specimen. A comparison of the X-ray diagram of the 2,4-di-*O*-methyl-L-rhamnose anilide with that of an authentic specimen of this anilide revealed that the two were identical.[21]

When a solution of the 2,4-di-*O*-methyl-L-rhamnose anilide (1.8 mg.) in methyl iodide (5 ml.) was treated under reflux with silver oxide (50 mg.) during 18 hours[9] the corresponding fully methylated anilide was formed. Extraction with acetone gave crystalline 2,3,4-tri-*O*-methyl-L-rhamnose anilide m.p. and mixed m.p. 110° (after recrystallization from ether–light petroleum ether).

Of interest also were the characteristic yellow spots shown by the rhamnose derivatives when sprayed with *p*-anisidine–trichloroacetic acid reagent.[18] Di-*O*-methyl-D-xylose derivatives generally show dark brown colors while tri-*O*-methyl-D-xylose or its anilide gave a characteristic red color. These facts helped to eliminate the possibility that component 3 was a methyl xylose derivative.

(d) **Component 4; 2,3-Di-*O*-methyl-D-xylose.**—This sirupy component (1.9295 g.) was 2,3-di-*O*-methyl-D-xylose, $[\alpha]^{23}\text{D}$ +23.5° in water (*c* 1.3). *Anal.* Calcd. for $C_7H_{14}O_5$: OMe, 34.8. Found: OMe, 35.1.

The anilide formed in the usual way and recrystallized from ethyl acetate proved to be 2,3-di-*O*-methyl-D-xylose anilide m.p. and mixed m.p. 126°, $[\alpha]^{23}\text{D}$ +181° in ethyl acetate (*c* 1.0). *Anal.* Calcd. for $C_{13}H_{19}O_4N$: OMe, 24.5. Found: OMe, 24.5.

(e) **The Isolation of 2-*O*-Methyl- and 3-*O*-Methyl-D-xylose from Component 5.**—Component 5, consisting of a sirup (39.7 mg.), had $[\alpha]^{23}\text{D}$ +30° in water (*c* 1.2). Paper chromatographic examination using solvent B indicated this fraction to be a mixture of two sugars corresponding in R_f values to 2-*O*-methyl-D-xylose and 3-*O*-methyl-D-xylose. This fraction was therefore separated into its respective components by sheet paper chromatography.

The sirup from the band having an R_f value corresponding to 2-*O*-methyl-D-xylose crystallized when nucleated with this sugar and recrystallization from ethyl ether yielded 2-*O*-methyl-D-xylose m.p. and mixed m.p. 132–133°.

The sirup from the band corresponding to 3-*O*-methyl-D-xylose crystallized when nucleated with 3-*O*-methyl-D-xylose and had m.p. and mixed m.p. 98–100° (after recrystallization from ethyl acetate).

From the known equilibrium specific rotations in water of 2-*O*-methyl-D-xylose (+35.9°) and 3-*O*-methyl-D-xylose (+14.8°) and the rotation of component 5 the amount of 2-*O*-methyl-D-xylose and 3-*O*-methyl-D-xylose in the mixture was calculated to be 29.2 and 10.5 mg., respectively. Since it is not unlikely that some cleavage of the aldobiouronic acid occurred during the graded hydrolysis of the methylated polysaccharide, the 3-*O*-methyl-D-xylose, was probably derived by partial cleavage of the 3-*O*-methyl-D-xylose unit of the methylated aldobiouronic acid.[3]

(f) **Component 6, (?) D-Xylose.**—This component, a dark yellow sirup amounting to 6.0 mg., appeared to be xylose from its R_f value (solvent A, B and C). It was by no means pure and it may not be of any constitutional significance. It failed to give a dibenzylidene dimethyl acetal derivative.

Acknowledgement.—The authors wish to thank the graduate school of the University of Minnesota for financial support during the initiation of this work.

