0.746 g. (96%, VII + epimer), m.p. 169–185° dec., were removed by filtration. A partial purification was accomplished by dissolving the solid in dilute bicarbonate (a minute amount of insoluble material was removed) followed by acidification with hydrochloric acid which gave a white solid, m.p. 173.5–185.5°.

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found (S): C, 76.77; H, 5.41.

Oxidation of the Hydroxyacid Mixture with Alkaline Potassium Permanganate.—A portion of the mixture (0.315 g., 0.00118 mole), was treated with 0.187 g. (0.00118 mole, 1.5 equivalents) of potassium permanganate by the method used in the oxidation of VI. This resulted in 0.289 g. (92%) of VIIa, m.p. 209.0–210.5°, showing no depression with the previously characterized VIIa.

ANN ARBOR, MICH.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Rearrangement of Bromofenchone by Base. The Structure of γ-Fencholenic Acid and the Synthesis of Dihydro-α-fencholenic Acid

BY D. S. TARBELL AND F. C. LOVELESS[1]

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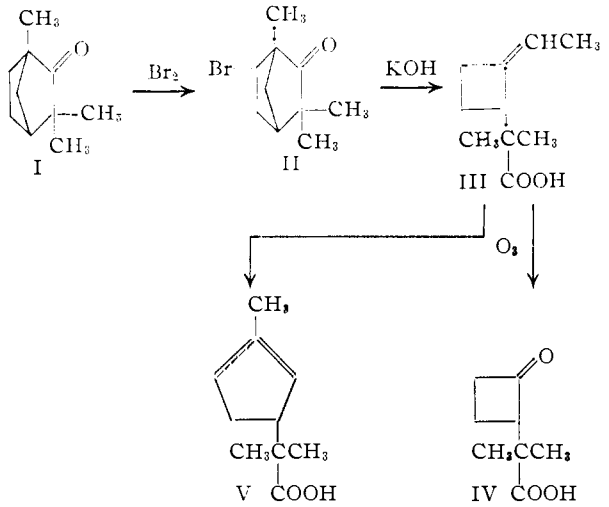
Bromination of *dl*-fenchone yields the hitherto undescribed crystalline *dl*-bromofenchone. Treatment of this with alcoholic alkali yields a mixture of *dl*-γ-fencholenic acid and the corresponding ester. Catalytic reduction of both γ- and α-*dl*-fencholenic acids yields the same acid, *dl*-α-(3-methylcyclopentyl)-isobutyric acid, the structure of which has been established by synthesis from 3-methylcyclopentanone by the Reformatsky reaction. γ-Fencholenic acid has been shown not to possess an ethylidenecyclobutane structure III as postulated by Semmler and Bartelt, but to be a methylenecyclopentane derivative VI; it yields formaldehyde and the expected cyclopentanone derivative on ozonization. The bromofenchone rearrangement is analogous to other base-catalyzed rearrangements and, although the position of the bromine has not been established rigorously, it is probably on the 10-carbon.

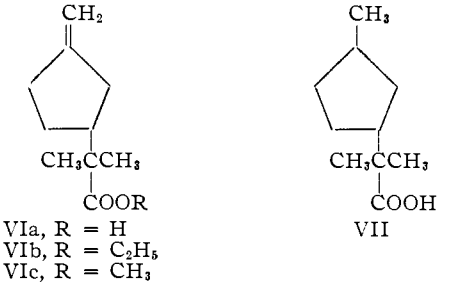
In connection with work on another problem in the fenchone field, we became interested in the report[2] that bromination of fenchone (I) yielded 6-bromofenchone (II), which was converted by base to γ-fencholenic acid; to this acid was assigned[2] structure III. The assignment of structure III



was based on ozonization to a keto acid, regarded as IV, which was characterized as the crystalline semicarbazone. The γ-fencholenic acid was reported to isomerize very readily on standing to α-fencholenic acid. The structure of the latter compound does not seem to have been established; the nitrile corresponding to it is formed by the action of sulfuric acid on fenchone oxime, and the α-fencholenic acid is obtained by hydrolysis of the nitrile.[3] The postulated[2] structure V (or a double bond isomer) is a reasonable one for α-fencholenic acid; we have provided synthetic evidence for its correctness below.

The bromination of fenchone and some transformation products of bromofenchone recently have been studied,[4] without establishing any of the structures involved.

If structures II-V are correct, the reactions involved are unusual; furthermore, the sequence might be useful for the preparation of cyclobutanone derivatives of an interesting type. We have, therefore, reinvestigated these compounds, have found that γ-fencholenic acid has the structure VI, rather than III, and have established the structures of γ- and α-fencholenic acids (VI and V) by the synthesis of the dihydrofencholenic acid VII. The position of the double bond in α-fencholenic acid is not, of course, established by this synthesis.



