and 0.5 g. of sodium metal), and was heated in a sealed tube at 170–180° for 2 hr. After cooling, the solution was diluted with water, acidified with hydrochloric acid, and warmed for 15 min. on a water bath. The solution was extracted with ether, and the ether solution was washed with aqueous bicarbonate, dried, and evaporated to leave 0.12 g. (80%) of colorless leaflets, m.p. 150°. Recrystallization from dilute ethanol raised the melting point to 153°; $[\alpha]_D^{18}$ +21.9° (c 2.47; EtOH). It showed no depression of the melting point on admixture with 3-desoxy-α-tetrahydro-α-santonin (VAb)[3b,c] m.p. 154°; $[\alpha]_D^{31}$ +20.8° (c 0.87; EtOH), prepared from IIAb by the Clemmensen reduction.

3-Desoxytetrahydro-β-santonin-d (VBd). By the Clemmensen method described above for preparing VB, the ketone-d (IIBd, 0.29 g.) was reduced to an oily product, which was fractionated to a colorless oil (VBd, 0.22 g., 80%), b.p. 73–75° at 3 mm. The oil (0.17 g.) was chromatographed on alumina (10 g.), and the elution with petroleum ether–benzene (2:1) gave 0.13 g. of colorless sirup, which solidified almost completely; m.p. 88–89°; $[\alpha]_D^{19}$ +60.0° (c 1.27; $CHCl_3$).

Anal. Calcd. for $C_{15}H_{24}O_2$: C, 76.22; H, 10.24. Found: C, 76.35; H, 10.01.

Attempt on isomerization of VBd into the corresponding compound (VAd)[3c] in α-santonin series by the procedure described for VBb was unfruitful.

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SHINJUKU-KU, TOKYO, JAPAN

[CONTRIBUTION FROM THE CITRUS EXPERIMENT STATION OF THE UNIVERSITY OF FLORIDA]

Derivatives of (+)-Limonene. I. Esters of *trans-p*-Menthane-1,2-diol[1]

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The hitherto unreported diacetate, dipropionate and dibutyrate esters of trans-*p*-menthane-1,2-diol have been synthesized from (+)-limonene in 50 per cent yield. Partial hydrogenation of (+)-limonene followed by hydroxylation with performic acid affords a crystalline mixture of *trans-p*-menthane-1,2-diols in 60 per cent yield. The diols are converted in 90–95 per cent yield to the diesters by reaction with the appropriate acid anhydride.

This paper describes a convenient synthesis of *trans-p*-menthane-1,2-diol and three of its diester derivatives. The preparation of *trans-p*-menthane-1,2-diol by the hydrogenation of *trans*-$\Delta^{8(10)}$-*p*-menthene-1,2-diol has been reported by Schmidt[2] and others.[3] Improved yields of this saturated diol have been obtained in this laboratory by first hydrogenating the exocyclic double bond of (+)-limonene and then hydroxylating the endocyclic double bond by reaction with performic acid.

Hydrogenation of freshly distilled (+)-limonene[4] (I) without solvent, at low pressure, over a 5 per cent platinum on Darco G-60 catalyst proceeds smoothly to afford Δ^1-*p*-menthene (II) in virtually quantitative yield. It is imperative to use only freshly distilled material, because the catalyst is rapidly poisoned by compounds (probably peroxides) formed in (+)-limonene stored in contact with air for as short a period as five days. The hydrogenation is highly exothermic and absorption of hydrogen almost ceases when one mole has been absorbed per mole of (+)-limonene. It has been found practicable to use the same catalyst for as many as thirty consecutive hydrogenations. Spent catalyst is easily reactivated by washing with acetone and drying for one hour at 110°. This ease of partial hydrogenation of (+)-limonene was first described by Vavon,[5] who used a heat deactivated platinum catalyst. More recently Fujita and Matsuura[6] accomplished the same partial hydrogenation using Adams' platinum catalyst in methanol solution.

