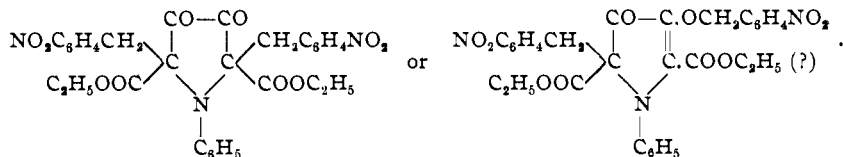


Di-(paranitrobenzyl)-N-phenyl α,α'-dicarbethoxy-β,β'-diketopyrrolidine,



The residue (above) insoluble in water and alcohol, which was apparently the chief product of the reaction, dissolved immediately in glacial acetic acid. When allowed to stand for about two days, the diparanitrobenzyl derivative finally separated in yellow prisms, which melted quite sharp at 132° to a clear oil. This compound was very soluble in boiling alcohol and separated, on cooling, in needle-like prisms which melted at 131-2° to a clear oil. It was insoluble in alkali and a mixture of the compound and the unaltered diethyl ester (m. p. 137°) melted at 109°. Nitrogen determination (Kjeldahl):

Calculated for $\text{C}_{30}\text{H}_{27}\text{O}_{10}\text{N}_8$: N, 7.13. Found: N, 6.98.

Behavior of N-phenyl α,α'-dicarbethoxy-β,β'-diketopyrrolidine towards Hydriodic Acid and Aluminium Amalgam.

Two attempts to reduce this compound with these reagents were unsuccessful. There was no evidence of saponification or reduction after boiling 3.0 grams of the pyrrolidine with 5 cc. of the acid for several minutes. It apparently underwent only slight decomposition by careful treatment and after being separated from the acid and decolorizing with a little sulfur dioxide water, it melted at 135-7° to an oil. By prolonged digestion, the ester was charred and was completely decomposed.

In a second experiment, the pyrrolidine was dissolved in 95 per cent. alcohol and the solution poured upon a large excess of aluminium-amalgam. After allowing to stand for 8-9 hours, when the evolution of hydrogen had ceased, the alcohol solution was filtered, concentrated and cooled. The unaltered diketopyrrolidine separated in needles and melted at 136-7°.

NEW HAVEN, CONN.

A SESQUITERPENE AND AN OLEFINIC CAMPHOR OCCURRING IN SOUTHERN CYPRESS.¹

BY ALLAN F. ODELL.

Received March 9, 1911.

While conducting a series of experiments on the oxidation products of sawdust, it was observed that the ethereal extract from the aqueous oxidation mixture of cypress sawdust left upon evaporation a very fragrant residue. The constant recurrence of this odor in connection with cypress wood led to an investigation of its nature.

The cypress in this section is entirely of the species *Taxodium distichum*,

¹ Paper read before the New Orleans Section, March 17, 1911.

consequently the sawdust, obtained from shingle mills, must have been uncontaminated by allied species, whose resins may differ in constitution.

About ten kilos of sawdust were extracted in a Marx apparatus with 95 per cent. alcohol, in lots of one hundred grams, for eight hours at a time, at the end of which all the alcohol-soluble constituents had been removed. On evaporation of the alcohol, about one hundred grams of a red, viscous resin were left. This was subjected to fractional distillation, at first in a vacuum, but afterward, on account of foaming in the distillation flask, it was found to succeed better by first distilling off the traces of the alcohol and water, to which the resin clung tenaciously at atmospheric pressure, and then fractionating the residue in a vacuum of 35 mm.

The first fraction came over between 180–190°, and consisted of 8 cc. of a light yellow, and very fragrant oil, which gives undoubtedly the essential odor of cypress, though in its concentrated condition it recalled the odor of vanilla somewhat.

The second fraction was collected between 217–222°, and consisted of about 50 cc. of a yellow, very viscous oil, smelling of empyreumatic products, and within twenty-four hours, resinifying to such an extent as to be entirely opaque and dark brown.

There were signs of a yet higher fraction, boiling between 235–245°, but the quantity was so small that it could not be purified with certainty. That which was obtained, solidified on cooling to a clear amber-colored, semi-solid mass.

The fraction boiling between 217–222° presented considerable difficulty in its purification, as the empyreumatic odor and the tendency to resinify were only removed after repeated fractionation, by which the original yield of oil was considerably reduced.

One very pure specimen was obtained by distillation in a cathode vacuum, in which its boiling point was reduced to 125°.

The oil was finally obtained as a yellowish-green, viscous, and almost odorless product, boiling at 218–220°₃₅, and 295–300°_{77.8}, and showing no resinification after standing in the light for a month.

Carbon and hydrogen were found on testing, and a combustion made with the Dennstedt apparatus gave C, 88.46; H, 11.20 per cent. The cryoscopic method gave a lowering corresponding to a molecular weight of 207. The Landesberger method gave an elevation corresponding to a molecular weight of 209, which would determine the compound as a sesquiterpene, C₁₅H₂₄.

The specific gravity was found to be 0.9647^{18°}_{4°}; n_D^{22} 1.5240. The calculated molecular refractivity is 62.55, that found by the Lorenz-Lorentz formula is 64.66; the difference is slightly greater than the increase due to one ethylene linkage.

