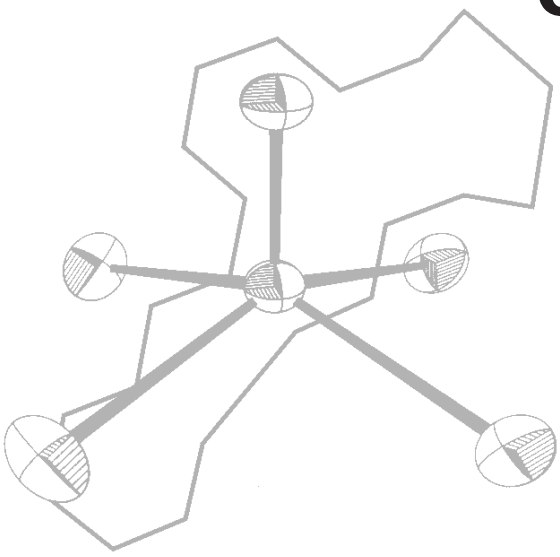
CSIRO PUBLISHING

Australian Journal of Chemistry



Volume 52, 1999

A journal for the publication of original research
in all branches of chemistry and chemical technology

www.publish.csiro.au/journals/ajc

All enquiries and manuscripts should be directed to
The Managing Editor
Australian Journal of Chemistry
CSIRO PUBLISHING
PO Box 1139 (150 Oxford St)
Collingwood Telephone: 61 3 9662 7630
Vic. 3066 Facsimile: 61 3 9662 7611
Australia Email: john.zdysiewicz@publish.csiro.au

Published by **CSIRO** PUBLISHING
for CSIRO Australia and
the Australian Academy of Science

Aust. J. Chem., 1999, **52**, 837-840

Four New β-Orcinol *meta*-Depsides from *Pertusaria* and *Siphula* Lichens

John A. Elix,[A] *Caroline E. Barclay,*[A] *Judith H. Wardlaw,*[A]
Alan W. Archer,[B] *Sen-hua Yu*[C] *and Gintaras Kantvilas*[D]

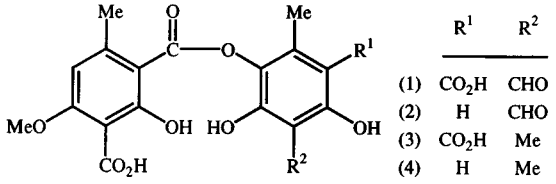
[A] Department of Chemistry, The Faculties, Australian National University, Canberra, A.C.T. 0200.
[B] National Herbarium of New South Wales, Royal Botanic Gardens, Sydney, N.S.W. 2000.
[C] Department of Biology, Nanjing Normal University, Nanjing 210097, People's Republic of China.
[D] Tasmanian Herbarium, G.P.O. Box 252-04, Hobart, Tas. 7001.

The new depsides decarboxyhypothamnolic acid [3-(2′,4′-dihydroxy-3′,6′-dimethylphenyloxycarbonyl)-2-hydroxy-6-methoxy-4-methylbenzoic acid] (4) and cryptothamnolic acid [3-(3′-formyl-2′-hydroxy-4′-methoxy-6′-methylbenzoyloxy)-4,6-dihydroxy-2,5-dimethylbenzoic acid] (6) have been detected in extracts of a Chinese *Pertusaria* species together with hypothamnolic acid (3) and their structures implied by means of chromatographic and spectroscopic comparisons with synthetic materials. Two further new depsides, neothamnolic acid [3-(5′,7′-dihydroxy-6′-methyl-1′-oxo-1′,3′-dihydroisobenzofuran-4′-yloxycarbonyl)-2-hydroxy-6-methoxy-4-methylbenzoic acid] (8) and lactothamnolic acid [3-(6′-formyl-5′,7′-dihydroxy-1′-oxo-1′,3′-dihydroisobenzofuran-4′-yloxycarbonyl)-2-hydroxy-6-methoxy-4-methylbenzoic acid] (9), have been isolated from the lichen *Siphula ramalinoides*, and the structure of these compounds followed from a combination of spectroscopic data, derivatization and degradation experiments.

