N-Methylnitraminoacetohydrazide (IV). To a solution of 180 ml. (2.39 moles) of 85% hydrazine hydrate and 200 ml. of methanol was added dropwise, with stirring, 235.2 g. (1.60 moles) of methyl *N*-methylnitraminoacetate. The temperature of the solution rose from 25 to 32°. After stirring for 30 min., the solution was cooled and a white solid precipitated. The product was collected, washed with cold methanol, and dried to give 179.3 g. (76.3%) of white solid, m.p. 81–84°. Recrystallization from ethanol raised the melting point to 84–85°.

Anal. Calcd. for $C_3H_8N_4O_3$: C, 24.32; H, 5.44; N, 37.83. Found: C, 24.70; H, 5.64; N, 38.00.

N-Methylnitraminomethyl isocyanate (VI). A mixture of 14.8 g. (0.1 mole) of *N*-methylnitraminoacetohydrazide, 125 ml. of water, and 125 ml. of chloroform was cooled to 0° and 9.2 ml. (0.11 mole) of 37% hydrochloric acid was added. Then a solution of 10.0 g. (0.11 mole) of 93% potassium nitrite in 20 ml. of water was added dropwise, keeping the temperature at 0–5°. The mixture was stirred for 15 min. and the chloroform layer was separated. The aqueous layer was extracted with two 150-ml. portions of chloroform. The combined chloroform extracts were washed with three 100-ml. portions of ice water, dried over sodium sulfate, and filtered. The solution was concentrated on the water aspirator at a temperature of 10–20° until the volume was decreased by half, to ensure the removal of the last traces of water. The solution was then warmed under a reflux condenser. At 40–50° the decomposition of the azide commenced. After the decomposition started, the solution was slowly heated to reflux. The solution was refluxed until the evolution of nitrogen had ceased (about 2 hr.) and concentrated *in vacuo*. The residue was distilled from a Claisen flask to give 9.0 g. (68.7%) of colorless liquid, b.p. 81–81.5° (2 mm.), n_D^{25} 1.4787.

Anal. Calcd. for $C_3H_5N_3O_3$: C, 27.70; H, 3.87; N, 32.30. Found: C, 27.32; H, 3.81; N, 32.74.

Methyl N-methylnitraminocarbamate (VII). A solution of 2.62 g. (0.02 mole) of *n*-methylnitraminomethyl isocyanate and 5 ml. of methanol was refluxed for 30 min. and concentrated *in vacuo* to give 3.0 g. (92.1%) of white needles, m.p. 65–67°. Recrystallization from methanol raised the melting point to 66–67°.

Anal. Calcd. for $C_4H_9N_3O_4$: C, 29.45; H, 5.56. Found: C, 29.76; H, 5.60.

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Reactions of Aliphatic Nitro Compounds

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The preparation of derivatives of the carboxylic acid groups in methyl 4,4-dinitropentanoate,[1] methyl 4-nitrazapentanoate,[2] and methyl 3-nitrazabutyrate[3] has been described. Aliphatic monoesters containing both the *gem*-dinitro and nitraza groups have also been reported. Feuer, Bachman, and May[4] prepared ethyl 3,5,5-trinitro-3-azapentanoate (I) and Frankel and Klager[5] reported the synthesis of methyl 3,5,5-trinitro-3-azahexanoate (II). Attempts by Feuer *et al.*[4] to hydrolyze I with concentrated hydrochloric acid resulted only in decomposition with evolution of oxides of nitrogen. The preparation of derivatives of the carboxylic acid group in II is reported in the present work.

$$\underset{\text{I}}{HC(NO_2)_2CH_2N(NO_2)CH_2CO_2C_2H_5}$$

$$\underset{\text{II}}{CH_3C(NO_2)_2CH_2N(NO_2)CH_2CO_2CH_3}$$

Hydrolysis of II with concentrated hydrochloric acid gave 3,5,5-trinitro-3-azahexanoic acid (II) in good yield, indicating that replacement of the acidic hydrogen atom in I with an alkyl group has a stabilizing influence on the molecule. Compound III was converted to 3,5,5-trinitro-3-azahexanoyl chloride (IV) and the corresponding azide (V). The azide was not isolated but decomposed *in situ* to form 2,4,4-trinitro-2-aza-1-pentyl isocyanate (VI). The isocyanate exploded violently on standing at ambient temperature but could be stored safely at −20° for several months. It reacted readily with methanol to form methyl *N*-(2,4,4-trinitro-2-aza-1-pentyl) carbamate (VII). Attempts to convert VI to 2,4,4-trinitro-2-aza-1-pentylamine hydrochloride (VIII) by treatment with concentrated hydrochloric acid were unsuccessful; the only compound isolated from this reaction was ammonium chloride.[6]

