standing for 1.5 hr, this was saturated with sodium chloride and extracted five times with ether. Evaporation of the ether gave a colorless solid which was refluxed with 40 ml of carbon tetrachloride to dissolve the benzoic acid. Not all of the solid went into solution. After cooling, the solid was collected, washed with carbon tetrachloride, and recrystallized from ether–petroleum ether to give 720 mg of colorless crystals, mp 194–195°.

Anal. Calcd for $C_{10}H_{16}O_5$: C, 55.54; H, 7.46. Found: C, 55.52; H, 7.52.

Resolution of (±)-Trichodesmic Acid.—A mixture of 21.6 mg of (±)-trichodesmic acid and 29.5 mg of cinchonidine was dissolved in 1.0 ml of methanol by heating. After standing in the refrigerator overnight, the colorless crystals were collected, washed with methanol, and recrystallized from methanol: yield 14 mg, mp 247–248° dec, $[\alpha]_D$ −95.5° (*c* 0.20, ethanol).

Anal. Calcd for $C_{29}H_{38}O_6N_2$: C, 68.21; H, 7.50; N, 5.49. Found: C, 68.36; H, 7.44; N, 5.46.

The filtrate from the above was evaporated under vacuum and the residue was recrystallized from methanol–ethyl acetate to give 16 mg of colorless crystals, mp 226–227° dec, $[\alpha]_D$ −72.5° (*c* 0.40, ethanol).

Anal. Calcd for $C_{29}H_{38}O_6N_2$: C, 68.21; H, 7.50; N, 5.49. Found: C, 68.09; H, 7.61; N, 5.29.

(+)-Trichodesmic Acid.—The cinchonidine salt, mp 247–248° (84 mg), was dissolved in 5 ml of 5% sulfuric acid and extracted five times with ether. The combine extracts were washed with water, dried, and evaporated to dryness under vacuum to give a residue of 32 mg. This was recrystallized from ether–petroleum ethr to give colorless crystals, mp 209–211° dec, $[\alpha]_D$ +2.96° (*c* 1.25, ethanol). A mixture melting point with trichodesmic acid,[14] mp 209–211°, was undepressed. The infrared (KBr) was identical with that published.[4]

Anal. Calcd for $C_{10}H_{16}O_5$: C, 55.54; H, 7.46. Found: C, 55.37; H, 7.42.

(−)-Trichodesmic Acid.—Decomposition of 141 mg of the cinchonidine salt, mp 226–227°, as above, gave a residue of 50 mg. Recrystallization from ether–petroleum ether gave 43 mg of colorless crystals, mp 201–203° dec, $[\alpha]_D$ −2.5° (*c* 0.4, ethanol). A mixture melting point with trichodesmic acid (mp 202–204°) was 193–197°. The infrared (KBr) spectrum had the same bands as (+)-trichodesmic acid but of less intensity.

Anal. Calcd for $C_{10}H_{16}O_5$: C, 55.54; H, 7.46. Found: C, 55.78; H, 7.49.

The cinchonidine salt, mp 226–227°, apparently contained a small amount of the diastereomer which would explain the lower melting point and specific rotation of (−)-trichodesmic acid. Because of insufficient material, it was not possible to repeat the resolution.

Trichodemic Acid Methyl Esters. A. (±)-Trichodesmic Acid.—A solution of 20 mg of (±)-trichodesmic acid in 3 ml of ether was treated with a slight excess of an etheral diazomethane solution. After 10 min the solution was evaporated to dryness under vacuum and the residue recrystallized from ether–petroleum ether to give 18 mg of colorless crystals, mp 116–119°.

Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88. Found: C, 57.56; H, 7.84.

B. (+)-Trichodesmic Acid.—In the same way, 25 mg of (+)-trichodesmic acid gave 23 mg of colorless crystals, mp 69–70°, $[\alpha]_D$ −6.83° (*c* 0.41, ethanol).

Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88. Found: C, 57.53; H, 7.80.

