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.

TOKYO, JAPAN RECEIVED JUNE 9, 1937

[CONTRIBUTION FROM DIVISION OF INSECTICIDE INVESTIGATIONS, BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, UNITED STATES DEPARTMENT OF AGRICULTURE]

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).

same ethoxy compound, but in addition an appreciable quantity of isoquassin, m. p. 221°, is formed.

Chromic acid in acetic acid solution has the same effect upon neoquassin that it has upon quassin; namely, it gives approximately a 50% yield of isoquassin. Since quassinol is readily obtained from isoquassin, this indirect route may be used to obtain quassinol from neoquassin. The yield of quassinol obtained by this procedure is also essentially the same as that from quassin because of the high yield of quassinol obtained from isoquassin.

As is the case with quassin, the action of acetic anhydride and sodium acetate upon neoquassin gives anhydroquassin. But, so far as could be determined, neither dehydroquassin nor the isomer picrasmin is formed. It is possible, however, to obtain dehydroquassin indirectly from neoquassin by the action of the acetylating reagent upon isoquassin. Under the conditions given for the formation of anhydroquassin from neoquassin, isoquassin gives only dehydroquassin.

The mechanism of the formation of these dehydro compounds, *i. e.*, dehydroquassin and quassinol, in non-oxidizing media is not clear. While numerous instances of partial dehydrogenation are on record, they involve the use of oxidizing agents as acceptors for the hydrogen. In the instances under consideration, however, the tertiary hydroxyl group apparently is involved, and probably hydrogen is eliminated as molecular hydrogen in somewhat the same manner that it is in the formation of acetone from isopropyl alcohol by the action of catalysts and heat.

Definite conclusions concerning this problem cannot be reached, however, until further information is available. The facts are therefore presented for the purpose of record.

The reactions under discussion are represented diagrammatically in the accompanying chart.

Experimental

Neoquassin.—This was prepared and purified as previously outlined.[1]

Action of Ethanolic Potassium Hydroxide upon Neoquassin.—Neoquassin, dissolved in ethanolic solutions of potassium hydroxide in the proportion of 1 g. to 10 cc. of solution, was refluxed for one hour. The concentrations of the potassium hydroxide solution ranged from 1 to 10%. The refluxed solutions were diluted with three volumes of water, the alkali was neutralized with hydrochloric acid, and the mixture allowed to crystallize. When the solutions contained as much as 3% potassium hydroxide, practically all the neoquassin was obtained unchanged. As the concentration of the alkali increased, the yields of neoquassin decreased. However, 5% potassium hydroxide gave good yields, and even with 10% alkali much of the neoquassin was recovered. From the standpoint of purification of neoquassin, 2.5% alkali is considered most favorable. The recovered neoquassin was recrystallized from 50% methanol. It separated in the usual crystalline habit with a melting point of 226°. Its optical crystallographic characteristics[2] were the same as those of untreated material, and when it was mixed with the latter there was no depression of the melting point.

Semidemethoxyquassin.—A suspension of 0.5 g. of neoquassin in 10 cc. of 10% hydrochloric acid and 20 cc. of water was refluxed for two and a half hours. The resulting solution was then set aside for three days to crystallize. The product obtained consisted of dense colorless prisms which usually melted at 205°, but at times they sintered at *ca.* 135° with the evolution of moisture and then melted at 205°. When the material thus obtained was recrystallized from ethyl acetate, it melted at 215° and cleared at 220°. It could be recrystallized conveniently from methanol by adding three volumes of water. When obtained in this manner it consisted of thick elongated rectangular plates, many of which were modified to pentagonal plates in which one end terminated in an acute angle. The material usually had a melting point of 215°, but at times it was obtained with a melting point of 210°. The melting point appeared to be somewhat dependent upon its state of agitation.

The material was the same as the semidemethoxyquassin obtained from quassin, as was shown by the facts that the two materials, recrystallized in the same way, did not cause a depression of the melting point and that the two substances had the same optical crystallographic properties.

