Synthesis of coruscanones A and B, metabolites of *Piper coruscans*, and related compounds

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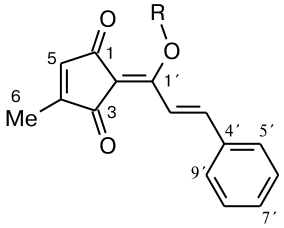
Base-catalyzed rearrangements of both individual 4-(acylmethylidene)butenolides and their mixtures prepared by condensation of citraconic anhydride with various phosphoranes occur successfully only in the presence of 5.2% MeONa in MeOH (molar ratio MeONa : substrate ≤ 10 : 1, room temperature, 1—2 h). Under these conditions, the yields of 2-cinnamoyl-4-methylcyclopent-4-ene-1,3-dione (coruscanone B) and 2-acetyl-4-methylcyclopent-4-ene-1,3-dione are 56 and 65%, respectively. With a considerable increase in the reaction temperature or the molar ratio MeONa : substrate, formal addition of MeOH to the C(4)=C(5) double bond of these triketones becomes an appreciable (or predominant) process. A reaction of coruscanone B with CH_2N_2 in ether gives coruscanone A as a ~3 : 2 mixture of (*Z*)- and (*E*)-methyl enolates (43%); other products (10%) result from the expansion and aromatization of the five-membered ring of the triketone. The simplest analog of coruscanone B, 2-acetyl-4-methylcyclopent-4-ene-1,3-dione, reacts with CH_2N_2 in a similar way.

Key words: citraconic anhydride, the Wittig reaction, 4-(acylmethylidene)butenolides, base-catalyzed rearrangements, 2-acylcyclopent-4-ene-1,3-diones, coruscanones A and B, O-alkylation, diazomethane.

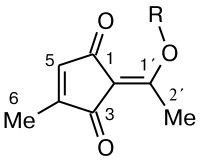
In the last few years, many biochemical and pharmacological investigations have been focused on cyclopentene β,β′-triketones (2-acylcyclopent-4-ene-1,3-diones) and methyl ethers of the corresponding enols produced by higher plants of the genera *Calythrix*, *Lindera*, and *Piper*. Some of them proved to be efficient antifungal,[1—3] antitumor,[2,4] and antiinflammatory agents,[5,6] as well as chimase,[7] chitin synthase 2,[3] and farnesyl-protein transferase inhibitors.[4]

During our systematic studies[8—13] of the physicochemical and biological properties of 2-acetylcyclopent-4-ene-1,3-diones, we needed to compare the biological activities of coruscanone B (**1**), its methyl enolate, coruscanone A (**2**) (both are the metabolites of *Piper coruscans*[1]), and their simplest synthetic analogs **3** and **4**. Coruscanone A (**2**) showed potent *in vitro* antifungal activity against the fluconazole-resistant strains *Candida albicans* and *Cryptococcus neoformans*, which are the main opportunistic fungi that attack AIDS patients with lowered immunity.[1,2]



1, 2

R = H (**1**, **3**), Me (**2**, **4**)



3, 4

Two known routes to coruscanone B (**1**) start from citraconic anhydride[1,2] and 2-acetylfuran.[14] The former method is simpler and more efficient, involving the conversion of citraconic anhydride into the corresponding 4-ylidenebutenolide and its base-catalyzed rearrangement into the target triketone **1**.

The goal of the present work was to obtain coruscanone B (**1**) and its simplest analog, triketone **3**, according to the aforementioned approach[1,2] and further conversion of triketones **1** and **3** into their methyl enolates **2** (coruscanone A) and **4**, respectively. Earlier, triketone **3** has not been synthesized in this way.

This approach was first employed for the synthesis of 2-isobutyroyl-4,5-dimethylcyclopent-4-ene-1,3-dione (calythrone) and related cyclopentene β,β′-triketones.[15,16]

In our experiments, the Wittig reaction of anhydride **5** with phosphorane **6** (benzene, 11-h reflux, Scheme 1) occurred regiospecifically at the unhindered carbonyl group of the substrate to give a ~9 : 1 mixture of known[1,2] (*E*)-butenolide **8** and undocumented (*Z*)-butenolide **10** in a total yield of 76%. These butenolides were isolated in the individual state by column chromatography on SiO_2. The column chromatography revealed no trace amounts of

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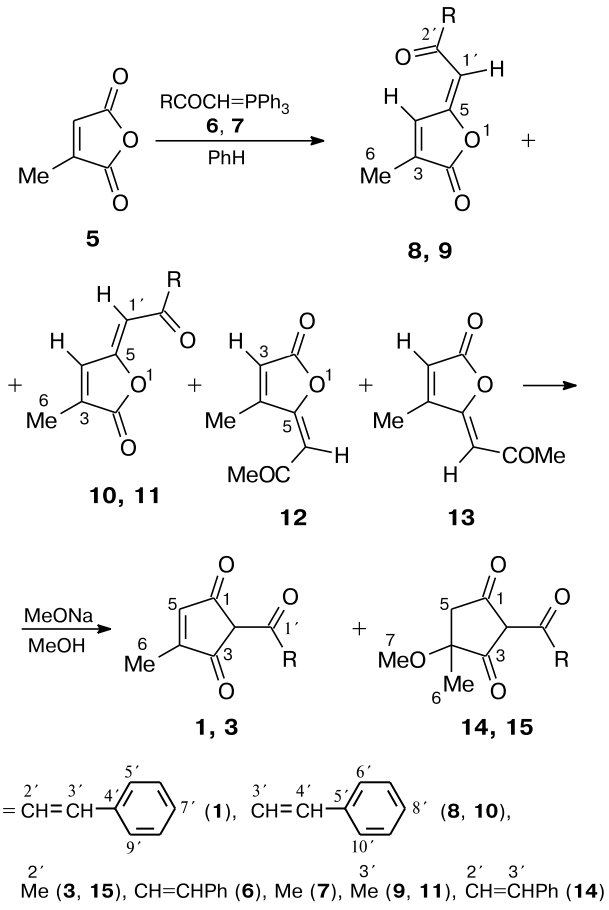
products that would result from an attack of phosphorane **6** at the sterically hindered carbonyl group of anhydride **5**. The Wittig reaction of anhydride **5** with a less bulky and less reactive phosphorane **7** (toluene, 16-h reflux) was regioselective, mainly occurring at the less hindered carbonyl group. However, apart from products **9** and **11**, their regioisomers **12** and **13** were also obtained in noticeable amounts (total yield of 14%). Compound **12** has not been documented hitherto. The ratio of butenolides **9** : **11** : **12** : **13** in the final mixture is 26 : 11 : 1 : 6 (^{1}H NMR data). The total yield of butenolides **9** and **11**—**13** was 89%.

Scheme 1



Butenolides **9** and **11**—**13** were isolated in the individual state by column chromatography on SiO_2. Compounds **12** and **13** can easily be distinguished from their regioisomers **9** and **11** by ^{1}H NMR spectroscopy. In the spectra of (*E*)-butenolide **12** and (*Z*)-butenolide **13**, the protons of the Me group in the β-position of the carbonyl-conjugated double bond C(3)=C(4)* resonate at δ 2.35 and 2.20, respectively, while the corresponding signals in the spectra of (*E*)-butenolide **9** and (*Z*)-butenolide **11** appear at δ 2.10 and 2.11, respectively. When comparing the ^{1}H NMR spectra of butenolides **8** and **10** with those of butenolides **9** and **11**, one can see that compounds **8** and **9** are (*E*)-isomers and compounds **10** and **11** are (*Z*)-isomers with respect to the exocyclic double bond C(5)=C(1′). The ^{1}H NMR spectra of these compounds show characteristic signals for H(4) and H(1′). In the spectra of (*E*)-butenolides **8** and **9**, the signals for H(4) appear at δ 8.11 and 7.98 (as a result of the deshielding effect of the carbonyl dipole of the COMe group), while the signals for H(1′) appear at δ 6.48 and 6.17, respectively (as a result of the deshielding effect of the cisoid O atom of the heterocycle). In the spectra of (*Z*)-butenolides **10** and **11**, the H(4) atoms resonate at δ 7.19 and 7.17 and the H(1′) atoms resonate at δ 5.71 and 5.49, respectively.

Base-catalyzed rearrangements of 4-ylidenebutenolides into the corresponding cyclopentene β,β′-triketones under the action of MeONa in MeOH were first described in Refs 15, 16. Three (*Z*)-4-ylidenebutenolides with structurally different ylidene side chains were obtained from dimethylmaleic anhydride and rearranged according to a general procedure under the following conditions: freshly prepared 0.8% MeONa in anhydrous MeOH, MeONa : substrate = 7.2—10.5 (mol/mol), 1-h reflux. The yields of triketones were 78—90%.

