(1H, *dd*, $J$ = 9.7 and 6.0 Hz, H-3), 6.14 (1H, *d*, $J$ = 6.0 Hz, H-4), 5.96 (1H, *d*, $J$ = 9.7 Hz, H-2), 4.60 (1H, *dd*, $J$ = 13.4 and 3.6 Hz, H-22), 4.54 (1H, *t*, $J$ = 3.0 Hz, H-6), 1.96, 1.88, 1.52, 1.48 (3H each, *s*, 28, 27, 21 and 19 Me).

*Withaphysalin E monoacetate* (3). A mixture of withaphysalin E (10 mg), $Ac_2O$ (0.5 ml) and pyridine (0.5 ml) was kept under dry conditions for 24 hr. The reaction mixture was freed from organic solvents *in vacuo* and purified by column chromatography (silica gel) to yield withaphysalin E monoacetate (3) as an amorphous powder (6 mg), mp 257–259°, EIMS *m/z*: 506 $[M-H_2O]^+$; UV $\lambda_{max}^{MeOH}$ nm: 226 (8300), 310 (4500); IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3440, 1750, 1700, 1652, 1225, 1012; $^1H$ NMR ($CDCl_3$): $\delta$6.93 (1H, *dd*, $J$ = 9.2 and 6.0 Hz, H-3), 6.33 (1H, *d*, $J$ = 6.0 Hz, H-4) 6.01 (1H, *d*, $J$ = 9.2 Hz, H-2), 5.56 (1H, *t*, $J$ = 3.0 Hz, H-6), 4.54 (1H, *dd*, $J$ = 12.1 and 3.8 Hz, H-22), 2.01 (3H, *s*, $-COCH_3$), 1.96, 1.88, 1.48 and 1.38 (3H each, *s*, 28, 27, 21 and 19 Me).

*Tetrahydrowithaphysalin E* (5). Withaphysalin E (1) (5 mg) in MeOH (2 ml) was hydrogenated over 5% Pd–C at room temp. and atm. pres. overnight, and the reaction mixture was purified by CC (silica gel) to furnish tetrahydrowithaphysalin E (5) as an amorphous powder (1.4 mg), EIMS *m/z*: 468 $[M-H_2O]^+$; $^1H$ NMR ($CDCl_3$): $\delta$4.49 (1H, *dd*, $J$ = 12.0 and 3.4 Hz, H-22), 3.94 (1H, *br*, H-6), 1.89, 1.81, 1.41 and 1.28 (3H each, *s*, 28, 27, 21 and 19 Me); CD (MeOH): $[\theta]_{250}+6490$, $[\theta]_{290}-3720$.

*Acknowledgement*—S.C.S. is grateful to CSIR, New Delhi for the award of a Senior Research Fellowship.

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# HOMOHEVEADRIDE, A CYCLONONADIENE BIS-ANHYDRIDE FROM *CLADONIA POLYCARPOIDES*

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**Key Word Index**—*Cladonia polycarpoides* Nyl. in Zwackh; Cladoniaceae; lichen; compound CS-1; cyclononadiene bis-anhydride; homoheveadride.

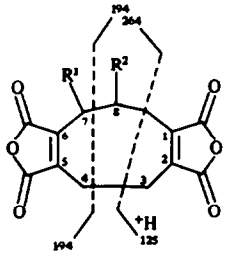
**Abstract**—The isolation of a novel cyclononadiene bis-anhydride, homoheveadride (8-butyl-7-pentylcyclonona-1,5-diene-1,2,5,6-tetracarboxylic dianhydride) from the lichen *Cladonia polycarpoides* Nyl. in Zwackh is reported.

## INTRODUCTION

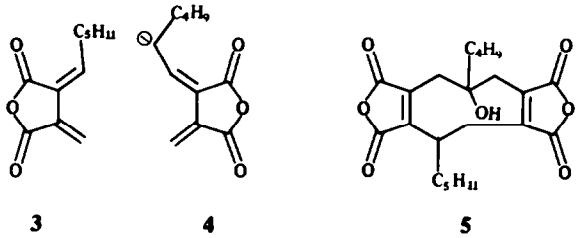
The terricolous, fruticose lichen *Cladonia polycarpoides* Nyl. in Zwackh (*Cladonia subcariosa* auct.) [1] is widely distributed in North America and Europe and also occurs in Japan, Australia and New Zealand. It contains norstictic acid and an additional compound which was tentatively identified as a fatty acid [2]. This compound was later examined by GC [3] and TLC; $R_f$ values of the compound, referred to as CS-1, in three standard solvent systems were published [4], and the presence of the compound in the lectotype of *C. polycarpoides* has recently been confirmed (Ahti, Personal Communication). In the present work, the compound was isolated from an Australian specimen of *Cladonia polycarpoides*; by analysis of the spectroscopic data, the compound was shown to have the nonadride structure, 8-butyl-7-pentylcyclonona-1,5-diene 1,2,5,6-tetracarboxylic dianhydride (1) [5, 6]. In view of the relationship with the nonadride, heveadride (2) isolated from *Helminthosporium hevea* [7], the name homoheveadride is suggested.

