solution was hydrogenated at a room temperature with 0.1 g. of 10% palladium-charcoal as a catalyst until 16.2 cc. of hydrogen was absorbed (one molar equivalent, 16.2 cc.). The catalyst was removed from the reaction mixture and the dihydro compound was precipitated from the filtrate with water and recrystallized from ethanol. m.p. 152-155°; \([\alpha]_D^{25} = +15.2^\circ\) (in 1.25% solution). Yield, 0.22 g. \textit{Anal.} Calcd. for \(C_{20}H_{32}O_2\): C, 78.94; H, 10.53. Found: C, 79.01; H, 10.48.

Hydrogenation of (B)—0.20 g. of (B), m.p. 160-161°, was hydrogenated similarly as in the case of (A) and 0.13 g. of dihydro compound of m.p. 172.5-175° was obtained, which showed a specific rotation of \([\alpha]_D^{25} = -15.8^\circ\) (in 1.8% solution). \textit{Anal.} Calcd. for \(C_{20}H_{30}O_2\): C, 78.94; H, 10.53. Found: C, 78.71; H, 10.39.

Dihydro-7-isodextropimaric acid—0.1 g. of 7-isodextropimaric acid was hydrogenated as above, and dihydro-7-isodextropimaric acid with m.p. 172-175° was obtained. 37.41 mg. was dissolved in chloroform-acetone (1:1) mixture to 2.0 cc. and the solution showed the specific rotation \([\alpha]_D^{21} = -16.0^\circ\).

Summary

The fraction of diterpenic acid, which had previously been isolated from the fruits of \textit{Juniperus japonica}, was reinvestigated and two isomers were obtained in a pure state. The one was a new diterpenic acid, \(C_{20}H_{30}O_2\), and the other was found to be identical with 7-isodextropimaric acid. (Received July 17, 1952)

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375. Tyunosin Ukita, Shoshichi Nojima, and Kinzo Nagasawa:
On the Santonin Analogs. II.* Reimer-Tiemann Reaction of 1-Methyl-2-hydroxy-5,6,7,8-tetrahydronaphthalene.

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Von Auwers and his collaborators\(^1\) discovered the fact that on Reimer–Tiemann reaction, both para- and ortho-substituted phenols, besides the expected phenolic aldehydes, gave a kind of ketone compounds containing chlorine, and proposed quinonoid structures (I) and (II) for the respective ketone compounds.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \quad \text{CH}_2 \quad \text{Cl}_2 \\
\text{OH} & \quad \text{O} \\
\text{(I)} & \\
\end{align*}
\]

Woodward\(^2\), and Arnold, et al.\(^3\) developed this reaction to obtain 2-keto-10-dichloromethyl-4,5,6,7,8-pentahydronaphthalene (IV) from 2-hydroxy-5,6,7,8-tetrahydronaphthalene (I), together with 1-aldehyde-2-hydroxy-5,6,7,8-tetrahydronaphthalene (V) and 2-hydroxy-3-aldehyde-5,6,7,8-tetrahydronaphthalene (VI), which were expected as the ordinary products of this reaction. Further, (IV) was converted into 2-keto-10-methyldecalin, which was confirmed to be the same compound with the authentic sample prepared by the ring closure method of Robinson\(^4\). Woodward’s work served as an indirect evidence for the paraquinonoid structure of (I) assumed by von Auwers.

\* Part I: This Journal, 72, 796(1952).

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1) K. von Auwers, et al.: \textit{Ber.}, 35, 465, 4207 (1902); \textit{Ann.}, 401, 303 (1913).


Harukawa, et al., \(^5\), recently reported a chlorine-containing compound as a product of Reimer-Tiemann reaction of 1-methyl-2-hydroxy-5,6,7,8-tetrahydronaphthalene (VII), and from the result of its ultraviolet absorption spectrum, they preferred the structure of 1-methyl-2-keto-10-dichloromethyl-4,9,10-hexahydronaphthalene (VIII) to 1-methyl-1-dichloromethyl-2-keto-4,9,10-hexahydronaphthalene (X) for their product. Moreover, they were of the opinion that the product might be more unstable against caustic soda if it had the structure of (X) with its dichloromethyl group in the ortho-position to the carbonyl group, analogous to the behavior of von Auwers' product (II) against alkali. However, they could not obtain any phenolic aldehyde corresponding to (VI).

