Unexpected Rearrangement in the Peroxytrifluoroacetic Acid-Mediated Baeyer–Villiger Oxidation of *trans*-3β-Hydroxy-4,4,10β-trimethyl-9-decalone Forming a 7-Oxabicyclo[2.2.1]heptane. Structure Proof and Total Synthesis of (±)-Farnesiferol-C[1]

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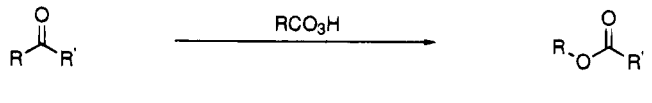
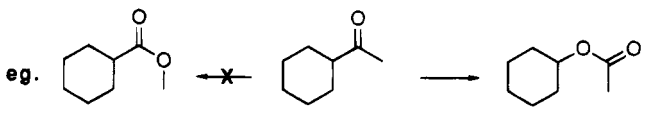
A rearrangement in the Baeyer–Villiger oxidation of *trans*-3β-hydroxy-4,4,10β-trimethyl-9-decalone (**2a**) and of OCH_2OMe (**2b**) and OTHP (**2c**) derivatives using peroxytrifluoroacetic acid is reported. The reaction involves trifluoroacetic acid catalyzed rearrangement of the initially formed hydroxy lactone **5a** giving the 7-oxabicyclo[2.2.1]heptane carboxylic acid **6**. This unexpected rearrangement is a useful preparation of the 7-oxabicyclo[2.2.1]heptane ring system and constitutes a stereoselective synthesis of the left-hand portion of the sesquiterpene-coumarin ether (±)-farnesiferol-C (**10**). The product **6** serves as an advanced, key intermediate from which a total synthesis and structure proof of this natural product is presented.

Introduction

The usefulness of the Baeyer–Villiger reaction as a means of preparing esters and lactones from carbonyl compounds eq 1 stems principally from the fact that the regiochemical aspects of this rearrangement are well defined. Thus the relative ease of migration of substituents attached to the carbonyl carbon atom has long been established as following the ability of these groups to stabilize a positive charge such that the migratory aptitude of carbonyl substituents in this reaction follows the order tertiary alkyl > cyclohexyl ≈ secondary alkyl ≈ benzyl ≈ phenyl > primary alkyl > cyclopropyl > methyl. This allows the regiospecific preparation of esters and lactones by choice of appropriate starting carbonyl compounds eq 2.[5]



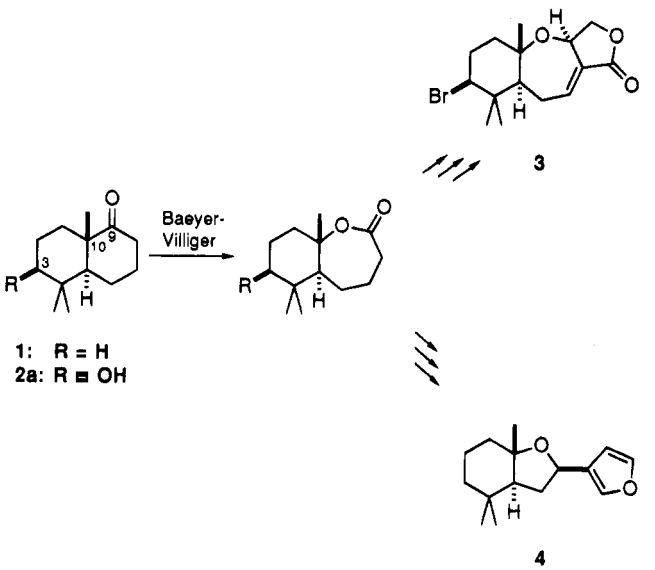
Equation 1



Equation 2

In work directed at the synthesis of monocyclofarnesyl natural products we aimed to use the Baeyer–Villiger reaction as a key to introducing strategically placed functionality which would enable us to convert the products into a variety of naturally occuring sesquiterpenes. Thus, the well known decalone **1**[6] and its 3β-hydroxy analogue **2a**,[6a,7,8] which have both served as useful starting materials in a number of terpene syntheses,[6b–d,7a,c,d,9] also presented themselves to us as ideal candidates from which for example aplysistatin (**3**)[10] and ancistrofuran (**4**)[11] might be accessible via oxidative Baeyer–Villiger cleavage of the C9–C10 bond and relevant subsequent manipulations (Scheme 1).

Scheme 1



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(5) March, J. *Advanced Organic Chemistry;* 3rd ed.; John Wiley and Sons, Inc.: New York, 1985; pp 990–991 and references cited therein. House, H. O. *Modern Synthetic Reactions*; 2nd ed.; W. A. Benjamin, Inc.: New York, 1972; pp 321–329 and references cited therein.

(6) (a) Snitman, D. L.; Tsai, M.-Y.; Watt, D. S.; Edwards, C. L.; Stotter, P. L. *J. Org. Chem.* **1979**, *44*, 2838–2842. (b) Cocker, J. D.; Halsall, T. G. *J. Chem. Soc.* **1957**, 3441–3445. (c) Sondheimer, F; Elad, D. *J. Am. Chem. Soc.* **1957**, *79*, 5542–5546. (d) Ototani, N.; Kato, T.; Kitahara, Y. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1730–1732. (e) Ohloff, G.; Giersch, W.; Schulte-Elte, K. H.; Vial, C. *Helv. Chim. Acta* **1976**, *59*, 1140–1157.

(7) (a) Sondheimer, F; Elad, D. *J. Am. Chem. Soc.* **1958**, *80*, 1967–1971. (b) Ireland, R. E. *Organic Synthesis*; Prentice Hall: Englewood Cliffs, NJ, 1969; pp 40–44 and 50–52. (c) Kalvoda. J.; Loeffel, H. *Helv. Chim. Acta* **1957**, *40*, 2340–2353. (d) King, F. E.; Ritchie, C. F.; Simmons, C. J. *Chem. Ind.* **1956**, 1230–1231.

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Results

In the case of the 3β-hydroxydecalone **2a** we have discovered an interesting and unexpected rearrangement, during the course of its Baeyer–Villiger oxidation with peroxytrifluoroacetic acid (CF_3CO_3H). Thus, treatment of the hydroxy ketone **2a** with CF_3CO_3H[12] in dichloromethane at room temperature resulted in the formation, not of the expected hydroxy lactone **5a**, but of the 7-oxabicyclo[2.2.1]heptane **6**. **6** was additionally characterized as its methyl ester **13** by reaction with diazomethane thereby supporting that this product was indeed a carboxylic acid and ruling out the expected ring expanded lactone. MS (M^+, 226) and combustion analysis corroborated the incorporation of one oxygen, while ^1H NMR (δ 9.07: COO*H*; δ 3.74 (d): *H*-C4; δ 2.32 (t): H_2-C3′; δ 1.29 (s): H_3C-C1*)*, ^{13}C NMR (δ 179.2: carboxyl; δ 86.8, 86.0: C1, C4*)* and IR (ν_{max} 3400–2400 cm^{-1}*)* were fully supportive of the ether/carboxylic acid structure **6**. Similar Baeyer–Villiger reaction of the methoxymethyl-(**2b**) and THP-(**2c**) protected derivatives[13] resulted in the same product **6**. Performing the reaction of THP-ether **2c** with CF_3CO_3H buffered with Na_2HPO_4[12b,c] resulted in the rapid deprotection to **2a** which, however, underwent only slow and incomplete Baeyer–Villiger oxidation to the hydroxy lactone **5a** and a very small amount of rearranged **6**. $NaHCO_3$ in the reaction mixture equally permited deprotection and very slow Baeyer–Villiger oxidation but completely suppressed the rearrangement to **6** (Scheme 2).

