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A NEW CLERODANE-TYPE BUTENOLIDE DITERPENE FROM  
THE BARK OF *POLYALTHIA LONGIFOLIA*

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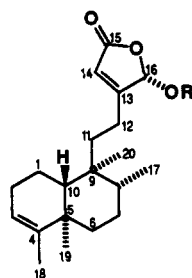
**ABSTRACT.**—A new  $\gamma$ -methoxybutenolide clerodane diterpene **2** has been isolated from the petroleum ether extract of the bark of *Polyalthia longifolia*. Its structure has been deduced by spectral analyses and by chemical correlation with the corresponding  $\gamma$ -hydroxybutenolide diterpene **1**, isolated earlier from this plant.

The plant *Polyalthia longifolia* Thw. (Annonaceae), locally known as "Dev-daru," is one of the 120 species constituting the genus *Polyalthia*. The bark has been used as a febrifuge in Indian folk medicine, and its aqueous extract is reported to be hypotensive in experimental animals (1). Earlier investigations on this plant have resulted in the isolation of a variety of compounds (2–10). In the course of our studies on the chemical constituents of Indian medicinal plants we have recently reported (11) the isolation of a new azafluorenone alkaloid, 6,7-dimethoxyonychine, from its bark. The same alkaloid has subsequently been described (12) again as a new natural product, designated polyfonthine, from the same plant and part but of Chinese origin. The name 6,7-dimethoxyonychine should be retained in preference to polyfonthine, since it was the first name assigned. We record herein our isolation of a new clerodane diterpene from the bark of *P. longifolia* collected locally.

Repeated cc of the petroleum ether extract of the bark furnished the new diterpene as a colorless oil which analyzed for  $C_{21}H_{32}O_3$ ,  $[M]^+$  332. The uv, ir,  $^1H$ -nmr,  $^{13}C$ -nmr, and mass spectral data of this compound were very similar to those observed for the  $\gamma$ -hydroxybutenolide clerodane diterpene **1**, isolated earlier from the leaves (8) and bark (9) of this plant, except for the following diagnostic features: (a) its ir spectrum lacked the hydroxyl absorption, (b) the  $^1H$ -nmr spectrum recorded an addi-

tional signal at  $\delta$  3.56 (3H, s), attributable to an aliphatic methoxyl, (c) the dioxygenated carbon resonance occurred further downfield by 5 ppm in the  $^{13}C$  nmr spectrum which also recorded the new methoxyl signal at  $\delta$  56.58 (q), and (d) in the eims the molecular ion peak was recorded at 14 mu higher. These observations, coupled with the appearance in its ms of the peak at  $m/z$  191 and peaks corresponding to the fragments arising out of it, strongly suggested the same A/B ring structures for both the diterpenes and indicated that this metabolite was the  $\gamma$ -methyl ether, i.e., the  $\gamma$ -methoxybutenolide **2**. To confirm the identity, the  $\gamma$ -hydroxybutenolide **1** was methylated (*p*-TsOH, MeOH, reflux) and purified by rapid cc to give a product which was found to be identical (co-tlc and superimposable ir spectra) with the new natural product, thus defining its total stereostructure as 16 $\alpha$ -methoxycleroda-3,13*Z*-dien-16,15-olide [**2**].

In the course of our structural assignment of the 16 $\alpha$ -hydroxy compound **1**,



- 1** R = H  
**2** R = Me

a definitive assignment of all the carbon resonances was made (9) by detailed  $^{13}\text{C}$ -nmr studies including XHCORR experiments. These studies necessitated the revision of  $^{13}\text{C}$ -nmr values for five carbons, C-6, C-7, C-18, C-19, and C-20, from those previously assigned (8). By analogy with these revised data the final  $^{13}\text{C}$  assignments of **2** have been shown here. Because the  $^{13}\text{C}$ -nmr values of C-13, C-14, and C-15 of the methoxy derivative showed excellent similarity to those reported for the  $\gamma$ -hydroxybutenolide **1** whose  $16S$  configuration (i.e.,  $16\alpha\text{-OH}$ ) had earlier been established (8) by an X-ray crystallographic analysis of the derived acetate, we infer the  $16S$  configuration for the methoxy compound as well. The only observation for which no reasonable explanation could be put forward is that the H-3 appeared somewhat downfield compared to the values reported for the same proton in related diterpenes. To our knowledge, this is the second report of the isolation of a  $\gamma$ -methoxybutenolide diterpene from a natural source, the earlier one being that of a labdane derivative from the aerial parts of *Conyza stricta* Willd. (13).

