in a glass tube 25 mm. in diameter and 65 mm. long. This ampoule was rotated to provide continuously renewed thin films of the ester. After 18 days, the excess tritium was removed and the residue was refluxed for 1 hr. with 0.6 ml. of 50% sodium hydroxide diluted with 10 ml. of ethanol. On addition of 25 ml. of water, the unsaponifiable material was removed by extraction with five successive 25-ml. portions of ether. Removal of labile tritium was accomplished by distillation of 1.5 l. of anhydrous ethanol from the soaps in 50-ml. batches. Finally, 9 ml. of 1*N* hydrochloric acid was added and the organic acids extracted with four successive 25-ml. portions of ether.

Gas chromatography of tritiated methyl oleate. Methyl oleate after exposure to tritium gas as well as after tritiation, saponification, alcohol exchange, acidification, and methylation (with diazomethane) was examined for chemical and radiochemical purity by gas chromatography on a 5-ft. Resoflex 296 column at 205° in the "Aerograph" instrument.[9] Simultaneously with the recording of thermal conductivity, an ion chamber–electrometer system recorded radioactivity (ion current) on the gas stream issuing from the thermal conductivity cell.[10] Alternatively radioactivity was determined by trapping the methyl esters in the effluent gas stream in vials containing 15 ml. of scintillation solution for minute intervals and by subsequent assay in the automatic "Tri-Carb Scintillation Spectrometer."[9]

Liquid partition chromatography of tritiated acids. Chemical and radiochemical purity of tritiated fatty acids (after alcohol exchange, *etc.*) was determined by the liquid-liquid partition chromatographic procedure of Nijkamp[11] which employs a methanol-isooctane solvent system on a silicic acid column. Alternate 1-ml. eluate fractions were (a) titrated in a nitrogen atmosphere with 0.2*N* potassium hydroxide to a thymol blue end-point using a Gilmont Microburet, and (b) diluted with 15 ml. of scintillation solution for assay of radioactivity with an automatic "Tri-Carb Scintillation Spectrometer." Quenching of fluorescence by fatty acids and by the chromatographic solvent was negligible.

Degradation of tritiated esters. Oxidative cleavage of the double bonds in the tritiated esters was accomplished by the method of Jones and Stolp[12] after addition of the inactive ester to the tritiated ester. This method involved saponification of the ester, oxidation of the acids as soaps at room temperature with periodate-permanganate solution, and subsequent extraction of all ether-soluble acids in a continuous extractor. Only traces of radioactivity remained in the aqueous layer. Removal of ether gave the acids for chromatographic identification.

Liquid-liquid partition chromatography of monobasic and dibasic acids from methyl oleate. Upper and lower phases of a water-alcohol-benzene mixture at equilibrium comprised the mobile and immobile phases, respectively. Silicic acid was used as the solid support.[12] All monobasic acids emerge as one peak and dibasic acids appear as separate peaks. Alternate 1-ml. eluate fractions were titrated and assayed with the scintillating spectrometer. Monobasic fractions were combined, acidified, and extracted. The acids were identified by the chromatographic procedure of Nijkamp,[1] titrated, and assayed for radioactivity.

PEORIA AND URBANA, ILL.

(9) Since the Department of Agriculture does not recommend the products of one company over those of another, the names are furnished for information only.

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[CONTRIBUTION FROM THE NAVAL STORES RESEARCH STATION[1]

Esters of Some Acids Derived from Terpenes[2]

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The preparation of vinyl monomers for use as internal plasticizers for polyvinyl chloride from acids derived from terpenes led to the preparation of six new vinyl esters. Acylpinolic acids were prepared by reaction of pinolic acid with the respective anhydrides and direct reaction with the acids in the presence of an acid catalyst. From the substituted pinolic acids, pinolic acid, pinonic acid, and 3-(1-methyl-1-hydroxyethyl)heptanedioic acid γ-lactone, the new vinyl esters were prepared by vinyl interchange with vinyl acetate in the presence of mercuric sulfate catalyst. Ethyl esters of these acids were prepared by azeotropic removal of water from the reaction mixture with *p*-toluenesulfonic acid as catalyst. The pinonic and pinolic ethyl and propyl esters have been previously reported. The identity of the ethyl esters obtained by direct esterification and those obtained by catalytic reduction of the vinyl esters was established by means of infrared analyses.

