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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(1) N. Zelinsky, *Ber.*, **41**, 2629 (1908).

(2) A. S. Dreiding and J. A. Hartman, *J. Am. Chem. Soc.*, **75**, 939 (1953).

(3) L. Bouveault and G. Blanc, *Comptes. rend.*, **137**, 61 (1905).

(4) E. G. E. Hawkins, D. L. J. Long, and F. W. Major, *J. Chem. Soc.*, 1462 (1955).

(5) M. S. Newman and W. M. Edwards, *J. Am. Chem. Soc.*, **76**, 1840 (1954).

Decolorizing charcoal was used when it was necessary to remove colored impurities from the esters.

The derivatives were dried under vacuum over phosphorus pentoxide and paraffin chips for 12 hr. at the temperature of boiling chloroform before the final melting points were determined.

All melting points were determined with the Koffler Microhotstage melting point apparatus using the calibrated thermometer supplied with the apparatus.

Carbon-hydrogen analyses were performed by Micro-Tech Laboratories, 8000 Lincoln Ave., Skokie, Ill.

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(6) G. Natta, P. Pino, and E. Mantca, *Gazz. chim. ital.*, **80**, 680 (1950); *Chem. Abstr.*, **46**, 905d (1952).