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Nonsteroidal Antiinflammatory Agents. V.[1] Photolysis of 6,11-Dihydro-11-oxodibenz[*b*, *e*]oxepin-3-acetic Acid

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Photolysis of 6,11-dihydro-11-oxodibenz[*b*, *e*]oxepin-3-acetic acid (**1**, oxepinac) in 1 N NaOH solution by sunlight gave 3-methyldibenz[*b*, *e*]oxepin-11(6*H*)-one (**2**), 2-methylanthraquinone (**3**), 4-carboxy-3-(2-methylphenoxy)phenylacetic acid (**4**) and 4-(2-carboxybenzyl)-3-hydroxyphenylacetic acid (**5**). Their structures were established by direct comparison with synthetic samples (**2**, **4**, **5**) and a commercial sample (**3**).

Keywords——sunlight photolysis; 6,11-dihydro-11-oxodibenz[*b*, *e*]oxepin-3-acetic acid; oxepinac; 3-methyldibenz[*b*, *e*]oxepin-11(6*H*)-one; 2-methylanthraquinone; 4-carboxy-3-(2-methylphenoxy)phenylacetic acid; 4-(2-carboxybenzyl)-3-hydroxyphenylacetic acid; antiinflammatory agent

In the previous paper,[2] the chemistry and some pharmacological properties of a series of 6,11-dihydro-11-oxodibenz[*b*,*e*]oxepinacetic acids were reported. Of these compounds, 6,11-dihydro-11-oxodibenz[*b*,*e*]oxepin-3-acetic acid (**1**, oxepinac) has been considered to be the most promising candidate as an antiinflammatory agent from pharmacological and toxicological points of view.[3]

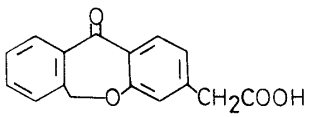
This paper deals with the photolysis of oxepinac (**1**) in 1 N NaOH solution by sunlight, as a part of our general physicochemical studies of **1**.

Photolysis and Isolation

A solution of oxepinac (**1**, 1.34 g) in 1 N NaOH (250 ml) was placed in a Kjeldahl flask (Pyrex). The flask was sealed and then exposed to sunlight for about 14 d (the total number of fine days). Thin-layer chromatography (TLC) of the resulting brown solution revealed several spots (Fig. 2) and compounds **1** to **5** were isolated after treatment of the solution as shown in Chart 1.

Structure Elucidation and Confirmation

The infrared (IR) spectrum of compound **2** showed no characteristic band of a carboxyl group near 1700 cm^{-1}. The proton nulcear magnetic resonance (^{1}H-NMR) spectrum in-



oxepinac (**1**)

Fig. 1

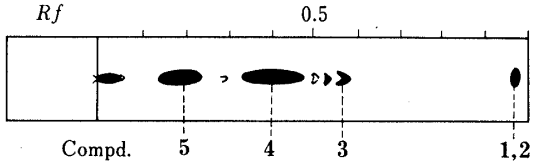


Fig. 2. Thin-Layer Chromatogram of a Solution of Oxepinac (**1**) in 1 N NaOH after Exposure to Sunlight

Solvent; lower phase of $CHCl_3$: MeOH : H_2O = 7 : 3 : 1.

