[a] Unless otherwise noted the yields of the free bases are based on the diphenyl dialkylacetamide. The yields of the salts are based on the pure free bases. [b] Analyses and rotations are by Mr. William Struck and staff of our Analytical Chemistry Laboratory. Infrared spectra are by Dr. James L. Johnson and associates of our Department of Physics. [c] This yield is based on diphenyl-N,N-dimethylacetamide. The free basic amide was not isolated in pure form. [d] Yield based on pure hydrochloride. [e] The infrared spectrum[b] as well as the analysis indicates that this is a hydrate. [f] Prepared from the corresponding free base which has been previously reported.[5] [g] This salt has been reported by Bockmühl and Ehrhart[4] with m.p. 182–183°, but no analytical figures were given. It was prepared from diphenyl-N,N-diethylamide [N. Maxim, *Compt. rend.*, **182**, 1393 (1926); *Ann. chim.*, **9**, 55 (1928)]. [h] This compound was isolated as a hydrate, m.p. 129–132°. *Anal.* Calcd. for $C_{27}H_{41}BrN_2O \cdot H_2O$: N, 5.52; Br, 15.75. Found: N, 5.44; Br, 15.65. A sample was dried giving the properties listed in the table. The hydrate was used for pharmacological study. [i] The free base was not isolated. The hydrochloride crystallized from an aqueous acid solution on the addition of ether. [j] This yield is based on diphenylacetyl-1-piperidine.[5,9] The free basic amide was not isolated in pure form. [k] In spite of repeated attempts by two laboratories a satisfactory carbon analysis could not be obtained. The results ranged from 56.66 to 58.09. Good analyses for the other elements were obtained without difficulty. [l] Yield based on the α,α-diphenyl-γ or δ-*t*-aminovaleroyl chloride acid sulfate. The intermediate free basic amide was not isolated in pure form. [m] $[\alpha]^{23}\text{D}$ +59° (1% in CH_3OH). [n] $[\alpha]^{23}\text{D}$ +7° (1% in CH_3OH). [o] $[\alpha]^{23}\text{D}$ −63° (0.6% in CH_3OH). [p] $[\alpha]\text{D}$ −6° (1% in CH_3OH). [q] Isolated as a hydrate as shown by infrared[b] spectrum but after drying analyzed as anhydrous material.

N,N-dimethylacetamide,[5,9] 9.7 g. (0.25 mole) of sodium amide and 500 ml. of dry toluene was heated under reflux with stirring for 3 hours. To 44.8 g. (0.226 mole) of 2-(2,2-dimethyl-1-pyrrolidyl)-ethyl chloride hydrochloride[10] was added a slight excess of aqueous sodium hydroxide and the mixture was extracted with 300 ml. of toluene in several portions. The toluene solution was dried over potassium carbonate and slowly added to the above suspension of the sodium derivative. The mixture was heated under reflux with stirring for 2 hours, cooled, washed with water and extracted with dilute hydrochloric acid. The aqueous acid solution was made basic with dilute sodium hydroxide and the product was extracted with benzene. After removal of the solvent an oil was obtained which crystallized from pentane and was recrystallized from hexane giving white crystals having the properties given in Table II (no. 5, base).

Hydrochloride.—This was prepared by treating a sample of the free base in ethyl acetate with a slight excess of ethanolic hydrogen chloride. It was recrystallized from ethyl acetate, m.p. 206–207° (no. 5, HCl).

Methobromide.—To a cold solution of 10 g. (0.0322 mole) of the free base in 100 ml. of methyl ethyl ketone was added a large excess of cold methyl bromide. The flask was stoppered, clamped and allowed to stand at room temperature for 2 days. The crystals which separated had the properties given in Table II (no. 5, CH_3Br).

N-Oxide Hydrobromide.—A solution of 14.6 g. (0.04 mole) of the above free base and 10 ml. of 30% hydrogen peroxide in 150 ml. of methanol was allowed to stand at room temperature for 2 days. The excess hydrogen peroxide was decomposed by adding a small amount of a slurry of platinum-on-charcoal and shaking for 2 hours. The solution was filtered and distilled to dryness under reduced pressure below 30°. The resulting gummy free base failed to crystallize. It was dissolved in acetone and made acidic with a slight excess of 48% hydrobromic acid, and diluted with ether. On standing, the gummy hydrobromide partly crystallized. This was rubbed with ethyl acetate giving a solid product. This was recrystallized from isopropyl alcohol giving light tan crystals having the properties given in Table II (no. 5 → O·HBr).

