Its ultraviolet spectrum shows one strong absorption peak at 285 mμ, log ε 4.48.

(b) **From 2-Benzylidene-α-decalol.**—Many dehydration experiments were performed using acetic anhydride, tosyl chloride, potassium hydrogen sulfate, boric acid and oxide, iodine, formic acid, Shaw solution, thionyl chloride in pyridine and conditions for xanthate preparation and decomposition. These methods either failed or gave the desired product in very poor yield. Of these the use of acetic anhydride is described. Three grams of 2-benzylidenecarbinol was refluxed in 200 ml. of acetic anhydride for 19 hours, then cooled and poured into 200 ml. of iced water. The oily layer was separated by decantation of the supernatant aqueous layer, taken up in ether and isolated by ether evaporation: 2.84 g. This was chromatographed through alumina using petroleum ether as solvent and eluant, from which 1.39 g. of semi-solid eluate was obtained having ultraviolet absorption in the 280 mμ region. This was rechromatographed with pentane from which 0.54 g. of crystalline product was secured in the first eluates. Recrystallization of this material gave a total of 0.33 g. (12%) of the pure 2-benzylidene-$\Delta^{1,9}$-octalin.

2-Keto-$\Delta^{1,9}$-octalin.—2-Benzylidene-$\Delta^{1,9}$-octalin (2.33 g.) was ozonized in 150 ml. of ethyl acetate at −60° for approximately three-quarters of the theoretical time. Zinc dust (1 g.) was added and the solution was concentrated *in vacuo*. Water was added next and the mixture refluxed for one hour. Ether extraction removed an oil which was treated directly with Girard T reagent. About 0.6 g. of ketonic material was isolated which upon evaporative distillation between 85–100° (0.1 to 1 mm.) yielded a total of 0.32 g. (20%) of 2-keto-$\Delta^{1,9}$-octalin, $n^{26}D$ 1.5213.[18] This substance absorbed at 238 mμ, log ε 4.15, in the ultraviolet region and had carbonyl absorption at 6.02 μ in its infrared spectrum.

The semicarbazone of the unsaturated ketone was prepared and crystallized from ethanol, m.p. 207–208°.

Anal. Calcd. for $C_{11}H_{17}ON_3$: C, 63.74; H, 8.27; N, 20.27. Found: C, 63.34; H, 8.40; N, 20.17.

(18) E. C. du Feu, F. J. McQuillin and R. Robinson, *J. Chem. Soc.*, 53 (1937); report the following values: 2-keto-$\Delta^{1,9}$-octalin, $n^{18}D$ 1.5238; semicarbazone, m.p. 208°; 2,4-dinitrophenylhydrazone, m.p. 168°.

Its ultraviolet spectrum displays a very intense maximum at 269 mμ, log ε 4.59.

Its 2,4-dinitrophenylhydrazone was also prepared and crystallized from ethyl acetate, m.p. 168–169°.

Anal. Calcd. for $C_{16}H_{18}O_4N_4$: C, 58.17; H, 5.49; N, 16.96. Found: C, 58.10; H, 5.52; N, 16.95.

β-Decalone.—2-Keto-$\Delta^{1,9}$-octalin (226 mg.) was hydrogenated at atmospheric pressure in ethyl acetate with platinum. After a 10% excess of an equimolar amount of hydrogen had been absorbed, the solvent and catalyst were removed leaving a colorless oil which was evaporatively distilled between 45–60° (35 mm.); 84 mg. (37%), $n^{27}D$ 1.4863.[19] The infrared spectrum of this material showed strong carbonyl absorption at 5.85 μ and none at 6.0 μ. Continued distillation between 70–120° (0.1 mm.) yielded 73 mg. (32%) of additional distillate, $n^{27}D$ 1.5099, having the same carbonyl absorption as above, but which was apparently contaminated with β-decalol.

A 2,4-dinitrophenylhydrazone derivative was prepared from the latter fraction. A small portion of this derivative was recrystallized to a m.p. of 164.5–166°. However, recrystallization of the main fraction from ethanol was accompanied by upward and downward fluctuations in m.p.'s after each subsequent recrystallization and by a concurrent appearance of yellow and orange crystals. Finally, a sample melting between 111–114° was analyzed. This erratic behavior is believed to be due to the non-homogeneity of a *cis–trans* mixture.

Anal. Calcd. for $C_{16}H_{20}O_4N_4$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.78; H, 6.46; N, 16.67.

The semicarbazone of this fraction was also prepared and crystallized from absolute ethanol, m.p. 175.5–176.5°.

