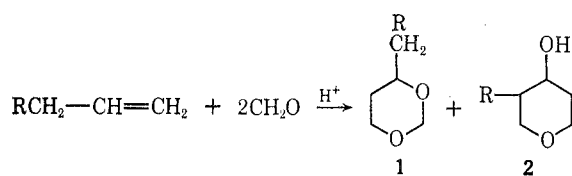


TABLE I
CONDENSATION OF 1-OLEFINS WITH FORMALIN^a



R	Conversion, %	Yield, ^b %	
		1	2
C ₂ H ₅	100	46	42
C ₃ H ₇	100	41	46
C ₅ H ₁₁	85	43	45
C ₇ H ₁₅	53	40	47
C ₉ H ₁₉	39	42	46

^a Reactions were carried out for 6 hr at 150° using 2 mol of olefin to 4.9 mol of 37% formalin 0.24 M in H₂SO₄. ^b Based on reacted olefin.

with nitrogen, and heated with stirring at 150° for 6 hr. After cooling, the product was extracted into ether and the ether extracts were washed with sodium carbonate solution and dried (MgSO₄); the ether was then removed. A portion of the residue was analyzed by glpc using the 5-ft column for the 1-decene and 1-dodecene reactions and the 10-ft column for the remainder. The order of elution is 2-alkanol, 4-alkyl-1,3-dioxane, dihydropyran, and 3-alkyltetrahydropyran-4-ol. The product 4-alkyl-1,3-dioxanes (Table II) and 3-alkyltetrahydropyran-4-ols (Table III) were isolated by fractionation through a 4 ft × 0.75 in. helices packed column.

Registry No.—1 (R = C₂H₅), 15601-78-2; 1 (R = C₃H₇), 2244-87-3; 1 (R = C₅H₁₁), 2244-85-1; (R = C₇H₁₅), 23433-02-5; 1 (R = C₉H₁₉), 24647-61-8; 2-*cis* (R = C₂H₅), 24647-33-4; 2-*cis* (R = C₃H₇), 24647-34-5; 2-*cis* (R = C₅H₁₁), 24647-35-6; 2-*cis* (R = C₇H₁₅), 24647-36-7; 2-*cis* (R = C₉H₁₉), 24647-37-8; 2-*trans* (R = C₂H₅), 24646-96-6; 2-*trans* (R = C₃H₇), 24646-97-7;

TABLE II
4-ALKYL-1,3-DIOXANES

R	Bp, °C	Pressure, mm	n _D ²⁰	Formula	Calcd, %		Found, %	
					C	H	C	H
C ₂ H ₅	60-61	16.0	1.4278	C ₇ H ₁₄ O ₂	64.6	10.8	64.7	10.9
C ₃ H ₇	62-63	8.0	1.4355	C ₈ H ₁₆ O ₂	66.6	11.1	66.7	11.1
C ₅ H ₁₁	105-107	12.0	1.4397	C ₁₀ H ₂₀ O ₂	69.8	11.6	70.0	11.8
C ₇ H ₁₅	132-134	12.0	1.4462	C ₁₂ H ₂₄ O ₂	72.0	12.0	72.0	12.1
C ₉ H ₁₉	128-130	1.5	... ^a	C ₁₄ H ₂₈ O ₂	73.6	12.3	73.7	12.4

^a Solidified, mp 41-42° from pentane, lit.³ mp 41.5-42.5°.

TABLE III
3-ALKYLTETRAHYDROPYRAN-4-OLS

R	Bp, °C	Pressure, mm	n _D ²⁰	Formula	Calcd, %		Found, %	
					C	H	C	H
C ₂ H ₅	112-114	16.0	1.4598	C ₇ H ₁₄ O ₂	64.6	10.8	64.5	10.6
C ₃ H ₇	105-106	8.0	1.4591	C ₈ H ₁₆ O ₂	66.6	11.1	66.4	11.0
C ₅ H ₁₁	95-99	0.5	1.4585	C ₁₀ H ₂₀ O ₂	69.8	11.6	69.8	11.8
C ₇ H ₁₅	168-170	12.0	1.4588	C ₁₂ H ₂₄ O ₂	72.0	12.0	71.9	12.0
C ₉ H ₁₉	150-154	1.5	1.4590	C ₁₄ H ₂₈ O ₂	73.6	12.3	73.6	12.3

acid catalyst to produce the expected spectrum of products with a rather considerable increase in dihydropyran formation.

