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.

CAMBRIDGE 39, MASS.

[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]

BY CARL DJERASSI, S. BURSTEIN, H. ESTRADA, A. J. LEMIN,[3a] A. E. LIPPMAN,[3b] A. MANJARREZ AND H. G. MONSIMER

RECEIVED JANUARY 23, 1957

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

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

(2) Supported by grants from the Rockefeller Foundation and from the Division of Research Grants of the National Institutes of Health, U. S. Public Health Service (grant No. RG-3863). We are indebted to Dr. H. Bravo (Instituto de Biologia, Mexico, D. F.) for the botanical identifications.

(3) (a) Postdoctorate research fellow at Universidad Nacional Autonoma de Mexico, 1954–1955. (b) Postdoctorate research fellow at Wayne State University, 1953–1955.

(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).

(7) C. Djerassi, S. K. Figdor, J. M. Bobbitt and F. X. Markley, *ibid.*, **79**, 2203 (1957), and earlier papers.

detailed investigation of the genus *Myrtillocactus*.

Britton and Rose[8] have assigned four species—*M. geometrizans*, *M. cochal*, *M. schenckii* and *M. eichlamii*—to this genus, which is indigenous to Mexico and Guatemala. *Myrtillocactus grandiareolatus* is usually considered a synonym[9] for *M. geometrizans*, but our chemical results indicate a distinct difference. Through the coöperation of Mr Howard E. Gates (Corona, California), Don Mariano Pacheco (Guatemala, C.A.) and Dr. Alberto Sandoval (Instituto de Quimica, Mexico, D.F.) it has been possible to secure specimens of all five species, which were investigated in the customary manner[4] for alkaloids and triterpenoid glycosides. All of these plants were rich in glycosides but did not contain any alkaloids, in agreement with earlier results among the *Cactaceae*[4] as well as other plant families[10] that glycosides and alkaloids usually do not occur in the same plant. In three instances, the non-glycosidic, neutral fraction was saponified[11] and was found to contain small amounts of triterpenes which were present in esterified form.

Myrtillocactus cochal (Baja California, Mexico) proved to be particularly rich in triterpenes. Acid hydrolysis of the glycosides yielded a neutral and an acidic fraction. The former consisted of essentially one triterpene which could be purified by direct crystallization and was found to be a new triterpene tetrol ($C_{30}H_{50}O_4$). With one exception (*M. schenckii*) this tetrol has proved to be the principal triterpene of all *Myrtillocactus* species and it has been encountered subsequently in only one species of another genus, namely, *Lemaireocereus chichipe*. We have named the substance chichipegenin and its structure elucidation[12] is being undertaken jointly with Dr. Alberto Sandoval and collaborators. The acidic portion consisted chiefly of one acid, cochalic acid, the structure (Ia) of which recently has been established.[13] Methylation of the mother liquors and chromatography gave in addition to methyl cochalate the methyl ester of a new trihydroxy triterpene acid which has now been named myrtillogenic acid and whose structure has been shown[1] to be IIa. Saponification of the oily, neutral, non-glycosidic constituents of this cactus furnished a small amount of longispinogenin (IIIa).[14] The co-occurrence of cochalic acid (Ia) and longispinogenin (IIIa), two triterpenes which differ only in the oxidation state of C-28, suggested that myrtillogenic acid (IIa) and the new tetrol chichipegenin might bear the same relationship to each other. This possibility was eliminated, however, when it was found that the lithium aluminum hydride reduction product (IVa) of myrtillogenic acid (II) was different from chichipegenin.

Myrtillocactus geometrizans (Central Mexico) exhibited qualitatively the same triterpene composition as *M. cochal* thus confirming the close botanical relationship of these two species. The common structural feature among its three triterpenes of known structure—cochalic acid (Ia), myrtillogenic acid (IIa) and longispinogenin (IIIa)—is the fact that they are oxygenated at positions 3, 16 and 28. Whether this also applies to the main constituent, chichipegenin, will have to be determined by degradation experiments which are now in progress.[12]

Myrtillocactus eichlamii is the only species of this genus which grows in Guatemala and it also contained chichipegenin, cochalic acid (Ia), myrtillogenic acid (IIa) and longispinogenin (IIIa), the latter being present in the non-glycosidic portion. In addition, there was encountered oleanolic acid (Va) (from the glycosidic fraction) and maniladiol (VI) (present in esterified form). The isolation of the latter is of interest since it has so far been found only in *manila elemi* resin[15] and in the cactus *Escontria chiotilla*.[5] Structurally, it fits nicely into the cactus triterpene pattern[4] according to which oxygenation is observed only in rings D and E aside from C-3.

