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MOULD METABOLITES—V

THE CONSTITUTION OF ERGOXANTHIN

D. J. ABERHART and P. DE MAYO
Department of Chemistry, University of Western Ontario, London, Canada

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Abstract—Ergoxanthin has been shown to have the gross structure of a lactonized seco-ergochrysin (IV).

THE isolation and constitution of a number of ergot pigments derived from a Portuguese ergot drug has recently been reported.[1] These chemical studies complemented the X-ray studies of Sim on ergoflavin (I)[2] and the chemical studies of Whalley *et al.*[3] Simultaneously with our publication, Whalley *et al.* published further work on other ergot pigments, with a general exchange of information, both groups having reached similar conclusions.[4] From this work the structures (II) and (III) were ascribed to the secalonic acids and the ergochrysins. The evidence available as to the stereochemistry of the various substances ascribed structures (II) and (III), was uncertain, and is irrelevant to the present issue.

Also contemporaneously with the above studies Franck *et al.* have provided independent evidence in favour of structures II and III, and have presented structural proposals for some other ergot pigments.[5]

Of the six pigments originally isolated,[1] aside from stereochemistry and the nature of the biphenyl junction, structures were ascribed to four in addition to that of the known ergoflavin. The remaining pigment possessed spectroscopic features which indicated that it was not, as were the remainder, composed of ergoflavin or secalonic units. It was termed ergoxanthin and was briefly characterized.*

The best analysis for ergoxanthin indicated the empirical formula $C_{31}H_{28}O_{14}\cdot H_2O$ and the mol. wt. was confirmed mass spectrometrically. The presence of a single methoxyl group was indicated in the NMR spectrum (Fig. 1) and confirmed by analysis.

* As already mentioned[1] the substance in the older literature termed 'ergoxanthin' is characterized so inadequately as to be unrecognizable. Since it was also most probably inhomogeneous the term has been appropriated for the present substance.

[1] D. J. Aberhart, Y. S. Chen, P. de Mayo and J. B. Stothers, *Tetrahedron* **21**, 1417 (1965).
[2] J. D. M. Asher, A. T. McPhail, J. M. Robertson, J. V. Silverton and G. A. Sim, *Proc. Chem. Soc.* 210 (1963).
[3] J. W. ApSimon, J. A. Corran, N. G. Creasey, K. Y. Sim and W. B. Whalley, *Proc. Chem. Soc.* 209 (1963).
[4] J. W. ApSimon, J. A. Corran, N. G. Creasey, K. Y. Sim and W. B. Whalley, *J. Chem. Soc.* 4130, 4144 (1965).
[5] B. Franck, O. W. Thiele and T. Reschke, *Chem. Ber.* **95**, 1328 (1962); B. Franck and E. M. Gottschalk, *Angew. Chem.* **76**, 438 (1964); B. Franck, G. Baumann, and U. Ohnsorge, *Tetrahedron Letters* 2031 (1965).

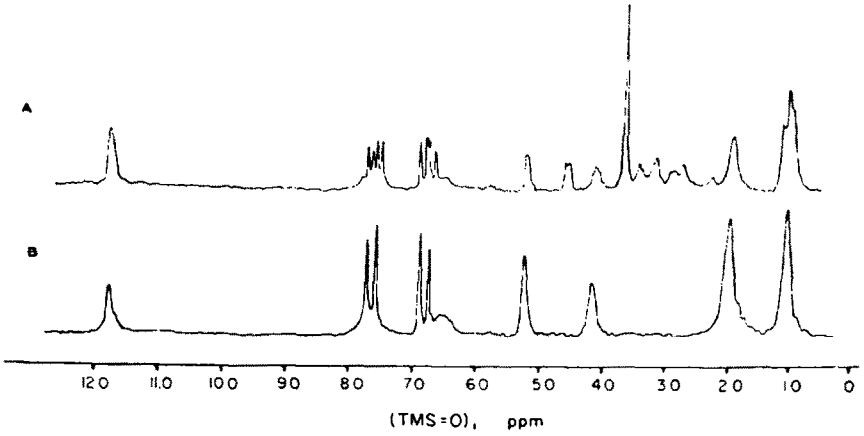


FIG. 1. NMR spectra of Ergoxanthin and Ergoflavin: A—Ergoxanthin; B—Ergoflavin.

