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Electrochemical Synthesis of a Tricyclo[5.4.0.0^{1,5}]undec-9-en-8,11-dione and Its Conversion to a Triqinane-type Compound

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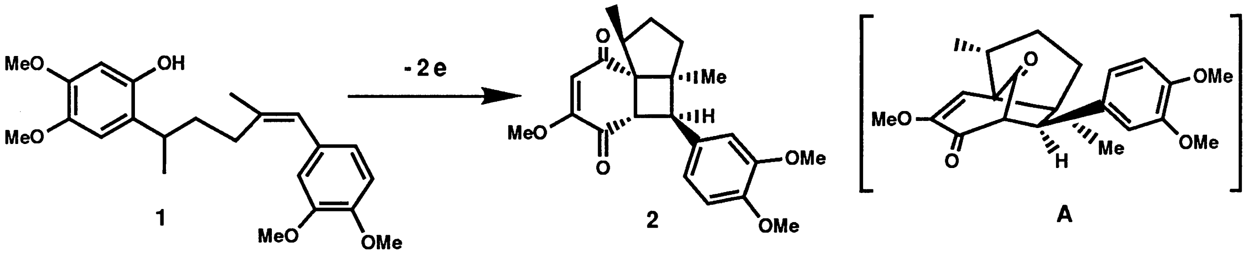
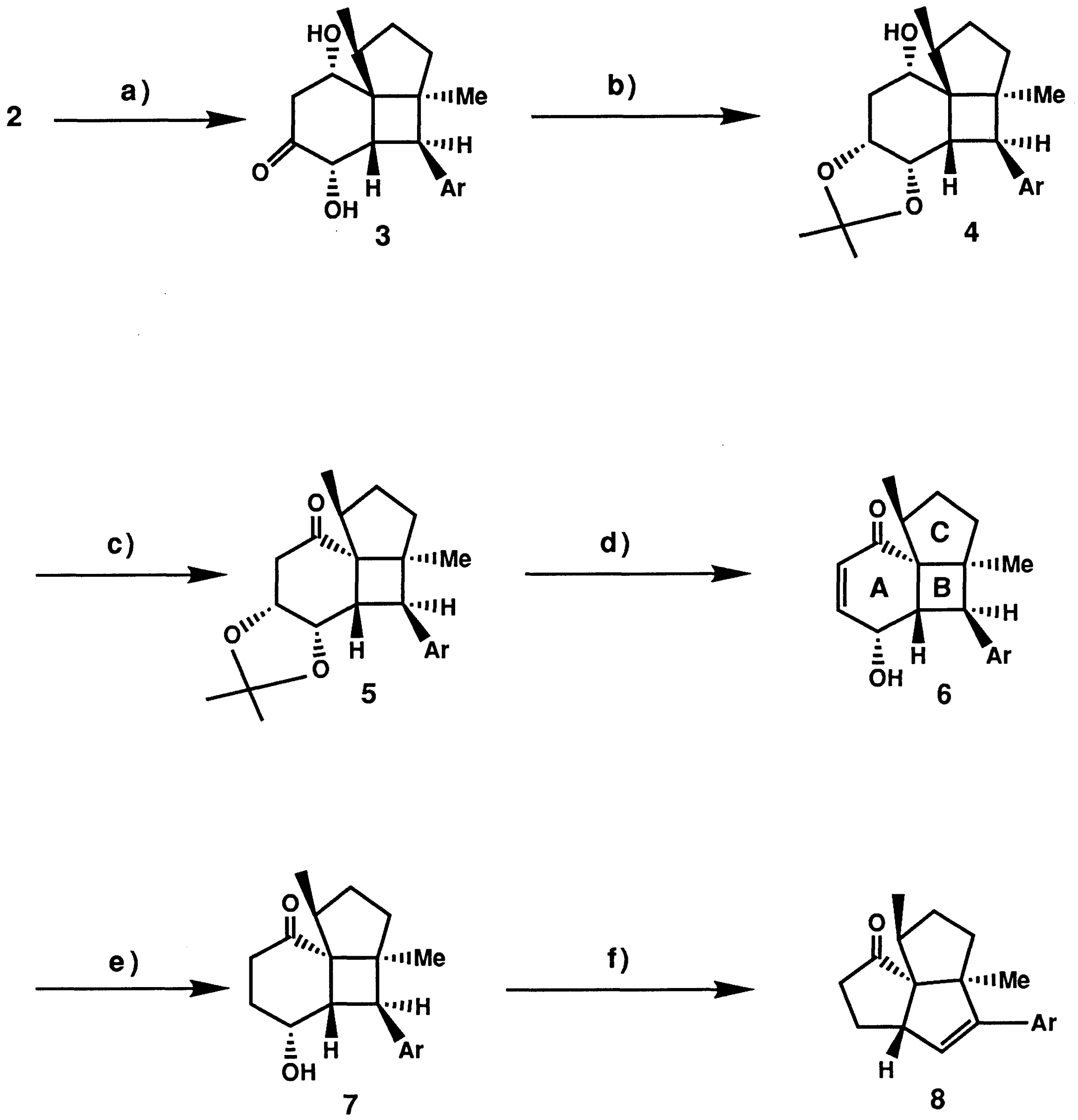
9-Methoxy-6ß-(3',4'-dimethoxyphenyl)-2ß,5α-dimethyltricyclo[5.4.0.0^{1,5}]undec-9-en-8,11-dione has been synthesized by using electrochemical oxidation of the corresponding phenol and then readily converted into a triquinane-type compound in 8 steps.

