γ-butyrolactone was added, with stirring, to 100 g. of polyphosphoric acid which have been heated to 50°. The resulting mixture was heated to 85–90° with stirring for 8 hr. and then poured onto ice and extracted with four portions of ether. The combined extracts were washed with sodium bicarbonate, dried over sodium sulfate, and concentrated. The residue, when cooled, solidified as yellow needles, m.p. 35–48°, yield 5.53 g. (50%). Recrystallization from an ether-hexane mixture and from ethanol afforded the pure hydroxy ketone as white needles, m.p. 48–49°. The infrared spectrum[7] of the product has bands at 3400 cm.$^{-1}$ (associated O—H) and 1670 cm.$^{-1}$ (conj. C═O); the ultraviolet spectrum[8] has maxima at 218 mμ (ϵ 10,300) and 272 mμ (ϵ 14,600).

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.26. Found: C, 67.88; H, 7.30.

A solution of 0.0518 g. (0.00027 mole) of the keto alcohol in 10 ml. of reagent acetone was cooled in a Dry Ice-acetone bath and treated, dropwise and with stirring, with a solution of 0.044 g. (0.00044 mole) of chromium trioxide and 0.15 ml. of concentrated sulfuric acid in 1.8 ml. of water. The mixture was allowed to warm to room temperature and stand over a 4-hr. period. The reaction mixture was concentrated, diluted with water, and extracted with ether. The ether solution was extracted with three 20-ml. portions of 5% aqueous sodium bicarbonate. Acidification of the combined bicarbonate extracts afforded 0.0329 g. (57%) of β-(*p*-methoxybenzoyl)propionic acid, m.p. 146–147°, which was identified by a mixed melting-point determination with an authentic sample. More vigorous oxidation of the keto alcohol with chromic acid in boiling acetic acid afforded *p*-anisic acid, identified by a mixed melting-point determination with an authentic sample, in 19% yield.

7-Methoxy-1-tetralone (I). β-(*p*-Methoxybenzoyl)propionic acid, m.p. 146–147° (lit.[9] 144.5–146.5°), was converted to γ-(*p*-methoxyphenyl)butyric acid, m.p. 60–60.8° (lit.[10] 61–62°) in 82% yield by low-pressure hydrogenolysis[10] in acetic acid solution at 65° in the presence of a 10% palladium-on-carbon catalyst and in 88% yield by high-pressure hydrogenolysis[11] of aqueous solution of the sodium salt of the acid at 200° in the presence of copper chromite catalyst. The reaction of 11.98 g. (0.0618 mole) of γ-(*p*-methoxyphenyl)-butyric acid with 150 g. of polyphosphoric acid at 90–93° for 15 min. followed by appropriate manipulations afforded 10.17 g. (93.5%) of 7-methoxy-1-tetralone, m.p. 56–62°. The pure tetralone, which crystallized from aqueous ethanol as pale yellow plates melting at 60.9–62° (lit.[9] 61–62.5°), has a band in the infrared[12] at 1685 cm.$^{-1}$ (conj. C═O) and exhibits ultraviolet[8] maxima at 222 mμ (ϵ 19,600), 253 mμ (ϵ 8900) and 323 mμ (ϵ 3100). The product formed a semicarbazone, m.p. 222–223.1° dec. (lit.[13] 224–226° dec.), in 72% yield and a crude 2,4-dinitrophenylhydrazone, m.p. 280–284°, in 99.5% yield. The pure *2,4-dinitrophenylhydrazone of 7-methoxy-1-tetralone* crystallized from ethyl acetate as red prisms, m.p. 285–286°. The ultraviolet spectrum[7] of the 2,4-dinitrophenylhydrazone has a maximum at 385 mμ (ϵ 31,400).

Anal. Calcd. for $C_{17}H_{16}N_4O_5$: C, 57.30; H, 4.53; N, 15.72. Found: C, 57.57; H, 4.39; N, 15.62.

