OCCURRENCE OF 2,7-DIHYDROXY-4-ISOPROPYL-2,4,6-CYCLOHEPTATRIEN-1-ONE (7-HYDROXY-4-ISOPROPYLTROPOLONE) IN WESTERN RED CEDAR (THUJA PLICATA DONN.)[1]

J. A. F. Gardner, G. M. Barton, and H. MacLean

ABSTRACT

The tropolones of western red cedar were collected as the green copper chelates deposited on copper–bronze screen exposed to the vapor from the heated wood in commercial kilns. Decomposition of the chelates with hydrogen sulphide yielded a new tropolone as well as the expected thujaplicins. Its infrared and ultraviolet absorption together with hydrogenation and oxidation reactions established it to be 2,7-dihydroxy-4-isopropyl-2,4,6-cycloheptatrien-1-one. Synthesis was achieved by persulphate oxidation of γ-thujaplicin. The natural substance is identical with the 7-hydroxyhinokitiol obtained by Nozoe from the diazonium salt of 7-aminohinokitiol and on the basis of color reactions and R_f appears to be the unknown "enol" previously noted by Zavarin and Anderson in paper chromatography of tropolone fractions of western red cedar and incense cedar. The concentration in the wood, determined by quantitative paper chromatography, ranged from 0.01 to 0.08%.

The generic name tropolone, originally suggested by Dewar (7), has come into general use for 2-hydroxy-2,4,6-cycloheptatrien-1-one and its derivatives which possess special characteristic properties due to the 1,2 arrangement of the carbonyl and hydroxyl groups on an unsaturated seven-membered carbon ring. The literature on the chemistry of these substances has been reviewed recently by Pauson (20) and also by Nozoe (15). In naming derivatives, the carbonyl is taken to occupy position 1 and the hydroxyl position 2. Because tropolones are considered to possess a highly mobile tautomeric system the formulae I*a* and I*b* are considered to represent a single substance. For such derivatives, the name has been based on the formula I*a*, which gives the lowest number for the position of the substituent, in this case 3 instead of 7. However, in the special case where the substituent X is another hydroxyl group, this convention is not altogether satisfactory.

In a symmetrical arrangement of the two hydroxyls about the carbonyl, as in formula II based on I(*b*), the effect of the neighboring carbonyl will be shared by two equal hydroxyl groups instead of one, and special characteristics assignable to this arrangement would be evident in contrast to that based on I(*a*). Thus in the case of II use of the 7 terminology rather than the 3 may be more accurately descriptive of the observed properties of the substance and may, therefore, be preferable. Accordingly, in this paper, which describes the isolation, characterization, and synthesis of a naturally occurring hydroxy tropolone, the 3 and 7 positions are differentiated for purposes of nomenclature.

Western red cedar heartwood (*Thuja plicata* Donn.) has been shown to be a rich source of the simplest naturally-occurring tropolones, the isomeric 3-, 4-, and 5-isopropyltropolones, III, IV, and V, known as α-, β-, and γ-thujaplicin respectively (2, 8). Although as much as 1.2% by weight of these potent natural preservatives occurs in the outer butt heartwood of mature trees (14), the preparation of research samples in the laboratory by steam distillation of the wood is tedious and expensive. The volatile oil must be recovered from a relatively large volume of aqueous distillate and consists of a mixture of the desired thujaplicins with thujic acid and its methyl ester (4).

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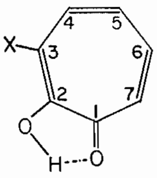
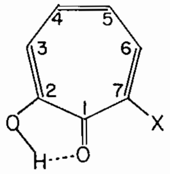
[1] *Manuscript received May 16, 1957.*
Contribution from the Vancouver Laboratory, Forest Products Laboratories of Canada, a Division of the Forestry Branch, Department of Northern Affairs and National Resources. Paper presented at the 40th Annual Conference, Chemical Institute of Canada, Vancouver, B.C., June 3–5, 1957.