In connection with our synthetic study on bioactive substances using electrochemical methods, two triquinanes (silphinene,1) and pentalenene2)) have been synthesized starting from the corresponding tricyclo[5.3.1.0^{1,5}]undec-9-en-8,11-diones which are electrochemically formed. We further carried out anodic oxidation of the phenol (**1**)3) in acetic anhydride4) including ^{n}Bu$_4$NBF$_4$[CCE: 2.1 mA (+800 - 1300 mV vs. SCE); 2 F/mol] to afford 9-methoxy-6ß-(3',4'-dimethoxyphenyl)-2ß,5α-dimethyltricyclo[5.4.0.0^{1,5}]undec-9-en-8,11-dione (**2**), in 66% yield, whose structure in the previous paper3) had been incorrectly assigned to be the tricyclo[5.3.1.0^{1,5}]undec-9-en-8,11-dione (**A**). As seen in Scheme 1, the stereostructure of **2** was unambiguously determined by reexamination of the spectral and chemical properties with the aid of an X-ray crystallographic analysis.



The tricyclic compound (**2**) was subjected to diisobutylaluminum hydride reduction followed by hydrolysis of the methyl enol ether group to afford a dehydroxy ketone (**3**)4) [IR(film) 3400 and 1715 cm^{-1}; δ (CDCl$_3$) 4.27 (1H, d, J= 6.2 Hz) (-CH-CH-OH) and 4.52 (1H, dd, J= 8.5, 10.2 Hz) (-CH$_2$-CH-OH)]. Furthermore, **3** was reduced with NaBH$_4$ and then directly converted into the corresponding acetal (**4**) [δ (CDCl$_3$) 3.31 (1H, d, J= 10.5 Hz) and 3.92-4.51 (2H, complex)], which was further treated with PCC-Celite to give a ketone (**5**) having the IR absorption band at 1690 cm^{-1}. When the acetal group of **5** was deprotected



Ar=3,4-dimethoxyphenyl

a) 1) DIBAL-H (3 equiv.) /toluene (-78 °C→room temp, 65 min), 2) 2 M aq. HCl (48% in 2 steps); b) 1) $NaBH_4$ /dioxane-MeOH (10:1) (0 °C→room temp, 50 min) (50%), 2) 2,2-dimethoxypropane and CSA (cat) /acetone (room temp, 11 h) (75%); c) PCC-Celite /CH_2Cl_2 (0 °C, 2 h) (73%); d) 2 M aq. HCl /dioxane (room temp, 5.5 h) (97%); e) H_2 /Pd-C /MeOH (room temp, 13 h) (85%); f) p-TsOH (cat) /toluene (refluxing temp, 3 h) (77%)

Scheme 1. Synthesis of a triquinane-type compound (**8**).

with 2 M aq. HCl, dehydration took place immediately to give an α,β-unsaturated ketone (**6**), the partial structure (A and B rings) of which was determined by ^{1}H NMR spectral data with the aid of decoupling experiments [δ ($CDCl_3$) 3.29, 3.90, 4.70, 6.14, and 6.76]. Then, **6** was subjected to catalytic hydrogenation to afford a ketone (**7**)$^{4)}$ with the IR absorption band at 1685 cm^{-1}. The stereostructure of **7** was unambiguously determined by an X-ray crystallographic analysis, as follows.