C. (−)-Trichodesmic Acid.—From 20 mg of (−)-trichodesmic acid after crystallization there was obtained 11 mg of ester, mp 69–70°. The infrared spectrum ($CHCl_3$) was identical with that above.

Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88. Found: C, 57.11; H, 7.86.

Registry No.—IV, 13136-61-3; V, 13136-62-4; VI, 13136-63-5; (+)-VII, 13136-64-6; (+)-VII cinchonidine salt, 13127-54-3; (+)-VII methyl ester, 13136-65-7; (−)-VII, 13136-66-8; (−)-VII cinchonidine salt, 13136-67-9; (−)-VII methyl ester, 13136-68-0; 2,3-diacetoxy-2,3-dimethyl-4-isopropylcyclopentanone, 13136-69-1.

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(14) This sample was supplied by Professor Yunusov. A sample of trichodesmic acid (insufficient for recrystallization) obtained from Professor Roger Adams in 1959 and stored at room temperature had a melting point of 202–204° which was not depressed on admixture with the synthetic acid. The authors are indebted to Professors Yunusov and Adams for these samples.

Monocyclic Terpene Alcohols. IV. Birch Reduction of *p*-Isopropylbenzoic Acid (Cumic Acid)[1,2]

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Selective reductions of the title compound with lithium and ethanol were achieved by careful control of the reaction conditions to promote either kinetically or thermodynamically controlled protonations of intermediate anions. Dihydro derivatives (*cis*- and *trans*-*p*-mentha-2,5-dien-7-oic acid and *p*-mentha-1,5-dien-7-oic acid) and tetrahydro derivatives (*cis*- and *trans*-*p*-menth-2-en-7-oic acid and *p*-menth-1-en-7-oic acid) could be prepared in high yields. On the light of the present findings, conflicting results described in the bibliography of the Birch reduction of *p*-alkylated aromatic acids are rationalized.

As a possible route to valuable intermediates in the synthesis of *p*-menthen-7-ols and *p*-menthadien-7-ols, we investigated the Birch reduction[3] of *p*-isopropylbenzoic acid (cumic acid I).

It is known[3a] that the influence of a carboxyl group in the reduction of a benzene ring outweighs that of other groups present and the formation of a 1,4-dihydro derivative is strongly favored. Thus, in a study of the reduction of aromatic acids and amides by sodium and alcohol in liquid ammonia, Kuehne and Lambert[4] reported that benzoic and *o*-toluic acids afforded the corresponding 1,4-dihydrobenzoic and 1,4-dihydro-*o*-toluic acids; however, under the same conditions, *p*-toluic acid gave mainly unconjugated tetrahydro acids. To account for the last result,

(1) Part III of this series: F. Camps, J. Castells, and J. Pascual, *J. Org. Chem.*, **31**, 3510 (1966).

(2) Supported by Grant FG-Sp-135 from the U. S. Department of Agriculture.

(3) (a) A. J. Birch, *Quart. Rev.* (London), **4**, 69 (1950); (b) A. J. Birch and H. Smith, *ibid.*, **12**, 17 (1958); (c) "Steroid Reactions," C. Djerassi, Ed., Holden-Day, Inc., San Francisco, Calif., 1963, pp 267–288; (d) H. Smith, "Organic Reactions in Liquid Ammonia. Chemistry in Non-Aqueous Ionising Solvents," Vol. 1, Part 2, John Wiley and Sons, Inc., New York, N. Y., 1963; (e) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, p 50.