The 2,4-dinitrophenylhydrazone of 6-methoxy-1-tetralone, m.p. 233–234° (lit.[14] 236–238°), has an ultraviolet[7] maximum at 396 mμ (ϵ 29,200).

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[6] The infrared spectra were determined with either a Baird, Model B, or a Perkin-Elmer, Model 21, infrared recording spectrophotometer fitted with a sodium chloride prism. The ultraviolet spectra were determined with a Cary recording spectrophotometer, Model 11 MS. The microanalyses were performed by Dr. S. M. Nagy and his associates.

[7] Determined in chloroform solution.

[8] Determined in 95% ethanol solution.

[9] D. G. Thomas and A. H. Nathan, *J. Am. Chem. Soc.*, **70**, 331 (1948).

[10] E. C. Horning and D. B. Reisner, *J. Am. Chem. Soc.*, **71**, 1036 (1949).

[11] This procedure developed by L. F. Fieser and W. H. Daudt, *J. Am. Chem. Soc.*, **63**, 782 (1941), was found to be more convenient in the present study.

[12] Determined in carbon tetrachloride solution.

[13] A. Muller, M. Meszaros, M. Lempert-Sreter, and I. Szara, *J. Org. Chem.*, **16**, 1003 (1951).

[14] F. J. Villani, M. S. King, and D. Papa, *J. Org. Chem.*, **18**, 1578 (1953).

The Triterpenes of *Heliabravoa chende*[1]

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A sample of the water-insoluble, "nonglycosidic", extracts of the giant Mexican cactus *Heliabravoa chende* (formerly *Lemaireocereus chende*),[2] kindly supplied by Prof. Carl Djerassi, was investigated for triterpenes. The sample was composed mostly of neutral material (A), and a small fatty acid fraction (B) which gave a negative Liebermann-Burchard test. Saponification of the neutral material (A) with 15% methanolic potassium hydroxide yielded an acid fraction (C) and a neutral fraction (D).

The acidic fraction (C) which was crude and only partly crystalline was washed several times with hexane. The hexane-insoluble residue, which proved to be oleanolic acid (I), was purified as its methyl ester (II).

Chromatography of the neutral fraction (D) over alumina gave oleanolic aldehyde (III) followed by erythrodiol (IV).

The presence of oleanolic aldehyde in *Heliabravoa chende* deserves special attention since this is the first instance of this triterpene being found in nature. However, its 3-acetyl derivative (V) had previously been prepared by Ruzicka and Schellenberg via a Rosenmund reduction of oleanolic acid chloride acetate.[3] In our hands, crude oleanolic aldehyde was obtained as a yellowish solid, m.p. 112–186°, which could best be purified as the acetate. Oleanolic aldehyde was also reduced in very high yields by lithium aluminum hydride to erythrodiol.

An interesting aspect of the present study is that oleanolic aldehyde is one more pentacyclic triterpene which should be added to the impressive

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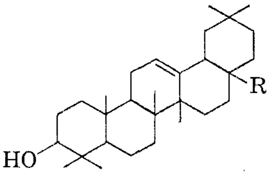
[1] This investigation was supported by a research grant (No. G5105) from the National Science Foundation.

[2] Helia Bravo and Don K. Cox, *Cactaceas Y Succulentas Mexicanas*, **3**, 3 (1958).

[3] L. Ruzicka and H. Schellenberg, *Helv. Chim. Acta*, **20**, 1553 (1937).

list of this class of compounds found in cacti.[4] Furthermore, oleanolic aldehyde conforms to the rule of possible oxygenation in cactus triterpenes only at C-15, 16, 21, 22, 28, and 30, besides the 3β-hydroxyl group.[4]



I. R = COOH
III. R = COH
IV. R = CH_2OH

EXPERIMENTAL

All infrared spectra on solids were run as potassium bromide pellets. All chromatograms employed acid-washed Brockman activity II-III alumina (*p*H 7). All melting points are uncorrected. All rotations were taken in chloroform. All triterpenes exhibited a triplet peak at 12.11, 12.24, and 12.46 μ due to the C-12,13 double bond. Elemental analyses are by Alfred Bernhardt Mikroanalytisches Laboratorium, Mulheim, Germany, and by Geller Microanalytical Laboratories, Bardonia, N. Y.

