J = 3 Hz, H-2'), 7.19 (q, J = 2, 9 Hz, H-6), 6.98 (d, J = 2 Hz, H-8), 6.94 (d, J = 2 Hz, H-3'), 4.35 (methoxy), 4.20 (d, J = 5 Hz, ether methylene), 3.12 (t, J = 5 Hz, epoxy), 1.38 (C-methyls) (in $CDCl_3$).

Anal. Calcd for $C_{17}H_{17}NO_4$: C, 68.23; H, 5.72; N, 4.68. Found: C, 68.1; H, 5.85; N, 4.61.

Further elution of the column with increasing amounts of benzene in hexane gave a further 3 g of 1. Fractions eluted with benzene and chloroform gave, after work-up, products which corresponded to the previously reported acridones, melicopidine, 1-hydroxy-2,3-dimethoxyacridone, and xanthevoidine.[11]

Acid Hydrolysis of 1 to Evoxine (2).—Two grams of 1 was added to a boiling 10% solution of oxalic acid. The solution was refluxed for 30 min. After cooling, the solution was made basic and extracted with ethyl acetate. The ethyl acetate extracts were dried and concentrated, whereupon the product, evoxine (2), crystallized: mp 151.5–154° (lit.[11] mp 155°); 1.76-g yield; $[\alpha]D$ +13° (EtOH).[17] The evoxine was identical in all respects with an authentic sample provided by Professor E. Ritchie.

In a similar manner **3** was converted into **4**: mp 145–147° (EtOAc); λ_{max}^{EtOH} 247, 277, ~296, 308, 320, 332 mμ; nmr δ 8.58 (d, J = 10 Hz, H-5), 7.93 (d, J = 2 Hz, H-2), 7.75–7.47 (m, H-6 and H-8), 7.37 (d, J = 2 Hz, H-3), 4.62 (methoxyl); (4.50–4.00 (m, ^{O}>CHCH$_2$O), 1.40 and 1.35 (C-methyls) (in $CDCl_3$).

Anal. Calcd for $C_{17}H_{19}NO_5$: C, 64.34; H, 6.03. Found: C, 63.7; H, 6.02.

Episulfide of 1.—To a solution of 0.45 g of KOH and 0.7 g of CS_2 in 10 ml of methanol was added 0.8 g of 1. The mixture was warmed to effect solution. After 36 hr water was added and after standing overnight the product (**8**) was collected by filtration: mp 167–169° after repeated crystallization from EtOAc–hexane; nmr δ 7.97 (d, J = 9 Hz, H-5), 7.58 (d, J = 2 Hz, H-2'), 7.24 (d, J = 9 Hz, H-6), 7.03 (d, J = 2 Hz, H-3'), 4.38, 4.15 (methoxyls), 3.27 (q,[18] ^{S}>CHCH$_2$O–), 1.65, 1.63 (C-methyls) (in $CDCl_3$).

Anal. Calcd for $C_{18}H_{19}NO_4S$: C, 62.5; H, 5.54; N, 4.34. Found: C, 63.0; H, 5.51; N, 3.98.

Registry No.—**1**, 24099-25-0; **3**, 24099-26-1; **4**, 24099-27-2; **8**, 24099-28-3.

Acknowledgments.—Initial studies on this problem were carried out at laboratories of the U. S. Department of Agriculture in Pasadena, Calif. The author is indebted to Dr. J. A. Lamberton, CSIRO, Melbourne, Australia, for a supply of plant material, and to Professor E. Ritchie of the University of Sydney for an authentic sample of evoxine.

(17) Johns, *et al.*, reported $[\alpha]D$ +20° (EtOH) for evoxine isolated from *Choisya ternata* H. B. and K. [S. R. Johns, J. A. Lamberton, and A. A. Sioumis, *Aust. J. Chem.*, **20**, 1975 (1967)]. Evoxine previously reported from *E. zanthoxyloides* showed $[\alpha]D$ +5° (EtOH).[11]

(18) This is the X part of an ABX pattern. The AB part was overlapped by the methoxyl resonances.

Interconversions of Some Diterpenic Constituents of *Podocarpus ferrugineus* D. Don.

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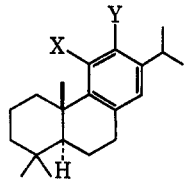
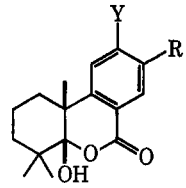
A chemical study of the diterpenic bark constituents of the New Zealand conifer *Podocarpus ferrugineus* D. Don. led for a variety of reasons to a need for their interconversion. Three such investigations are reported herewith.