I(a)



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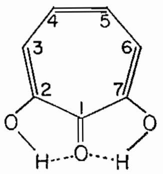

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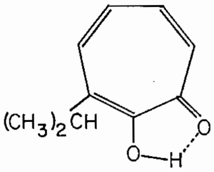

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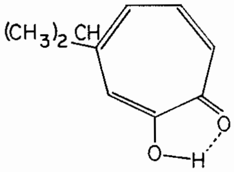

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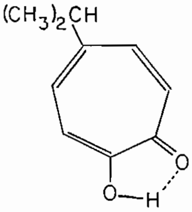


V

In a search for a simple inexpensive method of preparing large samples of the β and γ isomers, advantage was taken of the ability of the thujaplicins to combine directly with copper. At the temperature used in commercial kilns while drying cedar lumber, 75° to 95° C., a small proportion of the oil of the wood is volatilized and the thujaplicins therein coat any exposed copper with a stable water-insoluble green chelate compound. Thujic acid and its methyl ester, which are also present in the vapor, do not react with copper metal. Accordingly, sheets of copper–bronze screening were installed in the free spaces of commercial kilns being used for drying cedar lumber. After five weeks' exposure, the green deposit which had formed on the screens was washed off with chloroform and the solution concentrated. Decomposition of the copper chelates with hydrogen sulphide yielded an oily mixture of the thujaplicins. This procedure proved to be a convenient and inexpensive method of obtaining research samples of thujaplicin concentrates.

Vacuum distillation of the thujaplicin mixture gave a crystalline high boiling fraction which was not the expected γ-thujaplicin nor either of the lower boiling α and β isomers. After recrystallization from hexane or ethanol, the light-yellow crystals melted at 57.5–58° C. The thujaplicins, α, β, and γ, are colorless, have melting points of 34° C., 51–52° C., and 79–80° C. respectively, and cannot readily be recrystallized from ethanol because of very high solubility in that solvent.

The new substance in chloroform solution gave a red color in the organic layer when treated with aqueous ferric salt solutions and a green color with copper acetate solutions. These color reactions are characteristic of the thujaplicins and other tropolones (20). However, the colors obtained in both cases contained more yellow than those from thujaplicins. Furthermore, the red ferric color was stable to excess ferric ion and no green color was formed in the aqueous layer as is the case with the thujaplicins.

The substance was optically inactive, highly refractive (n_D^{70} 1.6170), distillable with steam, very soluble in organic solvents, and only slightly soluble in water.

Tests for nitrogen, halogen, methoxyl, and carbonyl content were negative. The Folin-Denis test for phenols and the coupling reaction with diazotized *p*-toluidine were positive. Analytical values for carbon and hydrogen content coincided with the theoretical for the molecular formula $C_{10}H_{12}O_3$, which requires a molecular weight of 180.2. Molecular weight determination by the Rast method gave results ranging from 178 to 224. However, isothermal distillation in acetone and freezing point depression in benzene gave values of 189 to 190.

Methylation with diazomethane gave a distillable oil (n_D^{22} 1.5828) which analyzed for methoxyl content as a dimethyl ether, $C_{10}H_{10}O(OCH_3)_2$. The crystalline copper chelate analyzed correctly as the monocopper derivative, $C_{10}H_{10}O_3Cu$. The infrared absorption spectra of both these derivatives exhibited no bands assignable to hydroxyl groups.

All of the above properties were in accord with the new substance being a tropolone and, moreover, the molecular weight and analytical and methylation data indicated it to be a thujaplicin containing one additional hydroxyl group.