In order to investigate the mechanism of this reaction we prepared the hydroxy lactone **5a** as above, or, more cleanly, via Na_2HPO_4-buffered Baeyer–Villiger oxidation of silyl ketone **2f** followed by desilylation of **5f** with *n*-Bu_4NF in THF. The spectral characteristics of this compound were quite different from **6**, in particular ^1H NMR (δ 3.37 (dd): H^{α}-C7; δ 2.75 (dd): H^{α}-C3; δ 2.55 (ddd): H^{β}-C3; δ 1.51(s): H_3C-C9a*)*, ^{13}C NMR (δ 174.8: lactone; δ 84.5, 77.2: C9a, C7*)* and IR (ν_{max} 3460, 1717 cm^{-1}) spectra, fully supportive this time of the desired ε-lactone **5a**.

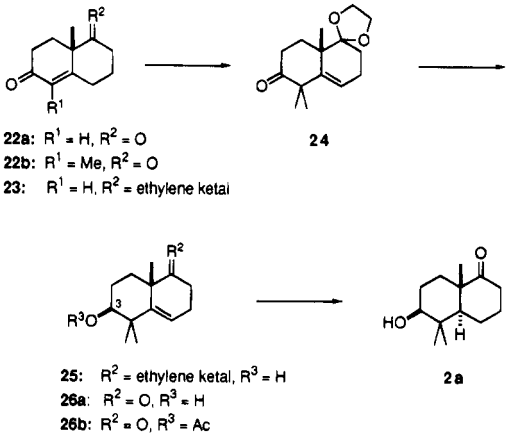
Subjection of hydroxy lactone **5a** to Baeyer–Villiger reaction conditions (containing both CF_3CO_3H *and* CF_3CO_2H) in the *presence* or *absence* of either Na_2HPO_4[12b,c] or $NaHCO_3$ provided unchanged hydroxy lactone **5a** ($NaHCO_3$), ether acid **6** exclusively (no additive) or a mixture of the two (Na_2HPO_4) (Scheme 2).

Furthermore, when the OCH_2OMe (**2b**) and OTHP (**2c**) derivatives were stirred at room temperature in CH_2Cl_2 containing a drop of CF_3CO_2H, the formation of the deprotected derivative **2a** was observed *within minutes*. Unbuffered *peroxy*trifluoroacetic acid resulted in very fast deprotection of **2b** or **2c**, followed by a gradual conversion to the 7-oxabicycloheptane **6** as judged by TLC. Oxidation of **2a/2c** with *m*-CPBA (with or without Na_2HPO_4) on the other hand gave only the corresponding lactone **5a/5c**. Evidently the strong acid CF_3CO_2H present in the unbuffered oxidation medium is required to promote the cleavage of the acyloxy group at C9a. *m*-CPBA (*and* its reduction product *m*-CBA) on the other hand neither promotes removal of acid labile C3β-OH protecting groups nor is it able to catalyze the rearrangement of **5a** to **6**.

3β-OAc (**2d**) and 3β-OBz (**2e**) derivatives were oxidized by unbuffered CF_3CO_3H to give exclusively the corresponding lactones **5d,e** respectively,[13] reflecting the fact that these protecting groups, as expected, were not removed under the acidic reaction conditions. Silyl ketone **2f** gave the corresponding lactone **5f** only under buffered conditions. In the absence of Na_2HPO_4 a complex mixture of products was observed (Scheme 2).

Total Synthesis of (±)-Farnesiferol-C (10). An inspection of the ether acid **6** reveals that it contains the same terpene skeleton as is found in the sesquiterpene-coumarin ethers farnesiferol-C (**10**) and creticacoumarin (**11**) isolated by Jeger and Arigoni[14] and Bohlmann,[15] respectively. Naturally occuring coumarins containing

(8) The synthesis of this well known hydroxy ketone **2a** has been the source of considerable confusion in the literature. As such the route beginning from the Wieland–Miescher ketone **22a** and proceeding via deconjugative bis-methylation of the monoketal **23**, hydride reduction of the ketone (**24** → **25**), deprotection, and olefin hydrogenation (**25** → **26a** → **2a**) has been claimed to be unreliable by Stotter and Watt and co-workers, particularly at the bis-methylation, hydride reduction, and catalytic hydrogenation steps (reportedly resulting in overmethylation, C3 epimeric alcohol mixtures and complex hydrogenation product mixtures, respectively).[6a]



In view of these difficulties, Stotter and Watt did in fact develop a new synthesis of **2a** similar in concept to the one at hand, but beginning with the vinyl methyl Wieland–Miescher ketone analogue **22b**.[6a] In complete contrast, however, Ireland had earlier claimed the route shown to be quite successful, the catalytic hydrogenation of hydroxy olefin **26a** amongst others apparently being quite viable, giving the desired hydroxy ketone **2a** in 80% yield.[7b] Professor Ireland kindly shed some light on this contradiction by informing us that the hydrogenation in question had indeed been "capricious" in his group and suggesting that, in view of the currency of Stotter's newer method, this would be the one to follow (personal communication).

Apparently though, both of the above groups seemed not to be aware, that the sequence from **22a** to **2a** had been successfully executed by Kalvoda and Loeffel[7c] many years earlier, with the only drawback being the nonselectivity of carbonyl reduction of **24** resulting from the use of lithium aluminum hydride instead of the subsequently introduced lithium tri-*tert*-butoxyaluminum hydride.

Contrary to Stotter's findings,[6a] we were able to cleanly reduce ketone **24** to give alcohol **25** uncontaminated by its epimer, by employing lithium tri-*tert*-butoxyaluminum hydride. Most significantly, however, the Swiss authors were able to cleanly hydrogenate the acetoxy olefin **26b** (instead of the alcohol **26a**) to a 7:3 mixture of *trans* and *cis* acetoxy decalones from which the *trans* isomer could be preferentially crystallized and hydrolyzed to the hydroxy ketone **2a**. We were able to routinely reproduce Kalvoda and Loeffel's proceedure.

(9) (a) Danieli, N.; Mazur, Y.; Sondheimer, F. *Tetrahedron* **1967**, *23*, 509–514. (b) Ghera, E.; Sondheimer, F. *Tetrahedron Lett.* **1964**, 3887–3891. (c) Sondheimer, F; Elad, D. *J. Am. Chem. Soc.* **1959**, *81*, 4429–4432.

(10) Pettit, G. R.; Herald, C. L.; Allen, M. S.; von Dreele, R. B.; Vanell, L. D.; Kao, J. P. Y.; Blake, W. *J. Am. Chem. Soc.* **1977**, *99*, 262–263.

(11) Baker, R.; Briner, P. H.; Evans, D. A. *J. Chem. Soc., Chem. Commun.* **1978**, 981–983.