A solution of water-insoluble *H. chende* extracts (100 g.) in ether was extracted with three 500-ml. portions of 10% potassium hydroxide. The combined base extracts were neutralized and extracted with ether to yield a dark brown oil (B, 2.72 g.) that consisted of fatty acids which were not characterized. Extraction with 10% hydrochloric acid gave no acid-soluble substance. Evaporation of the ether then gave 97 g. of neutral, water-insoluble material (A).

Hydrolysis of neutral fraction A. The neutral fraction (A) was heated under reflux for 6 hr. with 5 l. of 15% potassium hydroxide in methanol. The solution was then evaporated to half volume, cooled, and acidified with concentrated hydrochloric acid. The precipitated potassium chloride was filtered and washed copiously with ether. The combined filtrate and washings were evaporated to dryness, the residue dissolved in 2 l. of ether, filtered, and extracted 4 times with a total of 2 l. of 10% sodium hydroxide. The organic layer was dried, filtered, and evaporated to yield an orange-brown neutral mass (D, 69.5 g.).

The combined sodium hydroxide extracts were acidified with concentrated hydrochloric acid and extracted with ether. The ether washings were evaporated to yield an olive drab mass (C, 27 g.).

Oleanolic acid (I). In a typical run 500 mg. of the acidic fraction (C) was extracted with 3 separate 25-ml. portions of hot hexane, and then stirred for 5 min. with 50 ml. of cold hexane. The tan hexane-insoluble residue (200 mg.) was crude oleanolic acid (I). The hexane-soluble fraction was composed mainly of fatty acid material which was not further characterized.

Methyl oleanolate (II) was produced when an ether solution of crude oleanolic acid (456 mg., 1 mmole) was treated with an excess of ethereal diazomethane. The crude product was chromatographed in 4:1 benzene-hexane on 50 g. of alumina. Elution with 99:1 benzene-ether yielded 433 mg. (92%) of white solid, m.p. 190–196°. A recrystallization from methanol-water netted 428 mg. of white crystalline solid, m.p. 196–198°. Analytical sample m.p. 199–200°, $[\alpha]_D$ +75°.

Anal. Calcd. for $C_{31}H_{50}O_3$: C, 79.10; H, 10.71. Found: C, 79.32; H, 10.90.

This compound had an infrared spectrum identical to that of an authentic sample of methyl oleanolate.[5]

Acetylation of methyl oleanolate (II) with acetic anhydried in pyridine and 2 recrystallizations from methanol-ethyl acetate gave *methyl acetyl oleanolate* (VI), m.p. 222.5–223°, $[\alpha]_D$ +70°.

Anal. Calcd. for $C_{33}H_{52}O_4$: C, 77.29; H, 10.22. Found: C, 77.59; H, 10.13.

This compound gave an undepressed mixed melting point with an authentic sample of methyl acetyl oleanolate.

Lithium in liquid ammonia reduction of methyl oleanolate (VI). Reduction of methyl oleanolate (II) (150 mg., 0.032 mmole) with lithium in liquid ammonia[6] gave oleanolic acid (I), m.p. 304–308°. Two recrystallizations from aqueous methanol raised the melting point to 309–310°, $[\alpha]_D$ +80°.

Anal. Calcd. for $C_{30}H_{48}O_3$: C, 78.89; H, 10.59. Found: C, 78.81; H, 10.79.

A 39-mg. (26%) yield of *erythrodiol* (IV), m.p. 208–217°, was also obtained from the reduction. Two recrystallizations from aqueous ethanol gave m.p. 230–231°.

Acetylation of the above oleanolic acid (I) with acetic anhydride in pyridine followed by 3 recrystallizations from aqueous ethanol gave *oleanolic acid acetate* (VII), m.p. 266–268°, $[\alpha]_D$ +76°.

