

stilbene was obtained. This oxime could be crystallized from alcohol but ligroin proved to be a better solvent. A yield of 0.80 g. was obtained which crystallized in long colorless needles and melted at 152° (corr.). A mixed melting point determination showed that the oximes were unlike.

Summary

1. By means of the Grignard reaction both isomeric (α and β) *p*-dimethylamino-*p'*-chlorobenzoin have been synthesized. The benzoin as prepared by condensing *p*-dimethylaminobenzaldehyde and *p*-chlorobenzaldehyde was found to be *p*-chloro- α -hydroxybenzyl *p'*-dimethylaminophenyl ketone (β isomer) and has the structure $(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{-COCHOHC}_6\text{H}_4\text{Cl}$.

2. Under the influence of potassium cyanide, α -*p*-dimethylamino-*p'*-chlorobenzoin was found to rearrange and produce the β -isomer.

3. Upon reduction under suitable conditions, the α -benzoin produced *p*-dimethylaminobenzyl *p'*-chlorophenyl ketone. Under similar treatment, however, the β -benzoin produced the above ketone and also its isomer, *p*-chlorobenzyl *p'*-dimethylaminophenyl ketone. Nine new substances were prepared and characterized in the course of this work.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

THE AUTOXIDATION OF ALPHA NORMAL-AMYL CINNAMIC ALDEHYDE. CIS- AND TRANS-ALPHA-NORMAL-AMYL-CINNAMIC ACIDS

BY MARSTON T. BOGERT AND DAVID DAVIDSON¹

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Introduction

In the course of our study of the rates of autoxidation of commercial aldehydes,² we were led to examine the products resulting from the action of air on α -*n*-amylcinnamic aldehyde, $\text{C}_6\text{H}_5\text{CH}=\text{C}(\text{Am})\text{CHO}$. Since, in general, the action of air or oxygen on an aldehyde leads to the formation of the corresponding acid through the intermediate per-acid, thus³



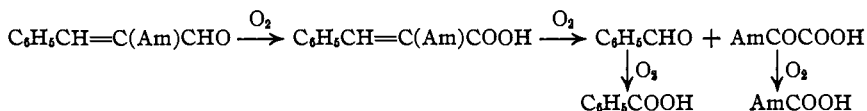
and, since unsaturated aldehydes such as crotonaldehyde and cinnamic aldehyde behave in accordance with this formulation, we expected that this aldehyde would yield α -amylcinnamic acid. Investigation revealed, however, that, when blown with air, α -amylcinnamic aldehyde undergoes

¹ Senior Research Assistant of the American Manufacturers of Toilet Articles.

² Bogert and Davidson, *Am. Perfumer Ess. Oil Rev.*, **24**, 587, 667 (1929-1930).

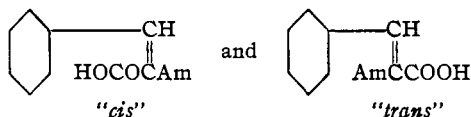
³ Baeyer and Villiger, *Ber.*, **33**, 1582 (1900); Jorissen and van der Beek, *Rec. trav. chim.*, **45**, 245 (1926); **47**, 286 (1928); H. L. J. Bäckström, *Medd. Vetenskapsakad. Nobelinst.*, **6**, No. 15 (1927).

a complex autoxidation reaction leading to the formation of caproic acid, benzoic acid and a form of α -amylcinnamic acid melting at 40° , as well as benzaldehyde and other, as yet unidentified, neutral substances. The production of the three acids mentioned indicates that both the aldehyde and the ethylene functions are attacked by oxygen, perhaps as follows



Two Alpha-Amylcinnamic Acids.—Since α -amylcinnamic acid had not previously been described in the literature, it was desirable to prepare it in order to compare it with the product obtained in the autoxidation of the aldehyde. Four methods of synthesis were employed: (1) the condensation of benzaldehyde with sodium heptanoate (Perkin-Stuart),⁴ (2) the condensation of benzaldehyde with methyl heptanoate by means of sodium (Claisen),⁵ (3) the condensation of benzal chloride with sodium heptanoate⁶ and (4) the condensation of benzaldehyde with methyl hexyl ketone by means of hydrogen chloride, followed by oxidation with sodium hypochlorite. In each case an α -amylcinnamic acid was obtained which melted at 80° and was entirely distinct from that obtained by the autoxidation of the aldehyde.

