Summary

Catalytic hydrogenation of 1,2-benzanthracene and of its 10-methyl and 10-acetoxy derivatives in the presence of Adams catalyst (usually with a promoter) results in the saturation of the terminal ring of the anthracene system, giving 5,6,7,8-tetrahydrides. With the acetoxy compound, which is more susceptible to attack than the other two substances, further hydrogenation results in the reduction of the other terminal ring. There is no indication that the hydrogenation of the benzanthracene derivatives proceeds through the intermediate fixation of hydrogen to the *meso*-positions, and indeed in one case a 9,10-dihydride was found to yield on hydrogenation a product quite different from the 5,6,7,8-tetrahydride obtained directly from the aromatic hydrocarbon.

On reduction with sodium and amyl alcohol, 1,2-benzanthracene and 10-methyl-1,2-benzanthracene are converted into 1′,2′,3′,4′,9,10-hexahydro derivatives.

New derivatives of the carcinogenically active 10-methyl-1,2-benzanthracene which have been submitted to biological tests include the 9,10-dihydride, the 1′,2′,3′,4′- and 5,6,7,8-tetrahydrides, and the 1′,2′,3′,4′,9,10-hexahydride.

CONVERSE MEMORIAL LABORATORY
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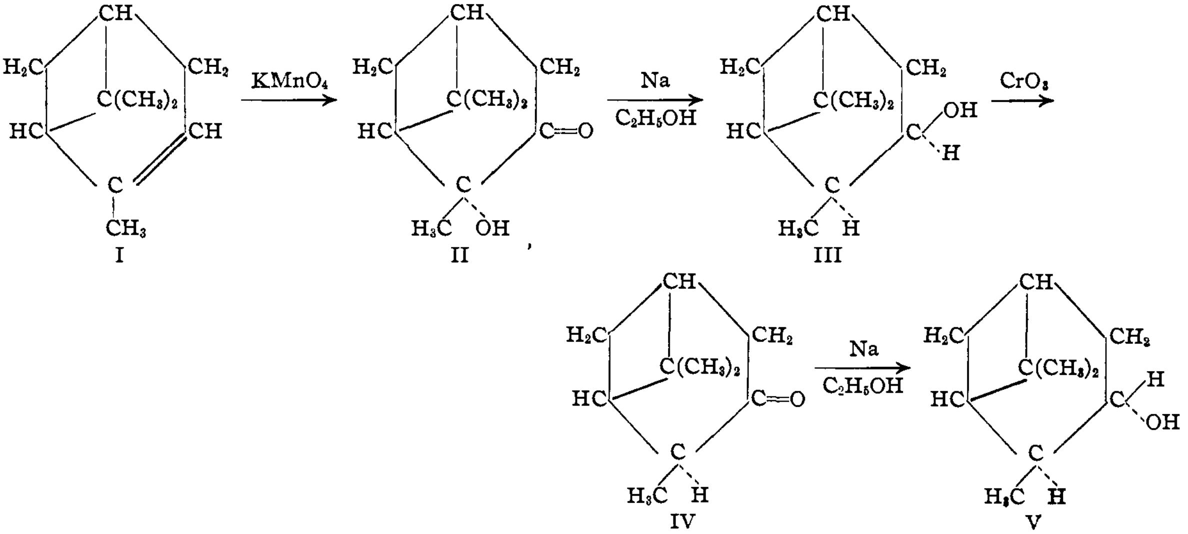
[CONTRIBUTION FROM THE DEPARTMENT OF APPLIED CHEMISTRY, TOKYO IMPERIAL UNIVERSITY]

Stereochemistry of Pinocampheols

BY TSUTOMU KUWATA

As pinocampheol is an alcohol of a bicyclic terpene, the existence of four diastereoisomeric compounds may be assumed. E. Gildemeister and H. Köhler[1] obtained *l*-pinocampheol (m. p. 67–68°) by reducing *l*-pinocamphone present in hyssop oil, and O. Wallach[2] synthesized *i*-pinocampheol (liquid) from nitrosopinene. H. Schmidt and L. Schulz[3] claimed to have prepared a new pinocampheol (m. p. 57°) by reducing *l*-pinocarveol from the oil of *Eucalyptus globulus*. The configurations of the pinocampheols, however, have not been studied extensively.

The present author has found a new method of synthesis of pinocampheol from α-pinene and has been able to confirm, to some extent, the diastereoisomeric relations between these alcohols.



When one mole of *d*-α-pinene (I) is oxidized in a medium of 90% aqueous acetone with powdered potassium permanganate corresponding to the amount of two atoms of oxygen, a new ketol, levorotatory 1-hydroxypinocamphone (II), is produced. The inversion of optical sign would be

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[1] E. Gildemeister and H. Köhler, *Chem. Zentr.*, **80**, II, 2158 (1909).

[2] O. Wallach, *Ann.*, **300**, 288 (1898).

[3] H. Schmidt and L. Schulz [*Schimmel Ber.*, 97 (1934)] named this pinocampheol *cis*-pinocampheol.

accounted for by the newly produced asymmetric carbon atom (2) in II. On reducing the ketol (II) with metallic sodium and absolute alcohol, *l*-*cis*-pinocampheol (III) has been obtained, which melts at 55–56° and resembles in many respects Schmidt's *cis*-pinocampheol.