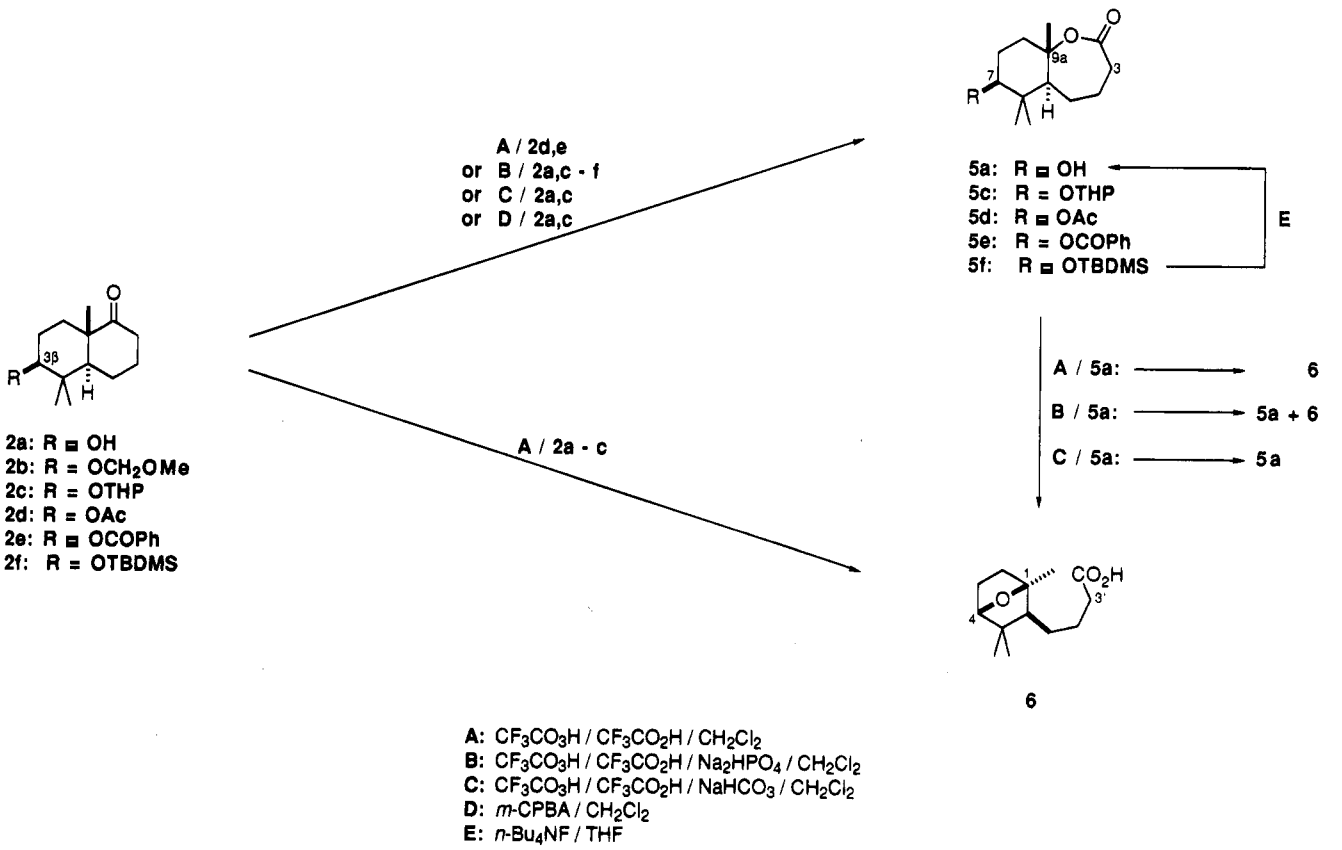
(12) (a) Sager, W. F.; Duckworth, A. *J. Am. Chem. Soc.* **1955**, *77*, 188–190. (b) Emmons, W. D.; Lucas, G. B. *J. Am. Chem. Soc.* **1955**, *77*, 2287–2288. (c) Hawthorne, M. F.; Emmons. W. D.; McCallum, K. S. *J. Am. Chem. Soc.* **1958**, *80*, 6393–6398.

(13) Demnitz, F. W. J.; Ph.D. Thesis; University of Cambridge, 1983.

(14) Caglioti, L.; Naef, H.; Arigoni, D.; Jeger, O. *Helv. Chim. Acta* **1959**, *42*, 2557–2570.

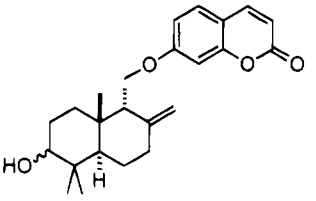
(15) Bohlmann, F.; Zdero, C. *Chem. Ber.* **1975**, *108*, 1902–1910.

Scheme 2

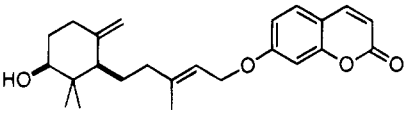


particularly 5C and 10C terpenoid units have been known for many years[16] but Jeger, Arigoni and their collaborators, studying nonvolatile components from the resin *Asa foetida* which is obtained from a variety of *foerula* species, isolated the farnesiferols A–C (**7, 9, 10**)[14,17] as some of the early coumarins containing sesquiterpenoid components. Subsequently Arigoni also obtained farnesiferol-D and -E (**12, 8**) from *galbanum*.[18,19] *Asa foetida* is considered to have sedative and vermifugal properties and is used as a spice in Iran and Afghanistan.

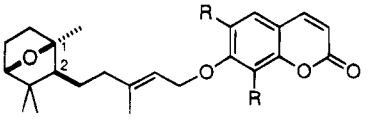
With respect to farnesiferol-C (**10**) Arigoni and coworkers did not unambiguously establish the relative configurations at the vicinal carbon atoms C1 and C2 of the 7-oxabicycloheptane unit. Nor did van Tamelen, in an early biomimetic synthesis[20] of farnesiferol-C (**10**), or Bohlmann in the isolation and structure determination of the closely related creticacoumarin (**11**),[15] resolve this stereochemical question. As such the stereochemical assignment relied upon "biogenetic precedent". In view of the stereochemical homogeneity of our ether acid **6** we were of course in a position to prove Arigoni's structural assignment of farnesiferol-C (**10**) by means of an unambiguous total synthesis of this natural product starting from our novel Baeyer–Villiger product. Our synthesis, shown in Scheme 3, does indeed prove the earlier structure proposal. Mukaiyama has in the meantime



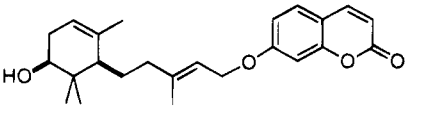
7: *Farnesiferol A*, 3β-OH
8: *Farnesiferol E*, 3α-OH



9: *Farnesiferol B*



10: R = H *Farnesiferol C*
11: R = OMe *Creticacoumarin*



12: *Farnesiferol D*

synthesized (+)-farnesiferol-C,[21] the antipode of the natural product, also corroborating the Swiss worker's

(16) (a) Murray, R. D. H. *Nat. Prod. Rep.* **1989**, 591–624. (b) Murray, R. D. H.; Méndez, J.; Brown, S. A. *The Natural Coumarins, Occurrence, Chemistry and Biochemistry*; Wiley: Chichester, 1982. (c) Dean, F. M. *Fortschr. Chem. Org. Naturst.* **1952**, *9*, 225–291.