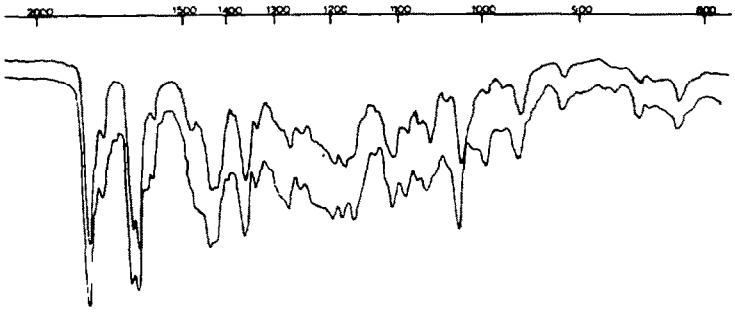


FIG. 2. IR spectra of Ergoxanthin and ψ-Ergoxanthin: Upper—Ergoxanthin; Lower—ψ-Ergoxanthin.

The presence of a strong band in the IR spectrum at 1793 cm^{-1} suggested the presence of a γ-lactone grouping as found, for instance, in ergoflavin (Fig. 2). In fact the comparison of absorption in that region with that of ergoflavin appeared to require the presence of *two* γ-lactonic functions in the ergoxanthin molecule. In addition there could be discerned comparatively weak absorption at 1739 cm^{-1} compatible, for instance, with presence of an ester or cyclopentanone.

Comparison of the NMR spectrum of ergoxanthin with that of ergoflavin indicated quite clearly (Fig. 1) the presence, in this substance, of an ergoflavin unit. This was confirmed by the appropriate decoupling by double irradiation.[1] The gross structural problem was, therefore, entirely concerned with the nature of the second unit.

The UV spectrum of ergoxanthin was closely similar to that of ergoflavin. Degradation with alkali under mild conditions[1] and redetermination of the spectrum both in acidic and alkaline solution (Table 1) also showed a parallel between the behaviour of ergoflavin and ergoxanthin. These results excluded the presence of a β-diketonic system, a fact already signalled by the green ferric chloride colour given by ergoxanthin: the β-diketones in the secalonic systems give a brown colour.

Ergoxanthin gave, under mild conditions,[1] a tetraacetate. Its IR and UV spectra (Table 2) were very similar to those of ergoflavin hexaacetate. Of these four acetyl functions, three must be attributed to the ergoflavin unit. The "xanthin" unit therefore

contains but one acylable hydroxyl group. Since the unit contains seven oxygen atoms this, together with the presumed lactones, leaves two presently unaccounted for if the ubiquitous γ-pyrone unit is also present.

On standing with diazomethane in ethereal solution for 24 hr ergoxanthin gave a trimethyl ether very similar in properties to ergoflavin tetramethyl ether (Table 2). Again, one hydroxyl function must be ascribed to the "xanthin" unit, which, in view of its reaction with diazomethane, must be acidic. The trimethyl ether could be acetylated under mild conditions to form a trimethyl ether monoacetate, which exhibited no hydroxyl absorption in the IR spectrum.

Ergoxanthin is stable to acid, but after 6 days refluxing with ethanolic hydrochloric acid, aside from 51% recovered starting material there is present also 34% of an acid (described below) and 15% of a substance which appeared to correspond in all properties with ergoxanthin except in that an ethoxyl group had replaced a methoxyl function. Under identical conditions ergoflavin was unchanged.