Although attempts to improve the selectivity of the Prins reaction under these conditions to either major product were unsuccessful, this procedure does represent a most convenient and useful synthesis of 4-alkyl-1,3-dioxanes and *cis,trans*-3-alkyltetrahydropyran-4-ols. A minimum of by-products is produced and the boiling point difference between the dioxane and tetrahydropyranol is sufficiently great that separation by fractionation is easily accomplished. Table I summarizes product yields from the condensation of a number of typical 1-olefins from 1-pentene through 1-dodecene using standard conditions. It is apparent that reaction rates are slower for the higher molecular weight olefins, probably because of decreased solubility, and more nearly optimum conditions would require longer reaction times, higher temperatures, more catalyst, or some combination thereof for complete conversion.

Experimental Section⁶

Condensation of 1-Olefins with Formalin.—A 1-l. Magnedrive autoclave constructed of Hastelloy C⁷ was charged with 2 mol of olefin (4.9 mol) of 37% formalin, and 5 ml of concentrated sulfuric acid. (One-half quantities were used for the 1-decene and 1-dodecene reactions.) The autoclave was sealed, flushed

2-*trans* (R = C₅H₁₁), 24646-98-8; 2-*trans* (R = C₇H₁₅), 24646-99-9; 2-*trans* (R = C₉H₁₉), 24647-00-5; formaldehyde, 50-00-0.

(6) All melting and boiling points are uncorrected. Olefins used were Phillips Petroleum Co. Pure Grade materials. Gas chromatographic analyses were carried out on a Perkin-Elmer Model 720 gas chromatograph using 5 ft and 10 ft × 0.25 in. columns of 20% Ucon LB-550-X on Chromosorb P.

(7) Autoclave Engineers, Inc., Erie, Pa.

Chemotaxonomy of the Rutaceae. VII.¹ Alkaloids in *Evodia zanthoxyloides* F. Muell.

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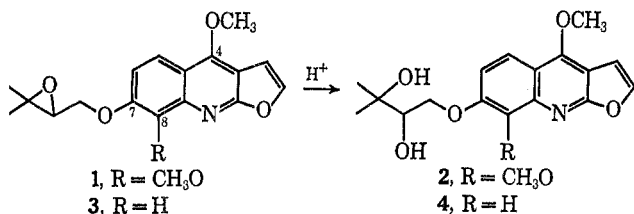
Received August 11, 1969

The alkaloids occurring in *Evodia zanthoxyloides* F. Muell. (Rutaceae) have been the subject of an extended investigation by Ritchie and coworkers.²

(1) Part VI: D. L. Dreyer and A. Lee, *Phytochemistry*, **8**, 1499 (1969).

(2) R. H. Prager, E. Ritchie, A. V. Robertson, and W. C. Taylor, *Aust. J. Chem.*, **15**, 301 (1962), and previous papers in this series.

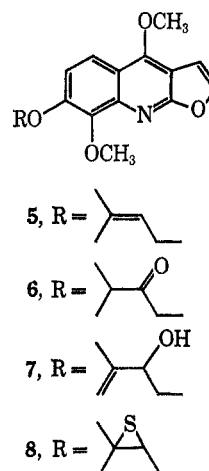
During a search for limonoids in *Evodia* species³ we have had occasion to isolate further furoquinoline alkaloids from this plant.⁴ An alkaloid, C₁₈H₁₉NO₅, mp 141–144°, crystallized from the crude extracts in 3% yield. Its ultraviolet spectrum was similar to that of skimmianine.^{6,7} The nmr spectrum showed aromatic resonances which compared well with those of skimmianine.⁸ In addition, resonances were present for two methoxy groups, a two proton doublet in the methoxy region, a one proton triplet at δ 3.25, and two C-methyl groups. The chemical shifts of the aliphatic resonances suggested the presence of an epoxy group in an isopentoxo side chain. On the basis of these data and biogenetic analogy, structure 1 was tentatively suggested. Proof of structure was obtained by mild acid hydrolysis to give the known alkaloid, evoxine (2).



Smaller amounts of a closely related, less polar, alkaloid were recovered from the mother liquors after chromatography on alumina. The uv spectrum indicated the material was a furoquinoline alkaloid and was similar to that reported for evolitrine.⁹ The nmr spectrum showed only one methoxy resonance. The downfield position of the methoxy resonance (δ 4.35) indicated the methoxy group was located at the 4 position.⁸ The aliphatic resonances again indicated the presence of an epoxyisopentoxo group. Acid hydrolysis of the alkaloid gave a glycol which is formulated as 4, analogously to evoxine (2).

