Tetrahedron. Vol. 27, pp. 871 to 877. Pergamon Press 1971. Printed in Great Britain

CLAISEN REARRANGEMENTS—II[1]

SYNTHESIS OF SIX NATURAL COUMARINS

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(*Received in the UK* 10 *September* 1970; *Accepted for publication* 28 *October* 1970)

Abstract—Pyrolysis of the natural coumarin, **1**, has been shown to give obliquetin, **2**, nieshoutin, **3**, and the out-of-ring rearrangement product, **10**. Methylation of **10** gave rutacultin, **11**. A convenient preparation of **1** and scopoletin, **6**, from aesculetin, **5**, is described.

A CONSEQUENCE of the recent investigations[2-7] of the heartwood constituents of *Ptaeroxylon obliquum* (sneezewood) has been the structural elucidation of many interesting new coumarins and chromones. In an earlier communication[3] dealing primarily with three of these chromones, we reported briefly the isolation of four new coumarins, namely **1** and **2** (which were not given trivial names), nieshoutin (**3**) and nieshoutol (**4**). Since then, Dean *et al.* has reported[5] that two of these coumarins, **2** and **3**, which they named obliquetin and cyclo-obliquetin respectively, were present amongst the many oxygen heterocycles which they isolated[5, 6] from *P. obliquum*. Herein we present information which corroborates the structures previously assigned[2, 3, 6] to three* of the sneezewood coumarins (**1**–**3**), and record details of their synthesis from aesculetin (**5**).

The existence of a coumarin nucleus in each of the $C_{15}H_{16}O_4$ isomers (**1**, **2** and **3**) was evident from their UV spectra which also indicated[7, 8] (see Table) that the coumarins were 6,7-dioxygenated. Moreover, their NMR spectra revealed that all three belonged to the class of simple coumarins bearing hydrogen at C-3 and C-4.[9]

Structure **1** was allocated to the isomer m.p. 81–82° on the basis of its conversion to scopoletin (**6**) on acid hydrolysis and its NMR spectrum which disclosed two *para* aromatic protons, one OMe group and a 3,3-dimethylallyloxy unit. In confirmation, **1** was readily derived from scopoletin by treatment with 3,3-dimethylallyl bromide and K_2CO_3 in acetone.

The related coumarin (**2**), was deduced from its NMR spectrum to contain a phenolic OH, one OMe group, one aromatic proton and a C_5H_9 residue. The five carbon fragment was present as a 1,1-dimethylallyl substituent,[10-12] since the NMR spectrum shows signals attributable to a vinyl group and two equivalent benzylic tertiary methyls. The marked change in the UV spectrum which accompanied the addition of base indicated[7] that the OH substituent was at C-7; thus since **2** is an aesculetin derivative, its OMe group must be at C-6.

The remaining coumarin, nieshoutin, which has been shown to be identical to cyclo-obliquetin (**3**) by direct comparison,† differs from **1** and **2** in the arrangement of

* Structure **4** has recently been confirmed[4] for the fourth coumarin, nieshoutol

† We are grateful to Dr. B. Parton for carrying out the direct comparisons by mixed m.p., TLC, IR and NMR

the C_5 unit which is present as a 2,3,3-trimethyldihydrofuran system. Thus signals in the NMR spectrum correspond to two benzylic tertiary methyls and a secondary methyl group on carbon bearing oxygen. Moreover, the OMe group in **3** can be placed at C-6 on the following evidence. **3** suffered demethylation on treatment with HBr/HOAc producing a phenol, **7** and the corresponding acetate. From UV evidence the intramolecularly H-bonded OH of the phenol was not at C-7. This necessitated the oxygen at C-7 to be the point of attachment of the dihydrofuran ring with the carbon residue therefore in the biogenetically more probable[13] C-8 position.