The remaining two Mexican species *M. grandiareolatus* and *M. schenckii* yielded only two triterpenes.[16] The principal constituent of the former was the above-mentioned chichipegenin accompanied by some oleanolic acid (Va) while the latter contained oleanolic acid (Va) and stellatogenin (VIIa).[17]

From these studies it can be concluded that chichipegenin is the most characteristic triterpene (followed by cochalic and myrtillogenic acids) of this genus since it has been isolated in large amounts from four species. The only species which did not contain it, *M. schenckii*, yielded triterpenes which are characteristic[4] of the genus *Lemaireocereus*, while the only species outside the genus *Myrtillocactus* where chichipegenin has been encountered has been *Lemaireocereus chichipe*.[12] It would appear that a botanical reinvestigation of these two species is in order and in view of the considerable taxonomic difficulties among the *Cactaceae* chemical criteria (such as triterpene content) might be used to good advantage.

Britton and Rose[4] have pointed out that botanically the genus *Myrtillocactus* has no close relatives and it has been placed next to *Lophocereus* only because plants of both genera show several flowers at each areole. Chemically these two genera are completely distinct[4] since all *Lophocereus* species are rich in alkaloids but do not contain any triterpenoid glycosides in marked contrast to the above described *Myrtillocactus* species.

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

(9) H. Bravo, "Las Cactaceas de Mexico," Imprenta Universitaria, Mexico, D.F., 1937, pp. 308–314.

(10) *Cf.* M. E. Wall, C. R. Eddy, J. J. Willaman, D. S. Correll, B. G. Schubert and H. S. Gentry, *J. Amer. Pharm. Assoc.*, **43**, 503 (1954).

(11) The observation that cactus triterpenes may sometime also be present in esterified form was first made by Dr. Alberto Sandoval working with *Lemaireocereus chichipe*.

(12) To be published.

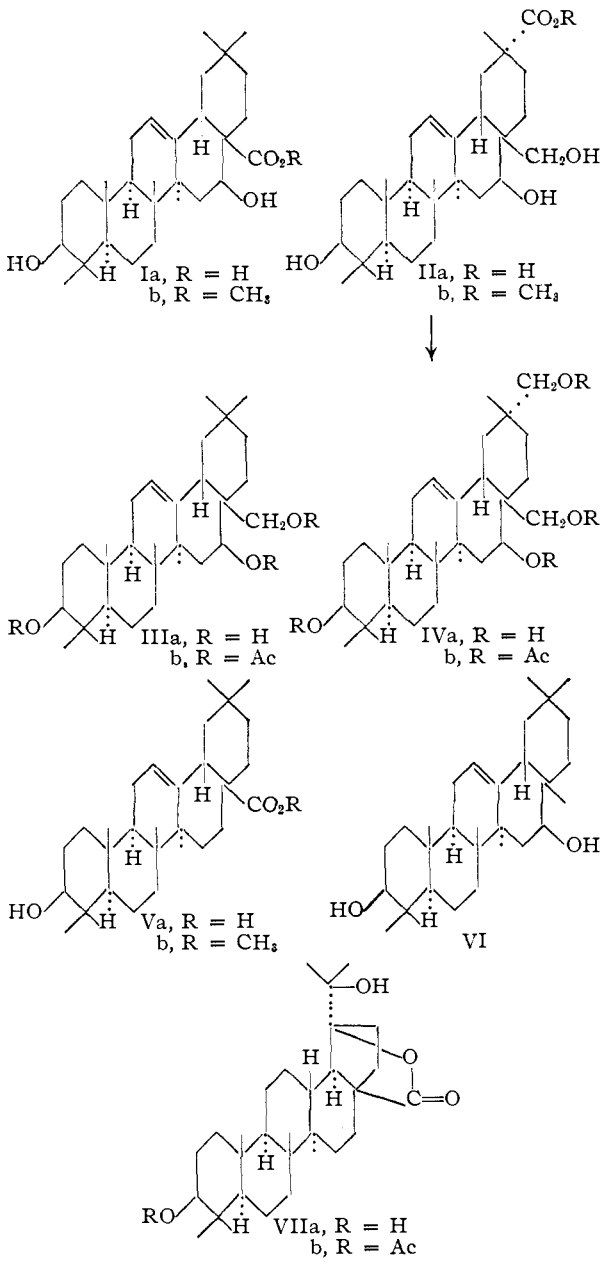
(13) C. Djerassi, G. H. Thomas and H. G. Monsimer, THIS JOURNAL, **77**, 3579 (1955).

