Aust. J. Chem., 1979, **32**, 927–9

The Structure of Conorlobaridone and Conloxodin. New Depsidones from the Lichen *Xanthoparmelia xanthosorediata*

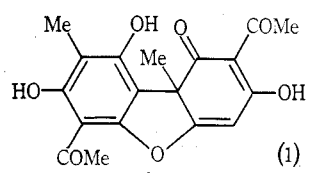
William R. Begg, Douglas O. Chester and John A. Elix

Chemistry Department, Australian National University, P.O. Box 4, Canberra, A.C.T. 2600.

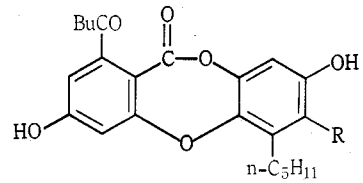
Abstract

The depsidones, conorlobaridone (4) and conloxodin (5), have been isolated from the lichen *Xanthoparmelia xanthosorediata*. The structure of these compounds followed from a comparison of the spectroscopic properties with those observed for the known cogenors, norlobaridone and loxodin.

Thin-layer chromatography of the crude extract of the Australian lichen, *Xanthoparmelia xanthosorediata* Elix, indicated that there were five major phenolic compounds present. Three of these compounds were known lichen metabolites, namely usnic acid (1), norlobaridone (2)[1] and loxodin (3).[2] These compounds were readily identified by comparison with authentic materials. As the chromatographic behaviour of the two remaining metabolites indicated that they were structurally related to the depsidones (2) and (3), they were named conorlobaridone and conloxodin respectively.

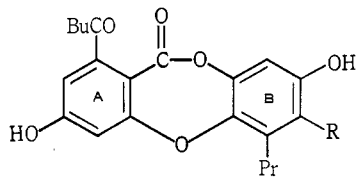


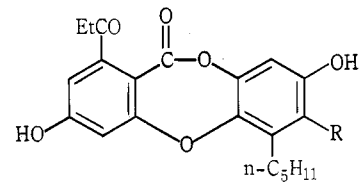
(1)



(2) R = H
(3) R = CO_2Me

The structure of conorlobaridone (4) and conloxodin (5) followed from the spectroscopic data. The ^1H n.m.r. spectra were very similar to those of norlobaridone (2) and loxodin (3) respectively, while the mass spectra indicated that the corresponding molecular ions were lighter by 28 mass units (i.e., norlobaridone, M 398, conorlobari-





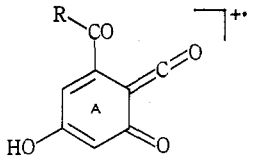
(4) R = H
(5) R = CO_2Me

(6) R = H
(7) R = CO_2Me

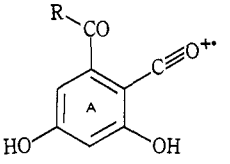
[1] Gream, G. E., and Riggs, N. V., *Aust. J. Chem.*, 1960, **13**, 285.
[2] Komiya, T., and Kurokawa, S., *Phytochemistry*, 1970, **9**, 1139.

done, M 370; loxodin, M 456, conloxodin, M 428). High-resolution mass measurements on the appropriate molecular ions confirmed the composition of the depsidones (4) and (5). From biosynthetic considerations a difference of 28 mass units probably arises from there being one C_2H_4 unit (that is one malonate-derived C_2-group) less on either ring A or ring B. Hence this evidence was consistent with either of the alternative formulations (4) or (6) for conorlobaridone and of (5) or (7) for conloxodin.

Mass spectrometry of lichen substances has proven very useful, not only in the determination of molecular weights, but also in structural elucidation.[3] In particular depsidones exhibit significant cleavage of the depside and ether linkage to give an odd and/or even electron daughter ion corresponding to the ring A fragment.[3] Thus the mass spectra of norlobaridone (2) and loxodin (3) exhibited significant peaks at *m/e* 220, 221, attributed to the ions (8) and (9).



(8) R = Bu
(10) R = Et



(9) R = Bu
(11) R = Et

As similar fragment ion peaks were observed in the mass spectra of conorlobaridone (4) and conloxodin (5) it appeared that ring A was identical in all four depsidones. No fragment ion peaks were observed at *m/e* 192 or 193 corresponding to the ring A fragments (10) and (11) expected from the alternative formulations (6) and (7). Furthermore, both norlobaridone (2) and conorlobaridone (4) showed prominent M − 57 fragments in the mass spectra. This was interpreted as loss of $^{\bullet}C_4H_9$ resulting from cleavage α to the carbonyl group of the acyl chain. Such α-fragmentation is facilitated in the case of alkyl aryl ketones.[4]

A comparison of the ^{1}H n.m.r. spectra of conloxodin (5) with loxodin (3) strongly supported the conclusion above. The CO_2CH_3, $ArCH_2$ and $ArCOCH_2$ resonances appear well downfield of the remaining aliphatic protons due to the deshielding effects of the respective aromatic and carbonyl moieties. In both (3) and (5) the $ArCOCH_2$ resonances appeared as a triplet, which indicated that these protons were adjacent to a further methylene group. If the structure of conloxodin were (7), the $ArCOCH_2$ resonances would be expected to appear as a quartet, split by the adjacent methyl group.

Hence the structures (4) and (5) can be assigned to conorlobaridone and conloxodin respectively.

Experimental

The general experimental details have been published previously.[5]

Extraction of Xanthoparmelia xanthosorediata *Elix*

The lichen material was collected on rocks, Kowen Forest, 16 km east of Canberra, A.C.T. (J. A. Elix—1830, MEL).