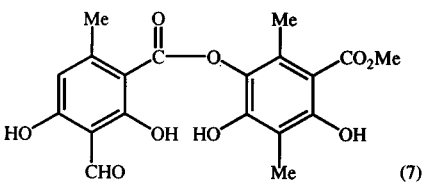
Introduction

para-Depsides and depsidones derived biosynthetically from β-orsellinic acid moieties are common lichen metabolites, but the related *meta*-depsides are much more restricted in number with only five representatives known, namely thamnolic acid (1),[1] decarboxythamnolic acid (2),[1] hypothamnolic acid (3),[1] haemathamnolic acid (5)[1] and dissectic acid (7).[2]

In this paper, we describe the characterization of four such new depsides, cryptothamnolic acid (6) and decarboxyhypothamnolic acid (4), present in a Chinese *Pertusaria* species, and neothamnolic acid (8) and lactothamnolic acid (9), present in the South American lichen *Siphula ramalinoides* Nyl. ex Crombie.



	R^1	R^2
(1)	CO_2H	CHO
(2)	H	CHO
(3)	CO_2H	Me
(4)	H	Me

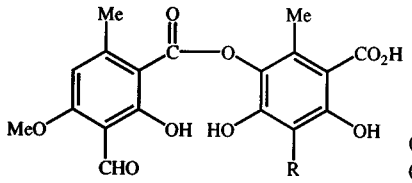


(7)

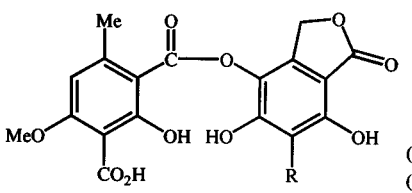
New Depsides Present in the *Pertusaria* Species

Thin-layer chromatographic (t.l.c.), high-performance liquid chromatographic (h.p.l.c.) and mass spectrometric analysis of the total acetone extract of an undescribed Chinese *Pertusaria* species indicated the presence of hypothamnolic acid (3) as the major constituent together with minor quantities of two related depsides. Subsequently we have undertaken the syntheses of decarboxyhypothamnolic acid (4) and cryptothamnolic acid (6) and found the chromatographic behaviour of these compounds to be identical with that of the minor depsides present in the lichen.

The successful synthesis of the depsides (4) and (6) was achieved by direct condensation of the appropriately substituted aromatic carboxylic acids and phenols in the presence