The Configuration of the Alpha-Amylcinnamic Acids.— $\text{C}_6\text{H}_5\text{CH}=\text{C}(\text{Am})\text{COOH}$ may be represented by the two space formulas



In harmony with the configurations of the two cinnamic acids we shall designate as "*cis*" that form of α -amylcinnamic acid in which the phenyl and carboxyl groups are *cis*.

The 40° acid differs from the 80° acid in that it forms an insoluble aniline salt in petroleum ether. By analogy with the behavior of the *cis*- and *trans*- α -methylcinnamic acids,⁷ this marks the 40° acid as the *cis* form. Striking confirmation of this configuration is obtained in the behavior of the two acids toward concentrated sulfuric acid. While the 80° acid dissolves readily to form a colorless solution from which it is precipitated unchanged by water, the 40° acid forms a deep blue solution from which ice precipitates a yellow, sweet-smelling oil, freezing at 4° (α -amylyndone).

⁴ Stuart, *J. Chem. Soc.*, **43**, 406 (1883).

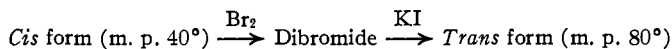
⁵ Claisen, *Ber.*, **23**, 977 (1890).

⁶ Badische Anilin und Sodafabrik. German Patent 17,467, 18,232 (1880); *Friedländer*, **1**, 26, 28 (1888).

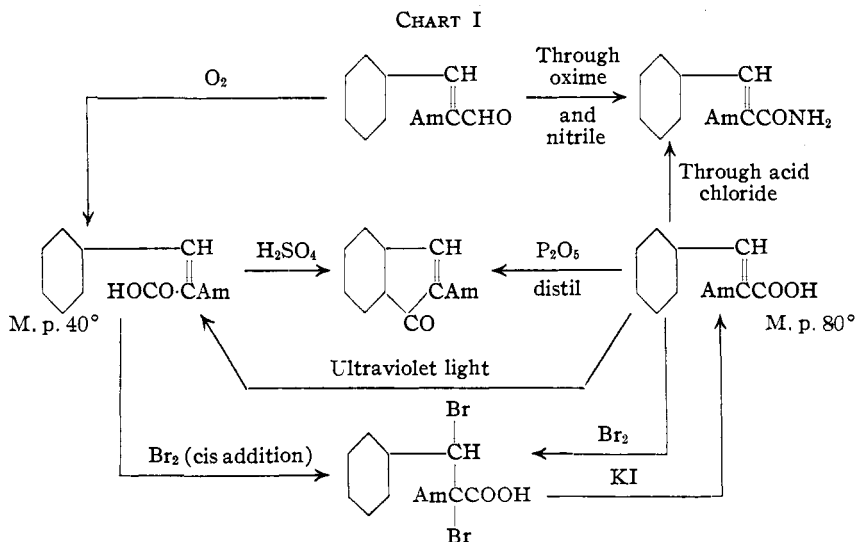
⁷ Stoermer and Voht, *Ann.*, **409**, 36 (1915).

Although the 80° acid is unattacked by cold concentrated sulfuric acid, it yields this same amylyndone when distilled with phosphorus pentoxide. That the two acids yield the same indone but with different ease at once establishes their isomerism and their respective configurations. The 40° acid, because of the readiness with which ring formation occurs between the ortho position in the benzene ring and the carboxyl group, is, therefore, the *cis*, while the 80° acid is the *trans* form.

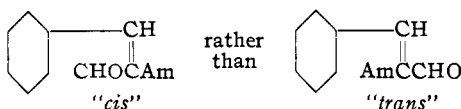
Further confirmation of the isomerism of the two acids is obtained in their yielding the same dibromide, melting at 143–144°. Since the latter can be reduced to the *trans* acid melting at 80° by means of potassium iodide, a means was had of converting the *cis* acid melting at 40° to its geometric isomer, thus



The reverse transformation of the *trans* to the *cis* form was accomplished by means of ultraviolet light. The reactions just discussed are summarized in Chart I.