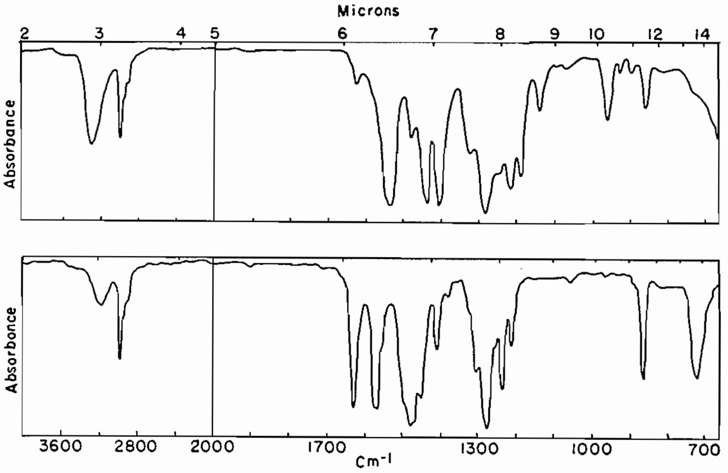


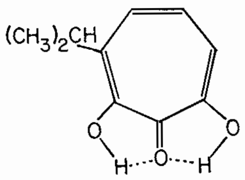
FIG. 1. Infrared spectrum of 2,7-dihydroxy-4-isopropyl-2,4,6-cycloheptatrien-1-one (upper) and 2-hydroxy-5-isopropyl-2,4,6-cycloheptatrien-1-one (lower).

Four different positions for an additional hydroxyl are available in α-thujaplicin (III), namely 4, 5, 6, and 7, and also in β-thujaplicin (IV), 3, 5, 6, and 7. However the product of substitution in the 3 position of β-thujaplicin would be equivalent to that of substitution in the 7 position of α-thujaplicin. Also in the symmetrical γ isomer (V) only the 3 and 4 positions are different and, of these, the product of substitution in the 3 positions would be equivalent to that of substitution in the 7 position in the β isomer. Thus a total of eight possible isomers were to be considered.

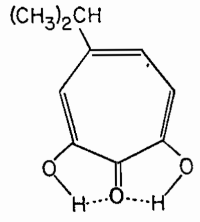
The infrared absorption spectrum, compared with that of γ-thujaplicin in Fig. 1, also indicated a substituted thujaplicin structure and was useful in indicating the position of the additional hydroxyl group. The bands in the spectrum of thujaplicin at 1265, 1440, 1468, 1558, 1618, and 3165 cm.$^{-1}$ have been considered by several investigators (3, 11, 12, 22) to be characteristic of the tropolone nucleus. The spectrum of the new substance shows bands at or near these frequencies, namely 1270, 1429, 1467, 1524–1530, 1613, and 3260 cm.$^{-1}$. The sharp band at 2950 cm.$^{-1}$ in the γ-thujaplicin spectrum has been ascribed to C—H stretching on the ring and the inflections at 2930 cm.$^{-1}$ and 2870 cm.$^{-1}$ to the isopropyl group. A similar band at 2955 cm.$^{-1}$ with inflections at 2930 cm.$^{-1}$ and 2870 cm.$^{-1}$ occurs in the spectrum of the new substance.

The broad absorption band of medium intensity at 3160 cm.$^{-1}$ in the case of γ-thujaplicin and at or near there in the case of other simple tropolones has been assigned to the hydroxyl group. The displacement from the free hydroxyl frequency of 3600 cm.$^{-1}$ has been attributed to rather strong intramolecular hydrogen bonding. In the new compound, the strong broad band at 3260 cm.$^{-1}$ indicates weaker hydrogen bonding, almost weak enough to be assigned to intermolecular polymeric association bonds. However, as this band does not disappear in dilute solutions in carbon tetrachloride and no dimeric or free hydroxyl bands appear in the 3450–3600 cm.$^{-1}$ region, intermolecular polymeric association bonds are ruled out since only intramolecular hydrogen bonds are independent of the concentration (5).