Hydroxylation of Δ^1-*p*-menthene (II) by the gradual addition of one equivalent of preformed performic acid followed by hydrolysis of the intermediate monoformate esters with alcoholic potassium hydroxide, affords a crystalline mixture of *trans-p*-menthane-1,2-diols (III) in 60% over-all yield from (I). Direct addition of II to the performic acid solution results in yields of III 20–25% less than obtained by the inverse addition procedure. Separation of the diols III by fractional crystallization affords 40–45% of one diol melting at 89° and 8–12% of another diol melting at 55°. By analogy with the work of Jefferies and Milligan[7] and Cole and Jefferies,[8] on the racemic *trans-p*-menthane-1,2-diols, the higher melting, more abundant diol probably has the conformation of their compound (I) (1-hydroxyneocarvomenthol) and the lower melting diol corresponds in structure to

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[1] Florida Agricultural Experiment Station Journal Series, No. 720.

[2] H. Schmidt, *Ber.*, **82**, 11 (1949).

[3] H. Meerwein, A. Ogait, W. Prang, and A. Serini, *J. prakt. Chem.*, **113**, 9 (1926).

[4] Samples of citrus d-limonene were supplied by Kuder Citrus Pulp Co., Lake Alfred, Fla.

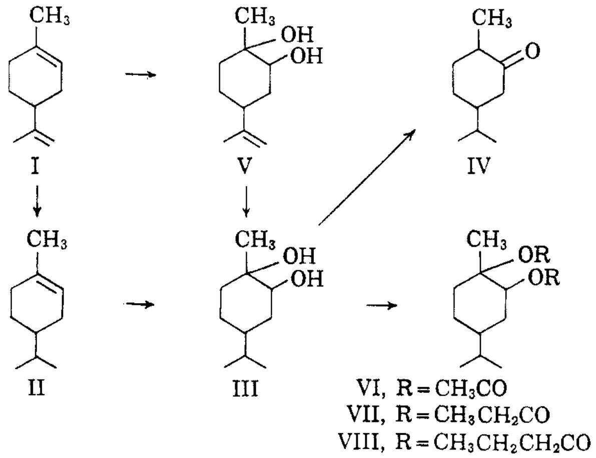
[5] M. G. Vavon, *Bull. soc. chim.* IV, **15**, 282 (1914).

[6] K. Fujita and T. Matsuura, *J. Sci. Hiroshima Univ.* **18A**, 455 (1955).

[7] P. R. Jefferies and B. Milligan, *J. Chem. Soc.*, 4384 (1956).

[8] A. R. H. Cole and P. R. Jefferies, *J. Chem. Soc.*, 4391 (1956).

their compound (II) (1-hydroxyisocarvomenthol). However, the infrared absorption of these optically active diols was not considered conclusive enough to establish conformations. Both *trans* diols are dehydrated by refluxing in 10% sulfuric acid to the same tetrahydrocarvone[2,7] (IV). The higher melting isomer may also be prepared in poor yield (14%) by performic acid hydroxylation of (+)-limonene (I) to $\Delta^{8(10)}$-*p*-menthene-1,2-diol (V) followed by catalytic hydrogenation. In this case only one unsaturated diol (V) could be isolated from the hydroxylation. Performic acid hydroxylation of (+)-limonene is, in contrast to the peracetic acid hydroxylations reported in the literature,[8,9,10] much too vigorous and a large part of the (+)-limonene is converted to water soluble polymers.



The higher melting diol is converted in 90–95% yield to the diacetate (VI), dipropionate (VII), or dibutyrate (VIII) ester by refluxing with the appropriate acid anhydride. The mixture of *trans*-diols (III) may also be converted directly, in comparable yield, to give a mixture of isomeric diesters. In this way saturated glycol esters may be prepared from (+)-limonene (I) in 50–55% yield.

EXPERIMENTAL

Preparation of 5% platinum on charcoal catalyst. The general procedure outlined by Kaffer[11] was followed with one modification, no hydrazine hydrate was used in the final stage of the preparation.