α,α-Diphenylacetyl-1-pyrrolidine.—A mixture of 106.1 g. (0.5 mole) of diphenylacetic acid, 73 ml. of thionyl chloride and 100 ml. of benzene was heated under reflux with stirring for 1 hour. The solvent and excess thionyl chloride were removed by distillation under reduced pressure and the crude acid chloride was diluted with 300 ml. of benzene. To this was added slowly with stirring a solution of 85.4 g. (1.2 moles) of dry pyrrolidine in 200 ml. of benzene. After standing at room temperature overnight or heating under reflux for 1 hour, the solution was washed with water. The benzene solution was concentrated by distillation, treated with decolorizing charcoal, and cooled. It crystallized giving 111 g. (84%) of white crystals, m.p. 163–165°.

Anal. Calcd. for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.66; H, 8.01; N, 5.38.

Diphenyl-N,N-diisopropylacetamide.—By a similar procedure this was prepared from diisopropylamine. It was recrystallized from *n*-pentane giving a 60% yield of amide, m.p. 53–55°.

Anal. Calcd. for $C_{20}H_{25}NO$: C, 81.31; H, 8.53; N, 4.74. Found: C, 81.26; H, 8.59; N, 4.88.

KALAMAZOO, MICHIGAN

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[9] V. G. Gokhale, N. L. Phalnikar and B. V. Bhide, *J. Univ. Bombay*, **16**, No. 5, 32–36 (1948); *C. A.*, **43**, 1144e (1949).

[10] R. B. Moffett, J. L. White, B. D. Aspergren and F. E. Visscher, THIS JOURNAL, **77**, 1565 (1955).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE A. M. TODD COMPANY]

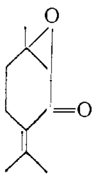
The Synthesis of Racemic Piperitenone Oxide and Diosphenolene

BY ROBERT H. REITSEMA[1]

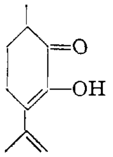
RECEIVED OCTOBER 12, 1956

The enolic diketone, diosphenolene, separated from the oil of *Mentha rotundifolia* has been synthesized by three methods. Piperitenone has been converted to a monoepoxide and this with acid gave diosphenolene. Pulegone was a useful starting material for two other methods. The syntheses provide further evidence that the structure of diosphenolene is 3,8(9)-*p*-menthadiene-2-one as previously proposed.

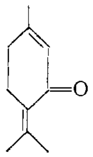
Mentha rotundifolia is one of the more interesting mint species and its oil contains constituents which are quite different from most other mint oils. It has been shown that the major constituent is piperitenone oxide (1,2-epoxy-4(8)-*p*-menthene-3-one) (I).[2] Associated with this keto oxide in the oil and readily obtained from it in the laboratory is a new enolic ketone called diosphenolene for which the structure of 3-hydroxy-3,8(9)-*p*-menthadiene-2-one (II) was proposed.[2]



I



II



III

The evidence for the location of the double bond

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[1] The Ohio Oil Company, Denver Research Center, Littleton, Colorado.

[2] R. H. Reitsema, THIS JOURNAL, **78**, 5022 (1956).

in piperitenone oxide at the 4–8 position giving an isopropylidene group was from chemical and spectroscopic evidence. The structure given for diosphenolene required the shift of the double bond to the 8–9 position. This was postulated particularly on the basis of the ultraviolet absorption maximum at about 306 mμ as could be calculated for the system C=CC=C(OH)C=O. Additional evidence for the view that this tautomeric form is predominant is given by the infrared spectrum. Diosphenolene shows a strong absorption at 884 cm.$^{-1}$ in agreement with the assignment of this region to the isopropenyl group.[3] Absence of significant absorption at 825 cm.$^{-1}$ makes the isopropylidene structure unlikely. The absorption at 1604 cm.$^{-1}$ is in agreement with the conjugated C=C group.[4]