Anal. Calcd. for $C_{11}H_{19}ON_3$: C, 63.12; H, 9.15; N, 20.08. Found: C, 62.95; H, 9.15; N, 19.99.

(19) The authors of ref. 17 report the following values for what they consider to be *cis*-β-decalone, arising from the palladium-on-strontium carbonate hydrogenation of 2-keto-$\Delta^{1,9}$-octalin, $n^{20}D$ 1.4888; semicarbazone, m.p. 182–183°. C. Mannich, W. Koch and F. Borkowski, *Ber.*, **70**, 355 (1937), give a m.p. of 192° for the semicarbazone of *trans*-β-decalone; W. Hückel, *Ann.*, **441**, 28 (1925), lists the following constants: *cis*-β-decalone, $n^{20}D$ 1.49265 and *trans*-β-decalone, $n^{19}D$ 1.48088.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

Terpenoids. III.[1] The Isolation of Erythrodiol, Oleanolic Acid and a New Triterpene Triol, Longispinogenin, from the Cactus *Lemaireocereus longispinus*[2]

BY CARL DJERASSI, R. M. MCDONALD AND A. J. LEMIN[3]

RECEIVED JULY 15, 1953

The Guatemalan cactus *Lemaireocereus longispinus*, although devoid of alkaloids, has proved to be a rich source of triterpenoid glycosides. Acid hydrolysis of the mixed glycosides produced oleanolic acid, previously isolated from another cactus, erythrodiol and a new triterpene, termed longispinogenin, which has been characterized as Δ^{12}-oleanene-3β,16β-x-triol.

In a recent communication[4] there was described an investigation of the triterpenoid constituents of the cactus *Lemaireocereus thurberi* and it was shown that oleanolic acid and a new triterpenoid lactone, thurberogenin, could be isolated. Prompted by this observation, we have undertaken an extensive investigation of certain other members of the *Cactaceae* family, particularly those of the subtribe *Cereanae*, and the present note concerns such an examination of the triterpenoid constituents of the cactus *Lemaireocereus longispinus*. This cactus is apparently restricted to Guatemala[5] and the plants used in the present study were obtained through the courtesy of Srta. Elizabeth Berlin from the gardens of Don Mariano Pacheco H. in Guatemala City.[6]

In contrast to the abundance of alkaloids in certain related genera,[7] *L. longispinus* proved to be devoid of alkaloids as had earlier been found to be

(1) Paper II, C. Djerassi, E. Wilfred, L. J. Visco and A. J. Lemin, *J. Org. Chem.*, **18**, 1449 (1953).

(2) This investigation was supported by a research grant (G-3863) from the National Institutes of Health, Public Health Service, Department of Health, Education and Welfare.

(3) Postdoctorate Research Fellow, 1953, on funds supplied by the U. S. Public Health Service.

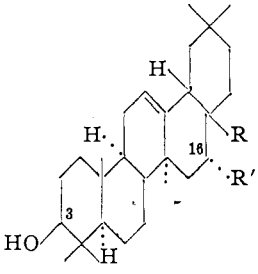
(4) C. Djerassi, L. E. Geller and A. J. Lemin, THIS JOURNAL, **75**, 2254 (1953).

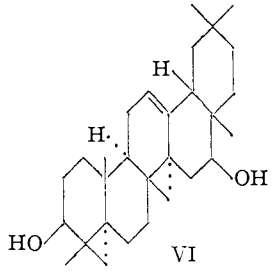
(5) N. L. Britton and J. N. Rose, "The Cactaceae," Vol. II, Carnegie Institution of Washington, Washington, D. C., 1920, p. 89.

(6) It is noteworthy that another Guatemalan cactus, *Nyctocereus guatemalensis*, which was obtained from the same source, has been found to be devoid of glycosides.

(7) C. Djerassi, N. Frick and L. E. Geller, THIS JOURNAL, **75**, 3632 (1953), and subsequent papers to be published from this Laboratory.

the case[4] with the closely related species *L. thurberi*, and it appears that the genus *Lemaireocereus* is not alkaloidipherous. However, considerable amounts of a semi-crystalline, water-soluble glycosidic fraction were obtained which yielded upon acid hydrolysis a neutral and an acidic component. The latter was readily identified as the known oleanolic acid (I)[8] and was characterized as the acetate and methyl ester. This is, therefore, the second[4] example of the occurrence of oleanolic acid (as a glycoside) in a cactus of the subtribe *Cereanae*, genus *lemaireocereus*.





