twice from ethanol–water (Norit) to give shiny white plates of anilide, m.p. 139–140° (lit. m.p. 140°).[6]

Anal. Calcd. for $C_{12}H_{13}NO$: C, 76.97; H, 7.00; N, 7.48. Found: C, 76.80; H, 7.03; N, 7.53.

Carbethoxycyclopentane.—Cyclopentane carboxylic acid (1.50 g.) was treated with diazoethane and distilled to give 1.72 g. (92%) of carbethoxycyclopentane, b.p. 87–90° (45 mm.), $n^{24}\text{D}$ 1.4325 (lit.[14] b.p. 89.3° (45 mm.), $n^{20}\text{D}$ 1.4360).

Carbethoxycyclopentane by Reduction of IX.—4-Carbethoxycyclopentene (IX) (140 mg.) was hydrogenated over 10% palladium on charcoal. Sixty-four milligrams of the saturated ester, $n^{23}\text{D}$ 1.4332, was isolated by preparative vapor phase chromatography. The infrared spectrum was identical to that of an authentic sample, and retention times on vapor phase chromatography were the same.

4-Hydroxymethylcyclopentene (X) **A.**—A solution of 2.68 g. of IX in 20 ml. of dry ether was added dropwise, with stirring and cooling, to a slurry of 1.50 g. of lithium aluminum hydride in 20 ml. of dry ether. The reaction mixture was stirred overnight and was then hydrolyzed by the addition of 6 ml. of water dropwise with cooling and stirring followed by stirring for an additional hour. The organic salts were removed by filtration and were dried over anhydrous magnesium sulfate. After removal of the drying agent and solvent, the residue was distilled to yield 1.63 g. (87%) of X, b.p. 98–99° (57 mm.), $n^{22}\text{D}$ 1.4670. An analytical sample was prepared by preparative vapor phase chromatography.

Anal. Calcd. for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 73.16; H, 10.37.

B.—A Grignard reagent was prepared by adding 4.12 g. of 4-bromocyclopentene[12] dissolved in 20 ml. of dry ether to 0.85 g. of magnesium turnings in 10 ml. of dry ether. The entire reaction was carried out under nitrogen with vigorous mechanical stirring. After the addition was complete, stirring was continued for 0.5 hr. At this point the nitrogen flow was diverted through a flask containing 3.0 g. of paraformaldehyde which had previously been dried over phosphorus pentoxide. This flask was immersed in an oil bath at 180°, causing the paraformaldehyde to depolymerize, yielding gaseous, monomeric formaldehyde which was swept into the Grignard solution by the nitrogen stream. After a good excess of formaldehyde had been introduced, the reaction mixture was stirred for an additional 0.25 hr. and then poured into ice–dilute hydrochloric acid. This mixture was extracted thrice with ether and the combined ether extracts were washed with sodium carbonate solution, then water, and dried over anhydrous magnesium sulfate. The drying agent and solvent were removed and the residue was distilled to give 1.04 g. (38%) of *X*, b.p. 105–108°, $n^{24}\text{D}$ 1.4697. This material had an infrared spectrum identical with that of the product obtained above in part **A**.

4-Dimethylhydroxymethylcyclopentene (IIB).—One gram of IX in 20 ml. of dry ether was added dropwise to the Grignard reagent prepared from 1.00 g. of magnesium, 3.00 g. of methyl iodide, and 50 ml. of anhydrous ether. The reaction mixture was stirred at room temperature for 0.5 hr., followed by hydrolysis with saturated ammonium chloride solution. The ethereal layer was removed and dried over anhydrous sodium carbonate. After removal of the drying agent and solvent, the product was isolated by preparative vapor phase chromatography to give 0.36 g. (40%) of IIB, $n^{26}\text{D}$ 1.4640.

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.82; H, 11.21.

Acknowledgment.—The authors are grateful to the General Aniline and Film Corporation for a generous gift of *cis*-but-2-ene-1,4-diol, and to the National Science Foundation for partial support of this work.

