Anal. Calcd. for $C_3H_5N_5$: C, 32.42; H, 4.54; N, 63.04. Found: C, 32.7, 32.5; H, 4.50, 4.72; N, 62.86.

Hydrogenation of 2.72 g. (0.098 mole) of 1-vinyl-5-aminotetrazole in glacial acetic acid at 50 p.s.i. using Adams platinum oxide as catalyst gave 2.70 g. (97.7%) of 1-ethyl-5-aminotetrazole, m.p. 149–150.5° after recrystallization from water. A mixture melting point with an authentic sample of 1-ethyl-5-aminotetrazole[10] was not depressed.

2-Vinyl-5-aminotetrazoles. The dehydrohalogenation of 40.47 g. (0.274 mole) of 2-(2-chloroethyl)-5-aminotetrazole was accomplished in the same manner as for the 1-isomer using potassium hydroxide in methanol. After evaporation of the methanol at reduced pressure, the crude product was extracted with three 50-ml. portions of methylene chloride. Distillation of the methylene chloride left 30 g. of oil which on distillation gave 23.39 g. (77.7%) of 2-vinyl-5-aminotetrazole, b.p. 75–77° at 0.8 mm., m.p. 47–49° after recrystallization from carbon tetrachloride. The melting point of a sample was unchanged by sublimation at reduced pressure.

Anal. Calcd. for $C_3H_5N_5$: C, 32.42; H, 4.54; N, 63.04. Found: C, 32.29; H, 4.65; N, 63.05.

1- and 2-Allyltetrazoles. A suspension of 70 g. (1.0 mole) of tetrazole in 400 ml. of 95% ethanol was neutralized to a phenolphthalein end point with a 50% aqueous solution of 41.2 g. (1.0 mole) of 97% sodium hydroxide. The suspension was heated to reflux, 121 g. (1.1 moles) of allyl bromide was added dropwise with stirring over a 10-min. period and the solution was refluxed overnight. The ethanol was then removed by distillation at atmospheric pressure and the residue was extracted with three 100-ml. portions of cold benzene. After drying the solution with anhydrous magnesium sulfate, the benzene was distilled at atmospheric pressure. The residue of mixed 1- and 2-allyltetrazoles was distilled at reduced pressures, yielding 36.3 g. (28.96%) of 2-allyltetrazole, b.p. 80–81° at 20 mm.

Anal. Calcd. for $C_4H_6N_4$: C, 43.62; H, 5.49; N, 50.89. Found: C, 43.51; H, 5.62; N, 51.22.

and 41.52 g. (37.36%) of 1-allyltetrazole, b.p. 101° at 1 mm.

Anal. Calcd. for $C_4H_6N_4$: C, 43.61; H, 5.49; N, 50.89. Found: C, 44.23; H, 5.45; N, 50.71.

1-Vinyl-4-methyl-5-iminotetrazole hydrochloride. 1-Vinyl-5-aminotetrazole (5.55 g., 0.05 mole) and 9.5 g. (0.055 mole) of redistilled methyl benzenesulfonate were mixed and heated on a hot plate in a small beaker. An exothermic reaction occurred when the temperature of the mixture reached about 100° and the beaker was removed from the hot plate. The reaction temperature rose spontaneously to 165°. After cooling, the mixture solidified. The product was dissolved in 50 ml. of methanol and made basic by the addition of 3.62 g. (0.055 mole) of potassium hydroxide in 25 ml. of methanol. The solution was then evaporated to dryness. The free base was extracted from the residue with three 50-ml. portions of chloroform and the insoluble potassium benzenesulfonate discarded. Evaporation of the chloroform solution yielded an oily yellow residue of 1-vinyl-4-methyl-5-iminotetrazole,[11] which was acidified with 5 ml. of concentrated hydrochloric acid. After the water was removed *in vacuo* on a steam bath, the 1-vinyl-4-methyl-5-iminotetrazole hydrochloride was recrystallized twice from 98% 2-propanol, yielding 2.56 g. (31.7%) of product, m.p. 214–215° (dec.).

