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CLAISEN REARRANGEMENTS—IV[1]

OXIDATIVE CYCLISATION OF TWO COUMARIN *o*-ISOPRENYLPHENOLS

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Abstract—Osthenol (**1**) has been found to react quantitatively with *m*-chloroperbenzoic acid in EtOAc or ether to furnish only the dihydrofuranocoumarin (±)-columbianetin (**6**). When $CHCl_3$ acidified with HCl was used, the sole product was the dihydropyranocoumarin (±)-lomatin (**7**). In a similar manner, 7-demethylsuberosin (**8**) was converted into (±) marmesin (**13**) and (±) decursinol (**14**).

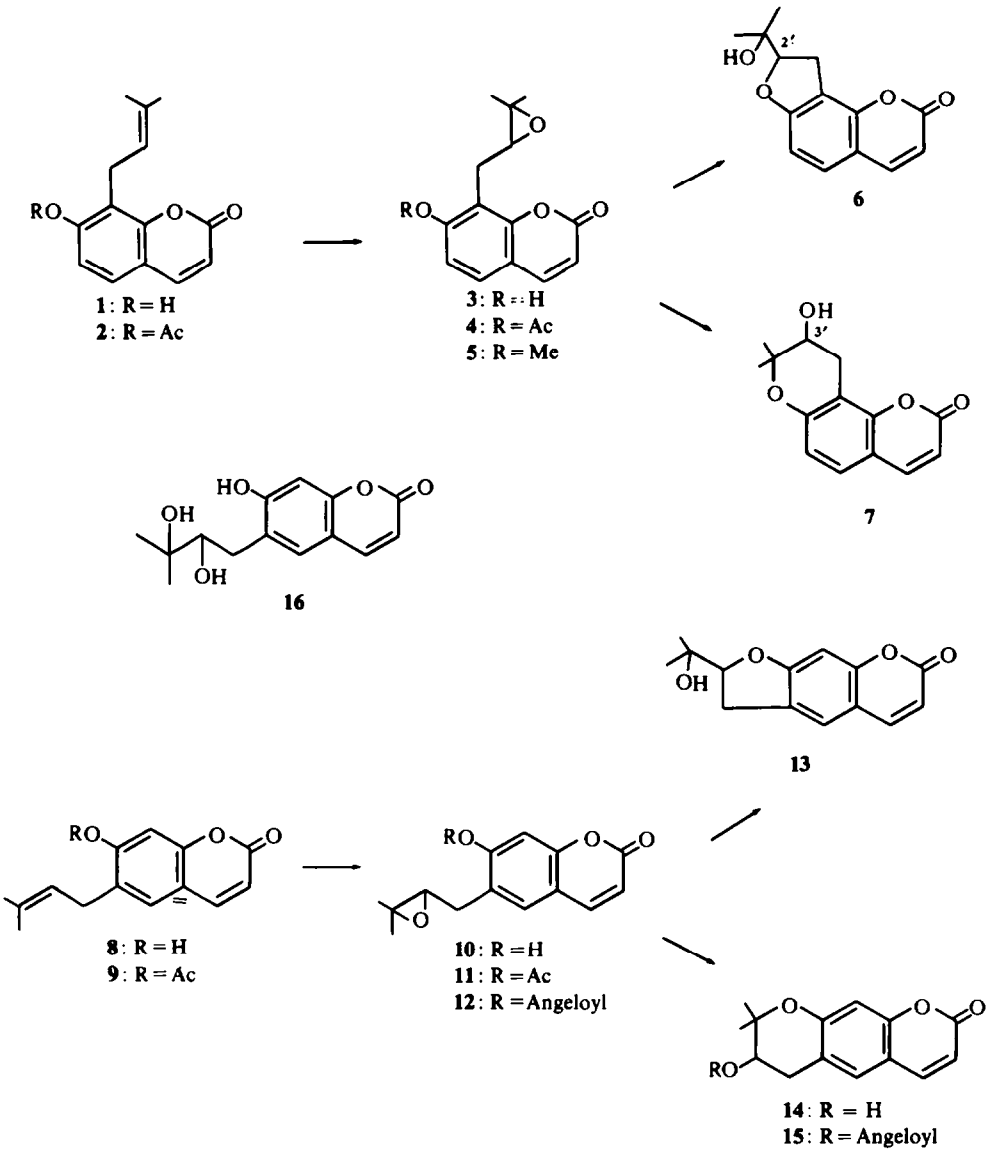
MANY NATURAL coumarins are known[2] in which the oxygenated heterocyclic nucleus is elaborated by the attachment on oxygen or carbon of at least one isoprenyl substituent. When the parent 3,3-dimethylallyl group is joined to the aromatic ring, it is invariably located *ortho* to an oxygen function as in osthenol[2](**1**) and 7-demethylsuberosin (**8**).[3] It is also common to find the C-5 unit in an oxygenated form as in meranzin[2](**5**) and peucedanol (**16**).[4] When considering the biogenesis of the 2′-(hydroxyisopropyl)dihydrofuran system,[5,6] as found in columbianetin[7] (= zozimol[8]) [**6**, 2′-(S)[9]], marmesin[10] [**13**, 2′-(S)[11]] and nodakenetin[12] [**13**, 2′-(R)[13]], or the 3′-hydroxy-2′,2′-dimethyldihydropyran system,[6] exemplified by lomatin[14] (=selinetin[15] =jatamansinol[16] =xanthogalol[17]) [**7**, 3′-(R)[6]] and decursinol*[18] [**14**, 3′-(S)[6]], either an epoxide (as in **3**) or a vicinal diol (as in **16**) may in principle[5] undergo biologically induced interaction with an *ortho* OH group. Although the exact intermediate leading to cyclisation is not yet known, it is perhaps significant that **16** is a stable compound[4] whereas the epoxyphenol (**3**) is only found naturally[2] as its methyl ether (**5**).