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[13] Similar results were obtained by G. S. Skinner and F. P. Florentine, *J. Am. Chem. Soc.*, **76**, 3200 (1954), who observed that cyclopentylmagnesium bromide gave only 10% of the corresponding tertiary alcohol on treatment with acetone.

[14] F. C. Whitmore, J. M. Crosby, W. S. Sloatman, and D. G. Clarke, *J. Am. Chem. Soc.*, **64**, 1801 (1942).

On the Structures of α-Dolabrinol and Isopygmaein

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During a paper chromatographic investigation[1] of the tropolones from a number of wood species in the family Cupressaceae we encountered five new tropolonic compounds, and recently[2,3] we determined the structures of two of them: pygmaein and α-thujaplicinol. This report deals with the isolation and structure determination of two further compounds, previousy designated as T-10 and T-0.1.

Preparative paper chromatography was applied to the mixture of α-thujaplicinol and the T-10 tropolone from *Cupressus pygmaea* (Lemm.) Sarg. Thick S&S 470 paper impregnated with dimethyl sulfoxide[4] was used, with isoöctane as eluent. The pure T-10 tropolone was obtained as a colorless oil and was purified by evaporative distillation.

The isolated T-10 material gave a red complex with ferric chloride solution, a green complex with copper acetate, and a yellow salt with sodium hydroxide. Its formula was $C_{10}H_{10}O_3$, with molecular weight (Rast) of 165 ± 10%. It exhibited a typical tropolonic electronic spectrum, similar to that of α-thujaplicinol and a typical infrared spectrum. Its n.m.r. spectrum also agreed with the tropolonic structure and indicated the presence of an isopropenyl side chain.

Hydrogenation of the isolated material, with palladium on charcoal as catalyst, indicated the presence of one double bond; the hydrogenated material was identical to α-thujaplicinol. The T-10 tropolone, accordingly, should possess the formula of 3-isopropenyl-7-hydroxytropolone, or α-dolabrinol (structure I).

So far only two natural tropolones with isopropenyl side chains—β-dolabrin and procerin[5,6]—

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

[2] E. Zavarin and A. B. Anderson, *ibid.*, **26**, 1679 (1961).

[3] E. Zavarin, A. B. Anderson, and R. M. Smith, *ibid.*, **26**, 173 (1961).

[4] C. A. Wachmeister and B. Wickberg, *Acta Chem. Scand.*, **12**, 1335 (1958).

[5] T. Nozoe, K. Takase, and M. Ogata, *Chem. Ind.* (London), 1070 (1957).

[6] J. Runeberg, *Acta Chem. Scand.*, **15**, 645 (1961).

have been definitely encountered, although infrared investigations of some roughly characterized tropolones indicate that more should be expected.[7]

Preparative paper chromatography by the 21% phosphoric acid–toluene method was applied to the isoöctane-soluble portion of the heartwood extract of *Papuacedrus torricellenis* (Schlechter) Li, in which the tropolone T-0.1 had been found.[1] A new tropolonic compound, m.p. 111–112°, was isolated in the form of white crystals. It gave the usual color reactions with ferric chloride, copper acetate, and sodium hydroxide, had a formula of $C_{12}H_{14}O_3$, a molecular weight of 194 ± 10% (Rast), and possessed a methoxy group. Its electronic absorption spectrum was similar to that of pygmaein and its infrared spectrum was characteristically tropolonic. It was further characterized as a 2:1 copper complex, m.p. 272.5–274.0°.

When α-thujaplicinol was methylated with about one equivalent of diazomethane, a 28% yield was obtained of a compound identical with that obtained from *P. torricellensis*. Accordingly the isolated material should be one of the three possible monomethyl ethers of α-thujaplicinol (structures II, III, and IV) of which one, 3-methoxy-4-isopropyltropolone or pygmaein, is known (structure IV).[2] Of the two remaining structures, II represents a derivative of 3-hydroxytropone. Investigations of the parent compound and its halogen derivatives[8] indicated that contrary to tropolones, the 3-hydroxytropones do not chelate with iron and that they exhibit no properties, spectral or other, associated with intramolecular hydrogen bonding. This should be even more true with structure II through steric interference of the methoxy group.

