of Sinor, being approximately 1° below ours, appear to be high in helium.

Figure 4 is a temperature-composition diagram for the 700, 800, 900, and 1000 psia isobars above 184° K. It can be seen from this diagram that the cricondentherm loci starts at the methane critical with a positive slope and increases with pressure. An estimate of the critical temperatures, based on extrapolation of the vapor and liquid curves for each isobar, is 190.55°, 190.64°, 190.70°, and 190.74° K, for 700, 800, 900, and 1000 psia, respectively. The pressure-temperature diagram, Figure 5, obtained from Figure 4 shows that the critical curve for helium–methane mixtures leaves the critical point of methane with a positive slope.

Figure 6 is a plot of K-values for helium and methane for the higher isotherms. It is interesting to note the change in the K-values of helium as the system goes from vapor-liquid to fluid-fluid equilibria. The slope of the 189.00° K isotherm is negative at the lower pressures, decreasing with increasing pressure. The 190.30° K isotherm has a very small negative slope at the lower pressures and, when considered with higher pressure data from (*5*), appears to pass through a minimum at about 1000 psia and then increases with increasing pressure. The 190.60° K isotherm, which is in the fluid-fluid region, originates at about 765 psia with a very steep positive slope which then decreases rapidly with increasing pressure. No unusual behavior is seen in the methane K's. The 190.30° K isotherm for methane was omitted for clarity.

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Methyl and Monoglycol Esters of Hydroxymethylabietanoic Acid and Their Derivatives

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A convenient and quantitative method is described for making the methyl and monoglycol esters of 12-hydroxymethylabietan-18-oic acid (I-1). A simple synthesis, starting from the glycol ester, for abietanyl diamines and diisocyanates is described. Several other new derivatives of I-1 are reported.

The Naval Stores Research Laboratory has been engaged for a number of years in making polyfunctional derivatives of resin acids. New glycols, hydroxy acids, amines, amino acids, amino alcohols, diamines, and diisocyanates have been reported (*1, 6, 7, 10, 11*).

This paper has three objectives: viz. to report a convenient quantitative route to resin acid esters; to point out a new simple route to abietanyl diamines and diisocyanates applicable to other similar derivatives described in the literature; and to give data on a number of new compounds prepared in connection with unpublished work.

A convenient method for converting 12-hydroxymethylabietan-18-oic acid (I-1) to a diisocyanate, and probably the simplest of published methods, was to prepare the dry sodium salt in dioxane (*6*), react the salt with ethylene chlorohydrin in dimethylsulfoxide (DMSO), react the glycol ester with tosyl chloride, and treat the ditosylate with ammonia to get the diamine. The diamine dihydrochloride was then converted to diisocyanate with phosgene (*11*).

A similar glycol ester was obtained by reacting a crude mixture of dihydro isomers of 12-hydroxymethylabietenoic acid and ethylene oxide by the method used by Lewis and Hedrick (*5*) and successfully converted to a diamine.

DISCUSSION

It is a well-known fact that the direct esterification of resin acids and rosin is difficult. Quantitative esterifications can usually be achieved by reacting the sodium salt with an alkyl halide. Dissolving rosin in dioxane, neutralizing with aqueous sodium hydroxide, and drying by distilling a water azeotrope gave a dry, crystalline salt which reacts readily with alkyl halides. Dioxane is a particularly good solvent for this reaction. This reaction works well with rosin and resin acids, but reactions with alkyl halides are not complete when the abietanyl moiety is substituted by hydroxyl groups that result from the addition of hydroxymethyl groups by reaction with formaldehyde (*1, 6, 8*) or oxonation of rosin (*4*). With compounds of this type

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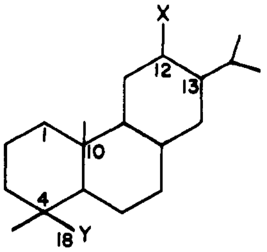
Table I. New Abietanyl Derivatives[a]