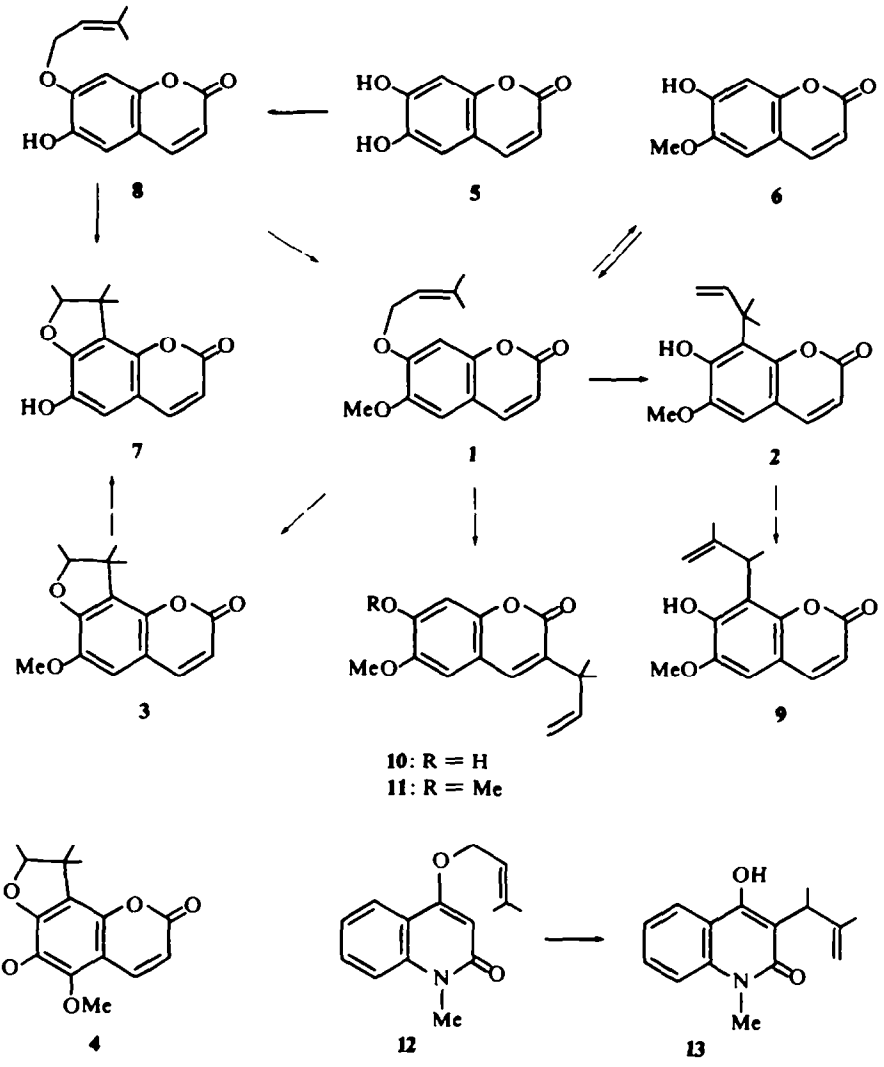
From a consideration of the structures deduced for the three coumarins, we conjectured that **2** and **3** might be derived synthetically from **1** by a Claisen rearrangement. For this purpose, **1** was prepared from scopoletin (**6**), which had been obtained by the method of Desai and Desai.[14] However, the low yields of **6** afforded[15] by this process (~20%) induced us to investigate an alternative synthesis of **1**. Thus aesculetin (**5**) when reacted with 3,3-dimethylallyl bromide and K_2CO_3 in refluxing acetone was converted in 63% yield to the 7-mono-ether* (**8**). Methylation of **8** with MeI and K_2CO_3 in acetone afforded **1** in high yield. This synthesis of **1**, when coupled with its facile acid-catalysed hydrolysis, provides a convenient synthetic route to scopoletin, the efficient preparation of which has been a subject of much interest.[17]

It has been reported[18] that pyrolyses of isoprenyl ethers of mono-oxygenated coumarins result in fragmentation to the parent phenols and isoprene. However, pyrolysis of **1** at 195°, apart from cleavage to scopoletin (30%), gave rise to three C-alkylated products. The desired *ortho* rearrangement product, **2** (9%) and its cyclised analogue, **3** (21%) were isolated and found to be identical with the samples of natural origin, thus confirming the structures which had been proposed earlier. From a consideration of related studies,[12, 19] there was the possibility that **9**, the product of an abnormal Claisen rearrangement, might have been one of the pyrolysis products.