The acid referred to above was obtained more simply by the following method. Dissolution of ergoxanthin in 0·1N NaOH at room temperature and standing overnight gave acidic material. This material on heating with acetic acid under reflux then gave this same acid. Brief treatment with diazomethane regenerated ergoxanthin.

It thus appeared that ergoxanthin was a methyl ester. The behaviour of this substance under acidic condition then became readily explicable as ester interchange, and furthermore the recognition of the carboxyl ester function accounted for the remaining two oxygen atoms.

Before proceeding to discuss the NMR data two chemical observations must be presented which are significant in that the behaviour observed is not paralleled in the chemistry of ergoflavin. This behaviour was particularly informative as to the nature of the "xanthin" unit.

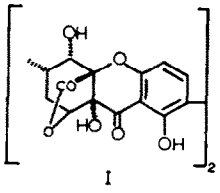
First, whilst acetylation under mild conditions gave, as described,[1] a tetraacetate in which no hydroxyl group could be discerned, heating ergoxanthin with acetic anhydride and pyridine for 15 hr gave a pentaacetate. This acetylation was accompanied by a significant change in the UV spectrum (an increase in extinction of about 10,000 near 243 mμ) implying some association of the acetate introduced last with the main chromophore.

The fifth acetate introduced was also shown to be of a different nature from the other four by its behaviour when exposed to acid. Under mild conditions specific hydrolysis took place with regeneration of the tetraacetate. Alkaline hydrolysis of the tetraacetate led to the formation of the acid, which could be methylated to regenerate ergoxanthin.

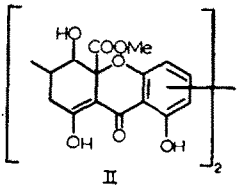
Secondly, and again in contrast with ergoflavin, under forcing conditions ergoxanthin gave a 2,4-dinitrophenylhydrazone. That this was not a hydrazide was indicated by the continued presence of the methoxyl group, and the study of the IR spectrum (carbonyl region) and UV spectrum and a comparison of these with those of model compounds.

The chemical evidence here presented is compatible with the structure (IV), and it is the purpose of the remainder of this discussion to indicate that this is not only compatible, but required by the evidence accrued from the NMR studies. The evidence for the ketonic ring will first be considered.

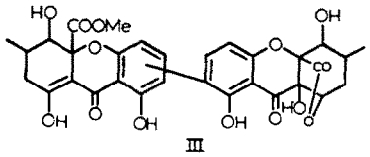
The general similarity in the IR spectrum, and the near identity of the UV spectrum



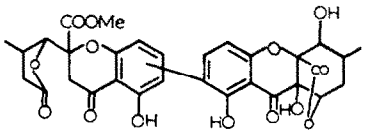
I



II

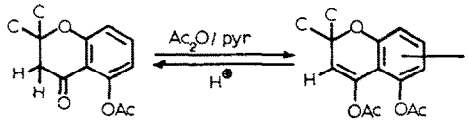


III



IV

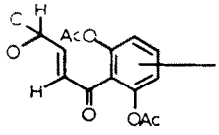
strongly suggested that the chromophores in the ergoflavin moiety and the "xanthin" moiety were identical. In addition the UV spectrum of ergoxanthin tetraacetate and ergoflavin hexaacetate were also very similar. Only on formation of ergoxanthin pentaacetate was there a dichotomy of behaviour. This extra, easily acid-hydrolysed, acetate had all the characteristics of an enol acetate. In the NMR spectrum of the pentaacetate there was present a signal at 4·53 ppm (doublet, $J \sim 4$ c/s) for one proton, that of the methine proton at a lactone terminus (see below). This represented a downfield shift of 0·05 ppm from the position in the tetraacetate which, since the shifts in the other methine protons (at 5·08 and 5·79) in the "flavin" nucleus are ca. 0.01 ppm indicated some change in the environment of this proton. A new proton signal, a singlet at 5·45 ppm not present in the tetraacetate had appeared, whilst a broader "singlet" of two protons at 3·03 ppm present in the tetraacetate disappeared on pentaacetate formation. These observations require the partial structures (V) and (VI) for the tetra- and pentaacetate respectively, the signals being attributed to a vinyl proton and to methylene protons adjacent to carbonyl respectively.