The propyl and allyl esters of pinolic and pinonic acids were prepared by direct esterification in the presence of *p*-toluenesulfonic acid. Dehydration and rearrangement of pinolic acid in the presence of *p*-toluenesulfonic acid was observed but not reported in detail.

In the course of investigating terpene derived materials for use in the preparation of polymerizable monomers of interest as internal plasticizers for polyvinyl chloride, vinyl esters were prepared from a number of terpene acids and derivatives of these acids. Two allyl esters were also prepared. For comparison purposes the corresponding ethyl and propyl esters were prepared by reduction of the unsaturated esters and by direct esterification.

The acids involved in this work were pinonic [3 - acetyl - 2,2 - dimethylcyclobutaneacetic acid), pinolic [3-(1-hydroxyethyl)-2,2-dimethylcyclobutaneacetic acid], pinolic acid acetate, pinolic acid propionate, pinolic acid butyrate, 3-(1-methyl-1-hydroxyethyl)heptanedioic acid γ-lactone, pinic acid [3-carboxy-2,2-dimethylcyclobutaneacetic acid], and several monoalkyl pinates. The esters

(1) One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) Presented at the meeting of the American Chemical Society, Atlantic City, New Jersey, September 13–18, 1959.

TABLE I

ACYLATED PINOLIC ACIDS

Acid	M.P.°	B.P.°, Mm.	Saponification Equivalent Found	Saponification Equivalent Calcd.	Yield, %	Empirical Formula	Analyses Carbon Calcd.	Analyses Carbon Found	Analyses Hydrogen Calcd.	Analyses Hydrogen Found
Pinolic acid acetate	71–73	126/0.1	113.5	114	60[a]	$C_{12}H_{20}O_4$	63.13	63.23	8.83	8.79
Pinolic acid propionate	—	132/0.1	123.7	123	45[b]	$C_{13}H_{22}O_4$	64.43	64.97	9.15	9.31
Pinolic acid butyrate	—	140/0.1	130.5	130	40[b]	$C_{14}H_{24}O_4$	65.59	65.14	9.44	9.56

[a] Maximum yield from anhydride process; yield generally less than 40%. [b] By catalytic process; yield generally about the same under same conditions.

TABLE II

VINYL ESTERS OF TERPENE DERIVED ACIDS

Acid	B.P.°, Mm.	n_D^{25}	Hydrogenation G./Mole H_2 Calcd.	Hydrogenation G./Mole H_2 Found	Yield, %	Empirical Formula	Analyses Carbon Calcd.	Analyses Carbon Found	Analyses Hydrogen Calcd.	Analyses Hydrogen Found
Pinonic	118/5.0	1.4640	210.26	208	69.5	$C_{12}H_{18}O_3$	68.54	68.10	8.63	8.63
Pinolic	114/3.0	1.4669	212.28	208	62.2	$C_{12}H_{20}O_3$	67.89	68.57	9.50	9.50
Pinolic acid acetate	138/2.5	1.45459	254.34	249	61.6	$C_{14}H_{22}O_4$	66.11	66.18	8.72	8.78
Pinolic acid propionate	145/2.0	1.4532	268.34	265	53	$C_{15}H_{24}O_4$	67.18	67.18	9.01	9.16
Pinolic acid butyrate	122/0.1	1.4507	282.37	281	54	$C_{16}H_{26}O_4$	68.05	68.07	9.28	9.41
3-(1-Hydroxy-1-methylethyl)heptanedioic acid γ-lactone	149/0.2	Solid	226.26	227.2	56	$C_{12}H_{18}O_4$	63.13	63.62	7.98	8.08

of the monoalkyl pinates are covered by two publications.[3]

The *cis-dl*-pinonic acid used was prepared by potassium permanganate oxidation of α-pinene.[4] The pinonic acid was reduced to *cis-dl*-pinolic acid by catalytic hydrogenation in alkaline media over platinum oxide catalyst. The procedure is a modification of that given by Delépine and Horeau.[5] 3-(1-Methyl-1-hydroxyethyl)heptanedioic acid γ-lactone was prepared from homoterpenyl methyl ketone, 3-(1-methyl-1-hydroxyethyl)-6-ketoheptanoic acid γ-lactone, *via* the Wilgerodt reaction.[6] The acylated pinolic acids were made from pinolic acid by reaction with acids in the presence of their anhydrides and esterification in the presence of *p*-toluenesulfonic acid with azeotropic separation of the water formed. Physical constants for the three acylpinolic acids prepared are given in Table I. The acylation of pinolic acids is complicated by the ease of dehydration and molecular rearrangement of this compound in the presence of dehydrating agents or strong acids. The behavior of pinolic acid under such conditions is currently under study and results should be published later.