TABLE. UV SPECTRA OF SOME DIOXYGENATED COUMARINS

Compound	λ_{max} in nm; log ε in parenthesis; *shoulder									
1	231	(4·25)	252	(3·76)	260	(3·69)	296	(3·75)	346	(4·09)
2	230	(4·08)	254	(3·60)	262	(3·56)	308*	(3·74)	346	(3·99)
2 in base			245	(3·75)	268	(3·73)			410	(4·31)
3	232	(4·19)	254	(3·50)	262	(3·46)	309*	(3·74)	346	(4·11)
6,7-diOMe-coumarin	229	(4·23)	251	(3·76)	257	(3·69)	293	(3·73)	344	(4·02)
5,7-diOMe-coumarin	218*	(4·04)	245	(3·75)	254	(3·75)	325	(4·15)		
7,8-diOMe-4-Me-coumarin	215*	(4·23)	247	(3·71)	255	(3·74)	315	(4·14)		
6	230	(4·11)	254	(3·68)	260	(3·63)	298	(3·68)	346	(4·07)
6 in base			242	(4·03)	278*	(3·64)			400	(4·36)
7	228	(4·17)	257	(3·48)	264	(3·48)	313*	(3·85)	349	(4·09)
7 in base	220	(4·44)	252	(4·28)	278	(3·73)	326	(3·80)	399	(3·92)
8	231	(4·37)	254	(3·91)	260	(3·91)	297	(3·96)	348	(4·22)
8 in base			254	(4·46)	274*	(4·06)	314	(3·98)	401	(4·00)
10	231	(4·25)	255	(3·76)	262	(3·72)	298	(3·80)	344	(4·21)
10 in base			243	(3·99)	279*	(3·67)			390	(4·40)

* Dean and Parton have also synthesised[7] this coumarin,[6, 16] by a similar procedure using dimethylsulphoxide as solvent. Under these conditions the 6-isomer is also formed[7]



Normally this was not found to be the case when preparative TLC was used to separate the reaction products. However when the reaction mixture was submitted to prolonged heating or if the phenolic components were extracted by mild base prior to TLC, **2** was absent and **9** now constituted ~10% of the mixture. The structure of **9** was evident from its NMR spectrum which was consistent with the presence of a 1,2-dimethylallyl group.[12] An investigation of this isomerisation is in progress to determine the factors involved.

The structure **10** of the third and most unexpected pyrolysis product (14%) was deduced spectroscopically. From its UV behaviour (see Table) **10** was a 7-OH-6-OMe-coumarin, while its NMR spectrum disclosed that two *para* aromatic protons were

present. However, the pair of doublets typical[9] of a 3,4-unsubstituted coumarin were absent having been replaced by a one-proton singlet at τ 2·52, the C-4 proton resonance.[9] Since there were resonances in the NMR spectrum corresponding to a 1,1-dimethylallyl substituent, this fragment must be attached to C-3. It is thought that **10** arises from **1** by a triple Claisen rearrangement[20] though whether it is a further rearrangement of the *ortho* dienone intermediate[10] leading to **2** or whether migration occurs via the C-6 *ortho* position* has not yet been clarified. Nickon and Aaronoff have shown[20] that a propenyl, but not a phenyl group can serve as an allyl acceptor in an out-of-ring Claisen migration and suggest[20] that similar rearrangements may proceed to ring systems having less aromatic character than phenyl.

The co-occurrence of the three coumarins **1–3** in sneezewood and their *in vitro* interconversion via the Claisen rearrangement might imply that their biogenesis could follow a similar pathway.[22] Significantly, Grundon *et al.* have shown[23] that in *Ravenia spectabilis*, the 3,3-dimethylallyl ether (**12**), via an abnormal Claisen rearrangement, is the biogenetic precursor of ravenoline (**13**). Again from a biogenetic viewpoint, the formation of **10** from **1** may be important bearing in mind the recent discovery[24] of a number of coumarins oxygenated at C-7 and substituted at C-3 by a 1,1-dimethylallyl group. One such coumarin, rutacultin, has recently been isolated[25] from tissue cultures of *Ruta graveolens* and its structure, **11**, now confirmed[25] by direct comparison with the methyl ether of **10**.

