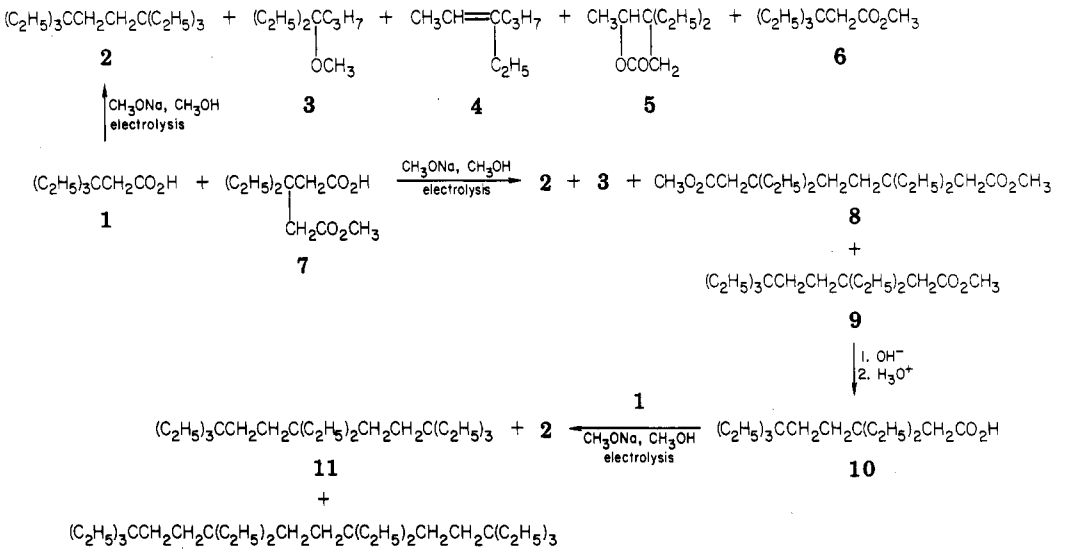
Scheme I



rative GC and identified as follows. **2**: bp 140–142 °C (20 mm); mp 7–8 °C; n^{25}_D 1.4524; ^{1}H NMR (CCl_4) δ 0.5–1.5, (m, 34, CH_2, CH_3); IR (neat) 2970 (s), 2935 (s), 2835 (s), 1460 cm^{-1} (m); viscosity in centistokes vs. temperature (°C), 5.24/37.8, 2.78/66.7, 1.67/98.9; D^{20}_4 0.8324; yield 81%.

Anal. Calcd for $C_{16}H_{34}$: C, 84.86; H, 15.14. Found: C, 84.95; H, 14.84. **3**: bp 72–76 °C (30 mm); n^{25}_D 1.4164; ^{1}H NMR (CCl_4) δ 0.5–1.0 (m, 9, CH_3), 1.1–1.7 (m, 8, CH_2), 3.03 (s, 3 H, OCH_3); IR (neat) 1090 (s), 1075 cm^{-1} (w); yield 11%.

Anal. Calcd for $C_9H_{20}O$: C, 74.93; H, 13.98. Found: C, 74.74; H, 13.72.

Trace quantities of three compounds were isolated by GC, and spectral analyses suggested the following structures. **4**:[11] ^{1}H NMR (CCl_4) δ 0.7–1.1 (m, 6, CH_3), 1.2–1.5 (m, 2,CH_2), 1.60 (d, 3, CH_3CH=), 1.8–2.3 (m, 4, =$C(CH_2)_2$), 5.0–5.4 (m, 1, CH=; IR (neat) 3190 (m), 2765–3060 (s), 1940 (m), 1840 (m), 1740 (m), 1670 cm^{-1} (m). **5**: ^{1}H NMR (CCl_4) δ 0.6–1.0 (m, 6, CH_3), 1.1–1.7 (m, 7, CH_2, CH_3), 2.20 (s, 2, CH_2CO_2), 4,27 (q, 1, CHOCO); IR 1775 cm^{-1} (s). **6**: ^{1}H NMR (CCl_4) δ 0.6–0.95 (m, 9, CH_3), 1.1–1.6 (m, 6, CH_2), 2.10 (s, 2, CH_2CO_2), 3.60 (s, 3, CO_2CH_3).

