very short time. The application of the latter is purely a technical problem. The possibility that it might prove of some practical use should be kept in mind. Meanwhile, we can consider the phenomenon described as the first photochemical memory model. As a matter of fact the search for such a reversible photochemical effect was originally undertaken at the suggestion of Dr. E. H. Frei of the Electronics Department, Weizmann Institute of Science, with the intention of building such a memory.

Experimental

Spectrophotometric Technique.—An attachment to the Beckman model D.U. quartz spectrophotometer was built, permitting the use of Dewar-type cells as described previously.[2]

Temperature Control.—The technique of work at low temperatures has been described in a former paper.[2]

Solvents.—Great care was taken to exclude traces of acid from all the solvents used. Methanol was distilled from KOH, ethanol was refluxed over CaO, and toluene, methylcyclohexane and petroleum ether were refluxed over and stirred with fused sodium before distillation.

Materials.—The syntheses of the four compounds studied are described in previous publications.[2]

Monochromatic Light.—The following combinations of Corning filters were used for the isolation of the individual monochromatic groups: for 365 mμ, 7380 + 5860; for 405 mμ, 3060 + 5970; for 436 mμ, 3389 + 5113; for 546 mμ, 3484 + 5120; for 578 mμ 3480.

The author is deeply indebted to Mr. M. Kaganowitch for the syntheses of the compounds investigated and to Mrs. Nelly Castel for her devoted technical assistance.

REHOVOTH, ISRAEL

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

Terpenoids. XXII.[1] Triterpenes from Some Mexican and South American Plants[2]

BY CARL DJERASSI, A. BOWERS, S. BURSTEIN, H. ESTRADA, J. GROSSMAN, J. HERRÁN, A. J. LEMIN, A. MANJARREZ AND S. C. PAKRASHI

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An examination of the triterpene content of ten plants from Mexico, Venezuela, Peru and Chile has resulted in the isolation of the following triterpenes: β-amyrin, maniladiol, erythrodiol, longispinogenin, oleanolic acid, gypsogenin, stellatogenin, betulin and betulinic acid.

The isolation[1,3] of a series of new triterpenes from certain giant cacti of the sub-tribe *Cereanae*, notably the genus *Lemaireocereus*, has encouraged us to continue the examination of related cacti and our results with seven species of the genera *Lemaireocereus*, *Trichocereus* and *Escontria* are reported herewith. In connection with the collection of these cacti, we also had the opportunity to obtain three plants (*Byrsonima spicata*, *B. crassifolia* and *Luffa operculata*) belonging to other families but which were investigated because there existed some evidence for believing that they may contain triterpenes.

The genus *Byrsonima* belongs to the *Malpighiaceae* family and only very few of its 500 species have been examined chemically.[4] It is interesting to note that extracts of the bark of the Mexican[5] *Byrsonima crassifolia* and the Peruvian[6] *B. spicata* (Cav.) Rich. have been used by the indigenous population for the expulsion of the placenta and the promotion of bleeding in females. Heyl[7] has reported the isolation from the bark of *B. crassifolia* of "byrsonimol" ($C_{29}H_{52}O$) with constants which are strongly reminiscent of β-amyrin (I) ($C_{30}H_{50}O$). Indeed, examination in these laboratories of bark samples of both *B. crassifolia* and *B. spicata* led to appreciable amounts of a single triterpene, identified as β-amyrin by comparison with authentic material.

The fruits of *Luffa operculata* (fam. *Cucurbitaceae*) form soapy solution in water and are referred to by the natives of Northern Peru[6] as "jaboncillo" (Sp. *jabon*, soap), which would indicate the presence of saponins. Mendoza and collaborators[8] have recorded the presence of a saponin in a related species of the cucumber family, *Luffa cylindrica* (Linn.) without however identifying the sapogenin.

(1) Paper XXI, C. Djerassi, J. A. Henry, A. J. Lemin and T. Rios, *Chemistry & Industry*, 1520 (1955).

(2) This represents part of a joint research program, financed by the Rockefeller Foundation, on Latin American plant products between Wayne University and the National University of Mexico. We are also indebted to the Division of Research Grants of the U. S. Public Health Service for financial assistance (Grant No. G-3863).