The presence of only one strong hydroxyl band moderately displaced in the spectrum suggested symmetrical placement of the two hydroxyl groups in the molecule about the carbonyl. This arrangement would account for weaker hydrogen bonding than in a simple tropolone since the influence of the carbonyl would be shared between two hydroxyls instead of one. Of the possible isomers only two would have this arrangement, the 7-hydroxy derivative (VI) of α-thujaplicin and the 7-hydroxy derivative (VII) o β-thujaplicin. Of these, the latter was more attractive because of the more nearly symmetrical placement of the isopropyl group in relation to the hydroxyls. In the former, the adjacent position of the isopropyl group would be expected to influence one of the hydroxyls, giving rise to two bands in the spectrum.



VI



VII

The band due to the C=O bond occurs in the 1610–1630 cm.$^{-1}$ region in tropolones, the large shift from normal frequencies being assigned to conjugation, ring strain, and to some extent intramolecular hydrogen bonding (11, 12). The band in this region in the spectrum of the new compound (1613 cm.$^{-1}$) is much less intense than the corresponding band for γ-thujaplicin (1618 cm.$^{-1}$). A non-symmetrical placement of the additional hydroxyl groups about the carbonyl, as in the 4, 5, or 6 position, would correspond to normal substituted tropolone structure and in dilute solution should give normal intensity in the 1610–1630 cm.$^{-1}$ region.

In investigating the hydroxylation of tropolone, Nozoe *et al.* (17) obtained the 5-hydroxyl derivative and small yields of the 3-hydroxyl (or 7-hydroxyl) derivative by alkaline persulphate oxidation. However, with α- and β-thujaplicin only the 5-hydroxyl derivatives were obtained (17). However, previously, in examining the diazo reactions of 7-aminohinokitiol (hinokitiol = β-thujaplicin) Nozoe, Kitahara, and Doi (16) obtained a crystalline product, m.p. 44–58° C., which was separated by fractional crystallization into three modifications melting at 59–60° C., 51–52° C., and 45–46° C. respectively. These analyzed correctly as the hydroxyl derivative and were believed by the authors to be tautomers of 7-hydroxyhinokitiol. No derivatives were described but in a later publication the ultraviolet absorption spectrum determined in iso-octane was given (18). The spectrum of the new substance from cedar in the same solvent (Fig. 2) appeared to be identical, exhibiting the same marked fine structure and enhanced intensity in the

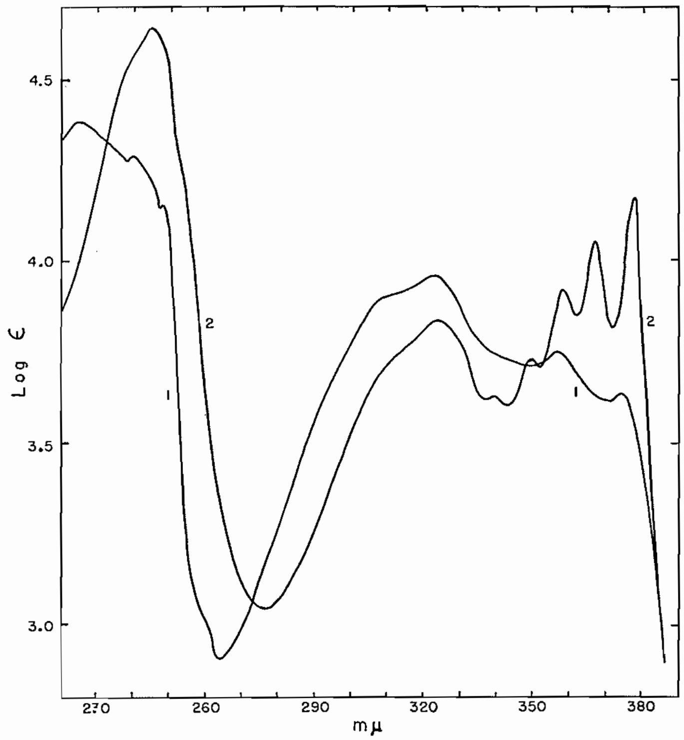


FIG. 2. Ultraviolet spectrum of 2-hydroxy-5-isopropyl-2,4,6-cycloheptatrien-1-one (Curve 1) and 2,7-dihydroxy-4-isopropyl-2,4,6-cycloheptatrien-1-one (Curve 2) in 2,2,4-trimethylpentane (iso-octane).

long wave region. Similar fine structure and enhanced intensity in this range compared with that of tropolone have also been observed for 3-hydroxy tropolone (2,7-dihydroxy-2,4,6-cycloheptatrien-1-one) (10, 18).