Electrolysis of a Mixture of 1 and 7. A solution of 36.4 g (0.23 mol) of **1** in 350 mL of dry methanol was added to a solution of the sodium salt of **7**, prepared by adding 25.0 g (0.15 mol) of 3,3-diethyl-1,5-pentanedioic anhydride to a solution of sodium methoxide, made from 6.9 g (0.3 mol) of sodium in 165 mL of methanol. The mixture was electrolyzed as described previously at 120 V and 20 amp for 4.5 h, when the amperage was 3. The solvent was removed by distillation, and the residue was dissolved in Et_2O, washed with 100 mL of H_2O and 100 mL of 1 N HCl, and dried. The Et_2O was distilled and the 43.1 g of residue was distilled through a spinning band column to give four major components: **2** (46%), **3** (11%), **8** (9.5%) [bp 135–136 °C (0.5 mm); n^{25}_D 1.4596; ^{1}H NMR (CCl_4) δ 0.6–1.0 (m, 12, CH_3), 1.0–1.6 (m, 12, CH_2), 2.14 (s, 4, CH_2CO_2), 3.60 (s, 6, CO_2CH_3); IR 1737 cm^{-1} (s)].

Anal. Calcd for $C_{18}H_{34}O_4$: 68.75; H, 10.90. Found: C, 69.02; H, 11.10. **9** (32%): bp 140–144 °C (2 mm); n^{25}_D 1.4550; ^{1}H NMR (CCl_4) δ 0.5–0.95 (m, 15, CH_3), 0.95–1.6 (m, 14, CH_2), 2.12 (s, 2, CH_2CO_2), 3.60 (s, 3, CO_2CH_3); IR 1740 cm^{-1} (s).

Anal. Calcd for $C_{17}H_{34}O_2$: C, 75.50; H, 12.67. Found: C, 75.45; H, 12.40.

Preparation of 10 and 3,3,6,6-Tetraethyl-1,8-octanedioic Acid. A mixture of 30.2 g (0.11 mol) of **9**, 52.8 g (0.8 mol) of 85% KOH, 135 mL of H_2O, and 55 mL of ethanol was heated at reflux for 18.5 h and worked up in the usual way. The acid (22.4 g, 78%) was recrystallized from CH_3CN; mp 48–50 °C.

Anal. Calcd for $C_{16}H_{32}O_2$: C, 74.94; H, 12.58. Found: C, 74.73; H, 12.53.

A similar saponification of 5 g of **8**, afforded 4.3 g (94%) of the dibasic acid.

Anal. Calcd for $C_{16}H_{30}O_4$: C, 67.09; H, 10.56. Found: C, 67.23; H, 10.55.

Electrolysis of a Mixture of 1 and 10. A mixture of 31.6 g (0.2 mol) of **1**, 25.6 g (0.1 mol) of **10**, 64.8 g (0.3 mol) of 25% sodium methoxide in methanol, and 400 mL of anhydrous methanol was electrolyzed for 3 h with an initial 110 V and 16 amp. The solvent was removed by distillation and the residue was diluted with petroleum ether, bp 60–65 °C. The solution was washed with H_2O and 10% HCl and dried over molecular sieves. The solvent was removed by distillation and the residue (43.5 g) was distilled through a spinning band column to give 10 fractions and a residue. The latter was recrystallized from acetone and afforded 5.4 g (27%) of **12**: mp 77–79 °C; ^{1}H NMR (CCl_4) δ 0.50–0.94 (m, 30, CH_3), 0.94–1.54 (m, 32, CH_2); IR 2950 (s), 2910 (s), 2850 (s), 1450 (s), 1370 cm^{-1} (m).

Anal. Calcd for $C_{30}H_{62}$: C, 85.22; H, 14.78. Found: C, 85.02; H, 14.69.

Redistillation of fractions 8–10 gave 10.4 g (32%) of **11**: bp 145–146 °C (0.8 mm); mp 39.5–41.5 °C (acetone); IR 2960 (s), 2935 (s), 2880 (s), 1460 (s), 1375 cm^{-1} (s).

Anal. Calcd for $C_{23}H_{48}$: C, 85.09; H, 14.91. Found: C, 84.90; H, 14.81.

Acknowledgment. We are grateful to P. R. Stapp who had prepared previously a sample of 3,3,6,6-tetraethyloctane and determined some of its physical properties.

