mophore in the vicinity of an asymmetric carbon atom[4] (ref. (2), p. 146). The latter possibility is apparently more important with Djerassi's ketonic compounds,[4,6,8] but the former might play an important role in nonketonic substances [*cf.* emetine, ref. (11)]. Three other nonketonic aromatic compounds for which data are available: estradiol,[17] 6-dehydroestradiol,[17] and *cis*-13-methyl-3,4-dimethoxy-5,6,7,8,9,10,13,14-octahydrophenanthrene,[6] show normal behavior; however, their dispersion curves were followed only down to 315, 335, and 337.5 mμ, respectively. The present findings, together with those mentioned in ref. (15), suggest that the investigation of other aromatic nonketonic substances might be of great interest.

EXPERIMENTAL

The codeine and morphine samples were commercial samples manufactured by the New York Quinine and Chemical Works and Merck and Co., respectively; they were obtained through the Pharmacy School of the University of Connecticut. The dihydrocodeine was obtained from the L. F. Small Collection through the kind cooperation of Dr. L. J. Sargent of the National Institutes of Health. The measurements were made with a Model No. 200S Rudolph Photoelectric Spectropolarimeter[18] at the Ohio State University. A 0.1 decimeter tube with quartz ends was used.

Morphine (I), R. D. in dioxane (*c* 0.209): $[\alpha]^{19}$ ($\underline{500}$ mμ), −160°; ($\underline{340}$), −1280°; ($\underline{298}$), 420°.

Codeine (II), R. D. in dioxane (*c* 0.358): $[\alpha]^{21-21.7}$ ($\underline{650}$ mμ), −130°; ($\underline{589}$), −200°; ($\underline{305}$), −1360°; ($\underline{300}$), 360°.

Dihydrocodeine (III), R. D. in dioxane (*c* 0.246): $[\alpha]^{20.7-21}$ ($\underline{600}$ mμ), −210°; ($\underline{589}$), −220°; ($\underline{305}$), −1580°; ($\underline{300}$), −1050°.

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Characterization of Cupressaceae Tropolones as Dicyclohexylamine Salts

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Although a number of reactions can be used to characterize tropolones through the preparation of derivatives, only a few reagents appear to be generally satisfactory. For instance, transition metal chelates tend to have rather high melting points[1,2]; the nuclear substitution often yields several isomers, and the parent tropolone cannot be readily recovered from the derivative.[1] Similarly, several isomers usually result from esterification or etherification of the tropolonic hydroxyl;[1] hydrochloride salts do not appear to be very convenient for handling, and melting points often seem insufficiently sharp.[3,4] Picrates and ethylenediamine salts have been used with success in the case of a number of synthetically prepared tropolones.[3,5,6]

In our work on the natural tropolones from the heartwood of *Cupressaceae* species, (*i.e.*, tropolones of relatively weak acidity, carrying alkyl, methoxy, or hydroxy substituents), a question of identification of the isolated compounds often arose. The formation of amine salts appeared rather promising, and as it was felt to be generally desirable to have several convenient reagents available,[7] the whole area was reinvestigated using a number of amines in combination with several tropolones.

No derivatives could be obtained by using aromatic amines. This is understandable in view of their weaker basicity. Assuming *p*K values of 9.42 and 3.02[10] for aniline and diethylamine, respectively, and a *p*K of 7.21 for β-thujaplicin,[1] a rough calculation indicated that the corresponding salts should be hydrolyzed to 96% in the first case, and to only 1.4% in the second. Experimentally, using aniline and cyclohexylamine with nootkatin in 0.05 *N* ethanol solution, and utilizing change in absorbance at 490 m. as the measure of the degree of ionization, it was found that, with aniline, the hydrolysis of the salt was 96% complete, whereas with cyclohexylamine, hydrolysis could not be detected by the method used.

The lower boiling amines and ammonia were unsuitable for preparation of derivatives, the adducts being unstable to recrystallization, drying, or heating because of the gradual volatilization of the amine from the salt. Thus, the ammonia salts of a number of tropolones tested transformed into

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[6] The formation of aliphatic amine salts is also commonly utilized for separation of resin acids. G. C. Harris and R. F. Sanderson, *Jour. Am. Chem. Soc.*, **70**, 334 (1948).

[7] Ethylenediamine apparently does not give any adduct with β-thujaplicin[8] nor with nootkatin.[9]

[8] T. Nozoe, E. Sebe, S. Mayama, and S. Iwamoto, *Sci. Rep. Tohoku Univ.*, **36**, 184 (1952).

