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NATURAL β-APO-4′-CAROTENOIC ACID METHYL ESTER IN THE FUNGUS *VERTICILLIUM AGARICINUM*

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Key Word Index—*Verticillium agaricinum*; fungi; neurosporaxanthin methyl ester; β-apo-4′-cartoenoic acid methyl ester.

Valadon and Mummery [1] isolated an unknown red band from the fungus *Verticillium agaricinum* which they called Red Band I. This carotenoid has been investigated further and on the following evidence was shown to be β-apo-4′-carotenoic acid methyl ester (**1**). It had the same absorption spectra in visible and infrared light and the same partition ratio as β-apo-4′-carotenoic acid methyl ester [2]. The hydride-reduced product of **1** and of synthetic β-apo-4′-carotenal (**2**) i.e. compound **3**, had the same visible and IR properties and could not be separated chromatographically. Further, when **1** was saponified it yielded β-apo-4′-carotenoic acid (**4**) identical in all respects to neurosporaxanthin isolated from the same fungus [3].

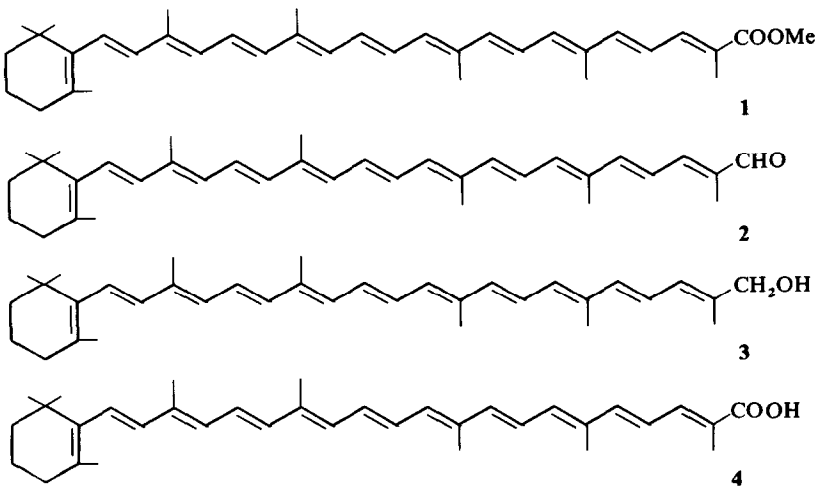
This is therefore the first demonstration of the methyl ester of neurosporaxanthin in the Fungi Imperfecti [4].

EXPERIMENTAL

V. agaricinum. Cultured as already described [3] and the carotenoids extracted by conventional methods and separated on an MgO–Celite (1:1) column. Red Band I was found below torulene on the column and purified further on TLC and on paper impregnated with Si gel [5].

Red Band I (**1**). Very similar absorption spectra in visible (~445, 473, 505 nm in *n*-hexane; 472, ~500 nm in MeOH) and IR light as β-apo-4′-carotenoic acid methyl ester [2]. When **1** was saponified using 10% KOH overnight, β-apo-4′-carotenoic acid (**4**) was obtained which could not be separated from neurosporaxanthin obtained from the same fungus [3]. Partition ratio of **1** in hexane–MeOH (5:95) was 93.5/6.5 whereas when it was converted to **4** the partition ratio changed to 1/9. R_f value of **1** on Si gel paper (SG 81) developed with Me_2CO–*n*-hexane (2:98) was 0.30. $LiAlH_4$-reduction of **1** in dry Et_2O resulted in the formation of β-apo-4′-carotenol (**3**) (~434, 459.5, 488 nm in *n*-hexane; ~431, 458, 487 nm in MeOH) whose partition ratio was 62/38. R_f value of **3** on Si gel paper (Me_2CO–*n*-hexane (2:98)) was 0.11.

Synthetic β-apo-4′-carotenal (**2**). When **2** (~450, 483, ~516 nm in *n*-hexane; 482, ~505 in MeOH), which had a partition ratio of 88/12, was subjected to $LiAlH_4$-reduction, the compound formed was β-apo-4′-carotenol. Further, when the hydride-reduced product of Red Band I (**3**) was oxidised with *p*-chloranil and I_2 in the presence of strong artificial light, the main product



formed could not be separated from synthetic **2** by chromatography. Its visible and IR absorption spectra were very similar to synthetic **2**. Red Band I was therefore identified as β-apo-4'-carotenoic acid methyl ester.

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PHLORACETOPHENONE DERIVATIVES IN *PRUNUS DOMESTICA*

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Key Word Index—*Prunus domestica*; Rosaceae; plum; ketones; domesticoside; phloracetophenone-4-methyl ether; phloracetophenone; coumarin; fraxinol.

