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TWO DITHIACYCLOHEXADIENE POLYACETYLENES FROM *CHAENACTIS DOUGLASII* AND *ERIOPHYLLUM LANATUM*

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Key Word Index—*Chaenactis douglasii*; *Eriophyllum lanatum*; Compositae; disulfide; polyacetylene.

Abstract—We have isolated two dithiapolyacetylenes from the roots of *Chaenactis douglasii* and from the plant roots as well as root cultures of *Eriophyllum lanatum*, namely 1-(2-methylethyn)-4-(hex-1,3-diyn-4-ene)-2,3-dithiacyclohexa-4,6-diene, and 1-(4-methylbut-1,3-diyn)-4-(but-1-yn-3-ene)-2,3-dithiacyclohexa-4,6-diene. We propose the trivial names thiarubrine A and thiarubrine B for these compounds.

INTRODUCTION

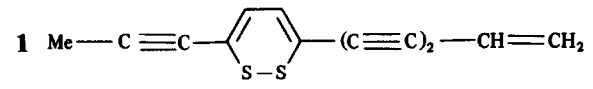
Dithiapolyacetylenes have been found in the roots of *Ambrosia eliator* L. and *Eriophyllum caespitosum* Dougl. [1] but there appears to be some doubt about the structures and the properties of these dithiacyclohexadienes, particularly with regards to their stabilities [1, 2]. We have now examined the methanolic extracts of roots of *Chaenactis douglassi* (Hook) H. & A. and root cultures of *Eriophyllum lanatum* (Pursh) Forbes [3] and isolated two dithiapolyacetylenes, thiarubrine A (1) and thiarubrine B (2), whose structural determination is described below.

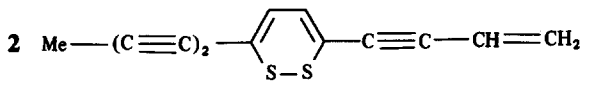
RESULTS AND DISCUSSION

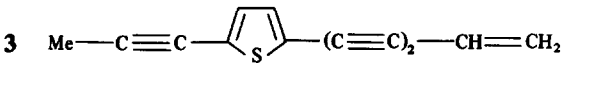
The two thiarubrines were readily separated on a reverse phase MCH-10 column thus providing a simple purification method. The mass spectral analyses showed a MW of 228 for each compound and distinctive fragmentation patterns which were characteristic of cyclic sulfur compounds [4]. The two ions $[M-109]^+$ $(H_2C{=}CH{-}C{\equiv}C)^+$ and $[M-145]^+$ $(Me{-}C{\equiv}C{-}C{-}S)^+$ showed that the major component from the roots of *C. douglasii* was thiarubrine A. The ions $[M-133]^+$ $(H_2C{=}CH{-}C{\equiv}C{-}C{-}S)^+$ and $[M-121]^+$ $(Me{-}(C{\equiv}C)_2{-}C{-}S)^+$ indicated that the major thiarubrine from *E. lanatum* was the B isomer. Both compounds gave high yields of the ions $[M-44]^+$ and $[M-45]^+$ suggesting close structural similarities with regards to the locations of the sulfur atoms. The results indicate the structures to be: A 1 and B 2.

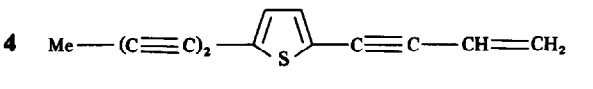
Although the compounds were stable in petrol to UV, irradiation in MeOH yielded two thiophenes as photoproducts (3 and 4), whose identities were confirmed by comparison of UV spectra with those of known compounds [5]. The yields of thiophenes (> 75%) from the thiarubrines indicate that the photo-induced reactions proceed without substantial carbon skeleton rearrangements. Both thiarubrines were stored in the dark for 2 months as a 1% solution in ethanol without loss of colour (490 nm) or changes in absorption spectra.