The bromination of fenchone has been carried out[2,5] with bromine in sealed tubes. This method proved unsatisfactory, and we tried several other brominating agents without much success. However, the treatment of *dl*-fenchone with bromine and copper powder[4] on the steam-bath for many hours yielded, in addition to much unchanged fenchone, a crystalline monobromofenchone, m.p. 44.5°, and oily material with the composition of a monobromofenchone. Previous workers[2,4,5] have not reported a crystalline bromofenchone. Bromination of *d*-fenchone by the same procedure yielded an oily monobromo compound, $[\alpha]_D$ +14.3°,

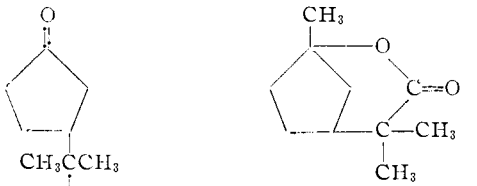
(1) Chas. Pfizer and Co. Fellow, 1956–1957.
(2) F. W. Semmler and K. Bartelt, *Ber.*, **40**, 432 (1907).
(3) G. B. Cockburn, *J. Chem. Soc.*, **75**, 501 (1899).
(4) L. Y. Bryusova, *J. Gen. Chem. USSR*, **10**, 1462 (1940).
(5) H. Czerny, *Ber.*, **33**, 2291 (1900).

which gave the same products as the crystalline bromo compound when treated with base.

The fact that the formation of the crystalline bromo compound did not involve rearrangement of the carbon skeleton during bromination was established by reduction to fenchone with zinc and acetic acid; the fenchone was identified by its infrared spectrum and by conversion to the oximes. The relationships are described in detail in the Experimental section.

Treatment of the crystalline bromofenchone with ethanolic potassium hydroxide yielded a mixture of γ-fencholenic acid VIa and the corresponding ethyl ester VIb. Both of these showed an infrared band at 873 cm.$^{-1}$, due to the exocyclic $=CH_2$ group. Although this value does not correspond exactly to the one (890 cm.$^{-1}$) reported for this group[6] in open-chain compounds, it agrees well with other compounds containing the exocyclic $=CH_2$ group.[7] This band at 873 cm.$^{-1}$ disappeared on catalytic reduction. The neutral product from the rearrangement in ethanol was considered to be the ester VIb because of the ester band in its infrared spectrum; hydrolysis converted it to an acid with the same infrared spectrum as the γ-fencholenic acid produced directly in the rearrangement. Esterification of γ-fencholenic acid with diazomethane gave the methyl ester VIc, which had the same infrared spectrum as the neutral product obtained from bromofenchone and *methanolic* alkali.

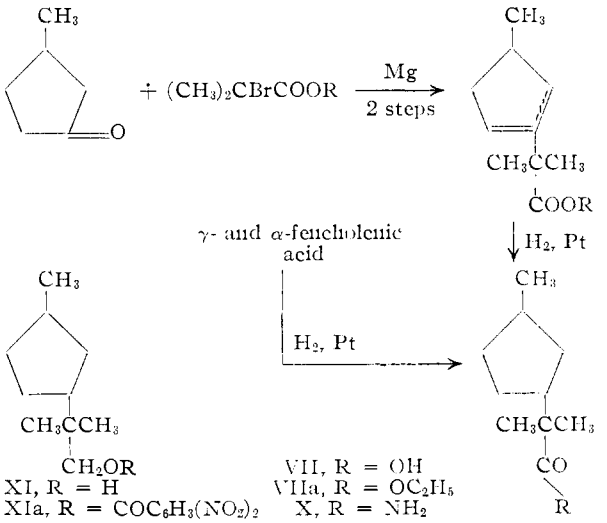
The correctness of structure VI for the γ-fencholenic acid obtained from bromofenchone in our experiments, and the incorrectness of structure III, was shown by ozonization to yield formaldehyde. This was identified in one run as the crystalline methone derivative,[7a] and in another run as the dinitrophenylhydrazone,[8] the purity of which was checked by running a paper chromatogram; the formaldehyde dinitrophenylhydrazone was not contaminated by any other dinitrophenylhydrazone. The other product of ozonization, which on the basis of structure VI should be the cyclopentanone derivative VIII instead of the cyclobutanone derivative III, had a carbonyl band at 1736 cm.$^{-1}$, in agreement with the cyclopentanone structure; a cyclobutanone should absorb[9] at about 1775 cm.$^{-1}$. Compound VIII also was characterized by preparation of a crystalline semicarbazone, whose composition agreed with that of structure VIII rather than with that of the lower homolog IV.