Our convenient three-step synthesis[1] of **1** from umbelliferone has enabled us to attempt the preparation of the epoxyphenol (**3**) and determine the conditions which might induce it to cyclise preferentially to (±)-columbianetin†(**6**) or (±)-lomatin (**7**).

Osthenol, when reacted with *m*-chloroperbenzoic acid in ether at 0° gave only one product which was identified from spectroscopic evidence (*vide infra*) as (±)-columbianetin (**6**). The observed nucleophilic opening of the epoxide ring of **3** at the less substituted carbon, leading to the dihydrofuran ring, was anticipated[27] under the effectively neutral conditions used. Identical results were obtained when EtOAc or CCl_4 were employed. However, with bench $CHCl_3$ more rapid oxidation ensured and the dihydropyranocoumarin (**7**) was now the sole product. This synthetically important result[17] can be explained if the opening of the epoxide ring in the latter

* While each of the alcohols **6**, **7**, **13** and **14** occurs naturally in one, or both, antipodal forms, they are more frequently encountered as esters. For example, the acetate[19] (libanoridine[20]), isovalerate[21], senecioate[21,22] (libanorin[23]), angelate (columbianadin[7] = zozimin[8]), epoxyangelate (columbianadinoxide[24]) and more complex esters (peulustrin[25] and isopeulustrin[24]) of columbianetin are known.

† A ten-step synthesis of **6** has recently been reported.[26]



case is catalysed by traces of HCl in the solvent with the reaction proceeding[28] *via* the more stable tertiary carbonium ion. In support of this hypothesis, **1** was again converted exclusively to **7** when AnalaR $CHCl_3$ acidified with HCl was employed as solvent. AR $CHCl_3$ however leading to a mixture of **6** and **7** (~1:2).

The reaction of 7-demethylsuberosin (**8**), which is also available synthetically[1] from umbelliferone, with *m*-chloroperbenzoic acid showed a similar solvent dependence. Using EtOAc, ether, CCl_4 or $ARCHCl_3$, only (±) marmesin (**13**) was formed. The dihydropyranocoumarin (±)-decursinol (**14**) was the sole product when $CHCl_3$

acidified with HCl was used, while reaction in $CHCl_3$ acidified with 1-naphthalenesulphonic acid was not selective, a mixture (~3:1) of **13** and **14** being produced.