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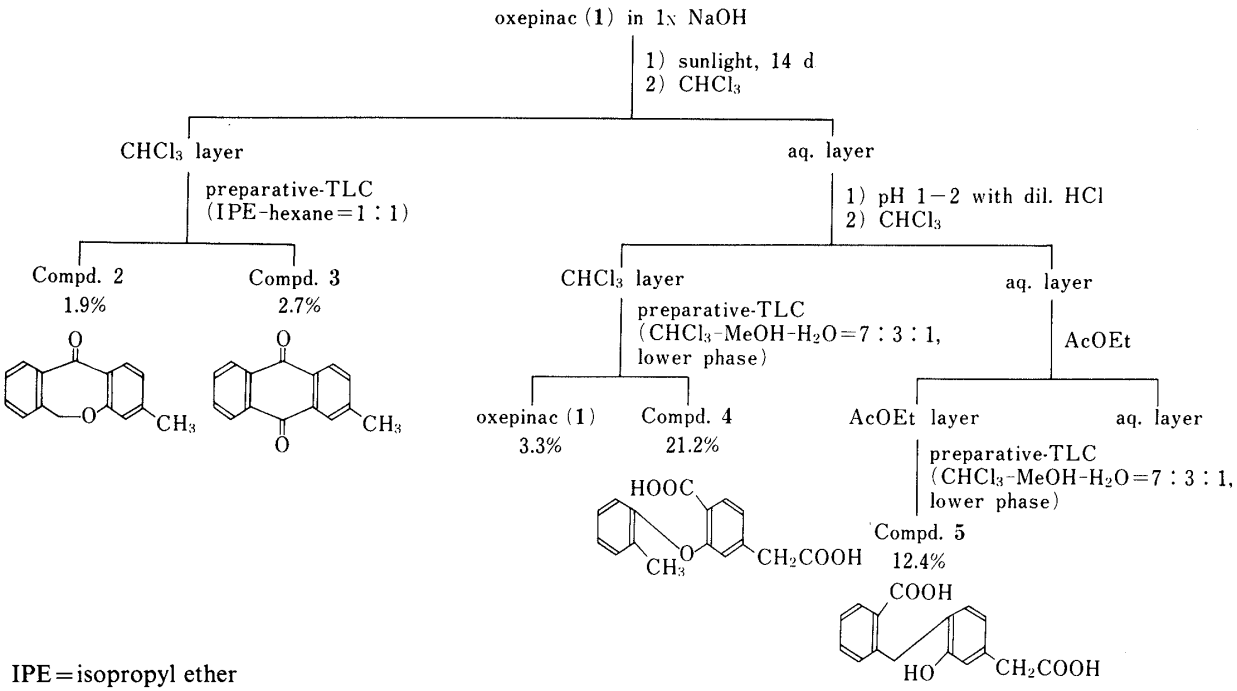

Chart 1. Isolation of the Products of Photolysis of Oxepinac (1)

dicated the presence of a methyl group (δ 2.39, 3H, s) in place of the methylene group of the acetic acid moiety of **1**. Consideration of the above results led to assignment of the structure as 3-methyldibenz[*b*,*e*]oxepin-11(6*H*)-one, which would be formed by the decarboxylation of **1**. This was confirmed by comparison with an authentic sample prepared according to the procedure of Stach *et al.*[4]

The ^{1}H-NMR spectrum of compound **3** indicated the disappearance of the C-6 methylene group of **1** and the presence of a methyl group (δ 2.53, 3H, s) in place of the methylene group of the acetic acid moiety of **1**. On the basis of the above results and the known conversion[5] of 3-methoxydibenz[*b*,*e*]oxepin-11(6*H*)-one to the quinone derivative with base, compound **3** was considered to be 2-methylanthraquinone. This was proved by comparison with an authentic commercial sample.

The elemental analysis and the mass spectrum (MS) of compound **4** indicated that the molecular formula was $C_{16}H_{14}O_5$, corresponding to addition of H_2O to $C_{16}H_{12}O_4$ (**1**). The ^{1}H-NMR spectrum (acetone-d_6) indicated the presence of a methyl group (δ 2.24, 3H, s) in place of the C-6 methylene group of **1**, suggesting fission of the O_5–C_6 bond and the conversion of the C-6 methylene group into a methyl group. The IR spectrum indicated the presence of a carboxylic acid group (1685 cm^{-1}) in place of the C-11 ketone group (near 1640 cm^{-1}) of **1**, suggesting fission of the C_{11}–C_{10a} or C_{11}–C_{11a} bond and the conversion of a ketone group into a carboxylic acid group. On the basis of the above results, compound **4** was considered to be 4-carboxy-3-(2-methylphenoxy)phenylacetic acid, in which the oxygen atom at the 5-position of **1** is bonded to the carbon atom at the 10a-position of **1**. This was confirmed by direct comparison with an authentic sample prepared as mentioned later.