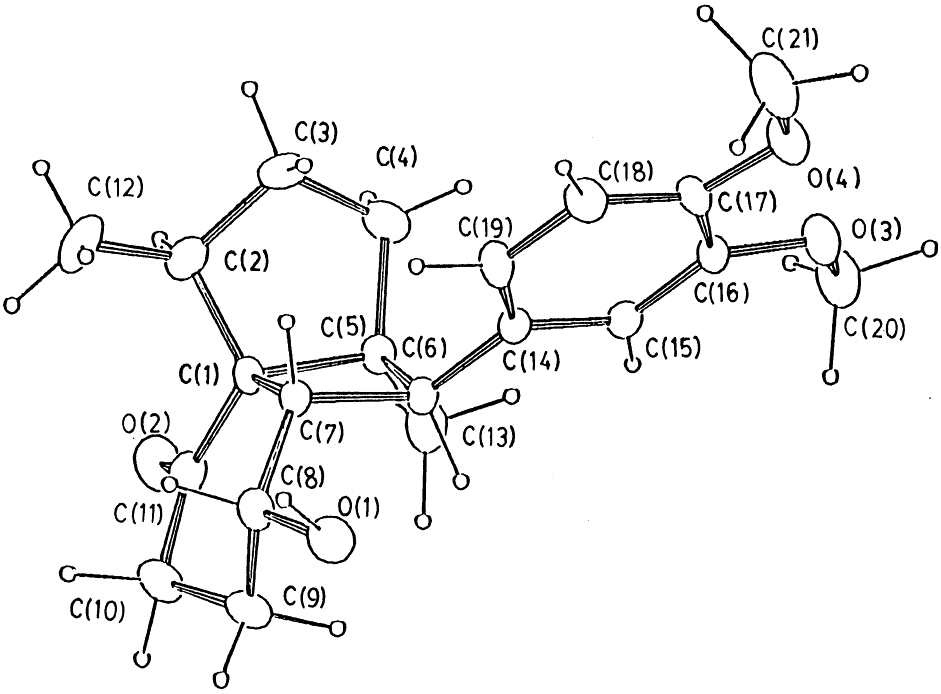


Fig.1. An *ORTEP* drawing of the molecule (**7**).

Crystal data : $C_{21}H_{28}O_4$, MW 344.5, orthorhombic, Pbca, a= 21.227(3), b= 7.8135(7), c= 22.161(3) Å, V= 3675.6(8) Å^3, Z= 8, Dx= 1.24 g cm^{-3}, μ(Mo K α)= 0.079 mm^{-1}.

Single-crystal X-ray diffraction measurement was performed on a Rigaku AFC-5 four-circle diffractometer with Mo Kα radiation up to 2θ= 55°. The structure was solved by direct methods and non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were located on difference syntheses and refined with isotropic thermal parameters. Final R is 0.048 for 1714 unique reflections.$^{5)}$ Therefore, the stereostructure of the tricyclic compound electrochemically produced must be represented by **2**. This is the first example of the intramolecular cyclization mode in our electrochemical studies.$^{6)}$

Finally, acid-catalyzed rearrangement of **7** gave rise to the desired triquinane-type compound (**8**), in good yield, whose structure was also confirmed by ^{1}H NMR spectral data with the aid of decoupling experiments. Further synthetic study on highly oxygenated triquinane-type sesquiterpenes is in progress.

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References

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3) S. Maki, T. Suzuki, S. Kosemura, Y. Shizuri, and S. Yamamura, *Tetrahedron Lett.*, **32**, 4973 (1991).

