a clear solution. The mixture was extracted with ethyl acetate (3 × 30 mL), the extract concentrated to 30 mL, washed with 1 N NaOH (3 × 30 mL), cooled to 0 °C, acidified to pH 2–3 with 1 N HCl, and again extracted with EtOAc (3 × 30 mL), the extract washed with water and dried over anhydrous Na_2SO_4, and the solvent removed to give colorless thick oil **13c**: 0.34 g (55% yield); IR ν_{max} (neat) 3400–3500 (br s), 1720, 1590 (br s), 1395, 1370 (s), 1270 (br s), 1170 (br s), 1080 (br s), 760, 740 (s) cm^{-1}; ^1H NMR δ 1.2 (s, 9 H), 1.45 (s, 9 H), 2.6 (m, 2 H), 3.3 (m, 2 H), 4.1 (m, 1 H), 4.9 (br s, 1 H); mass spectrum, m/e 276 [$(M + 1)^+$].

(*S*)-3-Hydroxy-4-aminobutyric Acid. After compound **13c**, 0.13–0.14 g (0.5 mmol) stood in 2 mL of 4 N dioxane–HCl at room temperature for 16 h, dioxane was blown off with N_2, and the precipitated solid was dissolved in 3.5 mL of water. The mixture was charged on a Dowex 50 W-X8 cation-exchange resin column (200–400 mesh, H^+ form, 9 cm × 1 cm), which was washed with water until the effluent was neutral and then eluted with 25–30 mL of 2 N ammonium hydroxide. Removal of the water at room temperature gave a white solid. Ethanol was added, and after an hour the solvent was removed and the residue dried under vacuum overnight. A light yellow solid, 57 mg (95% yield), was obtained: mp 214 °C (lit. 212–214 °C); $[\alpha]^{22}_D$ +20.1 (*c* 1.7, H_2O) [lit.[8a,b] $[\alpha]^{20}_D$ +18.3° (H_2O), $[\alpha]^{23}_{589}$ +20.4° (*c* 1.48, H_2O)]; IR ν_{max} (KBr) 3450, 3100–2500, 2150, 1665 cm^{-1}; ^1H NMR (D_2O, Me_4Si external standard) δ 2.3 (br d, J = 6 Hz, 2 H), 3.0 (m, 2 H), 4.1 (m, 1 H). Anal. Calcd for $C_4H_9NO_3$: C, 40.34; H, 7.56; N, 11.77. Found: C, 40.34; H, 7.73; N, 11.47.

Acknowledgment. We gratefully acknowledge the partial support of the research by United States Public Health Service Program Project Grant HL-18577 and by a grant from the Dow Chemical Co. Foundation. We thank the Rockefeller University Mass Spectrometric Biotechnology Research Resource supported by the Division of Research Resources, NIH, for obtaining the mass spectra. We also thank Dr. Joseph Vaughn for his help in measuring the NMR spectra.

Photoinduced Methanol-Incorporated Cyclization of *N*-(3-Phenylallyl)arenedicarboximides

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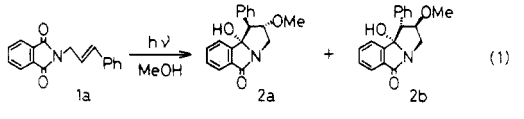
Irradiation of *trans-N*-(3-phenylallyl)arenedicarboximides **1b**, **1c**, and **1d** in methanol–acetonitrile (1/1 v/v) gave methanol-incorporated cyclization products **3a** + **3b**, **6a** + **6b**, and **7**, respectively. Chemical and spectroscopic evidence for the structure of the products is presented. The photocyclization of **1c** predominantly afforded the more sterically crowded product (**6a**). The suggested reaction mechanism, involving initial intramolecular electron transfer from the alkenyl moiety to the singlet excited state of the arenedicarboximide moiety, was supported by the examination of the fluorescence spectra, trans–cis isomerization during the cyclization, and the free-energy change associated with the electron transfer (ΔG_{et}). The calculated spin density of radical anion of naphthalene-1,2-dicarboximide rationalizes the photochemical result of **1c**.

