signals at 0.85d and 0.92d ($J = 7$, isopropyl), 0.85 (C-10 methyl), 1.17 (C-4 methyl), and 3.63 p.p.m. (methoxyl).

Anal. Calcd. for $C_{21}H_{34}O_3$: C, 75.40; H, 10.25. Found: C, 75.57; H, 10.25.

This substance was also obtained by oxidation of 0.06 g. of **10b** with an excess of ruthenium tetroxide in carbon tetrachloride.[31] After 1 hr. at room temperature the solution was filtered and mixed with a few drops of methanol, filtered again, washed with water, dried, and evaporated. Recrystallization of the residue from methanol–water furnished 0.03 g. of **18b**, m.p. 115–116°.

A solution of 0.1 g. of **18b** was refluxed with sodium methoxide in methanol for 6 hr. The recovered material was recrystallized from methanol–water, yield 0.07 g., identical in all respects with starting material.

Hydroboration of Methyl Levopimarate.—The major product, prepared by following the directions of Dauben and Coates,[14] melted at 123–124°, $[\alpha]^{25}\mathrm{D}$ +53° (*c* 1.08), lit.[14] 126–127.5°, $[\alpha]\mathrm{D}$ +56°, and was identical in all respects with the sample of **11b** prepared by methylation of **11a** from the hydrogenation of **2a**. The minor product[14] melted at 131–132°, lit.[14] m.p. 133–134°. The n.m.r. spectrum exhibited signals at 0.80 (C-10 methyl), 0.90 and 1.09 (slightly broadened isopropyl doublet), 1.17 (C-4 methyl), 3.62 (methoxyl), and 5.12 p.p.m. (H-14).

Oxidation of 11b.—Oxidation of 1.1 g. of **11b** by the literature method[14] and chromatography of the crude product over 35 g. of neutral alumina gave, in the benzene–petroleum ether (1:1) fraction, 0.65 g. of methyl $\Delta^{8(14)}$-12-keto-13α-H-abietenoate (**16b**), which, as reported previously,[14] did not exhibit a sharp melting point. The n.m.r. spectrum indicated the presence of a single substance, signals at 0.88 and 0.98 (superimposed doublets of isopropyl group), 0.98 (C-10 methyl), 1.20 (C-4 methyl), 2.40 (H-13?), 3.70 (methoxyl), and 5.52 p.p.m. (d, $J = 3$, H-14). Elution with benzene–petroleum ether (3:1) and benzene gave small amounts of gum. Elution with benzene–ether (20:3) gave 0.265 g. of methyl $\Delta^{13(14)}$-8α-hydroxy-12-ketoabietenoate (**21**) which after recrystallization from high-boiling petroleum ether melted at 135°, $[\alpha]^{23}\mathrm{D}$ +29°, λ_{max} 235 mμ (ϵ_{max} 6140). The n.m.r. spectrum had signals at 0.65 (C-10 methyl), 1.01d and 1.04d ($J = 7$, isopropyl group), 1.13 (C-4 methyl), and 3.68 p.p.m. (methoxyl). Admixture of an authentic sample of **21**, m.p. 135°, $[\alpha]\mathrm{D}$ +28°, prepared by the literature method[9] gave no melting point depression, and the n.m.r. spectra of the two samples were identical.

Methyl 12-Keto-8β,13βH-abietanoate (**19**).—Methyl $\Delta^{8(14)}$-12-keto-13αH-abietenoate (**16b**) was isomerized with sodium methoxide by the literature method[14] to methyl $\Delta^{13(14)}$-12-keto-8βH-abietenoate (**17**) which had n.m.r. signals at 0.93 and 1.04 (superimposed doublets of isopropyl group), 0.93 (C-10 methyl), 1.05 (C-4 methyl), 3.65 (methoxyl), and 6.32 p.p.m. (H-14) and was hydrogenated without further purification. After one recrystallization from methanol–water, the product (**19**) had m.p. 96–97°, lit.[14] m.p. 98.5–99.5°; n.m.r. signals at 0.85d and 0.89d ($J = 7$ and 6, isopropyl group), 0.93 (C-10 methyl), 1.22 (C-4 methyl), and 3.67 p.p.m. (methoxyl). The physical constants of this material differed from those of **18b** and the melting point was depressed on admixture of **18b**.