Using this procedure for rearrangement of (*E*)-butenolide **8** (0.78% MeONa in MeOH, MeONa : substrate = = 10.5 : 1, 1-h reflux), we unexpectedly obtained a mixture of coruscanone B (**1**) (21% yield) and undocumented methoxy triketone **14** (56% yield) (see Scheme 1). Under the conditions employed in Ref. 1 (5.2% MeONa in MeOH, MeONa : substrate = 10.0 : 1, room temperature, 3 h), the yield of coruscanone B (**1**) increased to 47% (against 62% in Ref. 1); however, methoxy triketone **14** was also obtained (9%).

Monitoring of the course of the reaction by chromatography revealed that the formation of coruscanone B is completed in 1 h. The yields of compounds **1** and **14** were 52 and 5%, respectively. These conditions for the rearrangement of (*E*)-butenolide **8** seem to be nearly optimum since the yield of coruscanone B (**1**) decreases under other conditions. For instance, for 2.5% MeONa in MeOH and MeONa : substrate = 5.0 : 1 (room temperature, 1 h), the yields of products **1** and **14** were 43 and 3%, respectively; for 8.2% MeONa in MeOH and MeONa : substrate = = 18.0 : 1 (room temperature, 1 h), the corresponding yields were 40 and 33%. As shown above, the formation of compound **14** is best promoted at elevated temperatures.

Methoxy triketone **14** can easily be transformed into coruscanone in 67% yield when treated with dry 6% HCl in MeOH at room temperature for 1 h. This makes the synthesis of coruscanone B (**1**) more efficient. Moreover,

* Numbering of the C atoms is shown on the structural formulas of the compounds.

the latter can be obtained not only from pure (*E*)-butenolide **8**. Rearrangement of a mixture of (*E*)- and (*Z*)-butenolides **8** and **10** under optimum conditions (5.1% MeONa in MeOH, MeONa : substrate = 10.0 : 1, room temperature, 1 h) afforded coruscanone B (**1**) in 56% yield, the yield of methoxy triketone **14** being 6%. Upon the conversion **14** → **1**, the total yield of coruscanone B was increased to 60%.

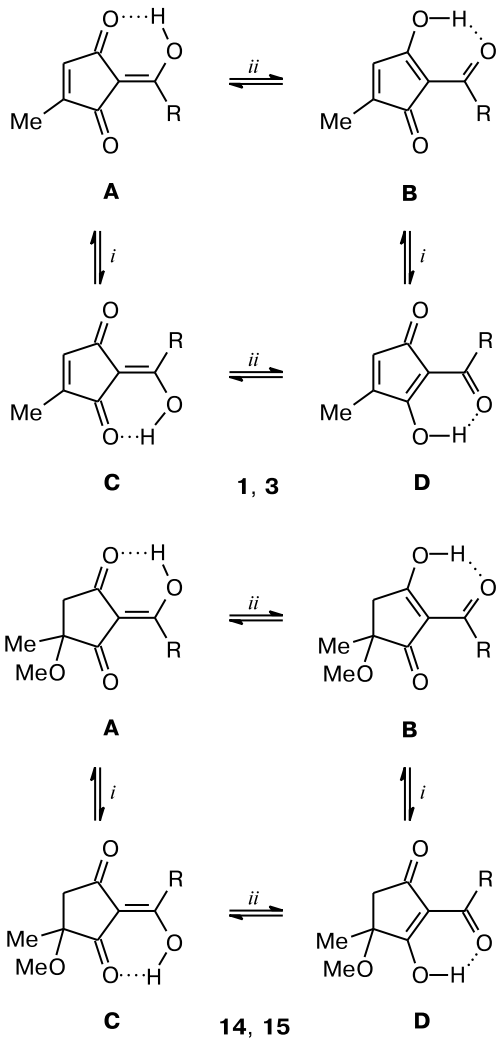
Rearrangement of less reactive acetonylidenebutenolide **9** (freshly prepared 5.5% MeONa in MeOH, MeONa : substrate = 5.0 : 1, room temperature, 2 h) gave a mixture of known triketone **3** (50% yield) and undocumented methoxy triketone **15** (2% yield). Under the same conditions (except that the ratio MeONa : substrate was increased to 10.0 : 1), the yield of triketone **3** was 61% and the yield of product **15** was 4%.

As in the synthesis of triketone **1**, triketone **3** can be obtained not only from pure (*E*)-butenolide **9**. Rearrangement of a mixture of butenolides **9** and **11**—**13** under the aforementioned optimum conditions gave triketone **3** in 65% yield. The yield of triketone **15** was 8%.

Because compounds **1** and **14** have close R_f values, their chromatographic separation is difficult. So we tried to separate them by extraction from a solution in $CHCl_3$ with aqueous saturated $NaHCO_3$. These triketones are both fully enolized in $CHCl_3$ and either can theoretically exist as a mixture of four enol species **A**—**D** (Scheme 2). Because each tautomer contains a fragment of a vinylogous carboxylic acid, these compounds exhibit pronounced acid properties. However, it turned out that methoxy triketone **14** is a stronger acid than triketone **1** and when treated with a solution of $NaHCO_3$ can easily be extracted from the organic phase as the corresponding salt. Treatment of the bicarbonate extract with 10% HCl liberated triketone **14**. Products **3** and **15** were separated in a similar way.

The spectroscopic characteristics of compound **1** fully agree with those of both natural[1,17] and earlier prepared synthetic coruscanone B.[1,2,14] In the ^{1}H NMR spectrum of coruscanone B (**1**), each signal for the Me, OH, and H(5) protons appears as a set of two similar signals, which suggests the presence of two enol forms of this compound in $CDCl_3$. One form is slightly dominant: the integral intensity ratio for analogous signals is ~11 : 9 in our case and 1.2 : 1 in natural coruscanone B.[1] The rate of exchange between tautomers **A** and **B** (see Scheme 2) in a solution of coruscanone B is two orders of magnitude higher than the NMR time scale and hence these tautomers cannot be differentiated spectroscopically. The same relates to tautomers **C** and **D**. At the same time, the rate of exchange between tautomers **A** and **C** or between tautomers **B** and **D** is comparable with the NMR time scale, which allows these equilibria to be seen in the spectrum. Earlier,[18] we found that triketone **3** obtained, like compound **1**, according to Scheme 1 exists in $CDCl_3$ as an equilibrium mixture of tautomers **A** and **C** in a ratio

Scheme 2



i. Slowly. *ii*. Rapidly.
R = CH=CHPh (**1**, **14**), Me (**3**, **15**)

of ~3 : 2. Quantum-chemical DFT calculations at the B3LYP/6-31G(d) level showed that enolization of triketone **3** should occur almost completely in the side chain since the total Gibbs energies (G_H) of tautomers **A** and **C** are lower by 5—6 kcal mol^{-1} than the corresponding G_H values of tautomers **B** and **D**. The difference in the G_H values between tautomers **A** and **C** is small, species **A** being slightly more favorable ($G_{H(C)} - G_{H(A)} \approx$ ≈ 0.8—1.0 kcal mol^{-1}). When comparing the ^{1}H and ^{13}C chemical shifts in the corresponding NMR spectra of triketone **3** and coruscanone B (**1**), one can conclude that triketone **1** also exists as an equilibrium mixture of tautomers **A** and **C** (see Scheme 2), the former being dominant. Tautomers **A** and **C** may be regarded as geometrical (*E*)- and (*Z*)-isomers, respectively, with respect to the double bond C(2)=C(1′).

The structure of undocumented methoxy triketone **14** was determined from ^{1}H and ^{13}C NMR, IR, and mass spectra. According to ^{1}H and ^{13}C NMR spectra, triketone **14** in $CDCl_3$ exists as an equilibrium mixture of two tautomers. A large difference between the ^{1}H chemical shifts of the CH_2 protons and the C(4)Me and OMe protons for these species suggests that the observed equilibrium is between tautomers **B** and **D** (~3 : 2, see Scheme 2) rather than between tautomers **A** and **C** as in the case of coruscanone B (**1**).

This conclusion is true for related methoxy triketone **15** also existing as an equilibrium ~3 : 2 mixture of tautomers **B** and **D** (^{1}H NMR data).