VIII IX

Treatment of γ-fencholenic acid with sulfuric acid gave a mixture of γ- and δ-lactones, according to the infrared spectrum, from which a pure crystalline δ-lactone IX was isolated; this was identical with the lactone obtained from α-fencholenic acid (V) by sulfuric acid treatment. Because of the possibility of rearrangement of one or both of the γ-fencholenic and α-fencholenic acid pair under acidic conditions, the observations just described do not necessarily prove that the two acids have the same carbon skeleton. This was established unequivocally, however, by catalytic reduction of both γ- and α-fencholenic acids to the same saturated acid VII, which was characterized in each case by conversion to the same crystalline amide X.

Since, as has been mentioned, the correctness of the proposed structure VI for α-fencholenic acid does not seem to have been conclusively demonstrated, we synthesized the saturated acid VII by the Reformatsky reaction of ethyl α-bromoisobutyrate on 3-methylcyclopentanone, going through the usual stages. The synthetic product was shown to be identical with the product obtained by reduction of both the α- and γ-acids, by comparison of the crystalline amides X; the mixed m.p. of the samples prepared by the various routes showed no depression, and the infrared spectra were identical. The synthetic ester VIIa and the material obtained by reduction of the γ-fencholenic ester were also compared through the crystalline dinitrobenzoate XIa, prepared from the alcohol XI obtained by lithium aluminum hydride reduction of the two samples of the ester. There was no depression in the mixed m.p.



Structure VII can exist as a pair of racemates; the synthetic route obviously leads to the same racemate as is obtained from the rearrangement of the γ- and α-fencholenic acids. This is not surprising, because catalytic hydrogenation is involved in all of the series, in the step in which the second asymmetric carbon is formed. Although the configuration of the side chains in VII is not known, one would expect the *trans* form to be more stable ther-

(6) N. Sheppard and D. M. Simpson, *Quart. Revs.*, **6**, 26 (1952).

(7) D. E. Applequist and J. D. Roberts, THIS JOURNAL, **78**, 4012 (1956); A. T. Blomquist and Y. C. Meinwald, *ibid.*, **79**, 5316 (1957). Camphene shows a band at 872 cm.$^{-1}$ (the present research).

(7)a D. Vorländer, *Z. anal. Chem.*, **77**, 247 (1929).

(8) W. M. D. Bryant, THIS JOURNAL, **54**, 3760 (1932).

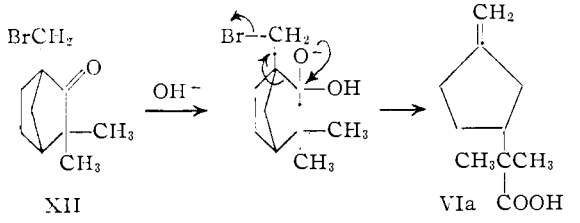
(9) R. N. Jones, P. Humphries and K. Dobriner, *ibid.*, **72**, 956 (1950); D. H. Whiffen and H. W. Thompson, *J. Chem. Soc.*, 1005 (1946).

modynamically. However, the *cis* form might be favored in a catalytic reduction, since the unsaturated compound would be adsorbed more readily on the catalyst surface with the alkyl side chain which is already attached to a saturated carbon "*trans*" to the catalyst surface. This would mean that the hydrogen added would be *trans* to this alkyl group, and hence that the two alkyl side chains would be *cis*.

The facile isomerization[2] of γ-fencholenic acid to the α-isomer (VI → V) is in agreement with both old and new observations[10] which show that 1-alkylcyclopentenes are much more stable than the isomers with the exocyclic double bond.

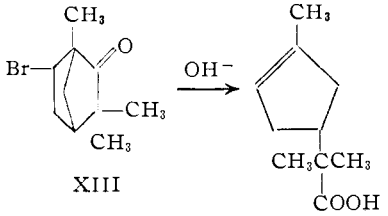
It should be noted that the amide X, prepared from γ-fencholenic acid derived from *d*-bromofenchone, melted only 4° higher than the *dl*-amide, obtained from the synthesis or from *dl*-bromofenchone, and showed no depression on mixed m.p.