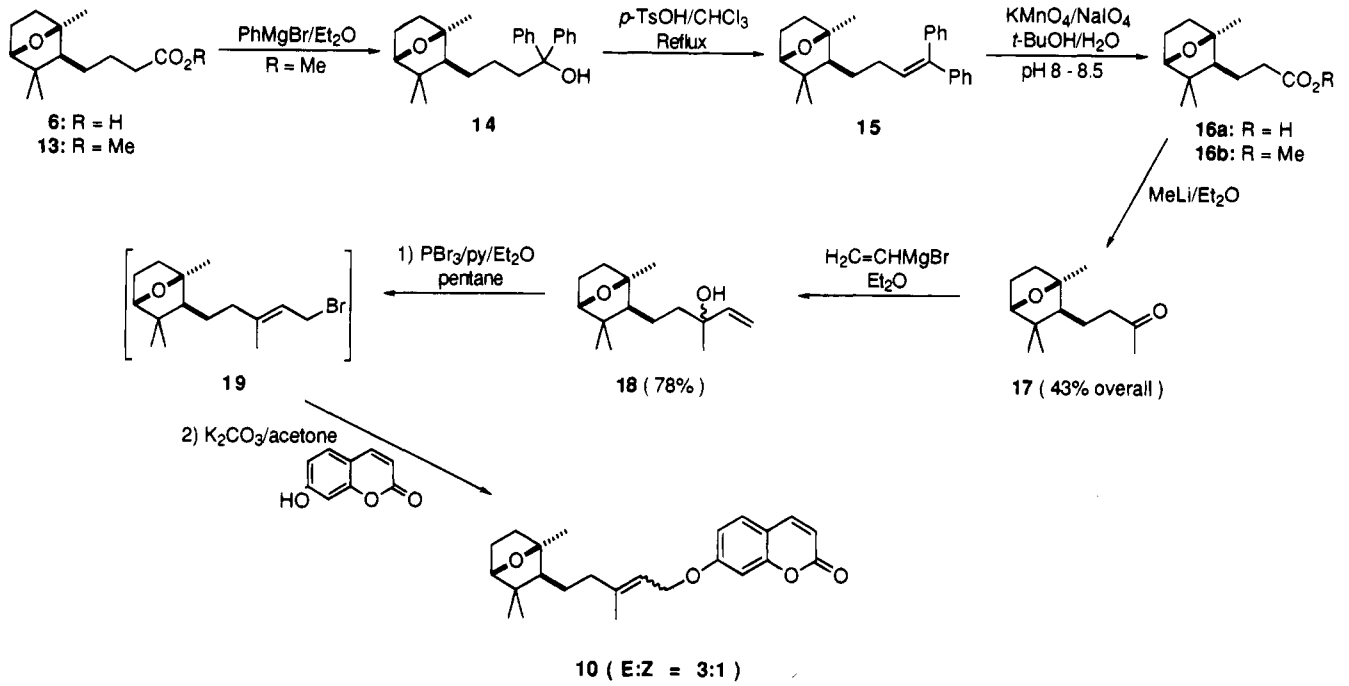
(17) Caglioti, L.; Naef, H.; Arigoni, D.; Jeger, O. *Helv. Chim. Acta* **1958**, *41*, 2278–2292.

(18) See also ref 11 cited in ref 20a.

(19) We thank Professor D. Arigoni for this information.

(20) (a) van Tamelen, E. E.; Coates, R. M. *J. Chem. Soc., Chem. Commun.* **1966**, 413–415. (b) van Tamelen, E. E.; Coates, R. M. *Bioorg. Chem.* **1982**, *11*, 171–196.

Scheme 3



assignment, namely a *cis* relationship between the alkyl side chain and the oxygen bridge. In fact it is exactly this oxygen bridge alongside the correct placement of the various substituents on the cyclohexane ring which makes up the major synthetic challenge of farnesiferol-C (**10**). As can be seen, our novel rearrangement in the formation of **6**, nicely solves this problem and forms, in a single reaction, the entire oxabicyclic unit of the natural product with all necessary substituents in the correct relative stereochemistry. Thus there remains only the synthetic manipulation of the side chain in order to secure farnesiferol-C (**10**).

Standard Barbier–Wieland degradation (CH_2N_2; PhMgBr; H^+/Δ; $KMnO_4/NaIO_4$) of **6** gave the lower homologue **16a**, treatment of which with MeLi (2 equiv) afforded the methyl ketone **17**. Finally, reaction of **17** with vinylmagnesium bromide provided the allylic alcohol **18** as the final precursor to the natural product. Much attention has been paid to developing methods for the controlled preparation of allylic chlorides from allyl alcohols without concomitant allylic rearrangement. However, for our purposes we required the rearranged allylic halide **19**,[22] treatment of which with potassium umbeliferate[21,22ab] would provide access to the desired farnesiferol-C (**10**). The well precedented use of PBr_3[22] proved successful in this endeavor. Thus, reaction of the tertiary allylic alcohol **18** with PBr_3 in the presence of pyridine resulted in the formation of the labile (presumed) rearranged bromide **19** which, after workup, was immediately treated with the potassium salt of umbelliferone in acetone to give a 3:1 mixture of farnesiferol-C (**10**) and its *Z*-double bond isomer.[22a,23]

Discussion

The formation of the 7-oxabicyclo[2.2.1]heptane **6** upon subjection of hydroxy lactone **5a** to the Baeyer–Villiger reaction conditions (containing CF_3CO_2H) previously employed in the conversion of **2a** to **6**, and the reluctance to do so either in the presence of base ($NaHCO_3$) or by employing *m*-CPBA (providing the *less acidic m*-CBA as a byproduct), is an indication that the reaction of hydroxy ketone **2a** proceeds via initial formation of the lactone **5a** followed by rearrangement to **6** in the presence of strong acid (CF_3CO_2H) (Scheme 4). The known ability of CF_3CO_2H to cleave tertiary esters would support the formation of the intermediate carbonium ion **21** which would then be captured by the 3β-hydroxy group to give **6** in a stepwise fashion fom **5a**. Supported by the conformational aspects of ring-A, however, whose 1,3 diaxial steric interactions of the methyl groups facilitate a flipping into the boat form,[24] we cannot completely discard a partially concerted character of this reaction wherein the hydroxy group in the boat-form **5a-boat** aids in expelling the protonated acyloxy leaving group. Also, in contrast to a similar case recently observed by us involving ketone **1**[25] we have not observed other products in this reaction, whose formation could also be explained by invoking a carbonium ion such as **21**.

Although the possibility of a concerted one-step mechanism from **2a** directly to **6**, invoking a similarly facile chair/boat equilibrium between the Baeyer–Villiger intermediates **20-chair** and **20-boat**[24] and subsequent

(21) Mukaiyama, T.; Iwasawa, N. *Chem. Lett.* **1981**, 29–32.

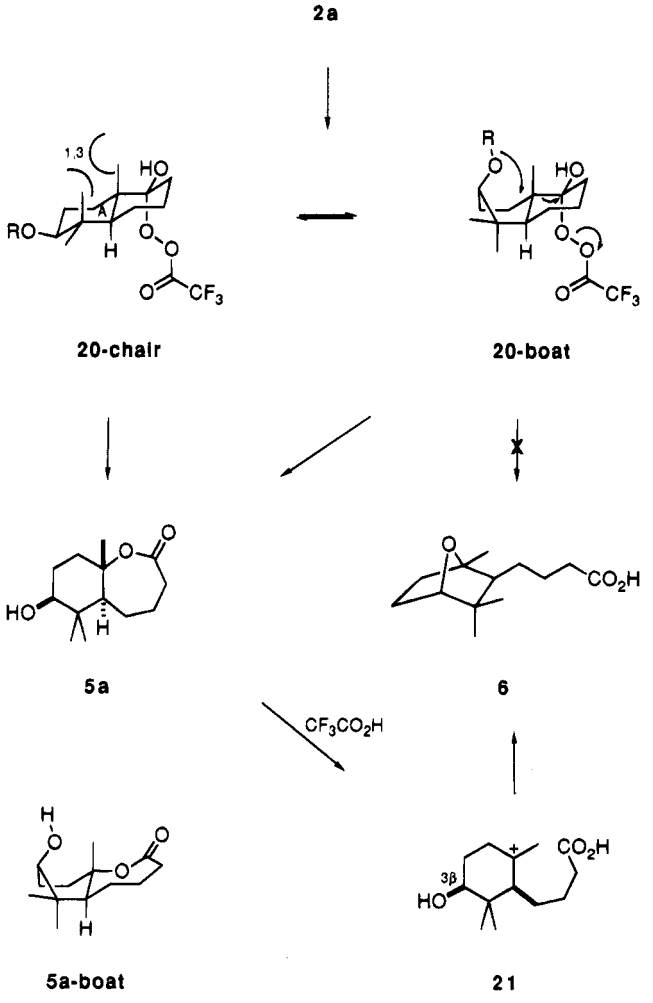
(22) (a) Babler, J. H. *J. Org. Chem.* **1976**, *41*, 1262–1264. (b) Bohlmann, F.; Körnig, D. *Chem. Ber.* **1974**, *107*, 1780–1783. (c) Isler, O.; Rüegg, R.; Chopard-dit-Jean, L.; Wagner, H.; Bernhard, K. *Helv. Chim. Acta* **1956**, *39*, 897–904. (d) Dauben, W. G.; Beasley, G. H.; Broadhurst, M. D.; Muller, B.; Peppard, D. J.; Pesnelle, P.; Suter, C. *J. Am. Chem. Soc.* **1975**, *97*, 4973–4980.

