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THE STRUCTURE OF LYCOXANTHIN AND LYCOPHYLL

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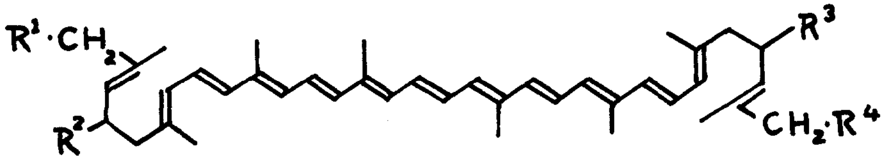
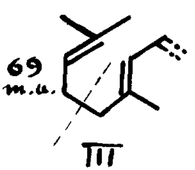
Lycoxanthin and lycophyll were first isolated from the berries of Solanum dulcamara by Zechmeister and Cholnoky (1) in 1936. The structures (I, II) were proposed from analytical data and by analogy with other phytoxanthins. The correctness of these formulae has been accepted in recent times by Goodwin, Land and Sissins (2) and by S.L. Jensen (3) in the course of comparison of lycoxanthin with rhodopin. However, although the assumed structures are in good agreement with much chemical evidence they have never been proved completely.

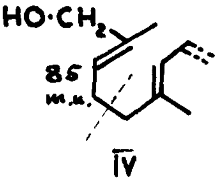
The molecular formulae for lycoxanthin ($C_{40}H_{56}O$) and lycophyll ($C_{40}H_{56}O_2$) have been confirmed by high resolution mass spectroscopy (552.4342 and 568.4283 respectively). The presence of hydroxyl groups (4) (ν_{max} $[CHCl_3]$ 3615 and 1008 cm^{-1}) and the aliphatic undecaene chromophore (λ_{max} $[C_6H_6]$ 521, 487 and 458 mμ; $10^{-3}\epsilon$ 141.8, 162.7 and 108.8, respectively) follow from the light absorption properties. The mass spectral studies confirm the number of hydroxyl groups in lycoxanthin (M^+-18) and lycophyll (M^+-18 and M^+-18-18 fragments). In lycoxanthin fragments at m/e 483 (M^+-69) and m/e 467 (M^+-85) indicate that one of the end groups is substituted with a hydroxyl group in the 1- or 3-position while the other (III) is unsubstituted. In the mass spectrum of lycophyll only the fragment at m/e 483 (M^+-85) appears.



	R¹	R²	R³	R⁴
I	H	OH	H	H
II	H	OH	OH	H
V	OH	H	H	H
VI	OH	H	H	OH



III



IV

The facts that lycoxanthin and lycophyll on oxidation with acetone according to the method of Oppenauer yield products with no shifts of λ_{max} compared with the starting materials, and that dehydro derivatives are not formed on treatment with ca. 0.01% chloroformic hydrogen chloride (5,6) show there are no hydroxyl groups in the positions allylic to the chromophore. But upon treatment with hydrogen chloride in chloroform under more drastic conditions 3,4-dehydrolycopene (λ_{max} $[C_6H_6]$ 547, 507 and 482 mμ) is obtained from lycoxanthin, and 3,4,3',4'-bis-dehydrolycopene (λ_{max} $[C_6H_6]$ 572, 533 and 495 mμ) from lycophyll. These dehydrolycopenes establish the carbon skeleton for both pigments and suggest the 3- and 3,3'-positions for the hydroxyl groups respectively, provided that no allylic rearrangement occurs on dehydration.

The proton magnetic resonance spectrum of lycoxanthin ($CDCl_3$) shows apart from olefinic protons, signals at: 8.39 (3H), 8.32 (6H), 8.19 (6H), 8.04 (12H), 7 86 (8H, complex), 6.00 (2H, doublet)τ . The 6.00τ doublet collapses to a singlet on shaking with D_2O and together with the 8.39τ singlet defines the group $:C(CH_3).CH_2OH$. The hydroxylated end group in lycoxanthin and by analogy both end groups in lycophyll* have the structure (IV).

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* Dr. P.M. Scopes (personal communication) has found no significant optical rotation at any observable wavelength for this compound.

The structures (V and VI) now proposed for lycoxanthin and lycophyll may be compared with that proposed by Jensen (7) for the C_{50}-carotenoid, dehydrogenans - P.439, which contains similar primary alcoholic end groups.

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