VI

I, R = COOH; R′ = H
II, R = CH_2OH; R′ = H
III, R = CH_2OH; R′ = OH
IV, R = COOH; R′ = OH
V, R = CH_3; R′ = OH

The neutral fraction from the hydrolysis was separated chromatographically into two components and the least strongly absorbed compound was identified as erythrodiol (II) by direct comparison with an authentic sample prepared[9] by reduction of oleanolic acid (I) with lithium aluminum hydride. Erythrodiol (II) does not seem to have been isolated previously as a glycoside and the only known source of this triterpene diol appears to be *Erythroxylon novogranatense* where it is present as the stearate.[10]

The material eluted last in the chromatogram of the neutral fraction was characterized as a triterpenoid triol, $C_{30}H_{50}O_3$, which we have named longispinogenin. Although its physical constants (m.p. 247–249°, $[\alpha]^{25}D$ +53°) show a marked resemblance to those of *Primula genin* A. (III)[11] (m.p. 254–255°, $[\alpha]D$ +53°), our triol was readily shown to be a new pentacyclic triterpene by its behavior on acetylation. Thus even very mild acetylation conditions result in the formation of a triacetate, while *Primula genin* A (III)[11] under similar conditions leads to the 3,28-diacetate.[12] A close relationship between these two triols is, however, shown by the following observations.

Gummosogenin, a new triterpene isolated in this Laboratory from the cactus *Machaerocereus gummosus*,[13] possesses two secondary hydroxyl and one carbonyl function and yields longispinogenin upon reduction with lithium aluminum hydride. Furthermore, Wolff–Kishner reduction[13] of gummosogenin leads to maniladiol (VI) from which it follows that longispinogenin must be Δ^{12}-oleanene-3β,16β,x-triol. The position of the third hydroxyl group will become apparent from degradation studies on gummosogenin which are now in progress.[13] A brief consideration of the configuration of the C-16 hydroxyl group in these triterpenes seems pertinent at this point.

Primula genin A (III) has been obtained by reductive methods[14] from echinocystic acid (IV). Since conversion of the carboxyl group of IV to methyl leads to an isomer V[14] of maniladiol (VI) which, however, yields maniladione upon oxidation, it is clear that maniladiol (VI) and echinocystic acid (IV) (and hence also *Primula genin* A (III)) are epimeric at C-16.[15] Maniladiol (VI) can be acetylated with extreme ease and even at 0° gives a considerable amount of 3,16-diacetate,[16] while the difference in reactivity of the C-3 and C-16 hydroxyl groups in echinocystic acid (IV)[17] is much more pronounced. On that basis, it appears that the C-16 hydroxyl group in maniladiol (VI) and longispinogenin is equatorial (β-configuration) and that in echinocystic acid (IV) and *Primula genin* A (III) is polar (α-configuration). The arbitrarily employed designation of maniladiol as a 16α-derivative[18] should now be reversed as shown in formula VI in order to be consistent with the presently employed stereochemical notations[8] in the triterpene field.

The obvious relationship of oleanolic acid (I) and erythrodiol (II) which differ only in the nature of the functional group at the C-28 position is apparently of significance in the biogenetic origin of these compounds since they are found together in the same plant. A detailed consideration of the biogenetic relationships of the various triterpenes in cacti must be deferred until a sufficient amount of information has been collected on the occurrence and structure of triterpenes in a number of representative cacti.

Experimental[19]

Isolation of Erythrodiol and Longispinogenin.—Stem cuttings (4.4 kg.) of *Lemaireocereus longispinus* were cut into

(8) We are employing the conventions proposed by T. G. Halsall, E. R. H. Jones and G. D. Meakins, *J. Chem. Soc.*, 2863 (1952); for stereochemical considerations, *cf.* D. H. R. Barton, *ibid.*, 1027 (1953) and W. Klyne, *ibid.*, 2916 (1952). The triterpene numbering system has been changed in accordance with the suggestions of J. Guider, T. G. Halsall and E. R. H. Jones, *ibid.*, 3024 (1953).

(9) The earlier described conversions of oleanolic acid to erythrodiol are considerably more involved (L. Ruzicka and H. Schellenberg, *Helv. Chim. Acta*, **20**, 1553 (1937); L. E. Orr, L. M. Parks, M. F. W. Dunker and H. H. Uhl, *J. Am. Pharm. Assoc.*, **34**, 39 (1945); V. Prelog, J. Norymberski and O. Jeger, *Helv. Chim. Acta*, **29**, 360 (1946).

(10) J. Zimmermann, *Rec. trav. chim.*, **51**, 1200 (1932).