Interestingly, the ^{1}H and ^{13}C NMR spectra of compound **14** in DMSO-d_6 show only one set of signals. Such a spectral pattern is probably explained by a much higher rate of exchange between DMSO-solvated enol forms **B** and **D**, which seems to pass through a triketone intermediate (in DMSO, the formation of this species is very likely[19]). Apparently, the rate of this exchange is higher than the NMR time scale and hence the ^{1}H and ^{13}C NMR spectra show signals for an average form of compound **14**.

The formation of considerable amounts of methoxy triketone **14** in the synthesis of coruscanone B prompted us to study the reaction scheme leading to this by-product. Fundamentally, it can form in two ways. According to the first way (Scheme 3), the methoxide anion attacks the electrophilic C(3) center of butenolide **8** and another MeONa molecule attacks the electrophilic C(2) center of intermediate **16**. The resulting double salt **17a** undergoes cyclization, through its tautomer **17b**, into salt **18**. Acid hydrolysis of the latter gives methoxy triketone **14**.

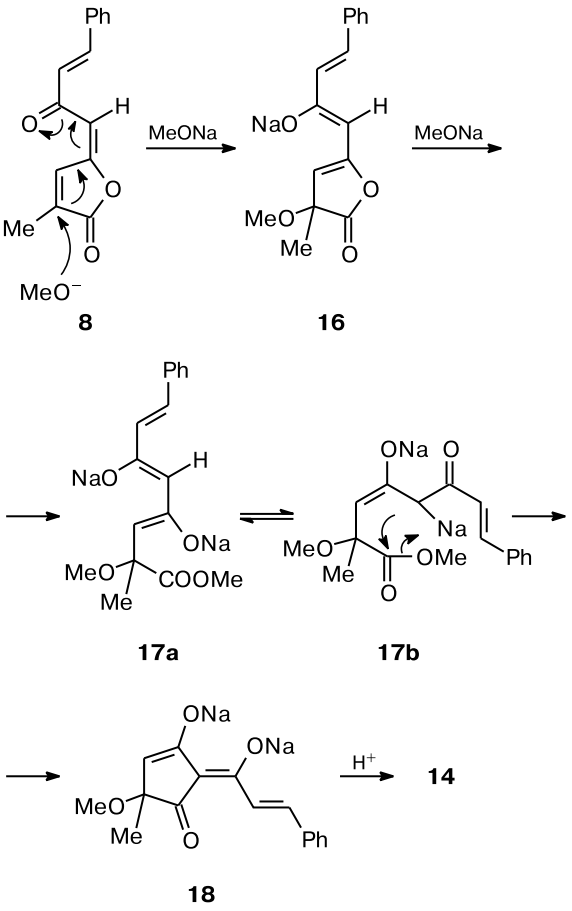
An alternative way involves an initial attack of the methoxide anion on butenolide **8** at the C(2) rather than C(3) atom (Scheme 4). The resulting coruscanone B salt **20** can be transformed, *via* conjugated addition of a second MeONa molecule, into double salt **18** and further into product **14** (acid hydrolysis).

To verify this assumption, we treated coruscanone B (**1**) with freshly prepared 5.2% MeONa in MeOH (MeONa : substrate = 10.0 : 1) in an inert atmosphere at room temperature for 1 h. Upon acid hydrolysis, the yield of methoxy triketone **14** was only 10%. Therefore, the formation of product **14** predominantly involves the conversion sequence **8** → **16** → **17** → **18** → **14** (see Scheme 3).

Under similar conditions, triketone **3** reacted with MeONa as well; however, the yield of product **15** was very low (~2%).

Our study of base-catalyzed rearrangements of 4-ylidenebutenolides **8**, **10** and **9**, **11**—**13** revealed the two most important conditions for the successful synthesis of triketones **1** and **3**: the reaction temperature must be ~20 °C and the molar ratio MeONa : substrate should not exceed

Scheme 3

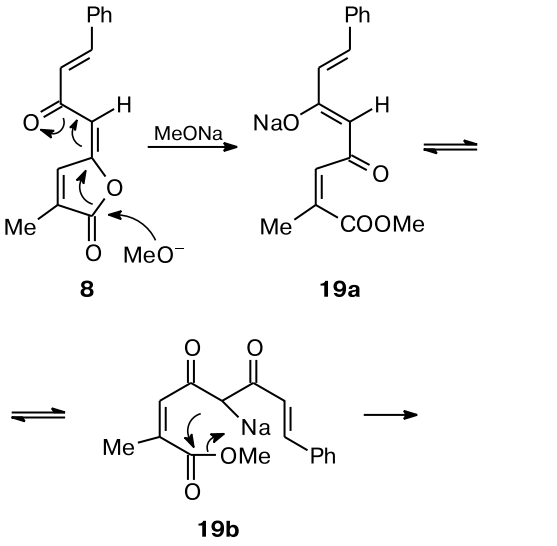


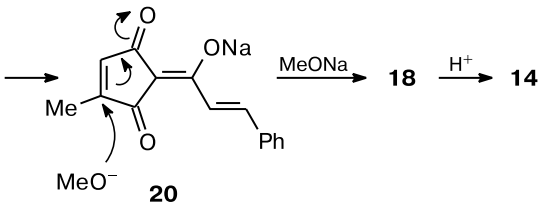
12 : 1 (an optimal value is 10 : 1). The reaction time is less important (1—2 h). When the reaction is carried out in boiling methanol, the fractions of methoxy triketones **14** and **15** increase substantially (note that rearrangements of 4-ylidenebutenolides prepared from dimethylmaleic anhydride produce no such compounds[15,16]).

To obtain coruscanone A (**2**), which is methyl enolate of coruscanone B (**1**), first we tried out relatively simple and rapid O-methylation with CH_2N_2. Diazomethane is known to be often employed earlier for the preparation of methyl enolates of cyclopentane β,β′-triketones, including natural ones.[20—23] However, a reaction of coruscanone B (**1**) with diazomethane gave a mixture of several products (Scheme 5), which were separated by column chromatography on SiO_2.

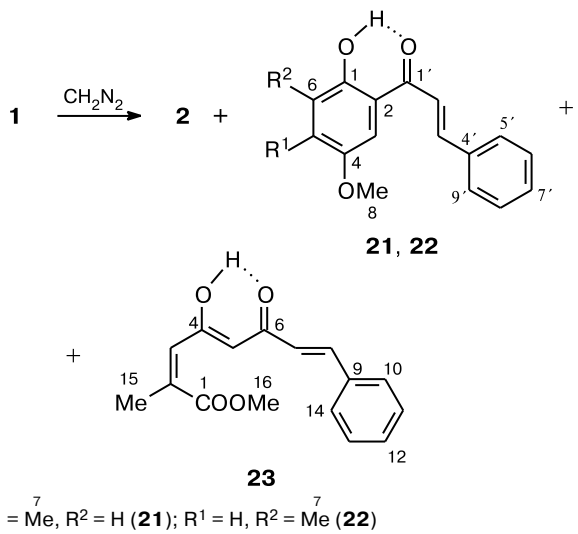
The target coruscanone A (**2**) was isolated as a ~3 : 2 mixture of (*Z*)- and (*E*)-methyl ethers **2A** and **2C** in 43% yield. The ratio of the isomers (relative to the double bond C(2)=C(1′)) was determined from the ^{1}H NMR spectrum in $CDCl_3$. Natural coruscanone A (**2**) exists in $CDCl_3$ as a ~1 : 1 mixture of (*Z*)- and (*E*)-isomers.[1] Apart from coruscanone A (**2**), we isolated a ~5 : 2 mixture of regioisomers **21** and **22** (2-cinnamoyl-4-methoxy-5(6)-meth-