(5) R = CHO
(6) R = Me

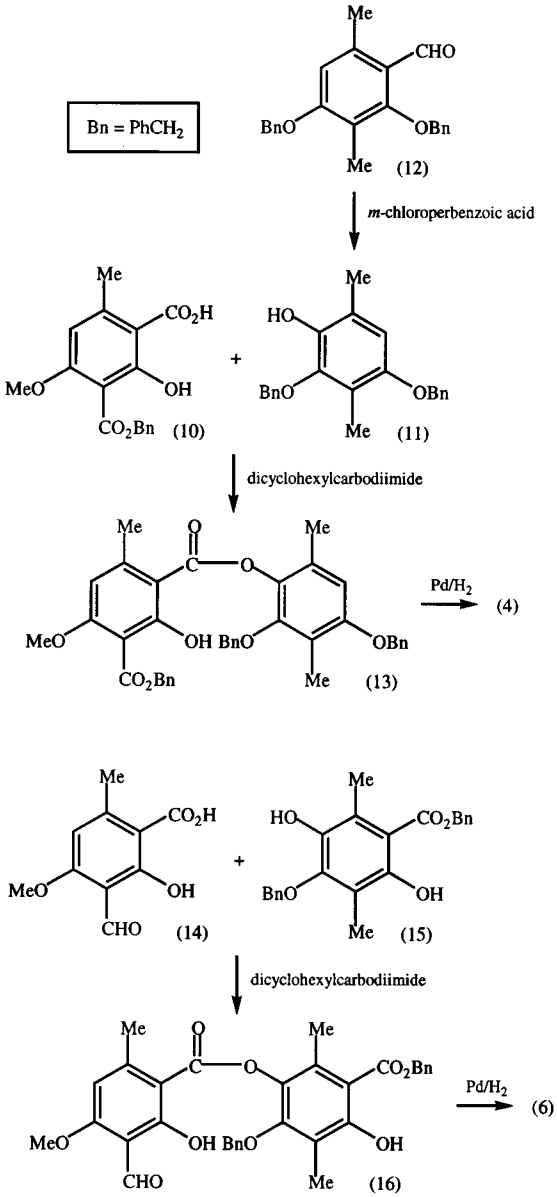


(8) R = Me
(9) R = CHO

Manuscript received 14 July 1999

10.1071/CH99085 0004-9425/99/090837

of dicyclohexylcarbodiimide (Scheme 1). Potentially reactive phenol and carboxy groups were protected by *O*-benzylation. We have successfully employed this route previously in the synthesis of similarly substituted natural depsides.[1,2] The mononuclear precursors (10),[1]* (14)[3]† and (15)[1]‡ had been synthesized previously, whereas 2,4-dibenzyloxy-3,6-dimethylphenol (11) was obtained from the corresponding aldehyde (12) by oxidation with *m*-chloroperbenzoic acid (Scheme 1). Depside ester formation between the acid (10) and phenol (11), and between the carboxylic acid (14) and the phenol (15) was achieved by treatment with dicyclohexylcarbodiimide and yielded benzyl 2′,4′-di-*O*-benzyldecarboxyhypothamnolate (13) and benzyl 4′-*O*-benzylcryptothamnolate (16) respectively. Hydrogenolysis of the esters (13) and (16) over palladized carbon produced the depsides decarboxyhypothamnolic acid (4) and cryptothamnolic acid (6) in high yield. The isolation of (4) and (6) from the lichen was not practicable given the minute quantities available.



Scheme 1

New Depsides Present in *Siphula ramalinoides* Nyl. ex Crombie

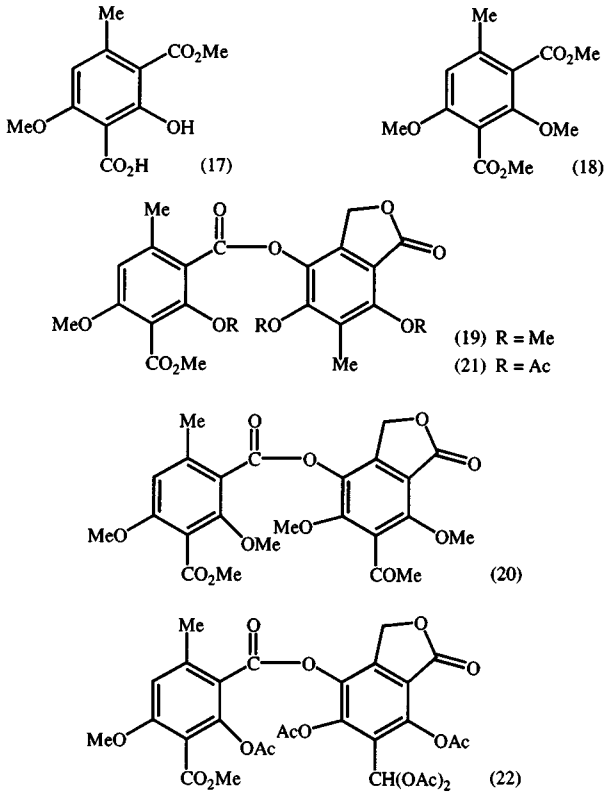
A preliminary chromatographic (t.l.c. and h.p.l.c.) and mass spectrometric examination of an acetone extract of the lichen *Siphula ramalinoides* indicated that this lichen contained two depsides of unknown structure. A subsequent preparative-scale extraction of this species followed. However, fractional crystallization and preparative-layer chromatography were unsuccessful in separating the two compounds present. The ^{1}H n.m.r. spectrum of this mixture exhibited three *C*-methyl resonances (δ 2.17, 2.47, 2.49), two *O*-methyl resonances (δ 4.05, 4.12), two methylene signals (δ 5.31, 5.32), two aromatic signals (δ 6.62, 6.47), a broad hydroxy resonance (δ 8.31) and an aldehyde resonance (δ 10.37). This mixture of compounds did not exhibit molecular ions in the positive-ion electron impact mass spectrum, but did exhibit fragment ions at *m/z* 226 and 209 as has been observed for thamnolic acid (1)[1] and hypothamnolic acid (3),[1] indicating that all four compounds probably contained the same A-ring moiety. This was confirmed by methanolysis of the mixture, whereupon the acid (17)§ was formed but the B-ring derivatives could not be isolated. On the basis of this spectroscopic and degradative data the tentative structures of neothamnolic acid and lactothamnolic acid were formulated as (8) and (9) respectively.