The configuration of III is probably the *cis*-form because the steric position of the hydroxyl group in III would be influenced mainly by the hydroxyl group formerly present in II which has a stronger valency field than the methyl group; under these conditions the reduction product in neutral as well as in alkaline medium has generally a *trans* configuration.[4]

When III is oxidized with chromic acid, *d*-pinocamphone (IV) is produced. The reduction product of IV with metallic sodium and absolute alcohol is *d*-pinocampheol (V), properties of which resemble Schmidt's *d*-*trans*-pinocampheol and also Gildemeister's *l*-pinocampheol with the exception of the sign of optical rotation. Owing to the steric effect of the methyl group (1), hydroxyl group of V should exist in the *trans* position with respect to the methyl group (1).

The exoendo isomerism of pinocampheols is left to future investigation.

In comparing the molecular refraction, it was recognized that the v. Auwers–Skita law[5] may hold between the pinocampheols.

	i-*cis*-Pinocampheol	*i*-Pinocampheol	*d*-Pinocampheol[6]
d^{20}_4	0.9799	0.9652	0.9648
n^{20}_D	1.4856	1.4831	1.4840
M_D	45.13	45.62	45.70
EM_D	−0.37	+0.12	+0.20

Experimental

l-**Hydroxypinocamphone (II).**—To a mixture of 150 g. of *d*-α-pinene (I) (b. p. 155–157°, d^{20}_4 0.8618, $[\alpha]_D$ +40.7) and 1.5 kg. of 90% aqueous acetone, 300 g. of powdered potassium permanganate was added little by little in the course of forty hours at 10–15°. The neutral product, most of which distils at 100–115°, 3 mm., was mixed with about four times its volume of petroleum ether and cooled as low as −20°. The ketol separated in small crystals and was recrystallized from petroleum ether. It formed thick plates or prisms. The ketol upon warming smells like camphor and dissolves readily in all organic solvents. It is insoluble in aqueous alkaline solution; m. p. 35.5–36.5°; $[\alpha]^{25}_D$ −18.56° (*c*, 14.44, alcohol).

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.58. Found: C, 71.68; H, 10.04.

The semicarbazone forms prisms from methanol; m. p. 230°, dec.

Anal. Calcd. for $C_{10}H_{16}O{=}N_2HCONH_2$: C, 58.61; H, 8.52; N, 18.65. Found: C, 58.63; H, 8.53; N, 18.56.

i-**Hydroxypinocamphone.**—This inactive ketol was prepared from *i*-pinene by the method above mentioned; m. p. 38.5–39.0°.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.58. Found: C, 71.32; H, 9.59.

The semicarbazone forms prisms from methanol; m. p. 213–214°, dec.

Anal. Calcd. for $C_{10}H_{16}O{=}N_2HCONH_2$: C, 58.61; H, 8.52. Found: C, 58.60; H, 8.45.

The acetyl ester was prepared by treating the ketol with acetic anhydride in pyridine. The ester is a mobile liquid having an agreeable odor: b. p. 104–108° (4 mm.); d^{25}_{25} 1.066; n^{25}_D 1.4770. *Ester value.* Calcd. for $C_{10}H_{15}O_2CO_2CH_3$: 267. Found: 247.

l-*cis*-**Pinocampheol (III).**—To 25 g. of *l*-hydroxypinocamphone dissolved in 250 cc. of absolute alcohol was added 25 g. of metallic sodium in small portions with vigorous stirring. When all the metallic sodium was dissolved, the reduction product was isolated in the usual manner; yield 20 g. *l*-*cis*-pinocampheol crystallizes in long needles having an odor resembling that of isoborneol: b. p. 84–87° (3 mm.); m. p. 55–56°; $[\alpha]^{20}_D$ −28.5° (*c*, 15.35, ether).

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.85; H, 11.77. Found: C, 77.86; H, 11.82.

The acetyl ester was obtained by heating the alcohol with acetic anhydride in the presence of sodium acetate. It is a mobile liquid and has an odor similar to isobornyl acetate: b. p. 82–84° (3 mm.); d^{20}_4 0.9781; n^{20}_D 1.4638. *Ester value.* Calcd. for $C_{10}H_{17}OCOCH_3$: 286.0. Found: 287.9.

The naphthyl urethan, prepared by treating with naphthyl isocyanate, forms small prisms from aqueous alcohol and melts at 87.5–88°. The phenylurethan derivative is difficult to crystallize.

Anal. Calcd. for $C_{10}H_{17}OCONHC_{10}H_7$: N, 4.33. Found: N, 4.38.

i-*cis*-**Pinocampheol.**—The alcohol, prepared from *i*-hydroxypinocamphone, is a viscous liquid: b. p. 90–95° (3 mm.), 214–217° (762 mm.); d^{20}_4 0.9799; n^{20}_D 1.4856. The phenylurethan derivative is a viscous liquid.

d-**Pinocamphone (IV).**—The oxidation of *cis*-pinocampheol was carried out by treating 6 g. of the alcohol dissolved in 60 cc. of acetic acid with 3 g. of chromic anhydride at ordinary temperatures: yield 5 g.; b. p. 61–64° (3 mm.); d^{20}_4 0.9631; n^{20}_D 1.4732; $[\alpha]^{18}_D$ +13.17°.

