taken up in 50 ml. of dry acetone. The ammonium chloride was removed by filtration and the acetone was evaporated to an oil. This oil was dissolved in ether and, on slow evaporation of the solvent, 1.9 g. (47%) of **methanetriacetic acid** precipitated, m.p. 115–118°. This material could not be recrystallized without large losses and was used directly in the next step.

(Glutaric Anhydride β-Acetic)-anhyride (VII).—Two grams of (0.02 mole) of acetic anhydride was added to 1.9 g. (0.01 mole) of methanetriacetic acid and the mixture was heated on the steam-bath for 15 minutes. Excess anhydride and acetic acid were removed by distillation *in vacuo* and the dark, residual oil was triturated with acetone. This induced the crystallization of needles that were recrystallized from acetone to give 0.6 g. of VII as colorless needles, m.p. 150–151°; $\lambda_{\max}^{\text{KBr}}$ 5.55, 5.60 and 5.70 μ.

Anal. Calcd. for $C_{14}H_{14}O_9$: C, 51.53; H, 4.32; neut. equiv., 54.4. Found: C, 51.45; H, 4.33; neut. equiv., 55.9.

Glutarimide-β-acetic Acid (IV).—A mixture of 30 g. (0.117 mole) of cyano ester III in 100 ml. of concentrated hydrochloric acid was stirred for one hour at room temperature. The reaction mixture was poured into 100 ml. of water and the resulting solution was evaporated on the steam-bath at a reduced pressure of approximately 50 mm. The yellow residual oil was taken up in 200 ml. of dry acetone leaving behind a small amount (*ca.* 10%) of ammonium chloride.

On concentration of the acetone to about 20 ml., colorless crystals were deposited. These were removed by filtration to yield 10 g. (50%) of the glutarimide, m.p. 168–170°. The analytical sample crystallized from acetone–hexane as colorless crystals, m.p. 172–173°, $\lambda_{\max}^{\text{KBr}}$ 5.82 and 6.00 μ.

Anal. Calcd. for $C_7H_9O_4N$: C, 49.12; H, 5.30; N, 8.18. Found: C, 49.15; H, 5.59; N, 7.89.

Yields in this reaction were subject to considerable variation because the hydrolysis conditions were difficult to duplicate, but usually they were in the range of 26–55%.

Glutarimide-β-acetyl Chloride. a. From the Sodium Salt of IV.—A solution containing 1.1 g. (0.008 mole) of glutarimide-β-acetic acid (IV) in 25 ml. of 95% alcohol was titrated to phenolphthalein with 1.0 *N* sodium hydroxide. The solvent was removed *in vacuo* and to the colorless solid was added 4.8 g. of thionyl chloride. The resulting slurry was heated on the steam-bath for 15 minutes and the excess thionyl chloride was removed by distillation under reduced pressure. The last traces were taken off by codistillation with dry benzene.

The dark red residue was taken up in warm benzene, filtered and the filtrate was concentrated to about 15 ml. On cooling there was deposited 0.5 g. (33%) of the acid chloride as colorless needles, m.p. 129–132°. A purified sample crystallized from acetone–hexane as colorless needles, m.p. 129–130°, $\lambda_{\max}^{\text{KBr}}$ 5.50 and 5.95 μ.

Anal. Calcd. for $C_7H_8O_3NCl$: C, 44.34; H, 4.25; Cl, 18.70. Found: C, 44.56; H, 4.39; Cl, 18.64.

The residue that did not dissolve in benzene was shown by infrared analysis to be a mixture of the acid and acid chloride. This mixture could be recycled so that the actual yield of acid chloride was probably higher than 33%.

b. From the Free Acid IV.—A slurry of 8.6 g. (0.05 mole) of the acid and 30 g. of thionyl chloride was heated under reflux for 30 minutes. The deep orange solution was cooled and the crystalline solid that precipitated was filtered rapidly, washed with dry acetone and stored immediately in a desiccator. The yield of impure acid chloride by this procedure was 6.3 g. (66%), m.p. 125–130°.

On some occasions the excess thionyl chloride was distilled under reduced pressure and the last traces were removed by codistillation with benzene. The orange residue then was triturated with cold acetone and dried. Yields of acid chloride, m.p. 126–131°, by this method were generally in the range of 50–55%. Repeated crystallizations of this impure material were seldom profitable and once-recrystallized acid chloride usually was employed in the Rosenmund reduction.

Glutarimide-β-acetaldehyde (V).—To a flask equipped with a gas inlet tube, stirrer and condenser were added 150 ml. of dry toluene, 3.4 g. (0.018 mole) of once-recrystallized glutarimide-β-acetyl chloride and 0.3 g. of 10% palladium-on-barium sulfate catalyst. The mixture was heated to reflux and hydrogen was passed through the system. The hydrochloric acid formed was titrated with standard alkali.

After three hours, 82% of the theoretical amount of acid had been titrated. The reaction was stopped and the hot toluene solution was filtered free of catalyst. On cooling, there was deposited long colorless needles of the aldehyde. These were removed and a second crop was obtained by concentrating the filtrate. In total, there was obtained 1.8 g. (64%) of the aldehyde, m.p. 121–123°. The analytical sample crystallized as colorless needles from acetone–hexane, m.p. 122–123°; $\lambda_{\max}^{\text{KBr}}$ 3.19, 3.73, 5.82 and 5.95 μ.

Anal. Calcd. for $C_7H_9O_3N$: C, 54.19; H, 5.84; N, 9.03. Found: C, 54.23; H, 5.47; N, 8.93.

The semicarbazone crystallized from dilute alcohol as colorless needles, m.p. 230–231°.

Anal. Calcd. for $C_8H_{12}O_3N_4$: N, 26.40. Found: N, 26.53.

When the catalyst was poisoned with quinoline and sulfur as suggested[19] in the literature, no aldehyde could be obtained in this reduction.

ITHACA, NEW YORK

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[19] E. B. Hershberg and J. Cason, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 627.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Terpenes. VII.[1] The Structures of the Dieucarvelones

BY G. BÜCHI AND W. S. SAARI

RECEIVED JANUARY 21, 1957

The structures of the isomeric dieucarvelones obtained earlier by Wallach have been reinvestigated. β-Dieucarvelone was shown to be a mixture of the α- and ε-isomers. The γ- and ϑ-isomers described by this author never could be isolated but two new isomers, ε and ζ, were found. Two substances reported by Rupe from the reaction of eucarvone with magnesium and methyl iodide were shown to be identical with α- and β-dieucarvelone. Chemical and spectroscopic findings are in agreement with structure III for these isomers. The conjugate bimolecular reduction of eucarvone is discussed.