ST. PAUL, MINNESOTA

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[21] The authors are grateful to Dr. W. N. Lipscomb of the University of Minnesota for carrying out these determinations.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Synthesis and Properties of Certain Spiro[4.4]nonenes[1]

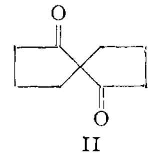
BY DONALD J. CRAM AND B. L. VAN DUUREN

RECEIVED OCTOBER 27, 1954

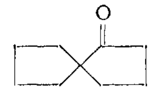
The synthesis of 1-spiro[4.4]nonene (VIII), 1,3-spiro[4.4]nonadiene (III) and 1,6-spiro[4.4]nonadiene (XVIII) are described, as well as the behavior of III as a dienophile in a Diels–Alder reaction.

The objective of this investigation was the exploration of the chemistry of the spiro[4.4]nonenes, the compound 1,3,6,8-spiro[4.4]nonatetraene (I) being the ultimate target for the work. Since 1,6-diketospiro[4.4]nonane (II)[2] was an obvious but expensive starting material, the model synthesis of 1,3-spiro[4.4]nonadiene (III) from the more available 1-ketospiro[4.4]nonane (IV) was developed first.


I


II


III


IV

The monoketone IV[3] was converted to its oxime which was reduced catalytically to provide 1-aminospiro[4.4]nonane[2] (V) which was dimethylated with formaldehyde and formic acid[4] to give 1-dimethylaminospiro[4.4]nonane (VI). This material was converted to the amine oxide VII which on pyrolysis gave 1-spiro[4.4]nonene (VIII).[5] The same olefin was obtained in better yield through the Hofmann elimination reaction, the infrared spectra and physical properties of the two olefin samples being identical.

Olefin VIII was characterized by quantitative catalytic hydrogenation to the known saturated spiro[4.4]nonane (IX).[6] Bromination of olefin VIII with N-bromosuccinimide gave an unstable oil which could not be purified, and which was converted directly to 3-dimethylamino-1-spiro[4.4]-nonene. Alkylation of this material led to the quaternary compound XI which when heated with silver oxide gave diene III. This material was thermally unstable and when distilled at atmospheric pressure appeared to dimerize to give the

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[1] This research was conducted under contract AF 33(616)-146 with the United States Air Force, the sponsoring agency being the Aeronautical Research Laboratory of the Wright Air Development Center, Air Research and Development Command.

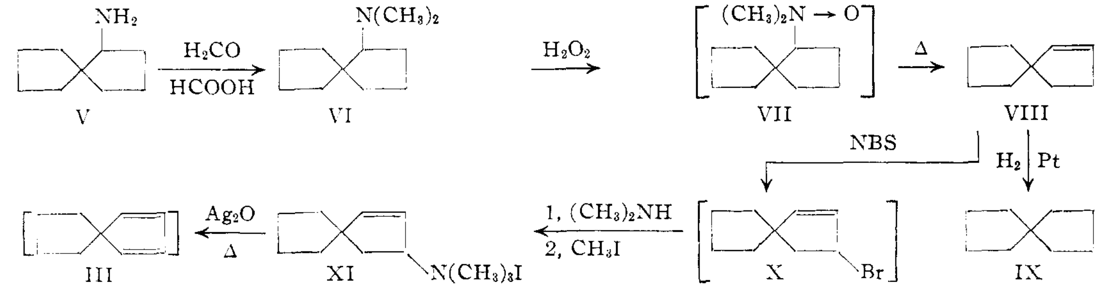
[2] D. J. Cram and H. Steinberg, THIS JOURNAL, **76**, 2753 (1954).