Recently, photoreactions involving electron-transfer processes have received much attention with regards to both the synthetic and mechanistic aspects in organic photochemistry.[1] In the course of studies on the photochemistry of imides, we and other groups have found in the photoreactions of phthalimide–alkene systems a variety of alcohol (solvent)-incorporated intramolecular cyclization[2] and intermolecular addition products,[3] which seems to occur via electron-transfer processes. A typical example is shown in eq 1. However, the imide compounds em-



(1)

ployed in the previous investigations have been confined to phthalimides, and only little information has been reported on the effect of arene structure of arenedicarboximides (aromatic imides).[4] Our studies have been focused on elucidation of the effect of extended π-conjugation system in the arene structure.[5] Here we report the results of intramolecular photoreactions of three types of *trans-N*-(3-phenylallyl)arenedicarboximide in methanol–acetonitrile, indicating that the methanol-incorporated photocyclization is characteristic for the series of the *N*-alkenylarenedicarboximides.

Results and Discussion

Irradiation of *trans-N*-(3-phenylallyl)naphthalene-2,3-dicarboximide (**1b**) in N_2-purged methanol–acetonitrile (1/1 v/v) gave two methanol-incorporated cyclization products [**3a** (55%) and **3b** (16%)] (eq 2). Support for the structure of **3a** was furnished by dehydration of **3a** to give **4** and by acid degradation of **3a** and **4** to **5a** (eq 3). The stereochemistry of **3a** and **3b** was deduced from the similarity of the ^1H NMR spectra (coupling constants between H^a–H^d) of **3a** and **3b** to those of **1a** and **1b**.[2a]

Irradiation of *trans-N*-(3-phenylallyl)naphthalene-1,2-dicarboximide (**1c**) in methanol–acetonitrile (1/1 v/v) gave mainly two methanol-incorporated cyclization products [**6a** (57%) and **6b** (34%)] together with the minor stereoisomers (eq 4). Acid treatment of **6a** and **6b** gave different

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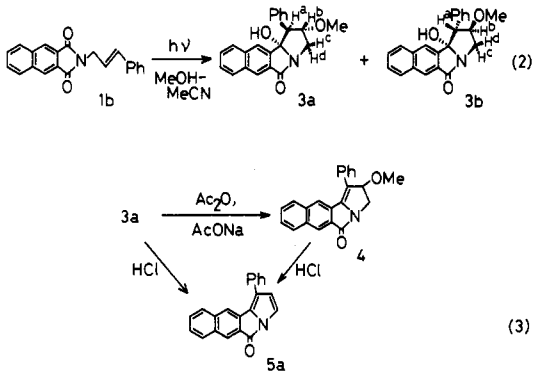
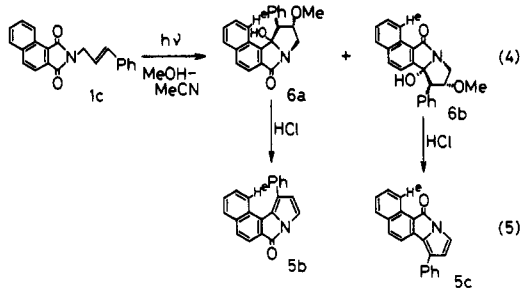
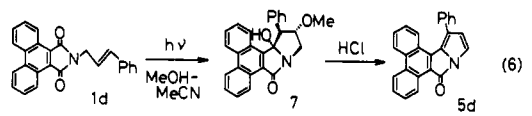


products [**5b** (58%) and **5c** (70%), respectively] (eq 5).



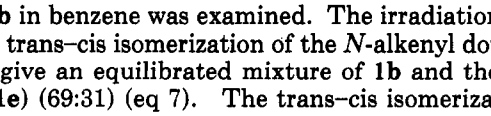
The structures of the compounds **6a**, **6b**, **5b**, and **5c** were assigned by their ^{1}H NMR spectra. It is well established that the protons which lie in the plane of carbonyl group and close to the oxygen atom are appreciably deshielded by the carbonyl group.[6] Thus, the large deshielding of H^e in **6b** (δ 8.7–8.9) and **5c** (δ 8.7–8.9) compared with those in **6a** (δ 8.2–8.4) and **5b** (δ 6.9–7.8) strongly supports the proposed structures. The fact that the yield of **6a** is higher than **6b** indicates that the photocyclization of **1c** predominantly afforded the more sterically crowded product (**6a**).