In 1899, and again in 1914, Wallach[2] reported that the reduction of eucarvone (I), with zinc in basic solution gave a series of compounds, $C_{20}H_{30}O_2$, which he named the dieucarvelones. Wallach found that these isomers could be separated by recrystallization from an acetic acid–water mixture into an α-isomer, m.p. 177°; β-isomer, m.p. 143°; γ-isomer, m.p. 128°; and a ϑ-isomer, m.p. 111°.

Because the α- and β-isomers only slowly decolorized a solution of bromine in acetic acid *with* liberation of hydrobromic acid and because they were not

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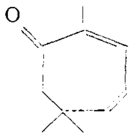
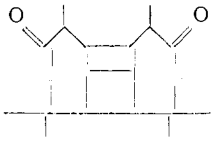
[1] Paper VI, G. Büchi and David Rosenthal, THIS JOURNAL, **78**, 3860 (1956).

[2] O. Wallach, *Ann.*, **305**, 223 (1899); **403**, 96 (1914).

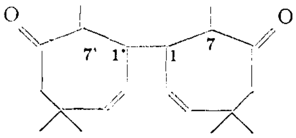
reducible over a palladium catalyst, he concluded that these compounds were saturated and proposed structure II for them. The γ-isomer, on the other hand, rapidly decolorized a solution of bromine in acetic acid with no liberation of hydrobromic acid. The unsaturated character of this isomer was furthermore ascertained by hydrogenation to a tetrahydro derivative over a palladium catalyst and structure III was proposed for the γ-isomer. The δ-isomer was isolated in such small yield that characterization was not possible.



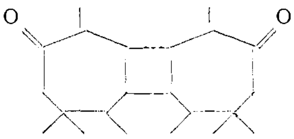
I



II



III



IV

In 1911, Rupe and Kerkovius[3] found that when eucarvone (I) was allowed to react with magnesium and methyl iodide two crystalline compounds for which they proposed structure IV ($C_{22}H_{36}O_2$) could be isolated in a total yield of 14%. They apparently did not realize that the melting points of their compounds and the corresponding oximes were identical with those of Wallach's α- and β-dieucarvelones.

The formation of both II and IV are mechanistically unsound in terms of present day theories and we therefore decided to reinvestigate these reactions. In this paper we describe work which shows that the dieucarvelones are most probably represented by III.

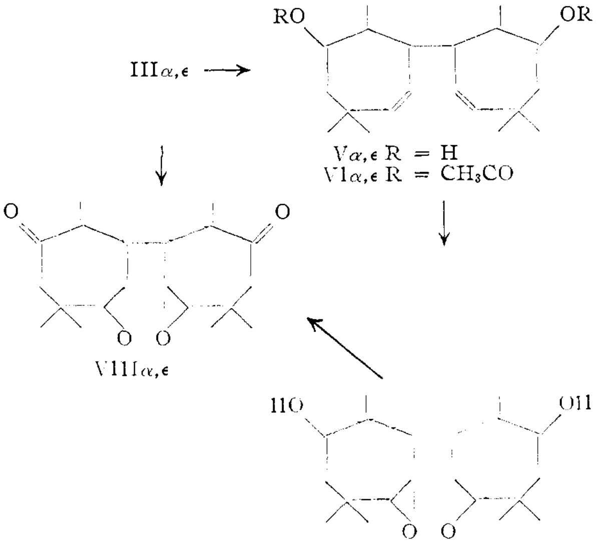
The α- and β-dieucarvelones were prepared easily by reduction of eucarvone with zinc dust in basic solution. Wallach's γ- and δ-isomers could never be isolated despite repeated recrystallization and chromatography of the crude reaction products, but two new isomers, ε- and ζ-dieucarvelone, were detected. Although the melting point of the ζ-isomer, 131°, is close to that of Wallach's γ-isomer, m.p. 128°, the two seem to differ markedly in their reactions with bromine in acetic acid solution.

When β-dieucarvelone, with a constant melting point of 142–144°, was chromatographed on active alumina, the α- and ε-isomers were obtained in yields of 23 and 77%, respectively. Both of these isomers were found to be stable to chromatography. Recombination of the α- and ε-isomers gave a mixture which was identical in all respects with the original β-dieucarvelone. Hence Wallach's β-dieucarvelone is not a pure compound but rather a mixture of the α- and ε-isomers. Confirmation was forthcoming from reduction of β-dieucarvelone with lithium aluminum hydride which yielded the α-glycol Vα in 23% yield and the ε-glycol Vε in 75% yield.

Repetition of Rupe and Kerkovius'[3] directions for the reaction of eucarvone with magnesium and methyl iodide gave two crystalline products in a total yield of 1% which appeared to be the compounds reported by them. These products were shown to be identical with α- and β-dieucarvelone by mixed melting point determinations.

Although none of the dieucarvelone isomers isolated decolorized a 5% solution of bromine in chloroform and all were saturated to tetranitromethane, we believe that they are in fact unsaturated since they all showed maxima in the infrared region at 3010, 1640 and 750 cm.$^{-1}$, characteristic of *cis*-disubstituted double bonds. Also the ultraviolet spectra of all the isomers exhibited strong end absorption at 210 mμ indicating unsaturation.

In order to further prove the unsaturated character of the dieucarvelone isomers, the α-glycol Vα obtained by a lithium aluminum hydride reduction of α-dieucarvelone (IIIα), was oxidized with perbenzoic acid. After seven days the α-glycol showed an uptake of peracid corresponding to 2.00 double bonds. Similarly the ε-glycol Vε derived from ε-dieucarvelone (IIIε) titrated for 1.96 double bonds after one day.



IIIα,ε

Vα,ε R = H
VIα,ε R = CH₃CO

VIIIα,ε

VIIα,ε

Furthermore we now have been able to hydrogenate the diacetate VIα, prepared from the α-glycol Vα, over Adams platinum catalyst in acetic acid solution to a tetrahydro derivative. The reduction is exceedingly slow and the fact that only this highly active catalyst is effective explains the negative results reported earlier by Wallach.[2] These findings as well as the inertness of α-dieucarvelone (IIIα) toward potassium permanganate (no reaction even in boiling pyridine) are only in agreement with the presence of two highly hindered double bonds in the molecule. It is significant that the three bands associated with the double bonds in the infrared spectra of the dieucarvelones are all present in every unsaturated derivative and disappear when any of the isomers, or their derivatives, are hydrogenated or converted to the epoxides. Contrary to Wallach's suggestion the dieucarvelones then must be bicyclic rather than tetracyclic.

