butyl peroxide were heated at 95° for 24 hours, after which the temperature was raised to 135° over a five-hour period and then to 180° over a three-hour period. In a typical non-catalytic run, the monomer was heated at 90° for 24 hours, 120° for seven hours, 170° for seven hours, and finally at 210° for seven hours. The polymers had high intrinsic viscosities corresponding to molecular weights of about 60,000. The methanol solubilities (ASTM designation D 703-49T) were about 2.0 to 2.5%.

Heat Distortion Point.—The heat distortion point was measured according to ASTM designation D 648-45T. The test bars were compression molded at 175° in a mold one-half inch by one-half inch by five inches (ASTM Designation D 647-49T). The heat distortion point was 117.8° (cor.) at 264 p.s.i. fiber stress (18.6 kg./cm.²).

Similar bars made of a commercial polystyrene had a heat distortion point of 88.0° (cor.) at 264 p.s.i. fiber stress.

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Terpenoids. X.[1] The Triterpenes of the Cactus *Lemaireocereus hystrix*

BY CARL DJERASSI AND A. E. LIPPMAN[2]

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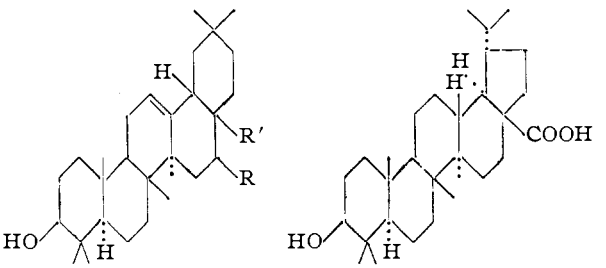
As part of a larger study on natural products present in giant cacti, there is under way in our laboratory an examination of all of the species of the genus *Lemaireocereus*, which appears to be particularly rich in triterpenoid glycosides. Since all of the species investigated so far (*Lemaireocereus thurberi*,[3] *L. longispinus*,[4] *L. dumortieri*,[5] *L. weberi*,[6] *L. stellatus*[7] and *L. pruinosus*[7]) are indigenous to Mexico or Guatemala, it seemed particularly appropriate to examine a *Lemaireocereus* species occurring in other parts of the American continent. The present note is concerned with *L. hystrix*, a cactus reaching up to 30 ft. in height and which represents the only *Lemaireocereus* species native to the West Indies.[8]

The plants were collected by one of us (A.E.L.) in the Mona district of Jamaica, B.W.I., and identified botanically by Mrs. Edith Robertson of the Botany Department, University College of the West Indies. In accordance with our earlier observations[3-5,7] on this genus that alkaloids and triterpene glycosides are not found in the same plant, the alcoholic extract of this cactus proved to be devoid of alkaloids but contained glycosidic material. Acid hydrolysis of the crude glycosides yielded a mixture of sapogenins which could be resolved into five components. The acid fraction consisted principally of oleanolic acid (I), but by methylation of the mother liquors followed by chromatography, it also was possible to isolate some betulinic acid (IV) methyl ester.

Chromatography of the neutral fraction furnished three substances. The least polar one, isolated in only trace amounts, was a high melting lactone, possible isomeric with thurberogenin[3] which was not studied further for lack of material. The material eluted after the lactone was identified as erythrodiol (II), a triterpene which, prior to our cactus studies, had been encountered (as the stearate) in only one plant, *Erythroxylon novogranatense*.[9] The most polar substance proved to be identical with longispinogenin (III), which was recently isolated for the first time from *L. longispinus*[4] and shown to be Δ^{12}-18β-oleanene-3β,16β,28-triol (III).[10] Erythrodiol (II) and oleanolic acid (I) also had been encountered[4] earlier in that cactus. It is thus quite striking that, insofar as the principal triterpenes are concerned, the Guatemalan cactus *L. longispinus* and the West Indian *L. hystrix* exhibit qualitatively almost the identical composition.