The α-thujaplicinol monomethyl ether isolated from *P. torricellensis* formed the ferric and copper complexes. Its ultraviolet spectrum, like that of pygmaein, revealed the strong absorption in the 350–375-mμ region, considered to stem from intramolecular hydrogen bonding.[9] Its infrared spectrum showed hydroxyl absorption in carbon tetrachloride solution at 3060 cm.$^{-1}$. The intensity of this band remained unchanged after dilution, indicating again the presence of an intramolecular hydrogen bond. The carbonyl peak was present at 1602 cm.$^{-1}$ (CCl_4), whereas in case of 3-hydroxytropones it was always found at a shorter wave length.

All of this evidence seems to eliminate structure II from consideration; accordingly the compound isolated from *P. torricellensis* must possess the structure of 3-isopropyl-7-methoxytropone, empirically isopygmaein (III).[10]

So far, pygmaein and isopygmaein have never been obtained together. It remains to be seen whether this means an exceptional selectivity on the part of the enzymatic methylation systems involved or the existence of formation mechanisms other than simple methylation of α-thujaplicinol.

In paper chromatographic experiments, demethylation with hydrobromic acid of a sample of pygmaein containing neither α-thujaplicinol nor α-dolabrinol resulted in formation of α-thujaplicinol, with a smaller amount of α-dolabrinol. As small amounts of the unknown tropolone T-4.5 always accompany pygmaein, T-4.5 may be a monomethyl ether of β-dolabrinol, probably corresponding to pygmaein. The work of separating and determining the structure of T-4.5 tropolone is being continued.

Experimental

Isolation and Characterization of α-Dolabrinol.—The residue from crystallization of the dicyclohexylamine salt of α-thujaplicinol[3] was combined with the remaining half of the crude dicyclohexylamine salts to give 23.5 g. of material. This was converted into free tropolones by the usual procedure[11] and distilled to give 11.2 g. of a viscous oil. A 934-mg. portion of the oil, as a stripe about 2 cm. thick, was chromatographed, using isoöctane as the mobile phase. A 14.5 × 58-cm. piece of S & S 470 chromatographic paper impregnated with 17% phosphoric acid was used. The positions of the fractions obtained were located by treating the paper with ammonia gas, and the corresponding zones were eluted with chloroform to yield solutions of pygmaein, of β-thujaplicin, and of a mixture of α-thujaplicinol and α-dolabrinol, which do not separate well by this method. The mixture was evaporated to dryness to give 449 mg., and α-dolabrinol was separated from α-thujaplicinol by paper chromatography, using only dimethyl sulfoxide-impregnated paper. Eluting α-dolabrinol and converting it into dicyclohexylamine salt gave 58 mg. of material, m.p. 139–142° (3% of the original tropolone mixture). Recrystallization from isoöctane raised the melting point to 141.5–142.5°.

Anal. Calcd. for $C_{22}H_{33}O_3N$: C, 73.50; H, 9.25. Found: C, 73.69; H, 9.31.

A 92-mg. portion of the above recrystallized material was converted into the free tropolone, and the resulting liquid obtained from two chromatographic runs was distilled at 1–2 mm. pressure. The bulk of the material distilled between 140° and 160° to give 43 mg. (94% yield) of a viscous oil, which could not be induced to crystallize.

Anal. Calcd. for $C_{10}H_{10}O_3$: C, 67.40; H, 5.66; mol. wt. (Rast), 178. Found: C, 67.39; H, 5.88; mol. wt., 165.

The benzylamine salt was prepared by the usual procedure

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[7] E. Pettersson and J. Runeberg, *Acta. Chem., Scand*, **15**, 713 (1961).

[8] R. B. Johns, A. W. Johnson, and M. Tisler, *J. Chem. Soc.*, 4605 (1954).

[9] M. Tsuboi, *Bull. Chem. Soc. Japan*, **25**, 368 (1952).