Since α- and β-dieucarvelone can be recovered in

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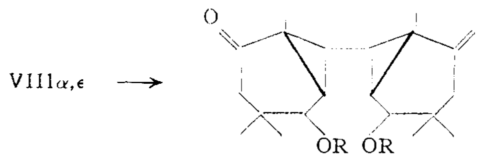
(3) H. Rupe and W. Kerkovius, *Ber.*, **44**, 2702 (1911). The analyses reported are also in agreement with $C_{20}H_{30}O_2$.

good yield from strenuous acid treatment, it is unlikely that they contain any three- or four-membered rings. This postulate is confirmed by the lack of significant absorption in the infrared in the regions usually associated with these groupings. Selenium dehydrogenation of the α-glycol Vα gave no aromatic compounds which could be detected spectroscopically and it is therefore unlikely that a six-membered ring is present in α-dieucarvelone. It is at any rate difficult to envision a change in the carbon skeleton of eucarvone under the conditions used in the preparation of III and structures containing two seven-membered rings seem much more plausible.

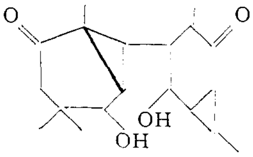
In agreement with structure III, α,α-dieucarvelone formed a hexadeutero derivative upon equilibration with alkaline deuterium oxide.

Oxidation of the α-diepoxyglycol VIIα with chromic acid in pyridine afforded α-diepoxydieucarvelone (VIIIα) which also could be obtained in good yield by epoxidation of α-dieucarvelone with trifluoroperacetic acid in the presence of a dibasic sodium hydrogenphosphate buffer. Similarly, ε-dieucarvelone (IIIε) yielded ε-diepoxydieucarvelone (VIIIε).

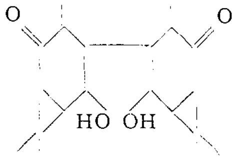
Treatment of α-diepoxydieucarvelone (VIIIα) with warm aqueous potassium hydroxide solution gave an isomeric compound which contained hydroxyl and carbonyl absorption in the infrared spectrum, a maximum in the ultraviolet spectrum at 216 mμ (ε 14,000) characteristic of cyclopropyl ketones,[4] was saturated to tetranitromethane and formed a diacetate (Xα). Only three structures (IX, XI and XII) fit these data. Since the dihydroxydiketone in question exchanged 3.76 hydrogens (after reconversion of –O–D to –O–H) upon equilibration with alkali in deuterium oxide, expression IXα must be the correct one.[5]



IXα,ε R, H
Xα,ε R, CH_3CO



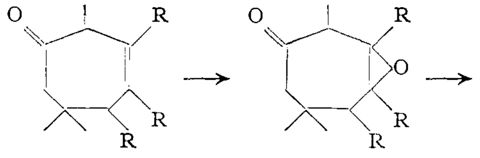
XI



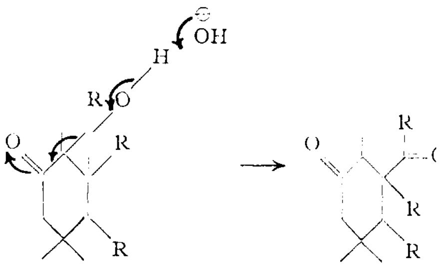
XII

An analogous dihydroxydiketone (IXε) which exchanged 3.88 H on deuteration was prepared by the same sequence from ε-dieucarvelone (IIIε). The two compounds were clearly different.

The conversion of VIII to IX involves a transannular displacement reaction and is similar to the one observed by Barton and Lindsey[6] with an epoxycyclononanone derived from caryophyllene. Conversions of cycloheptanes to bicyclo[4,1,0]heptanes seem to occur generally with great ease and other reactions of this type recently have been discovered by Corey, *et al.*[7] The presence of a cyclopropane ring in IXα and IXε excludes partial structures XIII for these two dieucarvelones because the corresponding dihydroxydiketones would have to be represented by XV. Compounds of this type are known to be unstable to base and to undergo rapid retroaldol reactions[8] (*cf.* XV → XVI) a behavior not observed with IX. Furthermore the β,γ-unsaturated ketones XIII would be expected to rearrange at least partially to the corresponding α,β-unsaturated ketones in the presence of acids or bases but no such transformations have been observed in the present investigation.



XIII, R = second ring XIV



XV XVI

A total of ten different isomers, namely, four *d,l*-pairs and two *meso* forms are possible from the parent structure III. Because α-dieucarvelone (IIIα) was not isomerized to any other isomer upon treatment with acid or base the methyl groups on C_7 and C_7' are already in the most stable configurations. The ε-isomer IIIε, on the other hand, was converted to an equilibrium mixture of the ε- and ζ-isomers on base-catalyzed isomerization. These facts clearly demonstrate that IIIα and IIIε cannot belong to the same (C_1, C_1', *syn* or *anti*) series and must have different configurations at C_1'. In agreement with this situation the α- and ε-isomers gave two different dihydroxydiketones (IXα and IXε).

Reduction of eucarvone (I) with zinc dust in the presence of ammonium chloride at 15° yielded only ε-dieucarvelone; under more strenuous conditions, however, a mixture of the ε- and α-isomers was

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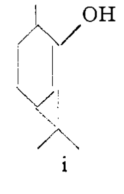
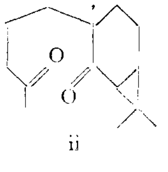
(4) R. H. Eastman and S. K. Freeman, THIS JOURNAL, **77**, 6642 (1955), and earlier references cited.

(5) Structures XI and XII have only three and two exchangeable hydrogens, respectively, because enols like i represent impossibly strained molecules. Similarly ii exchanged only five hydrogens (G. Büchi and D. M. White, THIS JOURNAL, **79**, in press (1957).



i



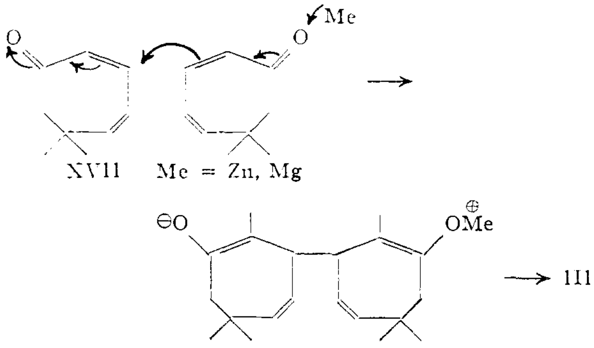
ii

(6) D. H. R. Barton and A. S. Lindsey, *J. Chem. Soc.*, 2988 (1951).

(7) E. J. Corey and H. J. Burke, THIS JOURNAL, **78**, 174 (1956).