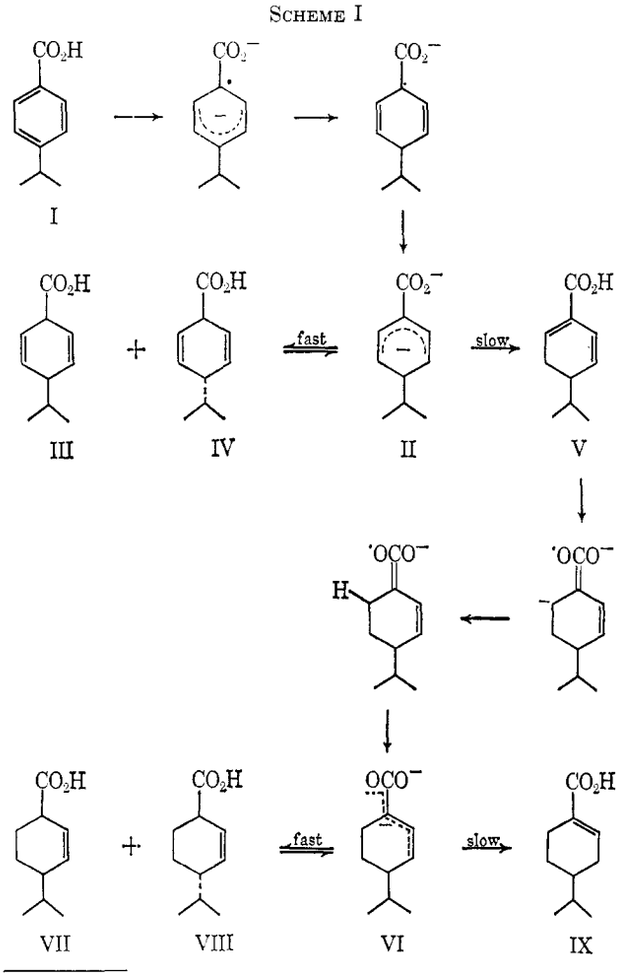
(4) M. E. Kuehne and B. F. Lambert, *J. Am. Chem. Soc.*, **81**, 4278 (1959).

these authors suggested that protonation of the possible intermediate anions takes place at the *ortho* or *meta* position to the carboxyl group, because the presence of the alkyl group decreases the charge density at the *para* position.

On the other hand, Markov and Ivanoff[5] obtained different results in the reduction of the ethyl ester and the amide of *p*-toluic acid by magnesium and alcohol in liquid ammonia. Under these conditions, the ethyl ester afforded the conjugated tetrahydro derivative and the amide the normal 1,4-dihydroamide. The authors pointed out that a mechanism different from that of the Birch reaction could operate in this case. The discrepancy of the above-mentioned results with current theory prompted us to use, in our study, Wilds and Nelson's modification[6] of the Birch method, because an interesting property of lithium is its lesser tendency to catalyze conjugation of double bonds.[7] Moreover, lithium has been found to be superior[6,8] to sodium or potassium in the reduction of many aromatic compounds.

Our results, summarized in Scheme I, show that a variety of dihydro and tetrahydro derivatives can be obtained in yields higher than 90% by a careful control of the reaction conditions. Structural assignments were made on analytical and spectral data and catalytic hydrogenation to the corresponding saturated compounds (see below). The nmr and glpc analysis of the methyl esters (prepared with diazomethane) were the methods of choice to control the course of the different reductions; both methods gave consistent results for tetrahydro derivatives, but anomalous results owing to thermal decomposition[9] were observed in the glpc analysis of dihydro compounds.

SCHEME I



Reduction of cumic acid (I) with 4 equiv of lithium, a slight excess of ethanol, short reaction times, and almost immediate addition of solid ammonium chloride afforded a liquid product that exhibited no ultraviolet absorption and the nmr spectrum of which pointed to the structure of a 1,4-dihydro derivative [an AB quartet of vinyl protons centered at τ 4.17 (4 H) and methine protons at τ 6.3 and 7.35]. The glpc analysis of the methyl esters of this product revealed the presence of the two expected isomers (III and IV) among other decomposition products; catalytic hydrogenation with platinum and ethanol afforded methyl *cis*- and *trans*-*p*-menthan-7-oates[10] in a 1:2 ratio, which should be that of dihydro acids III and IV in the starting product. Resolution of the liquid mixture of acids III and IV by treatment with thiourea and methanol[11] was unsuccessful. However, partial resolution of the esters of acids III and IV could be achieved by careful distillation at reduced pressure in a spinning-band column. Under the same reaction conditions described above, but without ammonium chloride addition, a crystalline acid, mp 102–105°, was isolated. Spectral data [ultraviolet λ_{max} 279.5 mμ (ϵ 2100)[12] and nmr vinyl protons at τ 2.95 (1 H), 3.6 (doublet, 1 H), and 4.25 (quartet, 1 H)] pointed to the structure V for this compound.

