Tetrahedron. Vol. 31, pp. 2966 to 2971. Pergamon Press 1975. Printed in Great Britain

CLAISEN REARRANGEMENTS—VII[1]

NOVEL REACTIONS OF THE COUMARIN, TOMENTIN

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(*Received in the UK 3 June 1975; Accepted for publication 3 July 1975*)

Abstract—The structure of tomentin has been confirmed as 5-hydroxy-6,7-dimethoxycoumarin (**2**), the derived 3,3-dimethylallyl ether giving a *para*-Claisen rearrangement product. Relief of strain in the corresponding 1,1-dimethylallyl ether has been found to result in a novel regiospecific *ortho*-Claisen rearrangement occurring on silica at room temperature. The structure **18** of the stable *ortho*-dienone formed has been confirmed by conversion of the corresponding dehydrodienone (**15**), obtained from the rearrangement of tomentin 1,1-dimethylpropargyl ether, to alloxanthoxyletin (**25**).

Recently, a new coumarin glycoside, tomenin, $C_{17}H_{20}O_{10}$, was isolated by one of us[2] from *Prunus tomentosa* wood. On acid hydrolysis, tomenin afforded glucose and a phenolic aglycone, tomentin, containing two OMe groups. A 5,6,7-trioxygenated coumarin nucleus followed from the identity of the methyl ethers of tomentin and fraxinol[3] (**1**), but since tomentin acetate and fraxinol acetate[3] were different, tomentin was necessarily either the 5-hydroxycoumarin (**2**) or the 7-isomer (**7**). Colour tests, which can however be misleading,[4] indicated that tomentin possessed structure **2**, but in the absence of chemical evidence, structure **7**, which has more recently been allocated[5] on spectral grounds to a new coumarin from *Artemisia scotina*, could not be rigorously excluded.

We felt that any ambiguity could be resolved by examination of the product from Claisen rearrangement of an unsymmetrically-substituted allyl ether of tomentin. Thus from the readily derivable 3,3-dimethylallyl ether, a *para* rearrangement[4,6] should result from **3** with a consequent double inversion of the allyl group giving **9**, whereas **8** should undergo an *ortho* rearrangement[4,7,8] to **11**. The NMR spectrum of the product would readily indicate[4,9] which pathway had been followed. Moreover, the Claisen rearrangement could serve a dual purpose, for if **11** were produced, it would possess the same carbon framework and oxygenation pattern as nieshoutol[10] (**13**), the sternutatory constituent of sneezewood, *Ptaeroxylon obliquum*.

From the practical viewpoint, the first-formed *ortho* Claisen rearrangement product of a 3,3-dimethylallyl aryl ether is prone to cyclise[4,7] to a dihydrofuran and may also undergo further rearrangement[7,11] under the reaction conditions; fission of the ether to isoprene and the parent phenol can also occur.[7,12] However, by carrying out the pyrolysis in the presence of butyric anhydride,[8,11] the first-formed phenol is trapped as its butyrate thereby preventing further reaction. The NMR spectrum of the butyrate, obtained in good yield when tomentin 3,3-dimethylallyl ether was heated in diethylaniline containing butyric anhydride, disclosed the characteristic resonances for a 3,3-dimethylallyl group attached to carbon[9] (Experimental). A *para* Claisen rearrangement had therefore presumably occurred providing strong support for the structure **2** originally proposed[2] for tomentin. Albeit unlikely, it was possible that the C-prenyl group could have arisen from an anomalous *ortho* rearrangement.[13] This possibility was however readily discounted for the phenol (**9**), obtained on hydrolysis of the butyrate, shows no OH-π H-bonding[8] in its IR spectrum. Moreover, the phenol was stable to hot acid, conditions which would have resulted in cyclisation to a dihydrofuran[14] had the phenolic OH and the dimethylallyl moiety enjoyed an *ortho* relationship. Additional NMR evidence for tomentin being the 5-hydroxycoumarin (**2**) came from the characteristic shielding[10] of the C-4 proton (0·23 ppm) in the spectrum of the derived toluene-*p*-sulphonate (**4**) compared with that of the parent phenol.

Since the structure of nieshoutol (**13**) has been deduced primarily from spectral evidence,[10] it was of interest to attempt to effect a partial synthesis of **13** from tomentin. It was envisaged that insertion of the requisite 5-carbon fragment at C-8 might be accomplished by the *para* Claisen rearrangement of the 1,1-dimethylallyl ether (**6**). Although the *ortho* rearrangement of 1,1-dimethylallyl aryl ethers is a known method for the insertion of a prenyl group *ortho* to a phenol,[15,16] the possibility of a *para* Claisen rearrangement in such an ether where both *ortho* positions are blocked has not yet been realised.