(8) M. S. Kharasch, T. Rudy, W. Nudenberg and G. Büchi, *J. Org. Chem.*, **18**, 1030 (1953).

produced. This implies that the ϵ-isomer is formed through the transition state of lowest activation energy. We are inclined to believe that the formation of these "dimers" occurs *via* a concerted process involving reduction and Michael addition (*cf.* XVII → XVIII → III).



XVII Me = Zn, Mg

XVIII

There is ample precedent for such conjugate bimolecular reductions of α,β-unsaturated aldehydes[9] as well as α,β-unsaturated ketones[10] and a general mechanism for such changes has recently been discussed by Brewster.[11] In the case at hand the reaction could theoretically take any one of three different paths: (a) 1,4-reduction → 1,4-addition; (b) 1,6-reductions → 1,6-addition and (c) 1,4-reduction → 1,6-addition. Although both 1,6-reductions[12] and 1,6-Michael additions[13] have been observed, studies of molecular models suggest that any 1,6-process is unlikely due to steric interference of the neighboring methyl groups. Inspection of molecular models also indicates that in the *syn*-series the transition state, regardless of the mechanism of bond formation, is slightly less strained than in the *anti* series. This notion leads to the assumption that the ϵ-isomer is represented by one of the two *meso* forms and is the product of *rate controlled* ketonization of the enol XVIII.[14] The ζ-isomer then becomes the *thermodynamically most stable* isomer of the *syn*-series. α-Dieucarvelone thus is the most stable isomer in the *anti*-series. It must be pointed out though that an unambiguous assignment of configuration is by no means possible mainly because very little is known about the conformations of cycloheptenes. The configurational problem at hand is identical with the one of the isomeric perhydrodiphenic acids which has been solved so brilliantly by Linstead and Doering.[15] We have not yet had the courage to embark on a similar project to determine the configurations for the dieucarvelones.

Acknowledgment.—We are greatly indebted to Firmenich and Co., Geneva, for financial assistance and to the National Institutes of Health for a fellowship to W. S. S. Further, we should like to thank Mr. D. Shew for the preparation of dieucarvelone.

Experimental[16]

Eucarvone (I).—Eucarvone was prepared from carvone according to the directions of Corey and Burke[7] and was obtained as a yellow oil, b.p. 73–76° (5.0 mm.), $n^{25}\text{D}$ 1.5066 (lit.[7] $n^{21}\text{D}$ 1.5080), in a 45% yield.

Dieucarvelone Isomers.[2]—A solution of 68 g. (0.453 mole) of eucarvone in 700 ml. of 95% ethanol was added to a solution of 57 g. of potassium hydroxide in 250 ml. of water. After adding 57 g. (0.872 mole) of zinc dust, the mixture was heated under reflux for 3 hours with vigorous stirring and then allowed to stand at room temperature for 3.25 hours. One liter of ice-water was added and the precipitate filtered with suction. An additional liter of water was added to the filtrate and the solution extracted with ethyl ether which was then dried over anhydrous magnesium sulfate. After filtering, the solvents were removed *in vacuo* to give 2.6 g. (3.8%) of a yellow oil which could not be crystallized.

The filtered solids were extracted with chloroform and the solution dried over anhydrous sodium sulfate. After filtering, the solvent was removed *in vacuo* and the oily residue recrystallized from ethanol to give a total of 8.1 g. (12%) of α-dieucarvelone with a m.p. of 177–178° which was not raised upon further recrystallization. The sample did not decolorize a 5% solution of bromine in chloroform and was saturated to tetranitromethane in chloroform.

Anal. Calcd. for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00; mol. wt., 302. Found: C, 79.42; H, 9.97; mol. wt., 300.

The infrared spectrum (KBr) contained maxima at 3008(w), 2955(s), 1699(s), 1640(w) and 752(s) cm.$^{-1}$. In chloroform, the carbonyl absorption was at 1692 cm.$^{-1}$.

The ultraviolet spectrum (EtOH) showed a maximum at 285 mμ (ϵ 115) with end absorption at 211 mμ (ϵ 1,700).

Continued fractional recrystallization of the mother liquors gave a total of 19.1 g. (28.3%) of β-dieucarvelone with a m.p. of 139–142° which was raised to 142–144° by further recrystallization from ethanol. The sample did not decolorize a 5% solution of bromine in chloroform and was saturated to tetranitromethane in chloroform.

The infrared spectrum (KBr) contained maxima at 2960(s) with a shoulder at 3020(w), 1691(s), 1647(w) and 752(m) cm.$^{-1}$. The carbonyl absorption in chloroform was at 1692 cm.$^{-1}$. The ultraviolet spectrum (EtOH) showed a maximum at 285 mμ (ϵ 68) with end absorption at 211 mμ (ϵ 2050).

Further fractional recrystallization of the mother liquors gave a series of fractions from which no pure compounds could be obtained by repeated recrystallization. All of the fractions were saturated to tetranitromethane and showed no significant absorption in the ultraviolet region. Fractional recrystallization of this mixture from an acetic acid–water mixture followed by repeated recrystallization of the fractions from ethanol gave no pure compounds. A total of 21.4 g. (31.5%) of this isomer mixture was obtained. Removal of the solvent *in vacuo* gave 12 g. (18%) of a yellow oil which would not crystallize even after chromatography on alumina, activity I.

Isolation of ϵ- and ζ-Dieucarvelone from the Zinc and Base Reduction of Eucarvone.—One gram of the dieucarvelone isomer mixture (m.p. 112–125°) mentioned above was

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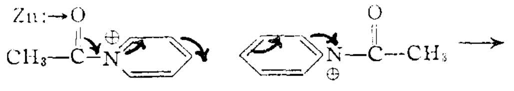
(9) C. Glacet, *Ann. chim.*, **12**, 293 (1947), and earlier papers cited.

(10) C. Harries and F. Hubner, *Ann.*, **296**, 295 (1897); the reduction of the closely related carvone is described in ref. 1; J. F. J. Dippy and R. H. Lewis, *Rec. trav. chim.*, **56**, 1000 (1937); J. F. Wiemann and C. Glacet, *Compt. rend.*, **226**, 923 (1948); R. C. Fuson and co-workers, THIS JOURNAL, **77**, 3776 (1955), and many earlier papers.

(11) J. H. Brewster, *ibid.*, **76**, 6361 (1954).

(12) *E.g.*



N,N,-diacetyltetrahydro-4,4,-bipyridyl; O. Dimroth and F. Frister *Ber.*, **55**, 3693 (1922).

(13) A. Eschenomoser, J. Schreiber and S. A. Julia, *Helv. Chim. Acta*, **36**, 482 (1953); J. W. Rolls, THIS JOURNAL, **75**, 2123 (1953); Y. Abe, *et al.*, *ibid.*, **78**, 1416 (1956).

(14) H. E. Zimmerman, *J. Org. Chem.*, **20**, 549 (1955).