Our interest in the Reimer-Tiemann reaction led to the reinvestigation of the same reaction carried out by Harukawa, et al. Besides the compound by them, we were able to obtain two new products, a phenolic aldehyde with m.p. 32~33°, and an oily product boiling at 130~132°/3 mm., which was an isomer of (VIII), and determined the structures of these compounds. The present paper deals with these results.

(VII) was treated with alkali and chloroform at 70~75° under the conditions of the Reimer-Tiemann synthesis, and the starting material was recovered by acidifying the aqueous layer. From the chloroform layer a brown oil was obtained from which, upon treatment with a small amount of benzine, a product (VIII), \(\text{C}_{12}\text{H}_{14}\text{OCl}_{2}\), melting at 154°, was crystallized out.

The residual oil, separated from (VIII), was distilled under diminished pressure, and from alkali-soluble fraction of the distillate was obtained a crystalline compound (IX), \(\text{C}_{12}\text{H}_{14}\text{O}_{2}\), melting at 32~33°, and from the alkali-insoluble fraction, using a chromatographic procedure, a yellow oily compound (X), \(\text{C}_{12}\text{H}_{14}\text{OCl}_{2}\), b.p. 130~132°, was obtained.

Evidently, (IX) is a phenolic aldehyde because it gives a violet black coloration in alcoholic solution by ferric chloride, a red color in aqueous fuchsin-bisulfite solution, and a semicarbazone, \(\text{C}_{13}\text{H}_{17}\text{O}_{2}\text{N}_{3}\), m.p. 267~268°, but it gave negative Beilstein's halogen test.

(IX) was reduced by the Wolff-Kishner method modified by Huang Minlon into a product, \(\text{C}_{12}\text{H}_{16}\text{O}\), m.p. 95~97.5°.

As for the position of the aldehyde group introduced into the starting compound (VII) by Reimer-Tiemann reaction, the only possible position would be 3, i.e. ortho to phenolic hydroxyl group, so it is largely possible that the structure of phenolic aldehyde could be formulated as (IX), and that of its reduction product as (XI).

Recently, Cocker\(^6\) synthesized 1,3-dimethyl-2-hydroxy-5,6,7,8-tetrahydronaphthalene (XI) according to the following route:

\(^5\) T. Harukawa, H. Ishikawa: This Journal, 70, 338 (1950).
Following this schema, (XI) was synthesized from a sample of \( \beta-(3,5\text{-dimethyl}-4\text{-methoxybenzoyl})\text{-propionic acid}, \) an intermediate compound of above route which was offered through the courtesy of Dr. Clemo and Dr. Cocker. The identity of our reduction product, m.p. 95\(^\circ\)~96.5\(^\circ\), with this authentic specimen was confirmed by mixed fusion, and, further, the melting point of the carbanilate, m.p. 181.5\(^\circ\)~182.5\(^\circ\), derived from the former was also in fair agreement with that of the authentic carbanilate reported in the Cocker's paper.

It is, therefore, convincingly evident that the phenolic aldehyde is 1-methyl-2-hydroxy-3-aldehyde-5,6,7,8-tetrahydronaphthalene as shown by (IX).

As for the structure of the product with b.p.3 130\(^\circ\)~132\(^\circ\), an isomeric compound with (VIII), it is largely possible to assign the formula shown by (X), if the product with m.p. 153\(^\circ\) has the structure (VIII) as assumed by Harukawa, et al., because the starting compound in our reaction was substituted by alkyl radicals both in the ortho- and para-positions to the phenolic hydroxyl group. This assumption could presumably be supported by the result reported by von Auwers, et al., who proposed the ortho-quinonoid structure (II) for the chlorine-containing ketone compound obtainable from o-cresol by the same reaction.