The structure 2,7-dihydroxy-4-isopropyl-2,4,6-cycloheptatrien-1-one (7-hydroxy-4-isopropyltropolone) (VII), favored for the new tropolone over the other seven possible isomers by the spectral data, was proved by a degradative experiment and synthesis (Fig. 3). Hydrogenation over Adams' catalyst used the theoretical 4 moles of hydrogen, yielding a crystalline product which analyzed correctly as the triol, $C_{10}H_{20}O_3$ (VIII). This product on oxidation consumed 2 moles of periodate and produced 1 mole of formic acid, in agreement with theory. The cleavage product from this oxidation was not isolated but was oxidized with alkaline permanganate to β-isopropyl adipic acid, identical with a synthetic sample. These results proved the vicinal arrangement of the three oxygens on the ring and fixed the relative position of the isopropyl group.

Of the three possible tautomeric structures which may be written to satisfy the vicinal arrangement of the carbonyl and two hydroxyl groups, the infrared absorption spectrum, as pointed out above, clearly indicates the symmetrical arrangement, i.e. a hydroxyl on each side of the carbonyl.

In the hydroxylation of simple phenols by treatment with alkaline persulphate solutions, satisfactory yields of the ortho isomer are obtained only when the para position is already substituted. Similarly in the case of tropolone, the product is a mixture of the 5- and 7(or 3)-hydroxy derivatives in which the former predominates. Blocking of the 5 position in tropolone with an isopropyl group as in γ-thujaplicin (corresponding to the

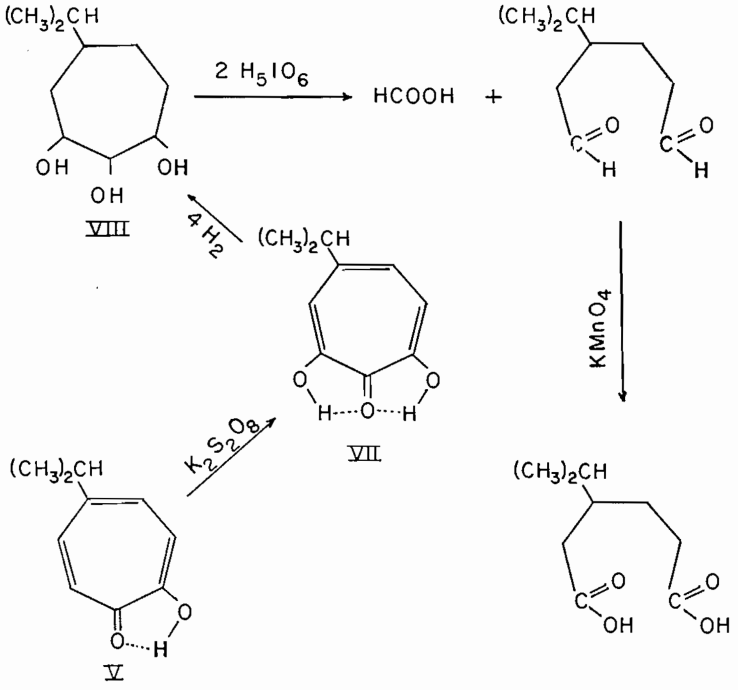


FIG. 3. Proof of structure of 2,7-dihydroxy-4-isopropyl-2,4,6-cycloheptatrien-1-one.

para position in phenol) should lead to hydroxylation only in the equivalent 3 and 7 positions (corresponding to ortho) and yield one isomer, the desired 2,7-dihydroxy-4-isopropyl-2,4,6-cycloheptatrien-1-one (VII). On this theory, the oxidation of γ-thujaplicin by alkaline persulphate was investigated. The product obtained in 28% yield was identical with the natural substance.