(3) *Inter al.*, (a) C. Djerassi, L. E. Geller and A. J. Lemin, THIS JOURNAL, **75**, 2254 (1953); (b) C. Djerassi, E. Farkas, A. J. Lemin, J. C. Collins and F. Walls, *ibid.*, **76**, 2969 (1954); (c) C. Djerassi, L. E. Geller and A. J. Lemin, *ibid.*, **76**, 4089 (1954); (d) C. Djerassi and A. E. Lippman, *ibid.*, **76**, 5780 (1954); (e) 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); (f) C. Djerassi and A. E. Lippman, *ibid.*, **77**, 1825 (1955); (g) C. Djerassi, G. H. Thomas and H. Monsimer, *ibid.*, **77**, 3579 (1955); (h) C. Djerassi, E. Farkas, L. H. Liu and G. H. Thomas, *ibid.*, **77**, 5330 (1955).

(4) *Cf.* C. Wehmer, "Die Pflanzenstoffe," G. Fischer, Jena, 1931, Vol. II, pp. 663–665.

(5) Its use has already been mentioned in the sixteenth century by Francisco Hernandez in his "Historia de las Plantas de Nueva Espana" (*cf.* Vol. I, p. 51 of 1942 edit., Imprenta Universitaria, Mexico, D.F.). See also survey on "Plant Materials Used by Primitive Peoples to Affect Fertility" by H. de Laszlo and P. S. Henshaw, *Science*, **119**, 626 (1954).

(6) Private communication from Dr. Ramon Ferreyra (Museo de Historia Natural "Javier Prado," Universidad Nacional Mayor de San Marcos, Lima, Peru) to whom we are greatly indebted for his continued assistance in supplying us with Peruvian plant materials and for the botanical identification.

(7) G. Heyl quoted in Elsevier's "Encyclopedia of Organic Chemistry," Amsterdam, 1940, Vol. 14, p. 596.

(8) A. S. Mendoza, P. Cruz and A. C. Santos, *Rev. Filip. Farm.*, **32**, No. 2, 49 (1941); A. S. Mendoza and A. C. Santos, *ibid.*, **32**, No. 7, 214 (1941). The presence of a saponin has also been mentioned in *Luffa acutangula* (K. S. Grewal and B. D. Kochhar, *Ind. J. Med. Res.*, **31**, 63 (1943)) and possibly *L. aegyptiaca* (S. Rangaswami and K. Sambumurthy, *Ind. J. Pharm.* **16**, 225 (1954)).

Acid hydrolysis of the crude saponin from *Luffa operculata* followed by purification of the methylated acidic fraction furnished gypsogenin (III), a sapogenin which had been isolated[9] from only very few plant sources limited to the genera *Gypsophila*, *Agrostemma* and *Saponaria*.

Chromatography of the acetylated mother liquors afforded two isomeric methyl ester acetates corresponding to dihydroxy acids of the empirical formula $C_{30}H_{48}O_4$, but insufficient material was obtained for structure determination.

The remaining plants to be discussed all belong to the *Cactaceae* family. *Escontria chiotilla* is a monotypic genus[10,11] and this tree-like cactus reaching up to 20 ft. in height and possessing many branches grows in Mexico in the southern region of the State of Puebla. In view of its botanical relationship to the genus *Lemaireocereus*, which has proved to be so rich in triterpenoid glycosides[1,3a-3e] it was of interest to determine its triterpene composition. Acid hydrolysis of the crude glycosidic fraction followed by chromatography furnished longispinogenin (V), a cactus triterpene isolated earlier from the Guatemalan *Lemaireocereus longispinus*[3c,12] and the Jamaican *Lemaireocereus hystrix*.[3d] In our initial studies,[3] the ether-soluble "non-glycosidic" portion which was relatively small was always discarded after being examined for any possibly alkaloid content. In this instance, the ether-soluble fraction represented an appreciable proportion of the total extract and since chromatography yielded no crystalline material, it was saponified on the assumption[13] that some triterpenes might be present in an esterified form. Indeed, chromatography of the neutral portion after saponification yielded two triterpenes. One of them proved to be again longispinogenin (V) while the other was identified as maniladiol (IV). We consider the isolation of maniladiol from a cactus to be of some biogenetic significance, particularly since it had earlier been reported from only a single plant source, *manila elemi* resin.[14] While our cactus studies,[1,3,12] have resulted in the isolation of a variety of new triterpenes, only four known ones have so far been encountered: oleanolic acid (II),[1,3a,3d,3e,12] erythrodiol (VI),[3d,12] betulinic acid (X)[3d,3e] and betulin (IX) (*vide infra*). Both the rare maniladiol (IV) and erythrodiol (VI)[15] together with the widely distributed oleanolic acid (II) fit nicely into the group of 3β,16β-dihydroxy-28-oxygenated cactus triterpenes exemplified by longispinogenin (V),[3c,12] gummosogenin (VII)[3c] and cochalic acid (VIII),[3g] the known representatives (II, IV and VI) lacking only an oxygen function at either C-16 or C-28. It is noteworthy that no 16α-hydroxytriterpene (*e.g.*, echinocystic acid, Primula genin) has been encountered among members of the *Cactaceae* family.