Ethoxyneoquassin.—A solution of 0.6 g. of neoquassin in 9 cc. of 99.8% ethanol and 0.9 cc. of concentrated hydrochloric acid was allowed to stand at room temperature for two days. Four volumes of water was then added, and the solution was allowed to crystallize for a day. Five-tenths gram of colorless crystals which melted at 165–167° was obtained. They were recrystallized to a constant melting point of 180° by separating the substance from a concentrated solution in acetic acid by the addition of water. Thus obtained they consisted of long, pointed, colorless rods. In parallel polarized light (crossed nicols) the extinction is parallel and the elongation is positive. η_α, 1.523 (crosswise); η_i, 1.535, a value shown crosswise but not definitely determined as the β value owing to the absence of interference figures: η_γ, 1.583 (lengthwise, frequently found).

Anal. Calcd. for $C_{24}H_{34}O_6$: C, 68.86; H, 8.19; $2OCH_3$ and $1OC_2H_5$, total alkoxyl, 25.6; mol. wt., 418.4. Found: C, 68.94; H, 8.35; alkoxyl, 25.4; mol. wt. (Rast), 376.

Action of Alcoholic Hydrochloric Acid upon Quassin.—One-tenth gram of quassin was treated with ethanolic hydrochloric acid in the same manner as was neoquassin in the preceding experiment. The material that separated

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(2) The optical crystallographic data and comparisons reported here were determined by George L. Keenan, of the Food and Drug Administration, U. S. Department of Agriculture. The values of the refractive indices are all ±0.003.

had a melting point of 160–165°. It was recrystallized from dilute acetic acid to a constant melting point of 180°, as outlined above. When it was mixed with ethoxyneoquassin there was no depression of the melting point. Its optical crystallographic properties were also identical with those of ethoxyneoquassin. These facts show that the two materials are identical.

Anal. Found: C, 69.00; H, 8.51.

The mother liquors from the first crop of crude crystals were set aside for further crystallization. After some time a material with a melting point of 208° was obtained. It was recrystallized to a constant melting point of 220° from its saturated boiling solution in *n*-butanol by the addition of eight volumes of *n*-butyl ether. It consisted of rosets and sheaves of spear-shaped rods. It was identified as isoquassin by its analysis, melting point, mixed melting point, and optical crystallographic properties.

Anal. Calcd. for $C_{22}H_{30}O_6$: OCH_3(2), 15.9. Found: OCH_3, 15.98.

Action of Chromic Acid upon Neoquassin, Isoquassin.—Neoquassin was treated with chromic acid according to the method previously outlined for the preparation of isoquassin from quassin. Eight-tenths gram of neoquassin yielded 0.5 g. of crude isoquassin which melted at 213°. It was recrystallized from its boiling methanol solution upon the addition of two volumes of water. Thus obtained it melted at 220–221°, and its identity was established by its analysis and by comparing its melting point, mixed melting point, and optical properties with those of an authentic sample prepared from quassin.

Anal. Calcd. for $C_{22}H_{30}O_6$: C, 67.67; H, 7.75. Found: C, 67.7; H, 7.4.