## RESULTS AND DISCUSSION

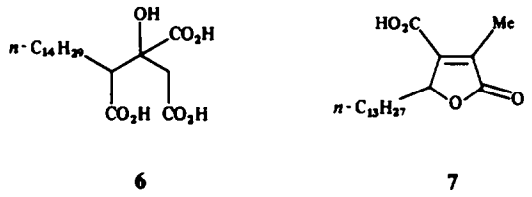
The molecular formula of homoheveadride was established as $C_{22}H_{28}O_6$ by high resolution mass spectrometry. The nonadride character of the substance was suggested by the high oxygen content and by the IR spectrum $\nu_{max}^{KBr}$ 1850, 1775 $cm^{-1}$ (anhydride). The arrangement of the alkyl groups shown in (1) followed from the mass spectral fragmentation pattern and the $^1H$ NMR spectra. The only strong peak (base peak) in the EIMS is at *m/z* 194 ($C_{11}H_{14}O_3$), an ion which can come from both



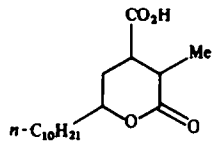
**1** $R^1$ = $n$-$C_5H_{11}$, $R^2$ = $n$-$C_4H_9$ homoheveadride
**2** $R^1$ = $n$-$C_3H_7$, $R^2$ = $C_2H_5$ heveadride



**3** **4** **5**



**6** **7**



**8**

halves of the molecule, as shown in (1). Subsequent fragmentation of this ion gives a number of ions at lower mass values, which were characterized by high resolution mass measurements; another pathway for fragmentation of the nine membered ring gives the ion at $m/z$ 264 ($C_{16}H_{24}O_3$); the conjugate fragment, after a hydrogen transfer, gives an ion at $m/z$ 125 ($C_6H_5O_3$). These results mainly parallel those reported for heveadride [7]. Any other substitution pattern in an isomeric structure would give rise to a number of other significant ion peaks from competing fragmentation pathways.

The $^1$H NMR spectrum (400 MHz) also can be interpreted in terms of (1). $H_A$-3, $H_A$-4 and $H_B$-3, $H_B$-4 give rise to an isolated, AA'BB' pattern at $\delta$3.15 and 2.20 (partly obscured) respectively; the remainder of the spectrum consists of one proton multiplets or in some instances overlapping multiplets upfield of $\delta$3.15, up to two three-proton triplets at $\delta$0.85 and 0.95. Thus *two* alkyl chains were present, and OCH groups were absent. By means of double irradiation experiments, 2D-COSY spectra, partially relaxed spectra, and $T_1$ measurements the chemical shifts of all the protons were assigned, both in the $C_4$ and $C_5$ side chains, and in the nonadiene ring. The data generally parallel, and extend those reported for heveadride [8]; but, unlike for that substance, ambient temperature spectra were satisfactory for interpretation. As with heveadride the stereochemistry at C-7 and C-8 has not been defined. The similarity of the optical rotation $[\alpha]_D$ +118° and a similar change to larger values at shorter wavelengths suggests that the stereochemistry of (1) is the same as that of (2).

Homoheveadride may be derived formally by the head-to-head concerted cycloaddition of two $C_{11}$ units, (3) and its derived anion (4) in an analogous fashion to that suggested for heveadride [7]. The $C_{11}$ precursor may be derived by decarboxylation–dehydration of the condensation product of octanoic acid (rather than hexanoic acid as in the case of heveadride) with oxaloacetic acid. That is, homoheveadride is another expression of the $C_n + C_4$ pathway, which has already been found to operate in lichens, producing acyclic acids such as caperatic acid (6), $\gamma$-lactonic acids such as lichesterinic acid (7) and $\delta$-lactonic acids such as acaranoic acid (8) [9]. The same precursors (3) and (4) give by alternative head-to-tail cycloaddition the hydroxylated byssochlamic acid homologue, scytalidin (5) [10].

Homoheveadride is the first cyclononadiene bisanhydride, or nonadride, to be isolated from a lichen; all other nonadrides have been isolated from various fungi [6].

## EXPERIMENTAL

Electron impact mass spectra (low and high resolution) were obtained with an A.E.I. MS902 mass spectrometer equipped with a DS30 data system. $^1$H NMR spectra (400 MHz) were measured in $CDCl_3$ on a Bruker WM-400 instrument [11].

