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TROPOLONES OF CUPRESSACEAE—III.

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Abstract—Twenty-two samples of heartwood from various *Cupressus* species were analyzed by paper chromatography to determine the tropolones present. Nootkatin and β-thujaplicin seem to occur in all species. Pygmaein, α-thujaplicinol, and α-dolabrinol occur only in the three cypresses from the California coast—*C. pygmea*, *C. goveniana*, and *C. abramsiana*. γ-Thujaplicin is found in large amounts in two closely related species, *C. forbesii* (southern California) and *C. guadalupensis* (Guadalupe Island, Baja California), as well as in *C. lusitanica*, a species known in cultivation only; it appears sporadically in *C. arizonica* and in the related species *C. glabra*. Hydronootkatinol and β-thujaplicinol are fairly common, usually in small amounts. α-Thujaplicin and β-dolabrin seem to be rare trace constituents.

INTRODUCTION

THE genus *Cupressus* (cypresses) consists of sixteen New World species, according to classifications by Wolf[1] and by Martinez,[2] and six Old World species, according to Dallimore and Jackson,[3] several of these species occur in two or more subspecies, varieties, or forms. One additional species, *C. lusitanica*, is known only in cultivation, with its origin subject to some controversy. However, since the morphological differences within this genus are rather subtle, the above classification is by no means universally recognized. Little[4] lists only seven of Wolf's twelve U.S. species. Other classifications usually fall between the two.[5,6,7] Table 1 summarizes the main relationships within the New and Old World cypresses, essentially in accordance with the ideas of Wolf, of Martinez, and of Dallimore and Jackson.

The present work continues our investigations of the distribution of tropolonic heartwood constituents throughout *Cupressus*.[8,9] Apart from its purely chemical interest, this could contribute to an understanding of taxonomic relationships involved. The structures of all known terpene and sesquiterpene-type tropolones are summarized in Table 2 with the names

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[1] C. B. WOLF, *El Aliso, The New World Cypresses*, Vol. 1, Part 1. Taxonomic and Distributional Studies of the New World Cypresses (1948).
[2] M. MARTINEZ, *Las Pinaceas Mexicanas*. Universidad Nacional Autonoma de Mexico, Mexico 20 D. F. (1963).
[3] W. DALLIMORE and A. B. JACKSON, *Handbook of Coniferae*. Edward Arnold, London (1931). 3rd Edn 1948, reprinted with corrections 1961.
[4] E. L. LITTLE, JR. *Check List of Native and Naturalized Trees of the United States*. U.S. Forest Service Agriculture Handbook 41 (1953). E. L. LITTLE, JR., *Madraño* **18**, 161 (1966).
[5] L. ABRAMS, *Illustrated Flora of the Pacific States*, Vol. 1. Stanford University Press, Stanford, California (1955).
[6] W. L. JEPSON, *A Manual of the Flowering Plants of California*. Independent Pressroom and Williams, San Francisco (1925).
[7] H. E. MCMINN and E. MAINO, *An Illustrated Manual of the Pacific Coast Trees*. University of California Press, Berkeley and Los Angeles (1959).
[8] E. ZAVARIN and A. B. ANDERSON, *J. Org. Chem.* **21**, 332 (1956).
[9] E. ZAVARIN, R. M. SMITH and A. B. ANDERSON, *J. Org. Chem.* **24**, 1318 (1959).

TABLE 1. RELATIONSHIPS OF *Cupressus* SPECIES

New World Species

Mexican species
- *C. benthami*, Endl.
- *C. lindleyi*, Klotsch
- *C. lusitanica*, Miller

Coastal species
- *C. forbesii*, Jeps.
- *C. guadalupensis*, Wats.

C. macnabiana, Murr.

Inland species
- subsp. *typica*, Wolf
- *C. bakeri*, Jeps.
- subsp. *matthewsii*, Wolf

- inland form
- *C. sargentii*, Jeps.
- coastal form
- *C. abramsiana*, Wolf
- *C. goveniana*, Gord.
- *C. pygmaea*, (Lemm.) Sarg.
- *C. macrocarpa*, Hartw.

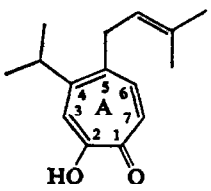
- *C. nevadensis*, Abrams
- *C. montana*, Wigg.
- *C. arizonica*, Greene
- *C. stephensonii*, Wolf
- *C. glabra*, Sudw.