Scheme 4





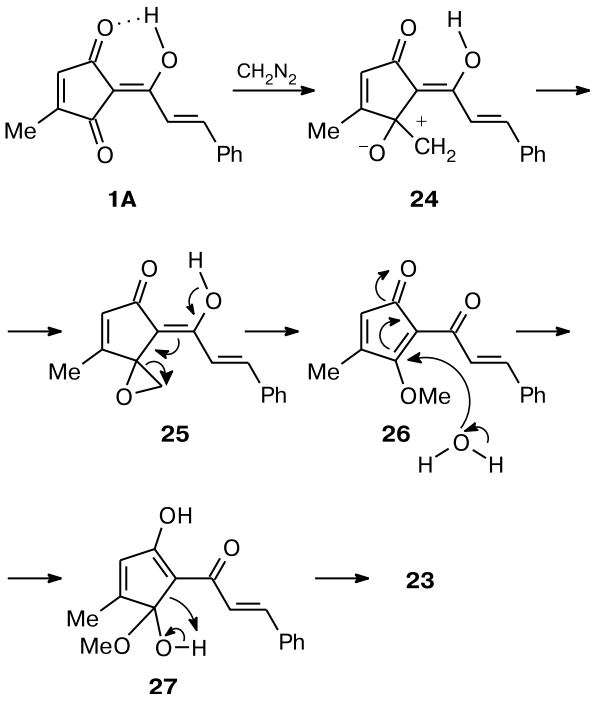
Scheme 5



$R^1 = \overset{7}{Me}$, R^2 = H (**21**); R^1 = H, $R^2 = \overset{7}{Me}$ (**22**)

ylphenols) in 10% yield. The position of the methyl group (at the C(5) or C(6) atom) in their structures and the (*E*)-configuration of the double bond C(2′)=C(3′) ($J_{(H2'),H(3')}$ = 15.4 Hz) were determined from the ^{1}H NMR spectrum. Apparently, the formation of these products results from an attack of a carbene on the carbonyl C(1) and C(3) atoms, respectively, of the five-membered ring of coruscanone B (**1**), which is followed by ring expansion and aromatization and O-methylation of the free OH group of the resulting hydroquinone (earlier,[24] this transformation was discussed in detail for a reaction of CH_2N_2 with 2-acetylindane-1,3-dione). The ratio **21** : **22** indicates that the carbene mainly attacks the less hindered carbonyl group of coruscanone B (**1**). Another product of this reaction was compound **23** (8%) identified as methyl octatrienoate from ^{1}H and ^{13}C NMR, IR, and mass spectra. The (*Z*)-configuration of the double bond C(2)=C(3) of this compound was determined from a strong NOE in the 2D NOESY spectrum of ester **23** between the spins of the C(2)Me and H(3) protons. The (*E*)-configuration of the double bond C(7)=C(8) is evident from $J_{H(7),H(8)}$ = = 15.9 Hz in the ^{1}H NMR spectrum. Apparently, this compound is produced by a reaction of very unstable cyclopentadienone enolate **26** with a water molecule (Scheme 6).

Scheme 6

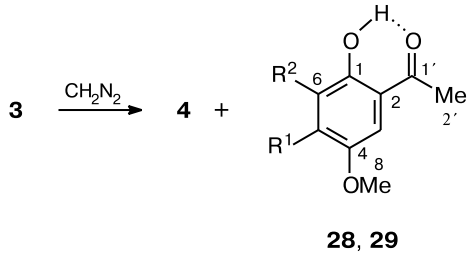


The presence of water traces in the reaction mixture is due to incomplete drying of a rapidly prepared solution of CH_2N_2 in ether. When the solution was dried thoroughly, product **23** was not formed.

Model β,β′-triketone **3** reacted with CH_2N_2 in a similar way; however, the yields and ratio of products differed from those in the case of coruscanone B (**1**) (Scheme 7).

A difficult-to-separate mixture of nearly equal amounts of (*Z*)- and (*E*)-enolates **4A** and **4C** (relative to the double

Scheme 7



28, **29**

$R^1 = \overset{7}{Me}$, R^2 = H (**28**); R^1 = H, $R^2 = \overset{7}{Me}$ (**29**)

bond C(2)=C(1′)) was isolated in ~50% yield. The yield of a ~3 : 2 mixture of regioisomers **28** and **29** (2-acetyl-4-methoxy-5(6)-methylphenols) was 25%. In this case, no product of the type **23** was detected.

A more suitable procedure for the synthesis of coruscanone A (**2**) involves methylation of coruscanone B (**1**) with Me_2SO_4 in dry acetone in the presence of anhydrous K_2CO_3. The yield of coruscanone A (**2**) as a ~3 : 2 mixture of (*E*)- and (*Z*)-methyl enolates was 77%; no by-products were detected. At the same time, methylation of model triketone **3** under similar conditions gave product **4** as a ~3 : 2 mixture of (*E*)- and (*Z*)-methyl enolates only in 20% yield.

Hence, the nature of the acyl substituent at the C(2) atom in triketones **1** and **3** substantially influences the outcomes of their reactions with CH_2N_2 and Me_2SO_4.

Experimental

Melting points were determined on a Boetius hot stage and are given uncorrected. IR spectra were recorded on a Bruker Vector 22 spectrophotometer in $CHCl_3$. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX-300 spectrometer (300.13 (^1H) and 75.47 MHz (^{13}C)) in $CDCl_3$ with Me_4Si as the internal standard. Mass spectra (EI) were measured on an AMD 604 S instrument (8 kW, direct inlet probe, ionizing energy 70 eV). The course of the reactions was monitored, and the purity of the products was checked, by TLC on Silufol UV 254 plates in benzene—acetone systems from 15 : 1 to 2 : 1. The products were isolated in the individual state by column chromatography on SiO_2 (Alfa Aesar, 70—230 μm) with hexane—acetone mixtures as eluents. Elemental analysis was carried out on a Flash E1112 C, H, N-analyzer.

Freshly distilled citraconic anhydride **5** (b.p. 85 °C, 5 Torr) was used. Phosphoranes **6** (see Ref. 1) and **7** (see Ref. 25) were prepared according to known procedures. A solution of diazomethane in ether was prepared in a separatory funnel by decomposition of *N*-methyl-*N*-nitrosourea with aqueous NaOH; the organic layer was dried over anhydrous Na_2SO_4.

(5*E*)-3-Methyl-5-(2-oxo-4-phenylbut-3-en-1-ylidene)furan-2(5*H*)-one (8) and (5*Z*)-3-methyl-5-(2-oxo-4-phenylbut-3-en-1-ylidene)furan-2(5*H*)-one (10). A solution of citraconic anhydride **5** (1.8 g, 16.1 mmol) in benzene (10 mL) was added under argon to a boiling solution of phosphorane **6** (5.5 g, 13.5 mmol) in anhydrous benzene (50 mL). The reaction mixture was refluxed for 11 h. The solvent was removed and the residue was chromatographed on SiO_2. Elution with hexane—acetone ((30 : 1)—(20 : 1)) gave butenolide **8** (2.2 g, 68%) as yellow needles, m.p. 158—159 °C (chloroform—ethanol, 1 : 1) (*cf.* Ref. 1: m.p. 160—161 °C). IR, ν_{max}/cm^{-1}: 1786 (C=O), 1652 (C=O), 1628 (C=C), 1617 (C=C), 1598 (C=C), 1577 (C=C). ^1H NMR ($CDCl_3$), δ: 2.11 (dd, 3 H, C(3)Me, J = 1.7 Hz, J = 0.6 Hz); 6.48 (quint, 1 H, H(1′), J = 0.6 Hz); 6.88 (d, 1 H, H(3′), J = 16.0 Hz); 7.42 (m, 3 H, H(7′), H(8′), H(9′)); 7.60 (m, 2 H, H(6′), H(10′)); 7.65 (d, 1 H, H(4′), J = 16.0 Hz); 8.11 (dq, 1 H, H(4), J = 1.7 Hz, J = 0.6 Hz).

Elution with hexane—acetone ((20 : 1)—(15 : 1)) gave butenolide **10** (0.245 g, 8%) as yellow needles, m.p. 190—192 °C (chloroform—ethanol, 1 : 1). IR, ν_{max}/cm^{-1}: 1798 (C=O), 1663 (C=O), 1630 (C=C), 1621 (C=C), 1600 (C=C), 1581 (C=C). ^1H NMR ($CDCl_3$), δ: 2.12 (dd, 3 H, C(3)Me, J = 1.7 Hz, J = 1.0 Hz); 5.71 (quint, 1 H, H(1′), J = 1.0 Hz); 6.80 (d, 1 H, H(3′), J = 16.0 Hz); 7.19 (dq, 1 H, H(4), J = 1.7 Hz, J = 1.0 Hz); 7.43 (m, 3 H, H(7′), H(8′), H(9′)); 7.59 (m, 2 H, H(6′), H(10′)); 7.78 (d, 1 H, H(4′), J = 16.0 Hz). Found (%): C, 75.12; H, 4.99. $C_{15}H_{12}O_3$. Calculated (%): C, 74.99; H, 5.03.