EXPERIMENTAL

M.ps were determined with a Kofler hot stage apparatus. IR spectra of CCl_4 solns were recorded by Mrs. F. Lawrie on a Perkin–Elmer 225 spectrometer; IR spectra of $CHCl_3$ solns were recorded on a Perkin–Elmer 257 spectrophotometer. NMR spectra of solns in $CDCl_3$ with TMS as internal standard were recorded by Mrs. S. Hamilton and Mr. J. Gall with a Varian T-60 spectrometer. Coupling constants quoted are observed values. Mass spectra were recorded by Mr. A. Ritchie with an AEI-GEC MS 12 mass spectrometer. Microanalyses were performed by Mr. J. M. L. Cameron and his staff. UV spectra were recorded for EtOH solns on a Unicam SP 800 spectrophotometer; λ (in base) refer to the above solns to which 2 drops 4N NaOH were added. Kieselgel G (Merck) was used for preparative TLC plates. Light petroleum refers to the fraction of b.p. 60–80°.

Coumarins from Ptaeroxylon obliquum

7-O-(3,3-*Dimethylallyl*) *scopoletin* (**1**). This coumarin, crystallised from ether–light petroleum as pale yellow needles, m.p. 80–81°, occurred as 0·03% of dried heartwood of *P. obliquum* (Found: C, 69·1; H, 6·1. $C_{15}H_{16}O_4$ requires: C, 69·2; H, 6·2%); mass spectral peaks at *m/e* 260(M^+), 192, 177, 164 and 149 (relative abundance 4, 100, 29, 16 and 10%); NMR signals at τ 8·24 (6H, bs), 6·12 (3H, s), 5·33 (2H, bd, J = 7Hz), 4·48 (1H, bt, J = 7Hz), 3·71 (1H, d, J = 10Hz), 3·12 (2H, s) and 2·34 (1H, d, J = 10Hz).

Hydrolysis of **1**. A soln of **1** (1g) in MeOH (20 ml) and dil HCl (20 ml) was refluxed for 2 hr then neutralised with NaOHaq. Most of the solvent was removed by evaporation and the residue diluted with iced water (100 ml). The ppt was filtered off, washed with brine and crystallised from MeOH to give **6** as colourless needles (0·65 g, 88%), m.p. 203–205° (lit.[17] 204°), identical by mixed m.p., TLC, IR and UV with an authentic sample of scopoletin.

Synthesis[15] *of* **1** *from* **6**. **6** (300 mg), AnalaR K_2CO_3 (272 mg) and freshly distilled 3,3-dimethylallyl bromide (330 mg) were stirred for 15 hr at 50° in AnalaR acetone (70 ml). After filtration and evaporation, the residue was extracted into EtOAc, the organic layer washed with $NaHCO_3$aq, with water to neutrality and dried. Freed from solvent, the resulting oil (390 mg, 96%) solidified on trituration with ether and crystallised from ether–light petroleum as needles, m.p. 80–81°, identical by mixed m.p., TLC, IR, UV and NMR with natural **1**.

* It is suggested[21] from a study of the rearrangement of catechol monoallyl ether to 3- and 4-allylcatechol that migration may proceed through both *ortho* positions

8-(1,1-*Dimethylallyl*) *scopoletin* (*obliquetin*[6]) (**2**). This unstable coumarin was isolated[3] from *P. obliquum* as pale yellow needles (from EtOAc–light petroleum) m.p. 141–143° (lit.[6] 138–139°); NMR signals at τ 8·29 (6H, s), 6·09 (3H, s), 5·02 (1H, bd, J = 11Hz), 5·00 (1H, bd, J = 18Hz), 3·79 (1H, d, J = 9·5Hz), 3·62 (1H, dd, J = 11 and 18Hz), 3·36 (1H, s) (disappears on addition of D_2O), 3·27 (1H, s) and 2·45 (1H, d, J = 9·5Hz). **2** was heated with butyric anhydride and pyridine to give the *butyrate* as a colourless oil which, after distillation at 150°/0·008 mm, solidified as a colourless solid, m.p. 104–106° (Found: C, 69·3; H, 6·65. $C_{19}H_{22}O_5$ requires: C, 69·05; H, 6·7%); NMR signals at τ 8·97 (3H, bt, J = 6·5Hz), 8·34 (6H, s), 8·24 (2H, m), 7·49 (2H, bt, J = 6·5Hz), 6·19 (3H, s), 5·12 (1H, dd, J = 10 and 1·5Hz), 5·07 (1H, dd, J = 18 and 1·5Hz), 3·71 (1H, dd, J = 10 and 18Hz), 3·66 (1H, d, J = 9·5Hz), 3·17 (1H, s) and 2·40 (1H, d, J = 9·5Hz).