(14) C. Djerassi, R. N. McDonald and A. J. Lemin, *ibid.*, **75**, 5940 (1953); C. Djerassi, L. E. Geller and A. J. Lemin, *ibid.*, **76**, 4089 (1954).

(15) R. Morice and J. C. E. Simpson, *J. Chem. Soc.*, 795 (1940).

(16) The neutral, non-glycosidic fraction was not investigated in this case.

(17) C. Djerassi, E. Farkas, L. H. Liu and G. H. Thomas, THIS JOURNAL, **77**, 5330 (1955).



Experimental[18]

Isolation of Triterpenes from *M. cochal.*[19]—Dried and ground plant (1.6 kg.) from 21 kg. of fresh cactus (furnished by Mr. Howard E. Gates, Corona, California) was extracted continuously for 4 days with ethanol in a Soxhlet extractor and the solvent removed to yield 475 g. of extract. This was washed thoroughly with ether to remove non-glycosidic material (see below) and then hydrolyzed by heating under reflux for 4 hours with 450 cc. of concd. hydrochloric acid and 800 cc. of ethanol. After reducing the volume to one-half, much water was added and the precipitate was collected and dried. Continuous extraction of this solid with ether in a Soxhlet apparatus (4 days) and cooling of the ether solution furnished 25.5 g. of crude **chichipegenin**, m.p. 278–285°, raised to 320–325° after two recrystallizations from ethanol. The ether filtrate was washed thoroughly with 5% potassium hydroxide solution (see below for isolation of acids), water, dried and evaporated, leaving 34 g. of neutral semi-solid. Extraction of this fraction with benzene left 14 g. of insoluble residue which after recrystallization from methanol–acetone yielded an additional 12 g. of chichipegenin (m.p. 304–310°). Chromatography of the benzene solution on 400 g. of acetic acid-deactivated alumina and elution with ether gave 2.0 g. of chichipegenin to raise the total yield to 39.5 g. (2.47% based on dry plant). The analytical sample was obtained from methanol–acetone and exhibited m.p. 322–325°, $[\alpha]D$ +60° (methanol).

Anal. Calcd. for $C_{30}H_{50}O_4$: C, 75.90; H, 10.62. Found: C, 75.56; H, 10.93.

Acetylation of a sample with acetic anhydride–pyridine at room temperature overnight followed by recrystallization from methanol–chloroform led to **chichipegenin tetraacetate**, m.p. 278–280, $[\alpha]D$ +30°.

Anal. Calcd. for $C_{38}H_{58}O_8$: C, 70.99; H, 9.09. Found: C, 70.78; H, 9.17.

The above alkali washes were combined and acidified. Extraction with ether gave *ca.* 40 g. of acidic residue, which upon crystallization from acetone yielded 15 g. of **cochalic acid (Ia)**, m.p. 300–302°.[13] The filtrate was evaporated, methylated overnight with excess diazomethane in methanol solution and then chromatographed on 800 g. of alumina deactivated with 10 cc. of 10% acetic acid. Elution with 8:2 benzene–ether provided 5.0 g. of crude methyl cochalate (Ib) (m.p. 175–180°)[13] raising the total yield of this triterpene to 1.25%.

Washing of the column with ether gave 3.1 g. (0.19%) of **methyl myrtillogenate (IIb)**, m.p. 232–236°. Recrystallization from methanol–acetone provided the analytical sample, m.p. 248–250°, $[\alpha]D$ +87°.

Anal. Calcd. for $C_{31}H_{50}O_5$: C, 74.06; H, 10.03. Found: C, 74.24; H, 9.98.

Acetylation with acetic anhydride–pyridine and recrystallization from methanol gave the corresponding **triacetate**, m.p. 147–149°, $[\alpha]D$ +76°.