The Configuration of Alpha-Amylcinnamic Aldehyde.—Having established the configuration of the α -amylcinnamic acids beyond a reasonable doubt, and recalling that the *cis* form of the acid had been obtained by autoxidation of the aldehyde, it appeared that the commercial aldehyde possessed the *cis* configuration



Further investigation, however, showed that commercial α -amylcinnamic aldehyde is really closely related to the *trans*- α -amylcinnamic acid, m. p. 80°, and that, therefore, it has the *trans* configuration.

Thus, direct oxidation of the aldehyde to the acid by means of silver oxide yielded *trans*- α -amylcinnamic acid, identical with that obtained by other syntheses. Furthermore, the series of reactions, $\text{RCHO} \longrightarrow \text{RCH}=\text{NOH} \longrightarrow \text{RCN} \longrightarrow \text{RCONH}_2$, yielded an α -amylcinnamamide, melting at 117°, which was also obtained from *trans*- α -amylcinnamic acid through the acid chloride.

We are forced to the conclusion that although ordinary α -amylcinnamic aldehyde is the *trans* form, it reacts with oxygen to give (among other products) the *cis* form of α -amylcinnamic acid.⁸ This inversion accompanying autoxidation may be explained by means of the following considerations. Stoermer and his co-workers have demonstrated that the *trans* forms of cinnamic acids are converted into the less stable *cis* forms by ultraviolet light.⁹ On the other hand, several investigators have found that the autoxidation of aldehydes is a chemiluminescent reaction.¹⁰ We may assume, therefore, that the radiation (or energy) emitted by the autoxidation of α -amylcinnamic aldehyde is absorbed by the product, namely, *trans*- α -amylcinnamic acid, which is thereby converted into its geometric isomer.

It is true that the experimental results do not enable us to decide whether this rearrangement of *trans* to *cis* configuration occurs wholly or partly in the initial aldehyde, the per-acid, or the *trans* acid stage but, in the absence of such evidence, we have assumed what seems to us the simplest interpretation of our observations.

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Experimental

Autoxidation of α -*n*-Amylcinnamic Aldehyde.—In a darkened chamber 136.1 g. (0.675 mole) of freshly distilled α -amylcinnamic aldehyde, boiling at 161–163° at

⁸ It should be mentioned that Erlenmeyer, *Ber.*, **38**, 2562 (1905), claims to have obtained *cis*-cinnamic acid (allocinnamic acid) from the partial autoxidation of cinnamic aldehyde, but no details are given.

⁹ Stoermer and Heymann, *Ber.*, **46**, 1256 (1913); **45**, 3099 (1912); Stoermer and Voht, *Ann.*, **409**, 36 (1915); Stoermer, Grimm and Laage, *Ber.*, **50**, 959 (1917); Stoermer and Foerster, *ibid.*, **52**, 1263 (1919).

¹⁰ Radziszewski, *Ann.*, **203**, 307 (1880); Perkin, *J. Chem. Soc.*, **41**, 365 (1882); Schorigen and Trautz, *Z. wiss. Phot.*, **3**, 121 (1905).

16 mm., contained in a gas wash bottle, was blown with air, the issuing gas being passed through a second wash bottle containing dilute sodium carbonate. The increase in acidity was determined occasionally by titrating 0.2 cc. of the oil dissolved in 25 cc. of alcohol with standard sodium hydroxide solution using phenolphthalein as an indicator. The progress of the reaction is indicated in Fig. 1. After forty-two days the residual oil weighed 131.5 g. (not allowing for 2.4 cc. which had been removed for titration) and contained approximately 0.47 mole of monobasic acids. The oil was agitated with a solution of 52 g. of sodium carbonate in 500 cc. of water and then treated with ether to aid in the separation of the neutral oil from the aqueous extract. A small amount of sodium bicarbonate separated and was filtered off. The aqueous layer was extracted a second time with ether and the ether layers combined (E).