Anal. Calcd. for $C_{32}H_{50}O_4$: C, 77.29; H, 10.22. Found: C, 77.59; H, 10.13.

Chromatography of neutral fraction (*D*). Part of the crude neutral fraction (D) (5.5 g.) was chromatographed on 400 g. of alumina. Elution with 2:3 benzene-hexane yielded a yellow oil (1.8 g., 33%), which appeared to be a fatty acid ester, gave a negative Liebermann-Burchard test, and was not further investigated. Subsequent elution with ether washed the remaining 3.5 g. of material off the column. The ether eluate was rechromatographed in 1:1 ether-benzene on 300 g. of alumina. Elution with 1:9 ether-benzene yielded *oleanolic aldehyde* (III) (1.05 g., 19%) as a yellowish solid, m.p. 112–186°. Employment of 4:1 ether-benzene then gave impure *erythrodiol* (IV) (2.24 g., 41%) as a white solid, m.p. 207–219°. Two recrystallizations from aqueous ethanol gave m.p. 230–231°, $[\alpha]_D$ +75°.

Anal. Calcd. for $C_{30}H_{50}O_2$: C, 81.39; H, 11.38. Found: C, 81.15; H, 11.03.

The erythrodiol isolated at this stage gave an undepressed mixed melting point with the erythrodiol isolated from the lithium in liquid ammonia reduction of methyl oleanolate (II). In addition, the infrared spectra of the 2 compounds were identical.

Acetylation of erythrodiol (IV) with acetic anhydride in pyridine and crystallization from ethanol-water gave *erythrodiol diacetate* (VIII), m.p. 179–184°. The analytical sample exhibited m.p. 186–188°, $[\alpha]_D$ +58°.

Anal. Calcd. for $C_{34}H_{54}O_4$: C, 77.52; H, 10.33. Found: C, 77.74; H, 10.13.

Acetylation of crude oleanolic aldehyde (III) with acetic anhydride in pyridine followed by chromatography on alumina and elution with 3:1 benzene-hexane yielded *oleanolic aldehyde acetate* (IX), m.p. 215–217°. Several recrystallizations from methanol gave m.p. 225–228°. Infrared peaks at 5.78–5.80 (ester and aldehyde superimposed), 8.07 (acetoxy), and 6.1 μ (double bond), in addition to the previously mentioned triterpene peaks.

Oleanolic aldehyde acetate oxime (X). To a solution of crude oleanolic aldehyde acetate (161 mg., 0.33 mmole) in 2 ml. of dry pyridine and 3 ml. of absolute ethyl alcohol was added hydroxylamine hydrochloride (69.5 mg., 1 mmole). The solution was heated under reflux for 6 hr., the solvent mixture evaporated, and the residue dissolved in 30 ml. of ether. The ether solution was extracted with three 15-ml. portions of 10% hydrochloric acid, once with 15 ml. of water,

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(4) C. Djerassi, *Festschrift Prof. Dr. Arthur Stoll*, Birkhauser, Basel, 1957, p. 330.

(5) The authors are indebted to Dr. Carl Djerassi for supplying all compounds for comparison studies.

(6) E. Wenkert and B. G. Jackson, *J. Am. Chem. Soc.*, 80, 217 (1958).

and dried. The crude product was chromatographed in 99:1 benzene-ether on 5 g. of alumina. Elution with 3:7 benzene-hexane yielded unreacted oleanolic aldehyde acetate (66 mg., 41%), m.p. 207–214°. Subsequent elution with ether yielded oleanolic aldehyde acetate oxime (X) (84 mg., 52%), m.p. 175–186°. Further purification of the latter fraction by recrystallizations from methanol-water yielded a colorless crystalline analytical sample, m.p. 189–200° dec.

Anal. Calcd. for $C_{32}H_{51}O_3N$: C, 77.21; H, 10.33. Found: C, 76.95; H, 10.10.

Infrared peaks at 2.93 (hydroxyl), 5.74 (ester), 8.07 (acetoxy), and 6.1 μ (double bonds), in addition to the previously mentioned triterpene peaks.