Registry No. **1**, 6637-50-9; **2**, 78715-64-7; **3**, 62813-72-3; **4**, 620-00-8; **5**, 78715-65-8; **6**, 78715-66-9; **7**·Na, 78739-30-7; **8**, 78715-67-0; **9**, 78715-68-1; **10**, 78715-69-2; **11**, 78715-70-5; **12**, 78715-71-6; 3,3,6,6-tetraethyl-1,8-octanedioic acid, 78715-72-7; 3,3-diethyl-1,5-pentanedioic anhydride, 4160-89-8.

(11) Church. J. M.; Whitmore, F. C.; McGrew, R. V. *J. Am. Chem. Soc.* **1934**, *56*, 1934.

Molecular Rearrangements and Fragmentations during the Aromatization of Diels–Alder Adducts Derived from 1-Benzylisobenzofuran

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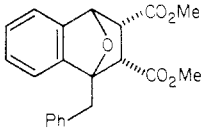
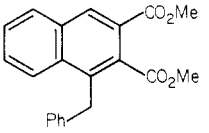
Received January 26, 1981

We have eariler reported[1] that 1-benzylisobenzofuran can be readily generated and captured as a Diels–Alder

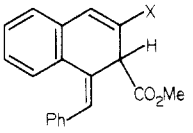
adduct. Aromatization (dehydration) of these adducts provided a convenient synthetic route to a variety of substituted polycyclic aromatic compounds. One observation made during these earlier studies was that acid-catalyzed aromatization of **1a** produced a mixture of naphthalenic, **2a**, and nonnaphthalenic, **3a**, products. Because this behavior was not observed when only one carbomethoxy group was present (i.e., **1b** → **2b**), it was thought that the increased steric interactions among the substituent groups as they became coplanar in the formation of **2a** permitted the alternative mode of dehydration forming **3a** to compete. The purpose of this report is to present evidence that suggests that the initial formation of compounds related to **3** is a general feature of these acid-catalzyed aromatizations as well as to describe an unusual molecular fragmentation.



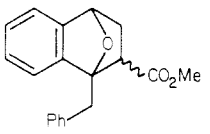
1a



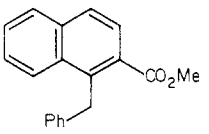
2a



3a, X = CO_2Me
b, X = H

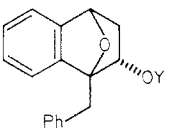


1b

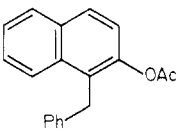


2b

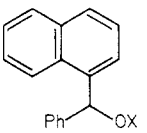
Attempts to aromatize the alcohol **4**[1b] with TsOH in refluxing benzene produced complex mixtures. Since it was possible that the anticipated 1-benzyl-2-naphthol might be thermally or oxidatively sensitive, dehydration was effected with TsOH in hot acetic anhydride in order to protect the hydroxy group by acetylation. At temperatures below 100 °C, the acetoxy derivative **5** was formed and thus **5** must be the intermediate in subsequent transformations. At 120 °C, **6** was formed but only in 30% yield. The major product (60% yield) was **7a**. These compounds were identified by isolation and comparison with an authentic sample[2] in the case of **6** and, after conversion of **7a** to **7b**, by comparison to authentic[3] **7b**.