Δ^1-*p-Menthene* (II). One hundred and twenty milliliters (100.8 g.) of freshly distilled (+)-limonene (I) (b.p. 175–176°, $[\alpha]_D^{23}$ + 118.7°, n_D^{23} 1.4722) was hydrogenated at room temperature in a Parr series 3910 low pressure hydrogenation apparatus at a starting pressure of 52 pounds using 1.3 g. of 5% platinum on Darco G-60 catalyst. One equivalent of hydrogen was consumed after 60 min. The temperature of the reaction flask rose to approximately 60° during hydrogenation. Removal of the catalyst by filtration afforded 121 ml. (97.6%) of Δ^1-*p*-menthene (II) (b.p. 174–176°, $[\alpha]_D^{23}$ + 109, n_D^{23} 1.4557). The physical constants for Δ'-*p*-menthene reported by Fujita and Matsuura[6] are: b.p. 77.5–78° at 35 mm., n_D^{25} 1.4533, $[\alpha]_D^{25}$ + 100.0°.

trans-p-Menthane-1,2-diols (III). A mixture of 200 ml. of 90% formic acid and 75.2 g. (0.752 moles) of 34% hydrogen peroxide was added dropwise over a period of 1 hr. to 120 ml. (0.717 moles) of Δ^1-*p*-menthene (II). The mixture was stirred and cooled in a water bath to maintain a temperature of 35° during the addition. Stirring at 35° was continued for an additional 2 hr. Five grams of sodium bisulfite was added to destroy peroxides and most of the formic acid was removed under vacuum at 50°, using a film evaporator. One hundred ml. of 95% ethanol was added to the colorless, oily residue and sufficient ethanolic potassium hydroxide to bring the *p*H to 11–12. This mixture was stirred for 3 hr. at room temperature, made to *p*H 6 with concentrated hydrochloric acid and all of the alcohol removed under vacuum at 50°. The residue was taken up in ether, the aqueous phase discarded and the ether solution dried over anhydrous sodium sulfate. After removal of the ether under reduced pressure, the residual oil (100.6 g.) was distilled. At 102–108° (1 mm.) 74.3 g. (60% from I) of *trans-p*-menthane-1,2-diols (III) distilled as a colorless, viscous oil. This oil slowly crystallized on standing at room temperature. The mixed diols were dissolved in 200 ml. of hot benzene, the solution was cooled, and 400 ml. of petroleum ether (30–60°) was added. The higher melting *trans*-diol crystallized as colorless prisms, m.p. 84–87°, 52.6 g. (43%). Several recrystallizations from a mixture of benzene and petroleum ether afforded material melting at 86.6–88.6° and having a rotation of $[\alpha]_D^{23}$ + 48° (10% acetone solution).

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.73; H, 11.70. Found: C, 70.13; 11.56.

The filtrate from the above diol was evaporated to dryness under vacuum and the residue dissolved in 100 ml. of petroleum ether. The lower melting *trans*-diol crystallized as colorless needles, m.p. 51–54°, 9.6 g. (7.8%). Several recrystallizations from petroleum ether afforded material melting at 54–55°, $[\alpha]_D^{23}$ + 25° (10% acetone solution).

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.73; H, 11.70. Found: C, 68.88, H, 11.79.

Tetrahydrocarvone (IV). Ten grams of *trans-p*-menthane-1,2-diol (III) (higher melting isomer, m.p. 87–89°) was refluxed for 2 hr. in 100 ml. of 10% sulfuric acid. During refluxing, 8.5 g. of colorless, steam distillable oil was collected in an oil separatory trap. Purification of this oil through the semicarbazone derivative afforded 5.0 g. (56%) of tetrahydrocarvone (IV), b.p. 55–56 (1 mm.), n_D^{23} 1.4545, $[\alpha]_D^{23}$ + 18 (reported,[2] b.p. 218–220°/745 mm.; n_D^{20} 1.4544; α_D^{20} + 13.3).

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.72; H, 11.76.

Semicarbazone, m.p. 185–189° (reported,[2] 190–191°).