Although we were unable to separate the naturally occurring mixture of (8) and (9), we were successful in separating and characterizing the corresponding permethyl and acetyl derivatives and in so doing confirming their assigned structures. Thus methylation of the mixture of (8) and (9) by treatment with excess ethereal diazomethane for a period of 3 days afforded a mixture of the corresponding permethyl derivatives which were separated by preparative-layer chromatography.

The faster moving band afforded the diester (18),¶ derived by cleavage of the A-ring moiety prior to, or during, diazomethylation. The second band contained methyl 2,4′,6′-tri-*O*-methylneothamnolate (19), and the third band methyl 2,4′,6′-tri-*O*-methyl-5′-*C*-methyllactothamnolate (20). The structure of the permethyl derivatives (19) and (20) followed from their respective ^{1}H n.m.r. and mass spectra. It is interesting that under these reaction conditions the 5′-formyl group of lactothamnolic acid (9) underwent *C*-methylation to give the corresponding methyl ketone (20).

The natural mixture of neothamnolic acid (8) and lactothamnolic acid (9) was acetylated by treatment with acetic

* 3-Benzyloxycarbonyl-2-hydroxy-4-methoxy-6-methylbenzoic acid.
† 3-Formyl-2-hydroxy-4-methoxy-6-methylbenzoic acid.
‡ Benzyl 4-benzyloxy-2,5-dihydroxy-3,6-dimethylbenzoate.
§ 2-Hydroxy-6-methoxy-3-methoxycarbonyl-4-methylbenzoic acid.
¶ Dimethyl 2,4-dimethoxy-6-methylbenzene-1,3-dicarboxylate.



anhydride and concentrated sulfuric acid, and the mixture of acetates so obtained was then methylated by reaction with ethereal diazomethane. Preparative-layer chromatography of the crude product afforded two major bands. The faster moving band yielded methyl 2,4′,6′-tri-*O*-acetylneothamnolate (21) and the slower band methyl pentaacetyllactothamnolate (22). Again the structures of these two derivatives followed from their spectroscopic properties.

Neothamnolic acid (8) and lactothamnolic acid (9) are further representatives of the β-orcinol *meta*-depsides, and may arise biosynthetically from the more common derivatives hypothamnolic acid (3) and thamnolic acid (1) by oxidation of the 2′-methyl group and subsequent lactonization.

Experimental

The general experimental details have been described previously.[4]

Chromatography

The lichen fragments were freed as far as possible from obvious organic substrate material and extracted with warm acetone for thin-layer chromatography (t.l.c.) or with warm methanol for high-performance liquid chromatography (h.p.l.c.). Compounds were identified by t.l.c. by using the methods standardized for lichen products[5–8] and by h.p.l.c. with retention index values (RI) calculated from benzoic acid and solorinic acid controls.[9] For t.l.c. standard R_F values were determined in three independent t.l.c. solvent systems: (A) toluene/dioxan/acetic acid (180 : 45 : 5); (B) hexane/t-butyl methyl ether/formic acid (140 : 72 : 18); (C) toluene/acetic acid (170 : 30). For h.p.l.c. a Spectra System, a Phenomenex Hypersil 5C18 column (250 by 4.6 mm) and a spectrometric detector operating at 254 nm with a flow rate of 1 ml/min were used. Two solvent systems were used: 1% aqueous orthophosphoric acid and methanol in the ratio 3 : 7 (*A*) and methanol (*B*). The run started with 100% *A* and was raised to 58% *B* within 15 min, then to 100% *B* within a further 15 min, followed by isocratic elution in 100% *B* for a further 10 min.