The aqueous layer was distilled to remove ether and volatile non-acidic constituents, about 300 cc. of water being collected. A mixture of 100 cc. of hydrochloric acid and 100 cc. of water was then added to the residue, and the distillation resumed, water being added from time to time. About 800 cc. of distillate (D) was collected, which contained a volatile oily acid (caproic). The residue (R) crystallized partially on standing overnight. D was made alkaline, concentrated by evaporation, acidified and distilled. The residue yielded crystals of a solid acid (benzoic). The distillate was treated as before, the oily acid finally being separated, dried over phosphorus pentoxide, and distilled (b. p. 201–208°; yield, 18.5 g.). When esterified with methyl alcohol and hydrogen chloride gas it yielded a fruity

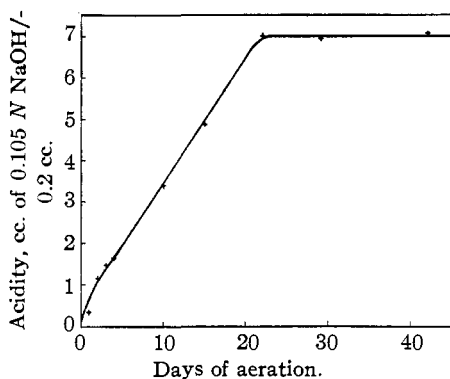


Fig. 1.

ester, boiling at 148–151°, which, when allowed to stand for two weeks with an equal volume of concentrated ammonia, yielded an amide, m. p. 99–100°. The acid was, therefore, *n*-caproic.

The residue (R) was filtered and the solid acid combined with the solid obtained in the purification of the caproic acid. When recrystallized from water, it yielded 7.5 g. of glistening platelets, melting at 121–122°. It was identified as benzoic acid by means of a mixed melting point, and examination of the methyl ester and amide.

The filtrate from residue (R) contained a dark oil which was distilled under diminished pressure giving the following fractions: (1) 6.7 g. partly solid, b. p. 130–190° at 18 mm., (2) 17.1 g. of a viscous yellow liquid, b. p. 190° at 18 mm., 215° at 14 mm., and a residue of 6.8 g. Fraction (1) was dissolved in dilute sodium hydroxide and the solution distilled to remove any non-acidic products formed in the distillation. The residue was then acidified with hydrochloric acid. The resulting oil yielded 2.9 g. of crude benzoic acid when extracted with hot water. Fraction (2), when chilled, deposited 2.8 g. of crystals melting at 38–39°. The filtrate was distilled, boiling mainly at 194° at 15 mm. The distillate yielded 3.6 g. of acid, m. p. 38–39°, while a further quantity was obtained from the oily filtrate and other residues by dissolving in petroleum ether and precipitating with aniline. The acid was purified by precipitating the aniline salt, m. p. 65°, decomposing the latter with dilute hydrochloric acid, separating the acid, dissolving in dilute sodium hydroxide, clarifying with norite, and finally liberating the acid. This separated as an oil which slowly crystallized (m. p. 40°). Further

precipitation of the aniline salt did not affect the melting point. The acid is exceedingly soluble in all common organic solvents.

Titration. 154 mg. required 8.56 cc. of standard alcoholic sodium hydroxide (0.0828 *N*). 155 mg. required 8.57 cc. Equivalent weight: calcd., 218. Found: 218, 219.

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.0; H, 8.3. Found: C, 76.9; H, 8.3.

These results indicate the substance to be an α -amylcinnamic acid.

The ether layer (E) which contained the oil from which the acids had been extracted with sodium carbonate was shaken twice with half-saturated sodium bisulfite solution. The bisulfite layers were combined and treated with hydrochloric acid, the sulfur dioxide removed by warming, and the resulting oil separated. It boiled at 174–177° and had the odor of *benzaldehyde*; yield, 1.3 g.¹¹ Its identity was confirmed by treating it with alcohol and concentrated ammonia, when colorless crystals, melting at 103°, were obtained (hydrobenzamide).

The ether layer from which the benzaldehyde had been separated was washed with sodium carbonate, dried with calcium chloride, and the ether evaporated. The residual oil weighed 61.7 g. It distilled with some decomposition at 17 mm., 49.0 g. yielding 25.6 g. of material boiling below 180° and 23.2 g. of a dark viscous residue. Redistillation yielded 12.2 g., boiling at 110–150° at 15.5 mm. (mainly at 143–150°) and 6.0 g. boiling at 150–170° at 15.5 mm. Both fractions yielded a small amount of a solid semicarbazone which has not been obtained sufficiently pure to be identified.