The elemental analysis and the mass spectrum of compound **5** indicated that the molecular formula was $C_{16}H_{14}O_5$, corresponding to addition of H_2O to $C_{16}H_{12}O_4$ (**1**). The IR spectrum indicated the presence of a carboxylic acid group (1680 cm^{-1}) in place of the C-11 ketone group of **1**, suggesting the conversion of a ketone group into a carboxylic acid group. The ^{1}H-NMR spectrum (acetone-d_6) showed a peak at δ 4.38 (2H, s) in place of the C-6 methylene group signal of **1** and the IR spectrum showed a new absorption band at 3320 cm^{-1}

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corresponding to a hydroxyl group, suggesting fission of the O_5–C_6 bond. On the basis of the above results, compound **5** was considered to be 4-(2-carboxybenzyl)-3-hydroxyphenylacetic acid, in which the carbon atom at the 6-position of **1** is bonded to the carbon atom at the 11a-position of **1**. This was confirmed by direct comparison with an authentic sample prepared as mentioned later.

Syntheses of the Products of Photolysis

Compound **4** was prepared by the route shown in Chart 2. Sandmeyer reaction of 4-

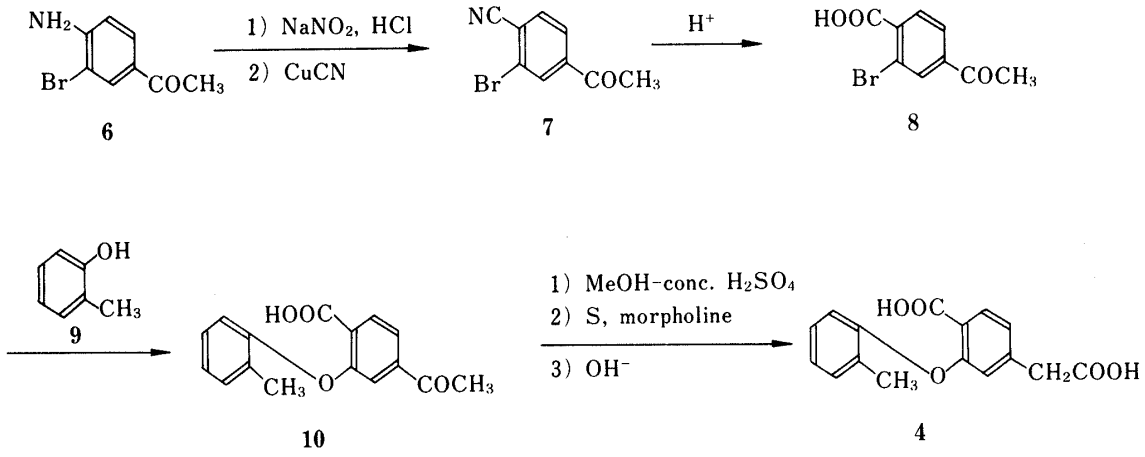

Chart 2

amino-3-bromoacetophenone (**6**)[6] gave 3-bromo-4-cyanoacetophenone (**7**, 36%). Compound **7** was hydrolyzed to the carboxylic acid derivative **8**, which reacted with *o*-cresol (**9**) in the presence of potassium carbonate and copper powder at 155—170 °C to give 4-acetyl-2-(2-methylphenoxy)benzoic acid (**10**). The esterification of **10** followed by Willgerodt-Kindler reaction and then hydrolysis gave **4**.

The synthesis of **5** is outlined in Chart 3. The esterification of 3-(2-carboxybenzyloxy)-