(15) R. P. Linstead and W. von E. Doering, THIS JOURNAL, **64**, 2009 (1942), and earlier papers.

(16) Melting points and boiling points are uncorrected. Microanalyses by Mmes. N. Alvord and G. Kula and Dr. S. M. Nagy, M.I.T.; deuterium analyses by Mr. J. Nemeth, University of Illinois. The infrared spectra were measured on a Baird recording spectrophotometer model B and the ultraviolet spectra on a Cary recording spectrophotometer model 11.

chromatographed in the usual manner on 100 g. of Merck acid-washed alumina, activity I. Elution with an 80% benzene–petroleum ether mixture gave a series of fractions one of which upon repeated recrystallization from ethanol gave ζ-dieucarvelone, m.p. 131–132°, in a low yield. The infrared spectrum of this sample was identical with that of ζ-dieucarvelone obtained by base isomerization of ϵ-dieucarvelone and there was no mixed melting point depression.

Several fractions were eluted with benzene which when recrystallized from ethanol gave α-dieucarvelone with a m.p. of 177–178°. No depression was observed upon mixed melting point with an authentic sample.

Elution with a 2–5% ethyl ether–benzene mixture gave a series of fractions which when recrystallized from ethanol gave ϵ-dieucarvelone with a m.p. of 151–152°. The infrared spectrum of this sample was identical with that of ϵ-dieucarvelone obtained from the chromatography of β-dieucarvelone and there was no mixed melting point depression.

Rupe and Kerkovius Grignard Reaction of Eucarvone (I).[3]—To 1.1 g. (0.045 mole) of magnesium and a few drops of methyl iodide was added dropwise with stirring a solution of 6.0 g. (0.040 mole) of eucarvone and 6.4 g. (0.045 mole) of methyl iodide over a period of 2 hours. After the solution had been stirred at room temperature for 0.5 hour more, it was poured onto a mixture of 100 ml. of 10% sulfuric acid and ice. The reaction was extracted with ethyl ether which was then washed with water and dried over anhydrous magnesium sulfate. After filtering, the solvent was removed *in vacuo* and the oily residue chromatographed on 90 g. of alumina, activity I. Several of the fractions which were eluted with a 80% benzene–hexane mixture partially crystallized after standing overnight. These were combined and recrystallized from ethanol to give 0.04 g. (0.66%) of α-dieucarvelone with a m.p. of 178–179°. No depression was observed upon a mixed melting point with an authentic sample.

Later fractions of the recrystallization gave 0.02 g. (0.33%) of β-dieucarvelone with a m.p. of 142–143°. No depression was observed upon mixed melting point with an authentic sample.

Lithium Aluminum Hydride Reduction of α-Dieucarvelone (IIIα).—A solution of 1.7 g. (0.00563 mole) of α-dieucarvelone in 50 ml. of tetrahydrofuran was added over a period of 10 minutes to a slurry of 0.43 g. (0.0112 mole) of lithium aluminum hydride in 30 ml. of tetrahydrofuran with stirring. The mixture was then heated under reflux for 6 hours, cooled and the excess hydride decomposed with 15 ml. of ethyl acetate followed by 10 ml. of water. The reaction mixture was filtered and the residue washed with methylene chloride. The solvents were removed *in vacuo* and the crude product recrystallized from ethanol to give 0.775 g. (45%) of the α-glycol Vα with a m.p. of 246–248°. An analytical sample had a melting point of 249–249.4°. The infrared spectrum (KBr) contained bands at 3268(s), 2994(w), 2890(s), 1618(w) and 750(s) cm.$^{-1}$.

Anal. Calcd. for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18. Found: C, 78.07; H, 11.31.

A perbenzoic acid titration of the α-glycol Vα proceeded as follows: after 1 day, it titrated for 0.94 double bonds 2 days, 1.45; 3 days, 1.75; 4 days, 1.94; 7 days, 2.00 double bonds.

The α-Diepoxyglycol VIIα.—A solution of 0.1 g. (0.000328 mole) of the α-glycol Vα in 20 ml. of chloroform containing 0.178 g. (0.077 mole) of perbenzoic acid was allowed to stand at room temperature for seven days. The chloroform solution was then washed with a saturated ferrous sulfate solution, water, a saturated sodium bicarbonate solution, water and then dried over anhydrous sodium sulfate. After filtering, the solvent was removed *in vacuo* and the oily residue recrystallized from methanol to give 0.08 g. (73%) of the diepoxide with a m.p. of 172–174° dec. Recrystallization from methanol gave an analytical sample with a m.p. of 175.4–176.0° dec. which was saturated to bromine and tetranitromethane in chloroform. The infrared spectrum (KBr) contained maxima at 3500 to 3200(s), 2958(s), 1255(m), 1235(m), 943(m), 933(m), 890(m), 860(m), 820(m), 795(w) and 775(m) cm.$^{-1}$, the bands at 2994, 1618 and 750 cm.$^{-1}$ which were present in the spectrum of the α-glycol Vα having disappeared.

Anal. Calcd. for $C_{20}H_{34}O_4$: C, 70.97; H, 10.13. Found: C, 71.19; H, 10.02.

The α-Diacetate VIα.—A solution of 0.375 g. (0.00123 mole) of the α-glycol Vα in 20 ml. of pyridine and 5 ml. (0.005 mole) of acetic anhydride was allowed to stand at room temperature overnight. The solvents were removed *in vacuo* and the residue chromatographed on 20 g. of acid-washed alumina, activity I to II. Elution with a 50% benzene–petroleum ether mixture gave a white solid which was recrystallized from methanol to give 0.356 g. (70%) of the α-diacetate with a m.p. of 199–201°. Recrystallization from methanol gave an analytical sample with a m.p. of 202.4–203.0°. The infrared spectrum (KBr) contained maxima at 2933(w), 2857(s), 1718(s), 1634(w), 1232(s) and 755(m) cm.$^{-1}$.

Anal. Calcd. for $C_{24}H_{38}O_4$: C, 73.80; H, 9.81. Found: C, 73.58; H, 9.74.

Reduction of the α-Diacetate VIα.—When 0.051 g. (0.000135 mole) of the α-diacetate was reduced with hydrogen in 8 ml. of glacial acetic acid, using 5 mg. of platinum oxide as a catalyst, the reduction was complete after 8 hours with the uptake of hydrogen equivalent to 2.07 double bonds. Filtration, evaporation of the solvent and crystallization of the residue from methanol yielded 0.030 g. (60%) of the α-tetrahydrodiacetate with a m.p. of 197.8–198.5°. The product was saturated to bromine and tetranitromethane in chloroform. A strong depression was observed upon mixed melting point with the α-diacetate VIα. The infrared spectrum (KBr) contained maxima at 2940(s), 1728(s) and 1240(s) cm.$^{-1}$, the bands at 2933, 1634 and 755 cm.$^{-1}$ present in the spectrum of the α-diacetate having disappeared.