Irradiation of *trans*-*N*-(3-phenylallyl)phenanthrene-9,10-dicarboximide (**1d**) in methanol–acetonitrile (1/1 v/v) gave mainly one methanol-incorporated cyclization product **7** (49%) together with the minor stereoisomers (eq 6). Acid treatment of **7** also gave **5d** (89%) (eq 6).



Absorption spectrum of **1d** in methanol–acetonitrile (1/1 v/v) was almost identical with that of *N*-methylphenanthrene-9,10-dicarboximide (**8**) in the wavelength region of >370 nm. Fluorescence spectrum of **1d** in methanol–acetonitrile (1/1 v/v) showed that the alkenyl moiety strongly quenched the fluorescence of the imide moiety (λ_{max} 480 nm) by a factor of 16 compared with that of **8**. From these results, we can conclude that the methanol-incorporated cyclization occurs directly from the singlet excited state of the imide moiety.

To obtain the further mechanistic information irradiation of **1b** in benzene was examined. The irradiation resulted in trans–cis isomerization of the *N*-alkenyl double bond to give an equilibrated mixture of **1b** and the cis isomer (**1e**) (69:31) (eq 7). The trans–cis isomerization



(6) Martin, R. H.; Defay, N.; Greets-Evrard, F. *Tetrahedron* **1964**, *20*, 1505.

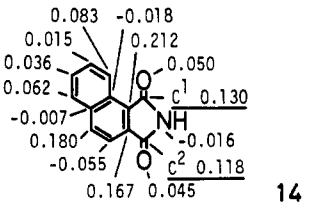
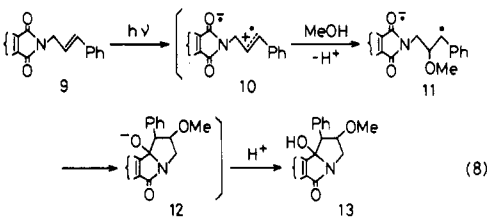


Figure 1.

seems to occur from the triplet excited state of the alkenyl moiety produced by intramolecular energy transfer from the imide moiety. In fact, no isomerization to **1e** was observed in methanol–acetonitrile (1/1 v/v) where irradiation of **1b** gave **3a** and **3b**.

A possible mechanism which can interpret the general feature of the photocyclization is shown in eq 8, in which **1b–d** are denoted as **9** altogether. The initial step of the



reaction is an electron-transfer process from the alkenyl moiety to the singlet excited state of the imide moiety. The approximate values of free-energy change associated with the intramolecular electron transfer (ΔG_{et}) can be estimated by using eq 9.[7] In this equation $E(D/D^+)$ is the

$$\Delta G_{et} = 23.06[E(D/D^+) - E(A^-/A)] - \Delta E_{0,0} \quad (9)$$

oxidation potential of the alkenyl moiety, $E(A^-/A)$ is the reduction potential of the imide moiety (–1.03 V for **8** in 0.5 M Et_4NClO_4/acetonitrile vs. Ag/0.01 M $AgClO_4$), and $\Delta E_{0,0}$ is the singlet excitation energy of the imide moiety (69 kcal/mol for **8** from the absorption and fluorescence spectra). For the oxidation potentials we have used +1.38 V for the alkenyl (styryl) moiety.[8] With these values, we can obtain a large negative value of ΔG_{et} (–13.7 kcal/mol) for **1d**, in agreement with the electron-transfer mechanism.

Although there have been a number of examples of solvent-incorporated addition in the photoreactions of electron donor–acceptor pairs,[9] the present photocyclization of *N*-(3-phenylallyl)arenedicarboximides is to be considered as an example of the solvent-incorporated intramolecular addition of alkenyl moiety to the carbonyl system.

One interesting problem here is which of the two types of carbonyl carbon atom in **1c** is attacked during the methanol-incorporated cyclization. Provided the reaction proceeds as shown in eq 8, the alkyl radical in **11** will attack the imide carbonyl carbon atom which is more reactive as the counteratom. The relative spin density in the imide radical anion moiety can be used to interpret this problem. The spin density of the radical anion of naphthalene-1,2-dicarboximide (**14**) is calculated by McLachlan method (on the basis of Hückel molecular orbital method),[10] and the results are shown in Figure 1. Spin density of C(1) carbonyl carbon atom of **14** is relatively low compared with

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that of C(2) carbon atom. Therefore, cyclization toward the C(1) carbon should be favorable. In our experiment **6a** predominated over **6b** by ca. 1.7 times.