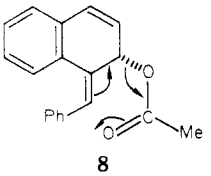
4, Y = H
5, Y = Ac



6



7a, X = Ac
b, X = H



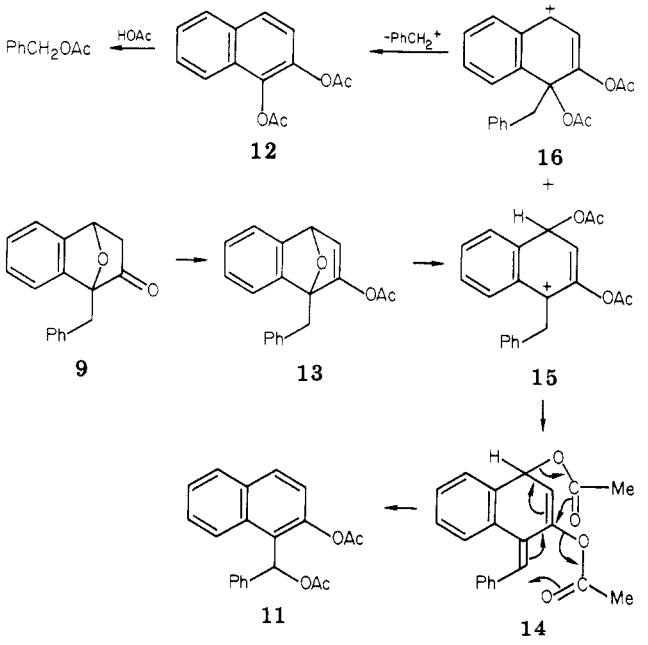
8

The formation of **7** can be rationalized by assuming the dehydration of **5** produced predominantly the nonnaphthalenic product **8**, which thermally rearranged to the observed acetate **7a**. Analogous [3,3]sigmatropic rearrangements have been reported elsewhere.[4] The present example strongly suggests that nonnaphthalenic products are kinetic dehydration products even with simply substituted Diels–Alder adducts such as **4**. In the present case, the nonnaphthalenic dehydration product is "captured" by the rearrangement of an acetoxy group; in other instances (e.g., **1b**) rearrangement of the nonnaphthalenic to the naphthalenic product (**3b** → **2b**) presumably occurs provided interactions of the substituent groups do not inhibit isomerization.

These observations prompted an attempt to dehydrate the ketone **9**[1b] with hot acetic anhydride–TsOH. The reaction product was separated by chromatography into two fractions. The first consisted of recovered **9** (13% recovery) and benzyl acetate (**10**; 36% yield). The second fraction consisted of a mixture of **11** and **12** in 21% and 58% yield, respectively (NMR analysis). The latter was isolated by vacuum sublimation and the former by chromatography of the nonvolatile residue, and identification was accomplished by comparison with authentic samples.[5,6]

The diol corresponding to **11** (i.e., 1-(α-hydroxybenzyl)-2-naphthol) is known to lose its α-hydroxybenzyl group under acidic[6] and oxidative[7] conditions. However, the diacetate **11** proved to be stable under the reaction conditions leading to its formation. The 1,2-diacetoxynaphthalene, **12**, must therefore be formed concomitantly with **11**.

The formation of **11** and **12** can be rationalized by assuming the initial formation of the enol acetate, **13**. Since this compound cannot "dehydrate" as can the alcohol **4**, it is suggested that the 1,4-epoxy bridge breaks to form the two intermediate acetylated carbonium ions **15** and **16**.



The former, **15**, would give rise to the diacetate **14** which can undergo two [3,3]-sigmatropic rearrangements[8] of the

(1) (a) Smith, J. G.; Wikman, R. T. *J. Org. Chem.* **1974**, *39*, 3648. (b) Smith, J. G.; Welankiwar, S. S.; Shantz, B. S.; Lai, E. H.; Chu, N. G. *Ibid.* **1980**, *45*, 1817.
(2) Claisen, L. *Justus Liebigs Ann. Chem.* **1925**, *442*, 210.
(3) Acree, S. F. *Chem. Ber* **1904**, *37*, 2753.
(4) Barton, D. H. R.; Magnus, P. D.; Pearson, M. J. *J. Chem. Soc. C* **1971**, 2231.
(5) Fieser, L. F.; Peters, M. L. *J. Am. Chem. Soc.* **1931** *53*, 793.
(6) Dilthey, W.; Dornheim, O. *J. Prakt. Chem.* **1937**, *149*, 55.
(7) Becker, H. D.; Bremholt, T. *Tetrahedron Lett.* **1973**, 197.
(8) Conceivably, these two rearrangements could occur stepwise, forming transient intermediates containing *gem*-diacetoxy groups or, alternatively, the rearrangements might proceed synchronously.

acyl groups, forming the observed product 11. Such a rearrangement is a somewhat more elaborate example of that seen for 8. The second intermediate carbonium ion, 16, stabilizes itself through loss of a benzyl cation[9] to form the second naphthalenic product, 12, and ultimately benzyl acetate, 10. The nearest precedent for this unusual fragmentation appears to be the previously mentioned decomposition of 1-(α-hydroxybenzyl)-2-naphthol.[6]

Experimental Section[10]