[10] The possibility that the isolated compound might be a Nozoe modification of pygmaein does not seem to hold. The isomers mentioned have never been obtained by simple methylation of a pure tropolone, and they interconvert easily even during recrystallization whereas the materials isolated from *P. torricellensis* were always stable.[14] In case of α-thujaplicin, Nozoe reports that the modification melting at 25.5–26.0° transformed into the one melting at 33–34° upon dissolution in concentrated sulfuric acid.[14b] When either pygmaein or isopygmaien was so treated, paper chromatography of the reaction products revealed no isomerization. As far as we are aware, the Nozoe modifications showed no mixed melting point depression of the lower melting modification. A 5° depression was obtained by mixing pygmaein with isopygmaein, and a 28° depression was obtained with their copper complexes. With the modifications of β-thujaplicinol, no difference was noted in positions of absorption maxima in electronic spectra,[9] but with isopygmaein and pygmaein the maxima were found at the different positions.

[11] E. Zavarin, R. M. Smith, and A. B. Anderson, *J. Org. Chem.*, **24**, 1584 (1959).

and recrystallized from isoöctane to yield needles, m.p. 97–98°.

Anal. Calcd. for $C_{17}H_{19}O_3N$: C, 71.56; H, 6.71. Found: C, 71.41; H, 6.59.

Spectral Characteristics of α-Dolabrinol.—Electronic absorption (isoöctane): λ_{max} 248.5 (log ε 4.31), 325 (log ε 3.68), 356 (log ε 3.60), 365 (log ε 3.69), 374 (log ε 3.79).

Infrared absorption (KBr pellets): 3250s, 2970w, 2930w, 1637w, 1613w, 1585m, 1540s, 1520s, 1455s, 1420s, 1375s, 1305s, 1285s, 1265s, 1240s, 1195s, 1100w, 1060m, 1040w, 1013w, 962m, 908m, 895m, 815m, 795m.

N.m.r. (shifts in p.p.m. relative to tetramethylsilane as +10.0; carbon tetrachloride solution): +7.8 (CH_3O; relative intensity 3.0); +5.0, +4.8 (CH_2=; rel. int. at doublet 2.0); +3.0 (H—aromatic; rel. int. 3.0); +1.15 (OH; rel. int. 2.0).

Hydrogenation of α-Dolabrinol.—Quantitative hydrogenation in acetic acid, with palladium on charcoal as catalyst, using the analytical sample of α-dolabrinol dicyclohexylamine salt, resulted in an absorption equivalent to 348 mg. of substance per mmole of hydrogen (*vs.* calculated 359 mg.).

In another experiment, 51.0 mg. of α-dolabrinol was hydrogenated in 4 ml. of 95% ethanol in presence of 12 mg. of 5% palladium on charcoal. The absorption of hydrogen stopped after 15 min. stirring. Filtration, evaporation to dryness, and evaporative distillation of the residue at 2 mm. pressure gave 44 mg. of α-thujaplicinol (85% yield). The material obtained, run as a smear, and its benzylamine salt run as potassium bromide pellets, showed infrared spectra identical with those of the authentic α-thujaplicinol and its salt. The dicyclohexylamine salt melted at 128–129° and the benzylamine salt 113.0–114.0°; these melting points were not depressed by admixture with authentic samples. Previously[3] the melting point of the benzylamine salt was reported as slightly lower. The higher melting point reported here was also reproduced with chromatographically purified α-thujaplicinol benzylamine salt. Insufficient separation of α-thujaplicinol from α-dolabrinol in previous experiments probably accounts for the discrepancy.

Isolation of Isopygmaein.—A 1.9-g. portion of the *n*-hexane-soluble part of the *Papuacedrus torricellensis* extract[1] was chromatographed on S & S 470 paper impregnated with 21% phosphoric acid, using toluene as eluent, as described above. The material separated into two fractions, and the fraction with lower R_f was eluted with chloroform. The evaporation residue of eluate was taken up in 15 ml. of warm isoöctane, treated with small amounts of charcoal, filtered, and cooled to −5°. The separated crystals after recrystallization weighed 22 mg. and melted at 111.0–112.0°.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27; mol. wt. (Rast), 194. Found: C, 68.15; H, 7.49; mol. wt., 206.

