named neochihuahuin, $C_{17}H_{22}O_5$, was obtained in about equal yield; it was tentatively assigned structure **9** on the basis of spectral data (ir and nmr, Table I).

Experimental Section[8]

Isolation of Chihuahuin (1) **and Artemisiifolin** (2).—Dried ground stems and leaves (1.86 kg) of *Ambrosia confertiflora* DC. (voucher[9] no. 257744; collection made on Aug 22, 1967, about 25 miles north of Chihuahua, Mexico) were extracted three times with a total of 15 l. of $CHCl_3$. Work-up of the extracts in the usual way[10] afforded 3.5 g of crude syrup. A second extraction yielded 21.5 g of crude syrup after work-up and a third and final extraction gave an additional 5.6 g of crude syrup. Column chromatography on silica gel of the first 3.5 g of crude extract yielded 0.5 g of chihuahuin and 0.42 g of artemisiifolin. In a second column chromatographic run, 15.8 g of crude syrup (10 g of the second extract and all of the third extract, 5.6 g) were dissolved in CH_2Cl_2 and chromatographed over silica gel (packed in CH_2Cl_2). The column was successively eluted first with 500 ml of CH_2Cl_2, followed by a CH_2Cl_2–ethyl acetate solvent mixture containing an increasing amount of ethyl acetate [400 (9.5:0.5), 400 (9:1), 600 (8.5:1.5), 1000 (4:1), 400 (3:1), 400 (7:3), 200 (3:2), 1000 (1:1), 200 ml (1:3)], 200 ml of ethyl acetate, and finally 500 ml of methanol. For the first 1100 ml of eluent, 100-ml fractions were taken (fractions 1–11); then 20–30-ml fractions were collected (no. 12–58) for the next 1200 ml of eluent, and finally 60-ml fractions were taken (no. 59–120) for the last 3500 ml of eluent. All fractions were monitored by tlc. Fractions 45–56 were combined and evaporated to dryness; the residue was redissolved in CH_2Cl_2. After the addition of a small amount of diisopropyl ether, the solution was allowed to stand at −20° for several days; chihuahuin crystallized out in long (5–6 mm) white rhombic needles (956 mg). The mother liquor gave an additional 725 mg of chihuahuin. One recrystallization from CH_2Cl_2–diisopropyl ether yielded pure chihuahuin (1), mp 168–170°,[11] $[\alpha]^{25}D$ +112° ($CHCl_3$, c 4.85).

Anal. Calcd for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24; O, 26.11. Found: C, 66.78; H, 7.40; O, 25.98.

Chihuahuin could be acetylated with Ac_2O and pyridine under standard conditions but the acetate **3** which was characterized by nmr (Table I), was not obtained crystalline.

Fractions 91–100 were combined and evaporated to dryness, and the residue was redissolved in CH_2Cl_2. After some n-hexane and a few seed crystals were added to the solution, it afforded, at room temperature, 1.30 g of artemisiifolin (2), mp 128–130°; the material was identical (ir, nmr, mixture melting point and tlc) with an authentic sample.[3a]

Dihydrochihuahuin (4).—To an ice-cooled solution of 405.4 mg of chihuahuin (1) (1.325 mmol) in 40 ml of methanol was added a freshly prepared solution of 105 mg of sodium borohydride (2.78 mmol) in 10 ml of methanol. After stirring the cold solution for 30 min, 20 ml of distilled water were added. The final solution was extracted with 200 ml of CH_2Cl_2. The organic layer was washed twice with water, dried over anhydrous magnesium sulfate, filtered, and evaporated to dryness to yield a colorless oil. After redissolving the oil in CH_2Cl_2, n-hexane was added until turbidity persisted. Dihydrochihuahuin (4) crystallized in needles at room temperature, 332 mg (81% of theory), mp 151–155°. The nmr spectrum of dihydrochihuahuin did not exhibit the characteristic pair of doublets for the C-11 methylene protons, but instead exhibited a new methyl doublet at 1.38 (J = 6 Hz).

Anal. Calcd for $C_{17}H_{24}O_5$: C, 66.21; H, 7.85; O, 25.94. Found: C, 66.36; H, 7.98; O, 25.79.

Pyrolysis of Dihydrochihuahuin (4) **and Its Acetate** (6).—Dihydrochihuahuin (20 mg) was heated under a water pump vacuum at 205° in a sublimation tube. After 5 min, the tube was rapidly cooled with ice water. A colorless oily residue (19 mg) was obtained and tlc (CH_2Cl_2:ethyl acetate, 1:1) indicated the presence of one major compound; an nmr spectrum of the material showed a characteristic doublet for an aldehyde proton (as in **5**) at 9.82. In a similar experiment 100 mg of dihydrochihuahuin acetate (**6**) afforded 95 mg of **7** as a crude oily residue (tlc, benzene:ethyl acetate, 3:1). An nmr spectrum (Table I) of the material was in agreement with structure **7**.