Detection of New Depsides (4) and (6) by Comparative Chromatography

The undescribed *Pertusaria* species was collected on bark, Lijiang, Mt. Yulongshan, Yunnan Province, China, 3300 m, Jinong Wu & Aitang Liu 82-195 (NNU). Comparative h.p.l.c. and t.l.c. indicated the presence of hypothamnolic acid (3) (major), decarboxyhypothamnolic acid (4) (minor) [standard t.l.c. R_F values:[5,8] R_F(A) 0.05; R_F(B) 0.15; R_F(C) 0.13; standard h.p.l.c.[9,10] RI 0.15], and cryptothamnolic acid (6) (minor) [standard t.l.c. R_F values:[5,8] R_F(A) 0.38; R_F(B) 0.32; R_F(C) 0.40; standard h.p.l.c.[9,10] RI 0.25]. The chromatographic behaviour of the latter two compounds was identical with that of the synthetic samples prepared below. The h.p.l.c. apparatus was coupled to a photodiode array detector for ultraviolet spectroscopic comparisons. By this means the spectra of the components eluting from the chromatogram were recorded and computer-matched against a library of ultraviolet spectra recorded for the authentic lichen metabolites under identical conditions. For the above substances the correlation of the ultraviolet spectra was greater than 99.9%. This composition was also consistent with the observed lichen mass spectrum with prominent fragment peaks observed at *m/z* 362, 346, 209, 194, 193, 192, 191, 180, 168, 165 (Found: *m/z* (mol. wt) 362.0999. $C_{18}H_{18}O_8$ requires mol. wt 362.1001. Found: *m/z* (mol. wt) 346.1051. $C_{18}H_{18}O_7$ requires mol. wt 346.1052).

2,4-Dibenzyloxy-3,6-dimethylphenol (11)

A solution of 2,4-dibenzyloxy-3,6-dimethylbenzaldehyde (12)[11] (0.5 g, 1.44 mmol) in anhydrous dichloromethane (50 ml) was added over 30 min to a stirred solution of *m*-chloroperbenzoic acid (3 mmol) in anhydrous dichloromethane (30 ml) at room temperature. The solution was stirred for a further 1 h and then the solvent was evaporated under reduced pressure. The residue was dissolved in ethyl acetate and the solution washed repeatedly with 10% sodium hydrogen carbonate solution, with saturated brine and then dried ($MgSO_4$). The crude formate obtained on evaporation of the solvent was dissolved in methanol (30 ml) and the solution cooled to 0°. A solution of 10% aqueous potassium hydroxide (20 ml) was then added with stirring under an atmosphere of nitrogen. After stirring was continued for a further 45 min at this temperature, the reaction mixture was poured into cold, dilute hydrochloric acid, extracted with ethyl acetate and the extract washed with water, brine and dried ($MgSO_4$). The residue obtained on evaporation of the solvent was purified by chromatography over silica gel using 10% ethyl acetate/light petroleum as eluent. The major band afforded the *phenol* (11) (0.24 g, 50%) as a colourless oil (Found: mol. wt 334.1570. $C_{22}H_{22}O_3$ requires mol. wt 334.1566). ^{1}H n.m.r. ($CDCl_3$) δ 2.23, 2.25, 2s, Me; 4.88, 5.01, 2s, CH_2; 5.24, s, OH; 6.55, s, H 5; 7.25–7.56, m, Ph. Mass spectrum *m/z* 334 (M, 3%), 91 (100).