The material was characterized further as copper complex (2:1), m.p. 272.5–273°.[12]

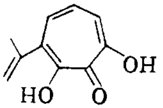
Anal. Calcd. for $C_{22}H_{26}O_6Cu$: C, 58.72; H, 5.82. Found: C, 58.52; H, 5.75.

Spectral Characteristics of Isopygmaein.—Electronic absorption (isoöctane): λ_{max} 373 (log ε 3.77), 358 (log ε 3.75), 326 (log ε 3.75), 313 infl. (log. ε 3.63), 250 (log ε 4.47).

Infrared absorption (KBr): 3220s, 2980m, 2890m, 1590m, 1555s, 1495m, 1475s, 1463s, 1445m, 1410s, 1390m, 1365m, 1337s, 1290s, 1243s, 1230s, 1210s, 1195m, 1168s, 1140s, 1095s, 1065m, 1035m, 990m, 920m, 855m, 800m, 783w, 760m, 675m. In carbon tetrachloride (0.23 *M*), the hydroxyl stretching peak shifted to 3060 cm.$^{-1}$ with decrease in intensity; neither intensity nor position was changed by dilution to 0.028 *M* solution. The carbonyl peak was found at 1602 cm.$^{-1}$.

The shift in position of the hydroxyl band upon dissolution was also observed for pygmaein. This was noted with other tropolones by Kuratani, *et al.*, and was explained by the existence of ring dimers with intermolecular hydrogen bonds in solid.[13]

Synthesis of Isopygmaein.—To a 595-mg. portion of α-thujaplicinol, n^{25}_D 1.6267, dissolved in 5 ml. of ethyl ether a solution of 150 mg. of diazomethane in 12 ml. of ethyl ether was added dropwise under stirring. The reaction was completed in a few minutes. The resulting mixture was evaporated to dryness, taken up in 20 ml. of warm isoöctane, treated with charcoal, filtered, and cooled to −5°. The separated crystals were filtered to give 138 mg. of material, m.p. 108–111° (28% yield); recrystallization raised the melting point to 110–111.5°. The substance obtained and its copper complex did not depress the melting point of the natural isopygmaein or its copper complex. Their infrared spectra and paper chromatograms were identical.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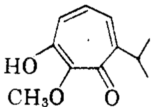
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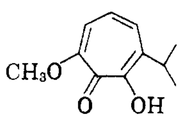
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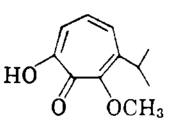
IV

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[12] At room temperature the copper complex of isopygmaein separated invariably in the form of gel-like voluminous material, either from alcohol or from isoöctane–chloroform mixture. The above crystalline modification was obtained by dissolving the material in hot isoöctane–chloroform mixture and removing the chloroform slowly on a steam bath.

[13] K. Kuratani, M. Tsuboi, and T. Shimanouchi, *Bull. Chem. Soc. Japan*, **25**, 250 (1952).

[14] (a) T. Nozoe, Y. Kitahara, and K. Doi, *Proc. Japan Acad.*, **27**, 282 (1951). (b) T. Nozoe, Y. Kitahara, K. Yamane, and T. Ikemi, *ibid.*, **27**, 193 (1951). (c) T. Nozoe, Y. Kitahara, E. Kunioka, and K. Doi, *ibid.*, **26**, (9) 38 (1950). (d) T. Nozoe and E. Sebe, *ibid.*, **26**, (9) 45 (1950).

Hydrogenolyses of Chloromethanes with Triphenyltin Hydride

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As part of a continuing study of the hydrogenolyses of organic halides with triphenyltin hydride, we are reporting on the stepwise hydrogenolyses of the chloromethanes.

When triphenyltin hydride was mixed with carbon tetrachloride at room temperature, an exothermic reaction took place which heated the solution to boiling. Chloroform was identified as one of the products by vapor phase chromatography, as well as by its n.m.r. spectrum. The companion product of the reaction, triphenyltin chloride, was identified by mixed melting point with an authentic

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[1] Taken from a portion of the dissertation submitted to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry, 1963.

[2] To whom inquiries should be sent.

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