The authors synthesized (I) and (II) according to the von Auwers' procedure in order to compare their ultraviolet absorption spectra with those of (VIII) and (X), and the results obtained are illustrated in Fig. 1 and Table 1.

The absorption curves of (I) and (II) differed remarkably from each other due to the positions of their two double bonds conjugated to the carbonyl groups; the former exhibiting its maximum at the short wavelength, 2350 Å with \( \log \varepsilon = 4.46 \), while the maximum of the latter shifted to the longer wavelength, 3050 Å, with smaller extinction coefficient, \( \log \varepsilon = 3.67 \). The same tendency was also witnessed in the spectra of (VIII) and (X), the former showing a maximum at 2360 Å with \( \log \varepsilon = 4.0 \), the latter at 3300 Å with \( \log \varepsilon = 3.62 \).

On the other hand, the oily product (X) was brominated by \( N\)-bromosuccinimide, and the bromide was converted into a product, \( C_{12}H_{19}OCl_{2}, \) m.p. 64\(^\circ\), by subsequent dehydrobromination with sodium acetate and acetic acid. This product was proved by mixed fusion to be identical with 1-methyl-1-dichloromethyl-2-keto-1,2-dihydronaphthalene (XII), which was recently reported as being synthesized by Dodson, et al.\(^7\) from 1-methyl-
2-hydroxynaphthalene by Reimer-Tiemann reaction. Therefore, the structure of the compound with b.p. 130~132° might well be represented as shown in (X).

However, there remains two possibilities, that the product may also be represented by the structural formula (X'), and that the product may be a mixture of the compounds having the structures (X) and (X').

The absorption maximum of the compound (II), $\lambda_{\text{max}}$ 3050 Å, is displaced to a considerably longer wavelength range as compared with acyclic 6-monosubstituted dienones, the maxima of which are reported to be very consistent in the location of $\lambda_{\text{max}}$ at 2700±10 Å. Such a displacement may be expected, as postulated by Evans and Gillam, from the location of two double bonds in the structure of (II) being involved in the single ring system.

Further, the latter authors generalized that the additional substituents at the C-atoms contained in a dienone system displaced the maximum of the base compound with almost constant increments. The increments empirically deduced by Evans and Gillam from several substituted dienone compounds amounted to 100 Å for each substituent and that by Fieser and Fieser for steroidal compounds amounted to 180 Å for each substituent at the γ and δ positions of a dienone system.

Based on these data, the absorption maximum of the compound with the structure of

(X), the dieneone system of which is similarly located in a single ring system as that in the structure of (II) and contains one additional substituent each at its γ and δ positions, may be calculated for \( \lambda_{\text{max}} \) 3250 Å or \( \lambda_{\text{max}} \) 3410 Å.

On the other hand, the compound which is represented with the structure (X'), the two double bonds of which are located over two ring systems and having one substituent at both γ and δ positions of the dieneone system, must have the absorption maximum at a rather shorter wavelength range, and the expected absorption maximum may probably be found almost at the same wavelength range as that of \( \beta^{15}\)-cholestadien-2-one (\( \lambda_{\text{max}} \) 2900 Å)\(^9\).

As the absorption maximum of the oily compound with b.p., 130-132° was found at \( \lambda_{\text{max}} \) 3300 Å, the structure of this compound might reasonably be represented by (X) rather than (X').

In conclusion, all of the expected reaction products from (VII) by the Reimer-Tiemann reaction were isolated and as (X) was proved to have the ortho-quinonoid structure, the assumption made by Harukawa, et al. that (VII) had the para-quinonoid structure was positively proved. However, the authors could not find any evidence that the dichloromethyl group situated at the ortho-position to the carbonyl group is unstable against alkali, because both (VII) and (X) were obtained in about the same yield.