Acids, Y = COOH	X
I-1	CH_2OH
I-2	CH_2NH_2
I-3	CH_2NH_2HCl
I-4	$CH_2CH_2NH_2$
I-5	$CH_2CH_2NH_2HCl$
I-6	CH_2COOH

Esters, Y = COOCH₃	X
II-1	CH_2OH
II-2	$CH_2OSO_2C_6H_4CH_3$
II-3	$CH_2OSO_2CH_3$
II-4	CH_2CN
II-5	CH_2NH_2
II-6	$CH_2NH_2HSO_3C_6H_4CH_3$
II-7	$CH_2NH_2HOOCC_6H_3(NO_2)_2$
II-8	$CH_2NH_2HOC_6H_2(NO_2)_3$
II-9	$CH_2CH_2NH_2$
II-10	$CH_2CH_2NH_2HOOCC_6H_3(NO_2)_2$
II-11	$CH_2CH_2NH_2HOC_6H_2(NO_2)_3$
II-12	$CH_2CH_2NHCOCH_3$
II-13	CH_2CH_2NCO
II-14	$CH_2CH_2NHCONHCH_2CH_2C_{21}H_{35}O_2$

Alcohols, Y = CH₂OH	X	
III-1	$CH_2CH_2NH_2$	
III-2	$CH_2CH_2NH_2HCl$	
III-3	CH_2NH_2	11
III-4	CH_2NH_2HCl	

Glycol ester and derivatives	Y	X
IV-1	$COOCH_2CH_2OH$	CH_2OH
IV-2	$COOCH_2CH_2OSO_2C_6H_4CH_3$	$CH_2OSO_2C_6H_4CH_3$
IV-3	$COOCH_2CH_2NH_2$	CH_2NH_2
IV-4	$COOCH_2CH_2NH_2HOOCC_6H_3(NO_2)_2$	$CH_2NH_2HOOCC_6H_3(NO_2)_2$
IV-5	$COOCH_2CH_2NCO$	CH_2NCO

[a] Elemental analyses for C, H, N, S, and Cl in agreement with theoretical values have been obtained and submitted for review.

and those described herein, the reaction is greatly facilitated by the presence of DMSO.

The facile reaction of the tosylates of these abietanyl glycols with ammonia as described is a good reaction which should be applicable to other pure and less pure rosin derivatives, described by Black and Hedrick (*1*), Levering and Glasebrook (*4*), and Royals and Greene (*8*).

Interest shown by other researchers in published work from this laboratory indicates that data on the new compounds in Table I should be of considerable value.

EXPERIMENTAL

Melting points are all uncorrected. Gas-liquid partition chromatography (GLPC) was carried out on an F&M 700 chromatograph using a 6-ft W-98 silicone Hewlett-Packard column at an oven temperature ranging from 215-250° C. Infrared spectra were determined on a Perkin-Elmer Model 21 spectrophotometer. Analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn. Elemental analyses for C, H, N, S, and Cl in agreement with theoretical values have been obtained and submitted for review.

12-Aminomethylabietan-18-oic Acid (I-2). Amino ester (II-5) (8 grams) in ethylene glycol (50 ml) was refluxed with potassium hydroxide (7 grams) for 18 hr. The potassium salt of the amino acid formed was treated with hydrochloric acid to get amino acid hydrochloride. The hydrochloride salt was taken up in methanol, heated with excess ammonia, cooled, and filtered to obtain the residue which was washed and dried; yield of I-2, 5 grams (65%); mp 315–320° C; hydrochloride (I-3), mp 320–324° C (from ethanol/ether); neut equiv 367.3; calcd 386.

12-(β-Aminoethyl)abietan-18-oic Acid (I-4). Amino ester II-9, when treated similarly, gave I-4, mp 300–310° C, and was characterized by its hydrochloride (I-5), mp 245–247° C; neut equiv 380.2; calcd 386. Amino acid I-4 was further characterized by its conversion to methyl acetylaminoethylabietan-18-oate (II-12); infrared bands at 2.95 and 6.14 (NH), 5.85 (acetyl), and 6.02 μ (CO); mp 143–145° C.

12-Carboxymethylabietan-18-oic Acid (I-6). This dicarboxylic acid was made by the alkaline hydrolysis of II-4 (*11*), yield 87%, mp 236–239° C (ether/hexane), neut equiv 184.5, calcd 182.