[9] Our observations.

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a viscous liquid under evolution of ammonia after a short storage period at room temperature and atmospheric pressure. The diethylamine salt of nootkatin decomposed in a similar way within one hour at 1 mm. pressure. Some salts of cyclohexylamine showed an extremely strong tendency to sublime, and the melting points had to be taken in a sealed tube.

In view of these findings, it seemed that the best procedure would involve the strongly basic amines of high boiling points which, to minimize any decomposition during recrystallization, should also have the solubility characteristics similar to those of the tropolones in question.

Among amines used, dicyclohexylamine appeared to give the best results. It is easily soluble in all common organic solvents, including saturated hydrocarbons, but is insoluble in water. Its basicity compares with that of other aliphatic amines, and it has a high boiling point (254°–256° at atmospheric pressure). Because of its high molecular weight, it is capable of giving high weight yields of derivatives. Thus, 1 g. of β-thujaplicin could theoretically yield 2.1 g. of the derivative. In all cases, the derivatives had a high tendency to crystallize. The yields in all cases were near theoretical, as the only losses were those inherent in the process of crystallization. The derivatives could be purified by recrystallization from isooctane or similar solvents or from ethanol/water mixtures. The melting points fell within the desired temperature range, were characteristic and sharp, with mixed melting points showing depressions from 5–12°. The original tropolones can be easily liberated by treating the derivatives with 10% sulfuric acid.[11]

Table I lists the dicyclohexylamine derivatives prepared from a number of tropolones, together with their melting points and analyses.

TABLE I[12]

DICYCLOHEXYLAMINE DERIVATIVES OF TROPOLONES

Tropolone	Melting point, °C.	Calcd. % C	Calcd. % H	Found % C	Found % H
β-thujaplicin	134–135	76.47	10.21	76.57	10.36
γ-thujaplicin	138–139	76.47	10.21	76.54	10.11
Nootkatin	114–115	78.40	10.48	78.42	10.56
Pygmaein[13]	86–87	73.56	9.93	73.70	9.74
3,5-Dibromo-α-thujaplicin	179–180	52.50	6.61	52.66	6.58
β-thujaplicinol	124–125	73.09	9.76	73.44	9.87

EXPERIMENTAL

Reagent. Monsanto's dicyclohexylamine was purified by fractional distillation, and the fraction that boiled within 120–121° at 8.3–8.5 mm. pressure was used in the experiments.

Preparation of a derivative. Pygmaein, 263 mg., m.p. 37.1–38.1°, was mixed with 500 mg. of dicyclohexylamine, and heated to 100° on a steam bath to effect solution. The resulting material was cooled to 0°, diluted with 5 ml. of cold isooctane, and allowed to stand for 1 hr. The separated crystals were filtered, the filtrate was reduced to 2 ml., cooled to 0°, and the second crop of crystals was recovered. The combined crystallization fractions were recrystallized from 10 ml. of isooctane to give 479 mg. of the derivative, m.p. 86–87° (94% yield).

Recovery of a tropolone from a derivative. A 246 mg. portion of nootkatin dicyclohexylamine salt, m.p. 113–114°, was stirred with 25 ml. of 10% sulfuric acid, and the precipitate was filtered, washed with 50 ml. of distilled water, air dried, and recrystallized from methanol-water to give 190 mg. of nootkatin, m.p. 93–94° (98% yield).

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[11] The hydrochloric acid salt of dicyclohexylamine is not very soluble in water.

[12] All melting points are corrected; microanalysis by Microchemical Laboratory, University of California, Berkeley, California.

[13] A methoxy thujaplicin isolated from *Cupressus pygmaea*, the structure of which will be the subject of a forthcoming publication.

Rates of Diisocyanate-Alcohol Reactions at Elevated Temperatures. Effect of Tri-*n*-butyl Amine Catalysis[1]

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Considerable work has been done in the past decade on the rates and mechanism of the reaction of organic isocyanates with hydroxyl-containing compounds to form urethanes, starting with the pioneering work of Baker and his associates.[2–6] It is difficult to relate many of the fundamental kinetic studies directly with the industrial production of polyurethanes. Hence, it was of interest to obtain reaction rate data on systems which

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[1] Paper presented in part before the Division of Polymer Chemistry, 134th meeting, ACS, Chicago, Ill., September 1958.

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