1 hour gave 1-*p*-anisyl-1-phenylethanediol (V), m.p. 103–104 after recrystallization from benzene–petroleum ether.

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.8; H, 6.6. Found: C, 73.3; H, 6.9.

Reduction of α-Hydroxy-1-*p*-anisyl-1-phenylacetaldehyde to 1-*p*-Anisyl-1-phenylethanediol (V).—The hydroxyaldehyde IV (0.5 g.) was reduced with lithium aluminum hydride in ether[17] to give 0.45 g. of solid, which after recrystallization from benzene–petroleum ether melted at 104–105°. The m.p. of a mixture with the sample obtained above showed no depression.

This glycol did not react with sodium bisulfite solution under conditions even more rigorous than those which caused the corresponding epoxide to rearrange.

Rearrangement of IV in Base.—A solution of 0.53 g. (0.0022 mole) of IV in 40 cc. of 50% aqueous methanol containing 1.0 g. of potassium hydroxide was heated under reflux for 1 hour. After the addition of 40 cc. of water and cooling a precipitate appeared, which after being filtered and dried, weighed 0.48 g., m.p. 85–100°. After two recrystallizations from chloroform–petroleum ether 0.25 g. (0.0010 mole, 46%) of 4-methoxybenzoin, m.p. 104–105°, was obtained.

Reaction of *p*-Anisylphenylacetaldehyde (III) with Perbenzoic Acid.—Redistilled III (2.0 g., 0.0089 mole) was allowed to stand for 12 hours with 30 ml. of chloroform containing 1.6 g. (0.0116 mole) of perbenzoic acid. The isolation procedure used above for the reaction of II with perbenzoic acid yielded an oil which did not crystallize and was then chromatographed on alumina. The column was eluted successively with benzene–petroleum ether ($^1/_4$) (200 ml.), pure benzene (200 ml.), and ether–petroleum ether ($^1/_1$) (250 ml.). The first 200-ml. fraction contained 0.70 g. (35%) of recovered starting material, $n^{27}\mathrm{D}$ 1.5860. The third fraction yielded a solid (0.59 g., 31%) which after recrystallization from benzene–petroleum ether was shown to be *p*-methoxybenzhydrol (0.42 g., 0.0020 mole, 23%), m.p. 68°. A mixed m.p. with authentic material showed no depression.

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[17] W. G. Brown, in R. Adams, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 489.

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p-*t*-Butylstyrene and its Polymers

BY L. L. FERSTANDIG, J. C. BUTLER AND A. E. STRAUS

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The commercial use of polystyrene is often limited by its relatively low heat distortion point. Some success has been attained in overcoming this difficulty, while retaining other desirable properties, by introducing substituents on the benzene ring. Work done in this Laboratory has shown that the new polymer made from *p*-*t*-butylstyrene has the highest heat distortion point (117.8° at 264 p.s.i. fiber stress) yet reported for alkyl-substituted polystyrenes.

p-*t*-Butylstyrene was synthesized by acetylation of *t*-butylbenzene, reduction of the *p*-*t*-butylacetophenone with lithium aluminum hydride to methyl-*p*-*t*-butylphenylcarbinol, and dehydration of the carbinol with potassium bisulfate. The reduction of the ketone with lithium aluminum hydride is an improvement, with respect to yields and simplicity, over those previously reported.[1,2]

p-*t*-Butylstyrene was polymerized in bulk, both thermally and with the aid of peroxide catalyst, to yield hard, clear and colorless polymers with high molecular weight and low methanol solubilities.[3] Some of the polymers were made from spectroscopically pure *p*-*t*-butylstyrene which had been purified by distillation and crystallization. The monomer prepared without the benefit of crystallization had about 2% of the *meta* isomer present. This material yielded a polymer of essentially the same properties as that of the pure *para* isomer.

It is interesting to note that copolymers made of styrene and *p*-*t*-butylstyrene show a straight-line relationship of heat distortion point and mole percentage composition; for example, a copolymer having the composition of 39 mole % *p*-*t*-butylstyrene and 61 mole % styrene has a heat distortion point of 100.6°.

Experimental

Methyl-*p*-*t*-butylphenylcarbinol.—About 400 ml. of absolute ether was added to 11.4 g. (0.3 mole) of lithium aluminum hydride in a nitrogen-filled flask. The mixture was stirred for about 15 minutes and then *p*-*t*-butylacetophenone[4] (176.0 g., 1.00 mole) was added over a period of 1.5 hours. Water was then added slowly until no more gas was evolved. The mixture was poured onto 200 g. of ice and water, and 700 ml. of 10% sulfuric acid was added. The ether layer was separated, and the aqueous layer was extracted twice with 200-ml. portions of ether. The combined ether layers were dried over anhydrous potassium carbonate and concentrated, leaving 178.1 g. of a white crystalline solid, m.p. 62–64° (100 weight % yield). The crude carbinol was recrystallized from mixed hexanes, yielding 164.0 g. (92.0 mole %) of methyl-*p*-*t*-butylphenylcarbinol, m.p. 66.6–67.4° (cor.).