(11) A. Margot and T. Reichstein, *Pharm. Acta Helv.*, **17**, 113 (1942); B. Bischof and O. Jeger, *Helv. Chim. Acta*, **31**, 1760 (1948).

(12) *Primula genin* A. (ref. 11) yields a diacetate (m.p. 220–221°, $[\alpha]D$ +31°) which is converted to a triacetate (m.p. 159–160°, $[\alpha]D$ −9.7°) upon more vigorous acetylation. Longispinogenin triacetate shows m.p. 219–221°, $[\alpha]D$ +73° and is thus readily distinguishable on that basis from *Primula genin* A.

(13) The details of the isolation and structure determination of gummosogenin will form the subject of a future communication.

(14) O. Jeger, C. Nisoli and L. Ruzicka, *Helv. Chim. Acta*, **29**, 1183 (1946).

(15) All of these compounds possess the 3β-hydroxyl group as demonstrated by appropriate correlations with β-amyrin.

(16) O. Jeger, M. Montavon and L. Ruzicka, *Helv. Chim. Acta*, **29**, 1124 (1946).

(17) W. R. White and C. R. Noller, THIS JOURNAL, **61**, 986 (1939).

(18) B. Bischof, O. Jeger and L. Ruzicka, *Helv. Chim. Acta*, **32**, 1911 (1949), employed a dotted line in order to emphasize the epimeric nature of the 16-hydroxyl group but they did not ascribe any stereochemical significance to this notation. See, however, D. H. R. Barton and N. J. Holness, *J. Chem. Soc.*, **78**, (1953).

(19) Melting points are uncorrected and were obtained on the Fisher–Johns block. The infrared absorption spectra were measured on a Baird Associates double beam recording spectrophotometer. All rotations were determined in chloroform solution. The microanalyses were carried out by Mr. Joseph F. Alicino, Metuchen, N. J.

small pieces, dried for three days at 80–90°, powdered and the dry material (812 g.) was extracted continuously in a Soxhlet extractor with 4 l. of ethanol for seven days until the extract was colorless. The dark brown solution was evaporated to dryness under reduced pressure and the residue (125 g.) was extracted continuously with ether until no more color was removed (5 hours). The ether extract did not contain alkaloids (Mayer reagent) and gave only traces of oily material when processed in the usual manner for triterpenes. The dark brown, semi-crystalline, ether-insoluble glycosidic fraction (103 g.) was refluxed for three hours with 1.5 l. of methanol and 300 cc. of concd. hydrochloric acid. During the hydrolysis a large amount of solid separated which after cooling and dilution with water was extracted with ether, washed with 10% potassium hydroxide solution, water and dried. Evaporation gave 11.4 g. of neutral material which was chromatographed on 200 g. of deactivated alumina.[20] Elution with benzene–ether (9:1) gave 2.7 g. of colorless crystalline material which crystallized from acetone as needles, m.p. 235–237°, $[\alpha]^{25}D$ +80°, $\lambda_{max}^{CHCl_3}$ 2.78 μ; no selective ultraviolet absorption above 215 mμ. The melting point was not depressed on admixture with **erythrodiol**, m.p. 235–237°, $[\alpha]^{25}D$ +76°, prepared as described below, and the infrared absorption spectra of the two specimens were identical.

Anal. Calcd. for $C_{30}H_{50}O_2$: C, 81.39; H, 11.38. Found: C, 81.25; H, 11.20.

Erythrodiol diacetate was obtained in nearly quantitative yield (acetic anhydride–pyridine, room temperature, 20 hours) as needles after crystallization from methanol, m.p. 183–185°, $[\alpha]^{25}D$ +58°, $\lambda_{max}^{CHCl_3}$ 5.81 and 8.00 μ. Identity with the sample of erythrodiol diacetate described below was established by infrared and mixture melting point comparison.

Anal. Calcd. for $C_{34}H_{54}O_4$: C, 77.52; H, 10.33. Found: C, 77.77; H, 10.26.

Isolation of Longispinogenin.—Further elution of the previously described chromatogram column with benzene–ether (1:1) gave 3.3 g. of colorless crystalline material, m.p. 240–242°, which after several crystallizations from acetone separated as needles with m.p. 247–249°, $[\alpha]^{25}D$ +53°, $\lambda_{max}^{CHCl_3}$ 2.75 and 2.86 μ, no selective ultraviolet absorption above 215 mμ, yellow color with tetranitromethane.

Anal. Calcd. for $C_{30}H_{50}O_3$: C, 78.55; H, 10.99. Found: C, 78.71; H, 10.95.