Anal. Calcd. for $C_4H_6N_6Cl$: C, 29.73; H, 4.99; N, 43.35; Cl, 21.94. Found: C, 29.74; H, 5.73; N, 42.79; Cl, 21.73.

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Lucernic Acid, A New Triterpene from Alfalfa

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Interest in the possible toxic physiological activity of alfalfa (*Medicago sativa*) saponins in poultry and animal feeds has led to further investigation of these saponins and their aglycones. Recent manuscripts have described the isolation and characterization of medicagenic acid from the "cholesteride" saponins of alfalfa.[1,2] Further examination of the fractions obtained during the isolation of medicagenic diacetate has led to the isolation of a new triterpene, $C_{30}H_{46}O_7$, which is shown to be a trihydroxy, monolactone, monocarboxylic acid.

Characterization studies of this triterpene—now named lucernic acid[3]—demonstrated the presence of 3 easily acylable hydroxyl groups, as shown by the formation of the triacetate (II) at room temperature with pyridine–acetic anhydride. The infrared spectrum (KBr pellet) of II shows bands at 1775, 1730, and 1250 cm.$^{-1}$, corresponding to a 5-membered lactone, acetate, and C—O stretching adsorption. The presence of lactone was confirmed by the consumption of 5 equivalents (3 acetyls, a lactone, and a carboxyl) of alkali during saponification of II with 0.1*N* KOH in methanol; upon neutralization of the salt the lactone ring closed. II gives no color with tetranitromethane in glacial acetic acid or with the Liebermann-Burchard reagent and shows no high terminal ultraviolet adsorption.

Periodic acid oxidation of the methyl ester (III) resulted in the consumption of one equivalent of the reagent, thus demonstrating the existence of a 1,2-glycol moiety in lucernic acid.

Biogenetic relationship of I to triterpenes previously isolated from alfalfa[2,4] might lead one to expect a β-amyrin structure; present information, however, gives only very limited clues as to the location of the functional groups.

Final characterization of I will necessitate correlation with the structure of a known triterpene.

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EXPERIMENTAL

Lucernic triacetate. Preparation of the saponin,[2] sapogenin, and sapogenin acetate,[1] has been previously described. Purification was accomplished by chromatography of II on 37 times its weight of magnesia-silica gel. Elution of the chromatographic column with benzene-alcohol (95:5) and repeated crystallization from aqueous methanol gave platelets, m.p. 297–299° $[\alpha]_D^{26} = +7.7$ (*c*, 4.9),[5] which showed no high terminal adsorption in the U. V. and gave no color with either tetranitromethane in glacial acetic acid or the Liebermann-Burchard reagent.

λ_{max}^{KBr} 1775, 1730, 1250 cm.$^{-1}$ For analysis it was dried *in vacuo* at 130°.

Anal. Calcd. for $C_{36}H_{52}O_{10}$: C, 67.0; H, 8.1; CH_3CO, 20.0, neutral eq. 644. Found: C, 67.0; H, 8.1; CH_3CO, 20.3, neutral eq. 637.

II was quantitatively saponified with 0.1*N* alkali in methanol.

Anal. Calcd. for 5 equivalents per mole (3 acetyls, 1 carboxyl, and 1 lactone) and the consumption of 0.378 meq. of alkali. Found: 0.388 meq. alkali were consumed.

Methyl lucernate triacetate was prepared by treatment of an etheral solution of II with diazomethane. Recrystallization from aqueous methanol afforded rodlike crystals, m.p. 273–275°; $[\alpha]_D^{25} = -5.9°$ (*c*, 0.5).