Vinylation of the acids was carried out by the vinyl interchange procedure of Adelman[7] using vinyl acetate and mercuric acetate–sulfuric acid catalyst. Physical constants of the vinyl esters prepared are given in Table II. The vinyl esters were catalytically reduced over 5% palladium on carbon. (Erratic results were obtained when platinum oxide was used.) The identity of the ethyl esters obtained with those prepared by direct esterification was established by infrared analyses. Vinylation of pinonic acid was also accomplished by the Reppe process.[8]

The allyl, ethyl, and propyl esters were prepared by direct esterification over acid catalyst in benzene or chloroform solution. The physical constants of the esters of pinonic acid, substituted pinolic acids, and 3-(1-hydroxy-1-methylethyl)heptanedioic acid lactone are given in Table III. The physical properties of the ethyl, propyl and allyl esters of pinolic acid are given in Table IV. The esters of pinolic acid were characterized by direct methods. Vapor phase chromatography showed only minor impurities, refractive indices of vinyl and allyl reduction products were in good agreement with the indices of the materials produced by direct esterification, and hydrolysis allowed isolation of good yields of unchanged pinolic acid. The ethyl and propyl esters of pinonic and pinolic acids were previously reported by Le-Van-Thoi.[9]

EXPERIMENTAL

The *cis-dl*-pinonic acid used was obtained by oxidation of α-pinene with potassium permanganate.[4]

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TABLE III

ETHYL, PROPYL, AND ALLYL ESTERS

Esters	B.P.°, Mm.	n_D^{25}	Molecular Weight		Yield, %	Empirical Formula	Analyses			
			Calcd.	Found			Carbon		Hydrogen	
							Calcd.	Found	Calcd.	Found
Ethyl pinonate	96–98/1.5	1.4496	212.28	210[a]	80–88	$C_{12}H_{20}O_3$	—	—	—	—
Propyl pinonate	125–128/5.0	1.4493	226.30	225[a]	76	$C_{13}H_{22}O_3$	68.99	68.66	9.81	9.88
Allyl pinonate	138–139/5.0	1.4611	224.28	220[b]	85	$C_{13}H_{20}O_3$	69.61	69.14	8.99	9.05
Ethyl pinolate acetate	76–78/0.5	1.4416	255.32	257[a]	75	$C_{14}H_{24}O_4$	65.59	65.77	9.44	9.68
Ethyl pinolate propionate	98–99/0.15	1.4423	270.36	268[a]	65	$C_{15}H_{26}O_4$	66.63	66.90	9.69	9.87
Ethyl pinolate butyrate	110–112/0.10	1.4415	284.39	283[a]	67	$C_{16}H_{28}O_4$	67.57	67.62	9.92	10.00
Ethyl-3-(1-methyl-1-hydroxyethyl) heptanedioate γ-lactone	122–124/0.25	1.4527	228.28	232[a]	69	$C_{12}H_{20}O_4$	62.58	63.10	8.74	8.96

[a] Determined by saponification equivalents. [b] Determined from hydrogenation (g./mole H_2 absorbed).

TABLE IV

PINOLIC ACID ESTERS

Esters	B.P.°, Mm.	n_D^{25}	Molecular Weight		Yield, %
			Calcd.	Found	
Ethyl pinolate	116–120/1.0	1.4539	214.30	216[a]	53.6
Propyl pinolate	153–154/1.0	1.4542	228.33	230[a]	69.2
Allyl pinolate	134–137/2.0	1.4619	226.31	225[b]	69.5

[a] Determined by saponification equivalents. [b] Determined from hydrogenation (g./mole H_2 absorbed) values.

cis-dl-Pinolic acid.[5] Crystalline, *cis-dl*-pinonic acid (736 g., 4 moles) was dissolved in excess alkali (200 g., 5 moles of sodium hydroxide in 1200 ml. water) and the solution was made up to 2 l. The solution was hydrogenated in a rocking autoclave in the presence of platinum oxide (1.4 g.) at 1500–1800 p.s.i.g. hydrogen pressure. Hydrogen absorption was rapid during most of the run but the last mole was absorbed very slowly. After hydrogen absorption ceased (about one week), the mixture was filtered and the solution acidified by slow dropwise addition of concd. sulfuric acid. The mixture was filtered and the crystalline pinolic acid washed free of sulfuric acid with water and air dried. Some oil, probably *trans*-pinolic acid, precipitated with the crystals, m.p. 91–96°. The melting point can be readily raised to 100–101° by recrystallization from water or ether–petroleum ether mixtures.