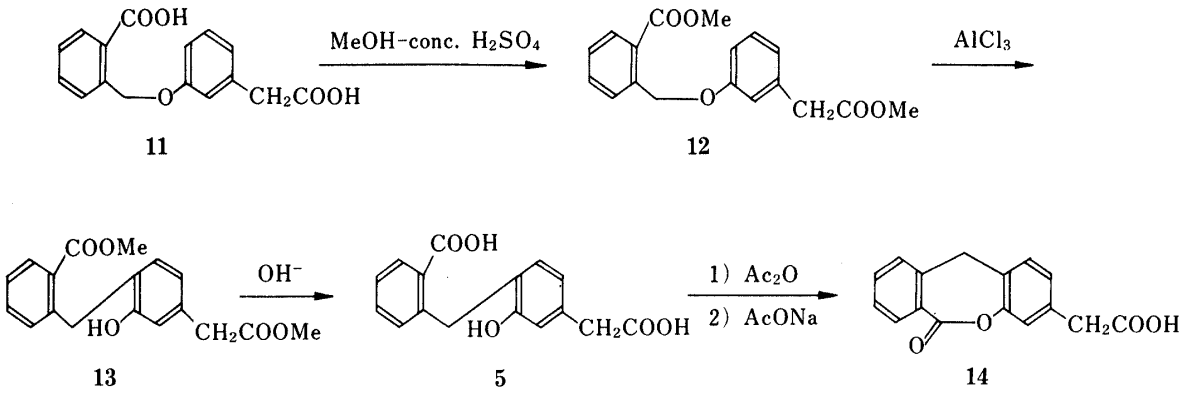

Chart 3

phenylacetic acid (**11**)[2] followed by alkyl aryl ether rearrangement reaction using aluminum chloride gave methyl 3-hydroxy-4-[2-(methoxycarbonyl)benzyl]phenylacetate (**13**, 29%). The hydrolysis of **13** with alkali gave **5**.

The ^{1}H-NMR spectrum of **5** showed a doublet signal at 7.02 (J=7.5 Hz) and cyclization of **5** under conditions similar to those reported by Baker *et al.*[7] gave the 7-membered lactone

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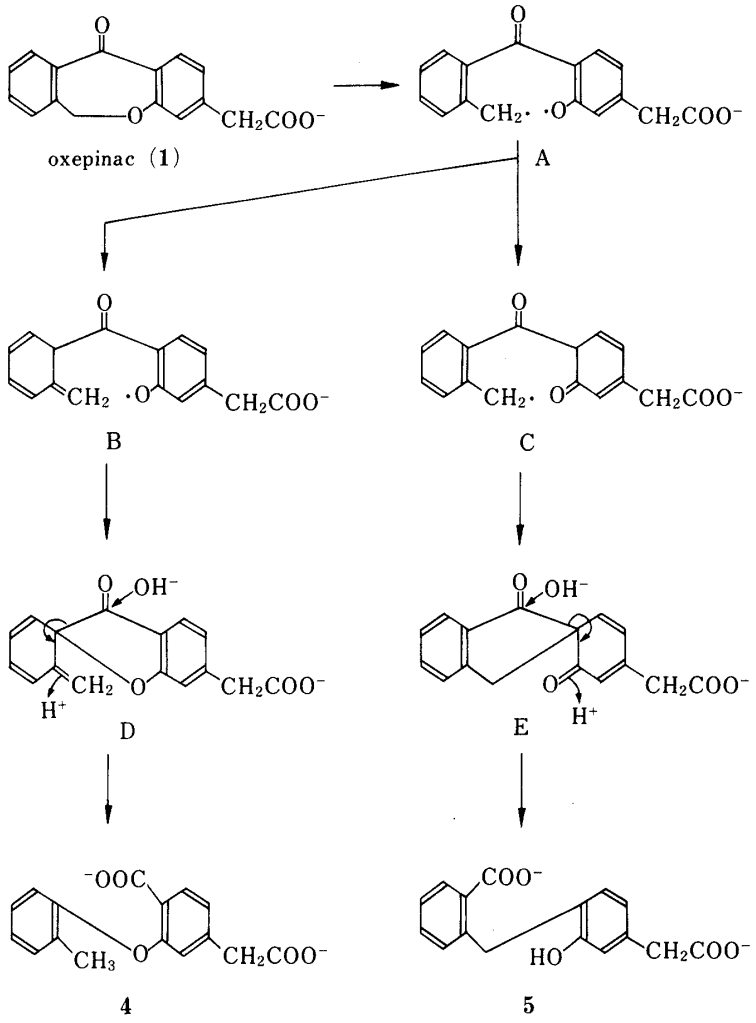

Chart 4

compound **14**. These results ruled out the possibility that **5** has other isomeric structure.

