which exhibited only a very small positive Cotton effect (peak at $[\alpha]_{310}$ +140°). Saponification to the keto acid, conversion to the oxime, and crystallization from ethyl acetate afforded a small amount (20 mg.) of pure oxime, m.p. 214–216°, $[\alpha]_D$ −82° (c, 0.81 in dioxane), whose infrared spectrum proved to be superimposable upon that of the keto acid oxime XIV[10,30] (lit.,[10] m.p. 223°, $[\alpha]_D$ −79.4° in dioxane).

Conversion of sclareol (XV) *to isomeric methyl* $\Delta^{8(10),13}$-*labdadien-15-oates* (XVIIIa, XVIIIb). Following the procedure of Bory and Lederer,[17] 50 g. of sclareol (XV)[15] was transformed to 21.3 g. of the crude aldehyde XVI and thence by oxidation with silver oxide and methylation to 19.5 g. of crude ester. Chromatography on 500 g. of Merck acid-washed alumina provided in order of ease of elution: (a) 2.0 g. of oxido ester[17] (resulting from addition of the C-8 hydroxyl group to the Δ^{13} double bond), m.p. 105–106°; (b) 1.7 g. of the hydroxy ester XVIIa, m.p. 130–131° after recrystallization from acetone-hexane (lit.,[17] m.p. 132–134°), $\lambda_{max}^{C_2H_5OH}$ 222 mμ, log ε 4.11, $\lambda_{max}^{CHCl_3}$ 2.87 (very sharp), 5.85, 6.07, 11.69 μ, whose mass spectrum[22] was identical with that of XVIIIa; (c) 1.4 g. of hydroxy ester XVIIb, m.p. 98–99° (lit.,[17] m.p. 99–101°), $\lambda_{max}^{C_2H_5OH}$ 220 mμ, log ε 4.17, $\lambda_{max}^{CHCl_3}$ 2.79 (weak and broad), 5.83, 6.06, 11.60 μ, the mass spectrum[22] being identical with that of XVIIIb.

An interesting distinction between the two hydroxy esters was noted in terms of their rotatory dispersion curves, a difference which persisted also in their respective dehydration products (XVIIIa,b). The higher melting hydroxy ester XVIIa (m.p. 130–131°) exhibited a plain[14] dispersion curve (c, 0.090 in methanol) which changed sign below 400 mμ: $[\alpha]_{589}$ +7°, $[\alpha]_{500}$ +7°, $[\alpha]_{400}$ +7°, $[\alpha]_{370}$ −7°, $[\alpha]_{350}$ −24°, $[\alpha]_{300}$ −42°, while the lower melting isomer XVIIb (m.p. 98–99°) possessed a plain dispersion curve (c, 0.098 in methanol) which remained positive: $[\alpha]_{589}$ +23°, $[\alpha]_{500}$ +23°, $[\alpha]_{400}$ +39°, $[\alpha]_{370}$ +55°, $[\alpha]_{350}$ +67°, $[\alpha]_{300}$ +120°.

A 2.0-g. sample of the higher melting hydroxy ester XVIIa in 40 cc. of pyridine was kept at room temperature for 15 hr. with 7 cc. of phosphorus oxychloride and the solution was then added cautiously to ice water. Ether extraction afforded 1.87 g. of material lacking an infrared hydroxyl band and chromatography on Merck acid-washed alumina provided in the petroleum ether eluates, 1.76 g. of colorless oil, which was distilled at a bath temperature of 140°/0.01 mm. The resulting unsaturated ester XVIIIa exhibited $\lambda_{max}^{C_2H_5OH}$ 218 mμ, log ε 4.14, $\lambda_{max}^{CHCl_3}$ 5.83, 6.07, 11.23, 11.63 μ, $[\alpha]_D$ +9.7° (c, 1.73), whose plain rotatory dispersion curve (c, 0.378 in methanol) behaved just like that of its precursor (XVIIa) in changing sign below 400 mμ: $[\alpha]_{589}$ +6°, $[\alpha]_{500}$ +8°, $[\alpha]_{400}$ +6°, $[\alpha]_{370}$ −2°, $[\alpha]_{350}$ −12°, $[\alpha]_{300}$ −72°, $[\alpha]_{285}$ −117°. The mass spectrographic, gas phase chromatographic, and NMR results have already been summarized in the Discussion.