(23) The product mixture contains (±)-farnesiferol-C as a major component along with three minor compounds which, due to their extreme inseparability (even by HPLC), we have not been able to fully characterize. To one of these we, however, tentatively assign the *Z*-double bond isomeric (±)-farnesiferol-C structure.

(24) (a) Barton, D. H. R.; Lewis, D. A.; McGhie, J. F. *J. Chem. Soc.* **1957**, 2907–2915. (b) Huffman, J. W. *J. Org. Chem.* **1959**, *24*, 447–451. (c) Djerassi, C; Finch, N.; Cookson R. C.; Bird, C. W. *J. Am. Chem. Soc.* **1960**, *82*, 5488–5493. (d) Holker, J. S. E.; Whalley, W. B. *Proc. Chem. Soc.* **1961**, 464. (e) Wendler, N. L. *Chem. and Ind.* **1958**, 1662–1663.

(25) Demnitz, F. W. J.; Freiberger, S.; Weber, H.-P. *Helv. Chim. Acta* **1995**, *78*, 887.

Scheme 4



collapse to **6** had been originally entertained by us, *our results clearly rule out this mechanistic scenario* and indicate the intermediacy of the *preformed* hydroxy lactone **5a** (Scheme 4).

Conclusion

An unusual outcome of the Baeyer–Villiger reaction of *trans*-3β-hydroxy-4,4,10β-trimethyl-9-decalone (**2a**) with CF_3CO_3H has been described. The initially formed hydroxy lactone **5a** undergoes CF_3CO_2H catalyzed cleavage of the lactone C–O bond and rearrangement to form a 7-oxabicyclo[2.2.1]heptane (**6**). The reaction constitutes a useful synthesis of this heterocyclic skeleton as shown here in a stereoselective synthesis and structure proof of the sesquiterpene (±)-farnesiferol-C (**10**).

Experimental Section

Materials and Methods. Melting points are corrected. ^1H NMR (90, 360, 400 MHz) and ^{13}C NMR (62.5, 100, 125 MHz) spectra were recorded using internal TMS or residual $CHCl_3$ protons as references. Infrared spectra (KBr, $CHCl_3$ solution, neat) were recorded as indicated. Flash chromatography was carried out using silica gel (EM Reagents, Kieselgel 60, 230–400 mesh). Analytical thin-layer chromatography was done on precoated Kieselgel 60 F_{254} 0.2 mm aluminum sheets. AR grade solvents were used without purification or, where necessary, were purified using standard procedures.[26] All commercial reagents were used without purification.

(26) Perrin, D. D.; Armarego W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; 2nd ed.; Pergamon Press: Oxford, 1980.

***trans*-3β-(Tetrahydropyranyloxy)-4,4,10β-trimethyl-9-decalone (2c).** A solution of the hydroxy ketone **2a**[7c] (330 mg, 1.57 mmol), dihydropyran (0.8 mL, 8.9 mmol, 5.7 equiv), and PPTS (several crystals) in dry CH_2Cl_2 (20 mL) was stirred at room temperature for 21 h. K_2CO_3 was added, and the mixture was filtered and concentrated. Flash chromatography of the residue (eluent: EtOAc:hexane; 1:4) afforded the diastereomeric THP-ether **2c** as a colorless oil (463 mg, 100%). ^1H NMR (400 MHz, $CDCl_3$) δ 4.65 and 4.50 (m, m, 1H), 3.85 (m, 1H), 3.40 (m, 1H), 3.14 and 2.94 (dd, dd, J = 11, 4 Hz; J = 11, 4 Hz, 1H), 2.49 (ddd, J = 14, 14, 7 Hz, 1H), 2.12 (m, 1H), 2.07–0.80 (br, 24H). IR (KBr) ν_{max} 2942, 2871, 1707, 1387, 1031 cm^{-1}. MS m/z (rel intensity) 294(M^+, 18), 276(4), 210(31), 193(25), 85(100). HRMS Calcd for $C_{18}H_{30}O_3$: 294.2195. Found: 294.2208.

***trans*-3β-[(*tert*-Butyldimethylsilyl)oxy]-4,4,10β-trimethyl-9-decalone (2f).** To a solution of the hydroxy ketone **2a**[7c] (1.35 g, 6.43 mmol) in dry CH_2Cl_2 (20 mL) were added DMAP (262 mg, 2.14 mmol, 0.33 equiv), *tert*-butyldimethylsilyl chloride (1.16 g, 7.69 mmol, 1.2 equiv), and triethylamine (1.2 mL, 8.61 mmol, 1.34 equiv). The reaction was heated to reflux for 5 days. The cooled reaction mixture was diluted with CH_2Cl_2 and washed with 0.5 M HCl (2x), water, saturated aqueous sodium bicarbonate, and brine. Drying (Na_2SO_4), filtration, and concentration gave a brown, solid residue which was chromatographed (eluents: pure hexane followed by hexane:EtOAc mixtures in the following proportions: 95:5, 9:1, 2:1 and 1:1) to give the silyl ether **2f** as a white solid (1.54 g, 74%) along with recovered hydroxy ketone **2a** (330 mg, 24%). Recrystallization from ethanol–water gave white plates, m. p. 95–97 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 3.15 (m, 1H), 2.57(ddd, J = 14, 14, 7 Hz, 1H), 2.19 (m, 1H), 2.08 (m, 1H), 1.80–1.45 (m, 7H), 1.14 (s, 3H), 1.11 (dd, J = 12, 4 Hz, 1H), 0.93 (s, 3H), 0.89 (s, 9H), 0.87 (s, 3H), 0.06 (s, 3H), 0.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.3, 78.6, 52.7, 48.7, 40.3, 37.5, 31.1, 28.4, 27.3, 26.4, 25.9, 21.0, 18.6, 18.1, 16.2, −3.8, −5.0. IR (KBr) ν_{max} 2954, 2870, 1702, 1470, 1363, 1256, 1116, 1099, 843, 771 cm^{-1}. MS m/z (rel intensity) 325(MH^+, 22), 268(30), 193(36), 175(100). Anal. Calcd for $C_{19}H_{36}O_2Si$: C, 70.37; H, 11.1. Found: C, 70.30; H, 11.1.