(5*E*)-3-Methyl-5-(2-oxopropylidene)furan-2(5*H*)-one (9), (5*Z*)-3-methyl-5-(2-oxopropylidene)furan-2(5*H*)-one (11), (5*E*)-4-methyl-5-(2-oxopropylidene)furan-2(5*H*)-one (12), and (5*Z*)-4-methyl-5-(2-oxopropylidene)furan-2(5*H*)-one (13). A solution of citraconic anhydride **5** (1.12 g, 10 mmol) in toluene (10 mL) was added under argon to a boiling solution of phosphorane **7** (3.18 g, 10 mmol) in anhydrous toluene (90 mL). The reaction mixture was refluxed for 16 h. The solvent was removed and the residue was chromatographed on SiO_2. Elution with hexane—acetone (45 : 1) gave butenolide **9** (0.8 g, 53%) as light yellow needles, m.p. 88—90 °C (ether—hexane, 1 : 1) (*cf.* Refs 26, 27: m.p. 88—89 °C). IR, ν_{max}/cm^{-1}: 1788 (C=O), 1720 (C=O), 1655 (C=C), 1615 (C=C). ^1H NMR ($CDCl_3$), δ: 2.10 (dd, 3 H, C(3)Me, J = 1.5 Hz, J = 0.5 Hz); 2.34 (s, 3 H, COMe); 6.17 (quint, 1 H, H(1′), J = 0.5 Hz); 7.98 (dq, 1 H, H(4), J = 1.5 Hz, J = 0.5 Hz).

Elution with hexane—acetone (38 : 1) gave butenolide **12** (0.027 g, 2%) as a viscous oil. IR, ν_{max}/cm^{-1}: 1815 (C=O), 1795 (C=O), 1725 (C=O), 1660 (C=C), 1618 (C=C). ^1H NMR ($CDCl_3$), δ: 2.33 (s, 3 H, COMe); 2.35 (d, 3 H, C(4)Me, J = 1.6 Hz); 6.21 (quint, 1 H, H(3), J = 1.6 Hz); 6.35 (d, 1 H, H(1′), J = 1.6 Hz). Found (%): C, 63.29; H, 5.32. $C_8H_8O_3$. Calculated (%): C, 63.16; H, 5.26.

Elution with hexane—acetone (35 : 1) gave butenolide **11** (0.33 g, 22%) as light yellow needles, m.p. 123—124 °C (ether—hexane, 1 : 1) (*cf.* Ref. 27: m.p. 125 °C). IR, ν_{max}/cm^{-1}: 1798 (C=O), 1724 (C=O), 1659 (C=C), 1617 (C=C). ^1H NMR ($CDCl_3$), δ: 2.11 (dd, 3 H, C(3)Me, J = 1.5 Hz, J = 1.0 Hz); 2.55 (s, 3 H, COMe); 5.49 (quint, 1 H, H(1′), J = 1.0 Hz); 7.17 (dq, 1 H, H(4), J = 1.5 Hz, J = 1.0 Hz).

Elution with hexane—acetone (33 : 1) gave butenolide **13** (0.18 g, 12%) as light yellow needles, m.p. 91—93 °C (ether—hexane, 2 : 1) (*cf.* Ref. 27: m.p. 92—94 °C). IR, ν_{max}/cm^{-1}: 1805 (C=O), 1789 (C=O), 1701 (C=O), 1671 (C=O), 1649 (C=C), 1622 (C=C). ^1H NMR ($CDCl_3$), δ: 2.20 (d, 3 H, C(4)Me, J = 1.4 Hz); 2.57 (s, 3 H, COMe); 5.59 (d, 1 H, H(1′), J = 0.5 Hz); 6.18 (dq, 1 H, H(3), J = 1.4 Hz, J = 0.5 Hz).

(2*Z*)-[(2*E*)-1-Hydroxy-3-phenylprop-2-en-1-ylidene]-4-methylcyclopent-4-ene-1,3-dione (1A) and (2*E*)-[(2*E*)-1-hydroxy-

3-phenylprop-2-en-1-ylidene]-4-methylcyclopent-4-ene-1,3-dione (1C, coruscanone B), (2*E*)-2-cinnamoyl-3-hydroxy-5-methoxy-5-methylcyclopent-2-en-1-one (14B) and (2*E*)-2-cinnamoyl-3-hydroxy-4-methoxy-4-methylcyclopent-2-en-1-one (14D). A solution of MeONa freshly prepared from metallic Na (0.664 g) in MeOH (20 mL) was added dropwise to a solution of butenolide **8** (0.7 g, 2.8 mmol) in dry MeOH (9 mL). The reaction mixture was stirred at room temperature for 1 h, poured into a mixture of ice and water (45 mL), and acidified with 2 *M* HCl to pH 1.0. The solvent was removed under reduced pressure and the product was extracted from the aqueous suspension with chloroform (4×15 mL). The combined organic extracts were washed with a saturated aqueous solution of $NaHCO_3$ (3×20 mL) and brine (3×15 mL), dried over anhydrous Na_2SO_4, and concentrated. The crude product was chromatographed on SiO_2. Elution with hexane—acetone (30 : 1) gave coruscanone B (**1**) (0.364 g, 52%), m.p. 127 °C (hexane) (*cf.* Ref. 1: m.p. 125 °C). A mixture of tautomers **1A** and **1C**. IR, ν_{max}/cm^{-1}: 3400—2600 (OH), 1709 (C=O), 1650 (C=O), 1631 (C=O, C=C), 1590 (C=C), 1573 (C=C). Major tautomer **1A** ((*Z*)-isomer). ^1H NMR ($CDCl_3$), δ: 2.11 (d, 3 H, C(4)Me, *J* = 1.7 Hz); 6.69 (q, 1 H, H(5), *J* = 1.7 Hz); 7.41 (m, 3 H, H(6′), H(7′), H(8′)); 7.65 (m, 2 H, H(5′), H(9′)); 7.72 and 7.80 (both d, 1 H each, H(3′), H(2′), *J* = 16.0 Hz); 12.10 (br.s, 1 H, C(1′)OH). ^{13}C NMR ($CDCl_3$), δ: 11.4 (C(6)); 103.1 (C(2)); 117.5 (C(2′)); 128.6 (C(5′), C(9′)); 129.0 (C(6′), C(8′)); 130.7 (C(7′)); 134.8 (C(4′)); 137.0 (C(5)); 143.2 (C(3′)); 158.0 (C(4)); 167.9 (C(1′)); 192.2 (C(3)); 200.7 (C(1)). Tautomer **1C** ((*E*)-isomer). ^1H NMR ($CDCl_3$), δ: 2.10 (d, 3 H, C(4)Me, *J* = 1.7 Hz); 6.61 (q, 1 H, H(5), *J* = 1.7 Hz); 7.41 (m, 3 H, H(6′), H(7′), H(8′)); 7.65 (m, 2 H, H(5′), H(9′)); 7.71 and 7.80 (both d, 1 H each, H(3′), H(2′), *J* = 16.0 Hz); 11.99 (br.s, 1 H, C(1′)OH). ^{13}C NMR ($CDCl_3$), δ: 10.6 (C(6)); 103.4 (C(2)); 117.6 (C(2′)); 128.7 (C(5′), C(9′)); 129.0 (C(6′), C(8′)); 130.7 (C(7′)); 134.8 (C(4′)); 140.7 (C(5)); 143.3 (C(3′)); 154.1 (C(4)); 167.7 (C(1′)); 191.7 (C(1)); 201.2 (C(3)). Coruscanone B (**1**). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 241 $[M + 1]^+$ (10), 240 $[M]^+$ (50), 239 $[M - 1]^+$ (6), 225 (4), 223 (3), 222 (4), 212 (12), 211 (27), 198 (9), 197 (44), 196 (16), 195 (100), 194 (10), 171 (33), 165 (13), 144 (13), 138 (15), 115 (25), 104 (13), 103 (20), 77 (23), 69 (18), 32 (90).