Longispinogenin triacetate, prepared by the acetic anhydride–pyridine method (room temperature), crystallized from methanol as needles with m.p. 219–221°, $[\alpha]^{25}D$ +73°, $\lambda_{max}^{CHCl_3}$ 5.80 and 8.00 μ. Repeated acetylation using more vigorous methods (acetic anhydride–perchloric acid and acetic anhydride–pyridine under reflux for 14 hours) gave the same triacetate.

Anal. Calcd. for $C_{36}H_{56}O_6$: C, 73.93; H, 9.65; acetyl, 22.01. Found: C, 73.95; H, 9.59; acetyl, 22.17.

Isolation of Oleanolic Acid.—The alkaline solution from the previously described hydrolysis deposited a semi-crystalline potassium salt which was filtered, dissolved in ethanol and acidified with dilute hydrochloric acid. The precipitated acid was filtered, washed with water and dried to give 22.4 g. of crude oleanolic acid (m.p. 288–292°) which after two crystallizations from ethanol had m.p. 306–308°, λ_{max}^{Nujol} 2.88 and 5.88 μ. The infrared absorption spectrum was identical with that of oleanolic acid and no depression in m.p. was observed on admixture with an authentic specimen. The acetate had m.p. 263–265° undepressed on admixture with an authentic specimen of oleanolic acid acetate; $\lambda_{max}^{CHCl_3}$ 5.80, 5.90 and 7.98 μ; the infrared spectrum was identical with that of oleanolic acid acetate. The methyl ester, prepared by diazomethane treatment in ether–methanol solution, crystallized from methanol–chloroform, m.p. 197–199°, undepressed on admixture with methyl oleanolate.

Erythrodiol (II) from Oleanolic Acid (I).—Oleanolic acid (1.15 g.) was dissolved in tetrahydrofuran (30 cc.) and added dropwise to a stirred suspension of lithium aluminum hydride (4.5 g.) in 300 cc. of ether. After continuous stirring for 25 hours the excess of reagent was decomposed by addition of water and the inorganic material taken into solution by addition of 300 cc. of 10% sulfuric acid. The organic layer was separated and washed with potassium hydroxide solution and water until neutral, dried and evaporated, yielding 0.935 g. of white crystalline material. Filtration through alumina in chloroform solution and crystallization from methanol gave **erythrodiol (II)**, m.p. 235–237°, $[\alpha]^{25}D$ +76°.[21] A sample was sublimed in high vacuum for analysis.

Anal. Calcd. for $C_{30}H_{50}O_2$: C, 81.39; H, 11.38. Found: C, 81.42; H, 11.49.

Erythrodiol diacetate prepared by the usual method had m.p. 184–185°, $[\alpha]^{25}D$ +59°.[22] This diacetate as well as the free diol were identical with the corresponding derivatives described above which had been isolated from the cactus.

(20) A suspension of 200 g. of activated alumina (Alcoa, grade F-20) in benzene was shaken with 6 cc. of 10% aq. acetic acid for 2 hours and then used directly.

(21) J. Zimmermann (ref. 10 and *Helv. Chim. Acta*, **19**, 247 (1936)) reported m.p. 232°, $[\alpha]D$ +75.4°.

(22) Reported[21] m.p. 186°, $[\alpha]D$ +59°.

DETROIT, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF DELAWARE]

The Configuration of Some Dichlorocamphanes

BY HAROLD KWART

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The dipole moments of the compounds known as bornyl dichloride and β-chlorocamphane have been measured. The configurational relationships of the two chlorine atoms in these compounds is deducible from the data. The steric course of the reactions by which these substances are formed is clearly understandable in terms of existing theory.

The structure of the principal dichlorination product of α-pinene (I) described by Aschan and others[1] has been identified as 2,6-dichlorocamphane on the basis of tricyclene formation when this product is treated with zinc or sodium. Although referred to by Simonsen and others[2] as bornyl dichloride, the previously reported evidence has not permitted a configurational assignment of the chlorine atoms; *i.e.*, whether *exo* or *endo*.

In general, the determination of configuration by methods involving reaction must depend on an intimate knowledge of the steric requirement for the reaction and other features of the reaction mechanism in entirely analogous systems. Conversion to tricyclene (V), therefore, affords no basis for configurational assignment, since these factors concerned with the process of formation are not sufficiently well understood. Furthermore, such

(1) O. Aschan, *Ber.*, **61**, 38 (1928); O. Brus, *Compt. rend.*, **180**, 1507 (1925).

(2) J. L. Simonsen, "The Terpenes," Vol. II, Oxford University Press, 1949, p. 167, and elsewhere in the text. See also reference 7.