The desired ether (**6**) was in principle derivable from the corresponding acetylenic ether (**5**) by partial hydrogenation.[15,16] Accordingly, tomentin was refluxed with 2-chloro-2-methylbut-3-yne, K_2CO_3 and KI in 2% aqueous acetone for 54 hr giving the ether **5** (45%). The spectral data for this compound were in complete accord with the proposed structure. In addition, three major by-products were detected. The least polar on TLC, a gummy coumarin (6%), was assigned structure **14** on the basis of its NMR spectrum which disclosed signals for two 1,1-dimethylpropargyl residues but no aromatic proton resonance. The structures of the remaining two compounds (11%), non-coumarin isomers of **5**, isolated as an inseparable 1:1 mixture, was not immediately apparent (*vide infra*).

The acetylenic ether (**5**) readily absorbed 1 mole of hydrogen when hydrogenated over 5% Pd-C poisoned with a carefully determined quantity of sulphur and

quinoline in xylene. After removal of the catalyst, by filtration through Celite, preparative TLC afforded in good yield a sharp-melting, bright yellow crystalline solid having the required formula, $C_{16}H_{18}O_5$. The spectral data of this compound were however not at all like those expected for a coumarin dimethylallyl ether. In contrast to **3** which shows maxima at 319 and 255 nm (log ϵ 4·07 and 3·66) and no base shift, the yellow solid exhibited maxima at 380, 316 and 257 nm (log ϵ 3·70, 3·95 and 3·82) which shifted to 338, 276 and 254 nm (log ϵ 3·84, 3·73 and 4·04) on addition of base. Furthermore two intense bands at 1678 and 1535 cm^{-1} were present in the IR spectrum of the hydrogenation product, though absent in the IR spectrum of **3**, while the α-pyrone CO band at 1760 cm^{-1} remained. The NMR spectrum disclosed signals at δ 1·53 (3H, bs), 1·60 (3H, bs), 2·70 (2H, d, J = 8·5 Hz), 3·15 (3H, s), 3·93 (3H, s), 4·87 (1H, bt, J = 8·5 Hz), 5·77 (1H, s), 6·08 (1H, d, J = 9·5 Hz) and 7·82 (1H, d, J = 9·5 Hz). It was immediately apparent that the expected 1,1-dimethylallyl unit was missing having been replaced by a 3,3-dimethylallyl unit, which, from the chemical shift of the methylene protons at δ 2·70, was attached to saturated carbon. Moreover, the single aromatic proton had shifted upfield from δ 6·42 in **2** to δ 5·77 while the two OMe resonances were now well split (δ 3·15 and 3·93) as compared with tomentin (δ 3·83 and 3·85) and its 3,3-dimethylallyl ether (δ 3·87 and 3·93).

Only the two cyclohexadienone structures (**18** or **19**) appeared to us to accommodate the spectral data, it being concluded that the ether (**6**), when formed, must have undergone an *ortho* Claisen rearrangement either spontaneously or during the isolation procedure. On TLC, the crude hydrogenation product gave an intense blue fluorescent spot anticipated for the coumarin ether structure **6**, but this turned yellow within a few seconds. During work up, even when the hydrogenation catalyst was rapidly removed using the minimum of Celite, 20% of rearrangement to the enone ensued, but the product did give NMR signals typical of a 1,1-dimethylallyl ether.[15] Whereas an EtOAc solution of this ether was stable to reflux, a clean, high yield conversion to the yellow enone took place rapidly at room temperature on addition of small amounts of Celite or Kieselgel G.

A new type of charge-induced Claisen rearrangement[17] had thus obtained, the sterically congested ether (**6**) giving rise at room temperature to only one product (**18** or **19**). From the spectroscopic data it was not however immediately apparent to which blocked *ortho* position this remarkably facile sigmatropic rearrangement had proceeded. Nonetheless, the significant difference in chemical shifts of the two OMe resonances mitigated in favour of **18**, while this structure satisfactorily accounted for the intense band at 1535 cm^{-1} which was attributed to the extended conjugation from the 7-OMe through to the pyrone CO group.

It was felt that chemical support for structure **18** could be obtained by reduction of the ketone group followed by aromatisation with loss of MeOH which should give the phenol (**21**), the synthetic precursor[1] of toddaculin (**22**). Sodium borohydride smoothly reduced the cyclohexadienone to the corresponding alcohol (**20**) which readily aromatised on treatment with hot methanolic acid or on pyrolysis at 195°. The product in each case however was 6,7-dimethoxycoumarin. Presumably protonation of **20** and loss of H_2O gave a carbonium ion which then suffered a retro-Friedel-Crafts fission of the resonance stabilised alkenyl group in preference to the desired C-OMe cleavage. This ease of loss of the C_5 fragment was also found on acid treatment of the parent enone (**18**) when tomentin (**2**) was the only isolable product. Since either structure (**18** or **19**) could have given these results, the thermal rearrangement of **5** was now studied in order to obtain definitive chemical evidence for **18**, rather than **19**, as the structure of the rearrangement product of **6**.

