Synthesis and Reactions of Isoprenyl Terminal Epoxides in the Chromone and Quinoline Series

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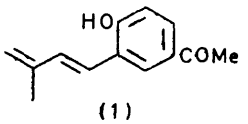
The prenylchromone peucenin (9a) was converted into the terminal olefin (11) and the terminal epoxide (13); acid- and base-catalysed cyclisation of the latter furnished a pyranochromone (14a), and the pyranoquinoline (21) was prepared similarly. The furochromone (±)-visamminol (8) was synthesised from peucenin.

ARYL isoprenoid dienes and their simple derivatives are a rare group of natural products, exemplified by the diene (1) isolated from *Helliantha uniflora* [1] and the coumarin (2) of *Thamnosa montana*.[2] Compounds formally derived from isoprenoid dienes by addition of adjacent aryl hydroxy-groups to the 1,2-double bond are better known [*e.g.* rotenone (3), the quinoline alkaloid (4),[3] and the chromone (5) [4]; isopropenyldihydrofurans of this type

[1] F. Bohlman and M. Grenz, *Chem. Rev.*, 1970, 103, 90.
[2] J. P. Kutney, T. Inaba, and D. L. Dreyer, *J. Amer. Chem. Soc.*, 1968, **90**, 813.
[3] J. Reisch, K. Szendrei, V. Papay, I. Novak, and E. Minker, *Tetrahedron Letters*, 1970, 3365.
[4] F. M. Dean, B. Parton, A. W. Price, N. Somvichien, and D. A. H. Taylor, *Tetrahedron Letters*, 1967, 3459.

have been synthesised from the corresponding hydroxy-isopropyl derivatives and by other methods.[5] The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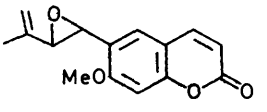
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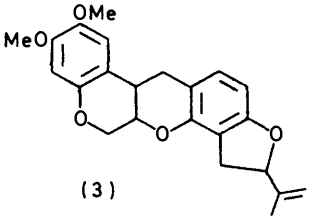
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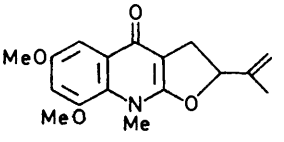
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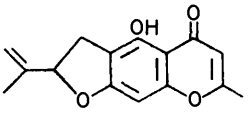
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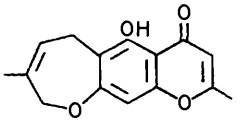
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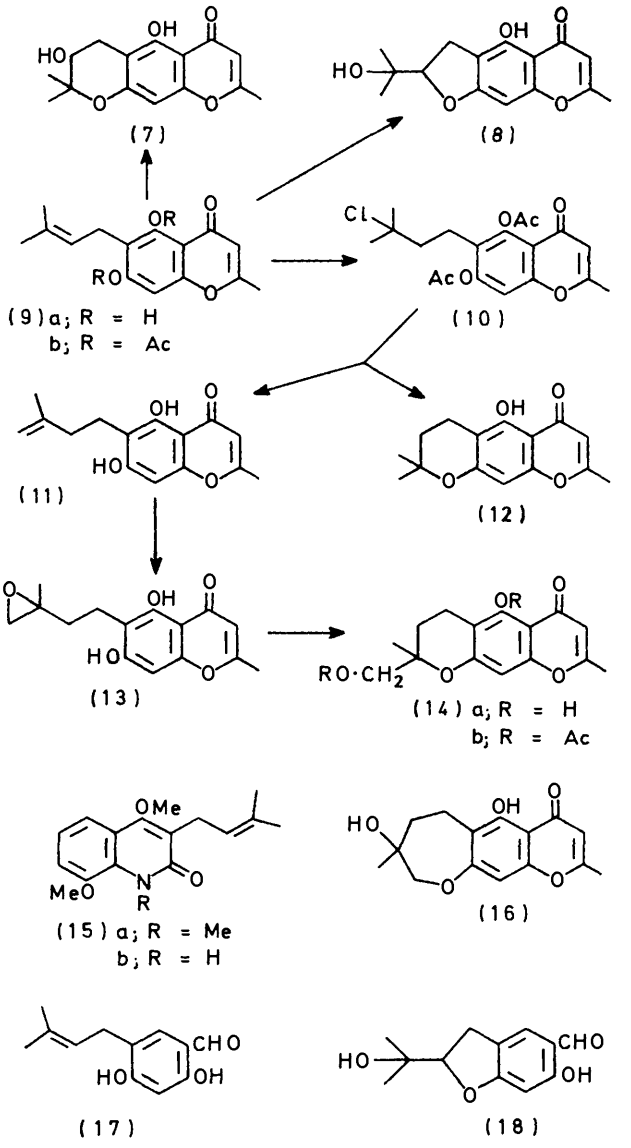
oxepinochromones of *Pteroxylon obliquum*,[4,6] *e.g.* deoxykarenin (6) represent carbon–oxygen bond formation at the terminal carbon atom of a prenyl group, perhaps through epoxidation of isoprenoid terminal olefins or dienes. As an extension of our interest in the biosynthesis of aryl isoprenoids and in the synthesis and oxidative cyclisation of 3-prenylquinolones,[7] we have studied the preparation and reactions of isoprenoid terminal olefins and now report our results in the chromone and quinoline series.