Aqueous sodium bicarbonate phase used for washing the organic extract was acidified with 2 *M* HCl to pH 1.0 and the product was extracted with chloroform (4×5 mL). The combined organic extracts were washed with brine (4×5 mL), dried over anhydrous Na_2SO_4, and concentrated. The crude product was chromatographed on SiO_2. Elution with hexane—acetone ((25 : 1)—(20 : 1)) gave triketone **14** (0.038 g, 5%) as light yellow crystals, m.p. 68—72 °C. A mixture of tautomers **14B** and **14D**. IR, ν_{max}/cm^{-1}: 3300—2200 (OH), 1702 (C=O), 1620 (C=O, C=C), 1597 (C=O, C=C), 1580 (C=C), 1554 (C=C). Major tautomer **14B**. ^1H NMR ($CDCl_3$), δ: 1.47 (s, 3 H, C(4)Me); 2.67 and 2.95 (both d, 1 H each, H(5), *J* = 19.1 Hz); 3.32 (s, 3 H, C(4)OMe); 7.45 (m, 3 H, H(6′), H(7′), H(8′)); 7.69 (m, 2 H, H(5′), H(9′)); 7.92 and 8.03 (both d, 1 H each, H(3′), H(2′), *J* = 16.0 Hz); 12.35 (br.s, 1 H, C(1′)OH). ^{13}C NMR ($CDCl_3$), δ: 21.7 (C(6)); 44.1 (C(5)); 52.0 (C(7)); 80.4 (C(4)); 110.0 (C(2)); 118.6 (C(2′)); 129.1 (C(5′), C(9′)); 129.5 (C(6′), C(8′)); 131.5 (C(7′)); 134.3 (C(4′)); 147.9 (C(3′)); 182.0 (C(1)); 199.5 (C(3)); 205.9 (C(1′)). Tautomer **14D**. ^1H NMR ($CDCl_3$), δ: 1.54 (s, 3 H, C(4)Me); 2.53 and 2.84 (both d, 1 H each, H(5), *J* = 18.4 Hz); 3.34 (s, 3 H, C(4)OMe); 7.44 (m, 3 H, H(6′), H(7′), H(8′)); 7.71 (m, 2 H, H(5′), H(9′)); 7.92 and 8.04 (both d, 1 H each, H(3′), H(2′), *J* = 16.0 Hz); 12.20 (br.s, 1 H, C(1′)OH). ^{13}C NMR ($CDCl_3$), δ: 22.0 (C(6)); 47.5 (C(5)); 52.1 (C(7)); 79.0 (C(4)); 110.5 (C(2)); 118.9 (C(2′)); 129.1 (C(5′), C(9′)); 129.5 (C(6′), C(8′)); 131.6 (C(7′)); 135.0 (C(4′)); 148.1 (C(3′)); 181.7 (C(1′)); 196.9 (C(1)); 207.2 (C(3)). Triketone **14**. ^1H NMR (DMSO-d_6), δ: 1.37 (s, 3 H, C(4)Me); 2.69 and 2.90 (both d, 1 H each, H(5), *J* = 18.8 Hz); 3.17 (s, 3 H, C(4)OMe); 7.51 (m, 3 H, H(6′), H(7′), H(8′)); 7.76 (m, 2 H, H(5′), H(9′)); 7.81 and 7.97 (both d, 1 H each, H(3′), H(2′), *J* = 16.0 Hz); 10.30 (br.s, 1 H, C(1′)OH). ^{13}C NMR (DMSO-d_6), δ: 21.7 (C(6)); 43.7 (C(5)); 51.3 (C(7)); 79.6 (C(4)); 110.0 (C(2)); 119.7 (C(2′)); 129.0 (C(5′), C(9′)); 129.3 (C(6′), C(8′)); 131.7 (C(7′)); 134.2 (C(4′)); 146.0 (C(3′)); 181.5 (C(1′)); 200.9 (C(1)); 201.4 (C(3)). MS, *m/z* (I_{rel} (%)): 272 $[M]^+$ (12), 243 (17), 242 (100), 200 (22), 172 (8), 171 (20), 144 (18), 138 (43), 131 (33), 116 (17), 115 (20), 103 (18), 77 (10), 73 (21), 69 (12), 43 (13), 42 (14), 41 (12), 32 (35). Found (%): C, 70.67; H, 5.89. $C_{16}H_{16}O_4$. Calculated (%): C, 70.57; H, 5.92.

Rearrangement of a mixture of butenolides 8 and 10. A ~9 : 1 mixture of (*E*)-butenolide **8** and (*Z*)-butenolide **10** (0.7 g, 2.8 mmol) in dry MeOH (10 mL) and MeONa freshly prepared from metallic Na (0.664 g) in MeOH (20 mL) were stirred at room temperature for 1 h. The workup described above gave coruscanone B (**1**) (0.392 g, 56%) and triketone **14** (0.046 g, 6%).

Conversion of triketone (14) into coruscanone B (1). A mixture of triketone **14** (0.095 g, 0.35 mmol) and a 6% solution of dry gaseous HCl in anhydrous MeOH (5 mL) was stirred at room temperature for 1 h. The reaction mixture was diluted with water (20 mL) and the product was extracted with chloroform (3×5 mL). The combined extracts were dried over anhydrous Na_2SO_4 and concentrated. The crude product was chromatographed on SiO_2. Elution with hexane—acetone (30 : 1) gave coruscanone B (**1**) (0.057 g, 67%), which is identical with the aforementioned sample.

(2*Z*)-2-(1-Hydroxyethylidene)-4-methylcyclopent-4-ene-1,3-dione (3A) and (2*E*)-2-(1-hydroxyethylidene)-4-methylcyclopent-4-ene-1,3-dione (3C), 2-acetyl-3-hydroxy-5-methoxy-5-methylcyclopent-2-en-1-one (15B) and 2-acetyl-3-hydroxy-4-methoxy-4-methylcyclopent-2-en-1-one (15D). A solution of MeONa freshly prepared from metallic Na (2.3 g) in MeOH (58 mL) was added dropwise to a solution of butenolide **9** (1.52 g, 10.0 mmol) in dry MeOH (40 mL). The reaction mixture was stirred at room temperature for 2 h, poured into a mixture of ice and water, and acidified with 2 *M* HCl. The acidic solution was treated as described above for the rearrangement of butenolide **8**. The product was chromatographed on SiO_2. Elution with hexane—acetone (25 : 1) gave triketone **3** (0.92 g, 61%) as light yellow plates, m.p. 43—47 °C (hexane) (*cf.* Ref. 28: m.p. 45—50 °C). A mixture of tautomers **3A** and **3C**. IR, ν_{max}/cm^{-1}: 3235—2300 (OH), 1718 (C=O), 1659 (C=O), 1630 (C=O), 1616 (C=O, C=C), 1590 (C=C). Major tautomer **3A** ((*Z*)-isomer). ^1H NMR ($CDCl_3$), δ: 2.07 (d, 3 H, C(4)Me, *J* = 1.7 Hz); 2.39 (s, 3 H, C(1′)Me); 6.63 (q, 1 H, H(5), *J* = 1.7 Hz); 12.28 (br.s, 1 H, OH). ^{13}C NMR ($CDCl_3$), δ: 11.3 (C(6)); 18.2 (C(2′)); 104.4 (C(2)); 136.3 (C(5)); 157.9 (C(4)); 177.2 (C(1′)); 192.3 (C(3)); 200.1 (C(1)). Tautomer **3C** ((*E*)-isomer). ^1H NMR ($CDCl_3$), δ: 2.06 (d, 3 H, C(4)Me, *J* = 1.7 Hz); 2.40 (s, 3 H, C(1′)Me); 6.56 (q, 1 H, H(5), *J* = 1.7 Hz); 11.97 (br.s, 1 H, OH). ^{13}C NMR ($CDCl_3$), δ: 10.4 (C(6)); 18.2 (C(2′)); 104.6 (C(2)); 140.6 (C(5)); 153.4 (C(4)); 177.0 (C(1′)); 191.8 (C(1)); 200.6 (C(3)). Triketone **3**. MS,

m/z (I_{rel} (%)):153 $[M + 1]^+$ (8), 152 $[M]^+$ (84), 138 (6), 137 (79), 135 (2), 134 (5), 124 (3), 123 (5), 110 (3), 109 (6), 108 (3), 107 (2), 106 (3), 105 (3), 95 (7), 83 (7), 81 (19), 69 (43), 57 (12), 55 (12), 53 (12), 44 (26), 40 (20), 35 (28), 32 (100).

Elution with hexane—acetone (15 : 1) gave triketone **15** (0.07 g, 4%) as light yellow crystals, m.p. 80—83 °C (benzene). A mixture of tautomers **15B** and **15D**. IR, ν_{max}/cm^{-1}: 3215—2210 (OH), 1710 (C=O), 1651 (C=O), 1634 (C=O), 1611 (C=O, C=C), 1585 (C=C). Major tautomer **15B** ((*Z*)-isomer). ^1H NMR ($CDCl_3$), δ: 1.43 (s, 3 H, C(4)Me); 2.54 (s, 3 H, COMe); 2.66 and 2.94 (both d, 1 H each, H(5), *J* = 18.6 Hz); 3.29 (s, 3 H, C(4)OMe); 11.90 (br.s, 1 H, OH). ^{13}C NMR ($CDCl_3$), δ: 21.2 (C(6)); 26.9 (C(2′)); 43.9 (C(5)); 51.8 (C(7)); 80.1 (C(4)); 109.7 (C(2)); 181.1 (C(1)); 198.7 (C(3)); 203.6 (C(1′)). Tautomer **15D** ((*E*)-isomer). ^1H NMR ($CDCl_3$), δ: 1.54 (s, 3 H, C(4)Me); 2.55 (s, 3 H, COMe); 2.45 and 2.76 (both d, 1 H each, H(5), *J* = 18.2 Hz); 3.30 (s, 3 H, C(4)OMe); 11.90 (br.s, 1 H, OH). ^{13}C NMR ($CDCl_3$), δ: 21.6 (C(6)); 26.6 (C(2′)); 46.9 (C(5)); 51.9 (C(7)); 78.9 (C(4)); 110.1 (C(2)); 180.7 (C(3)); 196.1 (C(1)); 205.0 (C(1′)). Triketone **15**. MS, *m/z* (I_{rel} (%)): 184 $[M]^+$ (10), 155 (16), 154 (100), 112 (59), 111 (9), 84 (11), 83 (30), 52 (48), 43 (8), 42 (26), 32 (39). Found (%): C, 58.73; H, 6.59. $C_9H_{12}O_4$. Calculated (%): C, 58.69; H, 6.57.