The above results with *Escontria chiotilla* not only confirmed on a chemical basis its close botanical relationship to the genus *Lemaireocereus*, but they also emphasized the importance of investigating the "non-glycosidic" fractions for their triterpene content and this was done with two of the four *Lemaireocereus* species mentioned below. Since the genus has been the most promising one, insofar as the isolation of triterpenes is concerned[1,3,12] we are attempting to secure every known species. The large majority grow only in Mexico[11] and certain Central American countries,[10] but a few can also be found in South America.[10] It has now been possible to examine a Venezuelan[16] species, *Lemaireocereus griseus*,[17] whose nearest geographical relative is the West-Indian *L. hystrix*, the triterpene composition of which has been reported recently.[3d] It was not unexpected, therefore, that precisely the same triterpenes were isolated from the very large glycosidic fraction, namely, oleanolic acid (II), longispinogenin (V), erythrodiol (VI), betulinic acid (X) and traces of an unknown triterpene lactone ("*hystrix* lactone"). Saponification of the non-glycosidic fraction[18] followed by chromatography furnished betulin (IX), representing the first isolation of this triterpene from a cactus. The occurrence of betulin (IX) and betulinic acid (X) in a cactus is not too surprising in view of their obvious structural similarity to the cactus triterpenes thurberogenin (XI) and stellatogenin (XII).[3f]

The remaining three *Lemaireocereus* species are native to Mexico[19] and one of them, *L. hollianus*[20] ("baboso"[21]) was found to be devoid of triterpenes, which may possibly be of some taxonomical importance. *L. treleasei* ("tunillo") occurs in the State of Oaxaca[22] and its triterpene content resembles that of *L. stellatus*[3e] since both oleanolic acid (II) and the lactone stellatogenin (XII) were obtained. In the case of *L. quevedonis*,[23] longispinogenin (V) was encountered in both the glycosidic and non-glycosidic fractions, while oleanolic acid (II) and betulinic acid (X) were isolated only in the former.

None of the above plants contained alkaloids, but since our laboratories are also concerned with novel

(9) Reference 7, pp. 557, 1050.

(10) N. L. Britton and J. N. Rose, "The Cactaceae," Carnegie Insitution of Washington, Washington, D. C., 1920, Vol. II, p. 65.

(11) H. Bravo, "Las Cactaceas de Mexico," Mexico, D.F., 1937, p. 233.

(12) C. Djerassi, R. N. McDonald and A. J. Lemin, THIS JOURNAL, **75**, 5940 (1953).

(13) This was based on the earlier observation of Dr. Alberto Sandoval, who isolated appreciable amounts of triterpenes after saponification of the ether soluble, non-glycosidic fraction of the Mexican cactus *Lemaireocereus chichipe*. His results will be reported in a subsequent paper dealing with the structure determination of a new triterpene "chichipegenin."

(14) R. Morice and J. C. E. Simpson, *J. Chem. Soc.*, 795 (1940). See also O. Jeger, M. Montavon and L. Ruzicka, *Helv. Chim. Acta*, **29**, 1124 (1947).