Dehydration of the *trans*-diol melting at 54–55° by the same procedure afforded a comparable yield of tetrahydrocarvone (IV). A mixture of the semicarbazone derivative with the semicarbazone prepared above showed no melting point depression.

$\Delta^{8(10)}$-*p-Menthene-1,2-diol* (V). A mixture of 30 ml. (0.184 mole) of (+)-limonene (I), 100 ml. of 90% formic acid, and 24 ml. (0.227 mole) of 29% hydrogen peroxide was stirred and cooled in a water bath to maintain a temperature of 35° for 1 hr. Unreacted (+)-limonene (10.8 ml.) was separated and the formic acid layer was run immediately into excess, aqueous sodium carbonate solution. The colorless oily upper phase was separated and dissolved in ethanolic potassium hydroxide (*p*H 10–11). After standing for 2.5 hr. at room temperature, the solution was brought to *p*H 6 with concentrated hydrochloric acid. Most of the ethanol was removed under vacuum and 100 ml. of water was added. The unsaturated diol crystallized as the hydrate in colorless plates. Removal of water of crystallization in a vacuum desiccator over sulfuric acid afforded 4.0 g. (19.6% conversion yield) of crystalline $\Delta^{8(10)}$-*p*-menthene-1,2-diol (V), m.p. 62–67°. Several recrystallizations from benzene–

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(9) J. Sword, *J. Chem. Soc.*, **127**, 1632 (1925).

(10) B. A. Arbusow and B. M. Michailow, *J. prakt. Chem.*, **127**, 92 (1930).

(11) H. Kaffer, *Ber.*, **57**, 1263 (1924).

petroleum ether (30-60°) afforded colorless prisms, m.p. 70–71.6°, $[\alpha]_D^{23}$ + 41 (10% acetone solution).

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.66; H, 10.66.

Hydrogenation of $\Delta^{8(10)}$-p-menthene-1,2-diol. Five grams of $\Delta^{8(10)}$-*p*-menthene-1,2-diol was dissolved in 150 ml. of 95% ethanol and hydrogenated at room temperature, using 2 g. of 5% platinum on Darco G-60 catalyst. The hydrogenation was complete in 10 min. The catalyst was removed by filtration and the filtrate concentrated to about 10 ml. Dilution with water afforded colorless crystals which were dried in a vacuum desiccator over concd. H_2SO_4. The dried product weighed 4.6 g. (92%) and melted at 86.4–88.4°. There was no melting point depression on admixture with a sample of *trans-p-menthane*-1,2-diol (III) (m.p. 86.6–88.6°) prepared by the hydroxylation of Δ^1-*p*-menthene (II).

Trans-p-menthane-1,2-diol-diacetate (VI). Thirty grams of *trans-p*-menthane-1,2-diol (III) (m.p. 89°) was refluxed for 2 hr. in 150 ml. of acetic anhydride containing 0.5 g. of anhydrous sodium acetate. The solution was poured into water and stirred to decompose excess anhydride. The diester was extracted with three portions of ethyl ether. The combined ether extracts were washed three times with sodium bicarbonate solution, twice with water, and dried over anhydrous sodium sulfate. After removal of the ether under reduced pressure, the residual oil was distilled. At 99° (0.8 mm.) 41 g. (92%) of colorless, slightly viscous oil was collected. The diacetate obtained by distillation was sufficiently pure for analysis $[\alpha]_D^{23}$ + 93, n_D^{23} 1.4498.

Anal. Calcd. for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44; Sapon. equiv., 128. Found: C, 65.34; H, 9.70; Sapon. equiv., 135.

Trans-p-menthane-1,2-diol-dipropionate (VII). Thirty grams of *trans-p*-menthane-1,2-diol (III) (m.p. 89°) was refluxed for 2 hr. in 150 ml. of propionic anhydride containing 0.5 g. of anhydrous sodium acetate. Excess anhydride was decomposed by water and the diester was extracted with ether as described in the case of the diacetate ester. After removal of the ether under reduced pressure, the residual oil was distilled. At 114° (0.8 mm.) 46 g. (94%) of colorless, slightly viscous oil was collected. The dipropionate obtained by distillation was sufficiently pure for analysis $[\alpha]_D^{23}$ + 83, n_D^{23} 1.4478.