Anal. Calcd. for $C_{21}H_{34}O_2$: C, 79.19; H, 10.76; O, 10.05; methoxyl, 9.74. Found: C, 78.91; H, 10.45; O, 10.35; methoxyl, 9.74.

Saponification of 0.18 g. of this ester XVIIIa was accomplished by heating under reflux for 1.5 hr. with 20 cc. of 3% methanolic potassium hydroxide. The oily acid (0.165 g.) was distilled at 160°/0.03 mm. and did not exhibit an ultraviolet absorption maximum, only a shoulder at 217 mμ, log ε 3.89 being observed, $[\alpha]_D$ +19.5° (c, 1.03), $\lambda_{max}^{CHCl_3}$ 5.89, 6.09, 11.20, 11.60 μ. The infrared spectrum was identical with that of copalic acid (VIa).

Anal. Calcd. for $C_{20}H_{32}O_2$: C, 78.89; H, 10.59. Found: C, 78.99; H, 9.97.

The dehydration of 2.0 g. of the lower melting hydroxy ester XVIIb (m.p. 98–99°) was performed exactly as described for XVIIa and proceeded in identical yield to afford an unsaturated ester (XVIIIb) with the following constants (see Discussion for mass spectrographic and gas phase chromatographic results): $\lambda_{max}^{C_2H_5OH}$ 219 mμ, log ε 4.14, $\lambda_{max}^{CHCl_3}$ 5.83, 6.06, 11.20, 11.56 μ,[31] $[\alpha]_D$ +48.1° (c, 1.18), the plain optical rotatory dispersion curve (c, 0.426 in methanol), remaining positive as had already been noted with its precursor XVIIb: $[\alpha]_{589}$ +50°, $[\alpha]_{500}$ +64°, $[\alpha]_{400}$ +119°, $[\alpha]_{370}$ +148°, $[\alpha]_{350}$ +174°, $[\alpha]_{300}$ +277°, $[\alpha]_{285}$ +353°.

Anal. Calcd. for $C_{21}H_{24}O_2$: C, 79.19; H, 10.76; O, 10.05; methoxyl, 9.74. Found: C, 79.19; H, 10.44; O, 10.34; methoxyl, 9.68.

Saponification led to the free acid, which after distillation at 160°/0.01 mm. exhibited $[\alpha]_D$ +38.2° (c, 1.16), $\lambda_{max}^{CHCl_3}$ 5.88, 6.10, 11.20, 11.50 μ, the infrared spectrum differing in the 8–9 μ region from that of copalic acid (VIa). The ultraviolet absorption spectrum showed an inflection at 217 mμ, log ε 3.95.

Anal. Calcd. for $C_{20}H_{32}O_2$: C, 78.89; H, 10.59; O, 10.51. Found: C, 78.86; H, 10.76; O, 10.72.

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[31] The principal difference between this spectrum and those of its isomer XVIIIa and methyl copalate (VIb) resided in the 8–9 μ region.

[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA SCHOOL OF FORESTRY]

On the Occurrence of α-Thujaplicinol in the Heartwood of *Cupressus pygmaea* (Lemm.) Sarg.

EUGENE ZAVARIN, ARTHUR B. ANDERSON, AND ROSALIND M. SMITH

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A new tropolone, α-thujaplicinol, and nootkatin, have been isolated from the heartwood of *Cupressus pygmaea* (Lemm.) Sarg. On the basis of spectroscopic data and degradative experiments, the structure of the first is deduced to be that of 6-isopropyl-7-hydroxytropolone.

In the course of paper-chromatographic investigation of the tropolonic fractions from heartwood of species mainly of the genera *Cupressus* and *Juniperus*, a number of spots that could not be related to any of the known tropolones appeared on the paper in several instances.[1] The heartwood of *Cupressus pygmaea*, a species growing in Mendocino County, California, seemed particularly rich in these materials. This report deals with the

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(1) E. Zavarin, R. M. Smith, and A. B. Anderson, *J. Org. Chem.*, 24, 1318 (1959).

determination of the structure of α-thujaplicinol, a tropolone type compound isolated from the heartwood of *Cupressus pygmaea* and designated previously as T-11.