Anal. Calcd. for $C_{24}H_{42}O_4$: C, 73.05; H, 10.73. Found: C, 72.75; H, 10.56.

Deuterium Exchange of α-Dieucarvelone.—A solution of 0.100 g. (0.00032 mole) of α-dieucarvelone in 4 ml. of 95% EtOD–D$_2$O and 0.05 ml. of 20% NaOD–D$_2$O was heated under reflux in an atmosphere of nitrogen for 15 minutes. After cooling, the solvents were removed *in vacuo*. Four ml. of a 95% EtOD–D$_2$O mixture and 0.05 ml. of deuterium oxide were added to the residue and the solution was heated under reflux in an atmosphere of nitrogen for 15 minutes, cooled and the solvents removed *in vacuo*. After this last exchange had been repeated two more times, deuterium oxide was added to the solid residue and the mixture extracted with ethyl ether which was then dried over anhydrous sodium sulfate. After filtering, the solvent was then removed *in vacuo*, the residue recrystallized from a 95% EtOD–D$_2$O mixture and then sublimed at 120° (0.1 mm.) to give 51 mg. (51%) of the deuterated α-dieucarvelone with a m.p. of 174–174.5°.

Anal. Calcd. for $C_{20}H_{24}D_6O_2$: D, 20.0. Found: D, 20.2.

Attempted Acid-catalyzed Isomerization of α-Dieucarvelone.—A solution of 0.5 g. (0.00166 mole) of α-dieucarvelone in 35 ml. of absolute ethanol and 10 ml. of 20% (vol.) sulfuric acid was heated under reflux for 5 hours. Ice-water was added to the solution and the product extracted with ether after saturating with sodium chloride. The ether solution was dried over anhydrous magnesium sulfate, filtered free from drying agent and the solvent removed *in vacuo*. The residue was recrystallized from ethanol and gave 0.32 g. (64%) of α-dieucarvelone with a m.p. of 177.5–178°. No depression was observed upon mixed melting point with an authentic sample.

Attempted Acid-catalyzed Isomerization of β-Dieucarvelone.—An identical experiment carried out with the β-isomer led only to recovered starting material (74%).

Oxidation of the α-Diepoxyglycol VIIα.—To a solution of 0.040 g. (0.000118 mole) of the α-diepoxyglycol in 5 ml. of pyridine was added 0.070 g. (0.00070 mole) of chromium trioxide. After the mixture had remained at room temperature for 2 days, water was added and the ketone extracted with chloroform. After drying over anhydrous sodium sulfate, the solution was filtered and the solvent removed *in vacuo* to give a dark brown solid. Recrystallization from a chloroform–methanol mixture gave 0.027 g. (69%) of crude α-diepoxydieucarvelone (VIIIα) with a m.p. of 285–290° dec. Further recrystallization raised the melting point to 295–296° dec. The infrared spectrum was identical with that of α-diepoxydieucarvelone obtained from epoxidation of α-dieucarvelone and there was no mixed melting point depression.

α-Diepoxydieucarvelone (VIIIα).—To 0.15 ml. (0.0053 mole) of 90% hydrogen peroxide in 1 ml. of methylene chloride was added slowly 0.9 ml. (0.0063 mole) of trifluoroacetic anhydride. The mixture was kept in an ice-bath and allowed to remain cool until 5 minutes after the addition of the anhydride was complete. This solution was then added dropwise with stirring to a solution of 0.5 g. (0.00166 mole) of α-dieucarvelone in 10 ml. of methylene chloride with 3 g. of dibasic sodium hydrogen phosphate present as a buffer. The solution warmed to reflux temperature during the addition and was then allowed to stand at room temperature for 15 hours with stirring. The solution was filtered, washed successively with a saturated solution of ferrous sulfate, water, a saturated sodium bicarbonate solution, water and then dried over anhydrous magnesium sulfate. After filtering, the solvent was removed *in vacuo* and the residue recrystallized from a chloroform–ethanol mixture to give 0.3 g. (52%) of α-diepoxydieucarvelone with a m.p. of 294–296° dec. Recrystallization from chloroform gave an analytical sample with a m.p. of 296.5–298.5° dec. which did not decolorize a 5% solution of bromine in chloroform and was saturated to tetranitromethane. The infrared spectrum (KBr) contained maxima at 2960(s), 1690(s), 1405(w), 1290(m), 1265(m), 1245(m), 1200(m), 945(m), 915(m), 890(w), 840(s), 815(s), 785(w) and 775(m) cm.$^{-1}$, the bands at 3012, 1639 and 750 cm.$^{-1}$ present in the infrared spectrum of α-dieucarvelone having disappeared.

Anal. Calcd. for $C_{20}H_{30}O_4$: C, 71.82; H, 9.04. Found: C, 71.58; H, 9.14.

ε-Diepoxydieucarvelone (VIIIε).—This compound was prepared in 63% yield by the method described for the α-isomer. Recrystallization from ethanol gave an analytical sample with a m.p. of 176.5–177.5° which was saturated to bromine and tetranitromethane in chloroform. A strong depression was observed upon mixed melting point with α-diepoxydieucarvelone. The infrared spectrum (KBr) contained maxima at 2950(s), 1694(s), 1296(m), 1286(m), 1277(m), 1240(w), 1195(s), 940(m), 924(w), 902(w) 845(m), 820(m) and 809(m) cm.$^{-1}$, the bands at 3012, 1639 and 750 cm.$^{-1}$ present in the infrared spectrum of ε-dieucarvelone having disappeared. In chloroform solution the carbonyl absorption was at 1684 cm.$^{-1}$.

Anal. Calcd. for $C_{20}H_{30}O_4$: C, 71.38; H, 9.04; mol. wt., 334. Found: C, 71.51, 71.63; H, 8.94, 9.09; mol. wt., 349.

Base Isomerization of α-Diepoxydieucarvelone (VIIIα).—A mixture of 0.33 g. (0.00099 mole) of α-diepoxydieucarvelone (VIIIα), 25 ml. of ethanol and 15 ml. of a 5% potassium hydroxide solution was heated under reflux with stirring. After 15 minutes solution was complete. The reaction mixture was then extracted with chloroform which was dried over anhydrous sodium sulfate. After filtering, the solvent was removed *in vacuo* and the residue recrystallized from chloroform to give 0.245 g. (74%) of the α-dihydroxydiketone IXα with a m.p. of 263–265°. Further recrystallization from chloroform gave an analytical sample with a m. p. of 265–266° which was saturated to tetranitromethane in chloroform and did not decolorize a 5% solution of bromine in chloroform.