Rearrangement of a mixture of butenolides 9 and 11—13. A ~26 : 11 : 1 : 6 mixture of (*E*)-butenolide **9**, (*Z*)-butenolide **11**, (*E*)-butenolide **12**, and (*Z*)-butenolide **13** (1.52 g, 10.0 mmol) in dry MeOH (40 mL) and MeONa freshly prepared from metallic Na (2.3 g) in MeOH (60 mL) were stirred at room temperature for 2 h. The workup described above gave triketone **3** (0.98 g, 65%) and triketone **15** (0.14 g, 8%).

Reaction of coruscanone B (1) with diazomethane. A 2% solution of CH_2N_2 in anhydrous ether (20 mL) was added in one portion to a solution of coruscanone B (**1**) (0.12 g, 0.5 mmol) in anhydrous ether (10 mL). The reaction mixture was kept at room temperature for 1 h. The solvent was removed and the residue was chromatographed on SiO_2. Elution with hexane—acetone (50 : 1) gave a 3 : 2 mixture of **(2*E*)-2-cinnamoyl-4-methoxy-5-methylphenol** (**21**) and **(2*E*)-2-cinnamoyl-4-methoxy-6-methylphenol** (**22**) (0.013 g, 10%) as a light yellow viscous oil. A mixture of isomers **21** and **22**. IR, ν_{max}/cm^{-1}: 3400—2400 (OH), 1713 (C=O), 1642 (C=O), 1628 (C=C), 1584 (C=C), 1575 (C=C), 1498, 1466, 1451, 1430, 1356, 1292, 1278, 1259, 1253, 1200, 1182, 1172, 1086, 1061. Ether **21**. ^1H NMR ($CDCl_3$), δ: 2.27 (s, 3 H, C(5)Me); 3.87 (s, 3 H, C(4)OMe); 6.85 and 7.19 (both s, 1 H each, H(6), H(3)); 7.45 (m, 2 H, Ph); 7.67 (m, 3 H, Ph); 7.57 and 7.92 (both d, 1 H each, H(2′), H(3′), *J* = 15.4 Hz); 12.61 (s, 1 H, C(1)OH). ^{13}C NMR ($CDCl_3$), δ: 15.9 (C(7)); 56.1 (C(8)); 110.0 (C(3)); 118.8 (C(2)); 120.6 (C(2′)); 125.2 (C(6)); 128.6 (C(5′), C(9′)); 128.9 (C(5)); 129.0 (C(6′), C(8′)); 130.8 (C(7′)); 134.7 (C(4′)); 145.3 (C(3′)); 151.1 (C(4)); 156.8 (C(1)); 193.6 (C(1′)). Ether **22**. ^1H NMR ($CDCl_3$), δ: 2.30 (s, 3 H, C(6)Me); 3.83 (s, 3 H, C(4)OMe); 7.05 and 7.21 (both d, 1 H each, H(5), H(3), *J* = 2.8 Hz); 7.45 (m, 2 H, Ph); 7.67 (m, 3 H, Ph); 7.61 and 7.92 (both d, 1 H each, H(2′), H(3′), *J* = 15.4 Hz); 12.74 (s, 1 H, C(1)OH). ^{13}C NMR ($CDCl_3$), δ: 16.9 (C(7)); 56.1 (C(8)); 108.9 (C(3)); 117.4 (C(2)); 120.4 (C(2′)); 120.5 (C(5)); 128.6 (C(5′), C(9′)); 129.0 (C(6′), C(8′)); 130.8 (C(7′)); 134.8 (C(4′)); 138.8 (C(6)); 145.0 (C(3′)); 150.4 (C(4)); 158.5 (C(1)); 192.8 (C(1′)). A mixture of isomers **21** and **22**. MS, *m/z* (I_{rel} (%)): 269 $[M + 1]^+$ (17), 268 $[M]^+$ (100), 267 $[M - 1]^+$ (20), 191 (11), 165 (8), 164 (48), 149 (12), 136 (8), 121 (6), 103 (5), 77 (5), 57 (5). Found (%): C, 76.23; H, 6.07. $C_{17}H_{16}O_3$. Calculated (%): C, 76.10; H, 6.01.

Elution with hexane—acetone (45 : 1) gave **methyl (2*Z*, 4*E*,7*E*)-4-hydroxy-2-methyl-6-oxo-8-phenylocta-2,4,7-trienoate** (**23**) (0.010 g, 8%) as light yellow crystals, m.p. 68—70 °C (ethanol). IR, ν_{max}/cm^{-1}: 1717 (C=O), 1633 (C=O), 1580 (C=C), 1575 (C=C), 1449, 1437, 1262, 1200, 1143, 1118. ^1H NMR ($CDCl_3$), δ: 2.37 (d, 3 H, C(2)Me, *J* = 1.5 Hz); 3.82 (s, 3 H, COOMe); 5.84 (s, 1 H, H(5)); 6.60 and 7.68 (both d, 1 H each, H(7), H(8), *J* = 15.9 Hz); 6.94 (q, 1 H, H(3), *J* = 1.5 Hz); 7.40 (m, 3 H, Ph); 7.55 (m, 2 H, Ph); 15.75 (s, 1 H, C(4)OH). ^{13}C NMR ($CDCl_3$), δ: 14.7 (C(15)); 52.6 (C(16)); 104.7 (C(5)); 123.9 (C(7)); 128.2 (C(11), C(13)); 129.0 (C(10), C(14)); 130.4 (C(12)); 132.2 (C(3)); 134.8 (C(9)); 139.9 (C(2)); 141.5 (C(8)); 168.1 (C(1)); 183.2 (C(4)); 184.5 (C(6)). MS, *m/z* (I_{rel} (%)): 273 $[M + 1]^+$ (13), 272 $[M]^+$ (88), 257 (6), 241 (23), 240 (100), 239 (8), 214 (9), 213 (73), 212 (21), 211 (9), 197 (10), 195 (13), 173 (29), 171 (15), 165 (9), 164 (18), 145 (20), 141 (20), 131 (74), 128 (26), 127 (22), 103 (35), 77 (24), 69 (26), 32 (18). Found (%): C, 70.69; H, 5.96. $C_{16}H_{16}O_4$. Calculated (%): C, 70.57; H, 5.92.