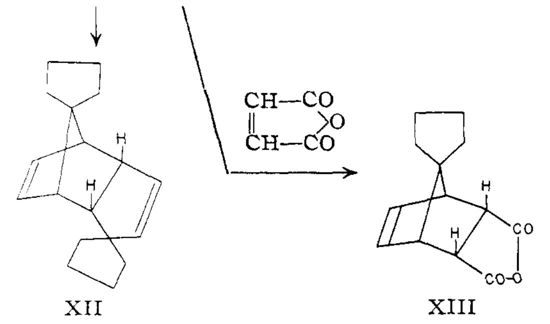
[3] (a) M. Qudrat-i-Khuda and A. K. Ray, *J. Indian Chem. Soc.*, **16**, 518 (1939); (b) M. Qudrat-i-Khuda and A. Mukherjee, *ibid.*, **16**, 532 (1939); (c) N. D. Zelinskii and H. V. Elagina, *Compt. rend. acad. sci.*, *U.R.S.S.*, **49**, 568 (1945), or *C. A.*, **40**, 6058 (1946).

[4] H. T. Clarke, H. B. Gillespie and S. Z. Weisshaus, THIS JOURNAL, **55**, 4571 (1933).

[5] For references to this *cis*-elimination reaction see: (a) A. C. Cope, T. T. Foster and P. H. Towle, THIS JOURNAL, **71**, 3939 (1949); (b) D. J. Cram, *ibid.*, **74**, 2137 (1952); A. C. Cope, R. A. Pike and C. Spencer, *ibid.*, **75**, 3212 (1953); D. J. Cram and J. E. McCarty, *ibid.*, **77**, in press (1955).

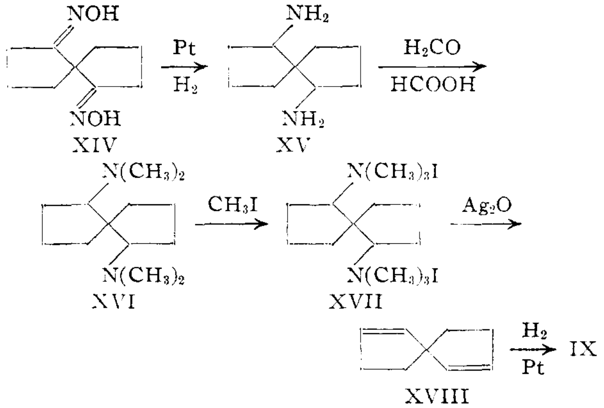
[6] N. N. Chatterjee, *J. Indian Chem. Soc.*, **14**, 259 (1937).



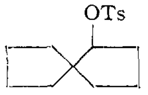


Diels–Alder product XII whose ultraviolet absorption spectra (only end-absorption at 220 mμ) indicated the absence of a conjugated system. The diene III was characterized as its maleic anhydride adduct. After this synthesis was completed, a report of the preparation of III by a different route came to our attention, the properties of the two samples of III and of the maleic anhydride adduct being the same.[7]

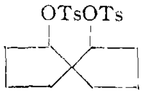
A similar synthetic route was applied to the bifunctional spiran system with 1,6-diketospiro[4.4]-nonane[2] (I) as the starting material, and the formulations indicate the reactions employed. The yields in this sequence were inferior to those in the monofunctional spiran model, probably because of the greater opportunity for side reactions in the bifunctional series. Diolefin XVIII was submitted to the action of N-bromosuccinimide and the resulting bromide was treated with dimethylamine. The resulting oil was converted to the methiodide which was an amorphous solid. When subjected to the Hofmann elimination reaction, the product appeared to be polymeric.



Attempts to prepare olefins VIII and XVIII by the base-catalyzed elimination of *p*-toluenesulfonic acid from compounds XIX and XX, respectively, failed. Although olefinic products were obtained,



XIX



XX

their physical properties did not correspond to VIII and XVIII, respectively, and this approach was abandoned.