Decahydro-7β-[(*tert*-butyldimethylsilyl)oxy]-6,6,9aβ-trimethyl-2-oxo-1-benzoxepin (5f). A solution of peroxytrifluoroacetic acid and trifluoroacetic acid in CH_2Cl_2 was prepared by adding a 60% solution of H_2O_2 (0.5 mL, 10.15 mmol) to a vigorously stirred solution of trifluoroacetic anhydride (3.5 mL, 24.8 mmol) in CH_2Cl_2 (46 mL) cooled to 0 °C. After stirring for 10 min the solution was taken to be ready and to be 0.2 M in trifluoroperacetic acid and 0.7 M in trifluoroacetic acid. Of this solution (21 mL, ≈4.26 mmol peracid, ≈1.7 equiv with respect to **2f**) was slowly added to a vigorously stirred slurry containing the silyl ether **2f** (810 mg, 2.5 mmol) and Na_2HPO_4 (10 g, 70 mmol, 28 equiv) in dry CH_2Cl_2 (100 mL) at −20 °C. Stirring was continued at 0 °C for 4 h, and more CF_3CO_3H solution was added (3.7 mL, 0.75 mmol, 0.3 equiv). After a further 1.5 h, solid $NaHSO_3$ was added and the mixture stirred vigorously for 30 min. Water was added, the layers were separated, and the aqueous phase was extracted with CH_2Cl_2 (3x). The combined organic phases were washed with saturated aqueous sodium bicarbonate, dried (Na_2SO_4), filtered, and concentrated. Flash chromatography (eluent: EtOAc:hexane; 1:4) afforded the starting silyl ether **2f** (314 mg, 39%) and the lactone **5f** (370 mg, 44%). Recrystallization from hexane gave white needles, mp 169–170 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 3.31 (dd, J = 11, 4 Hz, 1H), 2.75 (br dd, J = 16, 6 Hz, 1H), 2.55 (ddd, J = 16, 14, 2 Hz, 1H), 2.02 (br d, J = 14 Hz, 1H), 1.98–1.88 (m, 2H), 1.80 (br ddd, J = 14, 14, 4 Hz, 1H), 1.64 (m, 2H), 1.59–1.45 (m, 3H), 1.52 (s, 3H), 1.00 (s, 3H), 0.89 (s, 9H), 0.75 (s, 3H), 0.06 (s, 3H), 0.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 84.7, 77.8, 53.7, 40.9, 39.7, 37.1, 28.2, 28.1, 25.8, 25.7, 23.8, 21.9, 18.1, 14.8, −3.8, −5.0. IR (KBr) ν_{max} 2954, 2856, 1704, 1470, 1360, 1291, 1125, 1100, 834, 771 cm^{-1}. MS m/z (rel intensity) 340(M^+, 5), 325(22), 283(42), 75(100). Anal. Calcd for $C_{19}H_{36}O_3Si$: C, 67.06; H, 10.58. Found: C, 66.90; H, 10.6.

Decahydro-7β-hydroxy-6,6,9aβ-trimethyl-2-oxo-1-benzoxepin (5a). A solution of the silyl ether **5f** (263 mg, 0.773

mmol) in dry THF (20 mL) was treated with a 1 M solution of nBu$_4$NF in THF (1 mL, 1 mmol, 1.3 equiv) at room temperature under Ar. After 20 h stirring, more 1 M nBu$_4$NF in THF (0.2 mL, 0.2 mmol, 0.26 equiv) was added and the solution stirred for a further 4 h. The bulk of the THF was evaporated, the residue taken up in EtOAc and washed with dilute HCl, water, saturated aqueous $NaHCO_3$, and brine. Drying (Na_2SO_4), filtration, and concentration afforded a yellow oil which was flash chromatographed (eluent: EtOAc:hexane; 1:1) to give the hydroxy lactone **5a** as a colorless oil (145 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.37 (dd, J = 11, 4 Hz, 1H), 2.75 (br dd, J = 16, 6 Hz, 1H), 2.55 (ddd, J = 16, 14, 2 Hz, 1H), 2.09−1.43 (m, 10H), 1.51 (s, 3H), 1.10 (s, 3H), 0.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 84.5, 77.2, 53.8, 40.3, 39.9, 37.2, 28.0, 27.8, 25.6, 23.9, 21.9, 14.4. IR (KBr) ν_{max} 3460, 2946, 2870, 1717, 1366, 1211, 1123, 1040 cm^{-1}. MS m/z (rel intensity) 209 (M^+−OH, 8), 167(6), 149(42), 142(53), 126(40), 111(100). Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.70; H, 10.1.

Decahydro-7β-(tetrahydropyranyloxy)-6,6,9aβ-trimethyl-2-oxo-1-benzoxepin (5c). A solution of THP-ether **2c** (9 mg, 0.03 mmol) and m-CPBA (10 mg, 0.05 mmol, ≈ 1.6 equiv) in dry CH_2Cl_2 (5 mL) was stirred at 0 °C for 2 h and then at room temperature. After 20 and 25 h, an equal amount of m-CBPA was added. After a total of 42 h, the mixture was taken up in EtOAc and washed with dilute aqueous $NaHSO_3$ and $NaHCO_3$, dried (Na_2SO_4), filtered, and concentrated. The residue was flash chromatographed (eluent: EtOAc:hexane; 1:1) to give the THP lactone **5c** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.71 and 4.59 (m, m, 1H), 3.91 (m, 1H), 3.50 (m, 1H), 3.38 and 3.16 (dd, dd, J = 11, 4 Hz, J = 11, 4 Hz, 1H), 2.76 (br dd, J = 16, 6 Hz, 1H), 2.56 (ddd, J = 16, 14, 2 Hz, 1H), 2.10−1.45 (m, 15H), 1.61 (s, 3H), 1.14 and 1.01 (s, s, 3H), 0.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 102.2, 95.2, 86.3, 79.5, 63.0, 54.1, 53.9, 40.5, 40.0, 39.6, 37.1, 31.3, 31.1, 28.0, 27.7, 26.5, 25.5, 23.8, 23.0, 21.9, 20.2, 19.9, 15.4, 15.3. IR (KBr) ν_{max} 2944, 2869, 1720, 1387, 1123, 1032 cm^{-1}. MS m/z (rel intensity) 311(MH^+, 43), 227(74), 209(100).

2β-(3′-Carboxypropyl)-1α,3,3-trimethyl-7-oxabicyclo-[2.2.1]heptane (6). To trifluoroacetic anhydride (6.5 mL, 46.2 mmol) in dry CH_2Cl_2 (15 mL) was added 85% aqueous H_2O_2 (0.86 mL, 30 mmol) at 0 °C. The mixture was stirred vigorously for several minutes until it became homogeneous and then for about 2 min with removal of cooling. Of this solution (12.5 mL, ≈4 equiv) was added to a solution of the hydroxy ketone **2a** (882 mg, 4.2 mmol) in dry CH_2Cl_2 (50 mL) at 0 °C. Stirring continued at 0 °C for 30 min. and at room temperature for 3 h., after which time solid sodium bisulfite was added. After stirring for another 1 h the mixture was filtered through Celite and concentrated to afford a clear colorless oil which slowly crystallized. Recrystallization from pentane gave the ether acid **6** (757 mg, 80%) as plates, mp 59−60 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.07 (br s, 1H), 3.74 (d, J = 5 Hz, 1H), 2.32 (t, J = 7 Hz, 2H), 2.00−1.10 (m, 9H), 1.29 (s, 3H), 1.03 (s, 3H), 0.96 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.2, 86.8, 86.0, 55.7, 45.2, 38.9, 34.4, 27.3, 26.0, 25.7, 25.0, 23.2, 18.7. IR ($CHCl_3$) ν_{max} 3500, 3400−2400(br), 1711, 1461, 1385, 1156, 1001 cm^{-1}. MS m/z (rel intensity) 226(M^+, 47), 211(50), 208(14), 55(100). HRMS Calcd for $C_{13}H_{22}O_3$: 226.1569. Found: 226.1579. Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.80; H, 10.03.