Elution with hexane—acetone (20 : 1) gave a ~3 : 2 mixture of **2-(1-methoxy-3-phenylprop-2(*E*)-en-1(*Z*)-ylidene)-4-methylcyclopent-4-ene-1,3-dione** (**2A**) and **2-(1-methoxy-3-phenylprop-2(*E*)-en-1(*E*)-ylidene)-4-methylcyclopent-4-ene-1,3-dione** (**2C**, **coruscanone A**) (0.055 g, 43%) as small yellow crystals, m.p. 84 °C (hexane—acetone, 10 : 1) (*cf.* Ref. 1: m.p. 86 °C). A mixture of 2(*Z*)- and 2(*E*)-isomers. IR, ν_{max}/cm^{-1}: 1711 (C=O), 1666 (C=O), 1615 (C=C), 1578 (C=C), 1547 (C=C), 1445, 1309, 1279, 1222, 1208, 1181, 1057. 2(*Z*)-Isomer of coruscanone A. ^1H NMR ($CDCl_3$), δ: 2.09 (d, 3 H, C(4)Me, *J* = 1.6 Hz); 4.21 (s, 3 H, C(1′)OMe); 6.72 (q, 1 H, H(5), *J* = 1.6 Hz); 7.39 (m, 3 H, Ph); 7.62 (m, 2 H, Ph); 7.63 and 7.99 (both d, 1 H each, H(9), H(8), *J* = 15.9 Hz). ^{13}C NMR ($CDCl_3$), δ: 11.2 (C(6)); 64.7 (C(7)); 108.7 (C(2)); 121.1 (C(2′)); 128.5 (C(5′)); 128.9 (C(6′), C(9′)); 129.7 (C(8′)); 130.4 (C(7′)); 135.4 (C(4′)); 140.6 (C(5)); 142.9 (C(3′)); 156.4 (C(4)); 169.0 (C(1′)); 192.7 (C(3)); 194.2 (C(1)). 2(*E*)-Isomer of coruscanone A. ^1H NMR ($CDCl_3$), δ: 2.10 (d, 3 H, C(4)Me, *J* = 1.6 Hz); 4.22 (s, 3 H, C(1′)OMe); 6.71 (q, 1 H, H(5), *J* = 1.6 Hz); 7.39 (m, 3 H, Ph); 7.62 (m, 2 H, Ph); 7.63 and 7.97 (both d, 1 H each, H(9), H(8), *J* = 15.9 Hz). ^{13}C NMR ($CDCl_3$), δ: 11.3 (C(6)); 64.8 (C(7)); 108.7 (C(2)); 121.3 (C(2′)); 128.5 (C(5′)); 128.9 (C(6′), C(9′)); 129.7 (C(8′)); 130.7 (C(7′)); 135.4 (C(4′)); 140.3 (C(5)); 142.8 (C(3′)); 156.9 (C(4)); 168.8 (C(1′)); 191.9 (C(1)); 195.4 (C(3)). A mixture of **2A** and **2C**. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 255 $[M + 1]^+$ (13), 254 $[M]^+$ (77), 253 $[M - 1]^+$ (6), 240 (3), 239 (11), 226 (6), 225 (25), 223 (15), 213 (12), 212 (72), 211 (16), 210 (22), 199 (8), 198 (20), 197 (18), 196 (10), 195 (9), 189 (15), 188 (100), 185 (13), 167 (11), 166 (12), 165 (25), 158 (22), 155 (11), 153 (12), 152 (12), 137 (13), 128 (37), 127 (27), 115 (33), 103 (20), 102 (18), 77 (26), 45 (21), 32 (61).

Reaction of triketone 3 with diazomethane. A 2% solution of CH_2N_2 in anhydrous ether (20 mL) was added in one portion to a solution of triketone **3** (0.304 g, 2.0 mmol) in anhydrous ether (20 mL). The reaction mixture was kept at room temperature for 20 h. The solvent was removed and the residue was chromatographed on SiO_2. Elution with hexane—acetone (50 : 1) gave a ~3 : 2 mixture of **2-acetyl-4-methoxy-5-methylphenol** (**28**) and **2-acetyl-4-methoxy-6-methylphenol** (**29**) (0.090 g, 25%) as light yellow needles, m.p. 65—72 °C. A mixture of isomers **28** and **29**.

IR, ν_{max}/cm^{-1}: 3200—2400 (OH), 1641 (C=O), 1620 (C=C), 1583 (C=C), 1494, 1466, 1429, 1370, 1328, 1284, 1259, 1223, 1209, 1176, 1061. Ether **28**. ^1H NMR ($CDCl_3$), δ: 2.23 (s, 3 H, C(5)Me); 2.59 (s, 3 H, C(2)COMe); 3.77 (s, 3 H, C(4)OMe); 6.98 (s, 2 H, H(3), H(6)); 12.02 (s, 1 H, C(1)OH). ^{13}C NMR ($CDCl_3$), δ: 15.7 (C(7)); 26.8 (C(2′)); 55.8 (C(8)); 110.5 (C(3)); 118.5 (C(2)); 125.3 (C(6)); 128.8 (C(5)); 150.4 (C(4)); 157.3 (C(1)); 204.1 (C(1′)). Ether **29**. ^1H NMR ($CDCl_3$), δ: 2.23 (s, 3 H, C(6)Me); 2.58 (s, 3 H, C(2)COMe); 3.80 (s, 3 H, C(4)OMe); 6.76 and 6.98 (both d, 1 H each, H(5), H(3), J = 1.5 Hz); 12.19 (s, 1 H, C(1)OH). ^{13}C NMR ($CDCl_3$), δ: 16.9 (C(7)); 26.5 (C(2′)); 55.8 (C(8)); 109.5 (C(3)); 117.0 (C(2)); 120.2 (C(5)); 138.4 (C(6)); 151.1 (C(4)); 155.7 (C(1)); 203.1 (C(1′)). A mixture of isomers **28** and **29**. MS, m/z (I_{rel} (%)): 181 $[M + 1]^+$ (9), 180 $[M]^+$ (80), 166 (10), 165 (100), 162 (7), 147 (12), 137 (7), 119 (4). Found (%): C, 66.70; H, 6.73. $C_{10}H_{12}O_3$. Calculated (%): C, 66.65; H, 6.71.

Elution with hexane—acetone (8 : 1) gave a ~1 : 1 mixture of **(2*Z*)-2-(1-methoxyethylidene)-4-methylcyclopent-4-ene-1,3-dione** (**4A**) and **(2*E*)-2-(1-methoxyethylidene)-4-methylcyclopent-4-ene-1,3-dione** (**4C**) (0.166 g, 50%) as pale yellow crystals, m.p. 78—80 °C (hexane). A mixture of **4A** and **4C**. IR, ν_{max}/cm^{-1}: 1720 (C=O), 1699 (C=O), 1668 (C=O), 1624 (C=C), 1606 (C=C), 1579, 1376, 1316, 1246, 1073. (*Z*)-Isomer **4A**. ^1H NMR ($CDCl_3$), δ: 2.02 (d, 3 H, C(4)Me, J = 1.7 Hz); 2.60 (s, 3 H, C(1′)Me); 3.99 (s, 3 H, C(1′)OMe); 6.59 (q, 1 H, H(5), J = 1.7 Hz). ^{13}C NMR ($CDCl_3$), δ: 11.0 (C(6)); 14.3 (C(2′)); 56.1 (C(7)); 107.4 (C(2)); 140.0 (C(5)); 155.4 (C(4)); 174.2 (C(1′)); 193.3 (C(3)); 194.8 (C(1)). (*E*)-Isomer **4C**. ^1H NMR ($CDCl_3$), δ: 2.03 (d, 3 H, C(4)Me, J = 1.7 Hz); 2.59 (s, 3 H, C(1′)Me); 4.00 (s, 3 H, C(1′)OMe); 6.57 (q, 1 H, H(5), J = 1.7 Hz). ^{13}C NMR ($CDCl_3$), δ: 11.2 (C(6)); 14.3 (C(2′)); 56.2 (C(7)); 107.4 (C(2)); 139.3 (C(5)); 156.1 (C(4)); 173.9 (C(1′)); 192.9 (C(1)); 195.6 (C(3)). A mixture of **4A** and **4C**. MS, m/z (I_{rel} (%)): 167 $[M + 1]^+$ (17), 166 $[M]^+$ (100), 149 (13), 138 (31), 137 (32), 122 (29), 107 (32), 80 (30), 68 (31). Found (%): C, 65.15; H, 6.12. $C_9H_{10}O_3$. Calculated (%): C, 65.05; H, 6.07.

Reaction of coruscanone B (1) with dimethyl sulfate. Dry K_2CO_3 (0.94 g, 0.005 mol) was added under argon to a solution of coruscanone B (**1**) (0.15 g, 0.62 mmol) in anhydrous acetone (30 mL). The mixture was refluxed for 5 min, freshly distilled Me_2SO_4 (0.87 g, 7.0 mmol) was added dropwise, and reflux was continued for an additional 30 min. The precipitate was filtered off, the filtrate was evaporated to dryness, and the residue was chromatographed on SiO_2. Elution with hexane—acetone (20 : 1) gave a ~1 : 1 mixture of (*Z*)- and (*E*)-isomers of coruscanone A (**2**) (0.123 g, 77%), which is fully identical with the sample characterized above.

Reaction of triketone 3 with dimethyl sulfate. A mixture of triketone **3** (0.152 g, 1.0 mmol), freshly distilled Me_2SO_4 (1.06 g, 8.5 mmol), and dry K_2CO_3 (1.88 g, 0.01 mol) was refluxed in anhydrous acetone (30 mL) for 40 min. The precipitate was filtered off, the filtrate was evaporated to dryness, and the residue was chromatographed on SiO_2. Elution with hexane—acetone (7 : 1) gave a ~3 : 2 mixture of (*Z*)- and (*E*)-isomers of ether **4** (0.033 g, 20%), which is fully identical with the sample characterized above.

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