3-(2′,4′-Dihydroxy-3′,6′-dimethylphenyloxycarbonyl)-2-hydroxy-6-methoxy-4-methylbenzoic Acid (Decarboxyhypothamnolic Acid) (4)

A solution of 3-benzyloxycarbonyl-2-hydroxy-4-methoxy-6-methylbenzoic acid (10)[1] (170 mg, 0.54 mmol), 2,4-dibenzyloxy-3,6-dimethylphenol (11) (150 mg, 0.45 mmol) and dicyclohexylcarbodiimide (120 mg, 0.58 mmol) in anhydrous toluene (3 ml) and 1,2-dimethoxyethane (1 ml) was stirred at room temperature for 18 h. The solid was filtered off, the filtrate concentrated and purified by radial chromatography over silica gel using 2–10% ethyl acetate/light petroleum as eluent. The major band afforded the depside ester (13) (170 mg, 50%) as a colourless gum. ^{1}H n.m.r. ($CDCl_3$) δ 2.20, 2.21, 2.54, 3s, ArMe; 3.87, s, OMe; 4.85, 5.07, 2s, $ArOCH_2$; 5.41, s, CO_2CH_2; 6.32, 6.63, 2s, H 5,5′; 7.20–7.48, m, Ph.

A solution of the depside ester (13) (170 mg) in ethyl acetate (20 ml) was stirred in an atmosphere of hydrogen with 10% palladized carbon (25 mg) for 3 h. The catalyst was then filtered off and the solvent evaporated. The residue was crystallized from ethyl acetate to give *decarboxyhypothamnolic acid* (4) (85 mg, 87%) as colourless microcrystals, m.p. 270° (dec.) (Found: C, 59.5; H, 5.2. $C_{18}H_{18}O_8$ requires C, 59.7; H, 5.0%). ^{1}H n.m.r. ($CDCl_3$) δ 2.05, 2.16, 2.54, 3s, ArMe; 4.15, s, OMe; 6.27, 6.50, 2s, H 5,5′; 6.40, 7.30, 2s, 2′,4′-OH; 13.14, s, 2-OH. Mass spectrum *m/z* 362 (M, 0.8%), 209 (18), 192 (14), 191 (100), 165 (15), 152 (14), 149 (31), 105 (13).

5-(3′-Formyl-2′-hydroxy-4′-methoxy-6′-methylbenzoyloxy)-2,4-dihydroxy-3,6-dimethylbenzoic Acid (Cryptothamnolic Acid) (6)

A solution of 3-formyl-2-hydroxy-4-methoxy-6-methylbenzoic acid (14)[3] (80 mg, 0.38 mmol), benzyl 4-benzyloxy-2,5-dihydroxy-3,6-dimethylbenzoate (15)[1] (120 mg, 0.32 mmol) and dicyclohexylcarbodiimide (80 mg, 0.39 mmol) in anhydrous toluene (5 ml) and 1,2-dimethoxyethane (1 ml) was stirred at room temperature for 18 h. The precipitate was filtered off, the filtrate concentrated and the residue purified by radial chromatography over silica gel using 2–10% ethyl acetate/light petroleum as eluent. The major band afforded the depside ester (16) (67 mg, 37%) as a colourless gum. ^{1}H n.m.r. ($CDCl_3$) δ 2.16, 2.24, 2.53, 3s, ArMe; 3.94, s, OMe; 4.87, s, $ArOCH_2$; 5.42, s, CO_2CH_2; 6.22, s, H 5′; 7.25–7.52, m, Ph; 10.28, s, CHO; 11.74, 12.78, 2s, bonded OH.

A solution of the depside ester (16) (67 mg) in ethyl acetate (15 ml) was stirred in an atmosphere of hydrogen with 10% palladized carbon (25 mg) for 3 h. The catalyst was then filtered off and the solvent evaporated. The residue was crystallized from ethyl acetate to give *cryptothamnolic acid* (6) (32 mg, 70%) as cream microcrystals, m.p. 211–213° (Found: C, 58.2; H, 5.0. $C_{19}H_{18}O_9$ requires C, 58.5; H, 4.6%). ^{1}H n.m.r. ($CDCl_3$) δ 2.10, 2.18, 2.55, 3s, ArMe; 3.99, s, OMe; 6.42, s, H 5′; 8.05, br, OH, CO_2H; 10.29, s, CHO; 11.84, s, OH. Mass spectrum *m/z* 346 (0.06%), 210 (10), 194 (11), 193 (100), 191 (10).

