Anal. Calcd. for $C_{34}H_{54}O_5$: C, 75.23; H, 10.03; acetyl, 15.90. Found: C, 75.24; H, 10.05; acetyl, 14.52.

$\Delta^{12,15}$-Oleadiene-3β,28-diol Diacetate (XXVa).—The above triol diacetate XXIV (100 mg.) was treated with 5 cc. of pyridine and 0.5 cc. of phosphorus oxychloride at reflux temperature for 2 hours. After pouring into ice the product was extracted with ether and the ethereal solution was washed with dilute hydrochloric acid and water. Removal of solvent gave a residue which was chromatographed on 5 g. of alumina. The desired diacetate XXVa (65 mg.) was eluted with benzene and crystallized from chloroform–methanol to give colorless rods, m.p. 210–212°, $[\alpha]_D$ +53°.

Anal. Calcd. for $C_{34}H_{52}O_4$: C, 77.82; H, 9.99. Found: C, 77.56; H, 9.88.

The same product (mixture melting point and infrared comparison) was obtained when methyl Δ^{15}-dehydrooleanolate acetate (XXVb)[27] was reduced with lithium aluminum hydride and acetylated as described below for XXIXb.

Hydrogenation of $\Delta^{12,15}$-Oleadiene-3β,28-diol Diacetate to Erythrodiol Diacetate (XXVIb).—The hydrogenation of 43 mg. of the diene diacetate XXVa was carried out for 20 hours at room temperature and atmospheric pressure in 20 cc. of acetic acid in the presence of 180 mg. of platinum oxide catalyst. Removal of catalyst and solvent followed by recrystallization from chloroform–methanol gave 28 mg. of erythrodiol diacetate, m.p. 182–185°, $[\alpha]_D$ +62°, which was shown to be identical with an authentic specimen[2] by mixture melting point determination and comparison of the infrared spectra.

$\Delta^{12,21}$-Oleadiene-3β,28-diol Diacetate (XXIXb).—Methyl Δ^{21}-dehydroöleanolate acetate (XXIXa)[16] (220 mg.) was treated with excess lithium aluminum hydride in ether for 6 hours. After addition of ethyl acetate and dilute hydrochloric acid, ether extraction produced a gum which was acetylated with acetic anhydride and pyridine overnight at room temperature. Chromatography on 10 g. of alumina, elution with benzene and recrystallization from methanol and from dilute ethanol led to 110 mg. of colorless plates, m.p. 182–185°, $[\alpha]_D$ +38°.

Anal. Calcd. for $C_{34}H_{52}O_4$: C, 77.82; H, 9.99. Found: C, 77.37; H, 10.02.

Dehydration of Δ^{12}-28-Nor-oleanene-3β,15β-diol-22-one 3-Monoacetate (XXb) and Δ^{12}-28-Nor-oleanene-3,22-dione-15β-ol (XXc).—A 250-mg. sample of the crude 28-nor 3-monoacetate XXb in 10 cc. of a 4:1 mixture of glacial acetic acid and concd. hydrochloric acid was heated under reflux for 4 hours and the product was chromatographed on alumina. Elution with benzene–ether (4:1) furnished 110 mg. of solid (XXXa) which crystallized from methanol–chloroform as colorless needles, m.p. 240–245°, $[\alpha]_D$ −63°, λ_{max}^{EtOH} 326 mμ, ϵ 10,500; $\lambda_{max}^{CHCl_3}$ 5.80, 6.08 and 6.38 μ (double bond band nearly as intense as 5.8 acetate band).

Anal. Calcd. for $C_{31}H_{46}O_3$: C, 79.78; H, 9.94. Found: C, 79.77; H, 10.03.

Similar dehydration of the crude 28-nor-3,22-dione XXc proceeded in 65% yield to afford the diene-dione XXXb, m.p. 192–196° (from ethanol), $[\alpha]_D$ −47°, λ_{max}^{EtOH} 325 mμ, ϵ 12,500; $\lambda_{max}^{CHCl_3}$ 5.85, 6.08 and 6.35 μ.