Unlike the corresponding 1,1-dimethylallyl ether (**6**), the 1,1-dimethylpropargyl ether (**5**) was stable to silica but rearranged smoothly on pyrolysis at 130° to give only one *ortho* rearrangement product, a bright yellow solid later shown to be **15**. The UV spectrum of **15** is virtually identical to that of the cyclohexadienone obtained on rearrangement of **6** indicating that both had undergone Claisen rearrangement to the same *ortho* position. In the IR, intense bands at 1763 (pyrone), 1681 (enone) and 1538 cm^{-1} and a weak band at 1970 cm^{-1} (allene) were present, while the NMR spectrum disclosed a dimethylallenyl group attached to saturated carbon [δ 1·60 and 1·65 (each 3H, d, J = 3 Hz) and 5·12 (1H, septet, J = 3 Hz)][18] with similar chemical shift differences for the two OMe resonances (δ 3·21 and 3·87) as found for **18**.

Comparison of the mass spectra of **15** and **18** was most revealing. Whereas in the latter, the principle fragmentation pathway involved the rapid loss of the C_5 moiety, a fission which had already been noted chemically, the spectrum of the former revealed that loss of OMe was a facile process, the dimethylallenyl unit being retained until a fairly late stage in the breakdown. These observations encouraged us to attempt the elimination of MeOH from the alcohol (**23**) obtained on sodium borohydride reduction of **15**. When a solution of **23** in methanolic acid was warmed, MeOH was indeed eliminated, but the expected *o*-allenylphenol (**24**) proved unstable under the reaction conditions and cyclised to the corresponding chromenocoumarin, alloxanthoxyletin (**25**),[19] as the only isolable product. This however provided unequivocal evidence for the orientation of the C_5 side chain in **15**, and by inference, in **18**. Thus in the Claisen rearrangements of **5** and **6**, the former thermally and the latter induced by silica at room temperature, rearrangement in both cases had resulted in exclusive migration to the only *ortho* C atom bearing an oxygen substituent. Examples are known[20] where the *ortho-para* product distribution obtained from Claisen rearrangement of a substrate having an oxygen substituent on one *ortho* position accords with a preference for the allyl group to migrate via the oxygenated position. The regiospecificity observed in the Claisen rearrangements of **5** (and **6**) can however be interpreted more convincingly in terms of stabilisation of the transition states leading to the possible products (**18** or **19**).[21] In the rearrangement of **6** to **18**, delocalisation with the pyrone ring is retained, whereas this is lost in the transition state leading to **19**, and significantly no trace of this latter compound could be detected. It is noteworthy that the ether (**14**) also underwent similar regiospecific *ortho* migration at 150° in high yield, the spectral properties of the product being completely consistent with structure (**27**).

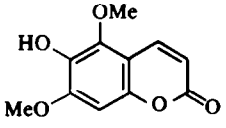
The remarkably rapid rearrangement of **6** on silica at room temperature can be attributed to two factors. It can be seen from models that there is considerable relief of strain in proceeding from **6**, with its bulky 1,1-dimethylallyl group, to the enone. Similar steric reasons have been advanced for the marked rate enhancement in the thermal cyclisation of propargyl ethers to chromenes when both α positions of the propargyl group carry

methyl substituents, the so-called *gem*-dimethyl effect.[22] The driving force for the rearrangement of **6** being alleviation of steric congestion, it would appear that silica is bringing about similar C–O bond weakening as is ascribed to boron trichloride[17] and trifluoroacetic acid[23] in charge-induced Claisen rearrangements, the rate of which can be increased by a factor of $\sim 10^{10}$ relative to the thermal reaction.[17]

It is most unusual to find an *ortho*-dienone like **18** as the stable product in the rearrangement of an allyl ether of a phenol having both *ortho* positions blocked, but having the *para* position free.[20] Thus the 3,3-dimethylallyl ether (**3**) smoothly underwent the *para* Claisen rearrangement to the *para*-(3,3-dimethylallyl)phenol (**9**), presumably via the *ortho*-dienone (**26**). However, the isomeric *ortho*-dienone (**18**) derived from **6**, differing only in the position of attachment of the two Me groups on the allyl moiety, was thermally stable, being recovered unchanged after heating to 200°. No trace of the expected phenol (**12**) was detected and consequently the desired interconversion with nieshoutol (**13**) has yet to be realised. Undoubtedly, further rearrangement of **18** to the *para*-dienone corresponding to **12** would result in a significant increase in steric congestion[24] thereby accounting for the thermal stability of **18**. Conversely, the further rearrangement of the *ortho*-dienone (**26**) will result in a comparable relief of steric strain, and consequently a *para* Claisen rearrangement is observed for **3**.