***p*-*t*-Butylstyrene.**[5]—Potassium bisulfate (6.4 g.) was fused in a 1-l. three-necked, round-bottomed flask equipped with a thermometer and a 9-inch long, 1-inch diameter, Vigreux column. Hydroquinone (2.0 g.), *t*-butylcatechol (1.0 g.) and the carbinol (188.1 g., 1.06 moles) were added. The system was evacuated to 100 mm. pressure. The pot was heated as rapidly as possible while still keeping the foaming under control. The reaction was completed in one hour and ten minutes with a maximum pot temperature of 195° and a maximum vapor temperature of 150°. The two-phase distillate was separated yielding 157.5 g. (93.2 weight %) of the dried crude *p*-*t*-butylstyrene and 17.6 g. of water.

The crude *p*-*t*-butylstyrene was mixed with 5 g. of *p*-*t*-butylcatechol and distilled at a 10:1 reflux ratio in a 0.75-inch by 32 inch column packed with McMahon saddles.[6] The yield of pure *p*-*t*-butylstyrene [b.p. 91.5° (9.0 mm.), $n^{20}\mathrm{D}$ 1.5270 and d^{20}_4 0.8883] was 123.0 g. (0.768 mole), or 72.5 mole % based on carbinol.

A portion of the *p*-*t*-butylstyrene was purified by low temperature crystallization in which the f.p. was raised from 37.2° (cor.) to a constant −36.9° (cor.).

Anal. Calcd. for $C_{12}H_{16}$: C, 89.93; H, 10.06. Found: C, 89.79, 89.78; H, 9.94, 9.95.

Polymerization.—The inhibitor was removed by alkaline washing, and the monomer was flash-distilled before each polymerization. Five-ml. samples of the monomer were placed in cleaned 10-ml. ampoules, cooled in a Dry Ice–acetone mixture, and the air was removed by evacuation to less than 1 mm. followed by flushing with nitrogen, repeating the cycle five times, ending with vacuum. The ampoules were sealed off and subjected to a varying heat cycle with or without added peroxides. In a typical catalytic run, the monomer and 0.02 to 0.04 weight % of di-*t*-

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[1] C. G. Overberger, C. Frazier, J. Mandelman and H. F. Smith, THIS JOURNAL, **75**, 3326 (1953).

[2] W. F. Huber, M. Renoll, A. G. Rossow and D. T. Mowry, *ibid.*, **68**, 1105 (1946).

[3] The poly-*p*-*t*-butylstyrene samples, even those fractionated to remove low molecular weight polymer, have an unexplained tendency to adhere to the fingers after handling. However, this is not due to ordinary tackiness, because the polymer does not adhere to paper nor to other samples of the same polymer, and its tack temperature [A. D. McLaren, T. T. Li, R. Rager and H. Mark, *J. Polymer Sci.*, **7**, 463 (1951)] is 174° compared to 106° for polystyrene.

[4] J. C. Butler, L. L. Ferstandig and R. D. Clark. THIS JOURNAL, **76**, 1906 (1954).

[5] C. S. Marvel and G. L. Schertz, *ibid.*, **65**, 2054 (1943).

[6] R. T. Struck and C. R. Kinney, *Ind. Eng. Chem.*, **42**, 77 (1950)

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*

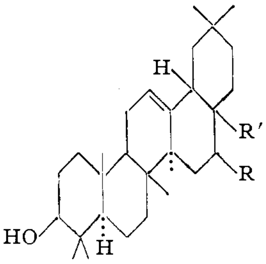
BY CARL DJERASSI AND A. E. LIPPMAN[2]

RECEIVED JULY 19, 1954

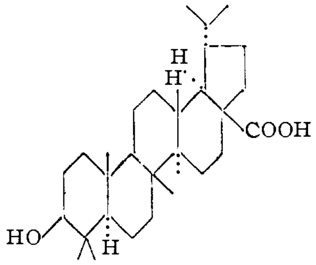
As part of a larger study on natural products present in giant cacti, there is under way in our laboratory an examination of all of the species of the genus *Lemaireocereus*, which appears to be particularly rich in triterpenoid glycosides. Since all of the species investigated so far (*Lemaireocereus 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$_2$OH
III, R = OH; R' = CH$_2$OH



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 corn-mill 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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(1) Paper IX, C. Djerassi and A. E. Lippman, *Chemistry & Industry*, 960 (1954).

(2) Postdoctorate research fellow, 1953–1954.

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

(4) C. Djerassi, R. N. McDonald and A. J. Lemin, *ibid.*, **75**, 5940 (1953).

(5) C. Djerassi, E. Farkas, A. J. Lemin, J. C. Collins and F. Walls, *ibid.*, **76**, 2969 (1954).

(6) C. Djerassi, C. R. Smith, S. P. Marfey, R. N. McDonald, A. J. Lemin, S. K. Figdor and H. Estrada, *ibid.*, **76**, 3215 (1954).

(7) L. H. Liu, unpublished observation from this Laboratory.

(8) N. L. Britton and J. N. Rose, "The Cactaceae," Carnegie Insitution of Washington, Vol. II, p. 86.

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

(10) C. Djerassi, L. E. Geller and A. J. Lemin, *Chemistry & Industry*, 161 (1954); THIS JOURNAL, **76**, 4089 (1954).

(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.