The semicarbazone, prepared in the usual manner, forms long prisms and has a m. p. 228°.

Anal. Calcd. for $C_{10}H_{16}{=}N_2HCONH_2$: N, 20.09. Found: N, 19.91.

i-**Pinocamphone.**—The inactive ketone has the following properties: b. p. 60–63° (3 mm.); d^{20}_4 0.9635; n^{20}_D 1.4730. Its semicarbazone melts at 207–209°.

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(4) Skita's law: A. Skita, *Ann.*, **431**, 1 (1923).

(5) *cis* Compounds are higher in specific gravity and refractive index, but smaller in molecular refraction as compared with *trans* compounds. K. v. Auwers, *Ann.*, **420**, 91 (1920); A. Skita, *Ber.*, **53**, 1792 (1920); A. Skita and A. Schneck, *ibid.*, **55**, 144 (1922).

(6) The data were determined in a supercooled state.

***d*-Pinocampheol** (V).—This was prepared from 3 g. of *d*-pinocamphone by reduction with 3 g. of metallic sodium and 30 cc. of absolute alcohol: yield 2.5 g. It forms long needles; b. p. 103–105° (13 mm.), m. p. 65–66°. In a supercooled state it shows d^{20}_4 0.9648; n^{20}_D 1.4840.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.85; H, 11.77. Found: C, 77.57; H, 11.89.

The phenylurethan derivative, recrystallized from aqueous methanol, melts at 74–75°.

Anal. Calcd. for $C_{10}H_{17}OCONHC_6H_5$: N, 5.12. Found: N, 5.08.

***i*-Pinocampheol.**—This alcohol is a viscous liquid; b. p. 82–84° (5 mm.); d^{20}_4 0.9652; n^{20}_D 1.4831. The phenylurethan derivative melts at 95–96°.

Acknowledgment.—The author wishes to express his thanks to Professor Y. Tanaka for kind advice.

Summary

Levorotatory 1-hydroxypinocamphone, a new terpene ketol, has been prepared from *d*-α-pinene by oxidizing the latter with potassium permanganate in 90% aqueous acetone medium. On reducing the ketol with metallic sodium and alcohol, *l-cis*-pinocampheol has been obtained, which gave *d*-pinocamphone by chromic acid oxidation. The reduction product of *d*-pinocamphone was *d*-pinocampheol which is a diastereoisomer of *l-cis*-pinocampheol.

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Quassin. II. Neoquassin

BY E. P. CLARK

In the first communication of this series[1] it was shown that, for the most part, the bitter material of quassia wood (*Quassia amara*) is a mixture of two isomeric substances, $C_{22}H_{30}O_6$. The one which predominates has a melting point of 206°. This was designated as "quassin." The other, which melts at 226°, was named "neoquassin." A method for the preparation and purification of these compounds was given, some reactions of quassin were reported, and several derivatives resulting therefrom were described.

Studies upon neoquassin similar to those made on quassin have now been completed, and the results are recorded here. Since there is a close structural relationship between the two isomers and the reactions of neoquassin are similar to those of quassin, a comparison of the results obtained with the two substances will be given as the reactions are presented.

Neoquassin crystallizes from dilute methanol as dense, colorless, six-sided prisms and quadrilateral plates which melt at 225–226°. Its specific rotation in chloroform solution is 46.6°. Like quassin, it contains two methoxyl groups and gives values corresponding to one active hydrogen by the Tschugaeff–Zerewitinoff method.

Boiling ethanolic potassium hydroxide solution in concentrations as high as 5% has no effect upon neoquassin, whereas the same reagent changes quassin to the extent that, as yet, no definite material has been obtained from it. The treatment is of value, however, as it has been used successfully in separating certain impurities from neoquassin.

The action of hydrochloric acid upon quassin and neoquassin is noteworthy. It was shown previously that constant boiling hydrochloric acid converts quassin to quassinol, with the elimination of two methoxyl groups and two hydrogen atoms. When neoquassin is subjected to the same conditions, no crystalline material is obtained. With boiling 3.5% aqueous hydrochloric acid, however, neoquassin gives excellent yields of semidemethoxyquassin, the same material that is obtained under identical conditions from quassin. With neoquassin, however, the yields are almost quantitative and the material is much purer, so that its subsequent purification is accomplished readily.

Neoquassin, when treated at room temperature with a 4% ethanolic hydrochloric acid solution, gives a compound $C_{24}H_{34}O_6$, m. p. 180°, which has one ethoxyl group. Since there is no evidence of a carboxyl group in neoquassin, the reaction indicates the presence of a highly basic, probably a tertiary, alcoholic hydroxyl group. Quassin subjected to the same reaction gives the

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(1) E. P. Clark, THIS JOURNAL, 59, 927 (1937).