7-Isopentenyl- δ -fagarine (5), the isopentyl derivative corresponding to 1, is a constituent of *Ptelea aptera* Parry (Rutaceae).¹⁰ The furoquinoline alkaloids found in this study are reasonable biogenetic intermediates to the furoquinoline alkaloids 2, 5, and 6 previously found by Cannon, *et al.*,¹¹ in this same plant. It is not apparent if the different results found in this study are a result of geographical or seasonal differences in the plant material from that previously used¹⁰ or if the products previously found are artifacts resulting from the acid employed in the isolation procedures.¹¹ The furoquinoline alkaloids, evoxine (2), evoxidine (6), and evodine (7), previously reported from *E. zanthoxyloides* have not been encountered occurring naturally in this study. Eastwood, *et al.*,⁷ suggested that evodine (7)² was not an artifact, since it was not

formed by treatment of evoxine with acid. The direct formation of evodine from the epoxy precursor during work-up cannot be ruled out. However, in this study only evoxine (2) was obtained from acid-catalyzed hydrolysis of 1.



An attempt to determine the absolute configuration of the side chain of 1 was undertaken. One possible approach is to introduce an optically active chromophore into the side chain which would adsorb to longer wavelengths of the furoquinoline chromophore. Trithiocarbonates are ideal derivatives for such studies since they adsorb well into the visible region¹² and sufficient knowledge is available on the interpretation of their ORD and CD curves in terms of absolute configuration.¹³

Treatment of 1 with potassium methyl xanthate, under conditions which might be expected to give the trithiocarbonate¹⁴ yielded instead only the episulfide (8).

Experimental Section¹⁵

Isolation.—Branch ends of *Evodia zanthoxyloides* (0.45 kg) containing seed clusters, collected June 1967, were ground and extracted with acetone. The extracts were concentrated, chloroform was added, and the solution was allowed to stand 48 hr during which time a crop of crystals was deposited. The product was collected to give 14 g of 1: mp 141–144° (EtOAc–hexane); $[\alpha]_D +13^\circ$ (CHCl₃); $\lambda_{\max}^{\text{EtOH}}$ 248 m μ (84,000), ~310, 320 (9000), 332 (8400), ~342; nmr δ 7.85 (d, J = 9 Hz, H-5), 7.54 (d, J = 3 Hz, H-2'), 7.20 (d, H-6), 6.95 (d, J = 3 Hz, H-3'), 4.30, 4.17 (methoxyls), 3.25 (t, J = 5 Hz, epoxy proton),¹⁶ 1.38 (C-methyls) (in CDCl₃).

Anal. Calcd for C₁₈H₁₉NO₅: C, 65.64; H, 5.81; N, 4.25. Found: C, 65.6; H, 5.86; N, 4.17.

Tlc of the crude extracts when sprayed with Ehrlich reagent gave indication of the presence of a polar limonoid.^{3,5} Solvent was removed from the mother liquors and the residue chromatographed over alumina. Elution of the column with 50% benzene in hexane eluted a nonpolar blue fluorescing spot which proved to be a monomethyl ether (3): mp 145–147° (EtOAc–hexane); $[\alpha]_D +50^\circ$ (CHCl₃); $\lambda_{\max}^{\text{EtOH}}$ 247 m μ (92,000), ~297, 308 (9600), 319 (9300), 331 (7400); nmr δ 8.09 (d, J = 9 Hz, H-5), 7.49 (d,

(12) C. Djerassi, H. Wolff, D. A. Lighner, E. Bunnenberg, K. Takeda, T. Komeno, and K. Kuriyama, *Tetrahedron*, **19**, 1547 (1963).

(13) K. Kuriyama and T. Komeno, "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," Heyden and Son, London, 1967, p 366.

(14) Cf. C. G. Overberger and A. Drucker, *J. Org. Chem.*, **29**, 360 (1964); see also, A. M. Creighton and L. N. Owen, *J. Chem. Soc.*, 1024 (1960); S. M. Iqbal and L. N. Owen, *ibid.*, 1030 (1960).

(15) Nmr spectra were taken at 60 MHz. The relative area of the peaks were consistent with their assignments.

(16) The ether methylene resonances were obscured by the methoxy resonances in CDCl₃, but were distinguishable in benzene.

(3) D. L. Dreyer, *Phytochemistry*, **5**, 367 (1966). For a review, see D. L. Dreyer, *Fort. Chem. Org. Naturstoffe*, **26**, 190 (1968).

(4) Tlc of the crude plant extracts (see Experimental Section) using Ehrlich's reagent as a detecting spray reagent⁵ also indicated the presence of limonoids; however, the amounts present were too small to permit isolation from the plant material on hand.

(5) D. L. Dreyer, *J. Org. Chem.*, **30**, 749 (1965).

(6) L. H. Briggs and R. C. Cambie, *Tetrahedron*, **2**, 256 (1958).