Prunus domestica, the tree of plum fruit, grows in India on Western temperate Himalayas. The sample under investigation was collected from Srinagar (Kashmir). A number of flavonoids were earlier isolated from the heartwood and studied [1]. The present communication reports the compounds isolated from an ether extract of the bark. The extract yielded four compounds, A–D, which were separated from one another and purified as described in the Experimental.

Compound A. $C_{15}H_{20}O_9$, mp 193–94°, was optically active. It gave a violet colour with alcoholic $FeCl_3$ (chelated phenolic —OH) and on acid hydrolysis, it yielded glucose and an aglucone. The IR spectrum of the glucoside showed the presence of hydroxyl groups, chelated carbonyl and phenyl ring. The UV maximum at 283 nm (log ε: 4.172) (in MeOH) was shifted to 337 nm with NaOMe (phenolic OH) and to 302 nm with $AlCl_3$–HCl (chelated carbonyl group). The NMR spectrum (TFA, δ) showed signals for a —COMe group attached to a benzene ring (2.90, *s*), one aromatic —OMe (3.95, *s*), sugar protons [5.4 (C-1') and 4.15–4.4] and two aromatic protons (6.3, *s*). The NMR spectrum of its pentaacetate ($CDCl_3$, δ) had peaks at 2.06 (12 H, *br. s*, four alcoholic acetate groups), 2.22 (3H, *s*, one phenolic acetate), 2.45 (3 H, *s*, —COMe group), 3.80 (3 H, *s*, —OMe), 4.25–5.30 (7 H, sugar protons) and 6.35 and 6.55 (ill-resolved doublets, $J = 3$ Hz, each integrating for one aromatic H). The above data indicate A to be a trisubstituted acetophenone with two free *meta* positions, the substituents being a hydroxy, a methoxy and a glucosyloxy group. Thus, A is a mono-*O*-glucoside of phloracetophenone monomethyl ether. The aglucone was conclusively identified as phloracetophenone 4-methyl ether by a direct comparison with an authentic sample. The following observations further showed that A is the hitherto unknown 6-*O*-glucoside. Thus, on ethylation and subsequent hydrolysis A yielded 2-*O*-ethyl-4-*O*-methylphloracetophenone (mp 134–35°) [Lit. mp 133–34°, [2]]. The glucoside could be hydrolysed with emulsin and on permethylation followed by Kiliani hydrolysis it gave 2,4-di-*O*-methylphloracetophenone and 2,3,4,6-tetra-*O*-methyl-D-glucose. It may be mentioned here that the 2-*O*-diglucoside of 4-*O*-methylphloracetophenone has been recently isolated from *Dorema hyrcanum* [3].

Compound B. mp 141–42°, was identified as 4-*O*-methylphloracetophenone by spectral data and direct comparison with an authentic sample. This is the first reported isolation of this compound from a natural source; the 2,4-dimethyl and trimethyl ethers of phloracetophenone are known to be naturally occurring [4, 5].

Compound D. Mp 169–71°, gave a brown colour with $FeCl_3$ and dissolved in aq. NaOH to give a deep yellow C_5H_5N) showing NMR peaks ($CDCl_3$, δ) at 2.30 (9 H, *s*, phenolic acetate), 2.48 (3 H, *s*, —COMe) and 6.9 (2 H, *s*, aromatic). These data indicated C to be phloracetophenone itself and this was confirmed by a direct comparison with an authentic sample. This is the first reported isolation of this parent compound from a natural source.

Compound D. mp 169–71°, gave a brown colour with $FeCl_3$ and dissolved in aq NaOH to give a deep yellow colour, which disappeared on acidification. The UV spectrum was typical of a coumarin and the IR spectrum showed appropriate bands for hydroxyl, lactone carbonyl and phenyl groups. The NMR spectrum ($CDCl_3$, δ) showed a singlet at 3.9 (6 H, two aromatic —OMe), a pair of characteristic doublets at 6.2 and 8.0 ($J = 11$ Hz) attributable to the C_3 and C_4 protons respectively and a singlet at 6.5 (1 H, aromatic). The above data showed D to be a dimethoxy-monohydroxycoumarin. The mp is in agreement with that of fraxinol (5,7-dimethoxy-6-hydroxycoumarin) [6] and the spectral data are fully compatible with this structure.

EXPERIMENTAL

Mps are uncorrected; comparisons with authentic samples were made by co-TLC, co-PC, co-IR and mmp.

Extraction. Air-dried bark (700 g, from a 8–10-year-old, 7-ft-tall tree) was extracted with hot petrol, Et_2O and EtOH respectively. The petrol extract contained mainly waxy matter. From the Et_2O extract was obtained a light pink-coloured solid (1.1 g).