V VI

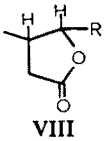
A plausible alternative for the pentaacetate formulation (VI) is VII. The vinyl proton here might also appear as a singlet if the coupling with the methine proton (see later) were small. However, the chemical shift of this proton might be expected to be to lower field (the fumaric ester olefinic proton is at 6·84 ppm). In addition a larger shift for this methine proton from its position in the tetraacetate might be expected, since it is now allylic. Furthermore, the specific hydrolysis of one acetate

in (VII) may be interpreted as supporting VI as against VII, as may the IR carbonyl absorption.



VII

The NMR spectrum of ergoxanthin (Fig. 1) in DMSO-d_6 exhibits all the signals characteristic of ergoflavin, and the characteristic couplings. In addition there is a signal at 277·7 c/s (one proton). This is evidently the signal found at 4·53 ppm in $CDCl_3$, referred to above. It is attributed to a methine proton on carbon bearing lactonic oxygen since it is not shifted on formation of the tetraacetate. This proton is coupled to another proton at ~175 c/s. Since certain of the methyl protons are also coupled to a proton at 175 c/s it may be presumed that this latter proton is that on a carbon bearing a methyl group. (The methyl group protons are also coupled with a proton at 120 c/s which is the location of the corresponding proton in the ergoflavin nucleus). These results require the part-structure (VIII) when it is recollected that, aside from the carbon atoms constituting V both a γ-lactone and a carbomethoxyl



VIII

group must be incorporated into the "xanthin" moiety. Since the group R must be attached through carbon and no other carbon atoms are available, the combination of V and VIII gives IV.

The structure arrived at is intuitively satisfying since it may be very simply derived from an ergochrysin (III) by cleavage of the β-diketone and lactonization. In fact the simplicity of the transformation required compelled a scrutiny of the operations performed in the isolation of ergoxanthin in case the biogenesis of this substance might have had an adventitious anthropomorphic impetus. As far as has been ascertained this is not the case, but the possibility cannot be excluded as may be judged from the following.

Two ergochrysins (A and B)[1] were available and each was allowed to react completely with 5 equiv of alkali. The resultant product was cyclized by refluxing in acetic acid and methylated with diazomethane. Both ergochrysins gave a number of products. The materials with the same R_F as ergoxanthin were isolated. That from ergochrysin B had an IR spectrum showing a general similarity to ergoxanthin, but was clearly different. That from ergochrysin A gave material with an IR spectrum (Fig. 2) of truly impressive similarity with ergoxanthin; and indeed on this evidence alone one might claim identity. However, closer inspection of the thin layer plates showed that the partially synthetic material presistently had a slightly lower R_F (0·36 as against 0·40) than ergoxanthin, and in fact whereas ergoxanthin is crystalline the new product was not.

The similarity of the spectra can, we believe, be interpreted as supporting the gross structure of IV, and it is therefore unlikely that ergoxanthin could be derived from

either ergochrysins A or B on isolation. The existence of a third ergochrysin (which must be required to be more sensitive as regards hydrolytic cleavage) and its conversion to ergoxanthin during isolation cannot be excluded.

TABLE 1. UV SPECTRA*

Compound	Neutral (95% EtOH)	Alkaline[a] (immediate)	Alkaline[b] (standing 2 hr)	Acidified[c]
Ergoflavin	207	237	273	246
	(25,000)	(20,200)	(17,200)	(19,500)
	241	286	391	270
	(19,300)	(13,600)	(9,400)	(15,000)
	279	414		360
	(20,000)	(11,800)		(6,600)
	380			
	(7,300)			
Ergoxanthin	209	239	273	250
	(25,400)	(17,500)	(16,000)	(19,100)
	268	282	394	267
	(23,600)	(13,700)	(9,500)	(16,700)
	373	407		361
	(8,000)	(11,800)		(7,600)

*

[a] Samples dissolved in 0·1N NaOH.