(7) F. W. Eastwood, G. K. Hughes, and E. Ritchie, *Aust. J. Chem.*, **7**, 87 (1954).

(8) A. V. Robertson, *ibid.*, **16**, 451 (1963).

(9) R. G. Cooke and H. F. Haynes, *ibid.*, **7**, 273 (1954).

(10) D. L. Dreyer, *Phytochemistry*, **8**, 1013 (1969).

(11) J. R. Cannon, G. K. Hughes, K. G. Neill, and E. Ritchie, *Aust. J. Sci. Res.*, **A5**, 406 (1952); *Chem. Abstr.*, **47**, 3857 (1953).

$J = 3$ 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 $\text{C}_{17}\text{H}_{17}\text{NO}_4$: 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; $[\alpha]_D^{20} +13^\circ$ (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); $\lambda_{\text{max}}^{\text{EtOH}}$ 247, 277, ~296, 308, 320, 332 m μ ; 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, $^{\text{O}}>\text{CHCH}_2\text{O}$), 1.40 and 1.35 (C-methyls) (in CDCl_3).

Anal. Calcd for $\text{C}_{17}\text{H}_{19}\text{NO}_5$: C, 64.34; H, 6.03. Found: C, 63.7; H, 6.02.

Epsulfide 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, $^{\text{S}}>\text{CHCH}_2\text{O}$), 1.65, 1.63 (C-methyls) (in CDCl_3).

Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_5\text{S}$: 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. Lambertson, 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 $[\alpha]_D^{20} +20^\circ$ (EtOH) for evoxine isolated from *Choisya ternata* H. B. and K. [S. R. Johns, J. A. Lambertson, and A. A. Sioumis, *Aust. J. Chem.*, **20**, 1975 (1967)]. Evoxine previously reported from *E. zanthoxyloides* showed $[\alpha]_D^{20} +5^\circ$ (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.

ERNEST WENKERT, JAMES D. MCCHESENEY,¹ AND DANIEL J. WATTS²

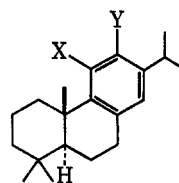
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Received November 19, 1969

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.

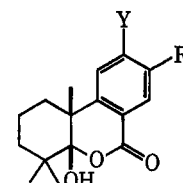
Ferruginol (1a), a major constituent,³ had to be converted into dehydroabietane (1b), a new natural product and minor constituent of the podocarp.⁴ While in a related case one of the Kenner procedures had been employed,⁵ it now was of interest to apply the recently discovered deoxygenation method of 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

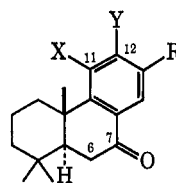
c, X = Y = OMe



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

b, R = Y = H

One of the minor bark constituents⁸ 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.



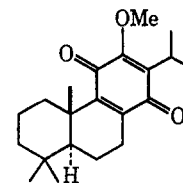
3a, X = Y = R = H

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



4

One more minor plant component⁵ 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-

(3) Cf. C. W. Brandt and L. G. Neubauer, *J. Chem. Soc.*, 1031 (1939).

(4) M. Kitadani, A. Yoshikoshi, Y. Kitahara, J. de Paiva Campello, J. D. McCheesney, D. J. Watts, and E. Wenkert, *Chem. Pharm. Bull.*, **18**, 402 (1970).

(5) E. Wenkert and B. G. Jackson, *J. Amer. Chem. Soc.*, **80**, 217 (1958).

(6) W. J. Musliner and J. W. Gates, *ibid.*, **88**, 4271 (1966).

(7) E. Wenkert, P. Beak, R. W. J. Carney, J. W. Chamberlin, D. B. R. Johnston, C. D. Roth, and A. Tahara, *Can. J. Chem.*, **41**, 1924 (1963).

(8) D. J. Watts, Ph.D. Dissertation, Indiana University, 1969.

(9) E. Wenkert and B. G. Jackson, *J. Amer. Chem. Soc.*, **80**, 211 (1958); E. Wenkert and J. W. Chamberlin, *ibid.*, **81**, 688 (1959).

(10) B. L. Mylari, unpublished result.

(11) B. L. Mylari, Ph.D. Dissertation, Indiana University, 1966.

(12) T. Kondo, M. Suda, and M. Teijima, *Yakugaku Zasshi*, **82**, 1252 (1962); *Chem. Abstr.*, **59**, 1685 (1963).

(1) National Science Foundation Cooperative Fellow, 1962–1965.

(2) Public Health Service Predoctoral Fellow, 1966–1969.