Anal. Calcd. for $C_{37}H_{56}O_8$: C, 70.67; H, 8.98. Found: C, 70.56; H, 9.11.

The ether washings of the original ethanolic cactus extract were evaporated and the dark green oil (25 g.) was heated under reflux overnight with 25 g. of potassium hydroxide and 250 cc. of methanol. Concentration, dilution with water and extraction with ether furnished 6.5 g. of a semi-solid which was chromatographed on 80 g. of acetic acid-deactivated alumina. All crystalline eluates were combined and recrystallized from acetone to give 2.5 g. (0.157%) of **longispinogenin (IIIa)**, m.p. 241–245°. Purification was best accomplished *via* its **triacetate** (m.p. 219–222°, $[\alpha]D$ +69°) which was shown to be identical with an authentic sample[14] by mixture melting point determination and infrared comparison.

Isolation of Triterpenes from *M. geometrizans*.[20]—The isolation was carried out exactly as above and the results differed only quantitatively from those observed with *M. cochal:* chichipegenin (0.62%), methyl cochalate (Ib) (0.25%), methyl myrtillogenate (IIb) (0.14%) and longispinogenin (IIIa) (0.0025%).

Isolation of Triterpenes from *M. eichlamii*.—The cactus was collected by Don Mariano Pacheco near Guatemala City and sun dried before being shipped to Detroit. From 1720 g. of dried, ground cactus, there was obtained 430 g. of ethanol extract which upon thorough washing with ether led to 319 g. of solid, tan-colored glycoside and 77 g. of neutral, non-glycosidic material.

Acid cleavage of the glycosides yielded 0.90% of chichipegenin, while chromatography of the methylated acid fraction gave 0.16% of **methyl oleanolate (Ib)** (m.p. 199°, $[\alpha]D$ +72°), 0.037% of **methyl cochalate (Ib)** and 0.028% of **methyl myrtillogenate (IIb)**.

Saponification of the non-glycosidic fraction followed by chromatography of the neutral fraction gave some β-sitosterol (m.p. 138–140°, $[\alpha]D$ −37°; **acetate**, m.p. 125–128°, $[\alpha]D$ −44°), 0.14% of **maniladiol (VI)** (m.p. 215–217°, $[\alpha]D$ +67°, identified by direct comparison with a sample prepared[14] from gummosogenin) and 0.83% of **longispinogenin (IIIa)**.

Isolation of Triterpenes from *M. grandiareolatus*.—This

(18) Melting points are uncorrected. Unless noted otherwise, rotations were measured in chloroform solution. We are indebted to Mrs. Dolores Phillips for the infrared spectra and to Dr. A. Bernhardt (Mülheim, Germany) for the microanalyses.

(19) A preliminary investigation was carried out by Dr. G. H. Thomas (see ref. 13).

(20) Collected at km. 205, of the Mexico–Laredo highway near the town of Zimapán.

cactus was collected near Zapotitlán on the road from Tehuacán Puebla to Huajuapan de León and from the glycosidic fraction there was obtained nearly 1% of **chichipegenin** and 0.2% of **methyl oleanolate (Vb)**.

Isolation of Triterpenes from *M. schenckii*.—A 1.54-kg. sample (dry) of cactus collected near Diaz Ordaz, Oaxaca, yielded only 55 g. of glycosidic material after alcoholic extraction and ether washing. Acid hydrolysis and chromatography of the neutral fraction gave 0.052% of **stellatogenin** (VIIa)[17] (m.p. 311–314°, $[\alpha]_D$ +40°; acetate VIIb, m.p. 323–326°, $[\alpha]_D$ +49°), identified by infrared comparison with an authentic sample,[6] while methylation of the acids and chromatography led to 0.136% of **methyl oleanolate (Vb)** (m.p. 197–199°).

Lithium Aluminum Hydride Reduction of Triacetyl Methyl Myrtillogenate.—Methyl myrtillogenate (IIb) triacetate (196 mg.) was heated under reflux for 12 hours with 1 g. of lithium aluminum hydride in 100 cc. of ether and was then processed in the manner described earlier[21] for oleanolic acid lactone. The crude Δ^{12}-**oleanen-3β,16β,28,29-tetrol (IVa)** (155 mg., m.p. 275–280°) was recrystallized from methanol to yield an analytical specimen, m.p. 280–283°, $[\alpha]_D$ +101° (methanol), no infrared absorption in the carbonyl region.