Discussion

Oxepinac (**1**) in 1 N NaOH was stable in the dark. Thus, compound **2** can be considered to arise by the photochemical decarboxylation of **1**. The quinone compound **3** is assumed to be formed from **2** by a mechanism similar to that proposed by Davies *et al.*[5] In addition, the pathways for the formation of **4** and **5** may be as shown in Chart 4. Fission of the O_5–C_6 bond of **1** and subsequent transfer of a radical ion results in the generation of radical B or C *via* radical A. Compound **4** or **5** is formed from B or C *via* the spiro intermediate D or E, respectively.

The photochemistry of dibenz[*b*,*e*]oxepin-11(6*H*)-one or its derivatives has not previously been reported.

Experimental

The following instruments were used. IR spectra: a Hitachi 285 spectrophotometer; ^{1}H-NMR spectra (tetramethylsilane as the internal standard): a Hitachi R-20B spectrometer (60 MHz); mass spectra: a Hitachi RMS-4 mass spectrometer (direct inlet, at 70 eV); melting points: a Yanagimoto melting point apparatus. All melting points are uncorrected.

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For column chromatography, silica gel (Merck, 70—230 mesh) was used. TLC and preparative TLC were carried out on Kieselgel 60 F_{254} precoated plates (Merck).

Physical, Spectral and Analytical Data for the Products of the Photolysis——Compd. **2**: 21.3 mg. mp 71—72 °C (ligroin–Et_2O). IR ν_{max}^{KBr} cm^{-1}: 1640. UV λ_{max}^{EtOH} nm: 276.0, 331.0. MS *m/e*: 224 (M^+). ^{1}H-NMR ($CDCl_3$) δ: 2.39 (3H, s), 5.18 (2H, s), 6.8—7.1 (2H, m), 7.3—7.7 (3H, m), 7.8—8.0 (1H, m), 8.17 (1H, d, J=7.5 Hz). *Anal.* Calcd for $C_{15}H_{12}O_2$: C, 80.33; H, 5.39. Found: C, 80.21; H, 5.33. Compd. **3**: 30.0 mg. mp 175—177 °C (EtOH). IR ν_{max}^{KBr} cm^{-1}: 1670. UV λ_{max}^{EtOH} nm: 256.5, 275.0, 327.5. MS *m/e*: 222 (M^+). ^{1}H-NMR ($CDCl_3$) δ: 2.53 (3H, s), 7.5—8.4 (7H, m). *Anal.* Calcd for $C_{15}H_{10}O_2$: C, 81.06; H, 4.54. Found: C, 81.30; H, 4.45. Compd. **4**: 303.4 mg. mp 189—190 °C (acetone–hexane). IR ν_{max}^{KBr} cm^{-1}: 3000—2500, 1685. ^{1}H-NMR (acetone-d_6) δ: 2.24 (3H, s,), 3.62 (2H, s), 5.0—6.5 (2H, br, disappeared after addition of D_2O), 6.75—6.95 (2H, m), 6.97—7.40 (4H, m), 7.92 (1H, d, J=8 Hz). MS *m/e*: 286 (M^+). *Anal.* Calcd for $C_{16}H_{14}O_5$: C, 67.12; H, 4.93. Found: C, 67.17; H, 5.11. Compd. **5**: 177.4 mg. mp 196.5—197.5 °C (AcOEt–$CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3320, 3000—2500, 1680. ^{1}H-NMR (acetone-d_6) δ: 3.52 (2H, s), 4.39 (2H, s), 6.70 (1H, dd, J=1.5, 7.5 Hz), 6.83 (1H, d, J=1.5 Hz), 7.02 (1H, d, J=7.5 Hz), 7.2—7.5 (3H, m), 7.94 (1H, m), 8.95 (3H, br, disappeared after addition of D_2O). MS *m/e*: 286 (M^+). *Anal.* Calcd for $C_{16}H_{14}O_5$: C, 67.15; H, 4.93. Found: C, 66.89; H, 4.90.