In conclusion, emphasis should be made on the generality of the solvent-incorporated addition (cyclization) of a double bond to an arenedicarboximide carbonyl system. We have already reported the corresponding photocyclization in the reaction of a wide variety of *N*-(2- and *N*-(3-alkenyl)phthalimides to form new five- and six-membered ring systems[2a,b] and of *N*-alkenylphthalimides with a more remote alkenyl double bond to attain medium-sized cyclic to macrocyclic compounds.[2c] Diversity in the behavior of the olefinic moiety responsible for the photocyclization was proved. This work reveals that a wide variety of arenedicarboximides can also be photocyclized and this technique for N heterocycle ring formation will have general synthetic utility.

Experimental Section

Melting points are uncorrected. NMR chemical shifts are reported in ppm (δ) relative to internal $SiMe_4$. UV irradiation was carried out with an Eikosha PIH 300-W high-pressure Hg lamp through Pyrex and saturated $CuSO_4$ aqueous solution filters with about 1-cm thickness [341 (50% transmittance), 330 (25%), 320 (5%), 310 nm (~0%)], under N_2 at ambient temperature. Column chromatography was done on Wakogel C-200 (silica gel, 74–149 μm).

Materials. Three *trans*-*N*-(3-phenylallyl)arenedicarboximides (**1b–d**) were prepared by the reaction of the corresponding arenedicarboxylic anhydrides and cinnamylamine[11] followed by dehydration (acetic anhydride). The imides were purified by column chromatography eluted with dichloromethane and then by recrystallization.

trans-*N*-(3-Phenylallyl)naphthalene-2,3-dicarboximide (**1b**): 23% based on naphthalene-2,3-dicarboxylic anhydride;[12] mp 235–237 °C (from chloroform–ethanol); ^{1}H NMR ($CDCl_3$) 4.57 (d, 2 H, NCH_2), 6.38 (dt, 1 H, CH_2CH=C), 6.82 (d, J = 16 Hz, 1 H, PhC*H*=C), 7.2–7.6 (m, 5 H, Ph), 7.5–7.8 (m, 2 H, Ar H), 7.9–8.2 (m, 2 H, Ar H), 8.28 (s, 2 H, Ar H); IR (KBr) 1772 (imide), 1715 (imide), 1395, 1350, 1122, 775 cm^{-1}. Anal. Calcd for $C_{21}H_{15}NO_2$: C, 80.49; H, 4.83; N, 4.47. Found: C, 80.85; H, 4.96; N, 4.35.

trans-*N*-(3-Phenylallyl)naphthalene-1,2-dicarboximide (**1c**): 35% based on naphthalene-1,2-dicarboxylic anhydride;[13] mp 141–143 °C (from benzene–ethanol); ^{1}H NMR ($CDCl_3$) 4.35 (d, 2 H), 6.19 (dt, 1 H), 6.62 (d, J = 16 Hz, 1 H), 7.0–8.1 (m, 10 H, Ph + Ar H), 8.5–8.9 (m, 1 H, Ar H); IR (KBr) 1760 (imide), 1708 (imide), 1428, 1384, 758 cm^{-1}. Anal. Calcd for $C_{21}H_{15}NO_2$: C, 80.49; H, 4.83; N, 4.47. Found: C, 80.21; H, 4.60; N, 4.38.

trans-*N*-(3-Phenylallyl)phenanthrene-9,10-dicarboximide (**1d**): 20% based on phenanthrene-9,10-dicarboxylic anhydride;[14] mp 231–234 °C (from chloroform); ^{1}H NMR ($CDCl_3$) 4.45 (d, 2 H), 6.35 (dt, 1 H), 6.75 (d, J = 16 Hz, 1 H), 7.1–8.0 (m, 9 H, Ph + Ar H), 8.5–8.8 (m, 2 H, Ar H), 8.9–9.2 (m, 2 H, Ar H); IR (KBr) 1772 (imide), 1696 (imide), 1440, 1395, 768, 735, 718 cm^{-1}. Anal. Calcd for $C_{25}H_{17}NO_2$: C, 82.62; H, 4.72; N, 3.85. Found: C, 82.47; H, 4.57; N, 3.79.