The position of the bromine atom in bromofenchone has not been established conclusively. The conversion of bromofenchone to γ-fencholenic acid is best represented as an example of the generalized β-elimination reaction.[11] On this basis, the reasonable position for the bromine atom is the 10-position (XII). If the bromine atom was in



XII VIa

the 6-position, as previously postulated,[2] one would expect that α-fencholenic acid, with the endocyclic double bond, would result directly from the action



XIII

of base. The formation of VIa from XIII would require a shift of the double bond from the endocyclic to the exocyclic position, which is not favored.[10]

Experimental[12]

Fenchone.—*dl*-Fenchone was a technical grade. Attempts to resolve *dl*-fenchone by reaction with *l*-menthyl N-aminocarbamate[13] were unsuccessful, due to the very low reactivity of the carbonyl group in fenchone; no derivative was formed on refluxing in ethanol or in Cellosolve for 25 days. *d*-Fenchone was prepared by three distillations of 750 g. of fennel seed oil (from S. B. Penick); 75 g. of *d*-fenchone was obtained, b.p. 170–180°, $[\alpha]_D$ 61°. The oxime, $[\alpha]_D$ 116° (*c* 0.928, ethanol), melted from 120 to 165°, and was apparently a mixture of *d*-fenchone β-oxime[14] (m.p. 123°, $[\alpha]_D$ 129°) and *d*-fenchone α-oxime[15] (m.p. 165°, $[\alpha]_D$ 47°), with the former predominating.

Bromination of Fenchone.—Bromination of fenchone in a sealed tube at 100° appeared to yield mainly polymeric material. Bromination at 100° and atmospheric pressure yielded only starting material, as did also treatment with N-bromosuccinimide and with pyridine hydrobromide perbromide.[16]

The procedure of Bryusova[4] was modified as follows: *dl*-Fenchone (Technical grade, 200 g.) and 4 g. of copper powder were heated to 90° in a four-necked flask fitted with stirrer, condenser, thermometer and dropping funnel. Bromine (210 g.) was added slowly over a period of 16 hours to the heated stirred solution, and the temperature was maintained at 90° with stirring for a total of 3 days. The reaction mixture was then subjected to steam distillation from the reaction flask, and 110 g. of steam-volatile oil was obtained; 95 g. of non-volatile material remained, and was saved.

Further purification was carried out on 294 g. of steam-volatile material and 241 g. of non-volatile product, isolated from three runs in which a total of 500 g. of fenchone and 525 g. of bromine was used. Distillation of the 294 g. of steam-volatile material gave 201 g. of fenchone (b.p. 36° (3 mm.)), and the remainder was separated into three fractions, boiling in the range 73–85° (4 mm.). These fractions crystallized partially on standing, and the crystalline bromofenchone was obtained by dissolving the oil in petroleum ether and cooling to −78°. Repetition of this procedure yielded 31.5 g. of crystalline bromofenchone, m.p. 43–44°, and 16 g. of oily bromofenchone, from which no more crystals could be obtained. Distillation of the 241 g. of non-steam-volatile bromination product gave 46.4 g. of bromofenchone, from which 25 g. of crystalline and 17 g. of oily product was obtained. The total yield of bromofenchone from 500 g. of fenchone was thus 56.5 g. of crystalline material and 34 g. of oily product.

The solid product melted at 44.5° after purification by sublimation, showed a carbonyl band at 1740 cm.$^{-1}$ and was optically inactive. The oily product showed $n^{20}D$ in the range of 1.5080, had an infrared spectrum practically identical with that of the crystalline material.

Anal. Calcd. for $C_{10}H_{15}BrO$: C, 51.96; H, 6.54. Found (crystalline product): C, 51.38; H, 6.54. Found (oil): C, 52.66; H, 6.74.

The analysis was carried out on a sample of oily bromofenchone from which the crystalline product had not been removed.

Bromination of *d*-Fenchone.—Bromination as above of *d*-fenchone (34 g., $[\alpha]_D$ 61°) yielded 6 g. of *d*-bromofenchone, $[\alpha]_D$ 14.3°, $n^{26}D$ 1.5068, which did not crystallize at −78°. Czerny[5] reported $[\alpha]_D$ 11.6°, $n^{12}D$ 1.5101.

Anal. Calcd. for $C_{10}H_{15}BrO$: C, 51.96; H, 6.54. Found: C, 51.58; H, 6.46.

Reduction of Bromofenchone to Fenchone.—Crystalline bromofenchone (10.0 g.) dissolved in 75 ml. of acetic acid was refluxed with 7.5 g. of zinc dust for 7 hours, the mixture was diluted with water and was extracted with benzene. The benzene extract was washed with water, then with several portions of aqueous bicarbonate solution, was dried, and after the solvent was evaporated, it yielded 6.7 g. of oil. The oil was converted to the oxime by refluxing for 25 hours in 200 ml. of methanol with 6.7 g. of hydroxylamine hydrochloride and 23 g. of potassium hydroxide. After the refluxing, water was added to the solution until it became cloudy. Cooling the solution yielded 1.0 g. of fenchone oxime, which had the same infrared spectrum as an authentic sample of the oxime prepared in the same way. The m.p. of the oxime (120°) differed from that of an authentic sample of *dl*-fenchone oxime (m.p. 155°), but by heating the 120° oxime to 170° and allowing it to crystallize, the m.p. was raised to 155°. When a mixture of 120° oxime and authentic *dl*-fenchone oxime (m.p. 155°) were heated together to 170°, the resulting solid melted at 147–150°. Apparently here we were dealing with isomerization of the β-oxime to the α-oxime.