2β-(3′-Carbomethoxypropyl)-1α,3,3-trimethyl-7-oxabicyclo[2.2.1]heptane (13). A small sample of the ether acid **6** (60 mg, 0.265 mmol) in Et_2O (5 mL) was treated with excess CH_2N_2 for 5 min. at 0 °C before quenching with several drops of formic acid. Filtration through a plug of florisil and concentration gave the methyl ester derivative **13** (60 mg, 95%) as a colorless oil. ^{1}H NMR (90 MHz, $CDCl_3$) δ 3.67 (1H, partially hidden under O-methyl singlet), 3.63 (s, 3H), 2.26 (br t, J = 7 Hz, 2H), 2.08−1.07 (m, 9H), 1.27 (s, 3H), 1.00 (s, 3H), 0.95 (s, 3H). IR (neat) ν_{max} 1740, 1466, 1386, 1368, 1250, 1170 cm^{-1}. MS m/z (rel intensity) 240(M^+, 23), 225(29), 222(10), 83(100). HRMS Calcd for $C_{14}H_{24}O_3$: 240.1726. Found: 240.1723. Saponification of this material with 5% KOH in refluxing MeOH:H_2O; 3:7 returned the ether acid **7** in >95%.

2β-(4′,4′-Diphenyl-4′-hydroxybutyl)-1α,3,3-trimethyl-7-oxabicyclo[2.2.1]heptane (14). A solution of the methyl ester **13** (357 mg, 1.49 mmol) in dry Et_2O (60 mL) was cooled to 0 °C under an atmosphere of nitrogen and treated dropwise with a 3 M ethereal solution of phenylmagnesium bromide (1.15 mL, 3.45 mmol, 2.3 equiv). The mixture was stirred at room temperature for 6 h and then quenched with 3 M HCl. The phases were separated, the aqueous layer was further extracted with Et_2O (4×), and the combined organic phases were washed with saturated aqueous $NaHCO_3$ and brine. Drying (Na_2SO_4), filtration, and concentration provided the diphenyl alcohol **14** as a pale yellow oil (518 mg, 96%). In practice this material was used without further purification. A small sample was purified by flash column chromatography (eluent: EtOAc:hexane; 1:4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.5 Hz, 4H), 7.31 (m, 4H), 7.22 (m, 2H), 3.67 (d, J = 5 Hz, 1H), 2.26 (m, 2H), 2.09 (s, 1H), 1.86 (ddd, J = 13, 8, 5 Hz, 1H), 1.64 (m, 1H), 1.48−1.10 (m, 7H), 1.23 (s, 3H), 0.93 (s, 3H), 0.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 128.1, 126.8, 126.0, 125.8, 86.6, 86.0, 78.2, 55.6, 45.1, 42.4, 38.9, 28.0, 26.0, 25.7, 23.9, 23.3, 18.7. IR (neat) ν_{max} 3400(br), 3065, 3024, 2960, 2870, 1599, 1496, 1465, 1448, 1389, 1368, 1189, 752, 700 cm^{-1}. MS m/z (rel intensity) 364(M^+, 4), 346(2), 331(1), 238-(12), 193(16), 183(100). HRMS Calcd for $C_{25}H_{32}O_2$: 364.24023. Found: 364.24030.

2β-(4′,4′-Diphenyl-3′-butenyl)-1α,3,3-trimethyl-7-oxabicyclo[2.2.1]heptane (15). A solution of the alcohol **14** (1.25 g, crude material) in $CHCl_3$ (130 mL) containing p-TsOH·H_2O (29 mg) was heated to reflux for 15 h. After cooling the solution to room temperature, solid K_2CO_3 was added and the mixture was stirred for 10 min. Filtration and concentration afforded a yellow oil (1.11 g) which was flash chromatographed (eluent: EtOAc:hexane; 7:93) providing the olefin **15** as a pale yellow oil (761 mg, 86% from **13**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.4−7.15 (m, 10H), 6.06 (t, J = 7 Hz, 1H), 3.68 (d, J = 5 Hz, 1H), 2.07 (m, 2H), 1.86 (ddd, J = 13, 8, 5 Hz, 1H), 1.64 (ddd, J = 17, 12, 5 Hz, 1H), 1.50−1.33 (m, 5H), 1.21 (s, 3H), 0.93 (s, 3H), 0.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 141.7, 129.9, 129.8, 128.1, 128.1, 127.1, 126.9, 126.8, 86.6, 86.0, 55.4, 45.2, 38.9, 29.8, 27.9, 25.9, 25.7, 23.3, 18.7. IR (neat) ν_{max} 3057, 3024, 2963, 2871, 1723, 1663, 1599, 1494, 1447, 1382, 1365, 1192, 829, 761, 702 cm^{-1}. MS m/z (rel intensity) 346(M^+, 10), 206(100), 193(78), 178(20), 167(15), 153(21), 115(52), 91(49).

2β-(2′-Carboxyethyl)-1α,3,3-trimethyl-7-oxabicyclo[2.2.1]-heptane (16a) and 2β-(2′-Carbomethoxyethyl)-1α,3,3-trimethyl-7-oxabicyclo[2.2.1]heptane (16b). To a stirred solution of the olefin **15** (342 mg, 0.99 mmol) in $tert$-BuOH (70 mL) was added a solution of $NaIO_4$ (1.27 g, 5.94 mmol, 6 equiv) and $KMnO_4$ (29 mg, 0.18 mmol, 0.18 equiv) in water (140 mL). 5% aqueous K_2CO_3 was slowly added dropwise to adjust the pH of the solution to 8.2. After stirring at room temperature for 16 h the reaction mixture was acidified with dilute HCl and extracted with EtOAc (5x). The combined organic layers were washed with water and brine and concentrated. The yellow-orange residue was then dissolved in EtOAc and the resulting solution extracted with 2.5% aqueous $NaHCO_3$ (4x). The combined aqueous phases were once again carefully acidified (0.5 M HCl) and extracted with EtOAc (4x). Finally, washing of the combined organic layers with brine, drying (Na_2SO_4), filtration, and concentration provided the crude carboxylic acid **16a** (176 mg, 84%) which in practice was used without further purification. A small portion was flash chromatographed (eluent: EtOAc:hexane; 3:7) giving a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (br s, 1H), 3.75 (d, J = 5 Hz, 1H), 2.32 (m, 2H), 1.90 (ddd, J = 13, 8, 5 Hz, 1H), 1.77−1.16 (m, 6H), 1.33 (s, 3H), 1.04 (s, 3H), 0.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.0, 86.7, 86.1, 55.3, 45.2, 38.9, 34.3, 26.0, 25.7, 23.3, 22.8, 18.7. IR (neat) ν_{max} 3650−2450(br), 2965, 2880, 1734, 1710, 1469, 1385, 1265, 1199 cm^{-1}. MS m/z (rel intensity) 212(M^+, 2), 197(5), 167(42), 149(100). HRMS Calcd for $C_{12}H_{20}O_3$: 212.14124. Found: 212.14120. This material was additionally characterized as its methyl ester: Treatment of a small sample of this acid **16a** with CH_2N_2 in Et_2O, concentration, and filtration through a small plug of silica gel provided the methyl ester derivative **16b**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (d, J = 5 Hz, 1H), 3.61 (s, 3H), 2.30

(m, 2H), 1.84 (ddd, J = 13, 8, 4 Hz, 1H), 1.75–1.40 (m, 5H), 1.28 (s, 3H), 1.11 (dd, J = 9, 6 Hz, 1H), 0.99 (s, 3H), 0.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 86.6, 86.1, 55.4, 51.5, 45.2, 38.9, 34.1, 25.9, 25.7, 23.3, 22.9, 18.7. IR (neat) ν_{max} 2963, 2885, 1741, 1439, 1392, 1365, 1256, 1198, 1166 cm^{-1}. MS m/z (rel intensity) 226(M^+, 2), 211(1), 195(1), 183(16), 167(35), 149(100). HRMS Calcd for $C_{13}H_{22}O_3$: 226.15689. Found: 226.15690.

