Lycoxanthol, a Hydroquinone Diterpenoid from *Lycopodium lucidulum* Michx.

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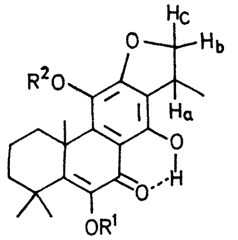
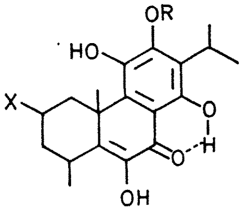
Summary Structure (I) is suggested for a yellow hydroquinone diterpenoid obtained from *Lycopodium lucidulum.*

WHILE examining the non-alkaloidal constituents of *L. lucidulum* we encountered a previously unknown bright yellow pigment, m.p. 249° which for convenience we called lycoxanthol and for which we suggest the structure (I). This represents the first reported occurrence of this type of diterpenoid in any Lycopodium species.

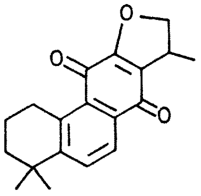
The bewildering array of physical data obtained for lycoxanthol, $C_{20}H_{24}O_5$ (anal., and M^+ 344·1634 *m/e*), became meaningful after recognition of the complex chromophore λ_{max} (EtOH) 265 (ϵ 12,250), 288 (8600) 334 (6100), and 385 (8600) nm as being virtually identical with that of certain coleon B derivatives[1] such as (II) (λ_{max} 262, 285, 333, and 390 nm) and (III) (λ_{max} 263, 284, 326, and 383 nm). The i.r. spectrum showed the presence of more than one hydroxy-group (3490 and 3320 cm^{-1}) and one of these is favourably placed to chelate strongly with a carbonyl group (1640 cm^{-1}). Acetylation of lycoxanthol (I) afforded a diacetyl derivative (IV) (M^+ 428 *m/e* and i.r. 1770 and 1205 cm^{-1}) and methylation by methyl iodide (K_2CO_3 in acetone) gave successively a mono-methyl (V), a di-methyl (VI), and with difficulty a tri-methyl ether (after 2, 8, and 30 h, respectively). Other than signals from the introduced acetyl and *O*-methyl groups, the n.m.r. spectra of lycoxanthol and the derivatives all showed a combination of three one-proton patterns at δ 3·76 (m. J 6, 7, and 9 Hz), 4·27 (d. of d. J 6 and 9 Hz), and 4·74 (t. J 9 Hz) corresponding to the protons of the dihydrofuran moiety (protons H_a, H_b, and H_c in structure I, resp.). Decoupling experiments confirmed this sequence and showed H_a to be coupled to the secondary methyl group (d. δ 1·39, J 7 Hz). These values compare favourably with those given for isocryptotanshinone (VII).[2]



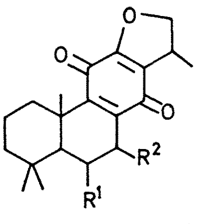
(I) $R^1 = R^2 = H$
(IV) $R^1 = R^2 = Ac$
(V) $R^1 = Me$, $R^2 = H$
(VI) $R^1 = R^2 = Me$



(II) R = H, X = OH
(III) R = H, X = H



(VII)



(VIII) $R^1 = O$, $R^2 = OH$
(IX) $R^1 = R^2 = H$

In the n.m.r. of lycoxanthol (I) in C_5D_5N apart from secondary methyl at δ 1·34, three methyl singlets were evident at δ 1·60, 1·62, and 1·89 and these correspond well to the *gem*-dimethyl and the angular methyl groups in the environments shown in structure (I). The impossibility of placing other substituents within the chromophore, the necessity of closing the ring, and biogenetic considerations leave no choice but to constitute ring A as shown. The mass spectrum of lycoxanthol reflects the stability of the conjugated system within the molecule in that the two major fragments are shown by precise mass determination to be $C_{15}H_{14}O_5$ (274·0860 *m/e*) and $C_{14}H_{14}O_5$ (262·0844 *m/e*) in which all five atoms of oxygen are retained.

Two *p*-quinonoid derivatives arose unexpectedly during the early stages of this work on lycoxanthol. The first, $C_{20}H_{24}O_5$ (344·1622 *m/e*) seems to arise by thermally initiated prototropy in the presence of silica gel, is compatible with structure (VIII). The other, $C_{20}H_{26}O_3$ (314·1880 *m/e*) is an aerial oxidation product of the colourless hydroquinone obtained by hydrogenation and hydrogenolysis of lycoxanthol. We suggest structure (IX) for this product which we hope to confirm shortly by synthesis.

We thank the National Research Council of Canada for operating and equipment grants.

(*Received, May 28th*, 1971; *Com.* 872.)

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[1] D. Karanatsios and C. H. Eugster, *Helv. Chim. Acta*, 1965, **48**, 471. M. Ribi, A. Chang Sin-Ren, H. P. Küng, and C. H. Eugster *Helv. Chim. Acta*, 1969, **52**, 1685.

[2] H. Kakisawa, T. Hayashi, and T. Yamazaki, *Tetrahedron Letters*, 1969, 301.