Structure of a Lichen Pigment Entothein and Its Identity with Secalonic Acid A, a Major Ergot Pigment

In the previous paper,¹⁾ we disclosed the triterpenic component of a lichen *Parmelia entotheiochroa* HUE. along with the existence of atranorin (depside) and a yellow pigment named entothein.²⁾ As a continuation of the chemical investigation on the lichen substances, we have been engaged in the structural study of entothein and have reached a conclusion as shown in the present communication that entothein is identical with secalonic acid A^{3,4)} (I), one of the major components of the ergot pigments. The finding revealed here seems to provide an insight of interest on the chemotaxonomical correlation between ergot and a fungus symbiotic in the above mentioned lichen.

Entothein (I) (isolated in 0.72% yield from the air dried lichen), C₃₂H₃₀O₁₄⁵⁾ (mass spectrum m/e : 638 (M⁺), 579 (base peak, M⁺-COOCH₃), mp 260° (yellow plates from CHCl₃-EtOH), $[\alpha]_D -73^\circ$ (CHCl₃), ultraviolet (UV) spectrum $\lambda_{\max}^{\text{EtOH}}$ mμ (log ε): 266 (sh.) (4.28), 340 (4.58); $\lambda_{\max}^{\text{EtOH-KOH}}$: 253 (4.42), 357 (4.55), infrared (IR) spectrum $\nu_{\max}^{\text{KBr}}$ cm⁻¹: 3480 (br., hydroxyl), 1742, 1726 (m.), 1608 (carbonyls), 1588, 1560 (benzene ring), nuclear magnetic resonance (NMR) spectrum (DMSO-d₆) τ : 8.90 (6H, d.-like, >CHCH₃×2), 7.9—7.2 (6H), 6.39 (6H, s., -COOCH₃×2), 6.4—6.0 (2H, >CHOH×2), 4.05 (2H, d., $J=5$ cps, >CHOH×2), 3.38, 2.55 (2H, each, ABq., $J=8$, aromatic *ortho* protons×2), -1.58 (2H, s., OH×2), exhibited red brown by FeCl₃, negative to Gibbs test and furnished a diacetate (II) (by *p*-toluenesulfonic acid and acetic anhydride treatment), C₃₂H₂₈O₁₂(OCOCH₃)₂, mp 245° (yellow plates from CHCl₃-MeOH), $[\alpha]_D -130^\circ$ (CHCl₃), positive (brown) to FeCl₃, UV $\lambda_{\max}^{\text{EtOH}}$: 267 (4.26), 337.3 (4.60), IR (KBr): 1760 (acetyl) 1745 (ester), 1620 (chelated ketone), 1615, 1592, 1565 (benzene ring), NMR (CDCl₃): 8.97 (6H, d., $J=5$, >CHCH₃×2), 7.86 (6H, s., -OAc×2), 7.7—7.1 (6H), 6.32 (6H, s., -COOCH₃×2), 4.65 (2H, d., $J=11$, >CHOAc×2), 3.52, 2.61 (2H, each, ABq., $J=8$, aromatic *ortho* protons×2), -1.53, -3.77 (2H each, s., -OH×4). On treatment with Ac₂O and NaOAc at reflux, entothein afforded an optically inactive acetate (=Y-Ac-E) (III), C₄₄H₃₈O₁₈, mp 208—209°, UV $\lambda_{\max}^{\text{EtOH}}$: 245.5 (4.96), 251 (5.01), 256.7 (5.01), 262 (4.87), 295 (4.11), IR (KBr): 1775 (acetyl), 1733, 1723 (ester), 1675 (conjugated ketone), 1610, 1595 (benzene ring), NMR (CDCl₃): 8.20, 8.09, 8.01 (6H each, all singlets totally six acetyls), 7.58 (6H, s., =C-CH₃×2), 6.32 (6H, s., -COOCH₃×2), 2.94, 2.55 (2H each, ABq., $J=8$, aromatic *ortho* protons×2), 2.85, 2.45 (2H each, br.s., aromatic meta protons×2), while on thermal decomposition (at 280°, 3 Torr) it yielded a benzoate derivative, mp 91—92°, UV $\lambda_{\max}^{\text{EtOH}}$: 245 (3.86), 304 (3.49), IR (KBr): 3420 (hydroxyl), 1697 (ester), 1618, 1597 (benzene ring), NMR (CDCl₃): 7.66 (3H, s., aromatic CH₃), 6.10 (3H, s., -COOCH₃), 3.97 (1H, s., -OH), 3.13 (1H, s.), 2.61 (2H, br.s) (aromatic protons), mass: M⁺ 166 (52.5%), 135 (base peak), 107 (44%), 77 (24.2%), whose physical properties are in good accord with methyl 3-hydroxy-5-methylbenzoate.^{3,4)} Y-Ac-E, on treatment with either collidine or pyridine at reflux gave

