washed with sodium bicarbonate solution and finally with cold water, and the chloroform solution then dried over calcium chloride. Addition of norite was necessary to clarify the solution. The solution was concentrated and finally diluted with petroleum ether, when the above acetyl derivative slowly separated in crystalline form. It was purified by crystallization from boiling ethyl alcohol and melted at 130°. The yield was 2.5 g. The compound did not contain nitrogen. The acetyl number was determined according to the method of Kunz.[4] This same change with loss of the cyanide radical of the cyanoglycoside can also be brought about by heating 1-cyano-2,3,4,6-triacetylglycose with glacial acetic acid at 150° for two hours.

Anal. 0.1181 g. of substance required 16.2 cc. of 0.09495 *N* sodium hydroxide solution. The equivalent amount of β-pentaacetylglycose corresponds to 15.9 cc. of the alkali solution.

Summary

Tetraacetylbromoglycose reacts with silver cyanide to form a cyanophoric glycoside, namely, 1-cyano-2,3,4,6-tetraacetyl-*d*-glycose melting at 76°.

NEW HAVEN, CONN. RECEIVED AUGUST 25, 1934

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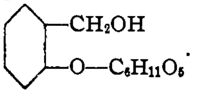
[4] KUNZ, THIS JOURNAL, **48**, 1982 (1926).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

The Structure of Populin

BY NELSON K. RICHTMYER AND ELEANOR H. YEAKEL

Populin, $C_{20}H_{22}O_8$, is a glucoside occurring in the bark, buds and leaves of certain species of poplar. It has long been known that alkaline cleavage produces benzoic acid and the glucoside salicin:



. Since populin can be oxidized to benzoylhelicin, which contains a free aldehyde group, it follows that the benzoyl group is attached not to the ortho CH_2OH, but to one of the hydroxyl groups in the glucose residue.[1] Kitasato,[2] in 1927, attempted to determine the location of the benzoyl group by an enzymatic hydrolysis of populin with taka-diastase, but was unsuccessful in obtaining the benzoyl glucose in a pure or crystalline form.

The following investigation was carried out with synthetic populin, prepared by the action of benzoyl chloride on salicin in the presence of aqueous alkali. The product, according to Dobbin and White,[3] who devised the method, is identical with the naturally-occurring glucoside.

From the methylation of populin by means of methyl iodide and silver oxide, there was obtained a beautifully crystalline tetramethylpopulin. From this the benzoyl group was removed readily by the action of hot sodium methylate. The resulting crystalline tetramethylsalicin has one free hydroxyl group, which, barring a shift during the process of methylation, represents the point of attachment of the benzoyl group in the original populin.

Acid hydrolysis of the tetramethylsalicin produced a sirupy trimethylglucose which was identified by conversion to the well-known 2,3,4-trimethyl-β-methylglucoside. Isolation of this derivative of 2,3,4-trimethylglucose shows that the benzoyl group was originally located on the sixth carbon atom of the glucose residue, and that populin may be designated as 6-benzoylsalicin.

That benzoylation of other glucosides leads to the introduction of the first benzoyl group in the 6-position was established by the reaction of benzoyl chloride with *o*-cresylglucoside. The product, 6-benzoyl-β-*o*-cresylglucoside, was identical with desoxypopulin; the latter was obtained by the hydrogenation of populin in the presence of palladium black, a reaction which is known to convert the ortho-CH_2OH to a -CH_3.

Experimental

Synthetic Populin.—A solution of 20 g. of salicin in 400 cc. of water was stirred vigorously while 25 g. of benzoyl chloride was added to it drop by drop in the course of about three hours; during that time the mixture was kept alkaline to phenolphthalein by the addition of aqueous potassium hydroxide. The product separated as a white granular solid which was filtered and washed well with water. The populin was separated from more highly benzoylated derivatives by extraction with boiling water; it crystallized from the cold solution in fine needles containing water of crystallization. A second crystallization, this time from alcohol, produced good-sized prisms which were solvent-free. The yield was only 8 g.; m. p. 178–179°, with sintering a few degrees lower. It showed $[\alpha]_D$ −2.0° in pyridine ($c = 5$).