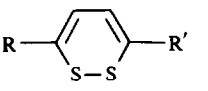
Bohlmann and Kleine [1] have suggested that the thiarubrines exist in equilibrium with their thioketone isomers (5). However, rotation around bond X

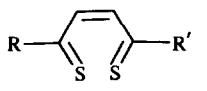


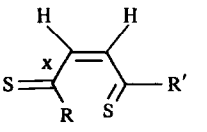












(thioketone form) would not result in sulfur orientation as depicted and a more likely orientation of the *cis*-form molecule would be as shown in **6**, where the S atoms are oriented in a more energetically favourable configuration [6]. The *trans*-form of the thioketone would not permit the formation of the –S–S– bond. The degree of reactivity of the cyclic dithiane ring is shown by the reaction of *n*-butyl mercaptide with 1,2-dithiacyclopentane. It is about 10^4 times faster than with its open chain analogue [7]; the explanation presented is that the large increase in rate results from the internal strain in the ring compound making it a highly reactive species. Consequently, since cyclopentyl and cyclohexyl dithiane ring systems are strained, it seems that a considerable energy input would be necessary for the thioketone system to rearrange to the dithiacyclohexadiene ring. It appears, therefore, that an equilibrium such as the one proposed [1] is highly unlikely. Further, the high degree of nucleophilic susceptibility of the dithiane ring suggests that it may be the reaction site for a number of biological reactions.

The ratio of thiarubrine A: thiarubrine B from the roots of *Chaenactis douglasii* is about 4:1 while that from the roots of *Eriophyllum lanatum* is about 1:4. The yields from the root cultures of *E. lanatum* are approximately the same as those from the plant roots thus making root cultures a suitable source of these compounds.

EXPERIMENTAL

Eriophyllum lanatum roots were cultured in SH medium [3] with 3% sucrose, 0.5 mg/l. NAA (α-naphthalene acetic acid) and a starting pH of 5.7. Roots were grown on a rotary shaker at 100 rpm in darkness at 25° in 3 l. Fernbach flasks containing 1.5 l. of medium. Flasks were inoculated with approximately 15 g of cultured roots and harvested 30 days later. Starting roots originated from stem explants cultured on medium as above, except that medium was solidified with 0.7% agar.

Roots (250 g) of *Chaenactis douglasii* or *Eriophyllum lanatum* were ground with 500 ml MeOH and after removal of the insoluble pulp by filtration, the solution was diluted with an equal vol. of H_2O and extracted 2 × with 1 l. portions of low bp petrol. The extracts were combined and dried ($MgSO_4$). The extract was then evapd to 500 ml and used as stock for subsequent purifications.

50 ml of the stock soln was reduced to 10 ml and applied to a silica gel-60 column (40 cm × 4 cm) which had been poured in petrol. The column, after the sample application, was eluted with low bp petrol (400 ml) and then with petrol containing 5% Et_2O. The thiarubrines were eluted between 500 and 600 ml; they had λ_{max} at 490 and 345 nm.

HPLC was carried out on a Varian 5000 instrument equipped with a MCH-10 reverse phase column operating isocratically with a solvent mixture of acetonitrile–H_2O (18:7). With a detector setting of 345 nm, the red compounds accounted for 91–92% of the material in the silica gel column fraction. The thiarubrines represented all of the absorbing material with the detector set at 490 nm. Yields from plants and from root cultures were approximately 1.0 mg/g fr. wt of combined thiarubrines.

The two compounds were collected by repeated HPLC, pooled, diluted with H_2O and extracted with petrol. The extract was dried and dissolved in absolute EtOH (λ_{max} 490, 345, 233 nm) (thiarubrine A); (λ_{max} 490, 345, 243 nm) (thiarubrine B). MS analyses were made on a Finnigan model 1020 GC MS equipped with a Finnigan 1020 data system. CIMS (70 eV) of the two thiarubrines yielded distinctive fragmentation patterns. The molecular ion in both cases indicated MWs of 228. Thiarubrine A: *m/z* (rel. int.): 228 $[M]^+$ (100), 83 $[M-145]^+$ (25), 119 $[M-109]^+$ (13), 183 $[M-45]^+$ (20), 184 $[M-44]^+$ (49). Thiarubrine B: *m/z* (rel. int.) 228 $[M]^+$ (100), 95 $[M-133]^+$ (20), 107 $[M-121]^+$ (13), 183 $[M-45]^+$ (16), 184 $[M-44]^+$ (35). The IR spectrum of thiarubrine A was done in CCl_4: significant peaks were Me–C≡C–, 1380 cm^{-1}; R–CH=CH_2, 980 cm^{-1}; –C–S–, 1244, 528 cm^{-1}.

The major component in each mixture of the thiarubrines was dissolved in MeOH and irradiated with UV-A (365 nm) for 30 min at a distance of 4 cm. After this period of exposure, most of the colour had disappeared from the soln. Solns irradiated in petrol did not lose their colour.

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