Anal. Calcd. for $C_{20}H_{30}O_4$: C, 71.82; H, 9.04. Found: C, 71.58; H, 8.82.

The infrared spectrum (KBr) contained maxima at 2540(s and broad), 2945(s), 1660(s and broad), 1430(m) and 1012 (m) cm.$^{-1}$. The ultraviolet spectrum (EtOH) showed maxima at 216 mμ (ε 14,000) and 282 mμ (ε 328).

The diacetate was prepared in the usual manner with acetic anhydride in pyridine. Recrystallization of the crude product from methanol gave an analytical sample with a m.p. of 275.5–277°. The infrared spectrum ($CHCl_3$) contained maxima at 2960(m), 1728(s), 1686(s), 1240 to 1210(s) and 1015(m) cm.$^{-1}$.

Anal. Calcd. for $C_{24}H_{34}O_6$: C, 68.86; H, 8.19. Found: C, 68.54; H, 8.17.

Deuterium Exchange of the α-Dihydroxydiketone (IXα).—A solution of 0.060 g. (0.00018 mole) of IXα, in 4 ml. of 95% EtOD–D_2O and 0.05 ml. of 20% NaOD–D_2O was heated under reflux in an atmosphere of nitrogen for 15 minutes. After cooling, the solvents were removed *in vacuo*. Four ml. of a 95% EtOD–D_2O mixture and 0.05 ml. of deuterium oxide were added to the residue and the solution was heated under reflux in an atmosphere of nitrogen for 15 minutes, cooled and the solvents removed *in vacuo*. After this last exchange had been repeated two more times, deuterium oxide was added and the solid residue filtered with suction and washed with 4 ml. of deuterium oxide. The residue was then dissolved in tetrahydrofuran and dried over anhydrous magnesium sulfate. After filtering, the solvent was removed *in vacuo* and the residue dissolved in methanol to exchange the hydroxyl deuteriums. The methanol was removed *in vacuo* and the crude product sublimed at 150° (0.1 mm.) to give 0.030 g. (50%) of the deuterated α-dihydroxydiketone with a m.p. of 262–263.5°. The infrared spectrum of the deuterated IXα showed no absorption in the –O–D region.

Anal. Calcd. for $C_{20}H_{26}D_4O_4$: D, 13.33. Found: D, 12.45.

Base Isomerization of ε-Diepoxydieucarvelone (VIIIε).—A mixture of 0.35 g. (0.00105 mole) of VIIIε and 40 ml. of a 5% potassium hydroxide solution was heated under reflux with stirring for 1.5 hours. After cooling, the solution was saturated with sodium chloride and extracted with chloroform which was then dried over anhydrous magnesium sulfate. Removal of the filtered solvent *in vacuo* and recrystallization of the residue from an ethanol–benzene mixture gave 0.245 g. (70%) of the ε-dihydroxydiketone IXε with a m.p. of 235–238°. Recrystallization from an ethanol–benzene mixture gave an analytical sample with a m.p. of 239–240.5° which was saturated to tetranitromethane and did not decolorize a 5% solution of bromine in chloroform.

Anal. Calcd. for $C_{20}H_{30}O_4$: C, 71.82; H, 9.04. Found: C, 71.52; H, 9.02.

The infrared spectrum (KBr) contained maxima at 3500(s and broad), 2945(s), 1682(s and broad), 1648(s), 1432(m) and 1005(m) cm.$^{-1}$. The ultraviolet spectrum (EtOH) showed maxima at 210 mμ (ε 11,200) and 280 mμ (ε 178).

The diacetate was prepared in the usual manner with acetic anhydride in pyridine. Recrystallization of the crude product from ethanol gave an analytical sample with a m.p. of 216.5–217.5°. The infrared spectrum ($CHCl_3$) contained maxima at 2980(m), 1275(s), 1686(s), 1250 to 1220(s) and 1013(m) cm.$^{-1}$.

Deuterium Exchange of the ε-Dihydroxydiketone IXε.—Using the method described above for the α-dihydroxydiketone IXα the deuterated ε-dihydroxydiketone, m.p. 237–239°, was obtained in 45% yield. The infrared spectrum of the deuterated IXε showed no absorption in the O–D region.

Anal. Calcd. for $C_{20}H_{26}D_4O_4$: D, 13.33. Found: D, 12.95.

Chromatography of β-Dieucarvelone. ε-Dieucarvelone (IIIε).—The chromatography of 60 mg. of β-dieucarvelone, with a constant melting point of 142–144°, on 6 g. of Merck acid-washed alumina, activity I, was carried out in the usual manner. Elution with benzene gave 14 mg. of a solid which when recrystallized from ethanol gave α-dieucarvelone with a m.p. of 177.0–177.8°. No depression was observed upon mixed melting with an authentic sample. A strong depression was observed upon mixed melting with β-dieucarvelone.

Elution of the column with a 5% ethyl ether–benzene mixture gave 45 mg. of a solid which when recrystallized from ethanol gave ε-dieucarvelone with a m.p. of 153.0–153.5°. The melting point was not raised upon further recrystallization. ε-Dieucarvelone did not decolorize a 5% solution of bromine in chloroform and was saturated to tetranitromethane in chloroform. No depression was observed upon mixed melting with β-dieucarvelone.

Anal. Calcd. for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00; mol. wt., 302. Found: C, 79.64; H, 10.07; mol. wt., 288.

The infrared spectrum (KBr) showed maxima at 2980(s) with a shoulder at 3017(m), 1692(s), 1645(w) and 755(w) cm.$^{-1}$. The ultraviolet spectrum (EtOH) shows a maximum at 285 mμ (ε 68) with end absorption at 210 mμ (ε 1,260).

A mixture of equal amounts of α- and ε-dieucarvelone was recrystallized from methanol. Pure α-dieucarvelone was obtained from the first fractions. The later fractions gave β-dieucarvelone with a constant melting point of 141–143°. The infrared spectrum of this sample was identical with that of β-dieucarvelone isolated from the zinc dust-base reduction of eucarvone and no mixed melting point depression was obtained.

Trifluoroperacetic Acid Reaction of β-Dieucarvelone.—The oxidation was performed as described for α-dieucarvelone (VIIIα). The product was recrystallized from a chloroform–methanol mixture to give 0.25 g. (7.5%) of α diepoxydieucarvelone (VIIIα), with a m.p. 260–270° dec. The melting point was raised to 296–298° dec. by further recrystallization from chloroform. The infrared spectrum was identical with that of an authentic sample of VIIIα and no mixed melting point depression was observed.