The Chromone Terminal Olefin (11) *and Epoxide* (13).—Our synthetic plan involved formation of an addition product of the 3-methylbut-2-enylchromone, peucenin (9a), suitable for conversion into the terminal olefin (11) by an elimination reaction.

Peucenin was prepared from 5,7-dihydroxy-2-methylchromone by the method of Seshadri and his co-workers [8] using 3,3-dimethylallyl bromide in methanolic sodium hydroxide; the 6,8-diprenyl derivative is formed in this reaction, as reported previously,[8] and we also isolated the 8-prenylchromone (heteropeucenin) (15%). Other procedures for *C*-allylation, for example by using the silver salt of 5,7-dihydroxy-2-methylchromone, were less satisfactory and gave a mixture of *C*- and *O*-allyl products in which the 6,8-diprenylchromone predominated.

Although hydration of 3-prenyl-2-quinolones and addition of halogen acids to the olefinic bonds of these compounds can be effected without participation of the adjacent oxygen function,[9,10] preliminary studies with peucenin (9a) indicated that cyclisation to chromans occurred readily in oxymercuration and in acid-catalysed addition reactions. The 5- and 7-hydroxy-groups of peucenin were protected, therefore, by acetylation. Reaction with hydrogen chloride in acetic acid at *ca.* 2° then furnished the tertiary chloride (10) quantitatively; its structure was confirmed by the n.m.r. spectrum (Table) and by mass spectrometry, which showed major fragmentations involving loss of halogen and benzylic cleavage. Since the proportion of least substituted


(7) (8) (9) a; R = H b; R = Ac (10) (11) (12) (13) (14) a; R = H b; R = Ac (15) a; R = Me b; R = H (16) (17) (18)

olefin formed in base-promoted dehydrohalogenation reactions increases with the steric size of the base,[11] we

[5] *E.g.* M. F. Grundon and K. J. James, *Tetrahedron Letters*, 1971, 4727; M. Nakazaki, Y. Hirsose, and K. Ikematsu, *ibid.*, 1966, 4735.

[6] P. H. McCabe, R. McGrindle, and R. D. H. Murray, *J. Chem. Soc.* (*C*), 1967, 145.

[7] M. F. Grundon and K. J. James, *Chem. Comm.*, 1971, 1311; R. M. Bowman, J. F. Collins, and M. F. Grundon, *J.C.S. Perkin I*, 1973, 626, and references given therein.

[8] A. C. Jain, P. Lal, and T. R. Seshadri, *Indian J. Chem.*, 1969, **7**, 1072.

[9] E. A. Clarke and M. F. Grundon, *J. Chem. Soc.*, 1964, 4190.

[10] J. F. Collins, G. A. Gray, M. F. Grundon, D. M. Harrison, and C. G. Spyropoulos, *J.C.S. Perkin I*, 1973, 94.

[11] H. C. Brown and I. Moritani, *J. Amer. Chem. Soc.*, 1953, **75**, 4112.

treated the tertiary chloride diacetate (10) with potassium 1,1-diethylpropyl oxide in 1,1-diethylpropyl alcohol. Elimination of hydrogen chloride was complete in 15 min at 70° and gave two major products, separated by chromatography. One compound (30%) was identified by its n.m.r. spectrum (Table) as the linear pyranochromone, isopeucenin (12). The required disubstituted olefin (11) could be separated from a small proportion of the trisubstituted olefin, peucenin (9a), only by preparative t.l.c. The structure of the terminal olefin was indicated by the n.m.r. spectrum (Table), which showed a two-proton broad singlet at τ 5·33 ($C{=}CH_2$) and a three-proton singlet at τ 8·23 [$C(CH_3){=}CH_2$] and by i.r. absorption at 890 cm^{-1} ($C{=}CH_2$).