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[1] See especially Piria, *Ann.*, **96**, 375 (1855).

[2] Kitasato, *Biochem. Z.*, **190**, 109 (1927).

[3] Dobbin and White, *Pharm. J.*, [IV] **19**, 233 (1904). See also Schiff, *Ann.*, **154**, 1 (1870).

Populin was obtained in smaller yield by adding slowly one equivalent of benzoyl chloride to an ice-cold solution of salicin in pyridine, and allowing the mixture to stand overnight at room temperature. A large amount of more highly benzoylated salicin resulted from this procedure.

β-*o*-Cresyl-*d*-glucoside.—The catalytic hydrogenation of salicin by means of palladium has been reported by Kariyone and Kondo,[4] and by one of us.[5] In the presence of 1 g. of palladium black, at room temperature and atmospheric pressure, one equivalent of hydrogen was absorbed in an hour by a solution of 7.5 g. of salicin in 175 cc. of water. The solution was decanted from the catalyst and a fresh portion of salicin in water added; this hydrogenation proceeded with the same speed as the first. Pure *o*-cresylglucoside was obtained by filtration, evaporation of the water, and crystallization of the residue from ethyl acetate. It crystallizes in needles, melts at 162–163°, and shows $[\alpha]_D$ −68.4° in water ($c = 2$).[6]

Desoxypopulin (6-Benzoyl-β-*o*-cresyl-*d*-glucoside) from Populin.—A solution of 5 g. of populin in 225 cc. of glacial acetic acid, with 2 g. of palladium black, was shaken with hydrogen for sixteen hours; one equivalent of gas was absorbed. The solution was filtered, diluted with water, and then nearly neutralized with solid sodium carbonate. The result was a gelatinous mass which showed no tendency to crystallize, but could be filtered. Crystals were finally obtained by dissolving the product in hot water and leaving the gel, which was formed when cold, in the icebox for several days. The main portion was crystallized by dissolving in hot water, cooling, and inoculating with the crystals already obtained. In the course of a week or more the rather stiff gel was transformed to small needles. The product, which contains water of crystallization, was dried to constant weight at 80° in a Fischer pistol; it absorbs moisture readily when exposed to the air again. The melting point was 148–149°, and $[\alpha]_D$ −13.3° in pyridine ($c = 2$).

Anal. Calcd. for $C_{20}H_{22}O_7$: C, 64.1; H, 5.9. Found: C, 63.7; H, 6.1.

Desoxypopulin from *o*-Cresylglucoside.—To a solution of 5 g. of *o*-cresylglucoside in 20 cc. of dry pyridine, cooled in ice, was slowly added 2.9 g. (1.1 equivalents) of benzoyl chloride. The mixture was allowed to stand overnight at room temperature, then poured on ice. The following day the solidified oil was filtered and extracted with boiling water; there was obtained the typical jelly which slowly rearranged to needles. The yield was less than one gram of anhydrous material, which melted at 148–149°, and showed no depression of melting point when mixed with desoxypopulin from populin itself.

Tetramethylpopulin.—The methylation of populin by means of methyl iodide and silver oxide was carried out in the usual way. Two methylations in methyl alcohol (or acetone) followed by a third methylation in methyl iodide as the solvent resulted in a mixture from which was isolated tetramethylpopulin, and a second solid, m. p. 148–150°, having the composition of a trimethylpopulin which was not further investigated (calcd. for 3 OCH_3 groups: 21.5%; found, 21.6%). The mixture was subjected to three additional methylations in methyl iodide, and again crystallized. From 25 g. of populin was obtained 20 g. of pure tetramethylpopulin; the remainder of the material was sirupy and doubtless contained considerable pentamethylsalicin as a consequence of partial loss of the benzoyl group, evidence for which was the odor of methyl benzoate noted after the several methylations.