Anal. Calcd. for $C_{30}H_{50}O_4$: C, 75.90; H, 10.62. Found: C, 76.00; H, 10.52.

Acetylation with acetic anhydride–pyridine and purification by alumina chromatography (elution with benzene) followed by recrystallization from methanol furnished Δ^{12}-**oleanen-3β,16β,28,29-tetrol tetraacetate (IVb)**, m.p. 182–183°, $[\alpha]_D$ +71°.

Anal. Calcd. for $C_{38}H_{58}O_8$: C, 70.99; H, 9.09. Found: C, 71.23; H, 9.47.

The difference in physical constants precluded identity with chichipegenin (and its acetate) and the infrared spectra were also different.

DETROIT, MICHIGAN
MEXICO 20, D. F.

(21) C. Djerassi, E. Farkas, A. J. Lemin, J. C. Collins and F. Walls, THIS JOURNAL, **76**, 2969 (1954).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE STATE UNIVERSITY]

Terpenoids. XXIX.[1] Iresin (Part 2).[2] A New Fundamental Sesquiterpene Skeleton[3,4]

BY CARL DJERASSI AND WERNER RITTEL[5]

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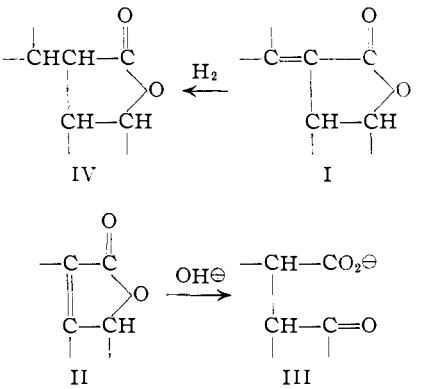
By means of various degradations, it has been shown that iresin possesses structure XXV (or the variant XXXII) based on a skeleton (XIII or XIV) which is unique among sesquiterpenes. Since this skeleton is always found in rings A, B and C of the higher (di- and tri)-terpenes, iresin represents an important link in the presently accepted biogenetic pattern of the lower and higher terpenes.

Recently,[2] there has been described the isolation and characterization of a novel sesquiterpene ($C_{15}H_{22}O_4$) which was named iresin. We should now like to record the salient experiments which led to the elucidation of the skeletal structure of this substance and which suggest that iresin occupies a unique position in terpene chemistry. Future papers will deal with various transformations of the functional groups of iresin and with its stereochemistry.

The nature of the four oxygen atoms already has been elucidated in the first paper[2] of this series and they were shown to be present as two reactive hydroxyl groups and as an α,β-unsaturated, five-membered lactone ring. The latter could, *a priori*, be of two types—the double bond being exocyclic (I) or endocyclic (II) with respect to the lactone ring—and it seemed important to differentiate between these two possibilities before initiating more drastic degradations.

Since α,β-unsaturated lactones of type II are known[6] to be convertible by base to the corresponding keto acids III, iresin was subjected to such treatment and was recovered unchanged (after acidification) even when heated with potassium *t*-butoxide. We conclude that the unsaturated lactone system of iresin is of type I and direct chemical proof for this supposition was afforded by ozonization experiments described below. The only double bond present in iresin is that conjugated with the



(1) Paper XXVIII, C. Djerassi, S. Burstein, H. Estrada, A. J. Lemin, A. E. Lippman, A. Manjarrez and H. G. Monsimer, THIS JOURNAL, **79**, 3525 (1957).

(2) Part 1, C. Djerassi, P. Sengupta, J. Herran and F. Walls, *ibid.*, **76**, 2966 (1954).

(3) Announced in part in a preliminary communication (C. Djerassi, W. Rittel, A. L. Nussbaum, F. W. Donovan and J. Herran, *ibid.*, **76**, 6410 (1954)).

(4) We are grateful to the Rockefeller Foundation for financial support.

(5) Ciba Ltd., Basel, Switzerland. Postdoctorate research fellow, 1953–1954.

(6) *Cf.* W. D. Paist, E. R. Blout, F. C. Uhle and R. C. Elderfield, *J. Org. Chem.*, **6**, 273 (1941); L. C. McKean and F. S. Spring, *J. Chem. Soc.*, 1989 (1954); J. B. Stenlake and W. D. Williams, *ibid.*, 2114 (1955).