cis-dl-Pinolic acid acetate, anhydride method. A solution of *cis-dl*-pinolic acid (46.5 g., 0.25 mole) in glacial acetic acid (70 ml.) was added slowly (3 hr.) to a stirred solution of acetic anhydride (50 ml., 0.53 mole) in glacial acetic acid (50 ml.) heated at reflux. After the addition was completed the mixture was heated for 30 min. longer. Water (20 ml.) was added and the acetic acid was distilled under vacuum. Distillation of the residue gave yields of 30–60%.

cis-dl-Pinolic acid acetate, catalytic method. A solution of *cis-dl*-pinolic acid (186 g., 1 mole) in 400 ml. of chloroform and a solution of 240 ml. glacial acetic acid and 20 g. *p*-toluenesulfonic acid in 200 ml. of chloroform were dried by azeotropic distillation of water with return of chloroform to the solution. The pinolic acid solution was added slowly (4 hr.) to the acetic acid-*p*-toluenesulfonic acid solution heated at reflux and the water formed was removed azeotropically. After the reaction was complete, the mixture was cooled and washed with 200 ml. of water. The wash was extracted with 25–30 ml. of chloroform and the extract combined with the original chloroform solution. The solution was stripped under 30–35 mm. pressure to a pot temperature of about 100°. The residue was washed to remove residual acetic acid, distilled bulb-to-bulb and then through a 2 × 20 cm. column packed with 6 mm. glass helices.

Generally a more crystalline material was obtained by the catalytic procedure. Pinolic acid propionate and butyrate were made by the above procedures but the yields were generally not as good.

dl-3-(1-Methyl-1-hydroxyethyl)heptanedioic acid γ-lactone was prepared from homoterpenyl methyl ketone *via* the Wilgerodt reaction according to the procedure of Halbrook and Lawrence.[6]

cis-dl-Vinyl pinonate. The vinylation procedure followed in each instance is that given by Adelman[7] except that the vinyl acetate to acid ratio was increased from 6:1 to 12:1. *cis-dl*-Pinonic acid (184 g., 1 mole) was placed in a 2-l. flask with 0.5 g. of copper resinate. Vinyl acetate (1110 ml., 12 moles) was distilled into the flask and cooled below 30°. Mercuric acetate (4.0 g., 0.0126 mole) was added and dissolved by stirring the mixture. Sulfuric acid (0.5 ml., 0.0093 mole) was added dropwise with very vigorous stirring. The flask was swept with nitrogen and allowed to stand at room temperature for 3 days. Sodium acetate (2 g., 0.024 mole) was added and the mixture was stirred 30 min. The excess vinyl acetate and most of the acetic acid formed in the reaction were removed by distillation under reduced pressure (25 mm.) to a pot residue temperature of 80°. The residue was then washed with water (2 × 50 ml.) and exhaustively extracted with saturated sodium bicarbonate solution to remove any unchanged acid. After drying over anhydrous sulfate, the residue was distilled to give water-white vinyl pinonate.

The other vinyl esters were prepared by this same procedure except vinyl-3-(1-methyl-1-hydroxyethyl)heptanedioic acid γ-lactone, which crystallized from the dried ether solution, on cooling, m.p. 47.8–48.6°. Distillation of this material generally resulted in considerable loss by polymerization or decomposition. The distilled material super cools and if not seeded may not crystallize.

In the case of vinyl pinolate the reaction mixture was

maintained at about 0° during and after addition of the sulfuric acid in order to avoid formation of the vinylidene compound at the hydroxyl group. Inasmuch as the reaction would be expected to be slower at this lower temperature, the reaction time was extended to 5 days.