N-Methylphenanthrene-9,10-dicarboximide (**8**) was prepared by the reaction of phenanthrene-9,10-dicarboxylic anhydride and methylamine followed by dehydration.

N-Methylphenanthrene-9,10-dicarboximide (**8**): mp 228–229 °C (from chloroform); ^{1}H NMR ($CDCl_3$) 3.16 (s, 3 H, NMe), 7.6–7.9 (m, 4 H, Ar H), 8.5–8.8 (m, 2 H, Ar H), 8.9–9.2 (m, 2 H, Ar H); IR (KBr) 1764 (imide), 1704 (imide), 1440, 1382, 770 cm^{-1}. Anal. Calcd for $C_{17}H_{11}NO_2$: C, 78.15; H, 4.24; N, 5.36. Found: C, 78.31; H, 4.31; N, 5.28.

Irradiation of 1b in Methanol–Acetonitrile. A solution of 400 mg (3.2 mmol) of **1b** in 400 mL of methanol–acetonitrile (1/1 v/v) was irradiated for 7 h under N_2 with stirring. Solvent was removed in vacuo, and the products were separated by column chromatography (eluted with dichloromethane–ether) to give 243 mg (55%) of **3a** and 71 mg (16%) of **3b**.

11bα-Hydroxy-2α-methoxy-1β-phenyl-1,2,3,11b-tetrahydro-5*H*-benzo[*f*]pyrrolo[2,1-*a*]isoindol-5-one (**3a**): mp 149–152 °C; ^{1}H NMR ($CDCl_3$) 3.45 (s, 3 H, OMe), 3.79 (dd, J = 2, 13 Hz, 1 H, H^c), 3.84 (d, J = 5 Hz, 1 H, H^a), 4.36 (m, 1 H, H^b), 4.4 (br s, 1 H, OH), 4.60 (dd, J = 6, 13 Hz, 1 H, H^d), 6.6–7.0 (m, 3 H, Ar H), 7.4–7.9 (m, 6 H, Ar H), 7.65 (s, 1 H, Ar H), 7.99 (s, 1 H, Ar H); IR (KBr) 3380 (OH), 1695 (amide), 1452, 1387, 1104, 1062 cm^{-1}. Anal. Calcd for $C_{22}H_{19}NO_3$: C, 76.50; H, 5.55; N, 4.06. Found: C, 76.82; H, 5.30; N, 3.98.

11bα-Hydroxy-2β-methoxy-1α-phenyl-1,2,3,11b-tetrahydro-5*H*-benzo[*f*]pyrrolo[2,1-*a*]isoindol-5-one (**3b**): mp 127–131 °C; ^{1}H NMR ($CDCl_3$) 2.78 (d, J = 4 Hz, 1 H, H^a), 3.33 (s, 3 H, OMe), 3.74 (d, J = 12 Hz, 1 H, H^c), 4.0 (br s, 1 H, OH), 4.02 (dd, J = 4, 12 Hz, 1 H, H^d), 4.40 (t, J = 4 Hz, 1 H, H^b), 7.51 (s, 1 H, Ar H), 7.3–8.0 (m, 9 H, Ar H), 8.21 (s, 1 H, Ar H); IR (KBr) 3300 (OH), 1678 (amide), 1108, 1082, 702 cm^{-1}. Anal. Calcd for $C_{22}H_{19}NO_3$: C, 76.50; H, 5.55; N, 4.06. Found: C, 76.28; H, 5.79; N, 3.96.

Dehydration of 3a. A solution of 100 mg of **3a** and 10 mg of sodium acetate in 10 mL of acetic anhydride was refluxed for 0.5 h. The cooled solution was poured into 50 mL of water, neutralized with sodium hydrogen carbonate solution, and extracted with chloroform. The extract was washed with aqueous sodium hydrogen carbonate solution and water and then dried. After evaporation of the solvent, column chromatography (eluted with dichloromethane–ether) of the residue gave 42 mg (40%) of **4**.