It is interesting to note that the band in the infrared associated with >C═C< stretching is different in dimer XII (λ 5.85 μ), in monoölefin VIII (λ 6.00 μ) and in diolefin XVIII (λ 6.18 μ). These bands are of medium intensity, and are the only ones found in the double bond region. The shift of the double bonds in diolefin XVIII toward the wave length commonly associated with conjugated dienes suggests that the π-electrons of each double bond interact in such a way as to increase the single-bond character of each function. A similar observation was made with 1,6-diketospiro[4.4]nonane (II) previously.[2]

Experimental[8]

1-Dimethylaminospiro[4.4]nonane (VI).—The 1-aminospiro[4.4]nonane (V) was prepared by the method previously employed[2,3c]; b.p. 95–99° at 25 mm. (reported[2] 90° at 19 mm.). Ten grams of 90% formic acid was cooled to 0°, and 5.3 g. of 1-aminospiro[4.4]nonane was added gradually. To this solution was added 7.5 g. of 35% aqueous formaldehyde, and the mixture was heated at 100° for three hours beyond the period during which gas bubbles were evolved, the total period of heating being 8–10 hours. The solution was allowed to cool to room temperature, 5 ml. of 15% hydrochloric acid was added, and the mixture was evaporated under reduced pressure. The residue was made alkaline with 25% sodium hydroxide, the solution was saturated with potassium carbonate and extracted with ether. The ether extract was dried, the solvent evaporated and the amine VI was distilled under reduced pressure to give 5.60 g. (87.5%), b.p. 98° (19 mm.), n^{25}D 1.4962.

Anal. Calcd. for $C_{11}H_{21}N$: C, 79.04; H, 12.54. Found: C, 78.84; H, 12.32.

1-Dimethylaminospiro[4.4]nonane Methiodide.—Treatment of the tertiary amine VI with an excess of methyl iodide at room temperature gave a crystalline methiodide which was purified by recrystallization from a methanol–ether mixture; m.p. 222–223°.

Anal. Calcd. for $C_{12}H_{24}NI$: C, 46.60; H, 7.76. Found: C, 46.46; H, 8.00.

1-Spiro[4.4]nonene (VIII). Method A.—1-Dimethylaminospiro[4.4]nonane (VI), 5.3 g., was added to 7.0 g. of 30% hydrogen peroxide, and the mixture was stirred at room temperature for 24 hours. The excess of hydrogen peroxide was destroyed with manganese dioxide, the solution was filtered, and the solvent was evaporated at 50° (20 mm.), the distillate being collected in a Dry Ice–acetone trap. The distillate then was acidified with 5 ml. of cold 15% sulfuric acid, and the olefin was extracted with pen-

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[7] R. Y. Levina and T. I. Tantsyreva, *Doklady Akad. Nauk., S.S.S.R.*, **89**, 697 (1953); *C. A.*, **48**, 6972 (1954).

[8] All melting points are corrected, boiling points are uncorrected.

tane. The pentane extract was washed with sodium bicarbonate solution, with water and dried. The solvent was evaporated through a fractionating column, and the residue was distilled at atmospheric pressure, bath temperature 140°, to give 2.0 g. of colorless liquid (51%), $n^{25}\mathrm{D}$ 1.4760.

Anal. Calcd. for C_9H_{14}: C, 88.52; H, 11.47. Found: C, 88.61; H, 11.61.

Method B.—To a solution of 5.6 g. of 1-dimethylaminospiro[4.4]nonane methiodide in 25 ml. of water was added freshly prepared (alkali-free) silver oxide (prepared from 5.6 g. of silver nitrate and 1.10 g. of sodium hydroxide). The mixture was stirred, first at room temperature for one hour and then at 50° for one hour. The silver iodide was collected and washed with water. The combined filtrate and washings were evaporated to dryness at 40° (20 mm.), and the residue was pyrolyzed at 100° (20 mm.), the distillate being collected in a Dry Ice–acetone trap. The olefin was isolated as described under method A. The product obtained was chromatographed on alumina with pure pentane as solvent. The olefin VIII was eluted quantitatively with pure pentane and redistilled: 1.65 g. (75%), $n^{25}\mathrm{D}$ 1.4770.