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

IV

Experimental[11]

Isolation of Oleanolic (I) and Betulinic (IV) Acids from *Lemaireocereus hystrix*.—The cactus was collected 0.4 mile west of the 12 mile post on the south side of the Palisadoes Road in Jamaica, B. W. I., and identified by Mrs. Edith Robertson, Department of Botany, University College of the West Indies. The fresh, despined plant (16.6 kg.) after cutting into small pieces and drying for 5 days at 80° gave 1.34 kg. of dry material which was ground in a cornmill and extracted ten times with 95% ethanol, refluxing each time for one hour. The combined filtrates were evaporated to dryness *in vacuo* and removal of water was ensured by repeated co-distillation with benzene. This extraction was carried out up to this stage under the supervision of Dr. Karl Reyle, Department of Chemistry, University College of the West Indies, and the extract was then shipped to Detroit for further processing.

The dry, alcoholic extract (144 g.) was extracted continuously with ether (Soxhlet extractor) until the extract was colorless; the insoluble residue (111 g.) was then hydrolyzed by refluxing for 4 hours with 700 cc. of methanol and 300 cc. of concd. hydrochloric acid. After concentration to one-half its volume, water was added and the insoluble brown material was collected. Neither the acid filtrate nor the original ether extracts gave any precipitate with Mayer reagent. The solid was continuously extracted with ether in order to remove the triterpenes and the extract was washed several times with 3% potassium hydroxide solution which resulted in the formation of a copious, light brown precipitate of potassium salt. The salt was filtered, suspended in dilute hydrochloric acid and the free acid was extracted with ether, yielding 12.7 g. of oleanolic acid (I), m.p. 293–298°. Several recrystallizations from chloroform–methanol and from ether raised the m.p. to 302–305°, undepressed upon admixture with authentic[3] oleanolic acid; $[\alpha]^{27}D$ +82.4°.

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(11) Melting points are corrected and unless noted otherwise were determined on the Kofler block. Rotations and infrared spectra were measured in chloroform solution. The microanalyses were carried out by Geller Laboratories, Hackensack, N. J.

Acetylation produced **oleanolic acid acetate**, m.p. 262–265°, $[\alpha]^{27}D$ +77.6°; a mixture melting point with authentic material[3] was undepressed.

The original aqueous, alkaline filtrate was acidified, extracted with ether and the ether extract together with the mother liquors from the recrystallization of oleanolic acid was methylated with diazomethane. Chromatography of the crude methyl esters (3.0 g.) on 300 g. of alumina (deactivated with 12 cc. of 10% acetic acid) and elution with benzene led to a series of crystalline eluates. The first two fractions (200 cc.) were combined and recrystallized from methanol to furnish 0.34 g. of long needles of **methyl betulinate**, still slightly contaminated with methyl oleanolate, m.p. 214–222°, undepressed upon admixture with an authentic specimen, $[\alpha]^{28}D$ +3.8°; identity was further confirmed by the preparation of **acetyl methyl betulinate**, m.p 201–203°, $[\alpha]^{27}D$ +16°, and by direct infrared comparison in each case with authentic samples of the corresponding betulinic acid derivatives. These physical constants are in reasonably good agreement with the literature values,[12] and aside from the infrared spectra the rotations are particularly characteristic of this series.

The intermediate eluates represented mixtures of methyl betulinate and methyl oleanolate, but from the last three crystalline eluates there could be isolated after several recrystallizations from methanol 0.45 g. of **methyl oleanolate**, m.p. 199–201°, $[\alpha]^{28}D$ +75°. The separation of methyl betulinate and methyl oleanolate appears to be impossible by crystallization due to mixed crystal formation, and even chromatography on alumina is inefficient.

Isolation of Neutral Triterpenes from *Lemaireocereus hystrix*.—The original alkali-washed ether solution of the triterpene mixture furnished 22.5 g. of brown, semi-solid material which was chromatographed in benzene solution on 300 g. of alumina (AlCOA, grade F-20) deactivated with 12 cc. of a 10% solution of acetic acid in water, 300-cc. fractions being collected. The first six fractions yielded oily material which was discarded. Fractions 7–16 (0.34 g.) after repeated crystallization from chloroform–methanol followed by sublimation at 200° (0.01 mm.) gave colorless crystals with the following constants: m.p. 331–334° (sealed capillary), $[\alpha]^{29}D$ +57.7°, $\lambda_{max}^{CHCl_3}$ 5.66 μ (five-membered lactone), no perceptible color with tetranitromethane.

