We have also determined the specific rotation of both *l*-ascorbyl palmitate and laurate. With the exception of water and petroleum naphtha, the temperature coefficient of solubility is high. Benzene and ethyl acetate are two of the best crystallizing solvents for purifying the esters.

Experimental

Solubility Determinations.[6]—Solubility in petroleum naphtha, boiling range 63–70°, and water was determined on saturated solutions obtained by shaking the solvent with excess solute until equilibrium, ascertained by analysis, was attained. With all the other solvents, equilibrium was approached from the solution side by allowing excess solute to crystallize. Dissolved ester was determined either by titration with 0.1 *N* sodium hydroxide[2] or by evaporation of solvent. At least two determinations were run; precision of duplicates was about five parts per thousand. Solubility of *l*-ascorbyl palmitate in glycerol could not be determined because the solution was a thick gel. Its solubility, however, appeared to be low. Results are summarized in Table I.

Specific Rotation.—Specific rotation was determined with a Bellingham and Stanley Glass Scale polarimeter that could be read directly to 0.01°. A 5–10% solution of the ester in 95% alcohol and a 4.00-dm. tube were employed.

l-Ascorbyl palmitate: $[\alpha]^{25.5}D + 23.3°$ (8.086 g. per 100 ml. of 95% ethanol solution). *l*-Ascorbyl laurate: $[\alpha]^{25.5}D + 26.6°$ (5.014 g. per 100 ml. of 95% ethanol solution).

TABLE I

SOLUBILITY AT 25 ± 0.10°: *l*-ASCORBYL ESTERS

Solvent	Sol.[a] g./100 g.	Solvent	Sol.[a] g./100 g.
Palmitate		Palmitate	
Water[b]	0.56	Ethyl acetate	4.9
Petroleum naphtha[c]	0.00	Ethyl cellosolve[e]	>33.9
Ethanol 95%[d]	23.5	Peanut oil	0.18
Benzene	0.45	Cottonseed oil	0.22
Ethylene glycol	0.18	Laurate	
1,2-Propylene glycol	6.6	Peanut oil	0.11
Dioxane	19.0	Cottonseed oil	0.08

[a] By titration. [b] Solubility by evaporation 0.31 g./100 g. Small and probably variable quantities of solute emulsified, thus accounting for the poor duplication between the results by titration and by evaporation. [c] B. p. range 63–70°. Solubility by evaporation 0.01 g./100. [d] Solubility by evaporation 23.4 g./100. [e] Insufficient material to complete determination.

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Preparation of Fluorothiophene

BY ROBERT T. VANVLECK

Chloro- and bromothiophene are offered in the industrial market and iodothiophene is reported in the literature, but no reference has been made to fluorothiophene. This compound has been prepared in these Laboratories in small yields by the reaction of antimony trifluoride with iodothiophene in the presence of nitromethane as a solvent. The preparation of fluorothiophene from 2-iodothiophene indicates that the fluoro compound is the 2-isomer.

Nitroethane, nitropropane and *t*-butylthiophene were found not suitable as solvents for the reaction. Various other methods for preparing fluorothiophene proved unsuccessful; they include the reaction of antimony trifluoride with either chloro- or bromothiophene, the reaction of aluminum trifluoride with chlorothiophene, and the reaction of fluoboric acid with thiophene diazonium chloride. This last reaction was studied in an unsuccessful attempt to adapt Flood's synthesis of fluorobenzene[1] to the preparation of the thiophene analog. It is possible that the diazonium chloride was not obtained due to the instability of the aminothiophene.

Experimental

A mixture of 150 g. (0.72 mol) of iodothiophene and 43 g. (0.24 mole) of antimony trifluoride in 250 ml. of nitromethane was heated in a flask at reflux temperature (90–100°) for five hours; the product fluorothiophene distilled over through a small column as formed plus some

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) Swern, Stirton, Turer and Wells, *Oil and Soap*, **20**, 224 (1943).

(3) Ambrose and DeEds, *Arch. Biochem.*, **12**, 375 (1947).

(4) Fitzhugh and Nelson, *Proc. Soc. Exptl. Biol. Med.*, **61**, 195 (1946).

(5) Chas. Pfizer and Company, New York, N. Y.

(6) Daniels, Mathews and Williams, "Experimental Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1929, pp. 111 and 341.

(1) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 295.