The possibility was examined that 7-hydroxy-4-isopropyltropolone (VII) did not occur in the cedar but had been generated from the thujaplicins by a copper catalyzed oxidation during the isolation procedure. Samples of steam volatile oil prepared from the wood in all glass apparatus were examined by the paper chromatographic technique for tropolones developed by Zavarin and Anderson (24). 7-Hydroxy-4-isopropyltropolone proved to be present in all samples tested. Furthermore it exhibited the same R_f and violet color reactions on paper as the unknown "enol" first noted by Zavarin and Anderson on paper chromatograms of the tropolone fraction of western red cedar and also incense cedar (*Libocedrus decurrens* Torr.).

The content of 7-hydroxy-4-isopropyltropolone in cedar was determined by quantitative paper chromatography of the steam volatile oil obtained by exhaustive steam distillation of the finely ground wood. The results for four samples of cedar heartwood are compared in Table I with the thujaplicin content determined by a colorimetric method (13).

In the richest sample, which also contained the highest thujaplicin content, the content of 7-hydroxy-4-isopropyltropolone was less than 0.1% of the wood and approximately one-tenth of the thujaplicin content. This low content and the relatively low order of toxicity to fungi compared with thujaplicin found in toxicity tests (21) indicate that 7-hydroxy-4-isopropyltropolone is a minor influence on cedar wood durability.

The high proportion (50%) of 7-hydroxy-4-isopropyltropolone in the tropolone fraction

TABLE I

CONTENT OF 7-HYDROXY-4-ISOPROPYLTROPOLONE AND THUJAPLICINS IN WESTERN RED CEDAR HEARTWOOD
(results in percentage of moisture-free wood)

7-Hydroxy-4-isopropyltropolone	Thujaplicins
0.01	0.026
0.01	0.16
0.05	0.44
0.08	0.78

obtained by use of the copper–bronze screen technique in spite of its relatively low concentration in the volatile oil may be due to its greater reactivity with copper as compared with the thujaplicins.

The extent of interference of 7-hydroxy-4-isopropyltropolone in the previously reported analytical method for thujaplicins in cedar wood (13) was determined by control tests. Owing to unfavorable solubility in the solvents prescribed and relatively poor color response, it was found that concentrations of up to 0.05% in the wood did not interfere.

Recently, the occurrence of another natural tropolone, chamaecin, in the essential oil of Formosan hinoki (*Chamaecyparis Taiwanensis* Masamune et Suzuki) has been reported (23). The authors suggested that chamaecin is an ether of 7-hydroxy-4-isopropyltropolone (7-hydroxyhinokitiol) based on analytical values and its rearrangement by alkali fusion to 2-hydroxy-4-isopropyl benzoic acid.

After completion of this paper a sample of pure 7-hydroxyhinokitiol, m.p. 57–58° C., synthesized from 7-aminohinokitiol by Nozoe *et al.* (16), became available together with its infrared absorption spectrum.* A mixed m.p. with 7-hydroxy-4-isopropyltropolone from western red cedar showed no depression and the infrared absorption spectra and R_f characteristics were identical.

EXPERIMENTAL

Evaporations were carried out under reduced pressure at 40° C. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Carbon and hydrogen microanalyses were done by Clark Microanalytical Laboratory, Urbana, Illinois, and W. Manser, Herrliberg, Switzerland. Infrared absorption spectra were determined on a Perkin-Elmer Model 21 spectrophotometer at the British Columbia Research Council. Ultraviolet absorption spectra were determined with a Beckman DU spectrophotometer.