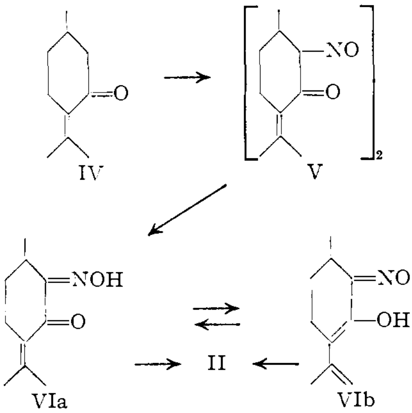
Piperitenone was treated with alkaline hydrogen peroxide by the general method of Treibs[5] to give a monoepoxide. Elementary analysis indicated the presence of a small amount of piperitenone in the product. The semicarbazone, prepared in aqueous suspension as for the active piperitenone oxide from *M. rotundifolia*, was identical to the *M. rotundifolia* ketone in respect to elementary analysis, ultraviolet absorption spectrum and in behavior in acid and base. The minor differences between the infrared spectra of the two appeared to be due to the necessary use of solid spectra.

The monoepoxide or its semicarbazone derivative could be converted to diosphenolene (II) readily by treatment with dilute acid. The product was identical in all respects to that obtained from piperitenone oxide obtained from *M. rotundifolia*. The reaction is analogous to the formation of diosphenol from piperitone oxide.[6]

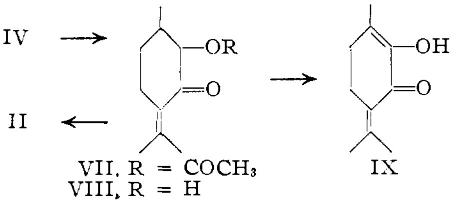
Other syntheses of diosphenolene started with pulegone which is more readily available than piperitenone. Conversion of pulegone into diosphenolene by two independent paths was possible.

The formation of bis-nitrosopulegone (V) by treatment of pulegone with amyl nitrite and hydrochloric acid was reported by Bayer and Prentice.[7] This had been converted to an isonitrosopulegone with ammonia. Heating the isonitroso derivative VI with dilute acid had given a low yield of nitrogen containing material which was not characterized. It has now been found that the isonitroso derivative can be converted to diosphenolene by acid treatment as already used for syntheses of diosphenolene reported above. The product was identical to diosphenolene from other methods of synthesis.

A possible synthetic route to diosphenolene from pulegone was by selenium dioxide treatment as reported by Cauquil.[8] The product was reported to be a diketone to which the structure of 4(8)-*p*-menthene-2,3-dione was given. This was a possible tautomeric form of diosphenolene, but the properties of this material did not agree with those of diosphenolene. Attempted duplication of the work gave a product in poor yield which was quite distinct from diosphenolene and in view of the other successful syntheses was not further studied.



The most useful synthesis of diosphenolene was a modification of the method used for the preparation of diosphenol from menthone.[9] Treatment of pulegone (IV) with mercuric acetate gave the desired 2-acetoxypulegone (VII). Hydrolysis and oxidation steps as with acetoxymenthone gave diosphenol (IX) instead of diosphenolene. It was found that acetoxypulegone was saponified readily and in the presence of excess alkali rearrangement of the bonds gave diosphenol. The formation of diosphenol occurred in the presence of 8% potassium hydroxide under reflux very quickly, and somewhat more slowly with 4% potassium hydroxide at 52°. It was possible to avoid this reaction by use of 1% alkali at lower temperatures. The resulting 2-hydroxypulegone (VIII) was then oxidized in good yield to diosphenolene under milder conditions than used for hydroxymenthone. The product from this synthesis also was identical to authentic diosphenolene.



Thus, the synthesis used, involving the conversion of ketone derivatives of piperitenone and pulegone to diosphenolene, provides further evidence for the proposed structures.

Acknowledgment.—The technical assistance of Mr. Verners J. Varnis and encouragement of this work by the A. M. Todd Company is gratefully acknowledged.

Experimental[10]

Epoxidation of Piperitenone.—To 5.0 g. of piperitenone[11]

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[3] D. Barnard, L. Bateman, A. J. Harding, H. P. Koch, N. Sheppard and G. B. B. M. Sutherland, *J. Chem. Soc.*, 915 (1950).

[4] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1956, p. 35.