## EXPERIMENTAL

**GENERAL EXPERIMENTAL PROCEDURES.**—Mp's were determined in open capillaries in a Toshniwal apparatus and are uncorrected. Uv and ir spectra were recorded on Shimadzu UV-160 and Shimadzu IR-408 spectrophotometers, respectively.  $^1\text{H}$ -nmr (100 MHz) and  $^{13}\text{C}$ -nmr (25 MHz, multiplicities determined by INEPT experiment) spectra were recorded in  $\text{CDCl}_3$  with TMS as internal standard on a JEOL FX-100 spectrometer. Eims (70 eV) was recorded on a Hitachi RMU-6L mass spectrometer using a direct inlet system. Optical rotation was measured in MeOH on a Perkin-Elmer 241 polarimeter. Cc was performed on Si gel (Qualigens, 60–120 mesh) and tlc on Si gel G (E. Merck, India). Petroleum ether used had bp 60–80°. Elemental analyses were performed at the Microanalytical Laboratory of the University College of Science, Calcutta.

**PLANT MATERIAL.**—The bark of *P. longifolia* was collected locally from Calcutta in July 1987. A voucher specimen has been preserved in the Chemistry Department of Bose Institute.

**EXTRACTION AND ISOLATION.**—The dried,

milled bark (3 kg) was extracted in a Soxhlet apparatus with petroleum ether. The residue obtained from the petroleum ether extract was subjected to cc. The early petroleum ether-EtOAc (9:1) eluates contained the crude diterpene. A second cc and elution with petroleum ether-EtOAc (19:1) furnished the diterpene **2** in 0.004% yield (122 mg).

**$\gamma$ -Methoxybutenolide 2.**—Colorless, viscous material,  $[\alpha]_D -48.8^\circ$  ( $c=0.114$ , MeOH); uv (MeOH)  $\lambda_{\text{max}}$  214 nm; ir ( $\text{CCl}_4$ ) 1797, 1768, 1645, 1455, 1370, 1205, 1120, 970, 895  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (100 MHz,  $\text{CDCl}_3$ )  $\delta$  5.88 (1H, s, H-16), 5.76 (1H, s, H-14), 5.64 (1H, br s, H-3), 3.57 (3H, s, OMe), 2.62–2.0 (4H, m), 1.89 (3H, d,  $J=1.5$  Hz, H<sub>3</sub>-18), 1.8–1.28 (10H, m), 1.13 (3H, s, H<sub>3</sub>-19), 0.87 (3H, s, H<sub>3</sub>-20), 0.84 (3H, d,  $J=5$  Hz, H<sub>3</sub>-17);  $^{13}\text{C}$  nmr (25 MHz,  $\text{CDCl}_3$ )  $\delta$  170.40, 168.26, 144.16, 38.56 and 38.03 (all s, C-15, -13, -4, and -5/-9, respectively), 120.17, 117.54, 104.20, 46.40 and 36.28 (all d, C-3, -14, -16, -10, and -8, respectively), 36.63, 34.70, 27.27, 26.68, 21.19, and 18.20 (all t, C-12, -6, -7, -11, -2, and -1, respectively), 56.58 (q, OMe), 19.78, 17.97, 17.79, and 15.75 (all q, C-19, -18, -20, and -17, respectively); eims  $m/z$  (rel. int.) 332 (10), 317 (14), 300 (19), 285 (81), 191 (85), 190 (92), 189 (100), 175 (38), 135 (56), 123 (65), 121 (74), 107 (81), 95 (76). *Anal.* found C 76.01, H 9.55; calcd for  $\text{C}_{21}\text{H}_{32}\text{O}_3$ , C 75.90, H 9.64%.

**Methylation of 1.**—A solution of  $\gamma$ -hydroxybutenolide diterpene **1** (230 mg) in MeOH (30 ml) containing a catalytic amount of *p*-TsOH was refluxed for 1 h, when tlc indicated complete consumption of the starting material. MeOH was then boiled off from the solution, maintaining its original volume by frequent addition of  $\text{H}_2\text{O}$ . It was then further diluted with  $\text{H}_2\text{O}$  (20 ml), basified with  $\text{NaHCO}_3$ , and extracted with  $\text{CHCl}_3$  (4  $\times$  50 ml). The  $\text{CHCl}_3$  extract was washed with  $\text{H}_2\text{O}$ , dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated, and the residue was purified by rapid cc. The methyl ether was obtained from the petroleum ether-EtOAc (19:1) eluates in 65% yield. It proved to be identical with the natural compound by co-tlc [petroleum ether-EtOAc (3:2), visualizer  $\text{I}_2$  vapor,  $R_f$  0.6 and 0.4 for **2** and **1**, respectively] and superimposable ir spectra.

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