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## Peucenin from Sneezewood (Ptaeroxylon obliguum)

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Peucenin (5,7-dihydroxy-6-isopentyl-2-methylchromone) is a major component amongst the interrelated chromones in sneezewood.

ALTHOUGH some tree-to-tree variation in components is evident, Dean and Taylor<sup>1</sup> apparently overlooked the presence of peucenin (I) in sneezewood [Ptaeroxylon obliquum (Thunb.) Radlk., previously P. utilé] during their isolation of the interrelated chromones heteropeucenin methyl ether (II), ptaeroxylin (III), and alloptaeroxylin (IV) from the timber.



Peucenin (I) was previously<sup>2</sup> isolated from the rhizome of the masterwort (Peucedanum ostruthium Koch.), and later synthesised.<sup>3</sup> It is readily isolated from sneezewood in good yield (1%), and was characterised as its 7-methyl ether and its 5-acetate 7-O-methyl derivative. New 7-acetate and 5,7-diacetate derivatives were formed. The ultraviolet spectrum of the 7-methyl ether of peucenin derived from sneezewood was identical with that of the synthetic compound, but significantly different from that of the methyl ether (II) of heteropeucenin.<sup>3</sup> Conclusive proof of the identity of peucenin from P. obliquum was provided by its selective hydrogenation with Adams catalyst; 1 mol. of hydrogen was absorbed, to give dihydropeucenin, followed by its conversion into the 7-methyl ether and the 5,7-diacetate.

The n.m.r. spectra of the derivatives of peucenin show a typical  $A_2X$  system ( $J \sim 7$  c./sec.) resulting from spin-spin coupling of the olefinic proton of the isoprenoid side-chain (triplet,  $\tau$  4.81-4.96) with its methylene protons (doublet,  $\tau$  6.69-6.73). These are absent in the case of the diacetate of dihydropeucenin, but in the latter the chromone nucleus survives (see Table), indicating that the exocyclic by double bond of the isopentenyl unit of peucenin is selectively hydrogenated under the above conditions. The monoacetate and monomethyl ether of peucenin both have the surviving hydroxyl proton far downfield ( $\tau - 3.28, -2.70$ ) indicating its strong hydrogen-bond to the carbonyl group. The hydroxyl therefore occupies the 5-position, and substitution is, as expected, in the 7-position in each instance.

It has been shown <sup>4</sup> that C-6- and C-8-linked flavone glycosides exhibit different shifts for protons in the 8and 6-positions on acetylation of a 5-hydroxyl; for example, keyakinin acetates  $\Delta \tau_8 = -0.40$ , hemiphloin acetates  $\Delta \tau_8 = -0.43$ , and isohemiphloin acetates  $\Delta \tau_6 = -0.23$ . Related data from peucenin lend support to 6-substitution of the isopentenyl group: peucenin 7-acetate  $\Delta \tau = -0.38$ , and peucenin 7-methyl ether  $\Delta \tau = -0.50$ . Such acetylation of peucenin 7-acetate and 7-methyl ether should only affect side-chain resonances if the isopentenyl substituent occupies the 6-position. Significant shifts are indeed observed (see Table), confirming the above spectral evidence.

The 6- and 8-substitution of the chromone nucleus by the isopentenyl group, as in peucenin and the methyl ether of heteropeucenin, respectively, within a single plant source (P. obliquum) is analogous to the natural

<sup>&</sup>lt;sup>1</sup> F. M. Dean and D. A. H. Taylor, J. Chem. Soc. (C), 1966,

<sup>114.
&</sup>lt;sup>2</sup> E. Späth and K. Eiter, Ber., 1941, 74, 1851.