[b] Same solution; no spectral changes occurred after 2 hr.

[c] Solution acidified with 6N HCl.

TABLE 2. COMPARISON OF ERGOXANTHIN AND ERGOFLAVIN DERIVATIVES

	Tri-OCH_3-ergoxanthin	Tetra-OCH_3-ergoflavin	Ergoxanthin tetraacetate	Ergoflavin hexaacetate
IR Spectrum ($CHCl_3$)	1798	1806	1810	1812
	1770	—	1780	—
	1747	—	1760	1757
	1691	1684	1745	—
	1596	1595	1698	1697
	1462	1458	1615	1616
			1565	1567
			1465	1456
UV Spectrum (95% EtOH)	250	252	242	240
	(24,500)	(29,200)	(26,400)	(29,600)
	337	348	330	338
	(4,400)	(5,650)	(4,600)	(5,250)

EXPERIMENTAL

NMR measurements were determined on a Varian DP-60 instrument in the solvents noted (5–10% w/v). Both $CDCl_3$ and DMSO-d_6 were obtained from Merck, Sharp and Dohme, Ltd. The spectra were calibrated by the usual side-band method and the audio oscillator was continuously monitored with an H-P 522B frequency counter. All peak positions are given relative to internal TMS. The double irradiation experiments were accomplished with an NMR Specialties, Inc., Model PD-60 homonuclear spin-decoupling unit.

The solvents for rotations are indicated parenthetically. M.ps were determined on the Kofler hot stage and are uncorrected. Kieselgel was used for TLC.

Ergoxanthin trimethyl ether. Ergoxanthin (160 mg) in chloroform (5 ml) was treated with excess ethereal diazomethane for 24 hr. The resultant mixture was separated by TLC (eluant: $CHCl_3$–AcOH; 9:1) and the major component (R_F 0·50), 89 mg. was isolated. It crystallized from $CHCl_3$–pet. ether in small colourless prisms m.p. 120–125° (dec), $[\alpha]_D$ −4° (*c*, 1·00, $CHCl_3$), ν_{max} 1798, 1770 (weak), 1747, 1691, 1596, 1462 cm^{-1} ($CHCl_3$), λ_{max}^{EtOH} 216 (20,000), 250 (24, 500), 337 (4,400) mμ. NMR spectrum ($CDCl_3$): δ 1·23 (6H, doublet, J ~ 6 c/s), a complex multiplet due to 7 protons in the region 100–180 c/s, 3·08 (2H, singlet), four OCH_3 groups 3·43, 3·56, 3·73; 4·13 (1H, multiplet) 4·48 (1H, doublet, J ~ 3 c/s), 5·42 (1H, doublet, J ~ 3 c/s) and two AB patterns = δ_A 6·91, δ_B 7·49, J_{AB} = 8·6 c/s; $\delta_{A'}$ 7·05, $\delta_{B'}$7·56, $J_{A'B'}$ = 8·5 c/s, arising from 4 aromatic protons. (Found: C, 61·30; H, 5·44; OCH_3, 17·10. Calc. for $C_{34}H_{34}O_{14}$: C, 61·26; H, 5·14; OCH_3 (IV), 18·62%.)