Anal. Calcd. for $C_{16}H_{28}O_4$: C, 67.57; H, 9.92; Sapon. equiv., 142. Found: C, 67.78; H, 9.96; Sapon. equiv., 146.

Trans-p-menthane-1,2-diol-dibutyrate (VIII). Thirty grams of *trans-p*-menthane-1,2-diol (III) (m.p. 89°) was refluxed for 2 hr. in 150 ml. of butyric anhydride containing 0.5 g. of anhydrous sodium acetate. Excess anhydride was decomposed by water and the diester was extracted with ether as described in the case of the diacetate ester. After removal of the ether under reduced pressure, the residual oil was distilled. At 131° (0.8 mm.) 50 g. (92%) of colorless, slightly viscous oil was collected. The dibutyrate obtained by distillation was sufficiently pure for analysis $[\alpha]_D^{23}$ + 74, n_D^{23} 1.4486.

Anal. calcd. for $C_{18}H_{32}O_4$: C, 69.19; H, 10.33; Sapon. equiv., 156. Found: C, 69.26; H, 10.47; Sapon. equiv., 154.

LAKE ALFRED, FLA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

α-Deoxykojic Acid and Some of Its Derivatives

CHARLES D. HURD AND SWIATOSLAW TROFIMENKO

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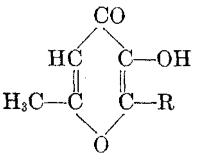
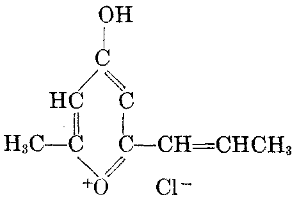
The allyl ether of α-deoxykojic acid was prepared and rearranged to 6-allyl-α-deoxykojic acid, from which the 6-propenyl and 6-propyl analogs were made. 3,5-Dinitrobenzoates were satisfactory derivatives for these compounds.

In connection with studies on kojic acid and related compounds it became of interest to prepare α-deoxykojic acid[1] and certain of its derivatives.

α-Deoxykojic acid (I) was synthesized from kojic acid by halogenation (thionyl chloride) to yield α-chloro-α-deoxykojic acid, followed by catalytic reduction of the latter. The allyl ether of I was prepared from allyl bromide, adapting conditions[2] employed earlier with kojic acid. The ether was an oil at room temperature that crystallized readily at ice temperature from one run but not from another. It isomerized rapidly to 6-allyl-α-deoxykojic acid (II) at elevated temperatures and gave evidence for slow isomerization at room temperature.

II was a crystalline solid, giving a strong violet color with ferric chloride. When it was treated with dry hydrogen chloride in ethanol it changed to a salt-like compound (V), the hydrochloride of 6-propenyl-α-deoxykojic acid (III). This compound lost hydrogen chloride on standing but more rapidly on heating to yield III. The latter was prepared more readily by treatment with base. V, III, and a mixture thereof all melted at the same temperature which would indicate that hydrogen chloride is lost prior to the attainment of the melting temperature, and that what melts is impure III. The 6-propenylkojic acid hydrochloride of McLamore and co-workers[2b] also melts a few degrees below the melting point of 6-propenylkojic





V

I, R = H
II, R = $CH_2CH{=}CH_2$
III, R = $CH{=}CHCH_3$
IV, R = $CH_2CH_2CH_3$

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(1) The α represents position on the side chain. α-Deoxykojic acid also has been called allomaltol by Yabuta, *J. Chem. Soc.*, **125**, 575 (1924).

(2) (a) C. D. Hurd and R. J. Sims, *J. Am. Chem. Soc.*, **71**, 2440 (1949); (b) W. M. McLamore, E. Gelblum, and A. Bavley, *J. Am. Chem. Soc.*, **78**, 2816 (1956).