Solvent was removed from the mother liquors and the oily residue recrystallized from ethanol to give 1.9 g. (57%) of ε-diepoxydieucarvelone (VIIIε) with a melting point of 167–171°. The melting point was raised to 176–177° by further recrystallization from ethanol. The infrared spectrum was identical with that of an authentic sample of VIIIε and no mixed melting point depression was observed.

Lithium Aluminum Hydride Reduction of β-Dieucarvelone.—A solution of 4.0 g. (0.0132 mole) of β-dieucarvelone in 100 ml. of tetrahydrofuran was added over a period of 20 minutes to a slurry of 0.86 g. (0.023 mole) of lithium aluminum hydride in 70 ml. of tetrahydrofuran with stirring. The mixture was then heated under reflux for 5 hours, cooled and the excess hydride decomposed with 10 ml. of ethyl acetate followed by 20 ml. of water. The reaction mixture was filtered and the residue placed in a Soxhlet extractor and extracted with chloroform. The solvents were removed *in vacuo* and the crude product recrystallized from methanol to give 0.9 g. (22.5%) of the α-glycol Vα with a m.p. of 248–249°. The infrared spectrum of this sample was identical with that of an authentic sample of the α-glycol and there was no depression upon mixed melting point.

Concentration of the mother liquors gave 3.0 g. (75%) of the ε-glycol Vε with a m.p. of 182–184°. Recrystallization from methanol gave an analytical sample with a m.p. of 182.6–183.8°. The infrared spectrum (KBr) contained bands at 3390(s), 3000(m), 2950(s), 1640(w), and 752(s) cm.$^{-1}$.

Anal. Calcd. for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18. Found: C, 78.33; H, 11.19.

A perbenzoic acid titration of the ε-glycol Vε proceeded as follows: after 10 hours, the glycol titrated for 1.38 double bonds; 24 hours, 1.96 double bonds.

Attempted Base Isomerization of α-Dieucarvelone.—A solution of 0.69 g. (0.00229) mole of α-dieucarvelone and 0.3 g. of sodium in 100 ml. of absolute ethyl alcohol was allowed to stand at room temperature for 48 hours. A saturated sodium chloride solution was added and the mixture extracted with chloroform which was then dried over anhydrous magnesium sulfate. After filtering, the solvents were removed *in vacuo* and the solid residue recrystallized from ethanol. The first fractions, 0.500 g., had a melting point of 174–175° which was not lowered when melted with an authentic sample of α-dieucarvelone. The later fractions had a lower melting point and were chromatographed on 5 g. of alumina, activity I. A series of fractions was obtained (0.073 g.) which when recrystallized from ethanol had a m.p. of 177–178° which was not lowered when melted with an authentic sample of α-dieucarvelone. A total of 0.573 g. (83%) of α-dieucarvelone was recovered from the reaction mixture.

Base Isomerization of ε-Dieucarvelone (IIIε).—A solution of 0.700 g. (0.00232 mole) of ε-dieucarvelone and 0.15 g. of sodium in 50 ml. of absolute ethyl alcohol was allowed to stand at room temperature for 48 hours. A saturated sodium chloride solution was added and the mixture extracted with chloroform which was then dried over anhydrous magnesium sulfate. After filtering, the solvents were removed *in vacuo* and the solid residue chromatographed on 70 g. of Merck acid-washed alumina, activity I. Elution with benzene followed by a 10% chloroform–benzene mixture gave 0.377 g. (54%) of ζ-dieucarvelone which when recrystallized from ethanol gave an analytical sample with a m.p. of 131.0–132.0° which did not decolorize a 5% solution of bromine in chloroform and was saturated to tetranitromethane in chloroform.

Anal. Calcd. for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00; mol. wt., 302. Found: C, 79.05; H, 9.86; mol. wt., 280.

The infrared spectrum (KBr) contained maxima at 3020 (m), 2930(s), 1700(s), 1640(w) and 755(m) cm.$^{-1}$. The ultraviolet spectrum (EtOH) showed a maximum at 290 mμ (ε 53) with end absorption at 210 mμ (ε 1,780).

Elution of the column with chloroform gave 0.285 g. (41%) of ε-dieucarvelone which when recrystallized from ethanol had a m.p. of 150–152°. Further recrystallization raised the melting point to 151.5–152.5° which was not lowered when melted with an authentic sample.

Zinc Reduction of Eucarvone (I).—A solution of 0.2 g. (0.00133 mole) of eucarvone and 1 g. of ammonium chloride in 10 ml. of an ethanol-water mixture was cooled to 10–15° with an ice-bath. Two grams of zinc dust was added and the slurry stirred vigorously at this temperature for 45 minutes. The mixture was then filtered and the filtrate extracted with ethyl ether which was dried over anhydrous magnesium sulfate. After filtering, the oily residue was recrystallized from methanol to give 0.025 g. (12.5%) of ε-dieucarvelone with a m.p. of 150.5–152.0°. The infrared spectrum of this sample was identical with that of an authentic sample and no mixed melting point depression was observed. Only uncrystallizable oils could be obtained from the mother liquors.

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

Terpenoids. XXVIII.[1] The Triterpene Composition of the Genus Myrtillocactus[2]

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All known species of the genus *Myrtillocactus* have been examined. While no alkaloids were encountered, seven triterpenes have been isolated of which only two have been found outside the cactus family. Cochalic acid, chichipegenin and myrtillogenic acid seem to be particularly characteristic of this genus and attention is called to possible taxonomic implications of these results.

The main purpose of our chemical investigations of giant cacti has been the isolation and structure proof of new alkaloids and triterpenes.[4] It was felt desirable to study, as far as possible, all species of a given genus which contained alkaloids or triterpenes since such results could be of biogenetic and taxonomic interest. Some fruitful conclusions already have been reached from examinations of the genera *Lemaireocereus*,[4,5] *Machaerocereus*,[6] and *Lophocereus*[7] and we should now like to report on a

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(1) Paper XXVII, C. Djerassi and H. G. Monsimer, THIS JOURNAL, **79**, 2901 (1957).

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(4) For a summary see "Cactus Triterpenes," by C. Djerassi in "Festschrift Arthur Stoll," Birkhäuser, Basel, 1957, pp. 330-352.

(5) See C. Djerassi, A. Bowers, S. Burstein, H. Estrada, J. Grossman, J. Herrán, A. J. Lemin, A. Manjarrez and S. C. Pakrashi, THIS JOURNAL, **78**, 2312 (1956), and earlier papers.

(6) C. Djerassi, L. H. Liu, E. Farkas, A. E. Lippman, A. J. Lemin, L. E. Geller, R. N. McDonald and B. J. Taylor, *ibid.*, **77**, 1200 (1955).

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