Anal. Calcd. for C_9H_{14}: C, 88.52; H, 11.47. Found: C, 88.41; H, 11.72.

The infrared absorption spectra of the olefins obtained by methods A and B were identical.

Catalytic Hydrogenation of VIII: Spiro[4.4]nonane (IX).—A solution of 100 mg. of VIII in 10 ml. of ethanol was hydrogenated with platinum as catalyst. One mole of hydrogen was absorbed rapidly. The resulting solution was filtered, 25 ml. of water was added and the hydrocarbon was extracted with pure pentane. The extract was dried, the solvent distilled through a fractionating column, and the residue was distilled at atmospheric pressure at a bath temperature of 160°, $n^{25}\mathrm{D}$ 1.4585 (reported $n^{20}\mathrm{D}$ 1.4610[7]).

Anal. Calcd. for C_9H_{16}: C, 87.10; H, 12.90. Found: C, 87.34; H, 13.19.

3-Dimethylamino-1-spiro[4.4]nonene Methiodide (XI).—To a solution of 1.5 g. of VIII in 10 ml. of carbon tetrachloride was added 75 mg. of benzoyl peroxide, 1.5 g. of anhydrous potassium carbonate and 2.0 g. of N-bromosuccinimide. The mixture was boiled under reflux with stirring for 90 minutes. After cooling to room temperature, the succinimide was collected, and the filtrate was washed, first with dilute sodium bicarbonate and then with water, and dried. The solvent was evaporated under reduced pressure. The yellow liquid residue was dissolved in 5 ml. of benzene and a solution of 2.0 g. of dimethylamine in 10 ml. of benzene was added cautiously. A vigorous exothermic reaction took place and a crystalline product separated. The mixture was allowed to stand for 12 hours, cooled in ice and acidified with cold 10% hydrochloric acid. The benzene layer was separated and washed with two 5-ml. portions of 10% hydrochloric acid. The combined aqueous solutions were made alkaline with 20% sodium hydroxide and the unsaturated tertiary amine was extracted into ether. The ether extract was dried over anhydrous potassium carbonate, filtered and the solvent was removed. A straw-colored liquid was obtained which was converted directly to the methiodide with an excess of methyl iodide. The crystalline methiodide XI, 1.85 g. (51.4%), was recrystallized from methanol–ether, m.p. 169–170°.

Anal. Calcd. for $C_{12}H_{12}NI$: C, 46.90; H, 7.16. Found: C, 46.74; H, 7.37.

Dimer of 1,3-Spiro[4.4]nonadiene (XII).—A solution of 1.10 g. of the methiodide, obtained in the previous experiment, in 5 ml. of water was heated with silver oxide and the olefin obtained as described under the preparation of VIII by method B above. The olefin was redistilled at atmospheric pressure, bath temperature 160–170°. Under these conditions the liquid became more viscous due to dimer (XII) formation, $n^{25}\mathrm{D}$ 1.5342.

Anal. Calcd. for C_9H_{12}: C, 90.00; H, 10.00. Found: C, 89.78; H, 10.09.

Maleic Anhydride Adduct of 1,3-Spiro[4.4]nonadiene.—The procedure employed was essentially that used for the preparation of the adduct from cyclopentadiene.[9] A solution of 0.50 g. of 3-dimethylamino-1-spirononene methiodide was converted to the hydroxide with silver oxide, and the hydroxide was pyrolyzed as described above. The distillate was extracted with two 5-ml. portions of benzene and the benzene extract was washed successively with cold dilute sulfuric acid, sodium bicarbonate solution and water. The benzene solution was dried, and 100 mg. of maleic anhydride was added. The mixture was allowed to stand at room temperature for 24 hours. Removal of the benzene left a crystalline residue which after one recrystallization from ether melted at 90–93°. The product was recrystallized from ether and sublimed at 75° (0.1 mm.) to give XIII, m.p. 102° (reported m.p. 98°[7]), yield 85%.