Steam distillation of the acetone extract of the *Cupressus pygmaea* heartwood sawdust gave a 2% yield[2] of volatile oil, a small part of which crystallized. The crystals were purified to yield 0.004% of nootkatin. The remaining oil was separated by the usual methods to give 8% neutral materials, 14.8% phenols, 69% tropolones, and 8.2% acids. During the separation it was noticed that part of the tropolones formed with dilute sodium hydroxide a salt of very low solubility; paper chromatography indicated that this was composed essentially of pygmaein.[1] The sodium hydroxide soluble part of the tropolonic substances on fractional crystallization of its dicyclohexylamine adduct gave crystals, m.p. 130.0–130.5°, which, when chromatographed, gave a spot corresponding to the T-11 compound. Liberation of the parent substance by means of dilute sulfuric acid and distillation gave a colorless oil, which could not be induced to crystallize.

The isolated material gave positive ferric chloride and copper acetate tests for tropolones. The molecular formula was $C_{10}H_{12}O_3$, as determined by elementary analysis and Rast molecular weight determination (192 ± 20%). It was characterized in addition to the mentioned dicyclohexylamine adduct by the preparation of the benzylamine adduct, m.p. 110–111°, and the copper chelate, m.p. 303.5–304.5°. The latter formed in 1:1 molecular ratio and did not show any hydroxyl bands in infrared[3] indicating that the tropolonic nucleus should carry a second hydroxyl.

The ultraviolet and infrared spectra of the isolated substance (Figs. 1 and 2) as well as of its copper complex were characteristically tropolonic[4] and very similar to those of β-thujaplicinol.[3] Run in various concentrations in carbon tetrachloride, the infrared 3230 cm.$^{-1}$ hydroxyl peak of the obtained material appeared as a singlet and did not change essentially its position or shape. This,[3] as well as the fine structure around 360 mμ in ultraviolet,[5] suggests the *ortho* placement of the second hydroxyl. The NMR spectrum exhibited *inter alia* a doublet at +8.70 and +8.82 p.p.m.[6] (J of 7 c.p.s.[7]) assigned to the isopropyl methyl protons and a multiplet at +6.26 p.p.m. assigned to the isopropyl tertiary hydrogen.

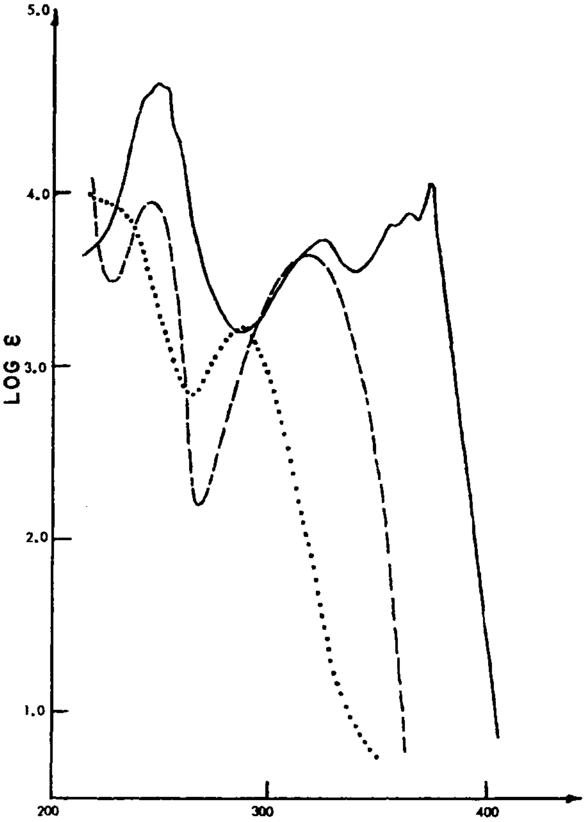

Fig. 1. Ultraviolet absorption spectra of α-thujaplicinol (——), 2-methoxy-3-isopropylbenzoic acid (......), and 3-isopropylsalicylic acid (------)