The differences which osthenol and demethylsuberosin display towards oxidation with *m*-chloroperbenzoic acid in AR $CHCl_3$ indicate that **1** is more sensitive than **8** to the acidity of the medium. Similar observations were made when monoperphthalic acid was the oxidant. Thus **8** gave only (±)-marmesin, as previously reported,[3] whereas **1** under identical conditions gave a mixture of **6** and **7** (~7:3). It is clear from these results that care should be exercised in the choice of solvent and reagent for epoxidations where the possibility of further acid-catalysed reaction exists.

It is possible to differentiate between isomers containing the hydroxyisopropyldihydrofuran and hydroxydimethyldihydropyran moieties, mainly by spectroscopic methods. In the NMR spectra of the former, the methylene and methine protons constitute an A_2X system resonating at $\tau \sim 6{\cdot}7$ (2H, d) and $\tau \sim 5{\cdot}2$ (1H, t) with $J = 9$–10 Hz, while the corresponding dihydropyran protons form an ABX system at $\tau \sim 7{\cdot}2$ (2H, m) and $\tau \sim 6{\cdot}3$ (1H, t).[24,29,30] Again, the tertiary and secondary OH resonances may be distinguished by measuring the NMR spectra in DMSO when the latter signal appears as a doublet through coupling with the adjacent methine proton.[29] This phenomenon may occasionally be observed with $CDCl_3$ as solvent (see experimental).

Chemically, the secondary alcohol acetylates more readily than the tertiary, and the downfield shifts of the methine protons on acetylation, ~1·2 and ~0·25 ppm respectively, serve as an additional method of discrimination.[31]

The dihydrofuran and dihydropyran systems can readily be identified by mass spectrometry. The principal pathway of fragmentation in the former[32] is loss of C_3H_6O, giving rise to an ion (M-58) which loses a hydrogen atom to give the base peak at M-59. An abundant ion at *m/e* 59 is also characteristic.[32–34] This species is not significant in the dihydropyran spectra where fission of the chroman ring gives the fragment ions M-70 and M-71 (base peak).[35]

High resolution IR studies on the alcohols **6**, **7**, **13** and **14** show that each exhibits a free and an intramolecularly H-bonded OH stretching absorption. For the secondary alcohols, the free OH bands appear at 3630 cm^{-1}, 10 cm^{-1} higher than those of the isomeric tertiary alcohols, while the corresponding bonded OH at 3590 cm^{-1} in the former is somewhat lower in frequency than that of the tertiary. Moreover there are readily discernible differences in the relative intensities of the free and bonded OH absorptions which should be of additional diagnostic value. Thus for the secondary alcohols the free OH is more intense than the bonded (~1·8:1), based on observed optical density measurements, whereas for the tertiary alcohols the reverse is true, the ratio being ~1:2·7.

From an examination of molecular models, the secondary OH may be either equatorial or axial in the half-chair conformations[31] of the dihydropyran ring. In the former, which should be energetically more favoured, intramolecular H-bonding to the dihydropyran oxygen is not possible, thus accounting for the observed, more intense, free OH band. In the dihydrofurans however in which intramolecular H-bonding is found to be more important, models show that the hydroxyisopropyl group will probably exist preferentially in a conformation in which the tertiary OH is H-bonded to the dihydrofuran oxygen.

At the outset of this work it was hoped that some evidence for the existence of the presumed epoxyphenol intermediates (**3** and **10**) might be adduced. However, it

would appear from our results that the epoxide ring, if formed, must undergo very rapid interaction with the phenolic OH.[27] With this in mind, the phenols **1** and **8** were acetylated prior to epoxidation. Both epoxyacetates (**4** and **11**), while substantially pure by NMR and TLC could neither be obtained crystalline nor freed from a small amount of **6** or **13**. Indeed, **4** and **11** were very sensitive to hydrolysis, both on TLC and with mild base, producing exclusively in each case the dihydrofuranocoumarin (**6** or **13**), the product which would have been anticipated from cyclisation of **3** or **10** under alkaline conditions.[27] In this context, it is interesting that Nielsen and Lemmich recently proposed[31] **12** as an alternative structure for the natural coumarin **15** on the premise that the observed hydrolysis product **14** could be derived from **12** on saponification. **15** was the preferred structure on spectroscopic grounds and **12** may now be firmly discounted on the basis of our observations.