The formation of 1,4-dihydro acids III and IV can be rationalized by kinetically controlled protonation[13] of the postulated intermediate anion II. On the other hand, if a thermodynamically controlled process occurs, protonation of the same intermediate anion leads to the more stable conjugated 3,4-dihydro acid V. Partial isomerization of acids III and IV into acid V was observed when addition of ammonium chloride was delayed. By the same token, acid V was easily further reduced with 3 additional equiv of lithium and the corresponding amount of ethanol to a liquid product when ammonium chloride was added and, in the absence of it, to a crystalline acid, mp 143–4°, which was identified as phellandric acid[14] IX (melting point, melting point of the *p*-bromophenacyl ester, and spectral data).

The above-mentioned liquid product exhibited no ultraviolet absorption and features of its nmr spectrum [vinyl protons at τ 4.23 (singlet, 2 H) and methine proton at τ 6.95] were consistent with those of a tetrahydro derivative. The presence in this liquid product

(5) P. Markov and C. Ivanoff, *Tetrahedron Letters*, 1139 (1962).
(6) A. L. Wilds and N. A. Nelson, *J. Am. Chem. Soc.*, **75**, 5366 (1953).
(7) A. J. Birch and D. Nasipuri, *Tetrahedron*, **6**, 148 (1959).
(8) H. L. Dryden, Jr., G. M. Webber, R. R. Burtner, and J. A. Cella, *J. Org. Chem.*, **26**, 3237 (1961).
(9) In an attempted preparative glpc of methyl ester of acid V on a 20 ft × 3/8 in. SE-30, 30% on Chromosorb P at 190°, using hydrogen as carrier gas, methyl benzoate and methyl cuminate were the main products isolated.
(10) J. Albaiges, J. Castells, and J. Pascual, *J. Org. Chem.*, **31**, 3507 (1966).
(11) H. van Bekkum, A. A. B. Kleis, D. Medema, P. E. Verkade, and B. M. Wepster, *Rec. Trav. Chim.*, **81**, 833 (1962).
(12) *Cf.* A. J. Birch, *J. Chem. Soc.*, 1551 (1950).
(13) For mechanism of this reaction, *cf.* (a) ref 3b; (b) ref 7; (c) ref 8; (d) A. P. Krapcho and A. A. Bothner By, *J. Am. Chem. Soc.*, **81**, 3658 (1959); **82**, 751 (1960); (e) J. F. Eastham and D. R. Larkin, *ibid.*, **81**, 3652 (1959); (f) A. P. Krapcho and M. F. Nadel, *ibid.*, **86**, 1096 (1964); (g) W. Hückel, B. Graf, and D. Münker, *Ann. Chem.*, **614**, 47 (1958).
(14) *Cf.* R. G. Cooke, A. K. Macbeth, and T. B. Swanson, *J. Chem. Soc.*, 808 (1940).

of the expected isomers VII and VIII (see below) was confirmed by glpc analysis (of the methyl esters) which showed two peaks in 1:2.5 ratio. The structure of these two components was established by catalytic hydrogenation of the methyl esters of acids VII and VIII with platinum and ethanol to the corresponding methyl *cis*- and *trans*-*p*-menthan-7-oates.[10] In the *trans* isomer VIII, the more favorable conformation has the C_1 methine proton "fixed" in a pseudo-axial position, which accounts for the broad band[15] observed (half-band width, 22 cps) in the nmr spectrum, whereas, in the *cis* isomer VII, the proton considered gives a narrow band (half-band width, 9 cps). Resolution of acids VII and VIII by thiourea was successful in this case; the *trans* isomer formed a complex which allowed isolation of *trans* acid VIII in a pure state (glpc), mp 16°,[16] whereas the *cis* acid VII was extracted from the mother liquors in 80% steric purity (glpc).