3-Bromo-4-cyanoacetophenone (7)——A solution of $NaNO_2$ (6.68 g, 0.968 mol) in H_2O (19 ml) was added to a solution of 4-amino-3-bromoacetophenone[6] (**6**, 20.0 g, 0.934 mol) in conc. HCl (24 ml) and H_2O (50 ml) at 5 °C. The resulting diazonium solution was added to CuCN solution[8] [prepared from $CuSO_4 \cdot 2H_2O$ (29.8 g, 0.119 mol) and NaCN (15.5 g, 0.316 mol)] at 40—50 °C over 0.5 h. The mixture was stirred for an additional 0.5 h, then insoluble material was filtered off and the filtrate was extracted with AcOEt. The extract was washed with H_2O, dried (Na_2SO_4) and concentrated to dryness *in vacuo*. The residue was subjected to column chromatography. Elution with C_6H_6 gave a crystalline substance, which was crystallized from hexane to give 3-bromo-4-chloroacetophenone (6.30 g, 28.9%) as colorless crystals, mp 78—79.5 °C (lit. 75 °C,[9] 85.5 °C[10]). ^{1}H-NMR ($CDCl_3$) δ: 2.57 (3H, s, CH_3), 7.51 (1H, d, J=8.5 Hz, C_5–H), 7.81 (1H, dd, J=1.5, 8.5 Hz, C_6–H), 8.18 (1H, d, J=1.5 Hz, C_2–H). MS *m/e*: 232 : 234 : 236 (=1 : 1.22 : 0.36). *Anal.* Calcd for C_8H_6BrClO: C, 41.15; H, 2.59. Found: C, 41.24; H, 2.80. Subsequent elution with the same solvent gave a crystalline substance, which was crystallized from AcOEt–hexane to give **7** (7.53 g, 36.0%) as colorless crystals, mp 129—130 °C. IR ν_{max}^{KBr} cm^{-1}: 2220 (C≡N), 1680 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 2.63 (3H, s, CH_3), 7.75 (1H, d, J=8.5 Hz, C_5–H), 7.99 (1H, dd, J=1.5, 8.5 Hz, C_6–H), 8.22 (1H, d, J=1.5 Hz, C_2–H). *Anal.* Calcd for C_9H_6BrNO: C, 48.24; H, 2.70; Br, 35.67; N, 6.25. Found: C, 48.28; H, 2.85; Br, 35.79; N, 6.22.

4-Acetyl-2-bromobenzoic Acid (8)——A solution of **7** (7 g, 0.312 mol) in conc. H_2SO_4 (35 ml), H_2O (35 ml) and AcOH (35 ml) was refluxed for 5 h. After cooling, the reaction mixture was adjusted with 10 N NaOH to pH 11 and washed with AcOEt. The aqueous layer was adjusted with conc. HCl to pH 1 and extracted with AcOEt. The extract was washed with H_2O, dried (Na_2SO_4) and concentrated to dryness *in vacuo*. The residue was crystallized from acetone–hexane to give **8** (7.09 g, 93.4%) as colorless crystals, mp 175—176 °C. IR ν_{max}^{KBr} cm^{-1}: 1722 (C=O), 1662 (C=O). *Anal.* Calcd for $C_9H_7BrO_3$: C, 44.47; H, 2.90; Br, 32.88. Found: C, 44.61; H, 3.01; Br, 33.10.