(10) O. Wallach, *Ann.*, **353**, 308 (1907); R. B. Turner and G. H. Garner, THIS JOURNAL, **79**, 253 [1957]; R. Fleck, *J. Org. Chem.*, **22**, 439 (1957).

(11) A. Eschenmoser and A. Frey, *Helv. Chim. Acta*, **35**, 1660 (1952); C. A. Grob and W. Baumann, *ibid.*, **38**, 594 (1955).

(12) All m.p.'s are corrected; microanalyses are by Miss Annette Smith and Micro-tech Laboratories.

(13) R. B. Woodward, T. P. Kohman and G. C. Harris, THIS JOURNAL, **63**, 120 (1941).

(14) M. Delépine, *Compt. rend.*, **178**, 1721 (1924).

(15) O. Wallach, *Ann.*, **272**, 104 (1892).

(16) C. Djerassi and C. R. Scholz, THIS JOURNAL, **70**, 417 (1948).

Conversion of the oxime from fenchone, regenerated from bromofenchone, to the nitriles,[8] followed by hydrolysis to *dl*-β-fencholenamide[8] yielded material of m.p. 81.5–82.5°; the amount was insufficient to recrystallize. *dl*-β-Fencholenamide prepared from β-fencholenic acid melted at 87–88°, and gave a mixed m.p. with the amide above, from the regenerated fenchone, of 81–86°.

***dl*-γ-Fencholenic Acid (VIa) and its Ester by Action of Base on Crystalline *dl*-Bromofenchone.**—*dl*-Bromofenchone (10 g., m.p. 43–44°) was refluxed for 3 hours in 85 cc. of absolute ethanol containing 7.5 g. of potassium hydroxide. A precipitate of potassium bromide appeared after a short time. The reaction mixture was diluted with water, and extracted with ether; the extract yielded 3.6 g. (47%) of ethyl *dl*-γ-fencholenate (VIb): it showed an ester carbonyl band at 1727, and the terminal methylene band at 873 cm.$^{-1}$.

Acidification of the aqueous layer, followed by the usual extraction procedure, yielded 1.70 g. (26%) of *dl*-γ-fencholenic acid; this showed the expected infrared absorption for a carboxylic acid.

***dl*-γ-Fencholenic Acid by Saponification of the Ester.**—The ethyl ester VIb (3.5 g.) obtained as above from *dl*-bromofenchone, was refluxed for 48 hours in a solution of 2 g. of potassium hydroxide in 80 ml. of dioxane and 20 ml. of water. The solvent was removed *in vacuo*, the residue was added to excess water, 0.4 g. of unreacted ester was removed by ether extraction, and the aqueous layer was acidified with mineral acid. The resulting oil was isolated by ether extraction, and yielded 1.80 g. of material whose infrared spectrum was identical with that of the γ-fencholenic acid obtained directly from the action of alkali on bromofenchone.

Methyl *dl*-γ-Fencholenate (VIc). A. By Esterification of the Acid VIa.—The γ-fencholenic acid (1.7 g.) obtained as above by action of base on *dl*-bromofenchone, was esterified with diazomethane prepared from 2 g. of nitrosomethylurea. The infrared spectrum was identical with that of the methyl ester obtained below, and was practically identical with that of the ethyl ester obtained above.

B. By Action of Methanolic Alkali on *dl*-Bromofenchone.—*dl*-Bromofenchone (5.0 g., m.p. 43–44°) was refluxed for 24 hours in 10 cc. of methanol containing 4.0 g. of potassium hydroxide. The reaction was worked up by the procedure described above, and 3.0 g. of the methyl ester was obtained.

Ozonization of *dl*-γ-Fencholenic Acid (VIa).—A solution of 1.00 g. of γ-fencholenic acid in 50 ml. of chloroform was ozonized at −78° for about 45 minutes. The mixture was then reduced catalytically with hydrogen and palladium-on-charcoal at −78° until no more hydrogen was absorbed. The mixture was then filtered and was extracted with water rapidly to avoid loss of low-boiling carbonyl compounds. Addition of purified solution of 2,4-dinitrophenylhydrazine[17] gave a precipitate of the dinitrophenylhydrazone of formaldehyde. Paper chromatography of this material showed[18] that no other dinitrophenylhydrazone was present, in addition to that of formaldehyde. Recrystallization of the sample gave a product melting at 162–165°, which gave no depression when mixed with an authentic sample.