[3] Huneck, S., Djerassi, C., Becker, D., Barber, M., Ardenne, M. von, Steinfelder, K., and Tümmler, R., *Tetrahedron*, 1968, **24**, 2707.
[4] McLafferty, F. W., 'Interpretation of Mass Spectra' (W. A. Benjamin: Reading 1973).
[5] Baker, C., Elix, J. A., Murphy, D. P. H., Kurokawa, S., and Sargent, M. V., *Aust. J. Bot.*, 1973, **21**, 137.

The dried thallus (1·09 g) was extracted with anhydrous acetone in a Soxhlet extractor for 48 h. The extract was then concentrated to yield 99·6 mg of brown solid. This residue was adsorbed on five silica gel plates (Merck silica gel $60F_{254}$ plates, 200 by 200 by 0·25 mm) and eluted with 15% acetic acid/toluene. At least eight distinct bands developed.

The first band (R_F 0·83) yielded usnic acid (1) (60 mg, 5·5%) which was recrystallized from benzene in yellow needles, m.p. 203–204° (lit.[6] 202–204°). The identity of this compound was confirmed by comparison with an authentic sample (t.l.c., ^{1}H n.m.r., m.m.p.).

The second band (R_F 0·41) contained loxodin (3) (10 mg, 0·9%) also identified by comparison with authentic material[2] (t.l.c., ^{1}H n.m.r., m.m.p.); mass spectrum *m/e* 456 (M, 100%), 428 (32), 424 (54), 398 (22), 396 (18), 367 (19), 341 (53), 221 (27), 220 (11).

The third band (R_F 0·36) yielded *conloxodin* (methyl 3,8-dihydroxy-11-oxo-1-pentanoyl-6-propyl-1*H*-dibenzo[*b*,*e*][1,4]dioxepin-7-carboxylate) (5) (7·3 mg, 0·8%) which crystallized from chloroform/carbon tetrachloride as colourless crystals, m.p. 137° (Found: M^+, 428·1461. $C_{23}H_{24}O_8$ requires M^+, 428·1422). The homogeneity of this compound was confirmed by ^{1}H n.m.r. spectroscopy and the fact that it exhibited one spot on t.l.c. in three independent solvent systems.

^{1}H n.m.r. δ ($CDCl_3$) 1·20–1·80, m, $3\times CH_2$, $2\times CH_3$; 2·72, t, *J* 8 Hz, $COCH_2$; 3·18, t, *J* 9 Hz, $ArCH_2$; 3·96, s, CO_2CH_3; 6·66–6·80, m, 3ArH. Mass spectrum *m/e* 428 (M, 100%), 396 (98), 384 (18), 370 (35), 221 ($C_{12}H_{13}O_4$, 14), 220 (22).

Bands four and five (R_F 0·29, 0·26) contained minute quantities of two unidentified fatty acids.

The sixth band (R_F 0·24) yielded norlobaridone (2) (9·1 mg, 0·9%) which was identified by comparison with an authentic sample[1] (m.p., m.m.p., t.l.c., ^{1}H n.m.r.); mass spectrum *m/e* 398 (M, 100%), 370 (59), 341 (30), 313 (22), 236 (20), 221 (19), 220 (5).

Table 1. T.l.c. data for conloxodin and conorlobaridone

On silica gel; A, benzene/dioxan/acetic acid 180/45/5; B, n-hexane/diethyl ether/formic acid 130/80/20; C, toluene/acetic acid 200/30

Compound	R_F(A)	R_F(B)	R_F(C)	Compound	R_F(A)	R_F(B)	R_F(C)
Atranorin (standard)	0·75	0·76	0·78	conloxodin (5)	0·40	0·39	0·30
Norstictic acid (standard)	0·41	0·32	0·27	norlobaridone (2)	0·50	0·36	0·21
Loxodin (3)	0·58	0·40	0·35	conorlobaridone (4)	0·35	0·35	0·14

The seventh band (R_F 0·20) contained *conorlobaridone* (3,8-dihydroxy-1-pentanoyl-6-propyl-1*H*-dibenzo[*b*,*e*][1,4]dioxepin-11-one) (4) (8·4 mg, 0·9%) which recrystallized from cyclohexane/acetone in colourless plates, m.p. 179–180° (Found: M^+, 370·1432. $C_{21}H_{22}O_6$ requires M^+, 370·1415). The homogeneity of this compound was confirmed by ^{1}H n.m.r. spectroscopy and the fact that it exhibited a single spot on t.l.c. in three independent solvent systems (see Table 1).

^{1}H n.m.r. δ (CD_3COCD_3) 0·81–6·79, m, $2\times CH_3$, $3\times CH_2$; 2·77, 2·81, 2t, *J* 8 Hz, $COCH_2$ and $ArCH_2$; 6·64, s, 2ArH; 6·87, 6·89, 2d, *J* 2·5 Hz, 2ArH. Mass spectrum *m/e* 370 (M, 100%), 342 (55), 313 (38), 286 (32), 233 (30), 221 ($C_{12}H_{13}O_4$, 8), 220 (4).

The final band (R_F 0·14) contained traces of a brown oil, again thought to be an unknown fatty acid.

Manuscript received 13 November 1978

[6] Asahina, Y., and Shibata, S., 'Chemistry of Lichen Substances' (Japanese Society for Promotion of Science: Tokyo 1954).