Ergoxanthin trimethyl ether monoacetate. Ergoxanthin trimethyl ether (41·4 mg), Ac_2O (16 ml) and pyridine (4 ml) were heated at 75° under N_2 for 15 min. The product was isolated by TLC (eluant: 7% acetic acid in $CHCl_3$) yielding 38·3 mg pure acetate which crystallized from 95% EtOH in white prisms, m.p. 238–240°, $[\alpha]_D$ −21° (*c*, 0·95, $CHCl_3$), ν_{max} 1804, 1752, 1696, 1598 cm^{-1} ($CHCl_3$), λ_{max}^{EtOH} 230 (24,500), 254 (30,000), 339 (5,350) mμ. NMR spectrum ($CDCl_3$): δ 1·05 (3H, doublet, J ~ 5 c/s), 1·30 (3H, doublet, J ~ 5 c/s), 2·21 (CH_3COO), 120–170 c/s (6H, multiplet); 3·07 (2H, singlet), methoxyls (4) at 3·39, 3·55, 3·58, 3·73; 4·48 (1H, broad singlet, W 1/2 ~ 4 c/s), 5·15 (1H, broad singlet, W1/2 ~ 4 c/s), 5·69 (1H, doublet, J ~ 3 c/s) and two overlapping AB patterns: δ_A 6·88, δ_B 7·43, J_{AB} = 8·6 c/s; $\delta_{A'}$ 6·95, $\delta_{B'}$ 7·51, $J_{A'B'}$ = 8·5 c/s, due to 4 aromatic protons. (Found: C, 61·44; H, 5·15. Calc. for $C_{36}H_{36}O_{15}$: C, 61·01; H, 5·11%.)

Acid treatment of ergoxanthin. Ergoxanthin (147·1 mg), 95% EtOH (70 ml), and 6N HCl (5 ml) were refluxed for 6 days, and the solvent evaporated. The resultant mixture (3 components) was separated by TLC (eluant: $CHCl_3$–AcOH; 4:1). The slowest moving component (R_F = 0·2) crystallized from $CHCl_3$ in round aggregates, m.p. 205–208° (dec). This compound was identical to demethylergoxanthin (described below).

The compound of intermediate R_F (0·65) formed yellow needles from 95% EtOH. It was identical in all respects with ergoxanthin.

The final product (R_F = 0·72) was not obtained crystalline, but was chromatographically pure: $[\alpha]_D$ +85° (*c*, 1·49, $CHCl_3$), ν_{max} 1796, 1745, 1649, 1626 cm^{-1} ($CHCl_3$), λ_{max}^{EtOH} 222 (19,000), 261 (20,000), 373 (6,600) mμ. NMR spectrum ($CDCl_3$): 1·22 (9H, multiplet), 2·13 (4H, multiplet), 2·83 (2H, multiplet), 3·14 (2H, broad singlet), 4·21 (2H, quartet, J ~ 7 c/s)—a 1H signal appeared buried beneath this quartet; 4·43 (1H, broad singlet), 5·29 (1H, broad singlet), two AB patterns (4H): δ_A = 6·60. δ_B = 7·48, J_{AB} ~ 8 c/s; $\delta_{A'}$ = 6·69, $\delta_{B'}$ = 7·56, $J_{A'B'}$ ~ 8 c/s; 11·87 (2H, singlet). (Found: C, 59·57; H, 4·56; OEt, 4·47. Calc. for $C_{32}H_{30}O_{14}$: C, 60·19; H, 4·73; OEt (I), 7·05%.) The compound gave a green colour with $FeCl_3$.

The hydrolysis of ergoxanthin. Ergoxanthin (114 mg) was treated with 0·1N NaOH (30 ml) overnight at room temp. The solution was acidified and extracted with AcOEt. The product was refluxed for 2 hr in glacial AcOH (30 ml), and the solvent evaporated. The resultant product, demethylergoxanthin, which was homogeneous on TLC (eluant: $CHCl_3$–AcOH; 4:1) gave round crystalline aggregates from $CHCl_3$, m.p. 205–208° (dec), $[\alpha]_D$ +41° (*c*, 0·98, MeOH), ν_{max} 1790, 1755, 1652, 1621 cm^{-1} (Kbr), λ_{max}^{EtOH} 258 (19,200), 369 (5,500) mμ. NMR spectrum (pyridine) δ 1·25 (6H, doublet, J ~ 5 c/s), 2·20 (4H, multiplet), 3·00 (2H, multiplet), 3·51 (2H, multiplet), 4·59 (1H, broad singlet, W 1/2 ~ 4 c/s), 4·94 (1H, broad singlet, W 1/2 ~ 4 c/s), 5·55 (1H, doublet, J ~ 3 c/s); the remaining peaks were lost under the solvent bands. (Found: C, 57·94; H, 4·56. Calc. for $C_{30}H_{26}O_{14}$·H_2O: C, 57·33; H, 4·48%.) The compound gave a green $FeCl_3$ colour.