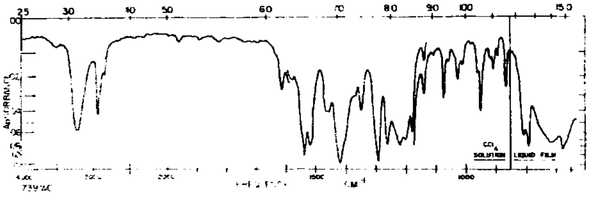

Fig. 2. Infrared spectrum of α-thujaplicinol

The determination of the isopropyl nature of the side chain by NMR methods, and the suggestion from infrared and ultraviolet data, that the additional hydroxyl is *ortho* positioned, reduce the number of the possible structural isomers to two, one of which corresponds to β-thujaplicinol. The isolated substance accordingly should possess the structure of 6-isopropyl-7-hydroxytropolone or of α-thujaplicinol (I), if named in conformity to the β-isomer.[8]

Treatment of the isolated compound with an excess of diazomethane in ethyl ether, followed by refluxing of the resulting methyl ethers with methanolic sodium methoxide, gave an aromatic acid, $C_{11}H_{14}O_3$, m.p. 66–67° (II), containing one methoxyl. Cleavage of the methoxyl with hydriodic/acetic acid mixture produced a corresponding

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[2] All yields referring to wood substance are calculated on dry wood basis.

[3] J. A. F. Gardner, G. M. Barton, and H. McLean, *Can. J. Chem.*, 35, 1039 (1957).

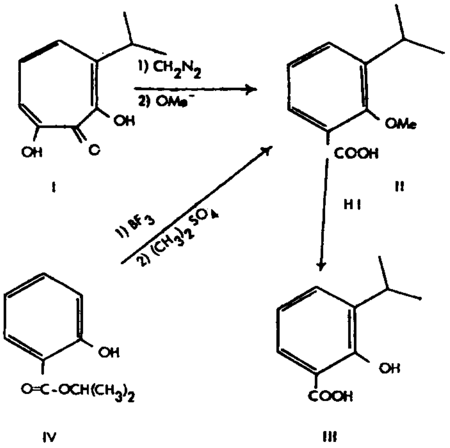
[4] P. L. Pauson, *Chem. Revs.*, 55, 19 (1955).

[5] T. Nozoe, S. Seto, S. Ito, M. Sato, and T. Katono, *Sci. Rep. Tôhoku Univ., Ser. 1*, 37, 191 (1953).

[6] The chemical shifts in parts per million were calculated in relation to tetramethylsilane peak as +10.

[7] J. D. Roberts, *Nuclear Magnetic Resonance*, McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 53.

[8] J. A. F. Gardner and G. M. Barton, *Can. J. Chem.*, 36, 1612 (1958).



hydroxy acid, $C_{10}H_{12}O_3$, m.p. 68–69°, (III). Contrary to II, III gave a violet color with aqueous ferric chloride, in the ultraviolet the benzenoid B-band moved from 287 to 317 mμ,[9] and in the infrared the carboxylic carbonyl peak shifted from 1695 to 1632 cm.$^{-1}$, [10] indicating a salicylic acid structure. The identity of the acid (III) was finally established by comparison with the 3-isopropylsalicylic acid synthesized by rearrangement of isopropyl salicylate (IV) with boron trifluoride.[11,12] This seems to determine unequivocally the structure of tropolone (I) as well as of its rearrangement product.

As far as is known, α-thujaplicinol has neither been isolated from any natural source nor synthetically prepared. It has been postulated as an intermediary product in alkaline peroxide oxidation of α- and β-thujaplicins.[13] Attempts to prepare it through diazotization of 3-amino-4-isopropyltropolone gave only 6-isopropylsalicylic acid.[14] Persulfate oxidation of α-thujaplicin resulted in formation of only 5-hydroxy-α-thujaplicin.[15] It has been chromatographically identified in *Cupressus pygmaea, abramsiana,* and *goveniana.*[1] Investigation is planned for its possible fungistatic activity toward wood destroying fungi.

EXPERIMENTAL[16]

Preparation of volatile oil. The sample of *Cupressus pygmaea* wood was collected in the Pygmy Forest, east of Fort Bragg, California. A 3022-g. heartwood sawdust portion, containing about 10% moisture, was extracted with acetone and the extract steam distilled using 39 l. of water. The oil contained in the final 16 l. of distillate solidified upon standing. It was filtered and recrystallized three times from 10 ml. of iso-octane to give 115 mg. of material, m.p. 95–96° (0.004% yield), found to be identical with nootkatin according to the mixed melting point and infrared techniques, using the compounds themselves and their copper chelates.