Syntheses of α -Amylcinnamic Acid, m. p. 80°. (1) **Perkin–Stuart Method.**—A mixture of 25 g. of benzaldehyde, 35 g. of sodium heptoate and 67 g. of heptioic acid was refluxed for thirty hours. The mixture was then distilled at 20 mm. from a bath at 180°. The residue was dissolved in boiling water and acidified with hydrochloric acid, the oil separated, the water layer extracted with ether, and the extract combined with the oil. The ether solution was extracted with sodium carbonate, the water layer extracted several times with ether to remove resinous material, warmed with norite on the hot-plate, and filtered. The almost colorless solution of sodium salts was then acidified, the oil extracted, the extract dried with sodium sulfate, the ether evaporated, and the oil distilled at 2 mm. Much heptioic acid was recovered and finally 1.6 g. (3.2%) of α -amylcinnamic acid boiling at 161° at 2 mm. and melting at 69° was obtained. When purified through the sodium salt the melting point rose to 74°, and from 75% acetic acid to 80°.

(2) **Claisen Method.**—The directions given in "Organic Syntheses" for the preparation of ethyl cinnamate¹² were adapted for the production of methyl α -amylcinnamate by substituting methyl heptoate for ethyl acetate. The excess of methyl heptoate was removed at 20 mm. and the residue distilled at 2 mm. The fraction boiling at 130–180° at 2 mm. and weighing 20 g. was saponified with methyl alcoholic potassium hydroxide and the acid separated. After steam distilling to remove heptioic acid, several recrystallizations from dilute alcohol yielded 6.5 g. (8%) of α -amylcinnamic acid melting at 76°. Further recrystallization from 75% acetic acid gave a product melting at 80°.

(3) **Badische Method.**—Seven grams of sodium was dissolved in 65 g. of heptioic acid, 16.1 g. of benzal chloride added and the mixture refluxed for thirty hours. The product was isolated as in (1); yield, 6.0 g. (28%), m. p. 80°.

¹¹ Much of the benzaldehyde produced must have been lost during the aeration, since a pronounced odor of benzaldehyde was noted in the issuing air after seventeen days.

¹² "Organic Syntheses," John Wiley and Sons, Inc., New York, 1929, Vol. IX, p. 38.

(4) The most satisfactory method of preparation of α -amylcinnamic acid involves the condensation of benzaldehyde with methyl hexyl ketone, followed by oxidation of the intermediate methyl α -amyl styryl ketone with hypochlorite. The details of this method will appear in a subsequent paper; yield, about 70%, m. p. 80°.

Titration. 151 mg. required 8.34 cc. of standard alcoholic sodium hydroxide (0.0828 *N*). 149 mg. required 8.24 cc. Equivalent weight. Calcd., 218. Found: 219, 218.

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.0; H, 8.3. Found: C, 77.0; H, 8.2.

Oxidation of α -Amylcinnamic Aldehyde with Silver Oxide.—To a boiling mixture of 5 g. of silver nitrate in 3 cc. of water, 2 g. of α -amylcinnamic aldehyde and 30 cc. of alcohol was added a hot solution of 2.5 g. of potassium hydroxide in 30 cc. of alcohol. The boiling was continued, water being added to replace the volatilized alcohol. After thirty minutes the alcohol was entirely removed. The clear straw-colored supernatant layer was decanted from the silver and the latter leached several times with boiling water. The combined liquors were acidified with acetic acid, whereupon slightly discolored *trans*- α -amylcinnamic acid, m. p. 78°, separated; yield, 1.7 g. (77%). Recrystallization from 75% acetic acid gave needles melting at 80°.

α -Amylcinnamaldoxime.¹³—50.5 g. of α -amylcinnamic aldehyde, 100 cc. of alcohol, 17.5 g. of hydroxylamine hydrochloride, and 34 g. of sodium acetate trihydrate were refluxed for an hour. On cooling and diluting with water, 44.2 g. of oxime, m. p. 74°, was obtained. It was recrystallized by dissolving in alcohol and diluting with water.

