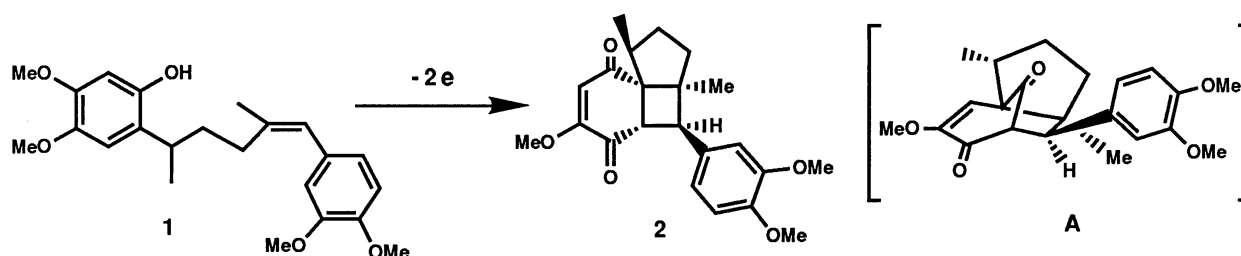


Electrochemical Synthesis of a Tricyclo[5.4.0.0^{1,5}]undec-9-en-8,11-dione
and Its Conversion to a Triquinane-type Compound

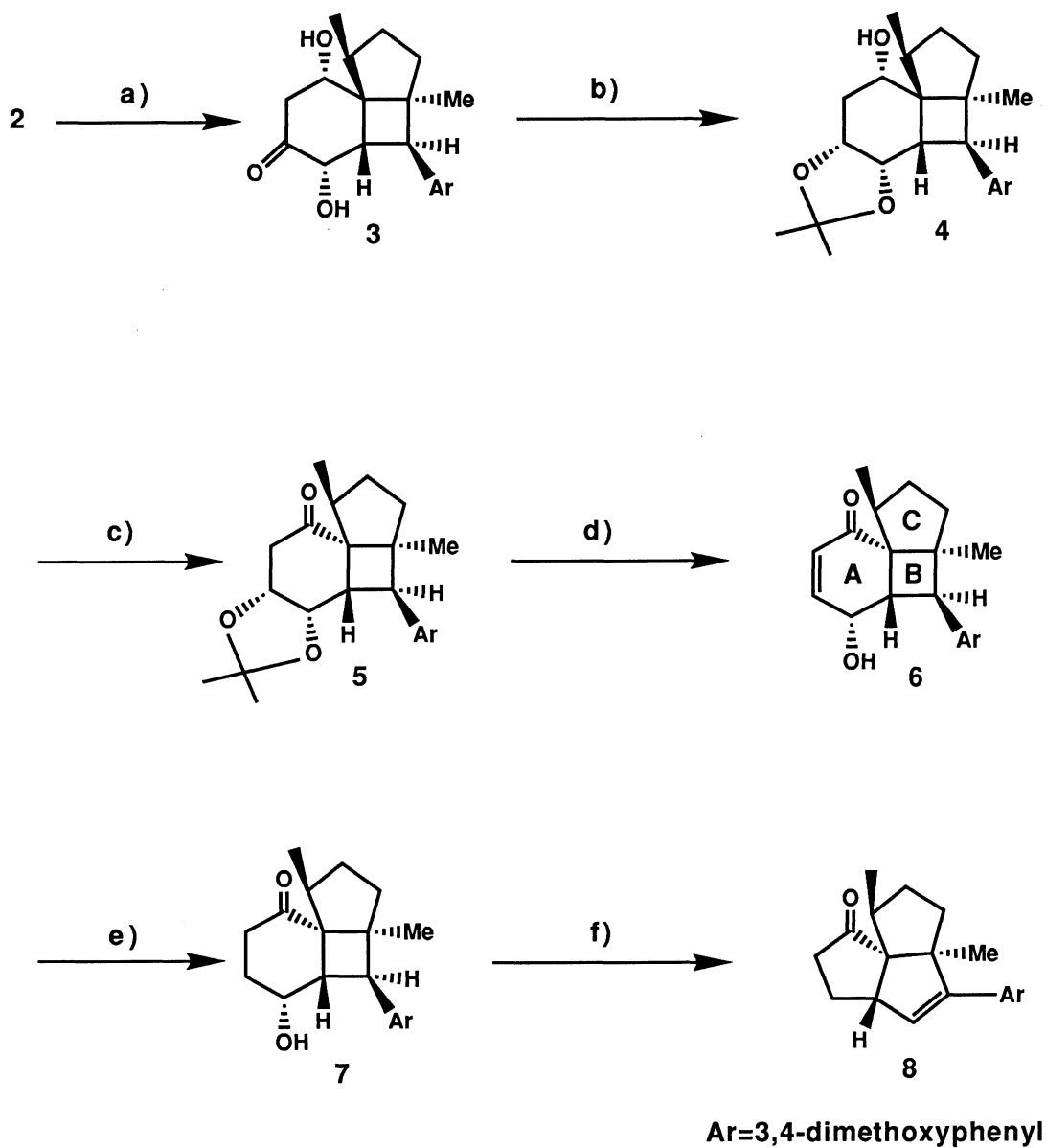
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9-Methoxy-6 β -(3',4'-dimethoxyphenyl)-2 β ,5 α -dimethyltricyclo[5.4.0.0^{1,5}]undec-9-en-8,11-dione has been synthesized by using electrochemical oxidation of the corresponding phenol and then readily converted into a triquinane-type compound in 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 ⁿBu₄NBF₄ [CCE: 2.1 mA (+800 - 1300 mV vs. SCE); 2 F/mol] to afford 9-methoxy-6 β -(3',4'-dimethoxyphenyl)-2 β ,5 α -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 (CDCl₃) 4.27 (1H, d, J = 6.2 Hz) (-CH-CH-OH) and 4.52 (1H, dd, J = 8.5, 10.2 Hz) (-CH₂-CH-OH)]. Furthermore, **3** was reduced with NaBH₄ and then directly converted into the corresponding acetal (**4**) [δ (CDCl₃) 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