Tetramethylpopulin crystallizes from a mixture of ether and petroleum ether in long lustrous needles. It is insoluble in water and petroleum ether, soluble in the usual organic solvents. It melts at 134–135°, and shows $[\alpha]_D$ −31.7° in chloroform ($c = 5$).

Anal. Calcd. for $C_{24}H_{30}O_8$: C, 64.5; H, 6.8; OCH_3, 27.8. Found: C, 64.4; H, 6.9; OCH_3, 28.0.

Debenzoylation to ω,2,3,4-Tetramethylsalicin.—A solution of 19.5 g. of tetramethylpopulin in 400 cc. of methyl alcohol was boiled for fifteen minutes with sodium methylate made from 1.9 g. of sodium (twice the theoretical amount) and 200 cc. of methyl alcohol. The mixture was then diluted with an equal volume of water, and the methyl alcohol removed by concentration *in vacuo*. The tetramethylsalicin, which separated in crystalline form during the process, was extracted with ether and recrystallized with the aid of petroleum ether. The yield was 13.5 g., or 90% of the theoretical.

ω,2,3,4-Tetramethylsalicin is insoluble in water and petroleum ether, soluble in the usual organic solvents. It crystallizes in small needles from ether–petroleum ether, melts at 137–138°, and shows $[\alpha]_D$ −46.4° in chloroform ($c = 3$).

Anal. Calcd. for $C_{17}H_{26}O_7$: C, 59.6; H, 7.7; OCH_3, 36.3. Found: C, 59.6; H, 7.7; OCH_3, 36.1.

Hydrolysis to 2,3,4-Trimethylglucose.—A total of 13.4 g. of the tetramethylsalicin, dissolved in a mixture of 200 cc. of ethyl alcohol and 400 cc. of 2-normal hydrochloric acid, was boiled for two hours with a reflux condenser. The alcohol was then removed by distillation, more water being added from time to time so that the volume in the flask was never less than 400 cc. There remained a colorless aqueous solution and a pink resinous solid, derived from the aglucone, which was removed by filtration but not further investigated. The aqueous solution was saturated with sodium sulfate and extracted thirty times by shaking with chloroform. The chloroform solution left upon evaporation 6.8 g. of a yellowish sirup (theoretical 8.7 g.) which did not crystallize when inoculated with either 2,3,6- or 2,4,6-trimethylglucose.

Conversion to 2,3,4-Trimethyl-β-methyl-*d*-glucoside.—The method has already been described for the 2,3,6-derivative.[7] The sirupy trimethylglucose obtained above, without being purified, was dissolved in 150 cc. of dry ether and saturated at −10° with dry hydrogen chloride gas. The solution turned reddish-brown as it stood overnight at room temperature. The excess hydrogen chloride was then removed by evaporation *in vacuo*, followed by solution of the residue in a fresh portion of dry ether, and

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(4) Kariyone and Kondo, *J. Pharm. Soc. Japan*, **48**, 684 (1928).

(5) Richtmyer, THIS JOURNAL, **56**, 1637 (1934).

(6) β-*o*-Cresylglucoside has also been prepared in a different way by Ryan [*J. Chem. Soc.*, **75**, 1056 (1899)], and by Kunz [THIS JOURNAL, **48**, 262 (1926)], but the rotation was not reported. The $[\alpha]_D$ value of +61.75° of Kariyone and Kondo [*J. Pharm. Soc. Japan*, **48**, 90 (1928) in German] obviously is incorrect in sign.

(7) Freudenberg, Andersen, Go, Friedrich and Richtmyer, *Ber.*, **63**, 1964 (1930).

repeating both processes several times. The resulting sirup was dissolved in 250 cc. of absolute methyl alcohol and shaken for two hours with 15 g. of silver carbonate. The colorless solution obtained by filtration was evaporated to dryness *in vacuo;* the addition of a little dry ether resulted in crystallization so that vacuum distillation became unnecessary.