(15) Prior to our cactus studies, erythrodiol (VI) had been isolated only from one plant, *Erythroxylon novogranatense* (J. Zimmermann, *Rec. trav. chim.*, **51**, 1200 (1932)).

(16) This cactus is very abundant in certain regions of Northern Venezuela and in fact practically lines the runways of the Caracas airport at Maiquetia. We are indebted to Dr. Werner G. Jaffe (Instituto Nacional de Nutricion, Caracas) and to Dr. Tobias Lasser (Instituto Botanico, Ministerio de Agricultura, Caracas) for the plant material which was collected near Maiquetia.

(17) Reference 10, pp. 87–88.

(18) This fraction had not been investigated (ref. 3d) in the case of *L. hystrix*.

(19) All of the Mexican cacti were collected by one of the authors together with Dr. Alberto Sandoval, who organized the plant expeditions. We are grateful to Dr. Helia Bravo (*cf.* ref. 11) of the Instituto de Biologia, Mexico, D.F., for assistance with the botanical identification.

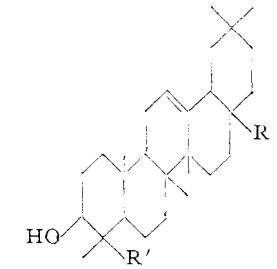
(20) Reference 10, p. 86.

(21) Reference 11, p. 250.

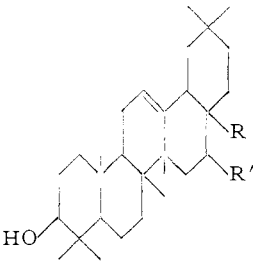
(22) Reference 11, p. 262.

(23) This cactus is reported (ref. 11, p. 266) to grow in the State of Sinaloa as well as near Acapulco and our specimens came from the latter location.

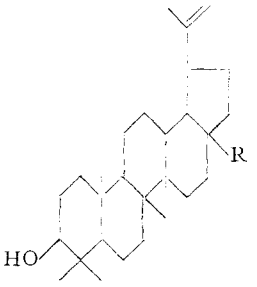
cactus alkaloids,[24] we have examined two South American *Trichocereus* species in view of Reti's isolation[25] of alkaloids from some Argentinian species of this genus. Both species, *T. chiloensis*[26,27] and *T. cuzcoensis*[28] proved to be essentially devoid of alkaloids and triterpenes; β-sitosterol and a long chain aliphatic alcohol were the only components which could be characterized.



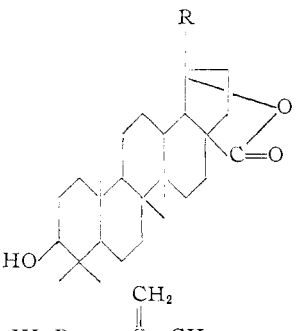
I, R = R′ = CH_3
II, R = CO_2H; R′ = CH_3
III, R = CO_2H; R′ = CHO



IV, R = CH_3; R′ = OH
V, R = CH_2OH; R′ = OH
VI, R = CH_2OH; R′ = H
VII, R = CHO; R′ = OH
VIII, R = CO_2H; R′ = OH



IX, R = CH_2OH
X, R = CO_2H



XI, R = $-C(=CH_2)-CH_3$
XII, R = $-C(OH)=(CH_3)_2$

Experimental[29]

Isolation of β-Amyrin (I) from *Brysonima crassifolia* and *B. spicata*.—The bark (10 kg.) of *B. crassifolia*, collected at Loma Bonita, Oaxaca, Mexico, was dried, ground to a powder and extracted three times each with 10 l. of boiling 95% ethanol. Filtration, followed by concentration to a volume of *ca.* 5 l. deposited 36 g. of solid (m.p. 190–192°) and an additional quantity (45 g.) was obtained by concentration of the mother liquors. Recrystallization from chloroform-methanol gave the analytical sample of β-amyrin,[30] m.p. 199–201°, undepressed upon admixture with an authentic specimen kindly provided by Prof. F. S. Spring (Royal Technical College, Glasgow), $[\alpha]D$ +90.5°.

Anal. Calcd. for $C_{30}H_{50}O$: C, 84.44; H, 11.81. Found: C, 84.26; H, 11.74.