Nieshoutin (*cyclo-obliquetin*[6]) (**3**). Isolated from *P. obliquum* as 0·02% dried heartwood, **3** crystallised from ether–light petroleum as pale yellow needles, m.p. 125–127° (Found: C, 69·5; H, 6·1. $C_{15}H_{16}O_4$ requires: C, 69·2; H, 6·2%); mass spectral peaks at m/e 260(M^+), 245, 231, 230, 227, 217, 213, 204 and 189 (relative abundance 100, 70, 11, 11, 15, 37, 16, 17 and 22%); NMR signals at τ 8·71 (3H, s), 8·57 (3H, d, J = 6·5Hz), 8·44 (3H, s), 6·11 (3H, s), 5·45 (1H, q, J = 6·5Hz), 3·82 (1H, d, J = 10Hz), 3·27 (1H, s) and 2·42 (1H, d, J = 10Hz).

Demethylation of nieshoutin. A soln of HBr in HOAc (45% w/v; 7 ml) was added to **3** (105 mg) in HOAc (7 ml) and the mixture heated at 75° for 18 hr. The cooled soln was poured into iced water (100 ml) and extracted with EtOAc. The organic layer was washed with brine to neutrality, dried and evaporated. The residual oil was resolved by TLC [ether–light petroleum (4:1)] into (i) *6-demethylnieshoutin*, **7** (38 mg, 36%), plates, m.p. 157–159° (from ether–light petroleum) (Found: C, 68·35; H, 5·65. $C_{14}H_{14}O_4$ requires: C, 68·3; H, 5·75%); $\nu_{max}^{CCl_4}$ 3573, 1738 and 1626 cm^{-1}; NMR signals at τ 8·71 (3H, s), 8·59 (3H, d, J = 6·5Hz), 8·43 (3H, s), 5·44 (1H, q, J = 6·5Hz), 4·50 (1H, bs) (disappears on addition of D_2O), 3·80 (1H, d, J = 9·5Hz), 3·18 (1H, s) and 2·47 (1H, d, J = 9·5Hz); (ii) recovered **3** (32 mg, 30%) identified by mixed m.p., TLC, IR and NMR: and (iii) *6-demethylnieshoutin acetate*, colourless needles (15 mg, 13%), m.p. 96·5–98° (from ether–light petroleum) (Found: C, 66·7; H, 5·7. $C_{16}H_{16}O_5$ requires: C, 66·65; H, 5·6%); NMR signals at τ 8·67 (3H, s), 8·58 (3H, d, J = 6·5Hz), 8·41 (3H, s), 7·66 (3H, s), 5·42 (1H, q, J = 6·5Hz), 3·79 (1H, d, J = 9·5Hz), 2·97 (1H, s) and 2·46 (1H, d, J = 9·5Hz).

Dimethylallylation of aesculetin. A mixture of K_2CO_3 (1 g) and **5** (1 g) in acetone (200 ml) was stirred at room temp for 2 hr. Dimethylallyl bromide (1 g) was added and the mixture refluxed for 20 hr. The inorganic solid was filtered off, washed with hot acetone, and the filtrate evaporated. The residue was dissolved in EtOAc and this soln washed repeatedly with NaOH aq (~0·5% w/v) until the basic layer was colourless. The EtOAc layer was washed with brine to neutrality, dried and evaporated. Crystallisation of the residue from ether–light petroleum afforded 6,7-bis(3,3-dimethylallyloxy) coumarin as pale yellow needles (0·40 g, 23%), m.p. 79·5–81° (lit.[7] 81°) (Found: C, 72·3; H, 7·1. Calc. for $C_{19}H_{22}O_4$: C, 72·6; H, 7·05%).