[5] W. Treibs, *Ber.*, **66B**, 610 (1933).

[6] R. H. Reitsema, THIS JOURNAL, **78**, 3792 (1956).

[7] A. Bayer and K. Prentice, *Ber.*, **29**, 1078 (1896).

[8] G. Cauquil, *Compt. rend.*, **208**, 1156 (1939).

[9] A. K. Macbeth and W. G. P. Robertson, *J. Chem. Soc.*, 3512 (1953).

[10] Unbracketed αD is used for observed rotations on homogeneous material taken without solvent at room temperature in a 1 decimeter tube. Ultraviolet absorptions were taken on a Model DU Beckman spectrophotometer in 95% ethanol. Infrared analyses by Anderson Physical Laboratories, Champaign, Illinois. Microanalysis by Clark Microanalytical Laboratory, Urbana, Illinois, and Microtech Laboratories, Skokie, Illinois.

[11] The sample of piperitenone was kindly provided by Dr. J. P. Bain of the Glidden Co., Jacksonville, Florida.

(n^{20}D 1.5296; reported[12] 1.5294) in 20 ml. of isopropyl alcohol cooled to −9° there was added dropwise with stirring, at equal rates through two dropping funnels, 4 ml. of 30% aqueous hydrogen peroxide and 4.0 ml. of 10% potassium hydroxide. The temperature was maintained below −2° during the addition and the mixture was stirred at this temperature for an additional five hours. After standing overnight in a refrigerator, the slightly yellow solution was diluted with 70 ml. of water containing sodium chloride. The mixture was extracted with three 10-ml. portions of ether, the ether layers were combined, dried over magnesium sulfate and distilled. After removal of ether, two main fractions, distilling at 12 mm. pressure were obtained: (a) b.p. 149–154°, 2.5 g., n^{20}D 1.5056; and (b) b.p. 154–160°, 1.54 g., n^{20}D 1.4948. These were recombined and 3.24 g. was redistilled through a 10 cm. helices packed column at 2 mm. pressure giving: (1) b.p. 84–87°, 0.28 g., n^{20}D 1.5065, $\lambda_{\max}^{\text{EtOH}}$ 260 mμ (ϵ 6,950); (2) b.p. 87°, 1.28 g., n^{20}D 1.5043, $\lambda_{\max}^{\text{alc}}$ 260 mμ (ϵ 6,040); and (3) b.p. 87–88°, 0.42 g., n^{20}D 1.5048.

The elementary analysis of the fractions showed the presence of some unreacted piperitenone mixed with the major product, piperitenone oxide. Chromatography also showed the presence of a low concentration of piperitenone with the main constituent not distinguishable from naturally occurring piperitenone oxide. The infrared spectrum of the product fractions showed the presence of all peaks found in the piperitenone oxide separated from *M. rotundifolia*. Eight additional minor absorption points correlated with the major absorptions of piperitenone. Separation of the epoxide from the starting material contaminant by distillation was difficult because of the limited amount of starting material and the similarity in boiling points. Regeneration from derivatives was not possible due to sensitivity of the oxide to acids and bases.

The semicarbazone was prepared from the reaction product by vigorously stirring a suspension of 0.4 g. with 0.45 g. of sodium acetate and 0.6 g. of semicarbazide hydrochloride in 6.6 ml. of water for 4.5 hours at room temperature. The liquid was decanted from the waxy solid after cooling. The solid was washed with warm methanol and recrystallized from methanol giving 0.15 g. of a white granular product, m.p. 168–169°, $\lambda_{\max}^{\text{EtOH}}$ 274.5 mμ (ϵ 10,950). The melting point varied slightly under different conditions of recrystallization, drying and melting point determination and 170–171° was observed at times.

Anal. Calcd. for $C_{11}H_{17}O_2N_3$: C, 59.17; H, 7.68; N, 18.82. Found: C, 59.17; H, 7.67; N, 18.88.

The semicarbazone of *d*-piperitenone oxide from *M. rotundifolia* melted at 177.5–178° and had the same ultraviolet absorption as the synthetic material with $\lambda_{\max}$ 10,700 at 274.5 mμ.[2] As a result of the very low solubility of the semicarbazones in suitable solvents, the liquid phase infrared spectra were not obtained. The spectra of the solids run pelletized with KBr were slightly different in minor respects. It is known that differences in crystal structure can lead to some differences in infrared spectra.[13] Whether this slight variation is the result of different crystal structures of the racemic and active materials, of different forms of the semicarbazones being isolated, or, less likely, of diastereoisomerism was not determined. All other properties of the two series were identical.