The acetate was recrystallized from methanol–ethyl acetate, m.p. 237–239°, $[\alpha]D$ +79°.

Anal. Calcd. for $C_{32}H_{52}O_2$: C, 81.99; H, 11.18. Found: C, 81.93; H, 11.25.

The benzoate was crystallized from chloroform–methanol, m.p. 232–234°, $[\alpha]D$ +93°.

Anal. Calcd. for $C_{37}H_{54}O_2$: C, 83.72; H, 10.25. Found: C, 84.28; H, 10.30.

Approximately the same amount (8 g. from 1 kg. of bark) of β-amyrin was isolated from *B. spicata*.

Isolation of Gypsogenin (III) from *Luffa operculata*.—The ground and dried fruit (863 g.), collected[6] in the Department of Piura in Northern Peru was refluxed three times each with 3 l. of ethanol and then concentrated to 1 l. After cooling, 19 g. of nearly white saponin separated. The filtrate was evaporated to dryness and processed in the standard manner[3] for alkaloids (negative) and triterpenes (small amounts which were not investigated further). The solid saponin was refluxed for 3 hours with 60 cc. of concd. hydrochloric acid and 220 cc. of methanol, concentrated *in vacuo* to a volume of 50 cc. and diluted with water. The resulting precipitate was extracted with ether in a Soxhlet extractor and the extract was separated into a neutral (0.9 g.) and an acidic (2.8 g.) portion. The acidic material was methylated with diazomethane and chromatographed on 70 g. of acid-washed alumina. Elution with 1:1 ether–benzene furnished 1.08 g. of solid (m.p. 162–172°) which for further purification was acetylated and rechromatographed; yield 0.92 g., m.p. 185–190°. Several recrystallizations from methanol yielded 0.74 g. of gypsogenin (III) acetate methyl ester,[31] m.p. 190–192°, $[\alpha]D$ +85°. Identity was established by mixture melting point determination and infrared comparison with an authentic sample from the collection of the late G. A. R. Kon[31] and kindly provided by Prof. D. H. R. Barton (University of Glasgow).

Anal. Calcd. for $C_{33}H_{50}O_5$: C, 75.24; H, 9.57. Found: C, 75.50; H, 9.65.

The oily 1:1 ethyl acetate–ether eluates from the original methyl ester chromatogram weighed 0.87 g. and were chromatographed after acetylation. Elution with benzene–ether (9:1) followed by recrystallization from methanol yielded *ca.* 20 mg. of colorless crystals, m.p. 132–135°.

Anal. Calcd. for $C_{35}H_{54}O_6$: C, 73.46; H, 9.54. Found: C, 73.35; H, 9.70.

Further elution with the same solvents (8:2 and 6:4) and recrystallization from methanol led to 40 mg. of crystals, m.p. 204–205°, $[\alpha]D$ +44°.

Anal. Calcd. for $C_{35}H_{54}O_5$: C, 73.64; H, 9.54. Found: C, 73.23; H, 9.38.

Isolation of Triterpenes from *Lemaireocereus griseus*.—The isolation procedure for this and the other cacti reported in this paper is similar to that reported earlier[3] from our laboratories and hence will not be described in detail. Exhaustive extraction of the dried cactus[16] with ethanol yielded 23% of ethanol-soluble material from which 1.5% (all yields are based on dry plant) of an ether-soluble fraction could be removed by repeated washing with ether. The "glycosidic" portion was hydrolyzed and separated into acidic and neutral components.

In view of the earlier[3d,3e] reported isolation of betulinic acid from two related species, special attention was paid to the careful, chromatographic purification of the methylated acidic fraction. Approximately 7% of crude methyl esters was obtained but complete separation was only achieved by chromatography of the acetate methyl esters which furnished 2% of **methyl acetyl betulinate** (m.p. 201–203°, $[\alpha]D$ +16°) and *ca.* 4% of **methyl acetyl oleanolate** (m.p. 216–220°).

Chromatography of the neutral fraction yielded in order of increasing polarity: 0.18% of a lactone (m.p. 340–346°, $[\alpha]D$ +49°, $\lambda_{max}^{CHCl_3}$ 5.67 μ), which proved to be identical with the material encountered in *L. hystrix*[3d]; 0.58% of **erythrodiol** (m.p. 225–229°, $[\alpha]D$ +70°; diacetate, m.p. 185–188°, $[\alpha]D$ +60°) and 0.82% of **longispinogenin** (m.p. 243–246°, $[\alpha]D$ +50°; triacetate, m.p. 222–226°, $[\alpha]D$ +67°).