Since epoxidation of aryl isoprenoids of type (11) containing terminal double bonds had not been reported, the course of the reaction could not be predicted readily and we decided to study first the reaction of peucenin (9a) with peroxy-acids. 3-Methylbut-2-enyl aryl compounds containing *ortho*-hydroxy-groups normally react with peroxy-acids to give a mixture of furo- and pyrano-derivatives by spontaneous cyclisation of an intermediate epoxide. With prenyl-coumarins and -chromones, furo-ring formation is suppressed by toluene-*p*-sulphonic acid,[12,13] presumably by directing the reaction through tertiary carbonium ions leading to pyrano-derivatives. Epoxidation of the prenyl derivative (17) in the presence of triethylamine gave a single product, the furo-derivative (18).[13] Such control was not observed in the epoxidation of 3-prenyl-2-quinolones, the *N*-methyl-2-quinolone (15a) affording a furoquinoline as sole product, even with sulphuric acid present, and the ratio of furo- and pyrano-compounds from the 2-quinolone (15b) being insensitive to the pH of the medium.[14] We confirmed that reaction of peucenin (9a) with *m*-chlorobenzoic acid in chloroform with addition of strong acid gave the pyrano-derivative, hamaudol (7), almost quantitatively. Epoxidation in the presence of potassium hydrogen carbonate furnished the furo-isomer, visamminol (8) (66%). The one-proton singlet at τ −2·92 in the n.m.r. spectrum indicated the presence of a 5-OH group hydrogen-bonded to carbonyl; the CH_2 resonances were at lower field than in the pyrano-isomer (7) (Table), as expected for a hydroxyisopropyl-dihydrofuro-derivative. Structure (8) for the product was confirmed by the mass spectrum, which showed a base peak at *m/e* 217 ($M - C_3H_7O$). Visamminol has been isolated from *Ammi visnaga* as the (+)-enantiomer,[15] but its synthesis has not been described previously. The reaction of peucenin with peroxy-acid affords only linear tricyclic products, strong intramolecular hydrogen bonding to the chromone carbonyl function apparently protecting the 5-OH group from participation.

We then studied the reaction of the terminal olefin (11) with *m*-chloroperbenzoic acid, expecting to obtain the epoxide (13) or the linear cyclisation products (14a) and (16). Epoxidation in AnalaR chloroform (containing 2% of ethanol) or in ethyl acetate was incomplete after several days and did not occur in acetone or after the addition of a radical inhibitor. Since epoxidation of olefins normally is faster in aprotic solvents, the reaction was repeated in chloroform free from ethanol; complete reaction occurred to give a single product, shown by n.m.r. spectroscopy (Table) to be the epoxide (13). Thus, resonances characteristic of a terminal oxiran ring occurred at τ 8·08 (2H, s, Me attached to oxiran ring) and at 7·0—7·5 (4H, m, overlap of $ArCH_2$ and oxiran ring proton signals). Benzylic cleavage (base peak *m/e* 205, $M - C_4H_7O$) was a major mass spectral fragmentation.

Cyclisation of the epoxide took place rapidly with toluene-*p*-sulphonic acid and more slowly with 2,6-lutidine in dimethylformamide and with sodium hydroxide to give the pyranochromone (14a) only. The n.m.r. signal at τ −2·95 (5-OH) indicated that cyclisation had occurred through the 7-OH group, and the pyrano-structure was suggested by close similarity of the spectrum to that of the pyranochromone (12), except for resonances at τ 6·30 (2H, s, $HO{\cdot}CH_2$) and at 8·70 (3H, s, pyran ring Me) instead of the six-proton singlet at τ 8·65 (CMe_2) (Table). However, the oxepinochromone (16), an alternative product of epoxide cyclisation, would be expected to have a similar n.m.r. spectrum, and in order

N.m.r. spectral assignments (τ values; 60 MHz)