Although oxidative cyclisations of *ortho*-isoprenylphenols initiated by peracids and leading generally to dihydrofurans have previously been reported,[3,34*] this study has served to demonstrate an extension of the synthetic utility of this reaction. By the correct choice of solvent, or the formation and subsequent hydrolysis of the epoxyacetates, cyclisation can be directed to produce either a five- or a six-membered ring exclusively. This procedure obviates the necessity for careful separation of mixtures of cyclic isomeric products.

EXPERIMENTAL

M.ps were determined with a Kofler hot stage. IR spectra (in CCl_4) were recorded by Mrs. F. Lawrie on Perkin–Elmer 225 and Unicam SP 100 spectrophotometers. NMR spectra (in $CDCl_3$) with TMS as internal standard were recorded by Mr. A. Haetzman 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. Kieselgel G (Merck) was used for prep. TLC. Alumina refers to Woelm basic. grade I. Light petroleum refers to the fraction of b.p. 60–80°. Unless otherwise stated. 85% *m*-chloroperbenzoic acid was employed for oxidations.

(±)-*Columbianetin* **6**. A cooled soln of the peracid (62 mg) in dry ether (2 ml) was added to a soln of **1** (60 mg) in ether (15 ml) at 0°. After 2½ hr. more peracid (15 mg) was added and the mixture stirred at 0° for 5 hr until TLC showed that reaction was complete. The mixture was filtered through a short column of alumina (0·5 g) which was further eluted with EtOAc. The combined eluates on evaporation gave (±)-columbianetin (53 mg, 83%) needles (from $CHCl_3$-light petroleum), m.p. 169–171° (lit.[26] 170–171°); NMR: τ 8·73 (3H. s). 8·63 (3H. s). 7·90 (1H. bs. disappears on addn of D_2O). 6·70 (2H. d, $J = 10$ Hz). 5·23 (1H. t, $J = 10$ Hz), 3·85 (1H, d, $J = 9·5$ Hz), 3·28 (1H, d, $J = 9$ Hz), 2·78 (1H, d, $J = 9$ Hz) and 2·42 (1H, d, $J = 9·5$ Hz); mass spectral peaks[32] at *m/e* 246 (M^+). 213. 188. 187. 176. 175. 160. 159. 131. 77 and 59 (relative abundance 43. 17. 86. 100. 15. 16. 37. 16. 24. 17 and 70%); ν_{max} 3620 and 3598 cm^{-1}.

(±)-*Lomatin* **7**. A soln of the peracid (50 mg) in AnalaR $CHCl_3$ (2 ml) was added to a soln of **1** (49 mg) in acidified $CHCl_3$ (1 ml) (prepared by shaking AnalaR $CHCl_3$ (50 ml) with 2 drops conc HCl) at 0°. After 20 min work-up as above gave (±)-lomatin (40 mg, 76%). needles (from EtOAc-light petroleum), m.p. 163–164° (lit.[36] 165–166°); NMR: τ 8·65 (3H. s) 8·62 (3H. s). 7·58 (1H. bs. disappears on addn of D_2O). 7·02 and 6·95 (2H. dd. $J = 17$ and 5 Hz). 6·13 (1H. t. $J = 5$ Hz). 3·80 (1H. d. $J = 9·5$ Hz). 3·25 (1H. d. $J = 9$ Hz). 2·78 (1H. d. $J = 9$Hz) and 2·43 (1H. d, $J = 9·5$ Hz); mass spectral peaks†. [35] at *m/e* 246 (M^+). 213. 188. 187. 177. 176. 175. 147. 91. 77. 71 and 43 (relative abundance 43. 12. 14. 12. 13. 100. 62. 13. 17. 11. 22 and 42%); ν_{max} 3630 and 3592 cm^{-1}.