Isolation of 7-Hydroxy-4-isopropyltropolone (VII)

Copper–bronze screen (18 mesh) was stretched over wooden frames in the free space of a commercial kiln being used for drying high grade western red cedar lumber at temperatures between 75° and 95° C. After 5 weeks of exposure, the screen which had become light green in color was removed from the kiln and washed with chloroform. The resultant green chloroform solution was filtered through hyflo supercel and concentrated. Removal of solvent left the crude crystalline copper derivatives of the tropolones (2.4 g. per sq. ft. of screen).

The copper derivatives were decomposed by saturating a chloroform solution with hydrogen sulphide and removing the precipitated copper sulphide by filtration. Solvent

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**Private communication from Tetsuo Nozoe, Chemical Institute, Tôhoku University, Sendai, Japan, March 27, 1957.*

removal left a mixture of tropolones as an oil which was distilled through a simple widmer (bath temp. 140–180° C./0.5 mm.). Yield from copper derivatives, 84%. The product distilling in the 150–180° C. range was light yellow in color and crystallized spontaneously.

Trituration with cold hexane, filtration, and recrystallization from hexane gave light yellow crystals, m.p. 54–55° C. Recrystallization from hexane, ethanol, or ethanol–water raised the melting point to 57.5–58° C., n_{D}^{70} 1.6170. Fractional crystallization of the lower boiling fractions gave additional material. A total of 62 g. was obtained from 122.5 g. of distilled tropolone mixture. Calc. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71; mol. wt. 180.2. Found: C, 66.67; H, 6.46; mol. wt. 190 by freezing point depression in benzene, 189 by isothermal distillation in acetone (6). For the infrared absorption spectrum in carbon tetrachloride see Fig. 1 and the ultraviolet absorption spectrum in iso-octane see Fig. 2.

Copper Chelate of 7-Hydroxy-4-isopropyltropolone (*VII*)

This was prepared in quantitative yield by shaking chloroform solutions of VII with 5% aqueous copper acetate solutions, washing with bicarbonate solution and water, and removing the solvent. Green needles, recrystallized from chloroform or chloroform–ethanol, m.p. 237–238° C. Calc. for $C_{10}H_{10}O_3Cu$: C, 49.69; H, 4.17; Cu, 26.29. Found: C, 49.66; H, 4.21; Cu, 26.34. $\nu_{\max}^{\mathrm{CCl}_4}$ in cm.$^{-1}$: no hydroxyl band, *2985*, 1621, *1525*, *1500*, *1423*, *1326*, *1305*, 1250, *1212*, 1185, 940, 900, 873, 838, 692.*

Dimethyl Ether of 7-Hydroxy-4-isopropyltropolone (*VII*)

Prepared by treatment with excess diazomethane in ether solution. The crude ether obtained after removal of the solvent was distilled in a Späth tube (bath temp., 50–155° C. at 0.5 mm.) to yield a yellow oil, n_{D}^{22} 1.5828. Calc. for $C_{10}H_{10}O(OCH_3)_2$: OCH_3, 29.7. Found: OCH_3, 29.4. $\nu_{\max}^{\mathrm{CCl}_4}$ in cm.$^{-1}$: no hydroxyl band, *2985*, *1630*, *1590*, 1505, *1469*, 1438, 1400, 1368, 1342, 1315, *1250*, *1238*, 1192, *1158*, *1132*, 1062, 991, 845.

Hydrogenation of 7-Hydroxy-4-isopropyltropolone (*VII*) *to the Triol* (*VIII*)

A solution of 7-hydroxy-4-isopropyltropolone (0.497 g.) in ethanol (75 ml.) was hydrogenated at atmospheric pressure in all glass apparatus using Adams' catalyst (0.2 g.). The absorption of hydrogen ceased in 20 minutes, the theoretical volume for absorption of 4 moles having been consumed. The residue (0.494 g.) crystallized after the removal of catalyst and solvent, m.p. 111–114° C. Recrystallization from ethyl acetate gave colorless needles, m.p. 112–113° C. Anal. Calc. for $C_{10}H_{20}O_3$: C, 63.79; H, 10.71. Found: C, 63.75; H, 10.76.