2-Methoxy-1-phenyl-2,3-dihydro-5*H*-benzo[*f*]pyrrolo[2,1-*a*]-isoindol-5-one (**4**): mp 149–152 °C; ^{1}H NMR ($CDCl_3$) 3.35 (s, 3 H, OMe), 4.05 (d, 2 H, CH_2), 5.35 (t, 1 H, CH), 6.7–8.1 (m, 9 H, Ar H), 8.30 (s, 1 H, Ar H); IR (KBr) 1696 (amide), 1380, 1228, 1090, 688 cm^{-1}. Anal. Calcd for $C_{22}H_{17}NO_2$: C, 80.71; H, 5.23; N, 4.28. Found: C, 80.83; H, 5.29; N, 4.16.

Acid Degradation of 3a and 4. To a solution of 50 mg of **3a** or **4** in 10 mL of chloroform was added a few drops of hydrochloric acid. After 1 day, the solution was washed with water and dried. After evaporation, column chromatography (eluted with dichloromethane) gave **5a** (33 mg, 77% from **3a** and 41 mg, 91% from **4**).

1-Phenyl-5*H*-benzo[*f*]pyrrolo[2,1-*a*]isoindol-5-one (**5a**): mp 160–163 °C; ^{1}H NMR ($CDCl_3$) 6.42 (d, J = 4 Hz, 1 H), 7.15 (d, J = 4 Hz, 1 H), 7.3–7.9 (m, 10 H, Ar H), 8.17 (s, 1 H, Ar H); IR (KBr) 1750 (amide), 1640, 1395, 1235, 735 cm^{-1}. Anal. Calcd for $C_{21}H_{13}NO$: C, 85.40; H, 4.44; N, 4.74. Found: C, 85.72; H, 4.38; N, 4.59.

Irradiation of 1c in Methanol–Acetonitrile. A solution of 400 mg (3.2 mmol) of **1c** in 400 mL of methanol–acetonitrile (1/1 v/v) was irradiated for 7 h. Solvent was removed in vacuo, and the products were separated by column chromatography (eluted with dichloromethane–ether) to give 250 mg (57%) of **6a** and 150 mg (34%) of **6b**. Minor products containing a methoxy group which were probably stereoisomers of **6a** and **6b**, were detected but not isolated in pure form.

11cα-Hydroxy-2α-methoxy-1β-phenyl-1,2,3,11c-tetrahydro-5*H*-benzo[*e*]pyrrolo[1,2-*b*]isoindol-5-one (**6a**): mp 176–179 °C (from benzene–ethanol); ^{1}H NMR ($CDCl_3$) 3.48 (s, 3 H, OMe), 3.74 (dd, J = 4, 14 Hz, 1 H), 4.00 (br s, 1 H), 4.3–4.5 (m, 2 H), 4.4 (br s, 1 H, OH), 6.5–7.0 (m, 5 H, Ph), 7.3–7.9 (m, 5 H, Ar H), 8.2–8.4 (m, 1 H, Ar H); IR (KBr) 3340 (OH), 1695 (amide), 1382, 1108, 768, 705 cm^{-1}. Anal. Calcd for $C_{22}H_{19}NO_3$: C, 76.50; H, 5.55; N, 4.06. Found: C, 76.85; H, 5.51; N, 4.14.

3aα-Hydroxy-2α-methoxy-3β-phenyl-1,2,3,3a-tetrahydro-10*H*-benzo[*e*]pyrrolo[2,1-*a*]isoindol-5-one (**6b**): mp 179–182 °C (from benzene–ethanol); ^{1}H NMR ($CDCl_3$) 3.38 (s, 3 H, OMe), 3.4–3.5 (m, 2 H, CH + OH), 3.72 (dd, J = 2, 12 Hz, 1 H), 4.02 (m, 1 H), 4.36 (dd, J = 6, 12 Hz, 1 H), 6.3–7.8 (m, 10 H, Ph + Ar H), 8.7–8.9 (m, 1 H, Ar H); IR (KBr) 3360 (OH), 1692 (amide), 1360, 1098, 838, 760 cm^{-1}. Anal. Calcd for $C_{22}H_{19}NO_3$: C, 76.50; H, 5.55; N, 4.06. Found: C, 76.79; H, 5.42; N, 4.11.