Preferential reduction[3e] of the conjugated double bond of acid V accounts for the formation of acids VII, VIII, and IX by the same mechanisms described above, although isomerization was found to be slower than in the case of the dihydro derivatives. In an independent experiment using sodium and the same conditions reported by Kuehne and Lambert, we obtained a mixture of 43% starting cumic acid (I), 7% 1,4-dihydro acids III and IV, 15% 3,4-dihydro acid V, and 35% tetrahydro acids VII and VIII (based on nmr analysis); when alcohol was the last reactant added, this ratio changed to 26:2:30:42.

In short, the rationale of all the above-mentioned results is that the slower reaction of sodium with the aromatic nucleus allows a simultaneous base-catalyzed isomerization of the initially formed 1,4-dihydro derivatives to the more stable 3,4-dihydro derivative, which in turn is easily further reduced to the tetrahydro stage by the still unreacted metal, precluding the isolation of 1,4-dihydro derivatives. On the other hand, the enhanced reducing power and lesser tendency to catalyze isomerization of lithium makes it possible to stop the reduction before undesirable reactions occur. We conclude, then, that it is not necessary to postulate a different mechanism for the Birch reduction of *p*-alkylated benzoic acids and that, by a careful control of the reduction conditions and the use of lithium as reducing agent, it is possible to isolate the normal 1,4-dihydro derivatives.

Experimental Section

Melting points were taken on a Kofler hot-stage apparatus and are corrected. Infrared spectra were measured on Perkin-Elmer Infracord 137 and Infracord 137 G spectrophotometers. Ultraviolet spectra were run on a Perkin-Elmer 137 apparatus. The nmr spectra were recorded on a Perkin-Elmer R-10 at 35° operating at 60 Mc/sec with TMS as internal reference. The glpc analyses were performed on a Barber–Colman 61-C instrument with β-ionization detector, on a silicone 550 Golay column, and an Aerograph A-705 with flame ionization detector on different columns. Preparative glpc separations were carried out on the latter instrument. Fractional distillation was achieved with a Büchi spinning-band column, Dr. H. Abegg system.

Starting Materials.—Compounds have been named as derivatives of *p*-menthane. Cumic acid was prepared by hydrogen peroxide oxidation[17] of commercial cuminaldehyde from Fluka A. G. Lithium wire was obtained from Fluka A. G. Commercial absolute ethanol was dried and distilled over calcium hydride before its use.

Apparatus.—In all cases, commercial ammonia was distilled into a well-dried three-necked round-bottomed 1-l. flask, externally cooled with a Dry Ice–acetone bath, and fitted with Dry Ice condenser, potassium hydroxide drying tube, Hershberg stirrer, and dropping funnel.

***cis*- and *trans*-*p*-Mentha-2,5-dien-7-oic Acids (III and IV).**—To a well-stirred solution of cumic acid (I) (19.8 g) in dry ethyl ether (120 ml) and liquid ammonia (350 ml) at −70° was added within 6 min lithium wire (3.3 g) cut in small pieces. Stirring was maintained under the same conditions for 12 min and then dry ethanol (30 ml) was added within 5 min. After 5 min, before the blue color was discharged, solid ammonium chloride (25.5 g) was added, and the cooling bath removed to eliminate the ammonia. The residue was acidified with dilute (1:1) hydrochloric acid under external cooling and extracted with ethyl ether. The organic layer was dried ($MgSO_4$), and solvent was evaporated to give a liquid product (18.3 g), bp 93° (0.05 mm), with no aromatic proton absorption (nmr) and the following spectral features: ultraviolet spectra gave no selective absorption; infrared (C_2Cl_4, S_2C), 2.9–4.4 (br), 5.86, 6.13, 6.22, 12.1, 13.2 μ; τ^{CCl_4} −0.78 (singlet, 1 H), 4.15 (fine split quartet, J = 9 cps, 4 H), 6.3 (broad, 1 H), 7.35 (broad, 1 H), 8.3 (broad, 1 H), 9.1 (doublet, J = 6 cps, 6 H).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.24; H, 8.52.