Ferruginol (**1a**), a major constituent,[3] had to be converted into dehydroabietane (**1b**), a new natural product and minor constituent of the podocarp.[4] While in a related case one of the Kenner procedures had been employed,[5] it now was of interest to apply the recently discovered deoxygenation method of Musliner and Gates.[6] Treatment of ferruginol (**1a**) with 5-chloro-1-phenyltetrazole and hydrogenation of the resultant 1-phenyl-5-tetrazoyl ether over palladium–charcoal yielded dehydroabietane (**1b**).[7]

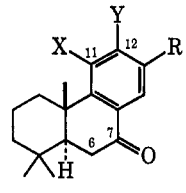


1a, X = H; Y = OH
b, X = Y = H
c, X = Y = OMe

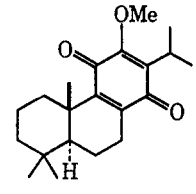


2a, R = *i*-Pr; Y = OMe
b, R = Y = H

One of the minor bark constituents[8] was the unusual B-seco-norditerpenic lactol **2a**. Its structure was determined by detailed spectral analysis and by comparison with the lactol obtained from chromic acid oxidation of 5-iso-7-ketodeoxypodocarponitrile enantiomer.[9] However, for direct structure proof a synthesis of the new product was desired. In this connection the incidental observation of the transformation of ketone **3a** into lactol **2b** on oxidation with oxygen and potassium *t*-butoxide,[10] a reaction which under controlled conditions converts 7-ketones into 6,7-diones,[11] assumed importance. A similar overoxidation converted sugiyl methyl ether (**3b**), another podocarp constituent, into lactol **2a**.



3a, X = Y = R = H
b, X = H; Y = OMe; R = *i*-Pr
c, X = OH; Y = OMe; R = *i*-Pr
d, X = Y = OMe; R = *i*-Pr
e, X = Y = OH; R = *i*-Pr



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One more minor plant component[8] proved to be cryptojaponol to which structure **3c** has been assigned.[12] The site of its O-methyl group, the only possibly questionable point of its structure, needed confirmation and a synthesis of the natural substance to be exe-

(1) National Science Foundation Cooperative Fellow, 1962–1965.
(2) Public Health Service Predoctoral Fellow, 1966–1969.
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cuted. A clue regarding the environment of the hydroxyl and methoxyl functions of cryptojaponol came from a study of the pyridine solvent shift of its proton magnetic resonance spectrum, $\delta_{CDCl_3} - \delta_{C_5H_5N} = 0.01$ ppm for the isopropyl methyl groups. Had the compound been a 11-methoxy-12-hydroxy isomer, the proximity of the hydroxyl and isopropyl groups would have led to strong deshielding of the latter in pyridine solution.[13] Structure **3c** was confirmed when hydrogenation of cryptojaponol and subsequent oxidation with *m*-chloroperbenzoic acid yielded royleanone methyl ether (**4**).[14] The synthesis of cryptojaponol (**3c**) was accomplished in the following manner. Chromic acid oxidation[9] of 11-methoxyferruginyl methyl ether (**1c**)[15] gave 11-methoxysugiyl methyl ether (**3d**). Demethylation of the latter with boron tribromide[16,17] and remethylation of the resultant catechol **3e** with diazomethane yielded the natural product (**3c**).

Experimental Section[18]

Dehydroabietane (1b).—A mixture of 200 mg of ferruginol (**1a**), 250 mg of 1-phenyl-5-chlorotetrazole, and 1.5 g of anhydrous potassium carbonate in 50 ml of acetone was refluxed for 18 hr. The cooled mixture was filtered and the filtrate evaporated under reduced pressure. Chromatography of the residue, 436 mg, on 6 g of Woelm neutral alumina, activity I, and elution with methylene chloride yielded 227 mg of oily ferruginyl 1-phenyl-5-tetrazoyl ether. A mixture of 160 mg of the ether and 200 mg of 10% palladium–charcoal in 20 ml of 95% ethanol was hydrogenated at 35 psi pressure for 48 hr. Filtration of the mixture and evaporation of the filtrate under reduced pressure yielded 160 mg of partly crystallized oil whose exhaustive extraction with petroleum ether gave 120 mg of clear oil. Chromatography of the latter on 6 g of silica gel and elution with petroleum ether afforded 33 mg of dehydroabietane (**1b**), mp and mmp 42–43°, ir and prm spectra identical with those of an authentic specimen,[7] while elution with methylene chloride led to recovery of 81 mg of starting ether.

Lactol 2a.—A solution of 125 mg of sugiyl methyl ether (**3b**) in 3 ml of dry *t*-butyl alcohol was added to a potassium *t*-butoxide solution (27 mg of potassium in 5 ml of dry *t*-butyl alcohol). Oxygen was bubbled into the mixture for 12 hr while it was being stirred and kept slightly above freezing temperature. Thereafter, 16 ml of 10% hydrochloric acid was added and the mixture extracted exhaustively with ether. The extract was dried over anhydrous sodium sulfate and evaporated. The solid residue, 110 mg, was chromatographed on an inverted dry column of silica gel G. Elution with chloroform gave first 35 mg of starting ketone **3b** and then 13 mg of lactol **2a**, mp and mmp 168–170°, ir and pmr spectra identical with those of the natural lactol.[8]

Anal. Calcd for $C_{20}H_{28}O_4$: C, 72.26; H, 8.49. Found: C, 72.43; H, 8.31.