3-Hydroxy-3,8(9)-*p*-menthadiene-2-one (Diosphenolene).—The synthetic piperitenone oxide (fraction 2 above) (0.5 g.) was added to 50 ml. of hot 10% sulfuric acid. Steam was passed into the mixture and 20 ml. of first fraction distillate and 35 ml. of second fraction distillate were collected. Both fractions gave very strong ferric chloride tests. Filtration of the first fraction after cooling gave white needles which were recrystallized from aqueous ethanol giving diosphenolene, m.p. 74–75°, $\lambda_{\max}^{\text{alc}}$ 306.5 mμ (ϵ 8,900), which showed no depression of melting point when mixed with material prepared by similar treatment of *M. rotundifolia* ketone.

Diosphenolene from Nitrosopulegone.—To a mixture of 50 g. of *d*-pulegone (n^{24}D 1.4861, α^{24}D 23.55°), 50 ml. of Skellysolve B, and 25 g. of amyl nitrite cooled in an ice-bath was added with stirring 13 drops of concentrated hydrochloric acid. The mixture became rather thick in ten minutes and was filtered. Repetition of the addition of acid to the cold filtrate gave three more crops of crystals which were washed with cold Skellysolve B. A total of 8.14 g. (15%) of air-dried crystals was obtained.

To 0.5 g. of the first crop covered with ether was added two drops of concentrated ammonia. This was allowed to stand until all was in solution and then 2 *N* sulfuric acid (about five drops) was added dropwise with stirring. The yellow crystals which appeared in the neutral mixture after separation and drying melted at 114.5–118°. Steam distillation of 0.32 g. of this crude product from 15 ml. of 10% sulfuric acid gave a few crystals in the condenser and white needles in the distillate upon cooling. These crystals gave a positive ferric chloride test and after recrystallization melted at 73–74° and failed to show depression in melting point when mixed with authentic diosphenolene. The ultraviolet absorption was in agreement with the previous spectrum of diosphenolene and showed a maximum absorption at 305 mμ (ϵ 9,200).

2-Acetoxy-4(8)-*p*-menthene-3-one (2-Acetoxypulegone).—A mixture of 85.5 g. of mercuric acetate and 41.0 g. of *d*-pulegone in 70 ml. of glacial acetic acid was stirred under gentle reflux for three hours. The liquid which had undergone numerous color changes was decanted from the layer of 47.7 g. of mercury into 800 ml. of water and extracted with three portions of ether. The organic layers were combined, washed twice with water, and dried over magnesium sulfate. Distillation after removal of ether and of acetic acid gave: 18.73 g. of recovered pulegone, b.p. 60–65° (3 mm.), n^{20}D 1.4863; 2.66 g. of an intermediate fraction, b.p. 75–92° (3 mm.), n^{20}D 1.4919; and 12.93 g. (44% of theoretical yield based upon recovered pulegone) of 2-acetoxypulegone, b.p. 96–98° (3 mm.), n^{20}D 1.4883. Redistillation of the main fraction through a short helices packed column gave a center cut, b.p. 102° (4 mm.), n^{22}D 1.4882, $\lambda_{\max}^{\text{alc}}$ 252 mμ (ϵ 6,010), α^{22}D −15.88.

Anal. Calcd. for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.35; H, 8.33.

The yield was not maximum and some undecomposed organic mercury derivatives remained as shown by the appearance of some mercury during the distillation.

Diosphenol from Acetoxypulegone.—2-Acetoxypulegone (5.8 g.) was stirred under reflux for 30 minutes with 50 ml. of 8% aqueous potassium hydroxide solution. After cooling, the orange oil was extracted with ether, the ether extracts dried and ether removed under vacuum leaving 3.5 g. (72%) of an oily solid. Recrystallization of this from methanol gave diosphenol, m.p. 82.5–83°, $\lambda_{\max}^{\text{alc}}$ 272 mμ (ϵ 8,800), positive ferric chloride test, which showed no melting point depression when mixed with an authentic sample.