With the rearrangement product (**15**) of the propargyl ether (**5**) to hand, it could be deduced from NMR that the yellow glass obtained in the condensation of tomentin with 2 - chloro - 2 - methylbut - 3 - yne (*vide supra*) was a 1 : 1 mixture of **15** and **16** which were separable by careful distillation. The more volatile isomer (**16**) was colourless and, possessing a less extensive chromophore than **15**, had a much simpler UV spectrum and significantly showed no strong absorption around 1530 cm^{-1} in its IR spectrum. Whereas the NMR spectra of the two isomers were virtually identical, their mass spectra differed significantly in that **16** lost the C_5 moiety immediately to give the base peak.

The pathway by which **15** and **16** are formed during the alkylation of **2** remains unresolved. Treatment of tomentin with 2 - chloro - 2 - methylbut - 3 - yne has resulted in O-alkylation and C-alkylation at the *para* position and both *ortho* positions of the phenol. Whereas reaction at oxygen and the *para* position resulted in exclusive introduction of a 1,1-dimethylpropargyl residue, alkylation at the two *ortho* positions resulted in exclusive introduction of a 3,3-dimethylallenyl group. 2 - Chloro - 2 - methylbut - 3 - yne is known to alkylate 2,4,6-trimethylphenol,[25] but in an ambident manner, giving mixtures of dimethylpropargyl and dimethylallenyl ethers and C-alkylated products. In tomentin, reaction of the alkynyl halide at the two *ortho* positions with sole introduction of the dimethylallenyl group is readily explicable on steric grounds. Using the same argument, reaction at the crowded *para* position should proceed similarly, models showing that severe steric compression results from the introduction of a dimethylpropargyl group; nonetheless, this is observed. To account more satisfactorily for the co-formation of **14**, **15** and **16**, it is suggested that tomentin reacts directly with the alkynyl halide but only at oxygen and the *para* position, giving **6** and the *para*-dienone (**17**). When **17** enolises, the resultant phenol is trapped by further O-alkylation to give **14**. Models show however that enolisation of **17** leads to a further increase in steric crowding and it is therefore conceivable that steric congestion in **17** is relieved by a *para* to *ortho* sigmatropic rearrangement and that **15** and **16** arise directly from **17**.



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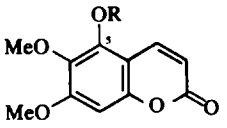
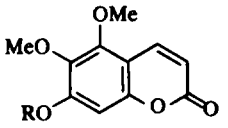
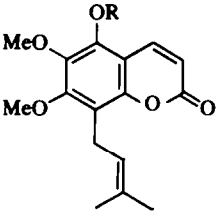


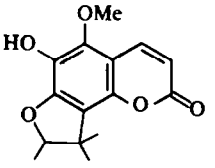
2: R = H
3: R = $CH_2CH{=}CMe_2$
4: R = Tos
5: R = $CMe_2C{\equiv}CH$
6: R = $CMe_2CH{=}CH_2$



7: R = H
8: R = $CH_2CH{=}CMe_2$



9: R = H
10: R = COPr



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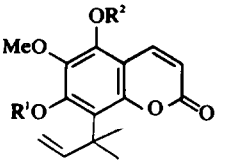
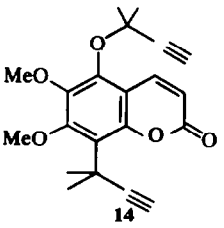


11: R' = H, R² = Me
12: R' = Me, R² = H



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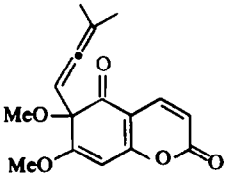

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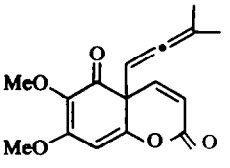

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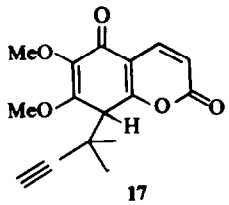
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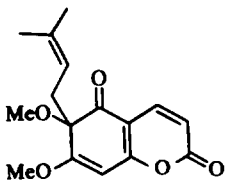
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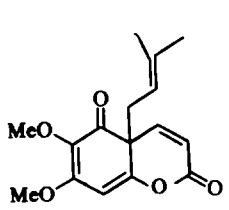
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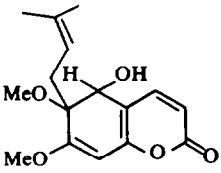
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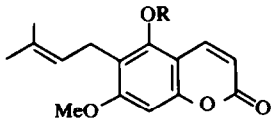
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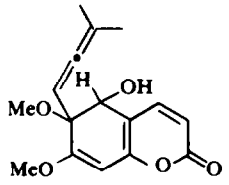
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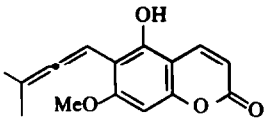
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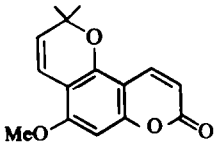
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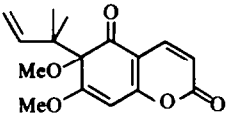
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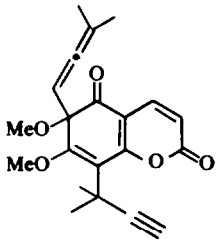
27