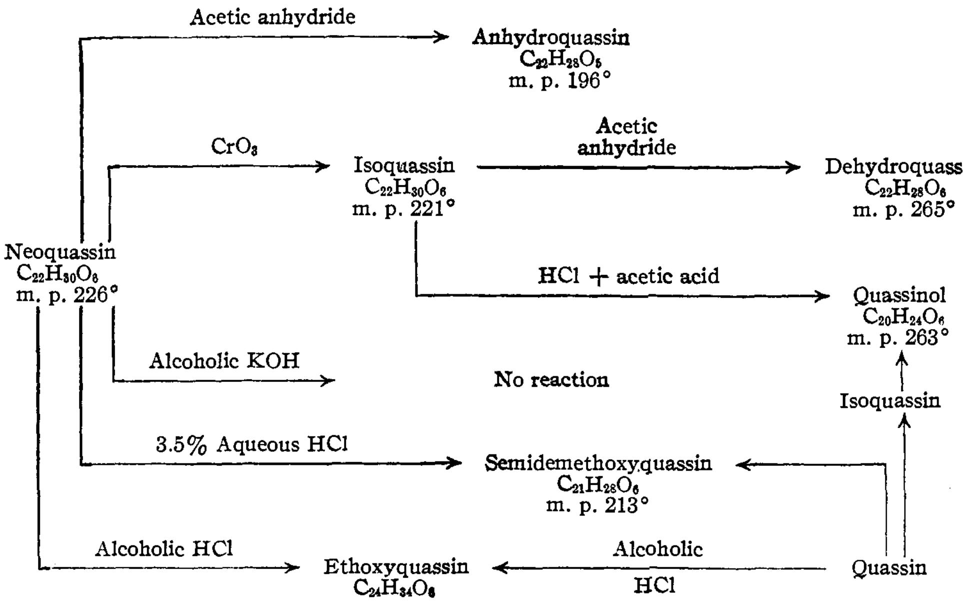
Action of Acetic Anhydride upon Neoquassin, Anhydroquassin.—A mixture of 1 g. of neoquassin, 0.25 g. of dry sodium acetate, and 8 cc. of acetic anhydride was boiled for one hour. The excess of anhydride was removed by distillation, and the residue was treated with water. The oily product soon crystallized and gave 1 g. of crude product. This was twice recrystallized from boiling methanol by adding an equal volume of water. The yield was 0.7 g. It began to sinter at 190°, flowed at 196°, and cleared at 198°. It consisted of irregular fern-shaped prisms which extinguished sharply in parallel polarized light (crossed nicols). In convergent polarized light (crossed nicols) no interference figures were observed, but the material was apparently biaxial. η_α, 1.575; η_β, indeterminate; η_γ, 1.615. The maximum and minimum indices were readily found.

The material was identified as anhydroquassin by comparing its melting point, mixed melting point, and optical properties with an authentic sample prepared from quassin.

The Action of Acetic Anhydride upon Isoquassin.—Isoquassin treated with acetic anhydride and sodium acetate exactly as was done with neoquassin gave a crude reaction product (0.45 g. from 0.5 g. of isoquassin) which melted between 210 and 230°. This was recrystallized from its solution in boiling methanol by adding an equal volume of water. The product consisted of long rods which melted at 263°. The methanolic mother liquors contained some unchanged starting material. The product melting at 263° was repeatedly recrystallized from one part of boiling acetic anhydride by the addition of two parts of *n*-butyl ether. It then consisted of colorless, spindle-shaped, elongated, six-sided rods which melted at 264°. In parallel polarized light (crossed nicols) the extinction was parallel and the elongation was usually negative, although some rods had positive elongation. In convergent polarized light (crossed nicols) partial biaxial interference figures frequently occurred and occasionally showed one optic axis in the center of the field. η_α, 1.560 (shown on irregular fragments); η_β, 1.575 (lengthwise); η_γ, 1.615 (crosswise).

Anal. Calcd. for $C_{22}H_{28}O_6$: C, 68.00; H, 7.27; OCH_3(2), 16.00. Found: C, 67.92; H, 7.43; OCH_3, 15.8.

DIAGRAMMATIC SUMMARY OF THE REACTIONS UNDER CONSIDERATION



Dehydroquassin prepared from quassin was reported previously[1] as having a melting point of 254°. As there was little doubt that the two materials under consideration here were the same, a new preparation was made from quassin and purified exhaustively by the method used for the preparation from isoquassin. In the process melting points between 256 and 263° were obtained, but it was found that in these preparations the proportions of the spindles and rods varied from one crystallization to another, and this accounted for the variation in melting points. The mixed melting points of the two preparations, *i. e.*, from quassin and isoquassin, were usually depressed slightly. The optical crystallographic properties of the two preparations were identical, however, so there is no doubt as to their identity.