<sup>&</sup>lt;sup>3</sup> A. Bolleter, K. Eiter, and H. Schmid, Helv. Chim. Acta, 1951, **34**, 186. <sup>4</sup> W. E. Hillis and D. H. S. Horn, Austral. J. Chem., 1966, **19**,

<sup>705; 1965, 18, 531.</sup> 

association of 6- and 8-methyl-5,7-dihydroxyflavanones, strobopinin and cryptostrobin in both Pinus parvifolia and P. peuce,<sup>5</sup> and of 6- and 8-C-glucosylflavones, for example orientin and iso-orientin (homo-orientin) in Aspalathus acuminatus,6 and vitexin and isovitexin (saponaretin) in Vitex lucens.<sup>7</sup>

During biogenesis of peucenin and the methyl ether of heteropeucenin in P. obliquum the isoprenoid unit may be introduced at a late stage<sup>8</sup> to either the 6- or the 8-position, following formation of the 2-methylchromone nucleus. Alternatively, peucenin might undergo a Wesseley-Moser-type rearrangement (ring isomerisation) to form heteropeucenin, followed by secondary conversion into the methyl ether (II), ptaeroxylin (III), and alloptaeroxylin (IV).

Prista<sup>9</sup> isolated a compound identical [crystalline appearance (photomicrographs), colour reactions (blue to ferric chloride), and melting point (210-215°)] with peucenin from the bark of P. obliquum. Its identification<sup>9</sup> as a 3,5,7-trihydroxy-2'-methoxyflavone diglucoside, ptaeroxylosin, is based on colour reactions 214° (210-212° in Pyrex) (lit.,<sup>2</sup> 212°) (Found: C, 68.8; H, 6.4. Calc. for  $C_{15}H_{16}O_4$ : C, 69.2; H, 6.2%),  $\lambda_{max}$ . (EtOH) 232, 259, 298 mµ, shifted to 270, 315, 372 on addition of aluminium chloride. Methoxyl groups are absent. The infrared spectrum (KBr disc) showed a carbonyl band (1650 cm.<sup>-1</sup>) partly overlapping the first benzenoid C=C stretching frequency (1620 cm.<sup>-1</sup>), as well as evidence of olefinic double bonds (845 and 813 cm.<sup>-1</sup>). On paper chromatograms the compound was blue under ultraviolet light, gave no reduction with ammoniacal silver nitrate, and gave a deep blue with ferric alum spray. In alcoholic solution it gave a blue with ferric chloride. Alkali fusion gave only phloroglucinol (paper chromatography).

Methylation of peucenin (50 mg.) in methanol with ethereal diazomethane at  $-15^{\circ}$  for 48 hr. gave the 7-0methyl derivative (12 mg.) as white crystals (from methanol) m. p. 108-110° (lit.,<sup>2,3</sup> 108-109°) [Found: C, 70.2; H, 6.8; OMe, 8.6%; M (Rast), 285, 293. Calc. for  $C_{16}H_{18}O_4$ : C, 70.1; H, 6.6; OMe, 11.3%; M, 278],  $\lambda_{\text{max.}}$  233, 260, 289, with inflections at 254 and 316 mµ (lit.,<sup>3</sup> peucenin methyl ether has  $\lambda_{max}$  233, 260, 293, with inflections at 254 and 316 m $\mu$ , while heteropeucenin methyl ether has

Nuclear	magnetic	resonance	spectra	$(\tau - values)$	

	Chromone nucleus					Side-chain				
Compound	-он	Arom.	Olef.	=C-CH <sub>3</sub>	OMe	O.	λc	Есн	CH2	$=C(CH_3)_2$
7-O-Methylpeucenin	-2.70	3.74	4.06	7.71	6.16			4.81	6.70	8·23, 8·34
7-O-Methylpeucenin 5-acetate Peucenin 7-acetate	-3.28	$3.36 \\ 3.34$	$4.10 \\ 3.92$	7·74 7·66	6·14	7·59 7·68		$\begin{array}{c} 4 \cdot 94 \\ 4 \cdot 84 \end{array}$	6.73 6.69 $(I \sim 7 \text{ c./sec.})$	8.26, 8.35 8.24, 8.31
Peucenin 5,7-diacetate		2.84	3.99	7.68		7- 7·57	5- 7·66	4.96	6.73 (J ~ 7 c./sec.)	8.24, 8.31
Dihydropeucenin 5,7-diacetate		2.92	<b>4</b> ∙05	7.74		7.58	7.68	α-CH <sub>2</sub> 7·49	$ \begin{array}{c} \beta \text{-} \text{CH}_2 + \gamma \text{-} \text{CH} \\ \sim 8 \cdot 6 \end{array} $	$\begin{array}{c} -\mathrm{C}(\mathrm{CH}_{3})_{2} \\ 9 \cdot 07 \\ (J \sim 6 \text{ c./sec.}) \end{array}$

of the phenolic and acidic products of alkali fusion, and is of doubtful validity. Prista's ptaeroxylosin might be peucenin.