2-Hydroxypulegone.—To 7.7 g. (0.0385 equiv.) of 2-acetoxypulegone was added with stirring 0.16 *N* aqueous potassium hydroxide at such a rate as to maintain the *p*H of the mixture between 8 and 10. After the first half hour at 25° when 41 ml. was added, the temperature was raised to 40° with a water-bath. After six hours 241 ml. (calculated 240 ml.) had been added and the rate of consumption of alkali had decreased to a very small value. The mixture was cooled and extracted with ether. No solid could be separated from the aqueous solution by neutralization with dilute sulfuric acid. Evaporation of ether from the organic extract left 4.66 g. (72%) of yellow oil which was distilled giving 3.74 g., b.p. 73–78° (3 mm.), n^{23}D 1.5048, $\lambda_{\max}^{\text{alc}}$ 254 mμ (ϵ 5,670), αD −5.65°. The crude product itself corresponded rather closely to the calculated analysis and was not purified further.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.56. Found: C, 70.85; H, 9.50.

Diosphenolene from Hydroxypulegone.—A mixture of 3.4 g. of 2-hydroxypulegone, 12.5 g. of glacial acetic acid and 4.65 g. of bismuth oxide was stirred at 110° for 10 minutes. The liquid was decanted from the bismuth metal (about 2.5 g.) into 250 ml. of water and the ether extracts were washed with water to remove acetic acid. Addition of ether caused more white solid to precipitate. This was removed by filtration and the organic layer was separated from the filtrate. The aqueous layer was extracted twice more with ether and the combined organic layers were washed with water to remove acetic acid. After drying the ether solution, ether was removed under vacuum leaving 3.19 g. (94%) of a light orange oil which suddenly crystal-

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(12) Y. R. Naves and G. Papazian, *Helv. Chim Acta*, **25**, 1023 (1942).

(13) H. Gilman, "Organic Chemistry," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 139.

lized to an oily solid. Recrystallization four times from methanol left 1.16 g. of white needles, m.p. 75–76°, λ_{max}^{alc} 304 mμ (ε 9,245). The material showed no mixed melting point depression with authentic diosphenolene prepared from piperitenone oxide. The ferric chloride test was very heavy dark green in color similar to the test with diosphenolene prepared in other ways.

KALAMAZOO, MICHIGAN

[JOINT CONTRIBUTION FROM THE INSTITUTO DE QUIMICA DE LA UNIVERSIDAD NACIONAL AUTONOMA DE MEXICO AND THE DEPARTMENT OF CHEMISTRY OF WAYNE STATE UNIVERSITY]

Terpenoids. XXX.[1] The Structure of the Cactus Triterpene Chichipegenin

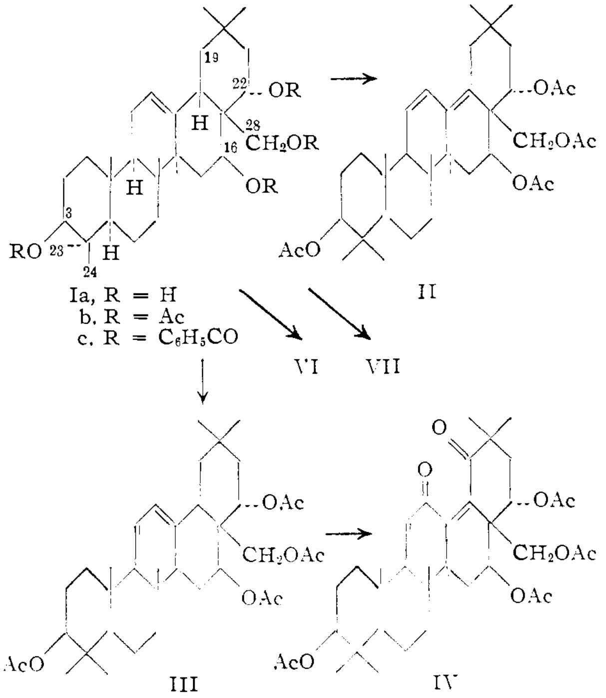
BY A. SANDOVAL, A. MANJARREZ, P. R. LEEMING,[2] G. H. THOMAS[3] AND CARL DJERASSI

RECEIVED APRIL 17, 1957

Chichipegenin—isolated from various *Myrtillocactus* species and from *Lemaireocereus chichipe*—has been converted *via* its 28-trityl ether VIa to longispinogenin (Va). Coupled with other degradation experiments, this leads to the conclusion that chichipegenin is Δ^{12}-oleanene-3β,16β,22α,28-tetrol (Ia), thus falling into the earlier established oxygenation pattern established for cactus triterpenes.