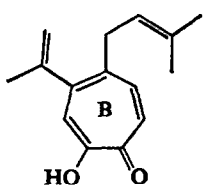
Old World Species

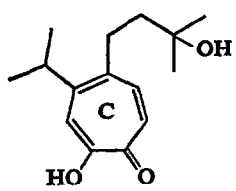
- *C. sempervirens* L.
  - var. *stricta*, *Alfon* (Eastern Mediterranean)
  - var. *horizontalis*, Gordon (Eastern Mediterranean)
- *C. dupreziana*, Camus (Sahara)
- *C. duclouxiana*, Hickel, (Yunnan, China)
- *C. torulosa*, Don. (Western Himalaya and western Szechuen, China)
- *C. cashmeriana*, Royle (apparently native to Tibet; unknown in wild state)
- *C. funebris*, Endl. (central China)

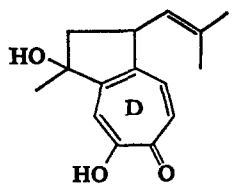
TABLE 2. STRUCTURES AND R_β VALUES FOR KNOWN TROPOLONES OF THE CUPRESSACEAE

Tropolone	Tropolone ring substitution	R_β (phosphoric acid)	R_β (dimethyl sulfoxide)	Color with $FeCl_3$: Before NH_3 exposure	Color with $FeCl_3$: After NH_3 exposure
5-Ethyltropolone	5-ethyl	—	—	—	—
α-Thujaplicin*	3-isopropyl	1·80	1·30	grey/green	brown/green
β-Thujaplicin*	4-isopropyl	1·00	1·00	brown	brown
γ-Thujaplicin*	5-isopropyl	0·78	0·87	green/brown	brown/green
β-Dolabrin*	4-isopropenyl	1·25	0·72	tan	brown
α-Thujaplicinol*	4-isopropyl, 3-hydroxy	1·90	1·07	purple	purple
β-Thujaplicinol*	4-isopropyl, 7-hydroxy	1·10	0·77	purple	purple
α-Dolabrinol*	4-isopropenyl, 3-hydroxy	1·90	0·76	purple	purple
Pygmaein*	4-isopropyl, 3-methoxy	1·60	1·20	green/grey	brown
Isopygmaein	3-isopropyl, 7-methoxy	0·35	0·60	green/grey	brown
Nootkatin*	See below (A)	1·90	1·36	green/buff	brown/green
Procerin	See below (B)	1·95	1·38	green/buff	brown/green
Hydronootkatinol*	See below (C)	0·05	0·10	green/grey	brown
Chanootin	See below (D)	—	—	—	—









* Present in *Cupressus* species.

of those known to occur in *Cupressus* indicated. The procedure involved in isolation and analysis of the individual tropolonic fractions was similar to the one described previously, with some improvements mentioned in the experimental part of this paper. The results are summarized in Table 3. In discussing the results only large qualitative differences are considered, as the number of trees investigated from each species was too small to allow

TABLE 3. COMPOSITION* OF THE TROPOLONE FRACTION OF EIGHTEEN *Cupressus* SPECIES

Species and individual sample number	Tropolone content %	β-Thujaplicin	Nootkatin	β-Dolabrin	α-Thujaplicinol	α-Dolabrinol	Pygmaein	Hydronootkatinol	γ-Thujaplicin	β-Thujaplicinol
C. sargentii (coastal)	0·02	●	●							
C. sargentii (inland)	0·17	S	●	+						S
C. abramsiana	0·07	●	●	+	S	+	+			
C. goveniana†	0·07	S	+	+	●	●	S			
C. pygmea†	1·40	S	S	+	●	●	●			
C. macrocarpa†	0·20	●	●							
C. guadalupensis 1	1·10	●	●						●	S
C. guadalupensis 2	0·03	S	●						S	
C. forbesii 1	0·30	+	●						●	+
C. forbesii 2	0·06	S	●						S	
C. lusitanica 1	0·09		+					S	●	+
C. lusitanica 2	0·12	●	+					S	●	+
C. lindleyi or *lusitanica* 1 (La Venta)	1·49	●	●					●	●	S
C. lindleyi 2 (Durango)	not. det.	●	S					S		
C. benthami 1	0·39	●	+					S		
C. benthami 2	not. det.	●	●					S		S
C. arizonica 1	1·10	●	●						S	S
C. arizonica 2 (Mexico)	0·60	S	●							
C. glabra 1	0·01	S	●						S	+
C. glabra 2	1·00	S	●							
C. nevadensis	0·10	S	●					+		
C. bakeri subsp. *typica*	0·50	●	●							
C. bakeri subsp. *matthewsii*	0·07	●	●							
C. macnabiana	0·10	S	●					+		+
C. sempervirens var. *stricta*†	2·20	S	●							
C. torulosa‡	2·60		●					+		
C. funebris	0·20	S	●							

* ●—main constituent, S—secondary constituent, +—trace constituent of the tropolonic fraction (not of wood).