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.55; H, 6.37. Found: C, 71.59; H, 6.67.

1,6-Diaminospiro[4.4]nonane.—A suspension of 10.0 g. of dioxime XIV (m.p. 227–230°)[2] and 0.30 g. of platinum oxide catalyst in 100 ml. of glacial acetic acid was shaken under 3–4 atmospheres of hydrogen for 48 hours. The solution was filtered, the solvent removed under reduced pressure, and the residue was made alkaline with 15% sodium hydroxide solution. A white crystalline substance separated and was filtered. This substance, after recrystallizations from methanol, melted at 227–231° and gave no depression of melting point on admixture with dioxime XIV. The aqueous alkaline solution was extracted with ether and the ether extract was dried over anhydrous potassium carbonate. Filtration of the mixture and removal of the solvent from the filtrate gave the amine XV which was distilled *in vacuo;* 4.89 g. (59%), b.p. 95–99° (2 mm.).

Anal. Calcd. for $C_9H_{18}N_2$: C, 70.13; H, 11.69. Found: C, 70.13; H, 11.43.

1,6-Bis-dimethylaminospiro[4.4]nonane (XVI).—A mixture of 4.0 g. of the diamine XV, 19.0 g. of 90% formic acid and 13.0 g. of 35% aqueous formaldehyde was heated on a steam-bath for 12 hours, and the ditertiary amine XVI was isolated as described above for the monotertiary amine. The product was distilled *in vacuo;* 2.60 g. (54%), b.p. 85° (0.5 mm.), $n^{25}\mathrm{D}$ 1.4950.

Anal. Calcd. for $C_{13}H_{26}N_2$: C, 74.28; H, 12.38. Found: C, 74.20; H, 12.31.

1,6-Bis-dimethylaminospiro[4.4]nonane Dimethiodide (XVII).—The ditertiary amine was converted to the dimethiodide with an excess of methyl iodide at room temperature, and the product was purified by crystallization from methanol, as colorless needles, m.p. 225–226°.

Anal. Calcd. for $C_{15}H_{32}N_2I_2$: C, 36.42; H, 6.47. Found: C, 36.52; H, 6.59.

1,6-Spiro[4.4]nonadiene (XVIII).—A solution of 2.45 g. of the dimethiodide in 10 ml. of water was treated with freshly prepared silver oxide (from 1.75 g. of silver nitrate and 0.42 g. of sodium hydroxide). The resulting hydroxide was pyrolyzed and the olefin isolated as described above. The olefin was purified by chromatography on alumina with pure pentane as solvent. The colorless liquid obtained from the column filtrates was distilled at atmospheric pressure (bath temperature 160°) to give 0.33 g. (55%) of olefin XVIII, $n^{25}\mathrm{D}$ 1.4815.

Anal. Calcd. for C_9H_{12}: C, 90.00; H, 10.00. Found: C, 89.42; H, 10.16.

Catalytic Hydrogenation of XVIII: Spiro[4.4]nonane (IX).—The diolefin was hydrogenated with platinum as catalyst, and the product was isolated and distilled, as described above for the hydrogenation of monoölefin VIII, $n^{25}\mathrm{D}$ 1.4590. The infrared absorption spectrum of the product was identical with that obtained by the hydrogenation of VIII.

***p*-Toluenesulfonate of 1-Hydroxyspiro[4.4]nonane.**—A mixture of 1.90 g. of *p*-toluenesulfonyl chloride, 1.40 g. of 1-hydroxyspiro[4.4]nonane[2] and 2.50 ml. of pyridine was allowed to stand at room temperature for 15 hours. The solution was then cooled in ice-water, 25 ml. of water was added, and the mixture was acidified with 10% hydrochloric acid. A water-insoluble oil separated. The mixture was extracted with ether, and the ether extract was washed, first with dilute sodium bicarbonate solution and then with water. The extract was dried, the solvent was removed and the crystalline residue was recrystallized from ether–pentane, m.p. 50°. The product was dried for a short period and analyzed immediately, since on standing the substance rapidly decomposes.