EXPERIMENTAL

M.ps were determined with a Kofler hot stage apparatus. IR spectra of CCl_4 solns were recorded on a Perkin Elmer 225 spectrophotometer. NMR spectra of solns in $CDCl_3$ with TMS as internal standard were recorded by Mr. J. Gall on a Varian T-60 or a Varian HA-100 spectrometer. Mass spectra were recorded by Mr. A. Ritchie with an AEI-GEC MS 12 mass spectrometer. UV spectra were recorded on a Unicam SP 800 spectrometer and refer to EtOH solns; λ_{max} (base) refers to EtOH solns to which 2 drops of 4N NaOH were added. Microanalyses were performed by Miss F. Cowan and her staff. Kieselgel G (Merck) was used for preparative TLC. Light petroleum refers to the fraction of b.p. 60–80°.

Tomentin. Tomentin[2] (2) showed NMR signals at δ 3·83 and 3·85 (each 3H, s), 6·19 (1H, d, J = 9·5 Hz), 6·31 and 6·42 (each 1H, s) and 7·98 (1H, d, J = 9·5 Hz); λ_{max} 323, 255 (sh) and 230 (sh) nm (log ϵ 4·13, 3·54 and 4·06), λ_{max} (base) 390, 333, 269 and 245 (sh) nm (log ϵ 3·68, 4·02, 3·88 and 3·95); mass spectral peaks at *m/e* 222 (M^+, 73%), 208 (12), 207 (100), 179 (19), 151 (42), 95 (19) and 69 (18). A soln of 2 (23 mg) and toluene-*p*-sulphonyl chloride (25 mg) in pyridine (1 ml) was kept for 75 hr, a further 20 mg toluene-*p*-sulphonyl chloride added and the soln left for 4 days. Work up gave a yellow glass (34 mg) which was separated by TLC (MeOH-$CHCl_3$, 1:199) into (i) *tomentin toluene-p-sulphonate* (4; 19 mg, 49%, 94% conversion), plates, m.p. 176–177° (from EtOAc) (Found: C, 57·25; H, 4·4. $C_{18}H_{16}O_7S$ requires: C, 57·45; H, 4·3%); λ_{max} 331, 296 and 255 (sh) nm (log ϵ 4·03, 3·98 and 3·96); NMR signals at δ 2·48, 3·63 and 3·93 (each 3H, s), 6·25 (1H, d, J = 9·5 Hz), 6·78 (1H, s), 7·37 (2H, d, J = 8 Hz), 7·75 (1H, d, J = 9·5 Hz) and 7·88 (2H, d, J = 8 Hz); mass spectral peaks at *m/e* 376 (M^+, 31%), 222 (77), 193 (100), 178 (15), 150 (15), 91 (41) and 69 (15); and (ii) tomentin (11 mg).

Pyrolysis of tomentin prenyl ether. Tomentin (70 mg) was added to a stirred suspension of K_2CO_3 (50 mg) in acetone (12 ml) and kept for 1 hr. 1 - Bromo - 3 - methylbut - 2 - ene (60 mg) was added and the mixture refluxed for 2 hr. After filtration and evaporation, the residue was dissolved in EtOAc and brine and the organic layer washed with K_2CO_3 aq (0·5% w/v), brine to neutrality and dried. 5 - O - (3 - *methylbut* - 2 - *enyl*) *tomentin* (3: 84 mg, 92%) crystallised from aqueous MeOH as plates, m.p. 80–81° (Found: C, 66·15; H, 6·15. $C_{16}H_{18}O_5$ requires: C, 66·2; H, 6·25%); ν_{max} 1744 and 1608 cm^{-1}; λ_{max} 319 and 255 (sh) nm (log ϵ 4·07 and 3·66); NMR signals at δ 1·70 and 1·78 (each 3H, bs), 3·87 and 3·93 (each 3H, s), 4·73 (2H, d, J = 7·5 Hz), 5·52 (1H, bt, J = 7·5 Hz), 6·23 (1H, d, J = 9·5 Hz), 6·63 (1H, s) and 7·93 (1H, d, J = 9·5 Hz); mass spectral peaks at *m/e* 290 (M^-, 7%), 222 (100), 207 (90), 193 (19) and 69 (92).