As pointed out recently,[4] the most characteristic triterpene of the genus *Myrtillocactus* of the *Cactaceae* family is a new tetrol, $C_{30}H_{50}O_4$. This substance has been named "chichipegenin" since it occurs also in large amounts in a single species of the genus *Lemaireocereus*, *L. chichipe*[5] (see Experimental section), and the taxonomic implications of this observation have already been commented upon.[4,6] We should now like to record the approach employed in the structure elucidation of this interesting triterpene.

Chichipegenin did not exhibit any infrared absorption in the carbonyl region but showed a strong band typical of one or more hydroxyl groups. Acetylation or benzoylation under mild conditions afforded the corresponding tetraacetate Ib and tetrabenzoate Ic, thus accounting for all four oxygen atoms. Furthermore, the ease of acylation indicated that these hydroxyl groups must either be primary and/or equatorially oriented secondary alcoholic functions. Since eventual correlation with a known triterpene was required for a definitive structure proof, it was important to establish to which broad class of triterpenes chichipegenin belonged. This was accomplished by examining the reactivity of chichipegenin tetraacetate toward selenium dioxide.



Oxidation in boiling acetic acid smoothly led to a diene, which on the basis of its characteristic triple ultraviolet absorption maxima[7] could be assigned the heteroannular $\Delta^{11,13(18)}$-formulation II, thus showing that chichipegenin was a member of the β-amyrin class of triterpenes. In order to eliminate position 19 as the site of one of the hydroxyl groups, the further oxidation of this diene II with selenium dioxide to the well known $\Delta^{9(11),13(18)}$-diene-12,19-dione IV[8] was attempted, but no pure product could be isolated. Reaction of chichipegenin tetraacetate Ib with N-bromosuccinimide did not lead to the desired $\Delta^{9(11),12,18}$-triene[9] but rather to an impure bromine-containing product in accordance with earlier observations in the queretaroic acid series.[10] However, with a limited amount of N-bromosuccinimide, it was possible to isolate

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[1] Paper XXIX, C. Djerassi and W. Rittel, THIS JOURNAL, **79**, 3528 (1957).

[2] Postdoctorate research fellow (1956–1957) at Wayne State University on funds supplied by the Division of Research Grants (grant No. RG-3863) of the National Institutes of Health, U. S. Public Health Service.

[3] Postdoctorate research fellow (1955) at Universidad Nacional Autonoma de Mexico under a grant from the Rockefeller Foundation.

[4] C. Djerassi, S. Burstein, H. Estrada, A. J. Lemin, A. E. Lippman, A. Manjarrez and H. G. Monsimer, THIS JOURNAL, **79**, 3925 (1957).

[5] N. L. Britton and J. N. Rose, "The Cactaceae," Vol. II, Carnegie Institution of Washington, Washington, D. C. 1920, p. 89. H. Bravo, "Las Cactaceas de Mexico," Imprenta Universitaria, Mexico, D. F., 1937, p. 258.

[6] C. Djerassi, 'Cactus Triterpenes' in "Festschrift Arthur Stoll," Birkhäuser, A. G., Basel, 1957, pp. 330–352.

[7] 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).

[8] A list of the various rings, C, D and E-substituted precursors leading to the same diene-dione (type IV) is given by D. H. R. Barton, N. J. Holness, K. H. Overton and W. J. Rosenfelder, *ibid.*, 3751 (1952), and by J. M. Beaton, J. D. Johnston, L. C. McKean and F. S. Spring, *ibid.*, 3660 (1953).

[9] *Cf.* L. Ruzicka, O. Jeger and J. Redel, *Helv. Chim. Acta*, **26**, 1235 (1943).

[10] C. Djerassi, J. A. Henry, A. J. Lemin, T. Rios and G. H. Thomas, THIS JOURNAL, **78**, 3783 (1956).