The chloroform layer from reduction of the ozonide was dried, and yielded a thick oil on evaporation of the solvent. This showed infrared bands among others, at 1736 cm.$^{-1}$ (corresponding to a cyclopentanone derivative (VIII) and ruling out the cyclobutanone structure (IV)) and at 1698 cm.$^{-1}$ (carboxylic acid).

The keto acid VIII, obtained by ozonization of another batch of *dl*-γ-fencholenic acid (0.5 g.) was allowed to stand in 5 ml. of ethanol and a few drops of water for 5 days at room temperature, along with 0.5 g. of semicarbazide hydrochloride and 0.75 g. of sodium acetate. The white crystals of the **semicarbazone of VIII** which formed (0.5 g.) were collected. They could be recrystallized in poor yield from methanol; the analytical sample was prepared for analysis by repeated washing with water, chloroform and acetone; it melted at 198–200° with decomposition.

Anal. Calcd. for $C_{10}H_{17}N_3O_3$: C, 52.85; H, 7.54. Found: C, 52.71; H, 7.66.

Semmler and Bartelt[2] reported the semicarbazone of the supposed cyclobutanone acid IV to melt at 192°, and to have the composition C, 51.06; H, 7.17. They did not identify acetaldehyde as a product of the ozonization. Their semicarbazone was recrystallized from methanol, which may have altered the compound.

Ozonization of Methyl *dl*-γ-Fencholenate (VIc).—This compound (1.728 g.) was ozonized in 100 ml. of chloroform for 120 minutes at room temperature, the exhaust gases being bubbled into two wash bottles filled with water. The two water solutions were added to a hot solution of 600 mg. of methone in 75 ml. of water. The white precipitate which formed was collected, and melted at 189.5–192.5°; it showed no depression on mixed m.p. with an authentic sample of the methone derivative of formaldehyde.

***dl*-α-(3-Methylcyclopentyl)-isobutyric Acid (VII). A. By Catalytic Reduction of *dl*-γ-Fencholenic Acid.**—γ-Fencholenic acid (1.0 g.) was reduced in ethanol with hydrogen and 100 mg. of 5% palladium-on-charcoal at room temperature and atmospheric pressure. The product showed the same infrared spectrum as the product obtained by reduction of *dl*-α-fencholenic acid. The amide melted at 126.5–128.5°, and gave no depression with the sample prepared below from the dihydro-α-fencholenic acid.

B. By Catalytic Reduction of *dl*-α-Fencholenic Acid.—The α-acid[3] (1.14 g.), was catalytically reduced as described above, and the product was identical with the one described above.

The amide was prepared using thionyl chloride and aqueous ammonia, and melted, after crystallization from hexane, at 128–129°.

Anal. Calcd. for $C_{10}H_{19}NO$: C, 70.95; H, 11.31; N, 8.28. Found: C, 70.83; H, 11.57; N, 8.20.

The *dl*-Lactone IX. A. From *dl*-γ-Fencholenic Acid.—*dl*-γ-Fencholenic acid (1.85 g.) was added to 10 ml. of concentrated sulfuric acid and allowed to stand at room temperature for 30 min. The solution was poured into ice-water, the mixture was extracted with ether, and the ether solution was washed with sodium bicarbonate solution. The ether layer was dried, and the 0.90 g. of partly crystalline residue was dissolved in petroleum ether, decolorized with charcoal and cooled to −78°; the white crystals (0.3 g.) melted at 72–74° and showed carbonyl absorption indicating some γ-lactone (1754 cm.$^{-1}$) as well as some δ-lactone (1709 cm.$^{-1}$). After three sublimations, the lactone melted at 71.2–72.8°, and showed only the δ-lactone peak. The optically active lactone IX is reported[19] to melt at 77–78°.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.32; H, 9.70.

B. From *dl*-α-Fencholenic Acid.—α-Fencholenic acid[3] (0.5 g.) was swirled for 2 min. with 5 ml. of concentrated sulfuric acid and was poured onto ice. The mixture was extracted with ether and the ether layer was washed several times with bicarbonate solution. Concentration of the dried ether solution yielded an oil, which gave a white solid on sublimation, m.p. 68.5–71.5°. It gave no depression on mixed m.p. with the lactone obtained from the γ-acid above, and had the same infrared spectrum.