A soln of 3 (22 mg) in N,N-diethylaniline (0·3 ml) and n-butyric anhydride (0·3 ml) was kept at 175° under N for 7 hr. The cooled mixture was diluted with iced water (15 ml), kept for 3 hr and extracted with EtOAc. The organic layer was washed with dil HCl (1% w/v), K_2CO_3 aq (0·5% w/v), brine to neutrality, dried and evaporated. The residue was purified by TLC (EtOAc-light petroleum, 3:7) and distilled at 170°/0·4 mm giving the *butyrate* (10) as a glass (18 mg, 66%) (Found: C, 66·65; H, 7·0. $C_{20}H_{24}O_6$ requires: C, 66·65; H, 6·7%); ν_{max} 1770, 1746, and 1608 cm^{-1}; λ_{max} 346 (sh), 328 (sh) and 294 nm (log ϵ 3·35, 3·65 and 3·86); NMR signals (CCl_4) at δ 1·08 (3H, t, J = 7 Hz), 1·70 and 1·85 (each 3H, bs), 1·60–2·10 (2H, m), 2·60 (2H, t, J = 7 Hz), 3·50 (2H, d, J = 7·5 Hz), 3·78 and 3·90 (each 3H, s), 5·17 (1H, bt, J = 7·5 Hz),

6·20 and 7·48 (each 1H, d, J = 9·5 Hz); mass spectral peaks at m/e 360 (M^+, 24%), 291 (24), 290 (86), 276 (60), 259 (36), 204 (23), 185 (43), 176 (29), 71 (41) and 43 (100).

A soln of **10** (27 mg) in EtOH (10 ml) was warmed with K_2CO_3 aq (0·5% w/v; 1 ml) on a steam bath for 5 min. The cooled soln was neutralised with 0·1 N HCl and the solvent removed by evaporation. Work up into EtOAc gave 8 - (3 - *methyl* - 2 - *butenyl*) - *tomentin* (**9**; 19 mg, 87%), needles, m.p. 154–158° (from ether-light petroleum) (Found: C, 66·2; H, 6·15. $C_{16}H_{18}O_5$ requires: C, 66·2; H, 6·25%); ν_{max} 3530, 1747, 1626 and 1618 cm^{-1}; λ_{max} 315, 256, and 232 (sh) nm (log ϵ 4·02, 3·95 and 4·03), λ_{max} (base) 406, 340 (sh), 326, 275 and 243 nm (log ϵ 3·56, 3·80, 3·89, 3·91 and 3·96); NMR signals at δ 1·70 and 1·83 (each 3H, bs), 3·47 (2H, d, J = 8 Hz), 3·93 (6H, s), 5·22 (1H, bt, J = 8 Hz), 6·18 (1H, s), 6·25 and 7·98 (each 1H, d, J = 9·5 Hz); mass spectral peaks at m/e 290 (M^+, 100%) 275 (79) and 247 (27%). **9**(4 mg) was recovered unchanged after refluxing a soln in MeOH (1 ml) with conc HCl (2 drops) for 90 min.