4) The spectral data for the new compounds are in accord with the structures assigned and only selected data are cited : **2** as an oil : $C_{22}H_{26}O_5$ [m/z 370.1779 (M$^+$)]; IR(film) 1760 (weak), 1700, 1650, 1600, and 1520 cm^{-1}; δ (CDCl$_3$) 0.87 (3H, d, J= 6.8 Hz), 1.27 (3H, s), 1.30 - 1.40 (2H, complex), 1.67 (1H, m), 1.76 (1H, m), 2.72 (1H, m), 3.51 (2H, s), 3.83 (3H, s), 3.88 (3H, s), 3.89 (3H, s), 6.20 (1H, s), 6.70 (1H, d, J= 1.8 Hz), 6.82 (1H, dd, J= 8.3, 1.8 Hz), and 6.86 (1H, d, J= 8.3 Hz). **3** as an oil : $C_{21}H_{28}O_5$ [m/z 360 (M$^+$)]*; IR(film) 3400 and 1715 cm^{-1}; δ (CDCl$_3$) 2.76 (1H, d, J= 9.2 Hz), 3.00 (1H, dd, J= 9.2, 6.2 Hz), 3.12 (1H, d, J= 10.2 Hz), 3.13 (1H, d, J= 8.5 Hz), 4.27 (1H, d, J= 6.2 Hz), 4.52 (1H, dd, J= 10.2, 8.5 Hz). **4** as an oil : $C_{24}H_{34}O_5$ [m/z 402 (M$^+$)]†; IR(film) 3500 cm^{-1}; δ (CDCl$_3$) 1.24 (3H, s), 1.45 (3H, s), 3.31 (1H, d, J= 10.5 Hz), and 3.92 - 4.51 (2H, complex). **5** as an oil : $C_{24}H_{32}O_5$ [m/z 400.2233 (M$^+$)]; IR(film) 1690 cm^{-1}; δ (CDCl$_3$) 4.37 (1H, dd, J= 7.8, 7.3 Hz), and 4.48 (1H, dt, J= 15.6, 7.8 Hz). **6** as an oil : $C_{21}H_{26}O_4$ [m/z 342.1792 (M$^+$)]; IR(film) 3500 and 1660 cm^{-1}; δ (CDCl$_3$) 3.29 (1H, ddd, J= 10.2, 7.3, 2.0 Hz), 3.90 (1H, d, J= 10.2 Hz), 4.70 (1H, dt, J= 7.3, 2.0 Hz), 6.14 (1H, dd, J= 9.3, 2.0 Hz), and 6.76 (1H, br.dd, J= 9.3, 2.0 Hz). **7** : mp 156-157 °C (from hexane - EtOAc); $C_{21}H_{28}O_4$ [m/z 344.2003 (M$^+$)]; IR(film) 3450 and 1685 cm^{-1}; δ (CDCl$_3$) 4.12 (1H, m). **8** as an oil : $C_{21}H_{26}O_3$ [m/z 326.1868 (M$^+$)]; IR(film) 1725, 1600, and 1500 cm^{-1}; δ (CDCl$_3$) 0.86 (1H, m), 0.96 (3H, d, J= 6.8 Hz), 1.10 (3H, s), 1.30 (1H, m), 1.52 (1H, m), 1.73 - 1.79 (2H, complex), 1.90 (1H, m), 2.17 (1H, ddd, J= 12.7, 7.3, 2.6 Hz), 2.25 (1H, ddd, J= 12.7, 7.3, 2.6 Hz), 2.49 (1H,m), 3.42 (1H, br.dd, J= 7.0, 2.5 Hz), 3.88 (3H, s), 3.89 (3H, s), 5.72 (1H, d, J= 2.5 Hz), 6.80 (1H, d, J= 8.3 Hz), 6.88 (1H, d, J= 2.0 Hz), and 6.91 (1H, dd, J= 8.3, 2.0 Hz).

   † The molecular ion peak has not been observed on high resolution mass spectra of both **3** and **4**, but their structures are supported by other spectral data.

5) Tables of atomic parameters, bond lengths and bond angles have been deposited with the Cambridge Crystallographic Data Centre.

6) Y. Shizuri, M. Ohkubo, and S. Yamamura, *Chem. Lett.*, **1989**, 113.

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