Summary

Certain reactions of neoquassin have been studied and compared with analogous reactions of quassin. The results indicate that the two substances are very closely related. A chart indicating these relationships is presented.

The experiments show that quassin contains two methoxyl groups and probably a tertiary hydroxyl group. The formation of anhydro and dehydro compounds is interpreted as involving reactions of the tertiary hydroxyl group.

WASHINGTON, D. C. RECEIVED OCTOBER 4, 1937

[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, MCGILL UNIVERSITY]

Studies on Reactions Relating to Carbohydrates and Polysaccharides. LIV. The Surface Tension Constants of the Polyethylene Glycols and their Derivatives[1]

BY A. F. GALLAUGHER AND HAROLD HIBBERT

In the liquid state, molecules are probably oriented under certain conditions. A number of liquids have been found which give abnormal values for the Ramsay and Shields constant K. Ramsay and Aston[2] noticed that in long normal aliphatic chains K increases with the number of CH_2 groups in the molecule. Hunten and Maass[3] have shown experimentally that the value of K rises with increase in the length of chain in a homologous series such as the fatty acids. From the point of view of orientation at the surface, it is not necessary to assume dissociation in order to explain the experimental facts. The calculation of the molecular surface to obtain the Ramsay and Shields constant is given by $(M/d)^{2/3}$, that is, it is assumed that the molecules are spherical or cubical in shape. Orientation would imply that a far larger number of molecules can occupy unit area in the case of the long chain derivatives. The longer the carbon chain, the greater the Ramsay and Shields constant, and this is in agreement with the experimental data given by Hunten and Maass.[3] Thus, there exists the possibility of a connection between orientation and abnormal values of the Ramsay and Shields constant. Accordingly, with a homologous series of polar compounds such as the polyethylene glycols, a determination of the surface tension constants such as the total surface energy and the parachor should yield data capable of interpretation in terms of the orientation theory.

Measurement of the Surface Tension.—The surface tension was measured by the capillary rise method. The temperature bath consisted of a four-liter Pyrex beaker, lagged with asbestos and filled with glycerol stirred with a motor-driven propeller. The temperature was regulated to 0.1° by a de Khotinsky thermo-regulator, fitted with a tapping device to prevent lag of the contacts. All temperatures were measured by means of a thermometer calibrated at the German "Reichsanstalt."

The tube in which the surface tension was measured is of the type used by Richards and Coombs[4] with the modification that millimeter scales were etched on the two arms of the tube. By calibrating these scales, the height of a column of liquid in the capillarimeter could be measured with great accuracy. The capillarimeter was made and kept vertical by the use of two plumb lines.

The capillary rise was measured by means of a cathetometer provided with a vernier scale reading to 0.002 cm. and kept vertical by means of a plumb bob. The lighting and observation of the meniscus was similar to that described by Richards and Coombs.

On account of the highly hygroscopic nature of the polyethylene glycols and some of their derivatives, special precautions were necessary to obviate the presence of moisture during the filling of the capillarimeter. An apparatus similar to that shown in Fig. 1 was attached to the top of the capillarimeter and was closed at the top. Through this, air, dried with concentrated sulfuric acid and phos-

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[1] Constructed from a thesis presented by A. F. Gallaugher to the Faculty of Graduate Studies, McGill University, in May, 1932, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy. For the first communication on this subject see THIS JOURNAL, **58**, 813 (1936). Original manuscript received March 9, 1936.

[2] Ramsay and Aston, *Z. physik. Chem.*, **15**, 101 (1894).

[3] Hunten and Maass, THIS JOURNAL, **51**, 159 (1929).

[4] Richards and Coombs, *ibid.*, **37**, 1656 (1915).