$$\text{II} \xrightarrow{\text{HCl}} \underset{\text{III}}{CH_3C(NO_2)_2CH_2N(NO_2)CH_2CO_2H} \xrightarrow{\text{SOCl}_2}$$

$$\underset{\text{IV}}{CH_3C(NO_2)_2CH_2N(NO_2)CH_2COCl}$$

$$\xrightarrow{\text{NaN}_3} \underset{\text{V}}{[CH_3C(NO_2)_2CH_2N(NO_2)CH_2CON_3]} \xrightarrow{\Delta}$$

$$\begin{tikzcd} & \underset{\text{VI}}{CH_3C(NO_2)_2CH_2N(NO_2)CH_2NCO} \arrow[ld, "CH_3OH"'] \arrow[d, "HCl"] \\ \underset{\text{VII}}{CH_3C(NO_2)_2CH_2N(NO_2)CH_2NHCO_2CH_3} & \underset{\text{VIII}}{CH_3C(NO_2)_2CH_2N(NO_2)CH_2NH_2 \cdot HCl} \end{tikzcd}$$

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[1] H. Schechter and L. Zeldin, *J. Am. Chem. Soc.*, **73**, 1276 (1951).

[2] M. B. Frankel and K. Klager, *J. Am. Chem. Soc.*, **78**, 5428 (1956).

[3] M. B. Frankel, *J. Org. Chem.*, **23**, 1811 (1958).

(4) H. Feuer, G. B. Bachman, and W. May, *J. Am. Chem. Soc.*, **76**, 5124 (1954).

(5) M. B. Frankel and K. Klager, *J. Am. Chem. Soc.*, **79**, 2953 (1957).

(6) The same results were observed in attempting to convert 2-nitrazapropyl isocyanate to 2-nitrazapropylamine hydrochloride.[3] This is in marked contrast to the facile preparation of 3-nitrazabutylamine hydrochloride from 3-nitrazabutyl isocyanate,[2] where the primary amino group is in a β position to the nitraza group.

EXPERIMENTAL[7,8]

3,5,5-Trinitro-3-azahexanoic acid (III). A mixture of 26.6 g. (0.10 mole) of methyl 3,5,5-trinitro-3-azahexanoate[6] and 75 ml. of concentrated hydrochloric acid was heated on the steam bath for 8 hr. On cooling, 15.1 g. (60.0%) of white solid separated, m.p. 133–136°. Recrystallization from ethylene dichloride raised the melting point to 139–140°.

Anal. Calcd. for $C_5H_8N_4O_8$: C, 23.82; H, 3.20; N, 22.22. Found: C, 23.96; H, 3.25; N, 22.56.

3,5,5-Trinitro-3-azahexanoyl chloride (IV). A mixture of 5.0 g. (0.02 mole) of 3,5,5-trinitro-3-azahexanoic acid and 25 ml. of redistilled thionyl chloride was refluxed for 8.5 hr. and concentrated *in vacuo* leaving 5.2 g. (96.8%) of white solid, m.p. 85–87°. Recrystallization from carbon tetrachloride raised the melting point to 87–88°.

Anal. Calcd. for $C_5H_7ClN_4O_7$: C, 22.19; H, 2.61; Cl, 13.10; N, 20.71. Found: C, 22.65; H, 2.95; Cl, 13.89; N, 21.27.

2,4,4-Trinitro-2-aza-1-pentyl isocyanate (VI). A solution of 35.1 g. (0.54 mole) of sodium azide in 250 ml. of water was cooled in an ice bath and a solution of 73.0 g. (0.27 mole) of 3,5,5-trinitro-3-azahexanoyl chloride in 200 ml. of acetone was added dropwise, keeping the temperature below 10°. The reaction mixture was stirred for 30 min. and extracted with three 150-ml. portions of chloroform. The chloroform solution was dried for 30 min. over sodium sulfate and placed in a one-liter flask arranged for distillation. About 110 ml. of chloroform was stripped off with the water aspirator to remove the last traces of water. The temperature was raised to 60° with a water bath and the azide was decomposed at atmospheric pressure. Dry chloroform was added periodically to keep the volume constant. After the nitrogen evolution had ceased, the solution was cooled to −10°, causing a white solid to separate. The product was collected and dried, the yield was 48.1 g. (72.0%), m.p. 97–100°. Recrystallization from ethylene dichloride raised the melting point to 102–103°. The compound exploded violently on standing at ambient temperatures but could be stored safely at −20° for several months.