Methylation of this product with an ethereal solution of diazomethane gave a liquid which exhibited two main peaks (90% of the mixture) with similar retention times, in a 1:2 ratio, by glpc analysis on a 20% SE-30 on Chromosorb W column at 180°. Methyl cuminate (9%) and three other minor unidentified products present in the mixture could be produced by thermal decomposition. Assignation of formulas III and IV to the main products of the mixture was substantiated by fast catalytic hydrogenation of the methyl ester (0.3 g) with platinum oxide (30 mg) in ethanol (15 ml) at room temperature and normal pressure to a liquid product (0.25 g) which exhibited two peaks in a 1:2 ratio (glpc) which were identified by their retention times as methyl *cis*- and *trans*-*p*-menthan-7-oate by comparison with pure specimens.[10]

Distillation of the mixture of methyl esters of acids III and IV (12.5 g) at reduced pressure in a spinning-band column afforded *cis* methyl ester of acid III (5.6 g), bp 88–90° (6 mm), in 53% steric purity and *trans* methyl ester of acid IV (5.7 g), bp 90–96° (6 mm), in 70% steric purity. Redistillation of the first fraction yielded the *cis* methyl ester (2.0 g), bp 88–89° (6 mm), in 71% steric purity and redistillation of the second fraction, the *trans* methyl ester (3.7 g), bp 95–96° (6 mm), in 80% steric purity. An attempted separation of acids III and IV with thiourea[11] in methanol was unsuccessful because both acids formed an inclusion complex.

***p*-Mentha-1,5-dien-7-oic Acid (V).**—The same above-mentioned procedure and amounts of reactants were used in this case. When the blue color disappeared, the solvent was evaporated without previous addition of solid ammonium chloride. The same work-up procedure finally afforded a product (19.6 g) with no aromatic proton absorption (nmr), which upon crystallization from ethyl ether at −50° yielded acid V (12.0 g), mp 102–105°, having the following spectral features: λ_{max}^{EtOH} 279.5 mμ (ϵ 2100); infrared (C_2Cl_4, S_2C), 2.9–4.4 (br), 5.92, 6.1, 6.3, 13.7, 14.1 μ; τ^{CCl_4} −2.18 (singlet, 1 H), 2.95 (broad, 1 H), 3.6 (doublet, J = 10 cps, 1 H), 4.23 (doublet, J = 10 cps, each band doublet, J' = 3 cps, 1 H), 7.7 (doublet, J = 3 cps, 2 H), 9.07 (doublet, J = 7 cps, 6 H).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.96; H, 8.49. Found: C, 71.72; H, 8.84.[18]

Preparation of *p*-bromophenacyl ester by the usual procedure[19]

(15) *Cf.* N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, p 79.

(16) R. L. Frank, R. E. Berry, and O. L. Shotwell [*J. Am. Chem. Soc.*, **71**, 3889 (1949)] gave mp 105° for an acid they claimed to be Δ^2-4-isopropyltetrahydrobenzoic acid. However, by comparison of the spectrum given with our results, we believe that they obtained a mixture of Δ^1- and Δ^2-4-isopropyltetrahydrobenzoic acids (VII, VIII, and IX).

(17) R. G. Cooke and A. K. Macbeth, *J. Chem. Soc.*, 1245 (1939).

(18) A better analysis could not be secured and C percentage diminished with time; the crystalline acid became finally a dark amorphous product.