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**Experimental**

Reimer-Tiemann Reaction of 1-Methyl-2-hydroxy-5,6,7,8-tetrahydronaphthalene (VII)—5 g. of 1-methyl-2-hydroxy-5,6,7,8-tetrahydronaphthalene (VII) was dissolved in 110 cc. of 10% aqueous sodium hydroxide in a flask equipped with an efficient reflux condenser and a dropping funnel. After the reaction mixture had been immersed in a water bath at 75°, pure chloroform was dropped in slowly from the funnel. On addition of the first few drops of chloroform, the solution colored yellow, and the color gradually deepened to orange with the additional amounts of chloroform. 20 g. of chloroform was added in the course of 2 hours. The reaction was then allowed to continue for 30 minutes, the water bath was removed and the reaction mixture was allowed to cool. The mixture was well shaken after the addition of ca. 50 cc. of chloroform. The chloroform layer (A) was washed several times with 5% aqueous sodium hydroxide, diluted hydrochloric acid solution, then water, successively, and dried over sodium sulfate. From the combined alkali-soluble fraction (B), (VII) was recovered upon acidification. The chloroform was evaporated from the fraction (A) and the residual oil furnished (VII) in crystalline form on standing in a refrigerator after a treatment with a small amount of benzine. This was separated from oily matter by filtration and recrystallized from methanol to colorless prisms, m.p. 154°-156°.

The residual oil, after removal of (VII), was distilled, giving a yellow oil, b.p., 115-125°. The ethereal solution of this oil was again extracted with 5% aqueous sodium hydroxide to give 0.95 g. of an alkali-soluble fraction (A') and 1.8 g. of alkali-insoluble fraction (B'). The former solidified and was recrystallized repeatedly from ligroine to recover 0.65 g. of the starting material with m.p. 110-112°. Evaporation of ligroine from the mother liquor gave 0.3 g. of a solid which yielded precipitation by addition of semicarbazide hydrochloride solution. This semicarbazone (m.p. 267-269°, yield 0.3 g.) was recrystallized from alcohol to colorless needles, m.p. 267-268°. Anal. Calcd. for C₁₀H₁₇O₂N₃: C, 63.16; H, 6.88; N, 17.00. Found: C, 63.49; H, 6.67; N, 17.04.

The semicarbazone was decomposed by warming with 20% hydrochloric acid and the reaction product was taken up in ether. On removal of the solvent, the ethereal solution yielded an oil which was distilled at 115-135°/4.5 mm. to give a yellow oil. After further distillation, the oil solidified and recrystallized from petroleum ether to colorless small prisms (IX), m.p. 32°-33°. The product showed the aldehyde-phenol characteristics, giving a red precipitation with alcoholic solution of 2,4-dinitrophenylhydrazine, a red color in aqueous fuchsin-bisulfite solution and a black violet color with ferric chloride in alcoholic solution, but it gave no Beilstein's halogen test. Anal. Calcd. for C₁₂H₁₄O₂: C, 75.69; H, 7.37. Found: C, 76.20; H, 7.25.

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1.9 g. of the alkali-insoluble fraction (B'), dissolved in 50 cc. of benzene, was poured through an alumina column. The chromatogram was eluted with methanol-ether (1:1). After evaporation of the solvent from the eluate, the residue was distilled under diminished pressure, giving 1.1 g. of a yellow oil (X) with b.p. 130°-132° as the main fraction. This neutral substance gave positive Beilstein's test and reacted gradually with an alcoholic solution of 2,4-dinitrophenylhydrazine but the reaction product could not be obtained as crystals. Anal. Calcd. for C_{12}H_{14}O:C, 58.75; H, 5.71; Cl, 29.00. Found: C, 58.80; H, 5.53; Cl, 29.20.

The flask-residue of above distillation, 1.5 g., was again treated by the chromatographic procedure, as stated above, to remove the resinous matter and 0.4 g. of (VIII) was obtained by elution of this chromatogram with acetone.