4-Acetyl-2-(2-methylphenoxy)benzoic Acid (10)——A mixture of **8** (6.6 g, 0.027 mol), *o*-cresol (**9**, 14.8 g, 0.137 mol), K_2CO_3 (9.40 g, 0.068 mol) and Cu powder (0.36 g) was heated at 157—170 °C for 2 h. After cooling, H_2O was added to the reaction mixture and the whole was washed with isopropyl ether. The aqueous layer was acidified with conc. HCl and extracted with isopropyl ether. The extract was concentrated to dryness *in vacuo* and the residue was purified by column chromatography using $CHCl_3$ as a solvent. The resulting product was crystallized from C_6H_6–hexane to give **10** (4.81 g, 65.5%) as pale yellow crystals, mp 132.5—133.5 °C. IR ν_{max}^{KBr} cm^{-1}: 1700 (C=O), 1680 (C=O). ^{1}H-NMR (acetone-d_6) δ: 2.26 (3H, s, CH_3–phenyl), 2.54 (3H, s, CH_3CO), 7.78 (1H, dd, J=1.5, 8.3 Hz, C_5–H), 8.02 (1H, d, J=8.3 Hz, C_6–H). *Anal.* Calcd for $C_{14}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 71.35; H, 5.35.

Methyl 4-Acetyl-2-(2-methylphenoxy)benzoate (15)——A solution of **10** (1.0 g, 0.0037 mol) in MeOH (50 ml) and conc. H_2SO_4 (0.5 ml) was refluxed for 4.5 h. The reaction mixture was concentrated to about 20 ml, poured into ice-cold water and extracted with $CHCl_3$. The extract was washed with H_2O, dried (Na_2SO_4) and concentrated to dryness *in vacuo* to give **15** as a pale yellow oil (1.0 g, 95.1%). ^{1}H-NMR ($CDCl_3$) δ: 2.26 (3H, s, CH_3–phenyl), 2.49 (3H, s, CH_3CO), 3.82 (3H, s, $COOCH_3$), 7.59 (1H, dd, J=1.5, 8.3 Hz, C_5–H), 7.91 (1H, d, J=8.3 Hz, C_6–H).

This compound was used for the next reaction without further purification.

4-Carboxy-3-(2-methylphenoxy)phenylacetic Acid (4)——A mixture of **15** (1.05 g, 0.0037 mol), sulfur (178 mg) and morpholine (2 ml) was refluxed under a nitrogen atmosphere for 17 h. H_2O was added to the reaction mixture and the whole was extracted with $CHCl_3$. The extract was concentrated to dryness *in vacuo*. A mixture of the resulting residue and KOH (2 g) in 95% EtOH (20 ml) was refluxed under a nitrogen atmosphere for 16 h and then concentrated to dryness *in vacuo*. H_2O was added to the residue and the mixture was washed with $CHCl_3$. The aueous layer was acidified with conc. HCl and extracted with AcOEt. The extract was concentrated to dryness *in vacuo* and the residue was purified by column chromatography using $CHCl_3$: MeOH = 10 : 1 and 5 : 1 as solvents. The resulting product was crystallized from acetone–hexane to give **4** (0.47 g, 44.4%) as colorless crystals, mp 189—190 °C. *Anal.* Calcd for $C_{16}H_{14}O_5$: C, 67.12; H, 4.93. Found: C, 66.90; H, 4.88.

Methyl 3-[2-(Methoxycarbonyl)benzyloxy]phenylacetate (12)——A solution of 3-(2-carboxybenzyloxy)-phenylacetic acid[2] (**11**, 30 g, 0.105 mol) in MeOH (300 ml) and conc. H_2SO_4 (5 ml) was refluxed for 22 h. The re-

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action mixture was concentrated to about 150 ml, poured into ice-cold water and extracted with $CHCl_3$. The extract was concentrated to dryness *in vacuo* and the residue was purified by column chromatography using $CHCl_3$ as a solvent to give **12** as a colorless oil (31.4 g, 95.3%). ^{1}H-NMR ($CDCl_3$) δ: 3.58 (2H, s, CH_2CO), 3.65 (3H, s, CH_2COOCH_3), 3.86 (3H, s, phenyl–$COOCH_3$), 5.47 (2H, s, CH_2O), 6.75—8.10 (8H, m, benzene protons). *Anal.* Calcd for $C_{18}H_{18}O_5$: C, 68.78; H, 5.77. Found: C, 69.00; H, 5.91.