(19) *Cf.* F. Wild, "Characterization of Organic Compounds," University Press, Cambridge, 1948, p 146.

gave a crystalline product: mp 88–89.5° (from ethanol); infrared (KBr), 5.82, 5.90, 6.10, 6.30, 12.1, 12.6, 14.1 μ; τ^{CCl_4} 2.3 (AB quartet, J = 14 cps, J' = 9 cps, 4 H), 3.0 (broad, 1 H), 3.62 (doublet, J = 11 cps, 1 H), 4.23 (doublet, J = 9 cps, 1 H), 4.75 (singlet, 2 H), 7.7 (narrow, 2 H), 9.06 (doublet, J = 6 cps, 6 H).

Anal. Calcd for $C_{18}H_{19}BrO_3$: C, 59.51; H, 5.28; Br, 22.00. Found: C, 59.47; H, 4.89; Br, 22.08.

Methylation with ethereal diazomethane solution afforded a liquid product: bp 61° (0.3 mm); $n^{25}D$ 1.4838; λ_{max}^{EtOH} 282.3 mμ (ϵ 2200); infrared (C_2Cl_4, S_2C), 5.82, 6.10, 6.30, 14.05 μ; τ^{CCl_4} 3.1 (broad, 1 H), 3.6 (doublet, J = 10 cps, 1 H), 4.22 (doublet, J = 10 cps, each band doublet J' = 3 cps, 1 H), 6.30 (singlet, 3 H), 7.75 (narrow, 2 H), 9.08 (doublet, J = 6 cps, 6 H).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.07; H, 9.19.

cis- and *trans*-*p*-**Menth-2-en-7-oic Acids (VII and VIII).**—The reaction was carried out in two stages. The first one was performed as the above-mentioned reduction of cumic acid (I) to *p*-mentha-1,5-dien-7-oic acid (V), only changing the amount of ethanol added (20 ml in this case). The residue of evaporation of ammonia was not hydrolyzed in this case but further reduced in a second stage in which ammonia was redistilled into the reaction flask and lithium wire (2.5 g) added; after stirring for 15 min, dry ethanol (22 ml) was dropped in within 10 min. After 10 min, solid ammonium chloride (44 g) was added and ammonia was allowed to evaporate; the residue was treated as usual to give a liquid product (19.0 g) which exhibited only one kind of ethylenic protons (nmr). Methylation of this product with ethereal diazomethane solution gave a mixture of two methyl esters in 1:2.5 ratio (glpc), which were separated by preparative glpc on a 20 ft × 3/8 in. 20% Carbowax 20 M on Chromosorb W column at 180° and identified as methyl esters of acids VII and VIII by their spectral features and catalytic hydrogenation on platinum oxide and ethanol at room temperature and normal pressure to the saturated methyl *cis*- and *trans*-*p*-menthan-7-oates.[10] More convenient for preparative purposes was the separation by means of thiourea.[11] The mixture of acids VII and VIII (19.0 g) was dissolved in dry methanol (150 ml), after which thiourea (30.0 g) was dissolved with heating in the solution obtained. Upon cooling, a precipitate (19.0 g) was formed, which was filtered off. By successive evaporations and crystallizations of the mother liquors, four crystalline fractions (20.1 g) were obtained. The joned fractions (39.1 g) were suspended in water (500 ml) and extracted with *n*-hexane (50 ml) three times. The combined *n*-hexane extracts were washed with sodium chloride saturated solution, dried (Na_2SO_4), and evaporated to give *trans*-*p*-menth-2-en-7-oic acid (VIII) (10.2 g). Distillation of this liquid acid under reduced pressure afforded the pure acid (glpc) as a low-melting solid: mp 16°; ultraviolet spectra gave no selective absorption; infrared (C_2Cl_4, S_2C), 2.9–4.4 (br), 5.88 μ; τ^{CCl_4} 1.7 (singlet, 1 H), 4.23 (AB triplet, J = 12 cps, 2 H), 6.93 (broad, 1 H), 7.5–8.9 (6 H), 9.08 (doublet, J = 6 cps, 6 H).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.63; H, 9.53.