Anal. Calcd. for $C_{29}H_{42}O_2$: C, 82.41; H, 10.02. Found: C, 82.71; H, 10.14.

Lithium aluminum hydride reduction (ether solution, 20°, 14 hours) of either XXXa or XXXb led to an oil which could not be crystallized even after chromatography and acetylation. The total product exhibited no carbonyl absorption in the infrared but showed λ_{max}^{EtOH} 275 mμ, ϵ 7,500, indicating that it possessed structure XXXc.

Reaction of Dumortierigenin Diacetate with N-Bromosuccinimide.—The diacetate XIXb was treated with N-bromosuccinimide using the conditions employed in the queretaroic acid series[1] or in the presence of calcium carbonate,[39] but in each case there was obtained a mixture which could not be separated completely. The predominant products appeared to be a bromo-triene[1] (m.p. 264–269°, λ_{max}^{EtOH} 317 mμ, ϵ *ca.* 10,000) and a ($\Delta^{9(11),12}$?)-diene (m.p. 224–234°, broad ultraviolet maximum at 285–290 mμ).

(39) G. G. Allan and F. S. Spring, *J. Chem. Soc.*, 2125 (1955).

DETROIT, MICHIGAN

COMMUNICATIONS TO THE EDITOR

THE SYNTHESIS OF CERTAIN DEGRADATION PRODUCTS OF THE ANTIBIOTIC 1703-18B. THE SYNTHESIS OF *neo*-INOSAMINE-2

Sir:

The isolation and characterization of a new inosamine, *neo*-inosamine-2 (V),[1] was reported recently from these Laboratories by Patrick and his coworkers.[3] This inosamine was obtained by hydrolysis of a new antibiotic (designated in these Laboratories as 1703-18B) with concentrated hydrochloric acid. We now wish to report the synthesis of this degradation product.

Catalytic oxidation[4] of *neo*-inositol (I)[5] gave an inosose, which was isolated as its phenylhydrazone derivative (47% yield), m.p. 201–204° (dec.).[6] (*Anal.* Calcd. for $C_{12}H_{16}N_2O_5$: C, 53.72; H, 6.01; N, 10.44. Found: C, 53.68; H, 6.21; N, 10.53).

Treatment of the phenylhydrazone derivative with benzaldehyde in the presence of benzoic acid[7] gave the inosose (69% yield), m.p. 218–220° (dec.). (*Anal.* Calcd. for $C_6H_{10}O_6$: C, 40.45; H, 5.66. Found: C, 40.49; H, 5.42). Hydrogenation of the inosose in the presence of platinum furnished an inositol (88% yield), m.p. 314° when dropped on a preheated block. (*Anal.* Calcd. for $C_6H_{12}O_6$: C, 40.00; H, 6.71. Found: C, 40.05; H, 6.91). This material and its hexaacetate, m.p. 252–253°, (*Anal.* Calcd. for $C_{18}H_{24}O_{12}$: C, 50.00; H, 5.60. Found: C, 50.28; H, 5.83) were identical with authentic samples of *neo*-inositol (I)[5] and its hexaacetate.

Reduction of the inosose with sodium amalgam followed by acetylation gave in 40% yield *myo*-

(1) The system of nomenclature proposed by Fletcher and his associates[2] is used in this paper.

(2) H. G. Fletcher, Jr., L. Anderson and H. A. Lardy, *J. Org. Chem.*, **16**, 1238 (1951).

(3) J. B. Patrick, R. P. Williams, C. W. Waller and B. L. Hutchings, THIS JOURNAL, **78**, 3652 (1956).