Anal. Calcd. for $C_{16}H_{23}SO_3$: C, 65.30; H, 7.48. Found: C, 65.50; H, 7.81.

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(9) O. Diels and K. Alder, *Ann.*, **460**, 98 (1928).

Bis-*p*-toluenesulfonate of 1,6-Dihydroxyspiro[4.4]nonane.—A mixture of 1.05 g. of 1,6-dihydroxyspiro[4.4]nonane, obtained by the catalytic reduction of the diketone,[2] 2.50 g. of *p*-toluenesulfonyl chloride and 5 ml. of pyridine was allowed to stand for 12 hours at room temperature. The mixture was then cooled in an ice-bath and acidified with ice-cold 10% hydrochloric acid. The crystalline solid was quickly filtered, washed with dilute sodium bicarbonate solution and dried in a vacuum desiccator; 2.0 g. (63%). The substance was recrystallized from methanol; m.p. 115° dec. Unlike the monotosylate, this substance was found to be stable at room temperature over a period of months.

Anal. Calcd. for $C_{23}H_{28}S_2O_6$: C, 59.47; H, 6.03. Found: C, 59.33; H, 6.08.

1,6-Diacetoxyspiro[4.4]nonane.—A mixture of 2.10 g. of the diol,[2] obtained by the catalytic reduction of the diketone,[1] 4.0 g. of acetic anhydride and 0.05 g. of acetyl chloride was heated on a steam-bath for 12 hours and the excess acetic anhydride was removed under reduced pressure, b.p. 152–153° (20 mm.). On standing, colorless crystals separated. The solid was separated by decanting the supernatant liquid and drying; wt. 0.70 g. Vacuum sublimation at 100° (0.50 mm.) gave an oil-free crystalline substance, m.p. 80°.

Anal. Calcd. for $C_{13}H_{20}O_4$: C, 65.00; H, 8.33. Found: C, 64.79; H, 8.14.

The liquid fraction, 1.30 g., did not yield any more crystalline material on standing and was redistilled for analysis, b.p. 152–153° (20 mm.), $n^{25}D$ 1.4788.

Anal. Calcd. for $C_{13}H_{20}O_4$: C, 65.00; H, 8.33. Found: C, 64.88; H, 8.29.

LOS ANGELES, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

Terpenoids. XVI.[1] The Constitution of the Cactus Triterpene Cochalic Acid. Partial Reductions of Methyl Diketoechinocystate[2]

BY CARL DJERASSI, G. H. THOMAS[3] AND H. MONSIMER

RECEIVED FEBRUARY 1, 1955

From the cactus *Myrtillocactus cochal*, there has been isolated a new triterpene acid, $C_{30}H_{48}O_4$, named cochalic acid (Ia). Oxidation of methyl cochalate furnished methyl diketoechinocystate (IIIa), while lithium aluminum hydride reduction led to the cactus triterpene longispinogenin (Vb). These transformations establish the constitution and stereochemistry of cochalic acid as 16β-hydroxyoleanolic acid (16-epiechinocystic acid). Rosenmund reduction of the acid chloride of diacetyl cochalic acid yielded the cactus triterpene gummosogenin (Va), thus establishing a further chemical connection in this class of closely related triterpenes. Reduction of methyl diketoechinocystate with sodium borohydride gives methyl 16-keto-oleanolate (IVc), while treatment with lithium in liquid ammonia results in elimination of the angular carbomethoxy group and formation of norechinocystenolorne (VIa).