p-Bromophenacyl ester, mp 92.5–93° (from ethanol), was prepared by the usual procedure: infrared (KBr), 5.74, 5.90, 6.30, 6.37, 12.13 μ; τ^{CCl_4} 2.35 (AB quartet, J = 14 cps, J' = 8 cps, 4 H), 4.20 (AB triplet, J = 12 cps, 2 H), 4.80 (singlet, 2 H), 6.8 (broad, 1 H), 7.6–8.9 (6 H), 9.10 (doublet, J = 6 cps, 6 H).

Anal. Calcd for $C_{18}H_{21}BrO_3$: C, 59.18; H, 5.80; Br, 21.88. Found: C, 59.19; H, 5.76; Br, 21.80.

Methylation with ethereal diazomethane solution gave a liquid product: bp 59° (0.4 mm); $n^{25}D$ 1.4650; infrared (film), 5.76, 6.10, 12.6, 13.7 μ; τ^{CCl_4} 4.3 (AB triplet, J = 12 cps, 2 H), 6.33 (singlet, 3 H), 7.0 (broad, half-band width 22 cps, 1 H), 7.6–8.9 (6 H), 9.10 (doublet, J = 6 cps, 6 H).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.07; H, 9.65.

From the mother liquor of thiourea treatment was obtained a liquid *cis* acid VII (6.0 g) of 80% steric purity (glpc): τ^{CCl_4} 1.5 (singlet, 1 H), 4.2 (narrow, 2 H), 6.95 (broad, 1 H), 7.6–8.9 (6 H), 9.08 (doublet, J = 6 cps). No crystalline *p*-bromophenacyl ester could be isolated. Preparative glpc of the methylated product on a 20 ft × 3/8 in. 30% XF 1150 on Chromosorb P column at 175° afforded pure (glpc) methyl ester of *cis* acid VII, which was a liquid: bp 55° (0.5 mm); $n^{25}D$ 1.4632; infrared (film), 5.77, 6.10, 12.3, 13.7 μ; τ^{CCl_4} 4.25 (narrow, 2 H), 6.33 (singlet, 3 H), 7.03 (broad, half-band width 9 cps, 1 H), 7.7–8.7 (6 H), 9.07 (doublet, J = 6 cps, 6 H).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.22; H, 10.54.

p-**Menth-1-en-7-oic Acid (IX, Phellandric Acid).**—Reaction was performed in the same way as in the precedent section but not ammonium chloride was added. Ammonia was evaporated and the residue was allowed to stay overnight at room temperature. After the usual work-up procedure, evaporation of the solvent gave a solid product, which was a mixture of acid IX (80%) and acids VII and VIII (20%) (based on nmr analysis). Recrystallization of the crude material yielded pure phellandric acid (6.2 g), mp 143–144° (lit.[14] mp 143–144°), from which a solid *p*-bromophenacyl ester was prepared, mp 86–86.5° (lit.[14] mp 86–86.5°). Spectral features are consistent with those of phellandric acid: λ_{max}^{EtOH} 214 mμ (ϵ 7600); infrared (KBr), 5.96, 6.11, 12.8, 13.5, 14.2 μ; τ^{CCl_4} 2.25 (singlet, 1 H), 2.85 (broad, 1 H), 7.2–8.95 (8 H), 9.06 (doublet, J = 5 cps, 6 H).

Registry No.—I, 536-66-3; III, 13132-44-0; III (methyl ester), 13132-45-1; IV, 13132-46-2; IV (methyl ester), 13132-45-1; V, 13132-48-4; V (*p*-bromophenacyl ester), 13132-49-5; V (methyl ester), 13132-50-8; VII, 13132-51-9; VII (methyl ester), 13132-52-0; VIII, 13132-53-1; VIII (*p*-bromophenacyl ester), 13132-54-2; VIII (methyl ester), 13132-55-3; IX, 586-88-9.