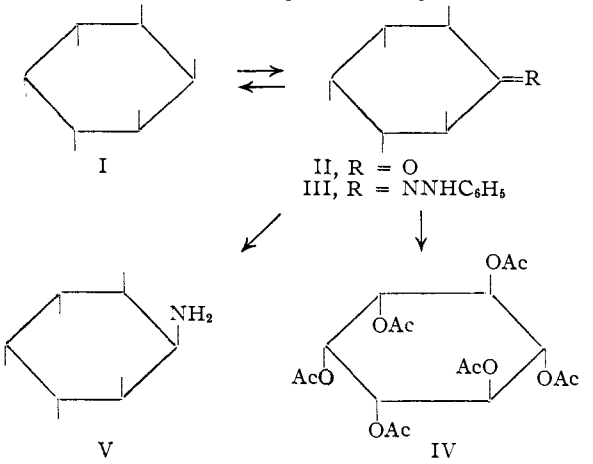
(4) For previous examples of the utilization of this technique in the inositol field see (a) K. Heyns and H. Paulsen, *Ber.*, **86**, 833 (1953); (b) **89**, 1152 (1956).

(5) S. J. Angyal and N. K. Matheson, THIS JOURNAL, **77**, 4343 (1955).

(6) All melting points were determined on the Kofler hot stage and are corrected.

(7) T. Posternak, *Helv. Chim. Acta*, **19**, 1333 (1936).

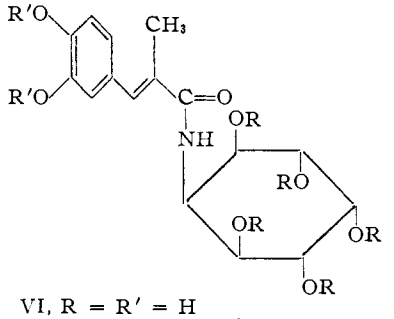
inositol hexaacetate,[8] m.p. 212–213°. (*Anal.* Calcd. for $C_{18}H_{24}O_{12}$: C, 50.00; H, 5.60. Found: C, 50.34; H, 5.69). Since *myo*-inositol and *neo*-inositol are formed by reduction of this inosose, the latter must be *neo*-inosose-2 (II); the phenylhydrazone derivative is represented by III.



I II, R = O III, R = $NNHC_6H_5$ V IV

The phenylhydrazone (III) was hydrogenated in the presence of a platinum catalyst to give in 53% yield an inosamine, m.p. 239–241° (dec.). (*Anal.* Calcd. for $C_6H_{13}NO_5$: C, 40.22; H, 7.31; N, 7.82. Found: C, 40.41; H, 7.73; N, 7.84). This inosamine gave a hexaacetate, m.p. 277–278°, (*Anal.* Calcd. for $C_{18}H_{25}NO_{11}$: C, 50.11; H, 5.84; N, 3.25. Found: C, 50.35; H, 6.02; N, 3.30), and an N-benzylidene derivative, m.p. 209–211° (dec.). (*Anal.* Calcd. for $C_{13}H_{17}NO_5$: C, 58.41; H, 6.41; N, 5.24. Found: C, 58.77; H, 6.49; N, 5.12). This synthetic inosamine was identical with the inosamine isolated from antibiotic 1703-18B and which has been shown to be *neo*-inosamine-2 (V).[3,9] Additionally, the hexaacetates[9] and the N-benzylidene derivatives[9] from the two sources were identical.

The 3,4-dihydroxy-α-methylcinnamic acid amide of *neo*-inosamine-2 (VI) has been postulated as the



VI, R = R′ = H
VII, R = CH_3CO–, R′ = C_2H_5CO–

$C_{16}H_{21}NO_8$ degradation product of the antibiotic 1703-18B,[10] and additionally, it appears to be at least isomeric, and possibly identical, with a portion of the antibiotic hygromycin.[11]

(8) M. Maquenne, *Ann. chim. phys.*, [6] **12**, 101 (1887).

(9) A sample of the material from the antibiotic was kindly furnished for comparison by Dr. J. B. Patrick.