Methyl 12-Hydroxymethylabietan-18-oate (II-1). The dry sodium salt of 12-hydroxymethylabietan-18-oic acid (I-1) was prepared by refluxing to remove water azeotropically, a mixture of the acid (224 grams, 0.66 mole), dioxane (2600 ml), hexane (200 ml), and sodium hydroxide (26.6 grams, 0.66 mole) in water (75 ml) in a 5-liter, 3-necked Morton flask fitted with a paddle stirrer (*6*). When water ceased to come off, about a liter of hexane/dioxane mixture was distilled, and DMSO was added to the remaining slurry of sodium salt. To the warm mixture was then added dropwise a solution of methyl bromide (119 grams, 1.25 moles) in DMSO (500 ml), followed by another 300 ml of the solvent. The mixture was warmed to get a clear solution, cooled, and then slowly stirred into water to precipitate the ester. The solid ester was collected, dissolved in ether, washed, and dried. Evaporation of the solvent gave 220 grams (94.4%) of II-1. GLPC chromatogram showed only one component, infrared bands at 2.79 (OH) and 5.8 μ (CO), mp 147–148° C.

Methyl 12-Tosyloxymethylabietan-18-oate (II-2). This compound was prepared by a standard procedure (*11*), yield 96%, infrared bands at 5.85 (CO) and 8.57 μ (tosylate), mp 145° C from acetone/methanol.

Methyl 12-Mesyloxymethylabietan-18-oate (II-3). Treatment of II-1 with methanesulfonyl chloride as for II-2 gave II-3, yield 96%, infrared bands at 5.82 (CO) and 8.54 μ (mesylate), mp 155° from acetone.

Methyl 12-Cyanomethylabietan-18-oate (II-4). This was prepared by a modification of Watson's procedure (*11*) from II-2. Tosylate II-2 (100 grams, 0.2 mole), sodium cyanide (20 grams, 0.4 mole), and DMSO (1800 ml) were reacted together at 35–40° C for 1 hr. The mixture was taken up in chloroform, washed with water, then with dilute hydrochloric acid and water, and dried. Removal of chloroform gave II-4, yield 68 grams (95%), mp 163° C from acetone/hexane. GLPC chromatogram had only one component, infrared bands at 4.48 (CN) and 5.85 μ (CO).

Cyano ester II-4 was also made from II-3, yield 95%.

Methyl 12-Aminomethylabietan-18-oate (II-5). This was made by a modification of Watson's procedure (*11*). A mixture of II-2 (15 grams, 0.03 mole) and DMSO (200 ml) was charged into a 1780-ml stainless steel bomb and chilled in DryIce/acetone. Liquid ammonia (200 ml) was added to the cooled mixture and the bomb heated at 50° C for 20 hr. After the excess ammonia was allowed to escape, the product was stirred into water and extracted with ether. The ether layer was washed with alkali and water and dried. Evaporation of the solvent gave the amino ester II-5 as a residue (10 grams, 95%) purified as the hydrochloride, mp 312–315° C from ethanol/ether. GLPC curve showed only one component, infrared bands at 2.96 and 6.3 (NH) and 5.85 μ (CO). Portions of II-5 were converted to the tosylate (II-6), mp 265–266° C; 3,5-dinitrobenzoate (II-7), mp 247–248° C; and the picrate (II-8), mp 230–232° C.

Methyl 12-(β-Aminoethyl)abietan-18-oate (II-9). Cyano ester (II-4) (25 grams), Girdler G-67RS (zirconium-promoted cobalt on kieselguhr) (3.75 grams), and *p*-dioxane (250 ml) were charged into a 1780-ml stainless steel bomb and chilled in Dry Ice/acetone mixture (*2*). Liquid ammonia (25 ml) was added, followed by hydrogen (to 2500 psig), and the batch was heated to 140–145° C. When the temperature rose to 145° C, hydrogen was introduced to 5000 psig and the heating continued for 5 hr. The bomb was cooled, ammonia allowed to escape, and the product was filtered to remove the catalyst. Evaporation of the solution gave 24 grams (95%) of II-9. GLPC chromatogram showed only one component, infrared bands at 2.95, 3.02, and 6.2 (NH) and 5.85 μ (CO); 3,5-dinitrobenzoate (II-10), mp 243–244° C; picrate (II-11), mp 220–222° C. The hydrochloride (mp 248–250° C from ethanol) had neut equiv of 403.4, calcd 400.