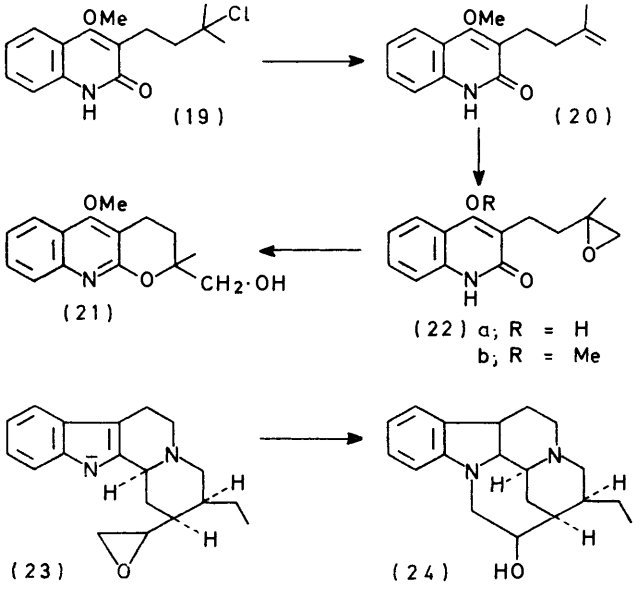
Compound	Solvent	5-OH	$ArCH_2$	$ArCH_2{\cdot}CH_2$	CMe_2	=CMe	$=CH_2$	CMe·O	$CH_2{\cdot}O$	CH·O
(7)	$CDCl_3$	−3·0	7·15(t)		8·61(s)					6·10(m)
					8·64(s)					
(8)	$CDCl_3$	−2·92	6·87(d)		8·15(s)					5·23(t)
					8·26(s)					
(9a) [a]	$(CD_3)_2CO$		6·62(d)		8·26(s)					
					8·30(s)					
(10)	$CDCl_3$		7·37(m)	8·10(m)	8·45(s)					
(11)	$(CD_3)_2CO$		6·75—7·45(m)			8·23(s)	5·33(s)			
(12)	$CDCl_3$	−3·03	7·29(t)	8·18(t)	8·65(s)					
(13)	$CDCl_3$		7·00—	8·05(t)				8·08(s)	7·00—	
			7·50(m)						7·50(m)	
(14a)	$CDCl_3$	−2·95	7·33(t)	8·20(t)				8·70(s)	6·30(s)	
(20)	$CDCl_3$		7·04(m)	7·66(m)		8·13(s)	5·19(s)			
(22b)	$CDCl_3$		7·25(m)	8·10(m)				8·53(s)	7·32(d)	
(21)	$CDCl_3$		6·97(m)	8·05(m)				8·60(s)		6·23(d)

[a] =CH− at 4·71(t).

[12] B. K. Bailey, P. G. Harrison, and W. Steck, *Canad. J. Biochem.*, 1971, **49**, 964.
[13] W. Steck, *Canad. J. Biochem.*, 1971, **49**, 2297.
[14] E. A. Clarke and M. F. Grundon, *J. Chem. Soc.*, 1964, 4196; R. M. Bowman and M. F. Grundon, *J. Chem. Soc.* (*C*), 1966, 1504.
[15] W. Bencze, J. Eisenbeiss, and H. Schmid, *Helv. Chim. Acta*, 1956, **39**, 923.

to distinguish between the primary alcohol (14a) and the tertiary alcohol (16) the n.m.r. spectrum of the product in [$^2H_6$]dimethyl sulphoxide was studied. Strong hydrogen bonding to the solvent reduced the rate of proton exchange, giving signals at τ 5·00 (1H, t, OH) and 6·55 (2H, m, CH_2·OH), the latter collapsing to a singlet on addition of deuterium oxide. The n.m.r. spectrum of the diacetate (14b) showed a two-proton singlet at τ 5·80 (CH_2·OAc), representing an upfield shift compared with the parent alcohol as expected for the acetate of a primary alcohol. The pyrano-formulation (14a) is established, therefore, by the n.m.r. data and was confirmed by the mass spectrum which showed a base peak at *m/e* 245 ($M - CH_2OH$).

2-Quinolone Terminal Olefin (20) *and Epoxide* (22b).—The isolation of an epoxide in the prenylchromone series, even with two *ortho* phenolic hydroxy-groups present, encourages us to investigate the preparation of an analogous quinoline derivative. In this case, however, cyclisation of an appropriate epoxide, for example (22a), could occur at either the 2- or the 4-oxygen function and protection of the 4-hydroxy-group was required to ensure the formation of linear tricyclic products. Fortunately, a suitable compound, the 4-methoxy-2-quinolone (19) was readily available.[10] Treatment of this tertiary chloride with potassium t-butoxide in dimethyl sulphoxide afforded the terminal olefin (20) (97%); its structure was indicated by i.r. absorption at 1640 cm^{-1} (NHCO) and by its n.m.r. spectrum (Table), which showed singlets at τ 5·19 (2H, C=CH_2) and 8·13 (3H, =CMe).