† Analysis as cited in Ref. 9.

‡ Small amounts of α- and β-thujaplicin, β-dolabrin and β-thujaplicinol in addition to nootkatin as the main constituent have been reported by Barreto and Enzell.[16]

consideration of more subtle distinctions. This is again connected with the difficulties inherent in the nature of this method. The tropolones are present mainly in heartwood and often occur in small amounts. Hence, their analysis requires relatively large quantities of the mature portions of trees so that sometimes a whole tree would have to be sacrificed. Since some cypress species are limited to one or two groves, often protected as a park, sampling of a statistically desirable number of individua is thus often impossible. Furthermore,

in some cases the groves have been damaged by fire and the young growth has not developed any heartwood. Other difficulties include the laborious procedure for isolating tropolonic fractions in a form suitable for the analysis and the somewhat temperamental and only semiquantitative nature of the paper chromatography methods available.

RESULTS AND DISCUSSION

To the present time ten of the fourteen known terpene- and sesquiterpene-type tropolones occurring in the Cupressaceae (Table 2) have been identified in the heartwood of *Cupressus* species (absent seem to be 5-ethyl tropolone,[10] isopygmaein,[11] procerin,[12] and chanootin[13]); in addition half a dozen or more probably tropolonic constituents have been noted and some have been isolated.[14] Two of the tropolones, nootkatin and β-thujaplicin, seem to occur in the heartwood of all *Cupressus* species and can be regarded as characteristic of this genus (Table 3). The presence of nootkatin also separates *Cupressus* from the closely related genus *Chamaecyparis*, where this compound is generally absent (exception being *Ch. nootkatensis* (D. Don) Spach).[15] α-Thujaplicinol, pygmaein, and α-dolabrinol are fairly rare constituents and always occur together; α-thujaplicin[16] and β-dolabrin also seem to be rare trace compounds. γ-Thujaplicin, β-thujaplicinol, and hydronootkatinol are more common and occasionally occur in rather large quantities.

The present work completes the analysis of eighteen of the twenty-three known *Cupressus* species. Of the remaining five species, *C. montana* and *C. stephensonii* are closely related to *C. arizonica*,[1,4] *C. duclouxiana* and *C. dupreziana* to *C. sempervirens*, and *C. cashmiriana* to *C. torulosa*.[3] Thus it seems unlikely that an analysis of these species would disclose anything new chemically.

The Old World species number six (Table 1). *C. sempervirens* var. *stricta* heartwood, analyzed on several previous occasions, contains nootkatin and β-thujaplicin.[9,17] *C. funebris* heartwood had not been examined previously. We found that it contained the same tropolonic constituents as *C. sempervirens*; and it yielded, in addition, a surprisingly large amount for a *Cupressus* of neutral aliphatic materials (12 per cent), which we have not yet examined. *C. torulosa* was investigated by Barreto and Enzel,[16] who found that it contained nootkatin and small amounts of α- and β-thujaplicin, β-dolabrin, and β-thujaplicinol. We reinvestigated this species and confirmed the presence of nootkatin as the main constituent. Other tropolones were present in amounts too small for identification.

The New World coastal species number seven and can be subdivided into a group of five related species, including *C. macrocarpa*, and into a group of two related species including *C. guadalupensis*. Four of the five species group grow in a few separated groves on the California coast from near Monterey to Fort Bragg. The fifth species, *C. sargentii*, has a somewhat wider distribution in California coast ranges between Santa Barbara and Mendocino counties and occurs possibly in two forms—inland and coastal. Analyses of