Dimethylpropargylation of tomentin. K_2CO_3 (0·83 g) and KI (0·14 g) were added to a soln of tomentin (0·56 g) in aqueous acetone (2% v/v; 66 ml) and the mixture stirred for 1 hr. 2 - Chloro - 2 - methylbut - 3 - yne (0·83 g) was added and the mixture refluxed for 6 hr. More K_2CO_3 (0·83 g) and 2 - chloro - 2 - methylbut - 3 - yne (0·83 g) were added and refluxing continued for a further 24 hr. Another addition of 2 - chloro - 2 - methylbut - 3 - yne (0·83 g) was made and a final 24 hr reflux carried out. Work up from the recovered inorganic solids gave tomentin (0·19 g) and from the filtrate a brown oil which was separated on TLC (ether-light petroleum, 1:1) into (i) the *ether* (**14**) as a pale yellow glass (33 mg, 4%, 6% conversion), b.p. 135°/0·1 mm (Found: C, 71·0; H, 6·45. $C_{21}H_{22}O_5$ requires: C, 77·15; H, 6·25%); ν_{max} 3309, 2110, 1740 and 1618 cm^{-1}; NMR signals at δ 1·73 and 1·92 (each 6H, s), 2·30 and 2·47 (each 1H, s), 3·80 and 3·98 (each 3H, s), 6·23 and 8·10 (each 1H, d, J = 9·5 Hz); mass spectral peaks at m/e 354 (M^+, 11%), 288 (55), 273 (100) and 67 (54); (ii) 5 - 0 - (1,1 - *dimethylpropargyl*)*tomentin* (**5**; 221 mg, 30%, 46% conversion), plates, m.p. 85–86° (from aqueous EtOH) (Found: C, 66·55; H, 5·95. $C_{16}H_{16}O_5$ requires: C, 66·65; H, 5·6%); ν_{max} 3310, 2125, 1747 and 1612 cm^{-1}; λ_{max} 350 (sh), 329, 313, 255 (sh), 246 (sh) and 225 nm (log ϵ 3·78, 4·01, 3·98, 3·60, 3·71 and 3·03); NMR signals at δ 1·72 (6H, s), 2·43 (1H, s), 3·78 and 3·90 (each 3H, s), 6·18 (1H, d, J = 9·5 Hz), 6·65 (1H, s) and 8·07 (1H, d, J = 9·5 Hz); mass spectral peaks at m/e 288 (M^+, 12%), 257 (45), 222 (100), 207 (100), 193 (23), 95 (28) and 69 (41); (iii) the mixture of allenes (**15** and **16**; 54 mg; 11% conversion) as a yellow oil which showed NMR signals at δ 1·48–1·70 (12H, m), 3·23 (6H, s), 3·88 and 3·93 (each 3H, s), 5·17 and 5·45 (each 1H, septet, J = 3 Hz), 5·70 and 5·73 (each 1H, s), 6·07, 6·18, 7·80 and 7·88 (each 1H, d, J = 9·5 Hz); and (iv) tomentin (10 mg). The 1:1 mixture of allenes was heated slowly in a sublimation tube at 0·1 mm until distillation commenced. The tube was then slowly withdrawn from the sublimation block as distillation proceeded until the block temp reached 145°, when heating was stopped. On cooling, the material at the upper end of the tube solidified and contamination from the yellow isomer (**15**) was removed by washing with ether. One further sublimation afforded the colourless *allene* (**16**), m.p. 148–150°; ν_{max} 1968 (weak), 1760, 1663, 1640 and 1604 cm^{-1}; λ_{max} 278 and 252 (sh) nm (log ϵ 4·06 and 3·98); NMR signals at δ 1·64, 1·66, 3·22 and 3·86 (each 3H, s), 5·45 (1H, septet, J = 3 Hz), 5·71 (1H, s), 6·33 and 7·91 (each 1H, d, J = 9·5 Hz); mass spectral peaks at m/e 288 (M^+, 43%), 257 (21), 222 (100), 207 (98), 193 (27), 69 (24) and 67 (39). The allene (**16**) was recovered unchanged after heating to 145° for 40 min.

The NMR spectrum of the 1:1 allene mixture (20 mg) in tetrachloroethene (0·4 ml) was unchanged when recorded at 100° and after heating to 155° for 40 min.

Hydrogenation and rearrangement. (a) 5% Pd-C (9 mg) was added to a soln of **5** (22 mg) in EtOAc (15 ml) and quinoline-sulphur poison[1] (0·07 ml) added. After hydrogenation at room temperature for 2 hr when the uptake of H_2 was 1 mole, the catalyst was removed by filtration through Celite 535 and the solvent evaporated with the minimum of heating, to give a yellow oil (29 mg). Purification on TLC ($CHCl_3$) gave the *enone* (**18**; 11 mg, 50%), yellow prisms, m.p. 111–113° (from ether) (Found: C, 66·45; H, 6·25. $C_{16}H_{18}O_5$ requires: C, 66·2; H, 6·25%); ν_{max} 1763, 1678, 1635, 1592 and 1535 cm^{-1}; λ_{max} 380, 316 and 257 nm (log ϵ 3·70, 3·95 and 3·82), λ_{max} (base) 338, 276 and 245 nm (log ϵ 3·84, 3·73 and 4·04), λ_{max} (reacidification) 281 nm (log ϵ 3·66); NMR signals at δ 1·53 and 1·60 (each 3H, bs), 2·70 (2H, d, J = 8·5 Hz), 3·15 and 3·93 (each 3H, s), 4·87 (1H, bt, J = 8·5 Hz), 5·77 (1H, s), 6·08 and 7·82 (each 1H, d, J = 9·5 Hz); mass spectral peaks at m/e 290 (M^+, 3%), 222 (100), 207 (65) and 69 (82).

(b) The hydrogenation of **5** was repeated as above, but the reaction mixture filtered rapidly through a thin pad of celite 535. Subsequent evaporation afforded a pale yellow oil which contained 20% of the enone (**18**) from NMR and showed NMR signals for **6** at δ 1·53 (6H, s), 3·83 and 3·97 (each 3H, s), 5·20 (1H, d, J = 18 Hz), 5·10 (1H, d, J = 10 Hz), 6·17 (1H, dd, J = 18 and 10 Hz), 6·23 (1H, d, J = 9·5 Hz), 6·67 (1H, s) and 7·92 (1H, d, J = 9·5 Hz).

A soln of **18** (15 mg) in EtOH-water (80% v/v, 10 ml) was warmed on a steam bath for 5 min with dil H_2SO_4 (2 ml). After dilution with water and extraction into EtOAc, work up gave tomentin (5 mg, 43%) identified by TLC, UV, IR and mass spectrum.

The enone (**18**) was recovered unchanged after heating at 150° for 15 min.