The remaining steam distillate was repeatedly extracted with a total of 7 l. of chloroform under addition of an excess of copper acetate during the later stages of extraction. The chloroform extracts were treated with an excess of hydrogen sulfide, evaporated to about 300 ml., filtered and evaporated to dryness to give 54.8 g. of an oil (1.97% yield).

Segregation of the volatile oil. The total amount of extract was dissolved in 130 ml. of *n*-hexane, treated with 100 ml. of 10% sodium hydroxide and cooled to +5°. The heavy, yellow precipitate of tropolone salts was filtered and washed with water and *n*-hexane to give 21.40 g. of sodium tropolonates. Chromatography indicated that this fraction was composed essentially of pygmaein.

The aqueous phase was separated from the filtrates, and the *n*-hexane solutions were extracted with 100 ml. of 10% sodium hydroxide in two portions. The separated organic layer gave 4.40 g. of neutral materials (8.0% in oil; 0.16% wood basis).

The *p*H of the aqueous extract was adjusted to 8.0 with carbon dioxide, the resulting liquid was extracted with 300 ml. of ethyl ether in four portions, and the extracts were washed with 300 ml. of water. The aqueous extracts were combined, acidified with an excess of hydrochloric acid, and extracted with 250 ml. of ethyl ether in four portions. The ether extracts gave 4.50 g. of acidic materials (8.2% in oil 0.16% wood basis). The material gave negative cupric acetate test for tropolones.

The ether extracts from the solution of *p*H 8.0 were combined and evaporated to dryness. The residue gave strong cupric acetate test for tropolones. It was dissolved in 400 ml. of *n*-hexane, and shaken with 400 ml. of 85% phosphoric acid in four portions.[17] The organic phase was separated to give 8.15 g. of phenolic oil (14.8% in oil; 0.29% wood basis).

The phosphoric acid solution was diluted with 2.5 l. of water containing 200 ml. of concd. ammonia, and extracted with 450 ml. of chloroform in five portions. The organic extract gave 18.55 g. of tropolonic oil. Thus, the amount of tropolones isolated from the volatile oil, together with pygmaein, isolated before as sodium salt, could be estimated as 37.75 g. (69% in oil; 1.36% wood basis).

Isolation and characterization of α-thujaplicinol. The total amount of tropolonic mixture separated by means of phosphoric acid was dissolved in 75 ml. of *n*-hexane, treated with 20 g. of dicyclohexylamine (1:1.07 molar ratio) and the separated precipitate washed with *n*-hexane to give 28.5 g. of yellow powder. Repeated crystallization of one half of this material from iso-octane/chloroform gave 5.5 g. of crystals, m.p. 129.2–130.7° (10% yield from the oil). Chromatograms showed composition essentially of T-11 tropolone.

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[9] According to P. Grammaticakis, [*Bull. soc. chim. France,* 821 (1953)], methylation of phenolic hydroxyl of salicylic acid causes hypsochromic shift of both benzenoid and K-ultraviolet absorption bands.

[10] L. J. Bellamy, *The Infrared Spectra of Complex Molecules,* Methuen & Co., London, 1954, 145.

[11] All isopropylsalicylic acids are known; (a) 3-isopropylsalicylic acid, m.p. 71–72°, M. Fileti, *Gazz. chim. ital.,* **16,** 113 (1886); (b) 4-isopropylsalicylic acid, m.p. 95–96° and 6-isopropylsalicylic acid, m.p. 122–123°, T. Nozoe, Y. Kitahara, and K. Doi, *J. Am. Chem. Soc.,* **73,** 1895 (1951); (c) 5-isopropylsalicylic acid, m.p. 116°, H. Meyer and K. Bernhauer, *Monatsh.,* **53** and **54,** 721 (1929).

[12] W. J. Croxall, F. J. Sowa, and J. A. Nieuland, *J. Am. Chem. Soc.,* **56,** 2054 (1934).

[13] T. Nozoe, *Festschr. Arthur Stoll,* Birkhauser, A. G. Basel, 1957, p. 765.

[14] T. Nozoe, Y. Kitahara, and K. Doi, *Proc. Japan Acad.,* **27,** 282 (1951).

[15] T. Nozoe, S. Seto, S. Ito, M. Sato, and T. Katono, *Proc. Japan Acad.,* **28,** 488 (1952).

