solution with chromic anhydride. The crude keto acid was purified by solution in alkali and reprecipitation by hydrochloric acid. The pale brownish flocculent precipitate which separated (yield, about 20%) was crystallized twice from benzene, and gave small white crystals, m. p. 154–155° (corr.), in agreement with the melting point reported by Tiemann and Krüger for their "trioxydehydroirene."

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.90; H, 7.27; neut. equiv., 220. Found: C, 70.70; H, 7.28; neut. equiv., 222.

Tiemann and Krüger purified their crude acid by solution in sodium carbonate and reprecipitation by carbon dioxide, but we found that method troublesome and unsatisfactory.

Our product gave a very definite iodoform test, indicative of the presence of the acetyl group. It is not clear why Tiemann and Krüger assigned to this acid a constitution which contained neither an acetyl nor a carboxyl group, although they recognized its acidic character. The structure we have proposed is what one would expect if the oxidation followed the same course as in the case of ionene (IX).[5]

As by-products in this oxidation, some unchanged irene was recovered, and a small amount of a substance of agreeable peppermint-like odor, which was not isolated in sufficient quantity for further study.

Alpha - (4 - methyl - 2 - carboxyphenyl) - isobutyric acid (XXIV) has been isolated by Bogert and Fourman[5] as one of the oxidation products of ionene. Attempts to obtain this acid, by the action of hypohalite upon a small amount of the foregoing ketone acid (XXIII), were not very satisfactory. The product melted at 139–144°, and was apparently a mixture of the acid sought (m. p. 131°) and the unaltered ketone acid (m. p. 154–155°). The quantity available was insufficient for further purification.

Alpha-(2,4-dicarboxyphenyl)-isobutyric Acid (4-Carboxy-alpha, alpha-dimethylhomophthalic Acid) (XXI).—Irene (VII) was refluxed for eight hours with an excess of saturated alkaline (sodium hydroxide) potassium permanganate. When cold, the reaction mixture was decolorized with sodium bisulfite, filtered from the precipitated manganese oxides, and the filtrate acidified with hydrochloric acid. The heavy white amorphous precipitate which separated was purified by solution in aqueous sodium hydroxide and reprecipitated by the addition of mineral acid. This is the "ioniregentricarboxylic acid" of Tiemann and Krüger. It has no sharp melting point, but passes gradually into its anhydride (XXII) when heated.

The neutralization equivalent of our acid was found to be 84; calculated for $C_{12}H_{12}O_6$, 84. The melting point of the anhydride was 214° (corr.); as compared with 214° reported by Tiemann and Krüger;[2] 214–215° (corr.), given by Pope and Bogert;[9] and 217° (corr.), found by Bogert and Fourman.[5]

Summary

1. The 1,1,2,6-tetramethyltetralin structure for irene (VII), proposed by Ruzicka, Seidel, and Schinz, has been supported by the synthesis of this tetralin from *m*-bromotoluene.

2. This synthetic irene (VII), which is a methyl homolog of ionene (IX), yields the same oxidation products as the irene (VII) prepared from the irone of the orris root.

3. The $C_{13}H_{18}$ formula given by Tiemann and Krüger for irene (VI), should be replaced by $C_{14}H_{20}$, in conformity with the results obtained by Ruzicka, Seidel, and Schinz, and with those reported above.

4. An explanation is offered as to why Tiemann and Krüger obtained C_{13} oxidation products from a C_{14} hydrocarbon.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF FRITZSCHE BROTHERS, INCORPORATED]

Identification of Citral in California Orange Oil

BY ERNEST S. GUENTHER AND CHARLES H. GRIMM

This investigation was undertaken for the purpose of identifying citral in California orange oil.