Conversion of Chihuahuin (1) **to Chamissonin Diacetate** (8) **and Neochihuahuin** (9).—To 106 mg of finely powdered chihuahuin (1) were added 1.85 ml of a 10% aqueous sodium hydroxide solution. Since chihuahuin did not dissolve at room temperature, the mixture was heated for 10 min on a steam bath[12] to give a lightly yellow colored solution which was cooled in ice water and then rapidly evaporated under high vacuum without applying heat. To the viscous oil-like residue thus obtained was added at ice-bath temperature 2 ml of glacial acetic acid. The acidified solution was evaporated (without heat) under high vacuum and the solid, somewhat sticky residue thus obtained was further dried for several hours. To this residue was added 2 ml of pyridine and 10 ml of acetic anhydride. The solution was allowed to stand at room temperature for 17 hr and then it was filtered from the solid material (sodium acetate) and the salt was washed with a few milliliters of ethyl acetate. Washings and filtrate were evaporated under vacuum to dryness to yield 167 mg of a yellow oil which was dissolved in ethyl acetate; the solution was washed several times with water to remove the last traces of sodium acetate. After the ethyl acetate extracts were dried over anhydrous magnesium sulfate, filtered, and evaporated, a crude yellow oil was obtained which contained two major constituents by tlc ($CHCl_3$:ether, 3:2), R_f values 0.56 and 0.40, the latter value was identical with that observed for a cochromatographed sample of chamissonin diacetate. Preparative thick layer chromatography of the crude oil (silica gel G; $CHCl_3$: ether, 3:2) yielded 28 mg of chamissonin diacetate (**8**) (23% of theory). After recrystallization of the crude material from 95% ethanol, 12.3 mg of **8**, mp 175–176.5°, was obtained. The material was identical (ir, nmr, mixture melting point, and tlc) with an authentic sample of chamissonin diacetate.

The less polar fraction from the thick layer plates (corresponding to the material with an R_f of 0.56) gave 35 mg of a partially crystalline material which gave, after trituration with n-hexane, 22 mg of crystalline material, mp 112–119°. Recrystallization of the crude crystals from ether n-hexane yielded 18 mg, mp 119–120°, of neochihuahuin (9): ir bands ($CHCl_3$) 1770 and 1742 (carbonyls), 1670 and 1638 (double bonds), 1230 cm^{-1} (acetate).

Anal. Calcd for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24. Found: C, 66.43; H, 7.38.

Registry No.—**1**, 25739-42-8; **3**, 25739-43-9; **4**, 25739-44-0; **6**, 25739-45-1; **7**, 25739-46-2; **9**, 25739-47-3.

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[8] All melting points are uncorrected. Analyses were determined by Dr. Alfred Bernhardt, Mikroanalytisches Laboratorium Elbach über Engelskirchen, West Germany.

[9] This voucher is deposited in The University of Texas at Austin Herbarium.

[10] See, for example, T. J. Mabry, H. E. Miller, H. B. Kagan, and W. Renold, *Tetrahedron*, **22**, 1139 (1966).

[11] The melting point of chihuahuin was determined by placing crystals on a hot plate at different temperatures. If inserted below 168°, polymerization occurred, and, if inserted above 170°, chihuahuin melted immediately.

[12] The Cope rearrangement required for the ultimate formation of neochihuahuin may have occurred during this step.

Isomerization of (−)-β-Pinene to High Optical Purity (−)-α-Pinene

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A recent publication[1] dealing with the isomerization of β-pinene to high optical purity α-pinene utilizing iron pentacarbonyl, has prompted us to disclose our method for carrying out this conversion.

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[1] Philip A. Spanninger and J. L. Von Rosenberg, *J. Org. Chem.*, **34**, 3658 (1969).

We encountered the need to prepare large quantities of high optical purity (−)-α-pinene in order to convert it to optically active pinonic acid, to be used during the course of another investigation.

The isomerization of β-pinene to α-pinene has previously been carried out with rosin acids,[2] palladium black saturated with hydrogen,[3,4] and more recently with iron pentacarbonyl.[1]

Each of the above procedures has certain drawbacks that are overcome by our present method. For example, although the palladium experiment gave almost quantitative conversion of β- to α-pinene, the conversion to the optically active product was only 82%. In addition, large amounts of palladium are required for large scale conversion.