Reaction of the terminal olefin with *m*-chloroperbenzoic acid in chloroform was not inhibited by the presence of ethanol in the solvent, and the epoxide (22b) was obtained. The n.m.r. spectrum (Table) showed a two-proton doublet at τ 7·32 (J 5 Hz) arising from geminal coupling in the oxiran methylene group and a three-proton singlet at τ 8·53 attributed to the methyl group attached to the epoxide ring. The base peak at *m/e* 228 in the mass spectrum apparently is due to the species formed by cyclisation of the epoxide and loss of the CH_2OH substituent from the resultant pyranoquinoline (21). The latter compound was obtained as the only product of cyclisation of the epoxide in reaction with either acid or base. Its structure was supported by the n.m.r. spectrum (Table), which showed resonance at τ 6·23 (2H, d, J_{gem} 2 Hz, CH_2·OH). In [$^2H_6$]dimethyl sulphoxide, the methylene resonance appeared at τ 6·58 as an unsymmetrical doublet (J 10 Hz) and collapsed to a singlet on addition of deuterium oxide. This accords with a primary alcohol structure and excludes formulation of the product as the isomeric oxepinoquinolone, although the result is less clear-cut than in the case of the analogous pyranochromone (14a) because of overlap of n.m.r. signals. The mass spectrum, however, also indicates the presence of a hydroxymethyl group (see before).

When the cyclisation of epoxides (13) and (22b) occurs in acidic media, electronic as well as steric factors clearly favour attack of phenolic oxygen at tertiary carbon to give six-membered pyran rings. The alternative mode of reaction was observed in the transformation (23) ⟶ (24), and exclusive formation of the seven-membered ring was attributed to the rigid geometry of the total ring system.[16] In our case, such steric control does not exist and the entropy effect unfavourable to the formation of a seven-membered ring is probably dominant, even when the cyclisation is conducted under basic conditions that might otherwise have resulted in faster reaction at the least substituted carbon of the oxiran.

EXPERIMENTAL

N.m.r. spectra were determined with a Perkin-Elmer R12 spectrometer (tetramethylsilane as an internal standard) and mass spectra with an A.E.I. MS902 spectrometer. In column chromatography, silica refers to 60—100 mesh, and alumina to Woelm Neutral Grade 3.

Peucenin (9a) [8].—Reaction of 5,7-dihydroxy-2-methylchromone [12] (25 g) with 3-methylbut-2-enyl bromide and sodium methoxide in methanol, chromatography of the product on silica, and elution with benzene–light petroleum (1 : 1) gave the 6,8-bis-(3-methylbut-2-enyl) derivative (22%), m.p. 142—144° (from light petroleum) (lit.,[8] m.p. 149—150°), τ ($CDCl_3$) −3·0 (s, 5-OH), 3·63 (s, 7-OH), 4·70 (s, 3-H), 4·70 (m, C=C*H*–CH_2), 6·55 (d, =CH–CH_2), 7·66 (s, 2-Me), and 8·22 (CMe_2), *m/e* 328 (M^+, 31%), 327 (M^+ — H, 96), 288 ($M^+ - C_3H_4$, 71), 275 (68), 263 (67), 235 (62), and 223 (100). Elution with benzene afforded a mixture which was separated by fractional crystallisation from benzene into peucenin (9a) (14%), m.p. 208—210° (lit.,[6] m.p. 212—214°), *m/e* 260 (M^+, 56%), 245 (M^+ — Me, 32), 217 ($M^+ - C_3H_7$, 72), 205 ($M^+ - C_4H_7$, 100), and 192 ($M^+ - C_5H_8$, 10), and the 8-(3-methylbut-2-enyl) derivative (heteropeucenin) (15%), m.p. 185—187° (lit.,[4] 193°), τ [$(CD_3)_2CO$] −2·83 (s, 5-OH), 3·65 (s, 6-H), 3·94 (s, 3-H), 4·72 (t, J 7 Hz, C=C*H*–CH_2), 6·60 (d, J 7 Hz, C=CH–CH_2), 7·60 (s, 2-Me), and 8·27 (CMe_2), *m/e* 260 (M^+, 91%), 245 (M^+ — Me, 100), 205

[16] D. D. O'Rell, F. G. H. Lee, and V. Boekelheide, *J. Amer. Chem. Soc.*, 1971, **93**, 3205.