(10) J. B. Patrick, private communication.

(11) (a) R. L. Mann, R. M. Gale, and F. R. van Abeele, *Antibiotics and Chemotherapy*, **3**, 1279 (1953); (b) R. L. Mann and D. O. Woolf, Abstracts of the 130th Meeting of the American Chemical Society, Atlantic City, p. 26-D.

The synthesis of VI was accomplished in the following manner. The N-benzylidene derivative of *neo*-inosamine-2 was acetylated to yield its penta-*O*-acetyl derivative (79% yield), m.p. 217–219°. (*Anal.* Calcd. for $C_{23}H_{27}NO_{10}$: C, 57.86; H, 5.70; N, 2.93. Found: C, 57.61; H, 6.09; N, 3.10). Selective hydrolysis of the latter with hydrochloric acid in tetrahydrofuran gave in 73% yield penta-*O*-acetyl-*neo*-inosamine-2 hydrochloride, m.p. 185–187°. (*Anal.* Calcd. for $C_{16}H_{23}NO_{10}\cdot HCl$: C, 45.13; H, 5.68; N, 3.29. Found: C, 45.39; H, 6.04; N, 3.40). Condensation of the latter material with α-methyl-3,4-dipropionoxycinnamoyl chloride gave in 69% yield 1,3,4,5,6-penta-*O*-acetyl-2-deoxy-2-(α-methyl-3,4-dipropionoxycinnamido)-*neo*-inositol (VII), m.p. 157–160°. (*Anal.* Calcd. for $C_{32}H_{39}NO_{15}$: C, 56.71; H, 5.80; N, 2.07. Found: C, 56.83; H, 5.60; N, 2.16). De-*O*-acylation of VII with triethylamine in methanol gave VI (71% yield), m.p. 256–259° (dec.). (*Anal.* Calcd. for $C_{16}H_{21}NO_8$: C, 54.08; H, 5.96; N, 3.94. Found: C, 53.71; H, 6.09; N, 4.06). This material was identical with the $C_{16}H_{21}NO_8$ degradation product[9,10] of the antibiotic 1703-18B.

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PARTITION COEFFICIENTS FROM GAS-LIQUID PARTITION CHROMATOGRAPHY

Sir:

The evaluation of heats and entropies of solution from gas–liquid partition chromatography has not been attempted in a systematic manner.[1] The method[2] by which results are presented in terms of a "corrected retention volume" is satisfactory if only ΔH is to be obtained, but if ΔS is also required, the study of the temperature variation of the partition coefficient (K) is the more straightforward method; where

$$K = \frac{\text{concn. of solute in stationary liquid phase}}{\text{concn. of solute in gas phase}} \quad (1)$$

both concentrations in g./ml. The partition coefficient so defined may be calculated from the zero-flow retention volume v_R^0 by the relation

$$K = \left[\frac{v_R^0}{\alpha X} - 1\right]\frac{\alpha}{\gamma} \quad (2)$$

where α = gas-space volume fraction of the column, γ = stationary liquid phase volume fraction of the column, X = total volume of the column.

This equation may be obtained from the results of James and Martin[3] or more simply by the following procedure, the principle of which is due to Glueckauf.[4] Let $f(c)$ = amount of solute contained

(1) Since this note was submitted a paper by Porter, Deal and Stross (THIS JOURNAL, **78**, 2999 (1956)) has appeared in which thermodynamic data are obtained in a systematic manner from GLP chromatography by a method analogous to the one described in this note.

(2) A. B. Littlewood, C. S. G. Phillips and D. T. Price, *J. Chem. Soc.*, 1480 (1955).

(3) A. T. James and A. J. P. Martin, "Proceedings of the International Congress on Analytical Chemistry," Heffer and Sons, Oxford, 1952, p. 359.

(4) E. Glueckauf, *Trans. Faraday Soc.*, **51**, 34 (1955).