Its solution in carbon tetrachloride absorbs two molecules of bromine, and there occurs at the same time a variable amount of substitution.

It was at first thought that this sesquiterpene was an impure specimen of cadinene on account of its conduct with moderately concentrated nitric acid. Its action with this was very violent, and yielded a yellow amorphous oxidation product, together with an acid similar in odor to iso-valeric. This yellow substance dissolved in potassium hydroxide to a red solution, and evolved a very fragrant ethereal odor on boiling. The solution of the sesquiterpene, however, in either chloroform or acetic acid, yielded an intense red color immediately on the addition of conc. sulfuric acid, and no intermediate green or blue as in the case of cadinene. Nor was there any appearance of violet as in the case of carrapene. The fact was later established that the compound contained only one ethylene linkage, which classes it with the somewhat rare tricyclic terpenes.¹

It is dextrorotatory, $[\alpha]_D^{20} = +6.53^\circ$ in a 10 cm. tube of the pure substance.

The properties of this compound are not characteristic of any other of the known tricyclic sesquiterpenes, and the name *cypressene* will be given to it to distinguish it in future investigations.

Preliminary experiments upon its oxidation yielded as products much carbon dioxide, and a considerable amount of the ill-smelling acid before mentioned, together with a compound, the nature of which has not been satisfactorily established.

All efforts to obtain the hydrochloride have, as yet, resulted in failure.

The fraction of the resin which distilled between 180–190° was refractionated, and though the quantity was small, a fairly pure distillate was obtained, boiling from 182–185°₃₅. It came over as a light yellow, very fragrant, mobil oil, which on combustion yielded the following: C, 80.28; H, 10.96; O, 8.76 per cent. The Landesberger method gave an elevation corresponding to a molecular weight of 182, giving to the substance the formula $C_{12}H_{20}O$.

Its density is 0.9469^{20°}, n_D^{20} 1.5040. The calculated molecular refractivity, in 53.16, that found by the Lorenz-Lorentz formula, is 56.29; the difference corresponds to two ethylene linkages within the limits of error.

Its solution in carbon tetrachloride adds four molecules of bromine, which result is in harmony with that obtained from its molecular refractivity.

The substance is probably an aldehyde, as it reduces ammoniacal silver nitrate solution readily; and it restores the color to decolorized fuchsin solution. It gives a precipitate when its alcoholic solution is boiled with an alcoholic solution of resorcinol and the mixture is poured into water.

¹ *Chem. Zentr.*, 1901, II, 1226.

It was slightly resinified by boiling with potassium hydroxide solution, but it failed to reduce Fehling's solution even upon continued boiling.

The quantity was not large enough to determine satisfactorily whether a sulfite compound was formed or not, and the attempt to prepare a small quantity of the semicarbazone was unsuccessful.

It is dextrorotatory.

An aldehyde with the formula $C_{12}H_{20}O$, with two ethylene linkages, would be an olefin, homologous with geraniol. The name *cypral* will be given to this compound, as at present no such homolog of the olefinic camphors is known.

As circumstances have made necessary the postponement of this work for several months, the details so far gathered have been given in this paper for the interest of those engaged in terpene investigations.

Summary.

The summary of the physical properties of the two new compounds described is as follows:

Cypressene, $C_{18}H_{24}$, a yellowish-green, viscous, and almost odorless oil, b. p. $218-220^{\circ}_{35}$ and $295-300^{\circ}_{77.8}$. Sp. gr. $0.9647^{18}/_4$. n_D^{22} 1.5240. $[\alpha]_D^{20} = 6.53^{\circ}$. *Cypral*, $C_{12}H_{20}O$, a light yellow, mobil, and very fragrant oil of b. p. $182-185^{\circ}_{35}$. Sp. gr. $0.9469^{20}/_4$. n_D^{20} 1.5040. Dextrorotatory.

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[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

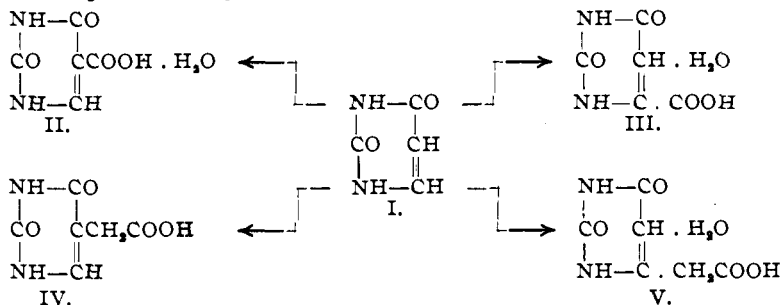
RESEARCHES ON PYRIMIDINES: SYNTHESIS OF CYTOSINE-5-ACETIC ACID.

[FIFTY-FIRST PAPER.]¹

BY TREAT B. JOHNSON (Experimental work by HARLEY T. PECK and JOSEPH A. AMBLER).

Received March 21, 1911.

If one considers only the carbon-substitution products of uracil (I), there are two possible uracilcarboxylic and two uracilacetic acids. They are represented by the structural formulas, II, III, IV, and V.



¹ A list of "Papers on Pyrimidines," previously published from this laboratory, is appended to this paper.