Anal. Calcd. for $C_5H_7N_5O_7$: C, 24.10; H, 2.83; N, 28.11. Found: C, 24.31; H, 3.11; N, 28.05.

Methyl N-(2,4,4-trinitro-2-aza-1-pentyl) carbamate (VII). A solution of 2.49 g. (0.01 mole) of 2,4,4-trinitro-2-aza-1-pentyl isocyanate and 15 ml. of methanol was refluxed for 4 hrs. and concentrated *in vacuo* leaving a quantitative yield of white solid, m.p. 98–100°. Recrystallization from isopropyl alcohol raised the melting point to 100–102°.

Anal. Calcd. for $C_6H_{11}N_5O_8$: C, 25.63; H, 3.94; N, 24.91. Found: C, 25.75; H, 3.81; N, 24.67.

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[7] All melting points are uncorrected.

[8] Microanalyses by Dr. A. Elek, Elek Microanalytical Laboratories, Los Angeles, Calif.

Isolation of β-Sitosterol from *Cassia Absus*, Linn.

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In 1935 Ahmad[1] examined an oil obtained from *Cassia absus*, Linn., and determined its composition in terms of the percentages of fatty acid (80%), glycerol (10.4%), and nonsaponifiable matter (8.4%) present. The latter was not further investigated. In 1954 Sen Gupta *et al.*[2] obtained a 2.2 % yield of an oil upon extracting the seeds of Cassia with petroleum ether. They too determined the fatty acid composition of the oil and also isolated a nonsaponifiable fraction. This material, m.p. 130,° afforded a benzoate, m.p. 142°, and an acetate, m.p. 115°, but was not investigated further.

In following the procedure of Siddiqui *et al.*[3] for the isolation of the alkaloid *Chaksine* from the seeds of *Cassia absus*, an ether-soluble, water-soluble fraction was obtained in 2% yield. Saponification of this oily substance afforded a semisolid nonsaponifiable fraction in 5% yield. From this material, by direct crystallization, was obtained β-sitosterol, m.p. 137–138, $\alpha]_D^{25}$ −30°, $\lambda_{\max}^{\text{Nujol}}$ 3400 cm.$^{-1}$ (OH), 840, 803 (tri-substituted olefin). It afforded a benzoate, m.p. 139–140°, $\lambda_{\max}^{\text{Nujol}}$ 1700 cm.$^{-1}$(—COO—), 1604, 1591, 715 (C_6H_5—), 840, 800 (trisubstituted olefin), and an acetate, m.p. 126–128°. Reduction over platinum resulted in the uptake of one mole of hydrogen and the formation of stigmastanol, m.p. 139–140°, $\lambda_{\max}^{\text{Nujol}}$ 3230 cm.$^{-1}$ (OH), $\alpha]_D^{25}$ + 30°. The properties of the compound, its acetate, benzoate, and dihydro derivative agree with those reported by Bernstein and Wallis[4] for β-sitosterol isolated from cottonseed oil. It is likely that β-sitosterol was the material isolated in crude form by Sen Gupta *et al.*[2]

The mother liquors from the crystallization of β-sitosterol were acetylated and chromatographed on alumina. In this manner additional β-sitosterol was isolated (as its acetate) together with an oily saturated hydrocarbon of as yet unknown structure.

Note added in proof: Since the completion of this work, I. Sen Gupta and E. Mosettig, *J. Ind. Chem. Soc.* **35,** 210 (1958) have identified the material isolated in ref. 2 as β-sitosterol.

EXPERIMENTAL[5]

β-Sitosterol. One kilogram of ground seeds of *Cassia absus*, Linn., was stirred three times as a slurry in 1500 ml. of 0.3% methanolic hydrogen chloride, each for 24 hr. at room temperature, and then filtered. The filtrates were each neutralized with ammonia, brought to *p*H 5 with acetic acid and evaporated to dryness. A total of 212 g. of brown sirup was obtained in this manner. The sirup was taken up in 600 ml. of water and exhaustively extracted with ethyl ether.

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[1] Z. Ahmad, *Z. Untersuch. Lebensm.*, **70,** 166 (1935).

[2] I. Sen Gupta, K. Singh and R. P. Sood, *Research Bull. East Panjab Univ.*, No. 48, 63 (1954).

[3] S. Siddiqui and Z. Ahmad, *Proc. Ind. Acad. Sci.*, 2A, 421 (1935).

[4] S. Bernstein and E. S. Wallis, *J. Org. Chem.*, **2,** 341 (1937–38).

[5] Melting points are uncorrected. Analyses by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y. Infrared spectra were determined in Mellon Institute by H. M. Nelson and G. L. Carlson on a Baird model A infrared spectrophotometer.