Reduction of oleanolic aldehyde (III) with lithium aluminum hydride in ether resulted in a 99% yield of erythrodiol (IV), m.p. 216–221°. Recrystallizations from methanol-water gave m.p. 230–232°.

The erythrodiol obtained above gave an undepressed mixed melting point with the erythrodiol obtained either naturally, or by metallic reduction of methyl oleanolate (II). Furthermore, the infrared spectra of these samples were identical.

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Derivatives of Some Cycloalkylcarbinols

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During the synthesis of a series of compounds for a study of cycloalkylmethylbromides, it became necessary to characterize a number of cycloalkylcarbinols. A survey of the literature showed that a number of these carbinols had been synthesized and characterized. No systematic approach to the subject, however, could be found. It was the object of this work to prepare several derivatives of the alcohols with which we were concerned. The derivatives chosen for the characterization were the phenylurethanes, the α-naphthylurethanes, and the 3,5-dinitrobenzoates.

The phenylurethane of cyclopentylcarbinol has been reported to melt at 110°[1] and 108–108.5°[2] while that of cyclohexylcarbinol was reported to melt at 82°[3] and 74–75°.[4] The α-naphthylurethane of cyclohexylcarbinol has been reported to melt at 109.4–110.2°[2] and 109–110.2.°[5] The melting point of the 3,5-dinitrobenzoate of cyclohexylcarbinol has been reported as 94°.[6]

EXPERIMENTAL

The alcohols used in this work were prepared by the lithium aluminum hydride reduction of the corresponding ethyl cycloalkane carboxylates with the exception of cycloheptylcarbinol, which was prepared from the butyl ester. The esters were dropped slowly into a rapidly stirred refluxing ether solution of a slight excess of lithium aluminum hydride. The alcohols were isolated after decomposition of the excess hydride and the reaction complex. The alcohols were purified by fractional distillation under reduced pressure.

The urethane derivatives were prepared from equimolar quantities of the alcohol and isocyanate. The reagents were mixed and heated on a steam bath for 0.5 hr. The resulting solids were removed and recrystallized from petroleum ether until the melting points were constant.

The 3,5-dinitrobenzoate esters were prepared by mixing the alcohol with a 10% molar excess of 3,5-dinitrobenzoyl chloride and heating the mixture over a low flame for 5–10 min. After cooling, excess acidic materials were removed from the precipitate by washing with 5% sodium bicarbonate solution. The crude esters were repeatedly recrystallized from ethanol-water mixture to constant melting points.

MELTING POINTS OF CYCLOALKYLCARBINOL DERIVATIVES

		Analysis			
		Calcd.		Found	
Compound	M.P.	C %	H, %	C, %	H, %
Cyclobutylcarbinol					
Phenylurethane	65.0–66.5°	70.21	7.38	70.10	7.33
α-Naphthylurethane	112.0–112.5	75.26	6.72	75.57	6.72
3,5-Dinitrobenzoate	98.5–99.5	51.42	4.32	51.27	4.33
Cyclopentylcarbinol					
Phenylurethane	104.5–106.5	71.19	7.83	71.31	7.85
α-Naphthylurethane	85.0–86.0	75.80	7.12	75.65	6.96
3,5-Dinitrobenzoate	89.5–90.5	53.05	4.80	53.06	4.76
Cyclohexylcarbinol					
Phenylurethane	82.5–83.5	72.06	8.22	72.03	8.18
α-Naphthylurethane	108.0–109.0	76.28	7.48	76.21	7.50
3,5-Dinitrobenzoate	95.0–96.0	54.53	5.24	54.69	5.22
Cycloheptylcarbinol					
Phenylurethane	61.0–62.0	72.83	8.57	72.64	8.45
α-Naphthylurethane	84.5–85.5	76.72	7.81	76.54	7.67
3,5-Dinitrobenzoate	79.0–80.0	55.89	5.64	55.49	5.63

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