**Wolff-Kishner-Huang Minion Reduction of (IX)**—A mixture of 1 g. (IX), 1.2 g. of potassium hydroxide, and 0.9 g. of 85% hydrazine hydrate in 10 cc. of diethylene glycol was refluxed for 1.5 hours, the water formed was removed by a take-off condenser, during this period the temperature of the solution being allowed to rise to 200°, and the refluxing was continued for additional 2 hours. The cooled solution was diluted with 50 cc. of water, poured slowly onto 40 cc. of N hydrochloric acid, and the colorless crystalline solid separated was dried. Repeated recrystallization from benzine gave fine needles, m.p. 95°-97.5°. Anal. Calcd. for C_{12}H_{16}O: C, 81.87; H, 9.09. Found: C, 82.10; H, 9.10.

The Carbanilate of 1,3-Dimethyl-2-hydroxy-5,6,7,8-tetrahydronaphthalene—0.2 g. of (XI) and 0.2 g. of phenyl isocyanate were warmed with a small amount of benzine at 60°-70° for 2 hours. The mixture was allowed to stand at a room temperature over night. After diluting with benzine, the solid precipitated was separated by filtration, and upon recrystallization from benzine colorless fine needles, m.p. 182°-182.5°, resulted. The analytical figures of this compound were in fair agreement with those of the authentic carbanilate prepared by Cocker. Anal. Calcd. for C_{23}H_{23}O_{2}N: C, 77.66; H, 7.07; N, 4.93. Found: C, 77.24; H, 7.17; N, 4.74.

**Formation of (XII) from (X)**—A mixture of 1 g. of (X), 1.45 g. of N-bromosuccinimide (2 molar equivalent), 0.21 g. of benzoyl peroxide, and 50 cc. of carbon tetrachloride was refluxed for 40 minutes. During the reaction the color turned to orange, then gradually to red, with refluxing of hydrogen bromide. After this period, 4.32 g. of potassium acetate and 2.16 g. of acetic acid were added and the mixture was refluxed for 2 hours, the color of the solution turned from red to original yellow. The reaction mixture was poured onto a mixture of ice and 4 g. of sodium hydroxide. The resultant two layers were separated and the carbon tetrachloride layer was washed successively with aqueous alkali, diluted hydrochloric acid, and water, and the evaporation of the solvent yielded a viscous yellowish brown oil, which on distillation, gave 0.81 g. of oily product boiling at 134°-142°/0.4 mm. It was further distilled at 115°-134° (0.1 mm.), yielding 0.6 g. of distillate. 0.21 g. of this oil was again refluxed with 0.15 g. of N-bromosuccinimide (one molar equivalent) and 10 cc. of carbon tetrachloride for an hour, the color of the mixture turned to orange and after additional 4 hours, the orange color disappeared and succinimide deposited in the flask. Cooling to room temperature and filtering with suction gave colorless crystals, m.p. 124°-126° (succinimide). From the filtrate, after washing and removal of the solvent, a very viscous brown oil was obtained. This was mixed with 10 cc. of carbon tetrachloride, 0.8 g. of sodium acetate, and 0.4 g. of acetic acid, and refluxed for an hour. Decomposition of the reaction mixture with water yielded 0.2 g. of solid which, after two recrystallizations from a small amount of benzine, furnished 0.15 g. of colorless fine prisms, m.p. 64°. The mixed melting point of the compound with an authentic sample prepared by the method of Dodson showed no depression.

**Ultraviolet Absorption Spectra**—The measurements were made in 95% ethanol solutions of the compounds in 1 cc. quartz cells with Beckman Model DU ultraviolet spectrophotometer.

**Summary**

1-Methyl-2-hydroxy-5,6,7,8-tetrahydronaphthalene was treated under the conditions of the Reimer-Tiemann synthesis, resulting in two new products. The structures of these compounds are discussed and it is concluded that the one possesses the structure of 1-methyl-2-hydroxy-3-aldehyde-5,6,7,8-tetrahydronaphthalene and the other, 1-methyl-1-dichloromethyl-2-keto-1,2,5,6,7,8-hexahydronaphthalene.

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10) This compound was isolated by T. Harukawa and H. Ishikawa. cf. Footnote 5).