(24) C. Djerassi, N. Frick and L. E. Geller, THIS JOURNAL, **75**, 3632 (1953); C. Djerassi, C. R. Smith, S. P. Marfey, R. N. McDonald, A. J. Lemin, S. K. Figdor and H. Estrada, *ibid.*, **76**, 3215 (1954).

(25) *Cf.* L. Reti and R. H. F. Manske and H. L. Holmes, "The Alkaloids," Academic Press, Inc., New York, N. Y., 1954, Vol. IV, pp. 23–28.

(26) Reference 10, p. 137.

(27) We would like to express our appreciation to Dr. Carlos Muñoz P. (Departamento de Investigaciones Agricolas, Ministerio de Agricultura, Santiago de Chile) for the botanical identification and for facilities put at our disposal. Srta. A. Ramirez and Sra. F. Sudzuki kindly assisted in the collection of the plant material.

(28) Reference 10, p. 135. The plants were obtained through the kind coöperation of Prof. Cesar Vargas of the University of Cuzco, Peru.

(29) Melting points were determined on the Kofler block and all rotations were measured in chloroform solution. We are indebted to Mrs. Dolores Phillips for the infrared measurements (Baird double beam infrared spectrophotometer). The microanalyses were carried out by Spang Microanalytical Laboratory, Plymouth, Mich., and by Geller Laboratories, Hackensack, N. J.

(30) See ref. 7, p. 532.

(31) G. A. R. Kon and H. R. Soper (*J. Chem. Soc.*, 617 (1940)) report m.p. 191°, $[\alpha]D$ +80°.

Identity was established in each instance by mixture melting point and infrared comparison with authentic specimens.

A 3.5-g. portion of the ether-soluble, "non-glycosidic" portion of the cactus extract, representing a dark green oil, was extracted with dilute acid in order to remove any alkaloids, but none were found. The residue was then refluxed for 3 hours with 30 g. of potassium hydroxide and 175 cc. of methanol and processed in the usual manner. Chromatography of the neutral material yielded 0.37 g. of crystals in the 1:2 ether–chloroform eluates. The analytical sample, obtained from methanol–chloroform, exhibited m.p. 248–251°, $[\alpha]_D$ +18°, and was sublimed at 240° and 0.01 mm.

Anal. Calcd. for $C_{30}H_{50}O_2$: C, 81.39; H, 11.38. Found: C, 81.47; H, 11.76.

The substance was identified as betulin (IX)[32] by conversion to the diacetate (m.p. 217–221°, $[\alpha]_D$ +20°) and direct comparison with an authentic sample (from birch bark) of betulin diacetate.

Examination of *Lemaireocereus hollianus*.—The fresh cactus stems (32 kg.) collected[19] approximately 7 km. from Zapotitlán on the Tehuacán-Puebla road were dried (4.33 kg.) and extracted in the customary manner. The ethanolic extract weighed only 177 g. (11 g. ether soluble) and after acid hydrolysis led to 5.8 g. of black, oily acidic fraction and 29 g. of black, neutral oil. Only small amounts of a nonpolar substance (m.p. 78°, eluted with benzene), probably similar to the aliphatic alcohol encountered with *T. chiloensis* and *T. cuzcoensis* (*vide infra*), could be obtained after chromatography.

Isolation of Triterpenes from *Lemaireocereus treleasei*.—The dried stems (3.75 kg. from 28 kg. of fresh material) of the cactus, collected[19] at Diaz Ordaz, State of Oaxaca, gave 1.07 kg. of ethanol extract of which 935 g. was ether insoluble. Acid hydrolysis followed by chromatography yielded a trace of (0.02%) of *thurberogenin* (XI),[3f,33] while the bulk of the material (0.64%) was eluted subsequently and identified as **stellatogenin (XII)** by direct comparison with authentic material[3e,3f,33]; m.p. 311–315°, $[\alpha]_D$ +40°, 3-monoacetate, m.p. 323–325°, $[\alpha]_D$ +49°.