($M^+ - C_4H_7$, 46), 192 ($M^+ - C_5H_8$, 63), 165 ($M^+ - C_4H_7 - C_3H_4$, 13).

5,7-*Diacetoxy*-6-(3-*chloro*-3-*methylbutyl*)-2-*methylchromone* (10).—A solution of peucenin diacetate [17] (9b) (6 g) in acetic acid (45 ml) previously saturated with dry hydrogen chloride was stirred at *ca.* 2° for 1 h. Evaporation gave the *chloride* (6·65 g), m.p. 145—147° (needles from benzene), *m/e* 354 (M^+ — CO, 16%), 320 (M^+ — HOAc, 61), 319 (M^+ — CO — Cl, 100), and 229 (M^+ — CO — C_4H_8Cl, 73) (Found: C, 59·9; H, 5·5. $C_{19}H_{21}ClO_6$ requires C, 60·0; H, 5·5%).

5,7-*Dihydroxy*-2-*methyl*-6-(3-*methylbut*-3-*enyl*)*chromone* (11).—The chloride (10) (6·65 g) was added in one portion to a solution of potassium (2·97 g) in 1,1-diethylpropyl alcohol (51 ml) and the solution was stirred at 70—75° for 20 min and added to iced water (400 ml). The mixture was stirred for 2 h and neutralised with acetic acid. The product, obtained by extraction with ethyl acetate, was chromatographed on silica. Elution with benzene–light petroleum (9 : 1) gave isopeucenin (12) (1·73 g), m.p. 133—135° (needles from hexane) (lit.,[6] 132°), *m/e* 260° (M^+, 73%), 245 (M^+ — Me, 18%), 217 ($M^+ - C_3H_7$, 44), and 205 ($M^+ - C_4H_7$, 100).

Elution with benzene gave the *terminal olefin* (11) containing some peucenin (9a), which was purified by preparative t.l.c. on fluorescent silica with chloroform as solvent; it was obtained as needles, m.p. 180—181°, *m/e* 260 (M^+, 43%), 245 ($M^+ - CH_3$, 7), 217 ($M^+ - C_3H_7$, 24), and 205 ($M^+ - C_4H_7$, 100) (Found: C, 69·4; H, 6·1. $C_{15}H_{16}O_4$ requires C, 69·2; H, 6·2%).

Hamaudol (7).[12]—Reaction of peucenin (9a) (40 mg) with *m*-chloroperbenzoic acid and toluene-*p*-sulphonic acid gave hamaudol (38 mg), m.p. 184—186° (needles from benzene) (lit.,[12] 186—188°) *m/e* 276 (M^+, 100%), 233 ($M^+ - C_3H_7$, 36), 205 ($M^+ - C_4H_7O$, 100), and 204 ($M^+ - C_4H_8O$, 56).

(±)-*Visamminol* (8).—A solution of peucenin (100 mg) in chloroform (40 ml) containing *m*-chloroperbenzoic acid (95 mg) was stirred at 0° with potassium hydrogen carbonate (2 mg) for 2·5 h, washed with aqueous sodium hydrogen carbonate, and evaporated. Preparative t.l.c. on silica with chloroform–ethyl acetate (4 : 1) afforded (±)-*visamminol* (70 mg, 66%), m.p. 144—145° [lit.,[15] 160—160·5° for (+)-visamminol], $\lambda_{max.}$ (EtOH) 299 (ε 13,500), 256 (18,600), 250 (18,800), 232 (19,700), and 215 nm (19,800), *m/e* 276 (M^+, 61%), 261 (M^+ — Me, 9), 243 (M^+ — Me — H_2O, 30), 218 ($M^+ - C_3H_6O$), and 217 ($M^+ - C_3H_7O$, 100).