$\lambda_{max}^{CCl_4}$ 1774, 1745 cm.$^{-1}$ $\lambda_{max}^{CS_2}$ 1235 cm.$^{-1}$ max

Anal. Calcd. for $C_{37}H_{54}O_{10}$. C, 67.5; H, 8.22; CH_3O, 4.71; CH_3CO, 19.6; mol. wt. 658. Found: C, 67.4; H, 8.32; CH_3O, 4.55; CH_3CO, 19.4; mol. wt. (Rast) 646.

Lucernic acid. Refluxing of II with 0.1*N* KOH in methanol, followed by neutralization, gave amorphous sapogenin. I proved to be almost insoluble in most organic solvents and could not be crystallized. $[\alpha]_D^{25} = +12.4°$ (pyridine) (*c*, 0.6).

λ_{max}^{KBr} 3155, 1745, 1704 cm.$^{-1}$

Anal. Calcd. for $C_{30}H_{46}O_7$: C, 69.2; H, 8.88. Found: C, 69.2; H, 8.86.

Methyl lucernate. Treatment of a suspension of I with diazomethane in ether gave crystalline III. Recrystallization from aqueous methanol afforded rodlike crystals, m.p. 347–350° $[\alpha]_D^{25} = +25.5°$ (*c*, 0.4).

λ_{max}^{KBr} 1758, 1724 cm.$^{-1}$

Anal. Calcd. for $C_{31}H_{48}O_7$: C, 69.9; H, 9.02; CH_3O, 5.82. Found: C, 69.9; H, 9.13; CH_3O, 5.71.

Periodic oxidation of methyl lucernate. 50 mg. of III was dissolved in 4 ml. absolute alcohol. To this solution was added 1 ml. of 0.63M H_5IO_6. The solution was left in the dark at room temperature and analyzed periodically by the standard As_2O_3 technique.

Anal. Calcd. for 1 glycol, or consumption of 0.0866×10^{-3} moles periodate. Found: 0.0833×10^{-3} moles of periodate were consumed.

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(5) All melting points were made on a Kofler block. Unless noted otherwise, rotations were measured in chloroform solution.

Organophosphorus Compounds. V.[1] Dialkyl Phosphorofluoridates

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Dialkyl phosphorofluoridates were first prepared in 1932 by Lange and Krueger[3] using silver phosphorofluoridate and alkyl iodide. They also observed the high toxicity of the compounds. Schrader[4,5] later elaborated a synthesis using halogen exchange of the corresponding dialkyl phosphorochloridates. McCombie and Saunders[6,7] also worked out this reaction independently. Chapman and Saunders[8] reacted phosphorus oxydichlorofluoride with alcohols to prepare dialkyl phosphorofluoridates.

We found considerable difficulty in the preparation of phosphorus oxydichlorofluoride as the main product, using the Swarts reaction.[9] Therefore, we investigated the use of the more readily available phosphorus oxyfluoride.

Phosphorus oxyfluoride was prepared by the Swarts reaction from phosphorus oxychloride without using antimony pentachloride catalyst with 94% yield (and 5% phosphorus oxydichlorofluoride).

$$POCl_3 + SbF_3 \longrightarrow POF_3 + SbCl_3$$

Similarly phosphorus oxyfluoride can be prepared from phosphorus oxybromide, according to Booth and Seegmiller.[10]

$$POBr_3 + SbF_3 \longrightarrow POF_3 + SbBr_3$$

During the course of our investigation we prepared dimethyl, diethyl, and diisopropyl phosphorofluoridate (DFP) from phosphorus oxyfluoride and the corresponding alcohols.

$$POF_3 + 2\ ROH \longrightarrow (RO)_2\ POF + 2\ HF$$

The HF was removed from the DFP before distillation by neutralization with dry ammonia or was bonded with pyridine.

There have been described the preparation of dialkyl phosphorochloridate under acid free conditions through the chlorination of dialkyl phosphite with *N*-chlorosuccinimide.[11] Previously,[12] we obtained dialkyl phosphorochloridates as acid

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