Anal. Calcd. for $C_{21}H_{34}O_3$: C, 75.40; H, 10.25. Found: C, 75.03; H, 10.13.

A solution of **19** in methanol was refluxed for 3.5 hr. with sodium methoxide. The recovered material (65% yield) melted at 95–96° and was identical in all respects with starting material.

Methyl 8α-Hydroxy-12-keto-13αH-abietanoate (**22**).—A solution of 0.1 g. of **21** in 150 ml. of ethanol was hydrogenated with 0.075 g. of prereduced platinum oxide at atmospheric pressure. After the uptake of 1 mole equiv. of hydrogen, the solution was filtered and concentrated to very small volume. The product which separated on cooling weighed 0.085 g. and was recrystallized twice from methanol–water: 0.06 g.; m.p. 162–164°; o.r.d. curve (*c* 0.046, methanol), $[\alpha]_{589}$ +22°, $[\alpha]_{308}$ +350°, $[\alpha]_{276}$ +230°, $[\alpha]_{250}$ (last reading) 400°; n.m.r. signals at 0.78 (C-10 methyl), 0.84 and 0.92d ($J = 7$, isopropyl group), 1.15 (C-4 methyl), and 3.68 p.p.m. (methoxyl).

Anal. Calcd. for $C_{21}H_{34}O_4$: C, 71.96; H, 9.78; O, 18.26. Found: C, 71.78, 72.11; H, 9.96, 9.62; O, 18.15, 18.40.

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[31] H. Nakata, *Tetrahedron*, **19**, 1959 (1963).

Resin Acids. V. Partial Synthesis of (−)-Rimuane[1,2]

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(−)-Rimuane has been synthesized from isopimaric acid. This defines the absolute configuration of the fully saturated hydrocarbon and hence that of rimuene itself.

The chemistry of the diterpene rimuene **1** has been the subject of many communications[3] but only recently has its structure been elucidated by two groups[4,5] and placed on a firm basis by the total synthesis of *dl*-rimuene by Ireland and Mander.[6] We describe here a partial synthesis of rimuane **2** which defines the absolute configuration at every center of this fully saturated hydrocarbon and hence that of rimuene itself.

Our starting material was the known γ-lactone **5**[7] obtained in two steps from naturally occurring isopimaric acid **3**[8] of known absolute configuration (Chart I).[9] Hydrolysis of **5** with potassium hydroxide in refluxing diethylene glycol[16] afforded the acid **6** whose n.m.r. and infrared spectra confirmed the presence of a trisubstituted double bond rather than the alternate tetrasubstituted $\Delta^{5(10)}$ isomer. This acid resisted catalytic hydrogenation with such catalysts as platinum oxide in acetic acid or ruthenium dioxide in ethanol but, in the former case, traces of lactone **5** were detected by infrared spectroscopy in the recovered material. Be-

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[1] Previous paper: W. Herz, H. J. Wahlborg, W. D. Lloyd, W. H. Schuller, and G. W. Hedrick *J. Org. Chem.*, **30**, 3190 (1965).

[2] Supported in part by grants from the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (GP-1962).

[3] For leading references see ref. 4.

[4] R. E. Corbett and S. G. Wyllie, *Tetrahedron Letters*, **No. 29**, 1903 (1964).

[5] J. D. Connolly, R. McCrindle, R. D. H. Murray, and K. H. Overton, *ibid.*, **No. 29**, 1983 (1964).

[6] R. E. Ireland and L. N. Mander, *ibid.*, **No. 46**, 3453 (1964).

[7] O. E. Edwards and R. Howe, *Can. J. Chem.*, **37**, 760 (1959).

[8] Isolated from WW gum rosin by the method of D. E. Baldwin, V. M. Loeblich, and R. V. Lawrence, *J. Org. Chem.*, **23**, 25 (1958).

[9] The structure and *relative* stereochemistry of isopimaric acid is represented[10,11] by **3**. Correlation[12,13] of isopimaric acid with sandaracopimaric acid, whose absolute stereochemistry has been defined by correlation with testosterone[14] and 3-acetoxyandrost-5-en-17-one,[15] therefore establishes that the *absolute* stereochemistry of isopimaric acid is also represented by **3**.