Royleanone Methyl Ether (4).—A mixture of 15 mg of cryptojaponol and 5 mg of 10% palladium–charcoal in 8 ml of ethanol was hydrogenated at atmospheric pressure and room temperature. Filtration of the mixture and evaporation of the filtrate yielded 14 mg of 7-deoxocryptojaponol, mp 164–165° (lit.[12] mp 163–164.5°). A solution of the latter and 10 mg of *m*-chloroperbenzoic acid in 5 ml of methylene chloride was left standing for 12 hr. A solution of 100 mg of sodium sulfite in 25 ml of water was added and the mixture stirred for 1 hr. The aqueous layer was extracted with methylene chloride, and the combined organic layer and extract was dried and evaporated. Thick layer chromatography of the residue, 8 mg, on silica gel G and elution with chloroform gave 3 mg of royleanone methyl ether (**4**), mp 118–120°, ir spectrum identical with that of an authentic sample.

Cryptojaponol (3c).—A solution of 530 mg of **1c**[15] and 500 mg of chromium trioxide in 60 ml of acetic acid and 15 ml of water was stirred at room temperature for 6 hr. It was poured into 250 ml of cold saturated brine solution and extracted with methylene chloride. The extract was washed with water, saturated sodium sodium bicarbonate, and brine solutions and dried. Solvent removal yielded 495 mg of oily ketone **3d** homogeneous on thin layer chromatography, 2,4-dinitrophenylhydrazone mp 215–217°.

Anal. Calcd for $C_{25}H_{36}O_6N_4$: C, 64.11; H, 6.92; N, 10.68. Found: C, 64.36; H, 6.83; N, 10.81.

A solution of 0.5 ml of freshly distilled boron tribromide in 5 ml of dry methylene chloride was added slowly to a solution of 250 mg of **3d** in 25 ml of methylene chloride at Dry Ice–acetone bath temperature. The solution was allowed to warm to room temperature slowly and then was evaporated under vacuum. Water, 50 ml, was added to the cooled solid residue and the mixture extracted with chloroform and with ether. The combined extracts were dried and evaporated. An ether solution of the solid residue (homogeneous on tlc and devoid of methoxy pmr signals) was treated with ethereal diazomethane. Evaporation of the solution and crystallization of the solid residue, 244 mg, from methanol gave cryptojaponol, mp and mmp 204–206°, ir and pmr spectral identical with those of an authentic sample.[19]

Anal. Calcd for $C_{21}H_{30}O_3$: C, 76.39; H, 9.09. Found: C, 76.69; H, 9.26.

Registry No.—**2a**, 24099-23-8; **3c**, 16755-52-5.

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(19) The authors are indebted to Professor T. Kondo for a gift of a specimen of the natural product.

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(18) Melting points were determined on a Reichert micro hot stage and are uncorrected.

Trichloroacetylation of Dipeptides by Hexachloroacetone in Dimethyl Sulfoxide under Neutral Conditions[1a]

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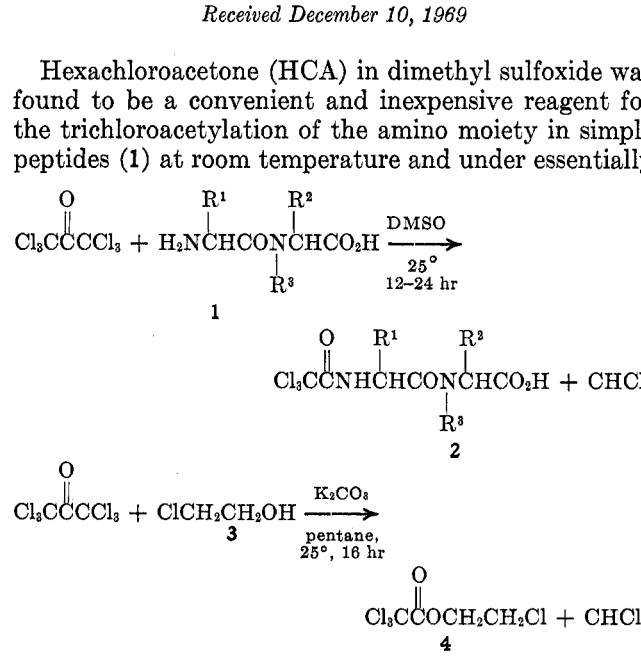
Hexachloroacetone (HCA) in dimethyl sulfoxide was found to be a convenient and inexpensive reagent for the trichloroacetylation of the amino moiety in simple peptides (**1**) at room temperature and under essentially



(1) (a) Presented at the 21st Southeastern Regional Meeting of the American Chemical Society, Richmond, Va., Nov 1969; (b) to whom inquiries should be addressed.