Reduction of **18** *and aromatisation.* $NaBH_4$ was added in 3 mg portions to a soln of **18** (45 mg) in EtOH (10 ml) until TLC indicated complete reaction. The mixture was neutralised with 0·1 N HCl, diluted with brine (20 ml) and extracted twice with ether-EtOAc (50% v/v). Evaporation afforded the alcohol (**20**) as a yellow glass (35 mg, 77%), ν_{max} 3593, 3425, 1740, 1600 and 1525 cm^{-1}; NMR signals at δ 1·65 and 1·73 (each 3H, bs), 2·45 (2H, bd, J = 8·5 Hz), 3·17 and 3·77 (each 3H, s), 4·30 (1H, s), 5·27 (1H, bt, J = 8·5 Hz), 5·33 (1H, s), 5·80 and 7·22 (each 1H, d, J = 9·5 Hz); mass spectral peaks at m/e 292 (M^+, 23%), 223 (42), 207 (90), 191 (53) and 163 (100).

A soln of **20** (16 mg) in MeOH (5 ml) containing conc HCl (0·3 ml) was refluxed for 10 min. The cooled soln was poured into iced water (15 ml) and extracted with EtOAc. Work up gave 6,7-dimethoxycoumarin (10 mg, 88%), m.p. 138–139°, identical (mixed m.p., UV, IR, NMR and mass spectrum) with an authentic sample.[26]

Pyrolysis of the propargyl ether. 5 - 0 - (1,1 - Dimethyl - propargyl)tomentin (25 mg) was heated at 130° in a sublimation tube for 20 min at 0·1 mm. TLC purification (EtOAc-light petroleum; 2:3) of the distillate gave the *allene* (**15**; 22 mg, 88%) which, on redistillation and allowing the distillate to stand for a week, solidified as yellow plates, m.p. 110–112° (Found: C, 66·5; H, 5·4. $C_{16}H_{16}O_5$ requires: C, 66·65; H, 5·6%), ν_{max} 1970, 1763, 1681, 1638, 1594 and 1538 cm^{-1}; λ_{max} 382, 312 and 255 nm (log ϵ 3·78, 3·99 and 3·82); NMR signals at δ 1·60 and 1·65 (each 3H, d, J = 3 Hz), 3·21 and 3·87 (each 3H, s), 5·12 (1H, septet, J = 3 Hz), 5·64 (1H, s), 6·04 and 7·79 (each 1H, d, J = 9·5 Hz); mass spectral peaks at m/e 288 (M^+, 3%), 260 (25), and 257 (100).

Conversion of **15** *to alloxanthoxyletin.* $NaBH_4$ was added in 3 mg portions to a soln of **15** (25 mg) in EtOH (4 ml) until TLC showed complete reaction. Work up furnished the alcohol (**23**; 24 mg; 95%) as a solid which decomposed quickly at room temperature. **23** showed NMR signals at δ 1·60 and 1·68 (each 3H, d, J = 3 Hz), 3·41 and 3·71 (each 3H, s), 4·71 (1H, s), 5·10 (1H, septet, J = 3 Hz), 5·32 (1H, s), 5·97 and 7·43 (each 1H, d, J = 9·5 Hz).

A soln of **15** (18 mg) in MeOH (2 ml) and dil HCl (0·3 ml) was warmed on a steam bath to 50°, allowed to cool and kept for 2 hr, after which it was diluted with water (10 ml) and extracted into EtOAc. Work up gave a glass which solidified on standing and on sublimation at 130°/0·1 mm gave **25** as colourless needles (6 mg, 38%), m.p. 110–112° (lit.[19] m.p. 116°), identical (mixed m.p., IR, UV, and mass spectrum) with an authentic sample.

Rearrangement of the ether (**14**). The ether **14** (18 mg) was heated at 140°/0·4 mm for 20 min. The distillate being the *allene* (**27**) as a deep orange glass (14 mg, 78%) (Found: C, 71·15; H, 6·4. $C_{21}H_{22}O_5$ requires: C, 71·15; H, 6·25%), ν_{max} 3310, 2103, 1966, 1757, 1679, 1614 and 1510 cm^{-1}; λ_{max} 400, 320 and 270 nm (log ϵ 3·47, 3·81 and 3·89); NMR signals at δ 1·57, 1·70, 1·73 and 1·78 (each 3H, s), 2·30 (1H, s), 3·32 and 4·10 (each 3H, s), 5·12 (1H, m),

6·12 and 7·90 (each 1H, d, $J = 9·5$ Hz); mass spectral peaks at m/e 354 (M^+, 27%), 339 (75), 323 (56), 287 (34), 193 (100) and 67 (34).

Acknowledgements—We are grateful to Prof. B. S. Joshi, Bombay, for a sample of authentic alloxanthoxyletin and to the S.R.C. for a maintenance award (to M.S.).

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