The EtOAc extract of the acidified aqueous layer was washed with brine, dried and evaporated. Crystallisation of the residue from MeOH yielded 7-O-(3,3-dimethylallyl) aesculetin (prenyletin) (**8**) as colourless needles (0·86 g, 63%), m.p. 143–144° (lit.[7] 146°) (Found: C, 68·35; H, 5·6. Calc. for $C_{14}H_{14}O_4$: C, 68·3; H, 5·75%); $\nu_{max}^{CCl_4}$ 3556, 1742 and 1631 cm^{-1}; NMR signals at τ 8·23 (6H, bs), 5·35 (2H, bd, J = 7Hz), 4·52 (1H, bt, J = 7Hz), 4·30 (1H, s) (disappears on addition of D_2O), 3·74 (1H, d, J = 10Hz), 3·19 (1H, s), 3·05 (1H, s) and 2·41 (1H, d, J = 10Hz).

7-O-(3,3-*Dimethylallyl*) *scopoletin* (**1**). K_2CO_3 (2 g) was added to a soln of **8** (1·7 g) in acetone (200 ml) and the mixture stirred at room temp for 1 hr. MeI (2·5 ml) was then added and the soln refluxed gently for 20 hr. The inorganic solids were filtered off and the solvent evaporated. The residue was dissolved in EtOAc, washed with K_2CO_3 aq (~0·5% w/v), with brine to neutrality, dried and evaporated. The residual solid on crystallisation from ether–light petroleum yielded **1** as needles (1·66 g, 91%), m.p. 80–81°.

Pyrolysis of **1**

(a) Compound **1** (500 mg) was pyrolysed at 0·05 mm in a sublimation block at 195°. Initially the material tended to sublime, so the tube was pushed further into the block. After 2 hr the oil was allowed to cool to room temp and separated by TLC ($CHCl_3$) into (i) **3**, which crystallised from ether–light petroleum as needles (106 mg, 21%), m.p. 124–125°, identified with the natural compound by mixed m.p., TLC and NMR; (ii) recovered **1** (21 mg, 4%); (iii) **2**, which crystallised from ether–light petroleum as needles (44 mg, 9%), m.p. 136–138°, identified with the natural compound by mixed m.p., TLC and NMR; (iv) 3-(1,1-*dimethylallyl*) *scopoletin* (**10**), which crystallised from light petroleum as yellow needles (71 mg, 14%), m.p. 132–135° (Found: C, 69·05; H, 6·25. $C_{15}H_{16}O_4$ requires: C, 69·2; H, 6·2%); $\nu_{max}^{CHCl_3}$ 3515, 1715–1705, 1612 and 1585 cm^{-1}; mass spectral peaks at m/e 260(M^+), 245, 217 and 205 (relative abundance 83, 83, 100 and 58%);

NMR signals at τ 8·55 (6H, s), 6·09 (3H, s), 4·96 (1H, bd, J = 18Hz), 4·93 (1H, bd, J = 10Hz), 3·82 (1H, dd, J = 18 and 10Hz), 3·65 (1H, bs) (disappears on addition of D_2O), 3·18 (1H, s), 3·14 (1H, s) and 2·51 (1H, s); and (v) **6**, needles (from MeOH) (105 mg, 30%), m.p. 203–205°.

(b) The residue from a similar pyrolysis of **1** (500 mg, 193°/0·06 mm, 2 hr) was separated with NaOH aq (0·5% w/v) into a base insoluble and a base soluble fraction. The former yielded a pale yellow oil (130 mg, 26%) which by TLC and NMR was mainly **3** with a small amount of starting material. The latter fraction was separated by TLC (2 × $CHCl_3$) into (i) 8-(1,2-*dimethylallyl*) *scopoletin* (**9**), which crystallised from ether–light petroleum as pale yellow needles (38 mg, 7·5%), m.p. 135–137° (Found: C, 69·1; H, 6·2. $C_{15}H_{16}O_4$ requires: C, 69·2; H, 6·2%); $\nu_{max}^{CHCl_3}$ 3500, 3400, 1715 and 1580 cm^{-1}; NMR signals at τ 8·49 (3H, d, J = 7Hz), 8·30 (3H, s), 6·09 (3H, s), 5·78 (1H, q, J = 7Hz), 5·03 (2H, bs), 3·75 (1H, d, J = 10Hz), 3·60 (1H, s) (disappears on addition of D_2O), 3·24 (1H, s) and 2·42 (1H, d, J = 10Hz); (ii) **10** (13%); and (iii) **6** (26%).