[10] W. Antkowiak, J. W. ApSimon, and O. E. Edwards, *J. Org. Chem.*, **27**, 1930 (1962).

[11] R. E. Ireland and J. Newbould, *ibid.*, **28**, 23 (1963).

[12] O. E. Edwards, A. Nicolson, and M. N. Rodger, *Can. J. Chem.*, **38**, 663 (1960).

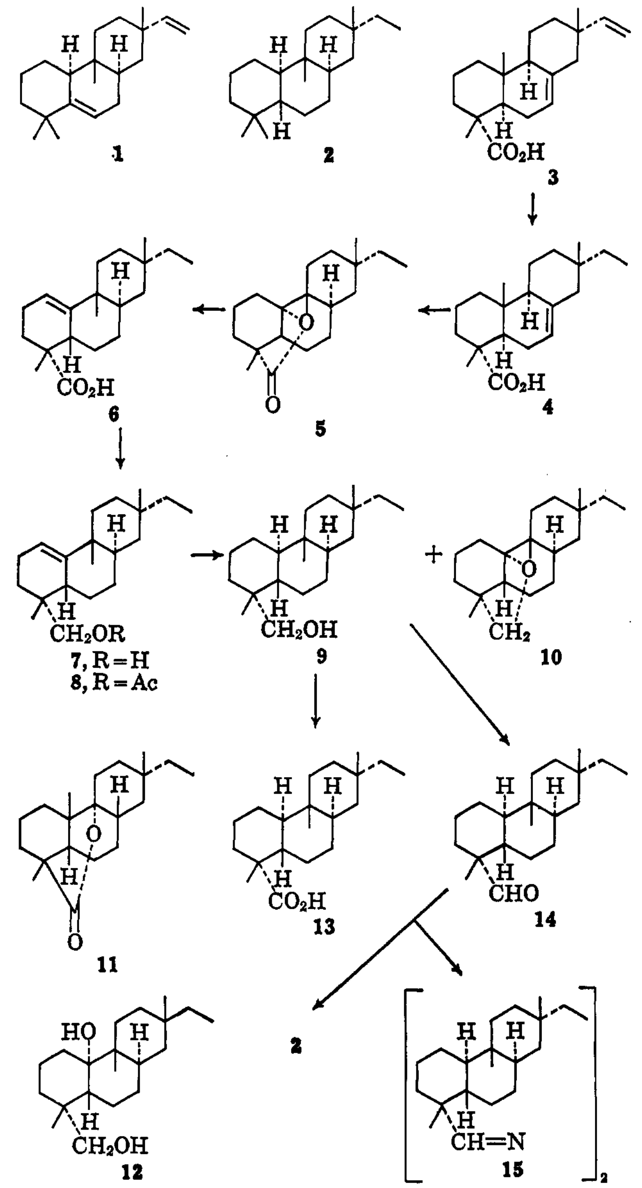
[13] J. W. ApSimon, B. Green, and W. B. Whalley, *J. Chem. Soc.*, 752 (1961).

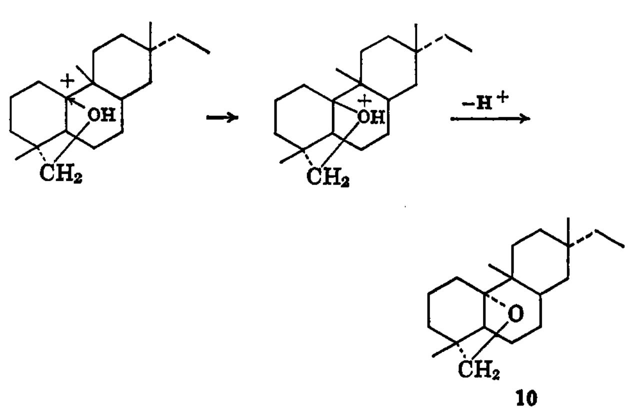
[14] A. K. Bose and S. Harrison, *Chem. Ind.* (London), 254 (1963).

[15] M. Fétizon and M. Golfier, *Bull. soc. chim. France*, 167 (1963).

[16] L. Van Thoi and J. Ourgaud, *ibid.*, 209 (1956).

CHART I





cause of this sensitivity of 6 to acids, we considered conducting further hydrogenation experiments on the alcohol 7 which was obtained in good yield from 6 by lithium aluminum hydride reduction.