(±)-*Marmesin* **13**. A soln of the peracid (20 mg) in EtOAc (3 ml) was kept with a soln of **8** (23 mg) in EtOAc (3 ml) at 0° for 4 hr. Work up afforded (±) marmesin (17·5 mg. 71%). plates (from benzene), m.p. 150–152° (lit.[3] 152–153°); NMR: τ 8·73 (3H. s), 8·62 (3H. s). 7·67 (1H. bs. disappears on addn of D_2O). 6·78 (2H. d.

* o-Allylphenol[38] and 3-isoprenylquinolones[27,29] also cyclise to dihydrofuran derivatives, through with the latter. dihydropyrans are sometimes observed.[29]

† The mass spectrum of **7** published by Das *et al.*[37] would appear to be in error.

$J = 9{\cdot}5$ Hz). 5·27 (1H, t, $J = 9{\cdot}5$ Hz). 3·87 (1H, d, $J = 9{\cdot}5$ Hz), 3·38 (1H, s), 2·83 (1H, s) and 2·47 (1H, d, $J = 9{\cdot}5$ Hz); mass spectral peaks[33] at *m/e* 246 (M^+). 213, 189, 188, 187, 175, 160, 159, 131, 77 and 59 (relative abundance 49, 24, 12, 85, 100, 16, 34, 14, 24, 15 and 60%); ν_{max} 3621 and 3596 cm^{-1}.

(±)-*Decursinol* **14**. A soln of the peracid (210 mg) in acidified $CHCl_3$ (3 ml) and a soln of **8** (207 mg) in acidified AnalaR $CHCl_3$ (3·5 ml) were mixed and kept at 0° for 1 hr. Work up gave (±)-decursinol (169 mg, 76%). needles (from EtOAc-light petroleum), m.p. 167–168° (lit.[31] 167·5–168·5°); NMR: τ 8·62 (6H, s), 7·37 (1H, d, $J = 6$ Hz, disappears on addn of D_2O), 7·13 and 7·00 (2H, dd, $J = 17$ and 5 Hz), 6·15 (1H, m, collapses to t, $J = 5$ Hz on addn of D_2O), 3·88 (1H, d, $J = 9{\cdot}5$ Hz), 3·32 (1H, s), 2·88 (1H, s) and 2·48 (1H, d, $J = 9{\cdot}5$ Hz); mass spectral peaks at *m/e* 246 (M^+), 213, 188, 187, 177, 176, 175, 148, 147, 91, 77, 71, 69, 51 and 43 (relative abundance 59, 10, 18, 13, 13, 100, 100, 11, 28, 15, 17, 27, 18, 17 and 53%); ν_{max} 3632 and 3588 cm^{-1}.

Pilot scale epoxidations. A cooled (0°) soln of the phenol (5 mg) in solvent (0·5–3 ml) and a cooled soln of the peracid (5 mg) in solvent (0·5–3 ml) were mixed and kept at 0° for 25–60 min, until no starting material could be detected by TLC. The dihydrofurocoumarins (**6** or **13**) can be readily distinguished from the dihydropyranocoumarins (**7** or **14**) by TLC in MeOH-$CHCl_3$ (1:199) with examination under UV light (λ 354 nm) and development with iodine.

(i) *7-demethylsuberosin*. (a) With EtOAc, CCl_4, ether and AnalaR $CHCl_3$, only **13** was formed; (b) with 'bench' $CHCl_3$ or AnalaR $CHCl_3$ acidified with HCl, the mixture turned yellow after 10 sec. After 5 min reaction was complete, the colour faded and only **14** was formed; (c) with AnalaR $CHCl_3$ and 1 ml of a saturated $CHCl_3$ soln of 1-naphthalenesulphonic acid there was no colour change but after 1 hr a mixture of **13** and **14** (~3:1) was formed; (d) With monoperphthalic acid in ether, only **13** was formed.