- a) 1) DIBAL-H (3 equiv.) /toluene (-78 °C→room temp, 65 min), 2) 2 M aq. HCl (48% in 2 steps);
 b) 1) NaBH₄ /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 /CH₂Cl₂ (0 °C, 2 h) (73%);
 d) 2 M aq. HCl /dioxane (room temp, 5.5 h) (97%); e) H₂ /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 ^1H 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.

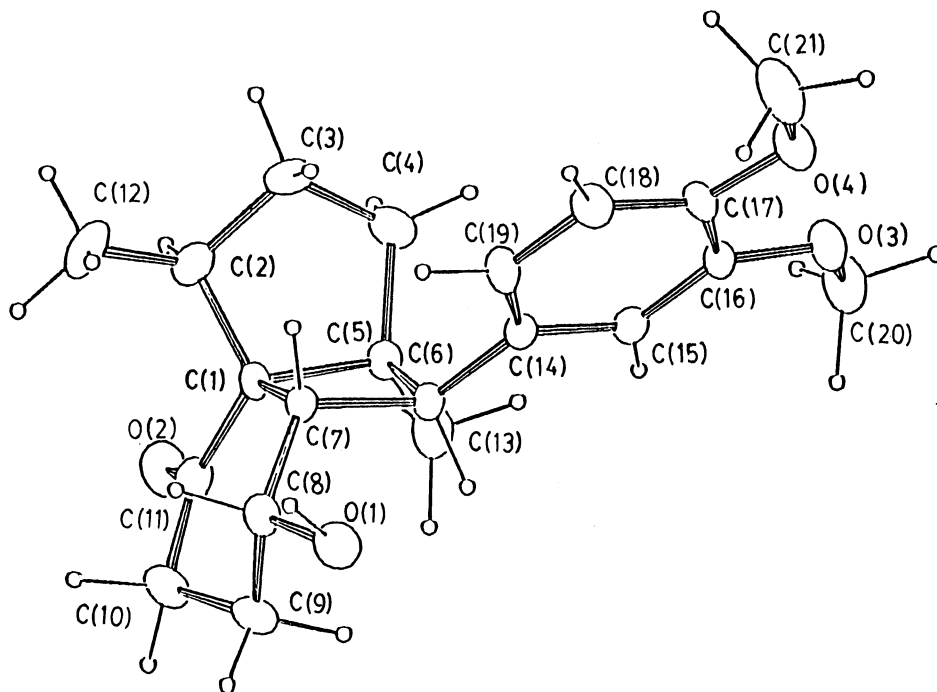


Fig.1. An ORTEP drawing of the molecule (**7**).

Crystal data : $\text{C}_{21}\text{H}_{28}\text{O}_4$, MW 344.5, orthorhombic, $Pbca$, $a = 21.227(3)$, $b = 7.8135(7)$, $c = 22.161(3)\text{ \AA}$, $V = 3675.6(8)\text{ \AA}^3$, $Z = 8$, $D_x = 1.24\text{ g cm}^{-3}$, $\mu(\text{Mo K } \alpha) = 0.079\text{ mm}^{-1}$.

Single-crystal X-ray diffraction measurement was performed on a Rigaku AFC-5 four-circle diffractometer with $\text{Mo K}\alpha$ radiation up to $2\theta = 55^\circ$. 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 ^1H 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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- 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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