Methylation of demethylergoxanthin. The above compound (10 mg) in AcOEt was methylated with excess ethereal diazomethane for 30 sec and the solvent and excess diazomethane evaporated. The major component of the resultant mixture was isolated by TLC (eluant: $CHCl_3$–AcOH; 9:1) and crystallized from 95% EtOH in needles, m.p. 185–188°. It was identical with authentic ergoxanthin in all respects.

Ergoxanthin pentaacetate. Ergoxanthin (40·4 mg), Ac_2O (12 ml) and pyridine (3 ml) were heated under N_2 on the steam bath for 15 hr. The solution was evaporated under red. press. and the product purified by TLC (eluant: 7% AcOH in $CHCl_3$). The product was an amorphous solid $[\alpha]_D$ −60° (*c*, 0·97, $CHCl_3$), ν_{max} 1810, 1780, 1750, 1745, 1698, 1625, 1460 cm^{-1} ($CHCl_3$); λ_{max}^{EtOH} 218 (26,000), 243 (37,800), 265 (inf. 21,800), 325 (4,500). NMR spectrum ($CDCl_3$): 1·02 (3H, doublet, J ~ 6 c/s), 1·20 (3H, doublet, J ~ 6 c/s), 1·87 (3H, singlet) 2·11 and 2·18 (12H ≡ 4 CH_3CO), complex multiplet

120–180 c/s (6H), 3·78 (3H, singlet), 4·53 (1H, doublet J ~ 3 c/s), 5·07 (1H, broad singlet, W 1/2 ~ 5 c/s), 5·45 (1H, singlet), 5·79 (1H, doublet, J ~ 5 c/s), two overlapping AB patterns: $\delta_A = 7{\cdot}01$, $\delta_B = 7{\cdot}39$, $J_{AB} \sim 8{\cdot}0$ c/s; $\delta_{A'} = 7{\cdot}09$, $\delta_{B'} = 7{\cdot}39$, $J_{A'B'} \sim 8{\cdot}5$ c/s (*ortho* aromatic protons). (Found: C, 59·31; H, 5·09; OCH_3, 3·08. Calc. for $C_{41}H_{38}O_{19}$: C, 58·99; H, 4·59; OCH_3 (I), 3·72%.)

Hydrolysis of ergoxanthin tetraacetate. Ergoxanthin tetraacetate (5 mg) in MeOH (5 ml) was treated with 0·1N NaOH (5 ml) and allowed to stand 24 hr at room temp. The mixture was then acidified, extracted with AcOEt, and the product heated with AcOH under reflux for 2 hr, after which the AcOH was evaporated under red. press. The product crystallized from chloroform, m.p. 205–208° (dec) and was identical with the material obtained from the hydrolysis of ergoxanthin (see below).

Hydrolysis of ergoxanthin pentaacetate. The pentaacetate (5 mg), in chloroform (2 ml) containing 3N HCl (2 ml) and MeOH (4 ml) was allowed to stand for 24 hr at room temp. After isolation the product was purified by TLC (eluant: 7% AcOH in $CHCl_3$). Its R_F value and IR spectrum were identical with that of ergoxanthin tetraacetate.