The vinylation of pinonic acid was accomplished by the Reppe procedure using pinonic acid in toluene with zinc pinonate as a catalyst. The yield of crude product, b.p. 115–150°, 1 mm., 393 g., was 80%. Fractionation of the crude product gave colorless vinyl pinonate (Table II), 50% yield, and 30% yield of a slight amber colored material. The second material was not completely characterized. However, it absorbed two equivalents of hydrogen and had an empirical formula, $C_{14}H_{20}O_3$. Polymers from bulk polymerization with benzoyl peroxide had the appearance of polystyrene foam and were insoluble in common solvents indicating crosslinking had taken place. Obviously two acetylene molecules had reacted with one molecule of pinonic acid. Vinylation of 3-(1-methyl-1-hydroxyethyl)heptanedioic acid γ-lactone by the same procedure was unsuccessful.

Characterization of cis-dl-vinyl pinolate. A 10-g. sample of freshly distilled vinyl pinolate was reduced over 5% palladium on carbon. Alcohol (50 ml., 95%) was used as the solvent and catalyst concentration was about 1%. After the reduction was completed, the solution was filtered and evaporated. Vapor phase chromatography showed the residue to contain ethyl pinolate with minor peaks corresponding to impurities in the vinyl pinolate. Five grams of the material was hydrolyzed by heating on the steam bath for about 4 hr. with excess 6*N* sodium hydroxide. The hydrolysis mixture was extracted with ether to remove the ethanol and the extracted solution was acidified. The acidified solution was extracted with three 15-ml. portions of ether; the ether solution was dried over sodium sulfate, filtered, and evaporated to yield 4.03 g., 91% of crystalline pinolic acid, m.p. 94.8–96.4. Mixed melting point with an equal quantity of 103–104° pinolic acid was 99–102.5°. Allyl and propyl esters also allowed good recovery of pinolic acid on hydrolysis and chromatographed samples showed even less impurities than the ethyl ester.

cis-dl-Ethyl pinonate. cis-dl-Pinonic acid (736 g., 4 moles) was placed in a flask with 95% ethanol (1 l., 17 moles), chloroform (1 l.), and *p*-toluenesulfonic acid (20 g.). The mixture was refluxed through a 2 × 20 cm. protruded metal packed column and the water which separated was removed through a liquid decanter. After separation of water ceased, the mixture was cooled, and treated with water until no further phase separation was noted. The chloroform layer was washed with sodium bicarbonate solution until the wash remained basic to *p*H paper and then dried over sodium sulfate. Evaporation and distillation of the residue yielded water-white ethyl pinonate.

The allyl and propyl esters of pinolic acid were prepared by this method. The ethyl ester, however, (probably because of long heating periods necessary to remove the water) is difficult to obtain in pure form if catalyst concentrations as high as this are used. Azeotropic removal of water from a mixture of pinolic acid ethanol and benzene in the absence of added catalyst has produced the purest *cis-dl*-ethyl pinolate although the yield was only about 50%.

Slow dehydration of the pinolic acid esters will take place if heating is continued beyond the time required to evolve one mole of water.

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, UNION CARBIDE CHEMICALS CO.]

Synthesis of Some Special Types of Glycidic Esters

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Glycidic esters have been found to undergo an ester exchange reaction with a wide variety of alcohols without concomitant destruction of the epoxide function. This exchange reaction was used for the preparation of certain unsaturated glycidic esters and diepoxides which are not readily obtained by other routes. Di-, tri-, and tetraepoxides containing the glycidic ester grouping have also been prepared by epoxidation of the corresponding unsaturated esters with anhydrous peracetic acid. The relative merits of these methods for the synthesis of glycidic esters are discussed.

A previous paper in this series described the preparation of saturated alcohol esters of α,β-epoxy acids by treatment of the esters of α,β-unsaturated acids with peracetic acid.[1] The present paper deals with the synthesis of some special types of glycidic esters, many of which are new, by methods which include 1) an exchange reaction of epoxy esters with alcohols, 2) an extension of the previously described peracetic acid epoxidation,[1] and 3) a combination of methods 1) and 2). Structural considerations govern the choice of method for the synthesis of a given glycidic ester. Other methods for the preparation of glycidic esters include the Darzens method[2] and the treatment of esters of α,β-unsaturated acids with peroxytrifluoroacetic acid.[3]

Esters of α,β-epoxy acids may be exchanged with alcohols under mild conditions without destruction of the oxirane rings. This appears to be a general reaction which works with saturated and unsaturated alcohols and glycols (Table I). Success with the ester exchange reaction depends on carrying it out under mild conditions (60° or below) in the presence of alcoholates of the alkali and alkaline

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