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- 2) Y. Asahina, "Lichens of Japan," Vol. II, Genus *Parmelia*, Res. Inst. for Natural Resources, Tokyo, 1952, p. 76.
- 3) B. Franck, E.M. Gottschalk, U. Ohnsorge, and F. Hüper, *Chem. Ber.*, **99**, 3842 (1966).
- 4) J.W. ApSimon, J.A. Corran, N.G. Creasey, W. Marlow, W.B. Whalley, and K.Y. Sim, *J. Chem. Soc.*, **1965**, 4144.
- 5) All the compounds given with the chemical formulae gave satisfactory analytical values. IR spectra were taken by the Hitachi EPI-G2 Grating Infrared Spectrometer and NMR spectra were measured at 100 Mc.

deep yellow grain crystals,⁶⁾ mp $>300^\circ$ (FeCl₃: green, conc. H₂SO₄: deep yellow with orange-green fluorescence), mass m/e : 566 (M⁺), UV $\lambda_{\text{max}}^{\text{EtOH}}$ 232 (4.52), 269.5 (4.60), 288.5 (sh) (4.52), 376 (4.04), IR (KBr): 1728 (ester), 1640 (conjugated ketone), 1610, 1580 (benzene ring).

The foregoing chemical and physical properties of entothien and its derivatives, in particular indicative of dimeric character based on their NMR spectra have led us to assume its identity with secalononic acid A or its related pigments³⁾ and furthermore to expect the identity of Y-Ac-E with a bis-benzophenone derivative (III) (previously described by Whalley, *et al.*⁴⁾ In fact, the direct comparisons (mixed mp, $[\alpha]_D$, IR, UV, TLC) of entothien with secalononic acid A performed kindly by prof. B. Franck and in this laboratory, and also of Y-Ac-E with III kindly done by Prof. W.B. Whalley have proved the correctness of the above assumption. Accordingly, the name of entothien hereafter must be replaced by secalononic acid A.

Chart 1

As has been revealed³⁾ in case of ergot pigments, the present lichen also contains some other minor yellow coloring substances which are currently under study in this laboratory.

In addition, three related lichens, *P. perisidians* Nyl., *P. aurulenta* Tuck. and *P. subaurulenta* Nyl. have been found to contain secalononic acid A in respective yields of 0.36, 0.005 and 0.17%.

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6) Although the compound exhibited single spot on TLC, as revealed by its NMR spectrum (CDCl₃): 7.60, 7.52, 7.50 (each singlet totally 6H, =C-CH₃ × 2), 6.06, 6.04 (each singlet totally 6H, -COOCH₃ × 2), 3.3—2.2 (8H, aromatic protons), -2.44, -2.66, -2.72 (each singlet totally 2H, -OH × 2), it appears to be a mixture of three bis-xanthone derivatives tentatively formulated as 1-hydroxy-6-methyl-8-carbomethoxy-xanthenes dimeric at 2,2'; 2,4' and 4,4', whose further elucidation is in progress.