Ergoxanthin-2,4-dinitrophenylhydrazone. 2,4-Dinitrophenylhydrazine (60 mg) was dissolved in MeOH (6 ml) plus 3N HCl (0·30 ml). To this was added ergoxanthin (62 mg), and the solution was refluxed for 3 hr (milder conditions furnished little or no derivative). The product was isolated by TLC (eluant: ether–benzene; 1:1, then $CHCl_3$–AcOH; 9:1) yielding 41 mg of orange product which formed prisms from MeOH, m.p. 212–215°, $[\alpha]_D$ +170° (*c*, 0·36, $CHCl_3$), ν_{max} 1798, 1745, 1625, 1600, 1505, 1438, 1340 cm^{-1} ($CHCl_3$), λ_{max}^{EtOH} 215 (32,300), 240 (28,500), 380 (26,600) mμ. NMR spectrum ($CDCl_3$): δ 1·25 (6H, doublet, J ~ 6 c/s), 2·12 (8H, multiplet), 2·87 (1H, multiplet), 3·13 (1H, multiplet), 3·76 (OCH_3), 4·35 (1H, broad singlet, W 1/2 ~ 4 c/s), 4·55 (1H, broad singlet, W 1/2 ~ 4 c/s), 5·26 (1H, broad singlet, W ½ ~ 4 c/s), and AB pattern: $\delta_A = 6{\cdot}60$, $\delta_B = 7{\cdot}50$, $J_{AB} = 9$ c/s due to two equivalent pairs of aromatic protons; an AB pattern (2H) = $\delta_A = 7{\cdot}33$, $\delta_B = 8{\cdot}37$, $J_{AB} = 8$ c/s, the low field pair being further split with J ~ 2 c/s; 9·15 (1H, doublet, J ~ 2 c/s); 11·40 (1H, broad singlet), 11·63 (1H, singlet), 11·89 (1H, singlet). (Found: N, 6·75. Calc. for $C_{37}H_{32}N_4O_{17}$: N, 6·96%.) Carbon and hydrogen analyses were not reproducible nor satisfactory.

Conversion of ergochrysin A *into ψ-ergoxanthin.* Ergochrysin A (331 mg) was treated with 0·1N NaOH (26·5 ml; 5 equivs) for 2½ hr at room temp. Then the mixture was heated on the steam bath for 1½ hr after which time all the alkali had been consumed. The solution was acidified and extracted with AcOEt, the extract was filtered through Na_2SO_4 and evaporated. The product was refluxed 1 hr in 25 ml glacial AcOH. Evaporation and methylation with diazomethane yielded a mixture of products, the major component having an R_F value close to that of ergoxanthin. This was isolated by TLC (eluant: $CHCl_3$–AcOH; 85:15), yielding 38·5 mg of chromatographically pure product. This could not be obtained in crystalline form, but was characterized as the amorphous compound: $[\alpha]_D$ +77° (*c*, 1·59, $CHCl_3$). The IR spectrum is shown in Fig. 2. λ_{max}^{EtOH} 272 (21,400), 370 (7,300). NMR spectrum ($CDCl_3$): 1·22 (6H, doublet, J ~ 6 c/s), 2·10 (3H, multiplet), a complex multiplet between 150 and 250 c/s (7H), 3·18 (2H, broad singlet), 3·72 (OCH_3), 4·32 (1H, broad singlet), 4·72 (1H, doublet, J ~ 6 c/s), 5·24 (1H, broad singlet), peaks due to 4 aromatic protons = $\delta_A = 6{\cdot}60$, $\delta_B = 7{\cdot}47$, $J_{AB} \sim 8{\cdot}4$ c/s; $\delta_{A'} = 6{\cdot}66$, $\delta_{B'} = 7{\cdot}53$, $J_{A'B'} \sim 8{\cdot}4$ c/s; 11·86 (2H, singlet). (Found: C, 59·08; H, 4·40; O, 36·39. Calc. for $C_{31}H_{28}O_{14}$: C, 59·62; H, 4·52; O, 35·86%.) The compound gave a green $FeCl_3$ colour.

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