Periodate Oxidation of the Triol (*VIII*)

The octahydro derivative (0.1095 g.) was dissolved in water, 0.1*M* sodium metaperiodate solution (25 ml.) added, and the total volume adjusted to 100 ml. with water. The solution was kept at room temperature in the dark for 4 hours before analysis. Periodate consumption was determined on an aliquot (5 ml.) by the usual arsenite method (9). Simultaneously formic acid production was determined on a similar aliquot using the iodometric method (1). Blank determinations were conducted in each case. Found: periodate consumption, 2.07 moles; formic acid formed, 0.995 moles.

Oxidation of Periodate Cleavage Product to β-Isopropyl Adipic Acid

The above periodate oxidation solution (70 ml.), remaining after withdrawal of the aliquots for analysis, was extracted with diethyl ether. After removal of the solvent, the residual oil was dissolved in water, the solution made alkaline with sodium bicarbonate,

Frequencies of peaks of high intensity are printed in italics.

and dilute potassium permanganate solution added dropwise until a pink color persisted. The mixture was filtered, acidified, and the excess permanganate decomposed with sodium bisulphite before extraction with diethyl ether. The ether solution was extracted with 5% sodium bicarbonate solution, the bicarbonate solution acidified, and the acid re-extracted into diethyl ether. Evaporation of the solvent gave colorless crystals (0.04 g.), m.p. 78–80° C. Recrystallization raised the melting point to 80–80.5° C. A mixed melting point with β-isopropyl adipic acid, m.p. 79–80° C., prepared by permanganate oxidation of 4-isopropylcyclohexanol (19), showed no depression.

Persulphate Oxidation of γ-Thujaplicin (V) to 7-Hydroxy-4-isopropyltropolone (VII)

γ-Thujaplicin (0.5 g.) was dissolved in 10% potassium hydroxide solution (5.7 ml.) and the solution stirred in an ice bath for 2 hours while potassium persulphate (0.99 g.) in water solution (20 ml.) was added through a dropping funnel. The solution turned from a yellow to brown color and some tar was deposited. After the mixture had been kept overnight at 15° C., it was acidified to pH 4 and extracted with ether (2×5 ml.). The extracted solution was then acidified to pH 2, heated 1 hour on the steam bath, adjusted to pH 4, and again extracted with ether (2×10 ml.). The solution was washed with water and dried over sodium sulphate before removal of the solvent to leave light yellow crystals (0.03 g.), m.p. after recrystallization from ethanol–water, 57–58° C. The substance had the same R_f and color reactions as 7-hydroxy-4-isopropyltropolone isolated from cedar wood and a mixed melting point showed no depression.

The ether extract obtained in the first extraction at pH 4 was extracted with 3 *N* sodium hydroxide solution (2×3 ml.) and the alkaline extract cooled to 0° C. The sodium salt (0.17 g.) of γ-thujaplicin crystallized out and was collected on a stainless steel filter. The filtrate was acidified and extracted with ether. Removal of the solvent left an oil (0.136 g.) which by paper chromatographic analysis contained γ-thujaplicin (0.09 g.) and additional 7-hydroxy-4-isopropyltropolone (0.046 g.). Yield based on γ-thujaplicin consumed, 28%.

Paper Chromatography

The qualitative technique of Zavarin and Anderson (24) using paper impregnated with phosphoric acid was employed. Toluene was used as developing solvent. For quantitative determinations, the appropriate areas of the paper were excised and eluted with isopropyl alcohol. By comparing the absorbance of the eluted solutions at 375 mμ with those prepared in exactly similar manner from standard solutions of reference samples, the concentrations of the various tropolones in the solutions examined were calculated.

ACKNOWLEDGMENTS

The authors are indebted to Nalos Lumber Company, Vancouver, B. C., for the use of a kiln.

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