The unsaturated alcohol 7 also proved to be resistant to catalytic hydrogenation with platinum oxide in acetic acid but, when a trace of perchloric acid was added, the reduction proceeded smoothly to give alcohol 9 in 65% yield after mild alkaline hydrolysis of the primary acetate formed by Fischer esterification. A second product, formed in 30% yield, was shown to be the ether 10 (see below). The proposed structure for alcohol 9 might be considered suspect because the acidic conditions employed could conceivably give rise to Wagner–Meerwein rearrangements reminiscent of those postulated for the formation of the δ-lactone 11 from γ-lactone 5.[7] Indeed, the generation of a carbonium ion at C-10 (a prerequisite for Wagner–Weerwein rearrangement) was demonstrated by the isolation of ether 10 which was presumably formed by nucleophilic attack at C-10 of a lone pair of electrons associated with the hydroxyl group and subsequent (or concomitant) expulsion of a proton. However, the stability of the carbon skeleton in 7 under the hydrogenation conditions was clearly demonstrated when 85% of 7 was recovered unchanged[17] from a blank experiment without catalyst or hydrogen present. The stereochemistry of the newly created center at C-10 is presumed to be as shown in formula 9 (H-10 α), since inspection of Dreiding models shows that hydrogenation would occur preferentially from the α side. Further support for the existence of an A/B *trans* junction is found in the demonstration that the functionalized group at C-4 is axial. The acid proton of 13 is shielded as compared with that of isohibaic acid (carboxyl group equatorial[18]). Conclusive proof for the correctness of the assumption is the identity (*vide infra*) of our partially synthetic material with (−)-rimuane from rimuene whose relative configuration at C-10 follows from the method of synthesis of the racemate.

The structure of the ether 10 was confirmed in two ways. First, chromic acid oxidation at 70° gave lactone 5 in 60% yield. Secondly, the ether was prepared unambiguously by dehydration[19] of diol 12 obtained by lithium aluminum hydride reduction of 5.

Oxidation of 9 with excess Jones reagent at room temperature gave an acid 13 which we propose to name tetrahydrorimuic acid (m.p. 204–205°, $[\alpha]_D$ −16°), the tetrahydro derivative of a new class of resin acids.

Oxidation of 9 with Jones reagent at 0° gave aldehyde 14 which when subjected to Huang-Minlon reduction afforded a 20% yield of hydrocarbon $C_{20}H_{36}$, m.p. 85–86°, $[\alpha]_D$ −7.5°, whose infrared spectrum showed bands at 1390 and 1370 cm.$^{-1}$ characteristic of a *gem*-dimethyl group and whose n.m.r. spectrum contained four singlets, each of intensity three protons, at 42.5, 47.5, 48.2, and 52 c.p.s. (60 mc.). These physical constants agree perfectly with those of a sample of rimuane prepared by Corbett and Wyllie[20] from naturally occurring rimuene. Hence our hydrocarbon is identical with rimuane whose stereochemistry is therefore correctly represented by 2. It would seem that the rotation of the "rimuane," $[\alpha]_D$ +68.5°, obtained by Briggs and coworkers[21] was reported incorrectly or that their

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[17] The remaining 15% was identified as the ether 10.

[18] W. Herz, D. Melchior, R. N. Mirrington, and P. J. S. Pauwels, *J. Org. Chem.*, **30**, 1873 (1965).

[19] K. S. Kulkarni, S. K. Paknikar, and S. C. Bhattacharyya, *Tetrahedron*, **20**, 1289 (1964).

[20] A personal communication from Professor Corbett states that his sample of rimuane had m.p. 86°, $[\alpha]_D$ −7.5°; n.m.r. singlets at 42, 48, 48, and 51.6 c.p.s. Professor Corbett was regretfully unable to furnish us with a sample for direct comparison. However our material was identical in all respects (infrared and n.m.r. spectra, melting point, and rotation) with a sample of (−)-rimuane which had been prepared from naturally occurring rimuene and was provided by Dr. L. N. Mander.

[21] C. H. Briggs, B. F. Cain, and J. K. Wilmshurst, *Chem. Ind.* (London), 995 (1958).

material differed in configuration from Corbett and Wyllie's rimuane. One possibility is that it may have been the 5*α*,10*α* epimer (AB rings *cis* fused) arising from hydrogenation from the *α* side of the molecule.