[16] All melting points are corrected; microanalysis by Microchemical Laboratory, University of California, Berkeley. Ultraviolet and infrared spectra were run on Beckman DK II and Perkin-Elmer Model 21 recording spectrophotometers, respectively, and NMR spectra on Varian Associates spectrometers.

[17] Y. T. Lin, T. B. Lo, and K. T. Wang, *J. Chinese Chem. Soc.* (Taiwan) **5,** 54 (1958).

From a 1.01-g. portion of this salt, the parent tropolone was regenerated by the procedure already described[18] and evaporatively distilled at 2 mm. pressure to give 448 mg. of a colorless oil (89% yield), n_D^{25} 1.6323, d_4^{22} 1.184.

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.81; H, 6.59; mol. wt. (Rast): Calcd.: 180. Found: 192 ±10%.

An analytical sample *of dicyclohexylamine salt* was prepared by crystallization from acetone to give rhomboidal crystals, m.p. 130.0–130.5°.

Anal. Calcd. for $C_{22}H_{35}O_3N$: C, 73.09; H, 9.76. Found: C, 73.01; H, 9.53.

A *benzylamine adduct* was prepared in the usual way,[18] and purified by recrystallization from iso-octane to give fine yellow needles, m.p. 110.2–110.8°.

Anal. Calcd. for $C_{17}H_{21}O_3N$: C, 71.05; H, 7.37. Found: C, 71.43; H, 7.35.

The *copper complex* was prepared by the usual procedure, and recrystallized from benzene/iso-octane to give a fine powder, m.p. 303.5–304.5° with previous darkening.

Anal. Calcd. for $C_{10}H_{10}O_3Cu$: C, 49.69; H, 4.17; Cu, 26.29. Found: C, 49.92; H, 4.45; Cu, 25.93.

Spectral characteristics of α-thujaplicinol (*I*). Ultraviolet: λ max 247.5 mμ (log ε 4.63); 324 mμ (log ε 3.73); 356 (log ε 3.82); 364 mμ (log ε 3.88); 372.5 mμ (log ε 4.05)—(iso-octane).

Infrared: 3230m, 2950m, 2860w, 1615w, 1585w, 1538s, 1520s, 1455–1470m, 1420s, 1350m, 1292s, 1262s, 1220s, 1200s, 1180s, 1140w, 1110w, 1075w, 1060w, 1027w, 1010w, 938w, 962, 950, 920, 910, 895, 866 (all weak)—carbon tetrachloride; 805m, 790m, 710m, 675m—(liquid film).

The influence of concentration on the hydroxyl singlet was determined by running the infrared spectra of the compound as liquid film (6.57*M*), and as 0.524, 0.262, and 0.040*M* carbontetrachloride solutions. The position of the hydroxyl peak shifted from 3260 to 3200 cm.$^{-1}$ when going toward more concentrated solutions. The shape of the peak remained the same; the ratio of the intensity of the hydroxyl peak to that of the strongest carbon-hydrogen stretching peak changed from 0.835 to 1.21, 1.35, and 2.20 going toward the more concentrated solutions.

NMR: (25% in carbon tetrachloride; 60 mc; tetramethylsilane as internal standard).[6] A singlet at +0.73 p.p.m. due to the two hydroxyls, an asymmetric multiplet with a main peak at +2.88 p.p.m. due to aromatic protons, a symmetric multiplet corresponding to isopropyl heptuplet with five peaks discernable and with a middle peak at +6.26 p.p.m. (J = 7.0), and the isopropyl doublet at +8.70 and +8.82 p.p.m. (J = 7.0) were observed; intensities of the above groups of peaks were roughly in the expected order of 2:3:1:6.

Special characteristics of α-thujaplicinol copper complex. Ultraviolet: λ_{max} 660 mμ (log ε 1.59); 397 mμ (log ε 3.62); 327 mμ (log ε 3.78); 270 mμ (log ε 4.42)—(ethanol).

Infrared: No OH stretching bands–carbon tetrachloride; carbonyl at 1615 cm.$^{-1}$—potassium bromide.

Ultraviolet of β-thujaplicinol copper complex: λ_{max} 670 mμ (log ε 1.50); 398 mμ (log ε 3.67); 326 (log ε 3.96); 266 mμ (log ε 4.38); 228 mμ (log ε 3.70)–(ethanol).