Extraction of Siphula ramalinoides *Nyl. ex Crombie*

The lichen material was collected on soil, Isla Clarence, Tierra del Fuego, Chile, S. Stenroos 2587, 18 January 1987 (H).

The dried lichen thallus (0.77 g) was extracted with anhydrous acetone (100 ml) in a Soxhlet extractor for 36 h. The acetone extract was then concentrated to give a mixture of neothamnolic acid (8) and lactothamnolic acid (9) as a yellow oil (0.134 g, 17%). ^{1}H n.m.r. (CD_3COCD_3) δ 2.17, 2.47, 2.49, 3s, ArMe; 4.05, 4.12, 2s, OMe; 5.31, 5.32, 2s, CH_2; 6.62, 6.74, 2s, ArH; 8.31, br s, OH; 10.37, s, CHO. Mass specrum *m/z* 226 (1%), 209 (12), 198 (2), 191 (32). This mixture could not be resolved by t.l.c. Standard t.l.c. R_F values:[5,8] R_F(A) 0.05; R_F(B) 0.20; R_F(C) 0.16. Standard h.p.l.c.[9,10] for neothamnolic acid (8) RI 0.13; lactothamnolic acid (9) RI 0.12.

Methanolysis of Mixture of (8) and (9)

A mixture of neothamnolic acid (8) and lactothamnolic acid (9) (29 mg) was boiled under reflux in anhydrous methanol for 2 h. The solvent was evaporated and the residue applied to a silica gel plate (20 by 20 by 0.1 cm) and eluted with 15% acetic acid/toluene. The faster moving band afforded 2-hydroxy-6-methoxy-3-methoxycarbonyl-4-methylbenzoic acid (17) (5.1 mg, 30%) as colourless microcrystals, identical with authentic (synthetic)[11] material (t.l.c., h.p.l.c., ^{1}H n.m.r., mass spectrum). ^{1}H n.m.r. (CD_3COCD_3) δ 2.32, s, ArMe; 3.84, 4.04, 2s, OMe; 6.57, s, H 5. Subsequent bands yielded mixtures of products and could not be resolved.

Methylation of Mixture of (8) and (9)

A solution of a mixture of neothamnolic acid (8) and lactothamnolic acid (9) (35 mg) in diethyl ether (10 ml) was added to excess ethereal diazomethane and the solution stored at room temperature for 3 days. The solvent was then evaporated and the residue applied to a silica gel plate (20 by 20 by 0.1 cm) and eluted with 30% ethyl acetate/light petroleum. Three major bands developed. The faster moving band afforded dimethyl 2,4-dimethoxy-6-methylbenzene-1,3-dicarboxylate (18) (2.1 mg, 9%) as colourless microcrystals, identical (t.l.c., h.p.l.c., ^{1}H n.m.r., mass spectrum) with authentic material.[12] ^{1}H n.m.r. (CD_3COCD_3) δ 2.34, s, ArMe; 3.81, 3.83, 3.90, 3.91, 4s, OMe; 6.51, s, ArH.

The second band yielded *methyl 2,4′,6′-tri*-O-*methylneothamnolate* (19) (5.0 mg, 12%) as a colourless oil (Found: C, 60.4; H, 5.0. $C_{23}H_{24}O_{10}$ requires C, 60.0; H, 5.2%). ^{1}H n.m.r. (CD_3COCD_3) δ 2.27, 2.51, 2s, ArMe; 3.84, 3.88, 3.91, 3.95, 4s, OMe; 4.09, s, CO_2Me; 5.18, s, CH_2; 6.61, s, H 5. Found: mol. wt 459.1294. $C_{23}H_{23}O_{10}$ requires mol. wt 459.1291. Mass spectrum *m/z* 459 (M − 1, 0.7%), 429 (15), 238 (29), 237 (100), 191 (22), 177 (10).