2β-(3′-Oxobutyl)-1α,3,3-trimethyl-7-oxabicyclo[2.2.1]-heptane (17). To a stirred solution of the crude carboxylic acid **16a** (176 mg, ≈0.83 mmol) in dry Et_2O (15 mL) at 0 °C under nitrogen was added a 1.6 M ethereal solution of methyllithium (1.15 mL, 1.84 mmol, 2.2 equiv). Stirring continued at 0 °C for 30 min. and at room temperature for 2 h. Another aliquot of methyllithium (0.26 mL, 0.5 equiv) was added and the solution stirred overnight. Acidification with 0.5 M HCl, extraction with EtOAc (4x), washing of the combined organic phases with brine, drying (Na_2SO_4), filtration, and concentration afforded a yellow oil (155 mg) which was flash chromatographed (eluent: EtOAc:hexane; 1:3) to give the methyl ketone **17** as a colorless oil (104 mg, 50% from **15**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (d, J = 5 Hz, 1H), 2.35 (m, 2H), 2.07 (s, 3H), 1.83 (ddd, J = 13, 8, 5 Hz, 1H), 1.67–1.34 (m, 5H), 1.27 (s, 3H), 1.08 (dd, J = 9, 6 Hz, 1H), 0.99 (s, 3H), 0.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.5, 86.6, 86.1, 55.4, 45.3, 43.8, 38.9, 29.7, 26.1, 25.7, 23.4, 21.6, 18.8. IR (neat) ν_{max} 2963, 2875, 1717, 1467, 1381, 1362, 1239, 1191, 1161 cm^{-1}. MS m/z (rel intensity) 167(M^+–Me–CO, 20), 149(100). HRMS Calcd for $C_{13}H_{22}O_2$: 210.16198. Found: 210.16190.

2β-(3′-Hydroxy-3′-methyl-4′-pentenyl)-1α,3,3-trimethyl-7-oxabicyclo[2.2.1]heptane (18). To a stirred solution of the methyl ketone **17** (104 mg, 0.49 mmol) in dry Et_2O (10 mL) at 0 °C under nitrogen was slowly added a 1 M ethereal solution of vinylmagnesium bromide (0.84 mL, 0.84 mmol, 1.7 equiv). Stirring continued at room temperature for 6 h. The reaction was quenched with saturated aqueous NH_4Cl. Separation of the phases, extraction of the aqueous layer with EtOAc (4x), washing of the combined organic phases with brine, drying (Na_2SO_4), filtration, and concentration afforded a yellow oil (119 mg) which was flash chromatographed (eluent: EtOAc: hexane; 22:78) to give the tertiary allylic alcohol **18** as a colorless oil (90 mg, 77%, 3.65:1 diastereoisomer ratio). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 (m, 1H), 5.22 (m, 1H), 5.08 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0 and 144.9 (2 x $CCH{=}CH_2$), 111.83 and 111.76 (2 x $CCH{=}CH_2$), 77.2 and 76.5 (2 x $CC(OH)$(Me)-). IR (neat) ν_{max} 3446, 2964, 2873, 1654, 1647, 1458, 1382, 1364, 1193, 994, 918 cm^{-1}. MS m/z (rel intensity) 220(M^+–H_2O, 12), 203(6), 177(6), 162(36), 153(22), 95(59), 81(100).

(±)-Farnesiferol-C (10). The tertiary allylic alcohol **18** (57.5 mg, 0.241 mmol) was dissolved in (2.2 mL) of a mixture of pentane:Et_2O:pyridine (65:43:1). The resulting solution was cooled to 0 °C and treated with a solution of PBr_3 (0.103 mL, 1.08 mmol) in dry Et_2O (2.1 mL). The reaction was stirred at 0 °C for 30 min and at room temperature for 3.5 h. Ice-cold water was then added and the mixture extracted with pentane (**4x**). The combined organic phases were washed with 1 M H_2SO_4 and with saturated aqueous $NaHCO_3$. Drying (Na_2SO_4), filtration, and concentration gave a yellow oil which was dissolved in dry acetone (5 mL) and treated sequentially with anhydrous K_2CO_3 (140 mg, 1.01 mmol) and umbelliferone (7-hydroxycoumarin) (44 mg, 0.27 mmol, 1.1 equiv based on **17**). The mixture was stirred at room temperature for 18 h and then filtered through a plug of Celite. The residue obtained after concentration was dissolved in EtOAc and the resulting solution washed with water and dilute aqueous $NaHCO_3$. Drying (Na_2SO_4), filtration, and concentration gave a yellow gum. Prepurification was achieved by flash chromatography (eluent: ethyl acetate:hexane; 1:4) to give a yellow gum which was taken up in diisopropyl ether. Placement in the freezer for *extended periods* resulted in the crystallization of ***(±)*-farnesiferol-C** as white blocks (35 mg, 38%). After several recrystallizations from diisopropyl ether a sample of constant mp (79–80 °C) [lit. 84–85 °C (Et_2O/hexane; for natural product; (−)-enantiomer);[17] 85–87 °C (synthetic (±)-farnesiferol-C)[20]] was obtained. The supernatant was a (2.7:2.5:1) mixture of three compounds whose identities were not established.[23] For (±)-farnesiferol-C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 9.5 Hz, 1H), 7.37 (d, J = 8.5 Hz, 1H), 6.85 (dd, J = 8.5, 2.4 Hz, 1H), 6.82 (d, J = 2.4 Hz, 1H), 6.25 (d, J = 9.5 Hz, 1H), 5.47 (br t, J = 6.5 Hz, 1H), 4.61 (d, J = 6.5 Hz, 2H), 3.72 (d, J = 5 Hz, 1H), 2.05 (m, 2H), 1.89 (ddd, J = 13, 8, 5 Hz, 1H), 1.77 (s, 3H), 1.68 (m, 1H), 1.52–1.38 (m, 4H), 1.33 (s, 3H), 1.18 (dd, J = 9, 6 Hz, 1H), 1.04 (s, 3H), 1.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 161.2, 155.8, 143.4, 142.6, 128.7, 118.4, 113.2, 113.0, 112.4, 101.5, 86.6, 86.0, 65.3, 55.2, 45.2, 39.6, 38.9, 26.1, 25.8, 25.7, 23.4, 18.9, 16.7. IR (neat) ν_{max} 2962, 2870, 1734, 1613, 1558, 1506, 1457, 1402, 1386, 1350, 1277, 1230, 1194, 1123, 999, 833 cm^{-1}. MS m/z (rel intensity) 382(M^+, 7), 365(5), 339(16), 284(5), 273(11), 220(15), 203(9), 177(8), 162(46), 153(30), 139(18), 135(31), 123(21), 107-(30), 95(76), 81(100). Anal. Calcd for $C_{24}H_{30}O_4$: C, 75.36; H, 7.91. Found: C, 75.58; H, 7.85.

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Supporting Information Available: Copies of spectra for the following new compounds. ^{1}H NMR: **5a**, **5c**, **7**, **10**, **14**, **15**, **16a**, **16b**, **17**, **18**; ^{13}C NMR: **5a**, **7**, **10**, **14**, **15**, **16b**, **17** (19 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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