α -Amylcinnamionitrile.—27.5 g. of the oxime was boiled for three hours with one and one-half moles of acetic anhydride and one gram of anhydrous sodium acetate. The mixture was cooled and cautiously treated with dilute sulfuric acid to decompose the excess of acetic anhydride. It was then largely diluted with water, the nitrile extracted with benzene, the extract washed with sodium carbonate solution and dried over sodium sulfate. The benzene was removed and the residue distilled. The product was practically pure α -amylcinnamionitrile, b. p. 173° at 18 mm., 165° at 13 mm. and 135° at 3 mm.; yield, 21 g. (83%).

Anal. Calcd. for $C_{14}H_{17}N$: C, 84.4; H, 8.5. Found: C, 84.4; H, 8.5.

α -Amylcinnamamide.—1.7 g. of the nitrile was refluxed for eight hours with a solution of 2 cc. of 50% sodium hydroxide and 15 cc. of *n*-propyl alcohol. Dilution of the alcoholic solution gave a solid, which was recrystallized from dilute alcohol and finally from ethyl acetate-petroleum ether, giving silky needles, m. p. 117°, identical with the product obtained below.

Anal. Calcd. for $C_{14}H_{19}ON$: C, 77.4; H, 8.8. Found: C, 77.4; H, 9.0.

α -Amylcinnamide from α -Amylcinnamic Acid.—One gram of α -amylcinnamic acid, m. p. 80°, was heated under reflux at 80–90° for one hour with 5 cc. of thionyl chloride. The excess of thionyl chloride was then distilled off and the residue treated with concentrated ammonia. The solid obtained was recrystallized from dilute alcohol and finally from ethyl acetate-petroleum ether, giving silky needles, m. p. 117°, identical with the product obtained above.

Action of Sulfuric Acid on 40 and 80° α -Amylcinnamic Acids.—1.09 g. of *cis*- α -amylcinnamic acid, m. p. 40°, was added to 11 cc. of chilled concentrated sulfuric acid. The acid readily dissolved, giving a deep blue solution. The mixture was stirred for a few minutes to complete solution and then poured on ice. The yellow oil was extracted with ether, the extract washed with water and then with 10% sodium carbonate. Evaporation of the ether gave 0.9 g. of a brown oil. Distillation at 20 mm.

¹³ Rutovski and Korlev, *J. prakt. Chem.*, 119, 272 (1928).

gave 0.65 g. of a golden brown oil, which solidified to a yellow solid, m. p. 4°, when placed in a freezing mixture. The oil had an odor resembling amyl salicylate. For identification and analysis, the substance was converted into its oxime; 0.65 g. of the indone gave 0.53 g. of golden yellow leaflets, which, when recrystallized from 80% methanol, melted at 75° and were identical with the product obtained below.

Anal. Calcd. for $C_{14}H_{17}ON$: C, 78.1; H, 7.9. Found: C, 78.4; H, 8.2.

A parallel experiment with 1.09 g. of *trans*- α -amylcinnamic acid, m. p. 80°, and 11 cc. of concentrated sulfuric acid gave a colorless solution, which when thrown on ice precipitated a colorless solid. Recrystallized from 75% acetic acid, this yielded 0.94 g. of needles, m. p. 80°. A mixture with *trans*- α -amylcinnamic acid also melted at 80°.

Formation of α -Amyl Indone from *Trans*- α -amylcinnamic Acid.—5.45 g. of *trans*- α -amylcinnamic acid, m. p. 80°, and 8 g. of phosphorus pentoxide were placed in a Claisen flask and well mixed by shaking. Distillation with a free flame at 17 mm. gave a golden brown distillate, b. p. 157–158° at 17 mm., which froze at 1–2° to a yellow solid. When added to concentrated sulfuric acid it formed a deep blue solution. Its odor was reminiscent of amyl salicylate; yield, 4.0 g. (80%). It was identified as α -amyl indone by conversion to the oxime according to the method of Schmidt and Söll.¹⁴ One gram of the indone was refluxed for one and one-half hours with 0.35 g. of hydroxylamine hydrochloride and 0.5 g. of barium carbonate powder in 15 cc. of methanol. The mixture was then cooled, filtered and diluted with water; 0.77 g. of yellow leaflets, m. p. 74°, were obtained and 0.28 g. of further material upon further dilution of the mother liquor. Recrystallization from twenty parts of methanol and five parts of water gave golden yellow leaflets, m. p. 75°, identical with the product obtained above.