The third major band afforded *methyl 2,4′,6′-tri*-O-*methyl-5′*-C-*methyllactothamnolate* (20) (2.1 mg, 5%) as a colourless gum (Found: C, 59.3; H, 5.0. $C_{24}H_{24}O_{11}$ requires C, 59.0; H, 4.9%). ^{1}H n.m.r. (CD_3COCD_3) δ 2.49, 2.55, 2s, ArMe, COMe; 3.88, 3.91, 3.92, 3.96, 4s, OMe; 4.16, s, CO_2Me; 5.21, s, CH_2; 6.61, s, H 5. Mass spectrum *m/z* 457 (M − OMe, 47%), 238 (100).

Sequential Acetylation and Methylation of Mixture of (8) and (9)

A mixture of neothamnolic acid (8) and lactothamnolic acid (9) (30 mg) was dissolved in acetic anhydride (5 ml), concentrated sulfuric acid (1 drop) added and the solution stored at room temperature for 16 h. Water (25 ml) was added and the solution stirred for 2.5 h. The mixture was extracted with ethyl acetate and the combined extracts were washed with water, brine and dried ($MgSO_4$). Excess ethereal diazomethane was added to the filtrate and the solution stored at room temperature for 16 h. The solvent was then evaporated and the residue applied to a silica gel plate and eluted with 50% ethyl acetate/light petroleum. Two major bands developed.

The faster moving band afforded *methyl 2,4′,6′-tri*-O-*acetylneothamnolate* (21) (2.0 mg, 5%) as a colourless gum (Found: C, 57.6; H, 4.0. $C_{26}H_{24}O_{13}$ requires C, 57.4; H, 4.4%). ^{1}H n.m.r. (CD_3COCD_3) δ 2.12, 2.18, 2.29, 2.46, 2.59, 5s, ArMe, COMe; 3.90. 3.93, 2s, OMe; 5.19, s, CH_2; 6.77, s, H 5. Mass spectrum *m/z* 513 (M − OMe, 0.5%), 471 (2.3), 191 (100).

The second band contained *methyl pentaacetyllactothamnolate* (22) (3.2 mg, 7%) as a colourless gum (Found: C, 54.4; H, 4.0. $C_{30}H_{28}O_{17}$ requires C, 54.5; H, 4.2%). ^{1}H n.m.r. (CD_3COCD_3) δ 2.07 (6H), 2.20, 2.31, 2.48, 2.58, 5s, ArMe, COMe; 3.90. 3.93, 2s, OMe; 5.22, s, CH_2; 6.77, s, H 5; 8.02, s, ArCH. Mass spectrum *m/z* 629 (M − OMe, 15%), 628 (33), 615 (30), 614 (100).

Acknowledgment

We wish to thank the Australian Research Council for generous financial support.

References

[1] Elix, J. A., and Norfolk, S., *Aust. J. Chem*., 1975, **28**, 2035.
[2] Elix, J. A., and Wardlaw, J. H., *Aust. J. Chem*., 1996, **49**, 539.
[3] Elix, J. A., and Norfolk, S., *Aust. J. Chem*., 1975, **28**, 399.
[4] Elix, J. A., Barclay, C. E., and Lumbsch, H. T., *Aust. J. Chem.*, 1994, **47**, 1199.
[5] Culberson, C. F., *J. Chromatogr.*, 1972, **72**, 113.
[6] Culberson, C. F., and Ammann, K., *Herzogia*, 1979, **5**, 1.
[7] Culberson, C. F., and Johnson, A., *J. Chromatogr.*, 1982, **238**, 483.
[8] Elix, J. A., and Ernst-Russell, K. D., 'A Catalogue of Standardized Thin Layer Chromatographic Data and Biosynthetic Relationships for Lichen Substances' 2nd Edn (Australian National University: Canberra 1993).
[9] Feige, G. B., Lumbsch, H. T., Huneck, S., and Elix, J. A., *J. Chromatogr.*, 1993, **646**, 417.
[10] Elix, J. A., Wardlaw, J. H., Archer, A. W., Lumbsch, H. T., and Plümper, M., *Australas. Lichenol.*, 1997, **41**, 22.
[11] Asahina, Y., and Asano, M., *Ber. Dtsch. Chem. Ges*., 1933, **66**, 894.
[12] Asahina, Y., and Yanagita, M., *Ber. Dtsch. Chem. Ges*., 1933, **66**, 36.