(ii) *Osthenol*. (a) With EtOAc, CCl_4 and ether only **6** was formed; (b) with bench $CHCl_3$ only **7** was formed; (c) with AR $CHCl_3$ a mixture (~1:2) of **6** and **7** was formed; (d) with monoperphthalic acid in ether a mixture of **6** and **7** (~7:3) was produced.

Osthenol acetate **2**. A soln of osthenol (44 mg) in Ac_2O (0·2 ml) containing pyridine (2 drops) was refluxed for 20 min. The cooled soln was poured into iced water and extracted with EtOAc. The organic layer was washed with $NaHCO_3$ aq (10%), with brine to neutrality, dried and evaporated. Crystallisation from aq EtOH gave the *acetate* as needles (44 mg, 85%), m.p. 94–95° (Found: C, 70·65; H, 5·85. $C_{16}H_{16}O_4$ requires: C, 70·6, H, 5·9%). NMR: τ 8·32 (3H, bs), 8·18 (3H, bs), 7·65 (3H, s) 6·52 (2H, bd, $J = 7$ Hz), 4·85 (1H, bt, $J = 7$ Hz), 3·63 (1H, d, $J = 9{\cdot}5$ Hz), 3·02 (1H, d, $J = 9$ Hz), 2·67 (1H, d, $J = 9$ Hz) and 2·37 (1H, d, $J = 9{\cdot}5$ Hz).

Epoxidation of **2** *and hydrolysis*. A soln of **2** (112 mg) in ether (6 ml) and a soln of the peracid (172 mg) in ether (3 ml) were mixed and kept for 1 hr. Work up gave the epoxyacetate (**4**) as a gum (99 mg, 84%). Although it was possible to separate **4** completely from small amounts of **6** by prep. TLC in MeOH–$CHCl_3$ (1:399), the recovered **4** always contained small amounts of **6**. **4** shows NMR signals at τ 8·68 (3H, s), 8·50 (3H, s), 7·62 (3H, s), 7·3–6·6 (3H, m), 3·63 (1H, d, $J = 9{\cdot}5$ Hz), 2·98 (1H, d, $J = 9$ Hz), 2·62 (1H, d, $J = 9$ Hz) and 2·35 (1H, d, $J = 9{\cdot}5$ Hz). The epoxyacetate (50 mg) in MeOH (10 ml) was stirred with 2% Na_2CO_3 (1 ml) for 1 min. Acidification with dil HCl and extraction into EtOAc gave (±)-columbianetin (43 mg, 94%), m.p. 169–171° after sublimation at 170°/0·02 mm and crystallisation from $CHCl_3$-light petroleum.

7-Demethylsuberosin acetate **9**. **9** (47 mg, 92%) derived from 7-demethylsuberosin (43 mg) crystallised from ether-light petroleum as prisms, m.p. 97–98° (lit.[3] 98–100°); NMR: τ 8·30 (3H, bs), 8·23 (3H, bs), 7·65 (3H, s), 6·73 (2H, bd, $J = 7$ Hz), 4·73 (1H, bt, $J = 7$ Hz), 3·65 (1H, d, $J = 9{\cdot}5$ Hz), 2·97 (1H, s), 2·72 (1H, s) and 2·37 (1H, d, $J = 9{\cdot}5$ Hz).

Epoxidation of **9** *and hydrolysis*. A soln of the peracid (131 mg) in EtOAc (1 ml) and a soln of **9** (150 mg) in EtAOc (8 ml) were mixed and kept for 1½ hr. Work up followed by purification on TLC ($CHCl_3$) gave the epoxyacetate (**11**) as a glass (116 mg), which always contained small amounts of **13**. **11** shows NMR signals at τ 8·63 (3H, s), 8·60 (3H, s), 7·60 (3H, s), 7·4–6·9 (3H, m) 3·72 (1H, d, $J = 9{\cdot}5$ Hz), 2·98 (1H, s), 2·60 (1H, s) and 2·40 (1H, d, $J = 9{\cdot}5$ Hz). **11** (70 mg) in MeOH (5 ml) was stirred for 1 min with 2% Na_2CO_3 aq (1 ml). Work up gave (±) marmesin, m.p. 150–152° (57 mg, 95%).

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