The glucoside was dissolved in ether, evaporated to dryness, and the crystalline residue extracted with boiling petroleum ether to remove it from a small amount of gummy material. Concentration of the petroleum ether left about 5 g. of the glucoside, which upon recrystallization melted at 93–94°, and showed $[\alpha]_D$ $-19.4°$ in water ($c = 2$). The physical constants and method of preparation identify it as the 2,3,4-trimethyl-β-methylglucoside.[8]

Grateful acknowledgment is made of a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences, which provided the microbalance, weights and palladium used in this work.

Summary

Populin, a glucoside occurring in certain species of poplar, has been methylated with methyl iodide and silver oxide. The resulting tetramethylpopulin was debenzoylated to a tetramethylsalicin, which on hydrolysis with hydrochloric acid yielded 2,3,4-trimethylglucose, identified by conversion to the crystalline 2,3,4-trimethyl-β-methylglucoside. This indicates that populin is 6-benzoylsalicin.

Evidence is presented that benzoylation of glucosides leads to the formation initially of the 6-monobenzoate.

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[8] See for example Oldham, THIS JOURNAL, **56**, 1360 (1934).

NOTES

p-Nitrobenzyl Esters of Organic Acids

BY T. LEONARD KELLY AND MARNELL SEGURA

During the course of a research the following *p*-nitrobenzyl esters were prepared which do not appear in the literature. Since the melting points of these are an aid in the identification of acids they are of value. They were prepared according to the method of Reid and co-workers[1] and were recrystallized to constant melting point. All melting points are uncorrected but were taken in a Fisher melting point apparatus with a set of Anschütz thermometers which gave correct melting points with various pure reagents.

p-NITROBENZYL ESTERS

Acid	M. p., °C.	Nitrogen, %	
		Calcd.	Found
o-Benzoylbenzoic	100.4	3.87	3.84
p-Cyanobenzoic	189.2	9.92	9.87
3,5-Dinitrobenzoic	156.8	12.06	12.14
Glutaric	69	6.93	6.81
Adipic	105.6	6.73	6.88
Suberic	85	6.30	6.26
Azelaic	43.8	6.11	6.18
Itaconic	90.6	7.00	7.10
Diphenic	182.6	5.46	5.63
		Halogen, %	
o-Bromobenzoic	109.8	23.78	24.17
m-Chlorobenzoic	107.2	12.16	12.14
o-Iodobenzoic	110.8	33.14	32.74
m-Iodobenzoic	121	33.14	33.47
p-Iodobenzoic	140.6	33.14	33.60

Caproic, caprylic, pelargonic and capric acids yielded oils which could not be induced to crystallize.

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[1] Reid and co-workers, THIS JOURNAL, **39**, 124, 701, 1727 (1917).

The Thermal Decomposition of Acetone

BY F. O. RICE, EDWARD L. RODOWSKAS AND WARREN R. LEWIS

It has been shown experimentally that when acetone is decomposed in quartz or Pyrex vessels it yields ketene and methane;[1] furthermore, it has been demonstrated that as the percentage decomposition of the acetone is decreased the yield of ketene approaches more and more closely to 100%[2] and therefore the over-all decomposition of acetone must be represented by the equation $CH_3COCH_3 \longrightarrow CH_4 + CH_2{=}CO$.

This reaction may occur either by migration of a hydrogen atom or by rupture of the molecule into CH_3 and CH_3CO, followed by a chain reaction[3]

$$CH_3COCH_3 + CH_3 \longrightarrow CH_4 + CH_3COCH_2 \quad (1)$$

$$CH_3COCH_2 \longrightarrow CH_2{=}CO + CH_3 \quad (2)$$

In order to determine whether the addition of methyl groups brings about a chain reaction in

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[1] Rice and Vollrath, *Proc. Nat. Acad. Sci.*, **15**, 702 (1929).

[2] Rice, Greenberg, Waters and Vollrath, THIS JOURNAL, **56**, 1760 (1934).

[3] It is of course possible that both of these reactions proceed simultaneously.