*Isolation of homoheveadride.* The compound was extracted from squamules (0.2 g) of *Cladonia polycarpoides*, collected and identified by one of us (AWA). The squamules were examined under low power (× 20) magnification before extraction and appeared to be free of soil and extraneous fungal growth. A voucher specimen, Archer 1795A, has been deposited in the National Herbarium, Sydney (NSW). The compound was extracted with acetone and separated from the accompanying norstictic acid by preparative TLC on silica gel using mobile phase C [4]. The UV absorbing zone corresponding to the compound, $R_f$ 0.8, was removed from the plate and extracted with acetone. Evaporation of the acetone gave homoheveadride (0.005 g, 2.5%) homogeneous by TLC; the substance separated from MeOH as a gel. $[\alpha]_D^{20}$ +118° ($CH_2Cl_2$ *c* 0.5), $[\alpha]_{578}$ +124°, $[\alpha]_{546}$ +144°, $[\alpha]_{436}$ +279°, $[\alpha]_{365}$ +494°. (Found: M$^+$, 388.1825; calc. for $C_{22}H_{28}O_6$: M$^+$ 388.1886). $\nu_{max}^{KBr}$ 2960, 2920, 2860, 1850, 1780, 1450, 1260, 1180, 920, 885, 760 cm$^{-1}$; $\lambda_{max}^{MeOH}$ 217, 240 (sh) nm. $^1$H NMR: $\delta$0.85 [3H, *t*, *J* = 7 Hz, (H-5')$_3$], 0.95 [3H, *t*, *J* = 7 Hz, (H-4")$_3$], 1.03 (2H, *m*, $H_A$-2', $H_A$-1"), 1.12 (1H, *m*, $H_B$-2'), 1.23 [4H, *m*, (H-3')$_2$, (H-4')$_2$], 1.34 (2H, *m*, $H_A$-2", $H_A$-3"), 1.50 (3H, *m*, $H_A$-1', $H_B$-2", $H_B$-3"), 1.77 (1H, *t*, *J* = 12 Hz, $H_A$-9), 2.00 (1H, *m*, $H_B$-1"), 2.20 (4H, *m*, $H_A$-3, $H_A$-4, H-8, $H_B$-1'), 2.41 (1H, *quint*, *J* = 5 Hz, H-7), 2.85 (1H, *dd*, *J* = 12 Hz, 3 Hz, $H_B$-9), 3.15 (2H, *m*, $H_B$-3, $H_B$-4). $T_1$-values (s): (H-5')$_3$, 1.5; (H-4")$_3$, 1.3; (H-4')$_2$, (H-3')$_2$, 1.0; (H-3")$_2$, (H-2")$_2$, 0.7; H-7, 0.7; others, *ca* 0.4. MS *m/z*: 388 (4%), 342 (1), 264 (4), 194 (100), 176 (9), 166 (11), 151 (7), 149 (7), 138 (8), 125 (20), 121 (10), 93 (7), 91 (9), 83 (9), 79 (11), 69 (16), 55 (19), 43 (19), 41 (30). HRMS measurements. Found: 264.1678 (calc. for $C_{16}H_{24}O_3$: 264.1725); 194.0925 (calc. for $C_{11}H_{14}O_3$: 194.0943), 176.0825 (calc. for $C_{11}H_{12}O_2$: 176.0837); 166.0981 (calc. for $C_{10}H_{14}O_2$: 166.0994); 138.0670 (calc. for

$C_8H_{10}O_2$: 138.0681); 138.0309 (calc. for $C_7H_6O_3$: 138.0317); 125.0235 (calc. for $C_6H_5O_3$: 125.0239).

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# 4-AMINOPHYSCION, AN ANTHRAQUINONE DERIVATIVE FROM DERMOCYBE (*AGARICALES*)

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**Key Word Index**—*Dermocybe*; Cortinariaceae; anthraquinones; erythroglaucin; physcion; 4-aminophyscion (4-amino-1,8-dihydroxy-6-methoxy-3-methyl-9,10-anthraquinone).

**Abstract**—The anthraquinones physcion, erythroglaucin and 4-aminophyscion (4-amino-1,8-dihydroxy-6-methoxy-3-methyl-9,10-anthraquinone) have been isolated from the fungal species *Dermocybe canaria* Horak (ined.). 4-Aminophyscion is reported for the first time as a natural product and represents the first fungal anthraquinone with an amino group.

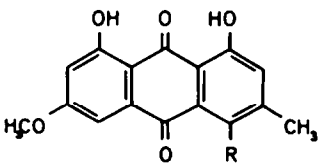
## INTRODUCTION

Anthraquinone derivatives occur in a great variety in species of the genus *Dermocybe* where they are responsible for the bright colours of the fruit bodies [1]. Since their occurrence and distribution has proved particularly useful in differentiating infrageneric taxa [2–4] we have examined anthraquinone pigments of *Dermocybe canaria* Horak (ined.), which is a bright yellow to orange coloured species reported from New Zealand.

## RESULTS AND DISCUSSION

Extraction of the dried carpophores of the fungus with methanol gave a deep red solution which was concentrated, diluted in hydrochloric acid and subsequently extracted with ethyl acetate to remove pigments from the aqueous phase. The anthraquinones **1** and **2** were separated by column chromatography. Compound **3** needed further isolation by preparative TLC.

The most abundant anthraquinone, yellow crystals, $C_{16}H_{12}O_5$, proved to be spectroscopically indistinguish-




1 R = H
2 R = OH
3 R = $NH_2$

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