3-Methylcyclopentanone was prepared in 51% yield by distillation of β-methyladipic acid with manganous carbonate.[20]

Ethyl α-(3-Methyl-1-hydroxycyclopentyl)-isobutyrate.[21]—Ethyl α-bromoisobutyrate (40 g.) in 150 ml. of anhydrous ether was added dropwise to 4.5 g. of dry magnesium turnings. After about 50 ml. of this solution had been added, the reaction was proceeding very vigorously, and 16.0 g. of 3-methylcyclopentanone was mixed with the remaining 150 ml. of ether solution, which was added at a rate sufficient to maintain gentle reflux. After the addition was complete, the mixture was refluxed with stirring for 2 hours, at which

(17) The solution was freshly prepared by dissolving 1 g. of 2,4-dinitrophenylhydrazine in 35 ml. of concentrated hydrochloric acid, with enough added water to produce a clear solution when cooled. The solution was then extracted with six 50-ml. portions of reagent grade benzene.

(18) The methanol–heptane system (F. E. Huelin and B. H. Kennett, *Chemistry & Industry*, 715 (1956)) was used. We are indebted to Dr. Alexander D. Cross of this Laboratory for the paper chromatogram.

(19) F. W. Semmler, *Ber.*, **39**, 2854 (1906).

(20) H. Lucas and D. Pressman, "Principles and Practices in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 284.

(21) B. Shive, W. W. Crouch and H. L. Lochte, THIS JOURNAL, **63**, 2979 (1941).

point most of the magnesium had reacted. Sulfuric acid (100 ml., 1 *M*) was added cautiously with stirring, the ether layer was separated and dried, and the solution was distilled until the b.p. reached 100°. At this point dehydration appeared to be starting. The residue in the distilling flask (24 g.) was chromatographed on 300 g. of alumina. The column was eluted with the following solvents in succession: petroleum ether, petroleum ether–ether (6:1), pure ether, ether–methanol (6:1, then 1:1), and pure methanol. Ten fractions were collected, most of the product coming off with petroleum ether (10.0 g.), and ether–methanol (6.0 g. and 4.5 g.). The last two fractions were apparently identical, showing similar infrared spectra with strong hydroxyl bands; they represented a combined yield of 32%. The first fraction of 10.0 g. showed no hydroxyl band. The analytical sample was prepared from fraction 10 (4.5 g.) by chromatographing twice more in the system above.

Anal. Calcd. for $C_{12}H_{22}O_3$: C, 67.25; H, 10.35. Found: C, 66.56; H, 10.39.

Ethyl *dl*-α-(3-Methylcyclopentyl)-isobutyrate (VIIa).—The hydroxyester above (6.0 g.) was dehydrated by heating to 125° for 15 hours with 10.0 g. of anhydrous magnesium sulfate; the mixture was thoroughly extracted with ether, which yielded, after evaporation, 5.05 g. of unsaturated ester showing no hydroxyl absorption in the infrared. This unsaturated ester (5.0 g.) was hydrogenated in ethanol with palladium-on-charcoal catalyst, with the absorption of the theoretical amount of hydrogen. The analytical sample was prepared by distillation (b.p. 84° (5 mm.)) of a sample from an earlier run which had not been chromatographed. Purification by chromatography is preferable, however.

Anal. Calcd. for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 73.19; H, 10.78.

***dl*-(3-Methylcyclopentyl)-isobutyric Acid (VII).**—The ester VIIa (3.0 g.) was refluxed for 72 hours with 2.0 g. of potassium hydroxide in 70 ml. of dioxane and 15 ml. of water. The mixture was worked up in the conventional way, and yielded 1.70 g. of unchanged ester and 600 mg. of the acid VII.

The amide of the synthetic acid was prepared with thionyl chloride and ammonia, and melted at 124–125°; its infrared spectrum was identical with that of the samples of amide prepared from samples VII obtained by catalytic reduction of both α- and γ-*dl*-fencholenic acids; further, a mixed m.p. with amide derived from the reduced α-acid showed no depression.

***dl*-2,2-Dimethyl-2-(3-methylcyclopentyl)-ethanol (XI).**—Ethyl α-(3-methylcyclopentyl)-isobutyrate (1.70 g., prepared by the Reformatsky reaction) dissolved in 25 ml. of anhydrous ether, was added dropwise to 0.65 g. of lithium aluminum hydride in 25 ml. of ether. The mixture was refluxed with stirring for 4 hours. Ethyl acetate (2 ml.) was added carefully, followed by 3.5 ml. of saturated sodium sulfate solution. The mixture was stirred for 15 minutes to coagulate the salts, which were then removed by filtration. The ethereal filtrate was dried and the solvent was removed, leaving 1.0 g. of 2,2-dimethyl-2-(3-methylcyclopentyl)-ethanol (XI).