Acid Degradation of 6a and 6b. Acid degradation of 50 mg of **6a** and **6b** was performed analogously as that of **3a** and **4** to give 25 mg (58%) of **5b** and 30 mg (70%) of **5c**, respectively.

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1-Phenyl-5*H*-benzo[*e*]pyrrolo[1,2-*b*]isoindol-5-one (**5b**): mp 158–160 °C; ^{1}H NMR ($CDCl_3$) 6.13 (d, J = 3 Hz, 1 H), 7.07 (d, J = 3 Hz, 1 H), 6.9–7.8 (m, 11 H, Ar H); IR (KBr) 1740 (amide), 1388, 1232, 768, 704 cm^{-1}. Anal. Calcd for $C_{21}H_{13}NO$: C, 85.40; H, 4.44; N, 4.74. Found: C, 85.66; H, 4.39; N, 4.50.

1-Phenyl-5*H*-benzo[*e*]pyrrolo[2,1-*a*]isoindol-5-one (**5c**): mp 136–139 °C; ^{1}H NMR ($CDCl_3$) 6.20 (d, J = 3 Hz, 1 H), 7.06 (d, J = 3 Hz, 1 H), 7.3–8.0 (m, 10 H, Ar H), 8.7–8.9 (m, 1 H, Ar H); IR (KBr) 1720 (amide), 1594, 1253, 820, 733 cm^{-1}. Anal. Calcd for $C_{21}H_{13}NO$: C, 85.40; H, 4.44; N, 4.74. Found: C, 85.76; H, 4.20; N, 4.80.

Irradiation of 1d in Methanol–Acetonitrile. A solution of 400 mg (2.5 mmol) of **1d** in 400 mL of methanol–acetonitrile (1/1 v/v) was irradiated for 7 h. The solvent was removed in vacuo, and the products were separated by column chromatography (eluted with dichloromethane–ether) to give 213 mg (49%) of **7**. Minor products having methoxy group, probably stereoisomers of **7**, were detected but not isolated in pure forms.

13cα-Hydroxy-2α-methoxy-1β-phenyl-1,2,3,13c-tetrahydro-5*H*-dibenzo[*e*,*g*]pyrrolo[2,1-*a*]isoindol-5-one (**7**): mp 197–200 °C (from benzene–ethanol); ^{1}H NMR ($CDCl_3$) 3.50 (s, 3 H, OMe), 3.6–3.8 (m, 1 H), 3.9–4.1 (m, 1 H), 4.1–4.5 (m, 2 H), 4.4 (br s, 1 H, OH), 6.6–6.9 (m, 5 H, Ph), 7.4–7.8 (m, 4 H, Ar H), 8.3–8.6 (m, 3 H, Ar H), 9.0–9.2 (m, 1 H, Ar H); IR (KBr) 3340 (OH), 1668 (amide), 1378, 1100, 758, 696 cm^{-1}. Anal. Calcd for $C_{26}H_{21}NO_3$: C, 78.96; H, 5.35; N, 3.54. Found: C, 79.17; H, 5.29; N, 3.49.

Acid Degradation of 7. Acid degradation of 50 mg of **7** was performed analogously as that of **3a** and **4** to give 39 mg (89%) of **5d**.

1-Phenyl-5*H*-dibenzo[*e*,*g*]pyrrolo[2,1-*a*]isoindol-5-one (**5d**): mp 214–217 °C; ^{1}H NMR ($CDCl_3$) 6.18 (d, J = 3 Hz, 1 H), 7.0–7.3 (m, 2 H), 7.4–7.8 (m, 9 H, Ar H), 8.5–8.7 (m, 2 H, Ar H), 8.9–9.2 (m, 1 H, Ar H); IR (KBr) 1730 (amide), 1380, 756, 738 cm^{-1}. Anal. Calcd for $C_{25}H_{15}NO$: C, 86.93; H, 4.38; N, 4.06. Found: C, 87.08; H, 4.28; N, 3.98.