[10] Y. T. LIN, K. T. LIN, K. T. WANG and B. WEINSTEIN, *Experientia* **22**, 140 (1966).
[11] E. ZAVARIN, *J. Org. Chem.* **27**, 3368 (1962).
[12] J. RUNEBERG, *Acta Chem. Scand.* **15**, 645 (1961); E. PETTERSSON and J. RUNEBERG, *Acta Chem. Scand.* **15**, 713 (1961).
[13] T. NORIN, *Arkiv Kemi* **22**, 129 (1963).
[14] C. ENZELL and M. KROLIKOWSKA, *Arkiv Kemi* **20**, 158 (1962).
[15] H. ERDTMAN, In *Fourth International Congress of Biochemistry*, Vol. 2, Biochemistry of Wood. Pergamon Press, Oxford (1958).
[16] H. S. BARRETO and C. ENZELL, *Acta Chem. Scand.* **15**, 1313 (1961).
[17] C. ENZELL and H. ERDTMAN, *Acta Chem. Scand.* **11**, 902 (1957).

all five species have been reported[8,9,18] (Table 3). We have reanalyzed *C. abramsiana* heartwood and examined that of the coastal form of *C. sargentii*. No β-thujaplicinol could be identified in heartwood extractives of the coastal form of *C. sargentii* while this constituent has been found previously in the inland form of this species. Since β-thujaplicinol has a tendency toward sporadic occurrence within a given species it seems dangerous to elaborate on any possible significance of its absence from this sample before more heartwood samples, particularly from other provenances, are analysed. The reanalysis of *C. abramsiana* revealed the presence of pygmaein in addition to the constituents reported previously. Thus no qualitative difference seems to exist between the tropolones of this species and those of *C. pygmaea* and *C. goveniana*. Furthermore, the occurrence of pygmaein, α-thujaplicinol and α-dolabrinol seems to clearly separate *C. abramsiana*, *C. goveniana*, and *C. pygmea* as a group from all of the other species of *Cupressus*.[19]

The remaining two coastal species are both of a more southern provenance: *C. guadalupensis* is indigenous to Guadalupe Island, Baja California. *C. forbesii* is a mainland species, represented by several groves in Orange and San Diego counties (southern California); it grows also in the northern part of Baja California, Mexico.

The heartwood of neither species had previously been examined for tropolones. Our analysis revealed not only the ubiquitous nootkatin and β-thujaplicin but also substantial amounts of γ-thujaplicin occasionally accompanied by some β-thujaplicinol in all samples of both species. The presence of γ-thujaplicin in large amounts sharply separates these two species from the previous five and to some extent also from the species of *C. arizonica* complex.

The six new World inland species can be split into a complex of five related species including *C. arizonica* and into a monospecific group including *C. bakeri*. The latter species has been further split by Wolf[1] into two subspecies *typica* and *matthewsii* although this separation does not seem to enjoy general acceptance.

The first five species are all of the more southern provenance: *C. nevadensis* is represented by several groves on Piute Mountain in Kern County (southern Sierra Nevada), *C. stephensonii*, the rarest of all New World cypresses, is found only on the southwestern slope of Cuyamaca peak, San Diego County, California; *C. montana* is indigenous to the San Pedro Martir mountains of northern Baja California, Mexico; *C. glabra* occurs in several areas near Flagstaff, Arizona, and *C. arizonica*, a rather variable species, is more widely spread throughout Arizona, New Mexico, and Texas, as well as several states of northern Mexico.

The analysis of three species of this complex—that for *C. nevadensis* is reported for the first time—indicated the presence of large amounts of nootkatin and β-thujaplicin in all cases. β-Thujaplicinol was encountered occasionally; moderate amounts of γ-thujaplicin were indicated in one of the two samples of *C. glabra* and in one of the two samples of *C. arizonica*. This sporadic appearance of γ-thujaplicin in the *C. arizonica* species complex explains why Enzell and Krolikowska[14] were unable to isolate it from their *C. arizonica* material.

Both subspecies of *C. bakeri* are indigenous to northern California, and southern Oregon,

[18] R. E. Corbett and D. W. Wright, *Chem. Ind. (London)* 1258 (1953).

[19] C. B. Wolf[1] regards *C. abramsiana* as morphologically intermediate between *C. goveniana* and *C. sargentii*. Chemically its relationship to *C. goveniana* is evident; nothing definite can be said regarding its relationship to *C. sargentii* without analysis of samples from a larger number of trees. However, the relative amounts of the tropolones characteristic for these three cypresses (α-thujaplacinol, α-dolabrinol, and pygmaein) are much lower in *C. abramsiana* than in the other two species, and this fact seems to support Wolf's thesis.

from Plumas to Jackson counties, where they occur in several separated groves. Erdtman[15] investigated the heartwood of this species but did not report where the sample was collected and gave no experimental data. We investigated the heartwood of both Wolf's subspecies and identified β-thujaplicin in addition to nootkatin, reported by Erdtman; we observed no difference between the two subspecies.