With iron pentacarbonyl, although an optical yield of 96.9% is obtained, one gets only a 45% conversion of β- to α-pinene.

We wish to report a very convenient method for preparing large quantities of optically pure -α-pinene, in excellent yield utilizing inexpensive benzoic acid.

Although this acid is strong enough to promote isomerization of β- to α-pinene, it apparently does not lead to side products caused by opening of the cyclobutane ring, nor to any δ-pinene which could be expected as a result from further isomerization of α-pinene.

Isomerization of β-pinene $\{[\alpha]^{25}\mathrm{D}\ -20.13°$ (neat) (optical purity 88.7%)$\}$, with 15 mol % benzoic acid for 48 hr at reflux temperatures produces α-pinene $\{[\alpha]^{25}\mathrm{D}\ -45.01°$ (neat) (optical purity 87.9%)$\}$, in essentially quantitative yields. This procedure which gives an optical yield of 99.0%, as well as the quantitative conversion of β- to α-pinene, makes this an excellent method for this isomerization reaction.

During this investigation, the isomerization was followed utilizing gas–liquid partition chromatography. The disappearance of β-pinene and the formation of α-pinene could be followed utilizing a Carbowax 20M column. Both starting material and product were identified by comparison of their known infrared and nmr spectra.

Chemicals.—β-Pinene was donated by the Crosby Chemical Company, Picayunne, Miss., and benzoic acid was purchased from Aldrich Chemical Company. The β-pinene was redistilled on a Nester–Faust lab still spinning-band column before use (purity 99.5+% by glc analysis.)

Analysis.—Gas chromatographic analysis was conducted on an Aerograph 90-P-3 equipped with a thermal conductivity detector, a 15-ft column of Carbowax 20M (20%) on Chromosorb W, 60–80 mesh, using helium as a carrier gas. Nuclear magnetic resonance spectra were run on a Joelco 60-MHz spectrometer and infrared spectra on a Perkin-Elmer Model 337 Infracord.

Isomerization Procedure.—Benzoic acid (200 g, 1.67 mol), 1100 ml (7.0 mol) of freshly distilled β-pinene, $[\alpha]^{25}\mathrm{D}\ -20.13°$, and 0.39 g of hydroquinone were placed into a 3 l. three-neck flask equipped with a magnetic stirrer, condenser, and gas inlet tube. The system was maintained under an inert atmosphere by passing N_2 through a bubbler at such a rate as to maintain a steady reflux. Heat was applied and this mixture was refluxed for 48 hr. During this reflux period, samples of the mixture were analyzed at 12-hr intervals to determine reaction progress by gas–liquid chromatography. At the end of the reflux period, the crude α-pinene mixture was carefully added to a stirring solution of saturated $NaHCO_3$ in a 4-l. beaker. After neutralization of the benzoic acid, the organic layer was separated, washed with three 500-cc portions of water, and then dried over anhydrous Na_2SO_4.

Distillation of the crude α-pinene through a Nester–Faust lab still spinning-band column yielded 895 g [95.5% yield of (−)-α-pinene]: bp 155–156°; $n^{25}\mathrm{D}$ 1.4645; $[\alpha]^{25}\mathrm{D}\ -45.01°$.

Registry No.—(−)-β-Pinene, 18172-67-3; (−)-α-pinene, 7785-26-4.

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Additions of Tributyltin Hydride to Terpenes

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The additions of tributyltin hydride[1] to optically active terpenes such as α- and β-pinenes, limonene, and camphene can be expected to proceed asymmetrically, to give an optically active product.

The analogous additions of organosilicon hydrides to these terpenes under irradiation with uv light or in the presence of chloroplatinic acid as catalyst have been thoroughly investigated by E. Frainnet[2,3] and R. Tanaka.[4] The addition of organotin hydrides to common α olefins has also been investigated; free-radical processes occur to give the tin terminated adducts.[5]

In the present experiments, azobisisobutyronitrile was mainly used as the radical generator and the reaction was carried out in a sealed tube at reaction temperatures from 75 to 200° for 24 hr. The yield of the adducts increased with the temperature rise.

β-Pinene and limonene gave 1:1 adducts in good yields, and formation of hexabutylditin, the inevitable side product, was small. α-Pinene, however, gave no real adduct even at the highest temperature (200°), no doubt because the internal double bond is relatively unreactive;[6] hexabutylditin and the products from contaminating terpenes predominated. With camphene, no substantial yield of adduct was obtained under any conditions despite of its terminal double bond. Analogous reactions were also studied with the five p-menthenes-1, -2 (*trans*), -3, -1(7), and

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