Natural chromones occur relatively infrequently compared with the wide distribution of structurally related Nevertheless, the isolated presence of coumarins. peucenin in both P. obliquum (Meliaceae) and P. ostru*thium* (Umbelliferae) does not appear to be of taxonomic significance.

## EXPERIMENTAL

The n.m.r. spectra were recorded on a Varian A-60 spectrometer, in deuterated chloroform, with tetramethylsilane as internal standard.

Peucenin and its Derivatives .- The ground wood (1.48 kg.) of P. obliquum was extracted for 2 days (Soxhlet) with chloroform; the dark red-brown tar (179 g.) recovered was redissolved in chloroform (200 ml.) and repeatedly washed with water for 48 hr. The chloroform layer yielded a dirty brown crystalline product (13.71 g.), which gave yellow crystals (9.3 g.) (from chloroform-methanol), m. p.  $\lambda_{max}$  260, 296, 330, with a single inflection at 254 mµ). N.m.r. spectroscopy confirmed the composition of the 7-methyl ether (see Table).

Acetylation of the methyl ether (50 mg.) with acetic anhydride-sodium acetate for 3 hr. gave 7-O-methylpeucenin 5-acetate (30 mg.), m. p. 126-127° (from ethanol) (lit.,<sup>2,3</sup> 125-126°). The presence of single methoxyl and acetyl groups was confirmed by n.m.r. spectroscopy.

Acetylation of peucenin (50 mg.) with acetic anhydridepyridine (0.4 ml.) at room temperature afforded a crystalline acetate (40 mg.), m. p. 87° (needles) (from ethanol) (Found: C, 68.1; H, 6.1.  $C_{17}H_{18}O_5$  requires C, 67.5; H, 6.0%). The monoacetate shows dimorphism, crystallising also as rhombs (from ethanol), m. p. 102-104°.

More drastic acetylation of peucenin (50 mg.) with acetic anhydride (0.5 ml.) and sodium acetate (0.1 g.) at the boiling point for 3 hr. gave the diacetate (45 mg.), m. p. 116°. The mono- and di-substitution of the acetates was confirmed by n.m.r. spectrometry (see Table).

Dihydropeucenin.-Peucenin (500 mg.) in methanol was hydrogenated with Adams catalyst (500 mg.); 1 mol. of hydrogen was absorbed. The crystalline product (350 mg.)

<sup>&</sup>lt;sup>5</sup> G. Lindstedt and A. Misiorny, Acta Chem. Scand., 1951, 5, 121.

 <sup>&</sup>lt;sup>6</sup> B. H. Koeppen and D. G. Roux, *Biochem. J.*, 1965, 97, 444.
 <sup>7</sup> R. M. Horowitz and B. Gentili, *Chem. and Ind.*, 1964, p. 498.

<sup>&</sup>lt;sup>8</sup> W. D. Ollis and I. O. Sutherland, "Recent Developments in the Chemistry of Natural Phenolic Compounds," ed. W. D. Ollis, Pergamon Press, London, 1961, p. 74.
 \* L. N. Prista, Anais Fac. Farm. Porto, 1951, 11, 81.

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had m. p. 207–208° (from ethanol) (lit.,<sup>2,3</sup> 206–207°). Dihydroheteropeucenin <sup>3</sup> has m. p. 191–192°.

Acetylation of dihydropeucenin (150 mg.) with acetic anhydride-sodium acetate, as above, gave the diacetate (130 mg.), m. p.  $101-103^{\circ}$  (lit.,<sup>2</sup> 99°). N.m.r. spectroscopy confirmed the presence of two acetyl groups; this was not evident from previous <sup>2</sup> analyses.

Methylation of dihydropeucenin (50 mg.) with diazo-

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methane, as above, gave the monomethyl ether, m. p.  $107\cdot5$ — $108\cdot5^{\circ}$  (lit.,<sup>2</sup> 106—107°).

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