The low yield of rimuane obtained in the above experiment was perhaps due to the axial orientation of the aldehyde group which is known to be more resistant to such reductions.[12,22]

Experimental[23]

Lactone 5.—Dihydroisopimaric acid (4), 3.1 g., prepared from isopimaric acid by hydrogenation with palladium-on-charcoal catalyst,[7] was lactonized by the method of Edwards and Howe[7] to give 3.08 g. of a gum which was chromatographed on 120 g. of silica gel. Elution with benzene furnished 1.90 g. (61%) of lactone **5** which crystallized from aqueous methanol as colorless needles, m.p. 107.5–108° (lit.[7] m.p. 105–106°), infrared band at 1765 cm.$^{-1}$

Unsaturated Acid 6.—A suspension of 2.45 g. of lactone **5** in 15 ml. of diethylene glycol containing 1.5 g. of potassium hydroxide was heated under reflux in a nitrogen atmosphere for 1.5 hr., then cooled, diluted with water, and extracted with ether (100 ml.). The ether extract was washed well with water, dried and evaporated to give 0.2 g. of unchanged lactone. The alkaline aqueous layer from the above extraction was cooled to −5°, carefully acidified with 100 ml. of 0.4 *N* acetic acid, then saturated with salt, and extracted with three 100-ml. portions of ether. The combined organic phase was washed well with water, dried, and evaporated to give 1.95 g. (80%) of acid **6** which crystallized from petroleum ether (b.p. 40–60°) as colorless prisms: m.p. 174–175°; $[\alpha]^{26}$D +173° (*c* 0.76); infrared bands at 2670, 1700 (acid), 1655, and 850 cm.$^{-1}$ (trisubstituted double bond); n.m.r. signals at 11.30 (broad, 1 proton, COO*H*), 5.33 (complex, 1 proton, H-1), 1.22, 0.93, and 0.83 p.p.m. (methyl singlets).

Anal. Calcd. for $C_{20}H_{32}O_2$: C, 78.89; H, 10.59. Found: C, 78.61; H, 10.20.

Unsaturated Alcohol 7.—A solution of 6.0 g. of **6** in 200 ml. of anhydrous ether was added slowly (2–3 min.) to a stirred suspension of 3 g. of lithium aluminum hydride in 250 ml. of anhydrous ether and the mixture was refluxed for 2 hr. and then treated cautiously with wet ether, water, and finally 2 *N* aqueous hydrochloric acid. The aqueous layer was extracted with ether and the extract was combined with the original ether layer which was washed with water, dried, and evaporated. The solid residue was chromatographed on a column of 150 g. of alumina; elution with benzene afforded 5.25 g. (92%) of alcohol **7** which crystallized from aqueous methanol as colorless needles: m.p. 120–121°; infrared bands at 3300, 1065, 1050, 1030 (alcohol), 1655, 860, and 840 cm.$^{-1}$ (trisubstituted double bond); n.m.r. signals at 5.35 (approximate triplet, 1 proton, H-1, J = 3 c.p.s.), 3.50, 3.31 (AB quartet, 2 protons, CH_2OH, J_{AB} = 10.5 c.p.s.), 0.92, 0.91, and 0.80 p.p.m. (methyl singlets).

Anal. Calcd. for $C_{20}H_{34}O$: C, 82.69; H, 11.80. Found: C, 82.44; H, 11.82.

Acetylation of **7** with acetic anhydride–pyridine gave the unsaturated acetate **8** as an oil: infrared band ($CHCl_3$) at 1730 and 1210–1240 cm.$^{-1}$ (broad, acetate); n.m.r. signals at 5.36 (complex, 1 proton, H-1), 3.88 (singlet, 2 protons, CH_2OAc), 2.07 (singlet, acetate), 0.93, 0.91, and 0.82 p.p.m. (methyl singlets).