(c) The residue from a pyrolysis of **1** (950 mg, 195°/0·02 mm, 4 hr) was separated by TLC resulting in the isolation of **9** (10%) from the complex reaction mixture.

(d) A soln of **1** (120 mg) in N,N-diethylaniline (1 ml) and butyric anhydride (0·6 ml) was heated at 180° for 15 hr under N_2. The residual oil was separated by TLC [EtOAc–light petroleum(1:2)] into (i) 3-(1,1-*dimethylallyl*) *scopoletin butyrate* (34 mg, 22%) which after distillation at 140°/0·03 mm solidified on standing to give plates, m.p. 98–99° (Found: C, 69·25; H, 6·7. $C_{19}H_{22}O_5$ requires: C, 69·05; H, 6·7%); NMR signals at τ 8·94 (3H, t, J = 6·5Hz), 8·50 (6H, s), 8·19 (2H, m), 7·41 (2H, t, J = 6·5Hz), 6·13 (3H, s), 4·91 (1H, d, J = 18Hz), 4·88 (1H, d, J = 10Hz), 3·79 (1H, dd, J = 18 and 10Hz), 3·06 (1H, s), 2·98 (1H, s) and 2·48 (1H, s); this butyrate (26 mg, 84%) was also derived from **10** (18 mg) when kept at room temp with butyric anhydride (0·1 ml) and dry pyridine (0·2 ml) for 4 hr; (ii) obliquetin butyrate (*vide supra*) (48 mg, 31%); and (iii) *scopoletin butyrate* (46 mg, 38%) which after distillation at 135°/0·03 mm partially solidified (Found: C, 64·35; H, 5·35. $C_{14}H_{14}O_5$ requires: C, 64·1; H, 5·4%); NMR signals at τ 8·96 (3H, t, J = 7Hz), 8·21 (2H, m), 7·43 (2H, t, J = 7Hz), 6·16 (3H, s), 3·65 (1H, d, J = 9·5Hz), 3·06 (1H, s), 2·97 (1H, s) and 2·38 (1H, d, J = 9·5Hz); this compound was readily formed (31 mg, 91%) when **6** (25 mg) and butyric anhydride (0·1 ml) in dry pyridine (0·2 ml) were kept for 4 hr at room temp.

Rutacultin (**11**). A mixture of the phenol **10** (35 mg), K_2CO_3 (40 mg) and MeI (0·1 ml) in acetone (10 ml) was kept at reflux for 4 hr. Work-up (*vide supra*) gave a residue which, on crystallisation from light petroleum, afforded 3-(1,1-*dimethylallyl*)-6,7-*dimethoxycoumarin* (**11**) as pale yellow needles, m.p. 103–104°. (Found: C, 70·1; H, 6·65. $C_{16}H_{18}O_4$ requires: C, 70·05; H, 6·6%); mass spectral peaks at m/e 274(M^+), 259, 231 and 219 relative abundance 100, 80, 95 and 46%). This compound was found to be identical with natural rutacultin.[25]

Pyrolysis of **8**. **8** (150 mg) was pyrolysed in a sublimation tube at 198° under partial pressure. After 15 min the oil solidified but heating was continued for a further 25 min. The cooled residue was separated by TLC [3 × MeOH–$CHCl_3$ (1:99)] into (i) a mixture (30 mg) of at least three compounds; (ii) **7** which crystallised from ether–light petroleum as plates (15 mg, 10%), m.p. 157–159°; (iii) a mixture (23 mg) of at least two compounds; (iv) 3-(1,1-dimethylallyl) aesculetin, as a colourless solid (15 mg, 10%); NMR (in DMSO-d_6) signals at τ 8·62 (6H, s), 5·01 (1H, d, J = 18Hz), 5·00 (1H, d, J = 10Hz), 3·83 (1H, dd, J = 18 and 10Hz), 3·27 (1H, s), 2·98 (1H, s) and 2·29 (1H, s); and (v) **5** (20 mg, 19%).

Acknowledgements—Two of us (MMB and PHM) are grateful to the SRC for maintenance awards.

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