5,7-*Dihydroxy*-2-*methyl*-6-[2-(2-*methyloxiran*-2-*yl*)*ethyl*]-*chromone* (13).—A solution of the olefin (11) (57 mg) and *m*-chlorobenzoic acid (53 mg) in ethanol-free chloroform (10 ml) was kept at 0° for 5 h, washed with aqueous sodium hydrogen carbonate, and evaporated. Crystallisation from benzene gave the *epoxide* in plates (40 mg, 66%), m.p. 136—138°, *m/e* 276·0996 (M^+, 17%; $C_{15}H_{16}O_5$ requires *M*, 276·0998), 275 (70), 245 ($M^+ - CH_3OH$, 73), 206 ($M^+ - C_4H_6O$, 40), and 205 ($M^+ - C_4H_7O$, 100). Satisfactory elemental analysis was not obtained.

7,8-*Dihydro*-5-*hydroxy*-8-*hydroxymethyl*-2,8-*dimethyl*-6H-*benzo*[1,2-*b*:5,4-*b'*]*dipyran*-4-*one* (14a).—The epoxide (13) in chloroform containing a trace of toluene-*p*-sulphonic acid was converted quantitatively in 2 h into the *pyranochromone* (14a), m.p. 114—116° (prisms from benzene), *m/e* 276 (M^+, 71%), 245 ($M^+ - CH_2OH$, 100), and 205 ($M^+ - C_4H_7O$, 48) (Found: C, 65·0; H, 6·0. $C_{15}H_{16}O_5$ requires C, 65·2; H, 5·8%). The diacetate (14b), m.p. 131—133°, was obtained by refluxing the chromone with acetic anhydride and sodium acetate.

The epoxide was converted completely into the pyranochromone in 2N-sodium hydroxide containing methanol after 20 h at 20°, and converted partially into the pyranochromone in dimethylformamide containing 2,6-lutidine after 24 h.

4-*Methoxy*-3-(3-*methylbut*-3-*enyl*)-2-*quinolone* (20).—A solution of the chloride (19) [10] (1·17 g) and potassium t-butoxide (2·83 g) in dimethyl sulphoxide (35 ml) was kept at 70° for 4 h, then water was added. Extraction with ether gave the *olefin* (0·99 g, 97%), m.p. 114—115° (needles from light petroleum), *m/e* 243 ($M^{+\cdot}$, 16%), 242 (63), 228 ($M^+ - CH_3$, 68), 212 (M^+ — OMe, 20), 188 ($M^+ - C_4H_7$, 100), and 130 (55) (Found: C, 74·0; H, 6·9. $C_{15}H_{17}NO_2$ requires C, 74·1; H, 7·0%).

4-*Methoxy*-3-[2-(2-*methyloxiran*-2-*yl*)*ethyl*]-2-*quinolone* (22b).—*m*-Chloroperbenzoic acid (345 mg) in chloroform (10 ml) was added to the olefin (20) (340 mg) in chloroform (20 ml), and the solution was kept for 12 h, washed with aqueous 5% sodium hydrogen carbonate, and evaporated. Trituration with ether gave the *epoxide* (190 mg, 53%), m.p. 129—132° (needles from chloroform–ether), *m/e* 259 (M^+, 33%), 228 ($M^+ - CH_2OH$, 100), 201 ($M^+ - CH_2O$, 3), 189 ($M^+ - C_4H_6O$, 14), 188 ($M^+ - C_4H_7O$, 13), and 130 ($M - CH_2O - C_4H_7O$, 14) (Found: C, 69·6; H, 6·6; N, 5·4. $C_{15}H_{17}NO_3$ requires C, 69·5; H, 6·6; N, 5·4%).

3,4-*Dihydro*-2-*hydroxymethyl*-5-*methoxy*-2-*methyl*-2H-*pyrano*[2,3-b]*quinoline* (21).—The epoxide (22b) (300 mg) in methanol (15 ml) and 2N-sodium hydroxide (5 ml) was kept for 24 h, diluted with water, and extracted with chloroform to give the *pyranoquinoline* as an oil (290 mg), which crystallised on addition of ether and separated from benzene in needles, m.p. 134—135°, *m/e* 259 (M^+, 16%), 229 ($M^+ - CH_2O$, 51), 228 ($M^+ - CH_2OH$, 100), and 188 ($M^+ - CH_2O - C_3H_5$, 29) (Found: C, 69·6; H, 6·6; N, 5·5. $C_{15}H_{17}NO_3$ requires 69·5; H, 6·6; N, 5·4%).

Treatment of the epoxide in chloroform with a trace of toluene-*p*-sulphonic acid gave the pyranoquinoline, identical (i.r. and n.m.r.) with an authentic sample.

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