

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-azahexanoate⁹ 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 C₆H₇N₃O₈: 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 C₆H₇ClN₃O₇: 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 C₆H₇N₅O₇: 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 C₆H₁₁N₅O₈: 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 Ahmad¹ 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, $\alpha_D^{25} -30^\circ$, $\lambda_{\max}^{\text{Nujol}}$ 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 (C₆H₅—), 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), $\alpha_D^{25} +30^\circ$. The properties of the compound, its acetate, benzoate, and dihydro derivative agree with those reported by Bernstein and Wallis⁴ 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.

EXPERIMENTAL⁵

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 pH 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.

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

(2) I. Sen Gupta, K. Singh and R. P. Sood, *Research Bull. East Punjab 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.

From the aqueous layer was eventually isolated chakaine iodide in 1.1% yield. The ethereal layer was dried and evaporated to afford 20 g. (2%) of a dark viscous neutral oil.

Saponification of 75 g. of neutral oil *via* ethanolic sodium hydroxide followed by the usual workup afforded 3.9 g. of a neutral, orange semisolid mass. The latter was crystallized from ethanol as a colorless solid (1.1 g.), m.p. 134–136°. Recrystallization from ethanol afforded β -sitosterol as colorless plates, m.p. 137–138°, $\alpha_D^{25} -30^\circ$ (c, 1.1 CHCl₃). (Lit.,⁴ m.p. 136–137°, $\alpha_D^{25} -36$.) Its infrared spectrum was superimposable on that of an authentic sample.

Anal. Calcd. for C₂₉H₅₀O: C, 84.0; H, 12.1. Found: C, 84.1; H, 11.9.

The mother liquors remaining after the crystallization of β -sitosterol were evaporated to dryness, then acetylated with acetyl chloride and pyridine. The crude mixture (2.0 g.) was chromatographed on neutral alumina (40 g.) to yield 0.7 g. of β -sitosterol acetate, m.p. 127–128°, and 0.3 g. of a colorless viscous liquid, $n_D^{27} 1.4954$. It showed absorption in the infrared characteristic of a saturated hydrocarbon, λ_{\max} . 2950 cm⁻¹, 2880, 1460, 1380.

β -Sitosterol acetate was prepared by treating 150 mg. of β -sitosterol with 8 ml. of acetyl chloride and a few drops of pyridine at 0°. Pouring the mixture on ice gave a colorless precipitate which crystallized from ethanol as colorless needles, m.p. 126–128°. (Lit.,⁴ m.p. 125–126).

Anal. Calcd. for C₃₁H₅₂O: C, 81.5; H, 11.5. Found: C, 81.1; H, 11.4.

To 100 mg. of β -sitosterol in 3 ml. of pyridine at 0° was added 3 ml. of benzoyl chloride. The solution was warmed on a steam bath for 10 min. after the initial exothermic reaction had subsided. The solution was poured on ice and the colorless precipitate removed by filtration. The β -sitosterol benzoate crystallized from ethanol as colorless needles, m.p. 139–140°. (Lit.,⁴ m.p. 145°).

Dihydro- β -sitosterol (Stigmastanol). To 100 mg. of platinum oxide in 13 ml. of acetic acid and 27 ml. of ethyl acetate was added 200 mg. of β -sitosterol and the mixture was shaken for 10 hr. under 40 lbs. of hydrogen pressure. The catalyst was filtered and the filtrate added to water to afford a colorless precipitate which crystallized from ethanol as colorless plates, m.p. 139–140°, depressed to 121–130° on admixture with β -sitosterol, $\alpha_D^{25} +30^\circ$ (c, 0.9 CHCl₃). (Lit.,⁴ m.p. 138–139°, $\alpha_D^{25} +25^\circ$).

Anal. Calcd. for C₂₉H₅₀O: C, 83.6; H, 12.6. Found: C, 83.5; H, 12.4.

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Chemistry of Lactones. II. Reaction of 2-Phenyl-4-benzylidene-5(4H)oxazolone with Benzene under Friedel-Crafts Conditions

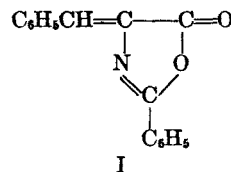
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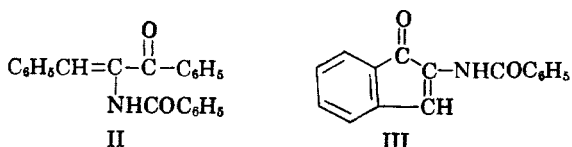
Oxazolones are often considered similar to cyclic anhydrides in their chemical reactions and might be expected to behave as acylating agents when treated with aromatic hydrocarbons in the presence of anhydrous aluminum chloride. Thus, succinic anhydride reacts with benzene under these condi-

(1) From the M.S. thesis of L.M.H., to be submitted to the Graduate School of Illinois Institute of Technology, 1958.

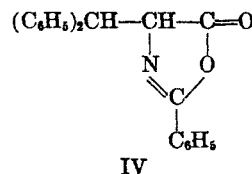
tions to form 3-benzoylpropionic acid. It was therefore of interest to study this reaction using 2-phenyl-4-benzylidene-5(4H)oxazolone (I) in place of anhydride. I has the added feature of an α,β -unsaturated carbonyl system.



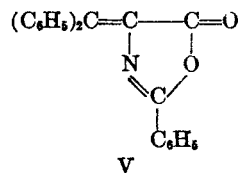
By analogy with cyclic anhydrides, it might be anticipated that I would react with benzene to give either 2-benzamidobenzalacetophenone (II) or 2-benzamidoindenone (III), formed by intramolecular cyclization.²



However, we did not isolate either II or III, the sole product being the saturated azlactone, 2-phenyl-4-diphenylmethyl-5(4H)oxazolone (IV), arising by 1,4 addition of benzene. The yield of IV after recrystallization was 62%.



This saturated azlactone has not been described previously and compounds with this type of structure are not readily obtainable by other routes, especially since attempts to prepare the unsaturated precursor, V, have failed.



The isolation of IV suggests the possibility of preparing interesting new compounds containing the diphenylmethyl moiety.

The structure of IV was established by elemental analysis, infrared and ultraviolet spectra, and by formation of the benzamide by aminolysis.

Whereas I exhibits a strong lactone carbonyl band at 1785 cm⁻¹,^{3a} typical of β,γ -unsaturated

(2) M. S. Newman and L. M. Joshel, *J. Am. Chem. Soc.*, 62, 972 (1940).

(3) (a) H. W. Thompson, R. R. Brattain, H. M. Randall, and R. S. Rasmussen in *The Chemistry of Penicillin*, Princeton University Press, Princeton, N. J., 1949, p. 387. (b) D. H. Whiffen and H. W. Thompson, *J. Chem. Soc.*, 1005 (1946).