Isolation of 1e (Irradiation of 1b in Benzene). A solution of 2 g (16 mmol) of **1b** in 400 mL of benzene was irradiated for 18 h under N_2. Solvent was removed in vacuo, and the residue was dissolved in 100 mL of ethanol by heating. When the mixture was cooled **1b** crystallized. After the crystals were filtered off the filtrate was concentrated to 50 mL. The plates of **1e** deposited on standing. The crystals were purified by repeated recrystallization from ethanol. The yield of **1e** was 130 mg (7%).

cis-*N*-(3-Phenylallyl)naphthalene-2,3-dicarboximide (**1e**): mp 175–177 °C; ^{1}H NMR ($CDCl_3$) 4.60 (dd, J = 2, 7 Hz, 2 H, NCH_2), 5.66 (dt, J = 7, 12 Hz, 1 H, CH_2CH=C), 6.60 (dd, J = 2, 12 Hz, 1 H, PhCH=C), 7.0–7.4 (m, 5 H, Ph), 7.5–7.8 (m, 2 H, Ar H), 7.9–8.1 (m, 2 H, Ar H), 8.25 (s, 2 H, Ar H); IR (KBr) 1772 (imide), 1715 (imide), 1400, 1350, 770 cm^{-1}. Anal. Calcd for $C_{21}H_{15}NO_2$: C, 80.49; H, 4.83; N, 4.47. Found: C, 80.65; H, 4.99; N, 4.21.

Structure of Dukunolides, Bitter Principles of *Lansium domesticum*

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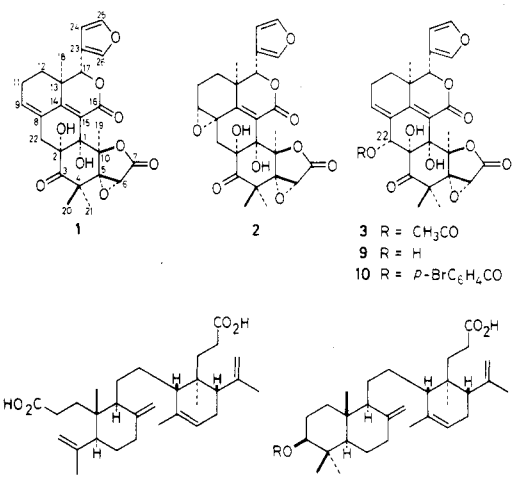
Characteristic bitter principles, named dukunolides A, B, and C, in seeds of *Lansium domesticum* have been proven to be skeletally new tetranortriterpenoids **1**, **2**, and **3**. The structure of **1** is definitely established by X-ray analysis, and that of **2** is confirmed by the chemical correlation with **1** by epoxidation. The absolute configuration of these compounds has been deduced from that of dukunolide C *p*-bromobenzoate, established by X-ray study.

Fruits of *Lansium domesticum* Jack v. duku, a Meliaceous plant, have been called "duku" traditionally and are a very popular dessert in southeast Asia. Kiang et al.[3] have reported the isolation of lansic acid **4** as a major constituent of this fruit skin in 1967. We have also investigated the skin constituents and characterized novel secoonocerane triterpene glycosides, lansiosides A, B, and C (**5–7**),[1] and their aglycone **8**.[2] The seeds of duku do not contain the onoceranoids **4–8** but gave skeletally new tetranortriterpenoids, named dukunolide A, B, and C (**1**, **2**, and **3**, respectively), as their bitter principles. We herein describe the isolation and structure determination of dukunolides.

Dukunolide A (**1**), mp 279–281 °C, was isolated as colorless needles in 0.03% yield from the powdered seed of *L. domesticum*. The molecular formula $C_{26}H_{26}O_9$ was determined on the basis of the mass spectrum and elemental analysis. The IR spectrum showed the presence of hydroxyls (3500 and 3300 cm^{-1}), carbonyls (1790, 1735, and 1670 cm^{-1}), and double bonds (1625, 1582, 1500, and 960 cm^{-1}). The existence of a $\alpha,\beta,\gamma,\delta$-unsaturated carbonyl moiety was suggested by the UV absorption spectrum (λ_{max} 292 nm ϵ 14 600). The ^{1}H NMR spectrum was rather simple as seen in Figure 3. The presence of 13 quaternary carbon signals in the ^{13}C NMR spectrum (Figure 6) made the structural study very difficult by conventional spectral analysis.

Chart I



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