Hydrogenation of 7.—A solution of 3.4 g. of **7** in 90 ml. of acetic acid containing 6 drops of 61% perchloric acid was shaken under hydrogen at 20-lb. pressure in the presence of 0.3 g. of platinum oxide for 20 hr. at room temperature. After removal of the catalyst by filtration through Celite, the filtrate was diluted with water and extracted with ether. The ethereal extract was washed with water twice, with 2 *N* aqueous sodium hydroxide twice, and again with water, dried, and evaporated. The oily residue was taken up in 100 ml., of hot 10% aqueous methanol and treated with 5 g. of potassium hydroxide on a steam bath for 1 hr., diluted with water, and extracted with two 200-ml. portions of ether. The washed and dried extract was evaporated to give a yellow oil which was taken up in hexane and chromatographed on a column of 100 g. of alumina prepared in hexane. Elution with hexane gave 1.16 g. of ether **10** (34%) which crystallized from aqueous methanol as colorless needles: m.p. 99.5–100°; infrared bands ($CHCl_3$) at 1040 and 1020 cm.$^{-1}$ (ether) no hydroxyl absorption; n.m.r. signals at 3.71 (singlet, 2 protons, CH_2–O–C–), 0.88, 0.80, and 0.77 p.p.m. (methyl singlets).

Anal. Calcd. for $C_{20}H_{34}O$; C, 82.69; H, 11.80. Found: C, 82.82; H, 11.54.

Elution with benzene–ether (9:1) gave 2.22 g. of alcohol **9** (65%) which crystallized from aqueous methanol as colorless needles: m.p. 100.5–101°; infrared bands at 3400 and 1035 cm.$^{-1}$ (alcohol); n.m.r. signals at 3.80, 3.48 (AB quartet, 2 protons, CH_2OH, J_{AB} = 11 c.p.s.) 0.95, 0.79, and 0.70 p.p.m. (methyl singlets).

Anal. Calcd. for $C_{20}H_{36}O$: C, 82.12; H, 12.40. Found: C, 82.12; H, 12.55.

Oxidation of 10.—A warm (70°) solution of 0.3 g. of **10** in 20 ml. of glacial acetic acid was treated with excess Jones reagent on a steam bath for 10 min. Methanol was added to decompose excess oxidant and the mixture was poured into water and extracted with two 100-ml. portions of ether. The ether extract was washed with water, 2 *N* aqueous sodium hydroxide, and water, dried, and evaporated to give an oily residue which was taken up in benzene and chromatographed on a column of 30 g. of silica gel prepared in benzene. Elution with benzene gave 0.20 g. of lactone **5** (60%) which crystallized from aqueous methanol, m.p. and m.m.p. 107.5–108.5°, identical spectroscopically with previously obtained **5**.

Conversion of Lactone 5 to Ether 10.—A solution of 2.3 g. of **5** in 50 ml. of anhydrous ether was added to a suspension of 0.85 g. of lithium aluminum hydride in 200 ml. of anhydrous ether and the mixture was refluxed 5 hr. The usual work-up afforded 2.18 g. of a white solid which crystallized from acetone as colorless needles of diol **12**: m.p. 191–192°; infrared bands at 3400, 3300, 1065, and 1055 cm.$^{-1}$ (alcohols), no carbonyl absorption; n.m.r. signals at 3.75, 3.20 (AB quartet, 2 protons, CH_2OH, J_{AB} = 11 c.p.s.), 0.92, 0.81, and 0.81 p.p.m. (methyl singlets).

Anal. Calcd. for $C_{20}H_{36}O_2$: C, 77.86; H, 11.76. Found: C, 78.10; H, 11.55.

A solution of 0.4 g. of diol **12** in 50 ml. of dry benzene containing 0.1 g. of *p*-toluenesulfonic acid was heated under reflux for 2 hr. after which time a pink-orange color had developed. The cooled solution was washed with two 50-ml. portions of 5% aqueous sodium bicarbonate solution and with water, dried, and evaporated. The yellow oily residue was taken up in hexane and chromatographed on a column of 20 g. of alumina prepared in hexane. Elution with hexane gave 0.35 g. of ether **10** which crystallized from aqueous methanol, m.p. and m.m.p. 98–99°, infrared spectrum identical with that of previously obtained material (see above).