Methyl 3-Hydroxy-4-[2-(methoxycarbonyl)benzyl]phenylacetate (13)——Aluminum chloride (90 g) was added to a solution of **12** (32.8 g, 0.104 mol) in 1,2-dichloroethane (60 ml) at 0—5 °C. The reaction mixture was stirred at room temperature for 40 min, poured into ice-cold water and extracted with $CHCl_3$. The extract was concentrated to dryness *in vacuo* and the residue was chromatographed using $CHCl_3$ as a solvent. Methyl 2-(chloromethyl)benzoate (5.97 g, 30.9%) was obtained from the earlier eluate, a portion of which was rechromatographed using the same solvent to give an analytical sample as a colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 3.89 (3H, s, CH_3), 5.02 (2H, s, CH_2), 7.97 (1H, m, C_6–H), 7.2—7.6 (3H, m, benzene protons). *Anal.* Calcd for $C_9H_9ClO_2$: C, 58.55; H, 4.91; Cl, 19.20. Found: C, 58.65; H, 4.99; Cl, 19.01. Further elution gave **13** (9.42 g, 28.7%), a portion of which was rechromatographed to give an analytical sample as a colorless oil. IR ν_{max}^{KBr} cm^{-1}: 3300 (OH), 1700 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 3.52 (2H, s, CH_2CO), 3.59 (3H, s, CH_2COOCH_3), 3.83 (3H, s, phenyl–$COOCH_3$), 4.21 (2H, s, phenyl–CH_2–phenyl), 6.6—7.4 (6H, m, benzene protons), 7.82 (1H, m, C_3–H), 7.88 (1H, s, OH). MS *m/e*: 314 (M^+). *Anal.* Calcd for $C_{18}H_{18}O_5$: C, 68.78; H, 5.77. Found: C, 68.81; H, 5.60. The final eluate gave methyl 3-hydroxyphenylacetate (9.53 g, 55.2%), a portion of which was rechromatographed to give an analytical sample as a colorless oil. IR ν_{max}^{neat} cm^{-1}: 3400 (OH), 1705 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 3.54 (2H, s, CH_2), 3.66 (3H, s, CH_3), 6.6—7.3 (4H, m, benzene protons). *Anal.* Calcd for $C_9H_{10}O_3$: C, 65.05; H, 6.07. Found: C, 64.84; H, 6.30.

4-(2-Carboxybenzyl)-3-hydroxyphenylacetic Acid (5)——A mixture of **13** (480 mg, 1.53 mmol) and KOH (0.28 g) in 60% EtOH (5 ml) was refluxed for 1.5 h and concentrated to dryness *in vacuo*. H_2O was added to the residue and the solution was adjusted with dil. HCl to pH 1. The resulting precipitates were collected and crystallized from AcOEt–$CHCl_3$ to give **5** (365 mg, 83.5%) as colorless crystals, mp 196.5—197.5 °C. *Anal.* Calcd for $C_{16}H_{14}O_5$: C, 67.12; H, 4.93. Found: C, 66.89; H, 4.90.

6,11-Dihydro-6-oxodibenz[*b*,*e*]oxepin-3-acetic Acid (14)——A solution of **5** (1.0 g, 3.49 mmol) in Ac_2O (4 ml) was heated at 50—55 °C for 10 min, then cooled. Sodium acetate (0.01 g) was added to the reaction mixture and the whole was stirred at room temperature for 20 min. Ice-cold water was added, and the resulting mixture was extracted with AcOEt. The extract was washed with H_2O, dried (Na_2SO_4) and concentrated to dryness *in vacuo*. The residue was purified by column chromatography using $CHCl_3$ and $CHCl_3$: acetone = 10 : 1 as solvents. The resulting product was crystallized from AcOEt–hexane to give **14** (545 mg, 58.2%) as colorless crystals, mp 159—160 °C. IR ν_{max}^{KBr} cm^{-1}: 1745 (C=O), 1710 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 3.63 (2H, s, CH_2CO), 4.02 (2H, s, phenyl–CH_2–phenyl), 7.94 (1H, m, C_7–H), 9.54 (1H, br, COOH). MS *m/e*: 268 (M^+). *Anal.* Calcd for $C_{16}H_{12}O_4$: C, 71.63; H, 4.51. Found: C, 71.89; H, 4.62.

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