Anal. Calcd. for $C_{30}H_{46}O_3$: C, 79.24; H, 10.20. Found: C, 79.58; H, 10.50.

The non-identity of this lactone with 18-isoöleanolic acid lactone[13] was demonstrated by the infrared spectrum and optical rotation; furthermore, earlier model experiments[5] had demonstrated that oleanolic acid is not lactonized under the conditions prevailing in the acid hydrolysis of the cactus glycosides. The substance appears to be isomeric with thurberogenin,[3,14] but lack of material precluded any further study.

Fractions 18–37 (benzene–ether, 9:1) were combined and recrystallized six times from acetone and acetone–hexane to furnish 0.9 g. of **erythrodiol (II)**, m.p. 229–231.5°, $[\alpha]^{29}D$ +74°, identified with authentic material[4] by means of mixture melting point and infrared comparison.

Anal. Calcd. for $C_{30}H_{50}O_2$: C, 81.39; H, 11.38. Found: C, 81.29; H, 11.36.

Erythrodiol diacetate showed m.p. 185–186°, $[\alpha]^{29}D$ +53°; the melting point of a mixture with authentic material was not depressed.

Chromatogram fractions 42–46 (ether) after two crystallizations from acetone yielded a total of 2.33 g. of **longispinogenin (III)**, m.p. 248–250° (Kofler), 253.5–254° (sealed capillary), $[\alpha]^{29}D$ +54°; identity with authentic longispinogenin from *L. longispinus*[4] was established by mixture melting point determination. The analytical sample was sublimed at 200° (0.3 mm.).

Anal. Calcd. for $C_{30}H_{50}O_3$: C, 78.55; H, 10.99. Found: C, 78.39; H, 10.94.

Acetylation at room temperature (12 hours) followed by recrystallization from methanol yielded **longispinogenin triacetate**, m.p. 220–222°, $[\alpha]^{29}D$ +71°. The infrared spectrum was identical with that of authentic longispinogenin triacetate.[4]

Anal. Calcd. for $C_{36}H_{56}O_6$: C, 73.93; H, 9.65; CH_3CO, 22.01. Found: C, 73.70; H, 9.59; CH_3CO, 21.99.

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Improved Synthesis of Amino Acid Benzyl Esters

BY BERNARD F. ERLANGER AND RONALD M. HALL

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Amino acid benzyl esters have been found to be useful intermediates for the synthesis of peptides because of their ability to be converted into acids by hydrogenolysis, enabling one to eliminate saponification procedures. When using the "carbobenzyloxy" method of peptide synthesis,[1] this decreases the number of steps and increases yields. Elimination of the need for saponification could also make possible the synthesis of peptides with alkali labile bonds.

Up to the present, benzyl esters of the following amino acids have been synthesized using various techniques: hydroxyproline,[2] glycine,[3-6] L-cysteine,[3] L- and D-glutamic acid (γ-ester),[7] (α-ester and dibenzyl)[8] L- and D-alanine,[5] L-leucine,[6] DL-phenylalanine,[6] ϵ-carbobenzyloxy-L-and-D-lysine[9] and L-proline.[10] The synthetic methods employed for the preparation of many of the amino acid benzyl esters are indirect and tedious and result in poor yields. It is because of this that the benzyl esters are not more widely used.

We are reporting a procedure which is simple and productive of good yields. It consists of the direct esterification of the amino acid in the presence of polyphosphoric acid[11] as the dehydrating agent. The reaction is carried out at temperatures of 90–105° (depending upon the amino acid) for four hours. We have prepared the benzyl ester hydrochlorides of L-alanine, DL-phenylalanine, L-leucine, L-phenylalanine, L-tyrosine and L-cysteine and L-cystine (by oxidation of L-cysteine benzyl ester). Analytical

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(11) Kindly supplied as a sample by Victor Chemical Works, Chicago 4, Illinois.