Methyl 12-(β-Isocyanatoethyl)abietan-18-oate (II-13). Phosgene was bubbled through a slurry of the hydrochloride salt of II-9 in *o*-dichlorobenzene and heated to refluxing until a clear solution was formed. The title compound was obtained as a brown solid (yield 95%) when the solvent was removed. Distillation (bp 200–202° C/0.12 mm Hg) gave a colorless solid, mp 111–112° C, which showed only one component in the GLPC chromatogram, infrared bands at 4.45 (CNO) and 5.85 μ (CO). It formed the symmetrical urea (II-14) (*3*) with II-9, mp 190–191° C.

12-(β-Aminoethyl)abietan-18-ol (III-1). Lithium aluminum hydride (LAH) reduction (*11*) of II-4 (0.02 mole) furnished the amino alcohol III-1 in 70% yield; GLPC chromatogram indicated only one component; infrared bands at 2.78 (OH) and 2.93, 2.98, and 6.3 μ (NH); mp 126–127° C from ether/hexane. The hydrochloride salt (III-2) with mp 312–315° C, neut equiv 377, calcd 372.

12-Aminomethylabietan-18-ol (III-3). LAH (0.02 mole) reduction of II-5 (0.01 mole) gave III-3 in 94% yield. GLPC curve showed only one component, infrared bands at 2.78 (OH) and 3 and 6.3 μ (NH), hydrochloride (III-4).

β-(Hydroxyethyl), 12-Hydroxymethylabietan-18-oate (IV-1). Extension of the method used for II-1 gave IV-1. Hydroxy acid I-1 (67.2 grams, 0.2 mole) was converted to the dry sodium salt as above, hexane/dioxane mixture was distilled to get a thick slurry. DMSO (250 ml) followed by solution of 2-chloroethanol (32.2 grams, 0.4 mole) in DMSO (100 ml) was added, and the mixture refluxed (temp 100° C) for about 4 hr. More DMSO (250 ml) was added during refluxing to keep the ester in solution. The product, when worked up as for II-1, gave 72 grams (94.7%) of IV-1. GLPC chromatogram showed only one component; infrared bands at 2.8 (OH) and 5.85 μ (CO); mp 109–110° C from acetone; hydroxyl equivalent calcd 190.3, found 188.5.

(β-Tosyloxyethyl), 12-Tosyloxymethylabietan-18-oate (IV-2). This ditosylate was prepared from 38 grams of the glycol ester of IV-1; yield 68 grams, 98%; mp 128–129° C from acetone/methanol; infrared bands at 5.85 (CO) and 8.6 μ (tosylate).

(β-Aminoethyl), 12-Aminomethylabietan-18-oate (IV-3). Ammonolysis of the ditosylate IV-2 by the method described under II-5 gave IV-3. A mixture of IV-2 (25 grams), DMSO (400 ml), and liquid ammonia (150 ml) heated at 50° C for 24 hr gave IV-3 (yield 13 grams, 94%) as a thick oily substance which refused to crystallize; infrared bands at 2.93, 3.02, and 6.15 (NH) and 5.87 μ (CO); di-3,5-dinitrobenzoate (IV-4), mp 205–206° C. The dihydrochloride (mp 293–295° C from ethanol) had neut equiv 228.7, calcd 225.8.

A crude mixture of 12-hydroxymethyldihydroabietic acids was reacted with ethylene oxide (to hydroxyl equiv 228, sap. equiv 400) and converted to a ditosylate. Complete replacement of the tosyl groups was achieved by ammonolysis in DMSO as above; 95% yield; mp di-3,5-dinitrobenzoate, 205–207° C.

(β-Isocyanatoethyl), 12-Isocyanatomethylabietan-18-oate (IV-5). The dihydrochloride salt of IV-3, under conditions similar to those for II-13, gave IV-5 in 58% yield, infrared bands at 4.45 (CNO) and 5.83 μ (CO). The diisocyanate (IV-5) and solid derivatives were difficult to purify. Analysis of the product was achieved by determining the isocyanate value (*9*).

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