This was characterized by preparation of the **3,5-dinitrobenzoate XIa**; the alcohol XI (1.0 g.) and freshly prepared 3,5-dinitrobenzoyl chloride (1.25 g.) in 5 ml. of anhydrous pyridine was heated on the steam-bath for 1.5 hours. The mixture was then poured into 10 ml. of saturated bicarbonate solution, and the resulting cloudy suspension was extracted with ether. The ether solution was washed with water and concentrated. The resulting oil was dissolved in ethanol, made turbid with water, and cooled. The crystals which formed melted, after recrystallization from ethanol–water, at 58.5–59.5°.

Anal. Calcd. for $C_{17}H_{22}N_2O_6$: C, 58.27; H, 6.33. Found: C, 58.13; H, 6.64.

A sample of this same derivative was prepared by lithium aluminum hydride reduction of ethyl dihydro-γ-fencholenate, followed by acylation with dinitrobenzoyl chloride. The two crystalline samples showed no depression on mixed m.p.

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[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE, THE WEIZMANN INSTITUTE OF SCIENCE]

Syntheses in the Terpene Series. V.[1] A Synthesis of DL-1,1,6α,10β-Tetramethyl-*trans*-decal-2β-ol-5-one, the Racemate of a Degradation Product of α-Amyrin

BY FRANZ SONDHEIMER AND DOV ELAD

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The previously described 1,1,10β-trimethyl-Δ⁸-octal-5β-ol-2-one benzoate (IIa) has been converted by a seven-step sequence to 1,1,10β-trimethyl-*trans*-decal-2β-ol-5-one benzoate (VIIb). The latter substance has been found to differ from the compound of King, *et al.*, to which structure VIIb had been ascribed, but the corresponding keto-acetate VIIc was identical with the substance prepared independently by Halsall, *et al.* Methylation of the keto-benzoate VIIb gave 1,1,-6α,10β-tetramethyl-*trans*-decal-2β-ol-5-one (Xa), which was shown to be the racemate of an optically active degradation product of α-amyrin and of ursolic acid. Condensation of the tetramethyl keto-benzoate Xb with sodium acetylide yielded the acetylenic carbinol XI, which appears to be a useful intermediate for syntheses in the triterpene field.

In Part III of this series[2] the conversion of the readily available 10-methyl-$\Delta^{1(9)}$-octalin-2,5-dione (Ia) *via* 1,1,10β-trimethyl-Δ⁸-octal-5β-ol-2-one benzoate (IIa) to 1,1,10-trimethyl-*trans*-decal-5-one (VIId) was reported. The last-mentioned substance, which was prepared independently by Cocker and Halsall[3] by a similar route, appears to be a useful intermediate for the synthesis of some of the diterpene alcohols and acids. However for the synthesis of members belonging to the onocerin[4] and pentacyclic triterpene group of substances, it was necessary to keep intact the C-2 oxygen function of IIa instead of removing it as had been done previously.[2,3] In this paper we describe the conversion of the ketol benzoate IIa to 1,1,10β-trimethyl-*trans*-decal-2β-ol-5-one (VIIa) and thence to 1,1,6α,10β-tetramethyl-*trans*-decal-2β-ol-5-one (Xa).[5] The latter was shown to be the racemate of the optically active substance Xa which had been obtained previously by the degradation of α-amyrin[6a] and of ursolic acid.[6b]

The majority of the diterpenes, the tetracyclic triterpenes and the pentacyclic triterpenes have all

(1) For Part IV, see F. Sondheimer and D. Elad, *Proc. Chem. Soc.*, 320 (1957).

(2) F. Sondheimer and D. Elad, THIS JOURNAL, **79**, 5542 (1957).

(3) J. D. Cocker and T. G. Halsall, *J. Chem. Soc.*, 3441 (1957).

(4) D. H. R. Barton and K. H. Overton, *ibid.*, 2639 (1955); K. Schaffner, R. Viterbo, D. Arigoni and O. Jeger, *Helv. Chim. Acta*, **39**, 174 (1956); J. D. Cocker and T. G. Halsall, *J. Chem. Soc.*, 4262 (1956).

(5) For a preliminary communication, see footnote 1.

(6) (a) R. Rüegg, J. Dreiding, O. Jeger and L. Ruzicka, *Helv. Chim. Acta*, **33**, 889 (1950); (b) D. Arigoni, H. Bosshard, J. Dreiding and O. Jeger, *ibid.*, **37**, 2173 (1954).