Action of Bromine on *Trans*- α -amylcinnamic Acid.—2.18 g. of *trans*- α -amylcinnamic acid, m. p. 80°, was dissolved in 25 cc. of carbon tetrachloride, and 0.6 cc. of bromine added to the solution in diffused daylight. Decolorization soon occurred, whereupon the carbon tetrachloride was removed by means of a current of air and the residue treated with petroleum ether and chilled; 2.3 g. of a dibromide m. p. 137–139° was obtained. Recrystallization from carbon tetrachloride–petroleum ether raised the melting point to 143–144°.

Anal. Calcd. for $C_{14}H_{13}O_2Br_2$: C, 44.5; H, 4.8. Found: C, 43.7; H, 4.6.

Transformation of *Cis*- α -amylcinnamic Acid, m. p. 40°, to *Trans*- α -amylcinnamic Acid, m. p. 80°.—1.09 g. of *cis*- α -amylcinnamic acid, m. p. 40°, was dissolved in a few cc. of petroleum ether and excess of bromine added to the solution in diffused daylight. As the bromine was absorbed, heat was evolved, a little hydrogen bromide appeared and a crystalline deposit formed on the walls of the flask. After four hours the flask was chilled, the mother liquor poured off and the crystalline deposit washed with petroleum ether; 1.13 g. of a flesh-colored cake was obtained which melted at 139–140°. Recrystallization from carbon tetrachloride–petroleum ether gave a colorless product, m. p. 143–144°. A mixture with the product obtained above also melted at 143–144°; 0.95 g. of this product, 1.7 g. of potassium iodide and 10 cc. of alcohol were refluxed for twenty minutes. The mixture was then diluted with dilute sodium bisulfite solution, whereupon a precipitate of 0.57 g. of crude *trans*- α -amylcinnamic acid was obtained, which, when recrystallized from 75% acetic acid, gave 0.39 g. of needles, m. p. 80° (mixed melting point). The acid obtained gave a colorless solution in concentrated sulfuric acid.

Transformation of *Trans*- α -amylcinnamic Acid, m. p. 80°, to *Cis*- α -amylcinnamic

¹⁴ Schmidt and Söll, *Ber.*, 40, 2455 (1907).

Acid, m. p. 40°.—2.18 g. of *trans*- α -amylcinnamic acid, m. p. 80°, spread out on a plate and placed at a distance of about fifteen inches from a Hanovia quartz mercury arc was irradiated for about 120 hours. The acid then melted at about 70° and gave a deep blue color with concentrated sulfuric acid. It was triturated with petroleum ether and filtered. The residue weighed 1.1 g., melted at 80° and gave a practically colorless solution in sulfuric acid. The petroleum ether extract was treated with several drops of aniline and seeded with the aniline salt of *cis*- α -amylcinnamic acid. A crop of long felted needles, m. p. 66° and weighing 0.41 g., was obtained. On decomposing the latter with dilute hydrochloric acid, 0.28 g. of *cis*- α -amylcinnamic acid, m. p. 38–39° (mixed melting point), was obtained. The product gave a deep blue color with sulfuric acid.

Summary

1. The α -amylcinnamic aldehyde of commerce is the *trans* isomer, since it is converted into *trans*- α -amylcinnamic acid by means of silver oxide, and into *trans*- α -amylcinnamamide through the oxime and the nitrile.

2. Autoxidation of α -amylcinnamic aldehyde proceeds readily at room temperature in the dark. Profound attack of the aldehyde ensues, leading to the production of caproic acid, benzoic acid and *cis*- α -amylcinnamic acid, m. p. 40°. The inversion of the *trans* to the *cis* form is accounted for by the chemiluminescence of the primary autoxidation.

3. Four methods of synthesis of α -amylcinnamic acid led to the same *trans* form, m. p. 80°.

4. The *cis* configuration of the 40° form of α -amylcinnamic acid is established by its ready formation of an indone. The *trans* form undergoes the same reaction, but only under much more vigorous conditions.

5. *Cis*- α -amylcinnamic acid is converted into the *trans* form through the dibromide.

6. *Trans*- α -amylcinnamic acid is converted to the *cis* form by means of ultraviolet light.

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