Rearrangement of the methylated α-thujaplicinol. The free α-thujaplicinol was obtained from 513 mg. of its dicyclohexylamine complex, m.p. 129.0–130.5°, and methylated with diazomethane using the known procedures. The resulting mixture was refluxed for 45 min. with a solution of 0.5 g. of sodium in 10 ml. of absolute methanol, acidified with dilute hydrochloric acid, treated with an excess of ammoniacal copper acetate solution and the separated copper tropolonates filtered off. The acidified filtrate was extracted with chloroform and the extract dried, filtered, and evaporated to dryness. The residue was dissolved in 5 ml. of isooctane, filtered from small amount of impurities, and treated with 0.25 g. of dicyclohexylamine. The resulting precipitate was filtered and recrystallized from iso-octane to give 20 mg. of material, m.p. 153–154° (4% yield).

When the same experiment was conducted using pygmaein, a monomethyl ether of α-thujaplicinol,[19] in the diazomethane methylation, a 31% yield of the above material was obtained.

An analytical sample of this salt was prepared by recrystallization from iso-octane/benzene to give clusters of small platelets, m.p. 155.5–156.5°.

Anal. Calcd. for $C_{23}H_{37}O_3N$: C, 73.56; H, 9.93. Found: C, 73.76; H, 10.00.

The parent acid was regenerated from 185 mg. of the dicyclohexylamine salt, m.p. 154.5–156.0°, with dilute sulfuric acid and evaporatively distilled at 2 mm. pressure to give 73.5 mg. of distillate which solidified to crystals, m.p. 65.8–66.8° (77% yield).

An analytical sample was prepared by recrystallization from *n*-hexane, to give small crystals, m.p. 67.5–68.5°.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27; OCH_3, 15.98. Found: C, 67.94; H, 6.91; OCH_3, 15.75.

Ultraviolet: λ_{max} 287 mμ (log ε 3.23)—(iso-octane). Infrared: Carboxylic carbonyl at 1695 cm.$^{-1}$–potassium bromide.

Preparation of 3-isopropylsalicylic acid (III). A 408-mg. portion of the acid (II), m.p. 65–67°, was refluxed for 2 hr. with a mixture of 8 ml. of 47% hydriodic acid and enough acetic acid to form a homogeneous solution and then diluted with water. The precipitate was filtered to give 328 mg., m.p. 65–67°; crystallization from *n*-hexane gave rhomboidal plates, m.p. 69–70°. The material was found to be identical with the synthetic compound by mixed melting point and infrared techniques.

Ultraviolet: λ_{max} 317 mμ (log ε 3.64); 245 mμ (log ε 3.95)–(isooctane). Infrared: Carboxylic carbonyl at 1632 cm.$^{-1}$–(potassium bromide).

Synthesis of 2-methoxy-3-isopropylbenzoic acid. The rearrangement was conducted using 21 g. of commercial isopropyl salicylate[20] according to the procedure of Croxall, *et al.*[12] The mixture of rearrangement products obtained was methylated four times using 80-ml. portions of 80% sodium hydroxide and 25-g. portions of dimethyl sulfate. The resulting liquid was made basic with an excess of sodium hydroxide, heated until clear, acidified with hydrochloric acid and extracted with *n*-hexane. The extract obtained was treated with 15.5 g. of dicyclohexylamine, the resulting precipitate filtered and recrystallized from *n*-hexane/benzene to give 3.7 g. of material, m.p. 155–156° (8.5% yield).

This salt as well as the free acid regenerated from it, m.p. 68–69°, were found to be identical by mixed melting point and infrared techniques with the corresponding dicyclohexylamine salt and the free acid obtained by rearrangement of the α-thujaplicinol methyl ethers.

Acknowledgments. The authors are indebted to Mr. William Dost of the California Redwood Association for the *Cupressus pygmaea* wood, to Mr. Alvin J. Berlin for NMR spectra and to Mr. G. M. Barton for a sample of β-thujaplicinol.

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[18] E. Zavarin, R. M. Smith, and A. B. Anderson, *J. Org. Chem.*, 24, 1534 (1959).

[19] To be published.

[20] Eastman Kodak, b.p. 120–122°/18 mm.