One additional New World species, *C. macnabiana*, grows in California over a fairly wide range, from Amador to Shasta counties in the Sierra Nevada and from Sonoma to Shasta counties in the coast ranges. In the tropolonic fraction of its heartwood we found traces of β-thujaplicinol and hydronootkatinol in addition to nootkatin and β-thujaplicin, which has been reported by Erdtman.[15]

The Mexican species had not been examined by others, previously. They include *C. benthami*, which occurs in a limited area in the states of Hidalgo, Vera Cruz, and Puebla; and *C. lindleyi*, with much wider range from Chihuahua in the north to Guatemala in the south. A third member of this group, *C. lusitanica*, is known only from the Old World, where it has been under cultivation for several centuries. Its origin was first placed in India, but later it was regarded as conspecific with the Mexican *C. lindleyi*. After a thorough investigation, Martinez[2] concluded that it differed from either *C. lindleyi*, or *C. benthami*, or the indian species.

We analyzed the heartwood of *C. benthami* from two localities in Hidalgo and found that the tropolonic fractions were composed essentially of nootkatin and β-thujaplicin with some hydronootkatinol and, in one case, β-thujaplacinol. Our analysis of *C. lindleyi*,[2] samples from Durango (central Mexico), was very similar to that of *C. benthami*. A heartwood sample of a cypress originally identified as *C. lindleyi*, growing near La Venta, Distrito Federal, contained, in addition to the above constituents, large amounts of γ-thujaplicin. Our two heartwood samples of *C. lusitanica*—one from Portugal and one from India, were similar to that from La Venta, with large amounts of γ-thujaplicin. Later it became clear that the tree from La Venta was not wild but planted. To our inquiry, Professor Martinez replied: ". . . *Cupressus* from La Venta is not native there. They are mostly in rows and were planted there sixty years ago. I have seen there some trees very similar to *C. lusitanica*. I don't know where the seeds were obtained. Perhaps they were imported." Obviously more morphological and chemical work must be done before one can solve the problem of the origin of *C. lusitanica*, although the coincident occurrence of large amounts of hydronootkatinol in all three species suggests close relationship.

We are continuing the chemotaxonomic studies of *Cupressus* by a different technique—GLC of the leaf oils—and hope to report on this work in the near future.

EXPERIMENTAL

Collection of wood specimens. The following samples were obtained from the localities described by Wolf,[1] and the page numbers refer to his publication: *C. abramsiana* from Bonnie Doon, p. 217; *C. sargentii* from Camp Meeker, p. 235, *C. guadalupensis* sample 1 from Guadalupe Island, p. 173; *C. guadalupensis* sample 2: seeds from Guadalupe Island, tree growing in Tilden Park, Contra Costa County, California; *C. forbesii* sample 1, from Otay Mountain, p. 165; *C. forbesii* sample 2, from Guatay Mountain, p. 163; *C. macnabiana* from Aetna Springs, p. 62; *C. bakeri* subsp. *typica* from Burney Springs, p. 75; *C. bakeri* subsp. *matthewsii* from Seiad Creek grove, p. 86; *C. nevadensis* from Red Hill, Piute Mountain, p. 119; *C. arizonica* sample 1: seeds from Chiricahua Mountains, p. 101, tree growing on the University campus, Riverside, California.

The following samples were collected in Mexico: *C. lindleyi* sample 1 near La Venta, Distrito Federal; *C. lindleyi* sample 2 in Predio Coyotes, Municipio de Pueblo Nuevo, Durango; *C. benthami* samples near Pachuca, Hidalgo; and *C. arizonica* sample 2 near Los Lirios, Coahuila. *C. glabra* sample 1 was obtained from near Flagstaff, Arizona, and sample 2 from a tree in the Eddy Arboretum, Institute of Forest Genetics,

Placerville, California. *C. lusitanica* sample 1 stemmed from the botanical garden of Coimbra, Portugal, its seeds probably from the forest of Bussaco in Portugal. Finally, the samples of *C. torulosa*, *C. funebris*, and *C. lusitanica* sample 2 were obtained from the Forest Research Institute and Colleges, New Forest, Dehra Dun, India.

Foliage and fruit were collected for reference in most cases, in addition to the heartwood. Where the trees grew in isolated and definite geographic locations, the identity of the collected material was obvious. In case of any doubt, assistance was obtained from the University of California Herbarium. The Mexican material was identified by Professor M. Martinez, National University of Mexico.