In continuation of our investigations[4] of natural products present in giant cacti, we have undertaken a study of the genus *Myrtillocactus*[5] which is indigenous to Mexico and Guatemala. Through the kind coöperation of Mr. Howard E. Gates of Corona, California, we have been able to secure specimens of *Myrtillocactus cochal*, a species growing chiefly in the Mexican State of Baja California.[6] The cactus did not contain alkaloids, but acid hydrolysis of the glycosides yielded a mixture of triterpenes from which a new acid could be isolated. We have named this substance cochalic acid and the present paper is concerned with the elucidation of its structure.[7]

Cochalic acid (Ia) is a dihydroxy acid ($C_{30}H_{48}O_4$) as demonstrated by the formation of a diacetate Ib, methyl ester Ic and methyl ester diacetate Id. Oxidation of the methyl ester diacetate Id with selenium dioxide in acetic acid furnished methyl diacetyl dehydrocochalate (II) which showed the levorotation and triple ultraviolet absorption maxima at 243, 251 and 260 mμ typical[8] of $\Delta^{11,13(18)}$-dienes of the β-amyrin series. Oxidation of methyl cochalate (Ic) with the chromium trioxide–pyridine reagent[9] led to a diketone, which could be identified as the known[10] methyl diketoechinocystate (IIIa) by direct comparison with an authentic sample.[11] Cochalic acid is, therefore, an isomer of echinocystic acid (IV) and can differ from it only in the configuration of the hydroxyl groups at C-3 and/or C-16.

It has been shown earlier[12] that gummosogenin (Va), a triterpene isolated from the cactus *Machaereocereus gummosus*, can be converted to maniladiol (Vc) thus demonstrating that both hydroxyl groups at C-3 and C-16 are β-oriented. Since longispinogenin (Vb), a triterpene triol obtained[13] from the cactus *Lemaireocereus longispinus*, has been related to gummosogenin (Va) by lithium aluminum hydride reduction[12] of the latter, two triterpenes (Va, Vb) of known structure and stereochemistry (at C-3 and C-16) were available for comparison. Lithium aluminum hydride reduction of methyl cochalate (Ic) produced longispinogenin (Vb); this established the stereochemistry of

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(1) Paper XV, C. Djerassi, W. Rittel, A. L. Nussbaum, F. W. Donovan and J. Herran, THIS JOURNAL, **76**, 6410 (1954).

(2) We are indebted to the Division of Research Grants of the U. S. Public Health Service for generous financial assistance (grant No. G-3863).

(3) Postdoctorate research fellow, 1954–1955.

(4) For leading references see paper XI, C. Djerassi, L. H. Liu, E. Farkas, A. E. Lippman, A. J. Lemin, L. E. Geller, R. N. McDonald and B. J. Taylor, THIS JOURNAL, **77**, 1200 (1955).

(5) N. L. Britton and J. N. Rose, "The Cactaceae," Carnegie Institution of Washington, Washington, D. C., 1920, Vol. II, pp. 178–181.

(6) H. Bravo, "Las Cactaceas de Mexico," Mexico, D. F., 1937, p. 312.

(7) Some of our results already have been reported in a preliminary communication (C. Djerassi and G. H. Thomas, *Chemistry & Industry*, 1354 (1954)).

(8) *Cf.* L. Ruzicka, G. Müller and H. Schellenberg, *Helv. Chim. Acta*, **22**, 767 (1939); D. H. R. Barton and C. J. W. Brooks, *J. Chem. Soc.*, 257 (1951).

(9) G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, THIS JOURNAL, **75**, 422 (1953).

(10) W. R. White and C. R. Noller, *ibid.*, **61**, 983 (1939).

(11) We are greatly indebted to Prof. C. R. Noller (Stanford University) for supplying this substance.

(12) C. Djerassi, L. E. Geller and A. J. Lemin, THIS JOURNAL, **76**, 4089 (1954).

(13) C. Djerassi, R. N. McDonald and A. J. Lemin, *ibid.*, **75**, 5940 (1953).