Approximately 0.1% of **oleanolic acid (II)** was isolated in the form of its methyl ester from the acid fraction, but the presence of small quantities of betulinic acid (X) was not excluded.

Isolation of Triterpenes from *Lemaireocereus quevedonis*.—This cactus (7.685 kg. of dry material from 60 kg. of fresh stems) was collected[19] at Piedra del Brinco near Acapulco and yielded 2.76 kg. of ethanol extract of which 2.4 kg. was insoluble in ether. The composition of this cactus is rather similar to that of *L. hystrix*[3d] since from the neutral triterpene mixture there was obtained *ca.* 0.4% of the "**hystrix lactone**" and 1.4% of **longispinogenin (V)**, while the acid fraction consisted of a mixture of **oleanolic (II)** and **betulinic acids (X)**. Chromatography of a 15-g. aliquot portion of the crude methyl esters led to 0.95 g. of methyl betulinate (m.p. 220–222°, $[\alpha]_D$ +4°), 4.0 g. of an intermediate fraction representing a mixture of the two components, and 6.0 g. of methyl oleanolate (m.p. 197–199°, $[\alpha]_D$ +69°).

Saponification of the "non-glycosidic" fraction as described above for *L. griseus* produced longispinogenin in 0.02% yield.

Isolation of Triterpenes from *Escontria chiotilla*.—Stems (18 kg. fresh, 2.46 kg. dry) of this cactus were collected[19] at km. 368 along the Mexico City–Oaxaca highway and yielded 574 g. of ethanolic extract, 480 g. of which was insoluble in ether. Almost the entire triterpene fraction obtained after acid hydrolysis proved to be neutral, and chromatography in the usual manner furnished **longispinogenin (V)** in 0.29% yield.

Saponification of 80 g. of the ether-soluble portion with 20% methanolic sodium hydroxide followed by chromatography of the neutral fraction on 2 kg. of alumina led to 2.4 g. of crude **maniladiol (IV)**[14] and 3.3 g. of longispinogenin (V). The maniladiol (m.p. 212–214°, $[\alpha]_D$ +68°) was converted to its 3,16-diacetate (m.p. 199–233°, $[\alpha]_D$ +82°) and 3,16-diketone (m.p. 208–210°, $[\alpha]_D$ +49°). The infrared spectra of the two derivatives were identical with those of specimens derived from gummosogenin (VII).[3e]

Examination of *Trichocereus chiloensis* and *T. cuzcoensis*.—When these two cacti[27,28] were processed in the above described fashion no triterpenes or alkaloids were encountered. In each instance, there was isolated β-sitosterol, m.p. and mixture melting point 137–138°, $[\alpha]_D$ −30° and an unidentified substance which from its infrared spectrum and nonpolarity during chromatography is believed to be a straight chain alcohol. The substance (m.p. 82–82.5°, $[\alpha]_D$ −11°) resembles *n*-nonacosan-10-ol (m.p. 82–83°)[34] but a mixture melting point was depressed (77–80°) and no further work was done with this material.

Anal. Found: C, 81.20, 81.08; H, 14.23, 14.16.

In order to be certain that no alkaloids were missed by the above procedure, a separate portion of *T. cuzcoensis* was processed by the procedure of Reti and Castrillon[35] which in the case of *T. candicans* led to the isolation of hordenine and candicine; no quaternary bases were encountered and only traces of non-phenolic basic material were noted. It is pertinent to mention that all of the *Trichocereus* species, which have been reported to contain alkaloids,[25] grow in a rather limited geographical area confined to Argentina.

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(32) Reference 7, p. 568.

(33) As pointed out earlier (ref. 3e), the isolation of trace quantities of thurberogenin (XI) in the presence of larger amounts of stellatogenin (XII) almost certainly indicates that the former was produced by dehydration of XII during the acid hydrolysis.

(34) We are indebted to Prof. F. S. Spring for a sample (*cf.* H. R. Bentley, J. A. Henry, D. S. Irvine, D. Mukerji and F. S. Spring, *J. Chem. Soc.*, 596 (1955)).

(35) Reference 25, p. 28.