Tetrahydrorimuic Acid (13).—A solution of 0.44 g. of **9** in 100 ml. of acetone was stirred at room temperature with 1.5 ml. of Jones reagent for 1 hr. The excess oxidant was destroyed by addition of methanol and the mixture was poured into water and extracted with three 75-ml. portions of ether. The combined extract was washed with water, dried, and evaporated to give a crystalline solid which crystallized from *n*-hexane as colorless needles (**13**): m.p. 204–205°; yield 0.43 g. (93%); $[\alpha]^{25}$D −16° (*c* 0.76); infrared bands ($CHCl_3$) 3200–2600 (br), 1720 (sh), and 1700 cm.$^{-1}$ (COOH); n.m.r. signals at 1.20, 0.77, 0.68 (methyl singlets), 0.75 (methyl triplet, J = 7 c.p.s.), 1.51 (singlet, 1 proton, COO*H*, removed on exchange with D_2O).

Anal. Calcd. for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18. Found: C, 78.41; H, 10.85.

Aldehyde 14.—Deaerated Jones reagent was added dropwise to a stirred solution of 0.65 g. of **9** in 50 ml. of acetone at 0° while nitrogen was bubbled through the reaction mixture. When the brown color persisted for 3–4 min. the excess oxidant was removed by addition of methanol and the stirred mixture was slowly diluted with water to give a crystalline precipitate which was collected by filtration and washed with water, yield

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[22] Professor Corbett has kindly informed us that a very similar conversion of isopimaric acid to rimuane was carried out in his laboratory (S. G. Wyllie, Ph.D. Thesis, University of Otago, Dunedin, New Zealand, 1964). However, the amount of isopimaric acid available was too small to permit analytical characterization of the intermediates and the final product was characterized by gas chromatography only.

[23] Melting points are uncorrected. Analyses were by Dr. F. Pascher, Bonn, Germany. Infrared spectra were run as Nujol mulls unless otherwise specified, rotations in chloroform. N.m.r. spectra were run on a Varian A-60 spectrometer in deuteriochloroform with tetramethylsilane as internal standard. Alumina used for chromatography was Alcoa grade F-20.

0.60 g. (92%), m.p. 80–85°. Repeated crystallization from methanol afforded aldehyde **14**: m.p. 97–98°; infrared bands at 2700, 1720, and 1720 cm.$^{-1}$ (aldehyde), no hydroxyl absorption; n.m.r. signals at 9.95 (singlet, 1 proton, C*H*O), 1.06, 0.80, 0.72 (methyl singlets), and 0.76 p.p.m. (methyl triplet, J = 6.5 c.p.s.). On exposure to air for 12 hr. it collapsed to an oil whose infrared spectrum ($CHCl_3$) now contained marked hydroxyl absorption and showed a considerable decrease in intensity of the carbonyl band at 1720 cm.$^{-1}$. The compound was therefore characterized as its azine (**15**) which crystallized from acetone as colorless needles, m.p. 201–202.5°, infrared bands at 1640 cm.$^{-1}$ ($C{=}N$).

Anal. Calcd. for $C_{40}H_{68}N_2$: N, 4.85. Found: N, 5.20.

Reduction of 14 to Rimuane 2.—A mixture of 0.45 g. of freshly prepared aldehyde **14**, 25 ml. of ethylene glycol, and 1 ml. of 95% hydrazine was refluxed for 1 hr., concentrated to b.p. 192°, and then allowed to cool for 10 min. Potassium hydroxide (3.2 g.), 0.5 ml. of hydrazine, and an additional 7 ml. of ethylene glycol were added and the mixture was refluxed for 2 hr., then cooled, diluted with water, and extracted with three 50-ml. portions of hexane. The organic extract was washed with aqueous sodium chloride and water, dried, concentrated to about 10 ml., and poured onto a column of 25 g. of alumina prepared in hexane. Elution with hexane gave 0.09 g. of rimuane **2** (20%) which crystallized from methanol as colorless needles: m.p. 85–86°; $[\alpha]^{26}\mathrm{D}$ −75° (c 0.74); infrared bands (CCl_4) at 1390 and 1370 cm.$^{-1}$ (*gem*-dimethyl group); n.m.r. signals at 0.87, 0.80, 0.79, 0.71 (methyl singlets), and 0.76 p.p.m. (center peak of methyl triplet).

Anal. Calcd. for $C_{20}H_{36}$: C, 86.88; H, 13.12. Found: C, 87.12; H, 12.78.

Elution with ether gave 0.35 g. of a colorless solid which crystallized from acetone as colorless needles, m.p. and m.m.p. 200–202°, identical with azine **15** described above.