Isolation of the tropolonic fractions. An acetone extract of the heartwood was obtained as described in our previous publications.[8,9] The acetone was evaporated to dryness, and the residue was extracted exhaustively with portions of isooctane on a steam bath, each time testing with a 5% $FeCl_3$ solution for the completeness of the extraction. Next the isooctane extract was treated with 5% NaOH, acidified with 25% acetic acid, and made alkaline again with 2 N NH_4OH. To the resulting liquid an excess of 5% cupric acetate solution was added, and the separated tropolonic copper complexes were extracted with several portions of $CHCl_3$. The $CHCl_3$ solutions were evaporated to dryness at room temperature under a current of air, the residue was dissolved in acetone, and the complexes were decomposed with H_2S and the filtrate was evaporated to dryness.

The resulting product contained tropolonic compounds together with various phenolics, the latter often in sizable amounts. The quantity of tropolones was estimated by the 85% phosphoric acid extraction procedure of Lin *et al.*[20] using an aliquot of the impure tropolonic fraction obtained. However, the tropolones separated in this way could not be used for analysis by paper chromatography, because phosphoric acid reacts with any troponoids that have a double bond in the side-chain,[21] so either the impure tropolonic mixtures were used directly or, if bad streaking was encountered, the material was evaporatively distilled at 200° and 1 mm pressure.

Paper chromatographic analysis. For more certain identification, we used both the phosphoric acid procedure of Zavarin and Anderson[8] and the dimethylsulfoxide procedure of Wachtmeister and Wickberg,[22] in conjunction with 5% ferric chloride and diazotized *o*-aminobiphenyl chromogenic sprays (Table 2). In the first procedure better separations were achieved by using 21% phosphoric acid solution for impregnation and toluene as the developing solvent; before its use, the impregnated paper was equilibrated for 48 hr in an atmosphere of about 60 per cent humidity at 23°, over a saturated solution of NaBr; it was developed under the same conditions.

It was possible to locate the spots belonging to individual tropolones by viewing the papers under u.v. light during the developing: the spots appeared dark-purple on a lighter background. The tropolones in general did not exhibit any fluorescence; procerin was an exception and gave rise to a strong fluorescence after brief irradiation with u.v. light while on the phosphoric acid-impregnated paper. No fluorescence resulted from irradiation of procerin absorbed on sulfoxide-impregnated paper. Since procerin and nootkatin are only partially separated by either procedure, this could afford a good method for distinguishing the two. Analysis by this method indicated that procerin was absent from all of the tropolonic mixtures that we obtained.

The R_β values for the tropolones encountered are listed in Table 2. In many cases unknown materials made their appearance in various parts of the chromatograms, usually as trace or secondary constituents. Only in the extracts of *C. arizonica* (Chiricahua Mountains), *C. guadalupensis* (Guadalupe Is.) and *C. forbesii* (Otay Mt.) was a major amount of an unknown constituent noted at R_β (21% H_3PO_4) of 1·5. The unknowns had R_β values of 0·65, 0·65, 0·06, 1·5, and 1·8 in the phosphoric acid procedure and of 0·2, 0·3, 0·4, 1·2, and 1·8 in the dimethylsulfoxide procedure.

Isolation of some constituents. In a few cases, extract constituents were isolated and identified by preparative methods.

The phenolic fractions from *C. benthami* and *C. lindleyi* obtained after removal of tropolones with 85% phosphoric acid, were composed largely of carvacrol, identified by the α-naphthyl urethanes, m.p. 114–116°, and 116–117°, respectively, no depression of melting points when mixed with authentic samples of a carvacrol α-naphthyl urethane. The same was true for the phenolic fraction of *C. pygmea*, where carvacrol (0·3 per cent in wood) was isolated by distillation and identified by i.r. methods.

γ-Thujaplicin was isolated from the *C. lusitanica* sample 2 (Portugal) extract by dissolving the material soluble in 85% phosphoric acid in CCl_4 and cooling. The filtered crystals melted after recrystallization from the same solvent at 76–78° and did not depress the melting point of an authentic sample.

White solid formed during decomposition of the copper tropolonates of *C. lindleyi* sample 1 (La Venta), with hydrogen sulfide in acetone solution. This was purified by treating its chloroform solution with decolorizing carbon and crystallizing from the chloroform; it gave pale yellow plates, m.p. 58–59·5°, which did

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not depress the melting point of an authentic sample of β-thujaplicinol. The isolation of hydronootkatinol from the same wood sample was described previously.[21]

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