According to H. D. Poore,[1] who made an investigation of California orange oil, decylic aldehyde is the only aldehyde present in this oil. Nelson and Mottern[2] identified citral in the oil of Florida Valencia oranges. In the isolation of citral from the terpeneless oil, Nelson and Mottern used the sodium sulfite method of Tiemann.[3] This might be the reason why H. D. Poore, who used sodium bisulfite, was unable to identify citral in California sweet orange oil. Semmler[4] had identified citral in Italian sweet orange oil as far back as 1891, but K. Stephan[5] found only decylic aldehyde in Italian orange oil. However, Stephan like Poore had used the bisulfite method in extracting the aldehydes from the terpeneless oil.

Y. R. Naves,[6] well aware of the existing contradiction between Semmler's and Stephan's findings

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(1) H. D. Poore, Tech. Bull. 241, U. S. Dept. of Agriculture, 1932.

(2) Nelson and Mottern, THIS JOURNAL, **56**, 1238 (1934).

(3) Tiemann, *Ber.*, **31**, 3318–3320 (1898).

(4) Semmler, *ibid.*, **24**, 202 (1891).

(5) K. Stephan, *J. prakt. Chem.*, [II] **62**, 523 (1900).

(6) Y. R. Naves, *Parfums de France*, **112**, 161 (1932).

and the possibility that a small amount of citral may escape observation if isolated by the bisulfite compound, established the presence of citral in sweet orange oil from French Guinea.

Because of the unmistakable odor of citral in California orange oil concentrates and terpeneless oils, and with a view to proving conclusively that citral is actually present in California sweet orange oil, we submitted this oil to a closer investigation.

Two thousand two hundred and fifty grams of absolutely pure California orange oil (a mixture of the oil from Valencia and Washington Navel oranges) supplied by the California Fruit Growers Exchange and of guaranteed manufacture, was distilled at reduced pressure (11 mm.), the limonene removed, and the residue steam-distilled. The so-called terpeneless oil (87 g.) was then examined for citral.

The aldehydes of the oil were separated by the Tiemann[3] method because by the usual method of shaking with a solution of sodium bisulfite the citral tends to go into solution as the stable dihydrosulfonic acid derivative from which this aldehyde cannot be regenerated.

The terpeneless oil was shaken for twelve hours with a solution of 20 g. of sodium sulfite and 27 g. of sodium bicarbonate in water. After standing for twenty-four hours at 2° the bisulfite compound was separated out. This was mainly the decylic aldehyde compound.

The aqueous solution was then separated from the oil and washed with ether, and an addition of 20% sodium hydroxide solution was made. The separated oil was then extracted with ether and careful evaporation of the ether gave an oil (2.2 g.) with a very pronounced odor of citral. The odor verification was made by five of our leading authorities.

The α-citral-β-naphthocinchoninic acid derivative was prepared according to Doebner[7] and purified by washing with ether. The yellow laminae melted at 199° and a mixture prepared in the same manner from pure citral gave no depression in the melting point.

The semicarbazone derivative was also prepared and recrystallized three times from methyl alcohol. This semicarbazone melts at 130 to 131°. (These data agree with the Wilson and Keenan[8] results which were reported on a mixture of α- and β-citral semicarbazones of melting point 132°.) When the mixture was treated with ether according to Parry,[9] crystals of α-citral semicarbazone were obtained which melted at 163°. We can thus assume that the citral in California orange oil is a mixture of the α- and β-varieties.

Semmler[4] reported the presence of citral in Italian orange oil, Y. R. Naves[6] in French Guinea orange oil, and Nelson and Mottern[2] in Florida Valencia orange oil. These findings are in agreement with those of the writers.

Summary

Citral in the form of α-β-isomerides has been shown to be present in California orange oil.

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[7] Gildemeister and Hoffmann, "The Volatile Oils," English translation, 2nd Edition, John Wiley and Sons, New York, N. Y., Vol. I, p. 412.

[8] Wilson and Keenan, *J. Assoc. Official Agr. Chem.*, **13**, 394 (1930).

[9] Parry, "Chemistry of Essential Oils and Artificial Perfumes," 3rd Revised Edition, D. Van Nostrand, Co., Inc., New York, N. Y., Vol. II, p. 173.