Notes

Resin Acids. VI. Stereochemistry of the Tetrahydropimaric Acids[1]

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Because of our interest in the mode of hydrogenation of substituted resin acids[2] our attention was attracted to a recent report[3] that hydrogenation of dihydropimaric acid **1** using a platinum catalyst gave two different tetrahydro acids depending on conditions employed. The first, m.p. 235–240°, $[\alpha]\mathrm{D}$ +13°, was formed at 20° and at atmospheric pressure and was apparently identical with a tetrahydropimaric acid, m.p. 238–240°, $[\alpha]\mathrm{D}$ +18°, previously obtained by Edwards and Howe[4] under similar conditions. The second, m.p. 166–168°, $[\alpha]\mathrm{D}$ +10°, was formed at 60° under 100 kg. pressure and was tentatively assigned[3] the *trans-anti-cis* structure **3**. Neither the French[3] nor Canadian[4] groups were definite about the stereochemistry of the high-melting acid which, it was suggested,[3] might be the *trans-anti-trans* isomer **12**. In an attempt to clarify the situation and, in particular, the seemingly unusual attack from the more hindered β side, we have effected an unambiguous synthesis of the tetrahydro acid **12** in the following way.

Hydroboration of methyl dihydropimarate **2** with diborane in diglyme followed by peroxide oxidation of the resultant alkyl boranes gave an approximately 1:1 mixture (see below) of alcohols **4** and **6** which could not be separated by chromatography on alumina and cocrystallized from aqueous methanol as colorless needles, m.p. 98–100°. The ratio of components was established by acetylation to the mixture of acetates **5** and **7** whose nuclear magnetic resonance (n.m.r.) spectrum contained doublets centered at 5.21 (0.55 proton, J = 12 c.p.s.) and 4.55 p.p.m. (0.45 proton, J = 10 c.p.s.) corresponding to H-14 in **5** and **7**, respectively. The slight predominance of **4** over **6** (55:45) was consistent with the expected, more favorable attack from the slightly less hindered α side of the molecule. The n.m.r. spectrum of the mixture of acetates **5** and **7** arising from acetylation of a *crude* alcohol mixture was essentially identical with that described above, confirming that no separation of the alcohols **4** and **6** had been achieved by chromatography or crystallization procedures.

The doublet at higher field (4.55 p.p.m.) was assigned to H-14 in acetate **7** rather than **5** for the following reason. Jones oxidation of the alcohol mixture gave an oil (obviously a mixture as indicated by its n.m.r. spectrum), alkaline treatment of which yielded a single ketone which represented the more stable isomer, presumably the *trans-anti-trans* isomer **8**. Reduction of **8** with sodium borohydride furnished the expected equatorial alcohol **6**, m.p. 150–152°, whose acetate **7** showed a one-proton doublet at 4.55 p.p.m. (J = 10 c.p.s.) in the n.m.r. spectrum but no trace of signals at 5.2 p.p.m.

The assignment of structure **7** to this acetate obviously depends on the establishment of the stereochemistry at C-8 in ketone **8**. Firstly, the optical rotatory dispersion (o.r.d.) curve of **8** showed the expected[5] negative Cotton effect, whereas a positive effect would be predicted from the octant rule[5] for the alternative $8\alpha,9\alpha$H- (BC *cis*-fused) 14-one. Secondly, the n.m.r. spectrum of **8** (methyl singlets at 1.19, 1.00, and 0.96 p.p.m.) showed no shielded methyl signal which would be expected of the C-10 methyl

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[1] Previous paper: W. Herz and R. N. Mirrington, *J. Org. Chem.*, **30**, 3195 (1965). Work supported in part by grants from the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (GP-1962).

[2] W. Herz, H. J. Wahlborg, W. D. Lloyd, W. H. Schuller, and G. W. Hedrick, *ibid.*, **30**, 3190 (1965).

[3] C. Asselineau, S. Bory, and A. Diara, *Bull. soc. chim. France*, 1197 (1964).

[4] O. E. Edwards and R. Howe, *Can. J. Chem.*, **37**, 760 (1959).

[5] W. Moffitt, A. Moscowitz, R. B. Woodward, W. Klyne, and C. Djerassi, *J. Am. Chem. Soc.*, **83**, 4013 (1961).