Preparation of 2-*endo*-Acetoxy-1-benzyl-1,4-epoxy-1,2,3,4-tetrahydronaphthalene (5). The alcohol 4 (51 mg, 2.5 mmol) was added to 1 mL of acetic anhydride containing 5 mg of *p*-toluenesulfonic acid, and the solution was heated under nitrogen at 55–60 °C for 4 h. The solution was poured onto ice, the product was extracted with ether, and the ether extract was washed with dilute sodium bicarbonate and water, dried ($MgSO_4$), and evaporated. The crude acetate, 5 (50 mg, mp 73–77 °C), was recrystallized from chloroform/60–80 °C petroleum ether: mp 76–78 °C; IR (Nujol) 1740, 1250, 1230, 1055, 755, 700 cm^{-1}; NMR ($CDCl_3$) 1.19 (dd, J_1 = 3 Hz, J_2 = 12 Hz, 1 H), 1.83 (s, 3 H), 2.4–3.0 (m, 1 H), 3.50 (s, 2 H), 5.10 (dd, J_1 = 3 Hz, J_2 = 9 Hz, 1 H), 5.31 (d, J = 5 Hz), 7.2–7.5 (m, 9 H). Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.59; H, 6.06.

Aromatization and Rearrangement of 4. The preceding reaction was repeated with 0.65 g (3.18 mmol) of 4, and the solution was heated at 120–125 °C for 4 h. The crude reaction product (0.61 g) on analysis by NMR showed a 2:1 ratio of **7a** to **6**. This was chromatographed on silica gel, using 10:3 mixture of 30–60 °C petroleum ether/benzene. 1-(α-Acetoxybenzyl)naphthalene (**7a**; 0.25 g, 29%) eluted first followed by 0.17 g of a mixture of **7a** and **6**, and finally 0.15 g (17%) of 2-acetoxy-1-benzylnaphthalene, 6, was collected, mp (from benzene) 49–52 °C. This latter compound was identical in its spectroscopic properties with an authentic sample:[2] mp 52–53 °C; IR (neat) 1750, 1360, 1200, 1170, 800, 750, 740, 730, 700, 690 cm^{-1}; NMR ($CDCl_3$) 2.26 (s, 3 H), 4.38 (s, 2 H), 7.1–8.2 (m, 11 H). The spectral properties of **7a** were as follows: IR (neat) 1740, 1365, 1230, 1020, 790, 770, 690 cm^{-1}; NMR ($CDCl_3$) 2.13 (s, 3 H), 7.2–8.2 (m, 13 H).

Conversion of 7a to 1-(α-Hydroxybenzyl)naphthalene (7b). Hydrolysis of **7a** (100 mg, 0.36 mmol) was effected by refluxing an ether solution (15 mL) of the compound under nitrogen with 0.05 g (1.3 mmol) of lithium aluminum hydride for 6 h. After destruction of the excess hydride with ethyl acetate, water was added and the ether layer was decanted, washed with water, dried ($MgSO_4$), and evaporated. The residual oil crystallized on treatment with 30–60 °C petroleum ether: 76 mg (90%); mp 75–79 °C; IR (Nujol) 3300, 1040, 970, 775, 755, 670 cm^{-1}; NMR ($CDCl_3$) 2.45 (br s, 1 H, exchanges with D_2O), 6.40 (s, 1 H), 7.0–8.2 (m, 12 H). These spectra were identical with those of an authentic sample[3] of **7b**, mp 89–91 °C.

Rearrangement and Decomposition of 1-Benzyl-1,4-epoxy-3,4-dihydro-2(1*H*)-naphthalenone (9). The ketone, 9 (2.78 g, 11.1 mmol), was dissolved in 30 mL of acetic anhydride containing 0.5 g of *p*-toluenesulfonic acid and heated under nitrogen for 24 h at 120 °C. The reaction products (3.5 g) were isolated as described above and chromatographed on silica gel, eluting with benzene. The first material collected (0.96 g, fraction A) was dissolved in hot ethanol. On cooling, the starting material, 9, crystallized (NMR, IR, mixture melting point). The filtrate, on evaporation, provided an oil with spectroscopic properties identical with those of benzyl acetate. Analysis (NMR) of this fraction gave a 36% yield of benzyl acetate and a 13% recovery of 9.

Following fraction A, two subsequent fractions were collected, fraction B (0.45 g) and C (1.92 g). The last fraction was sublimed under vacuum (0.05 mm) at 130 °C, and the sublimate was recrystallized from benzene/60–80 °C petroleum ether to provide 1,2-diacetoxynaphthalene, 12: mp 108–110 °C; IR (Nujol) 1760, 1240, 1210, 1190, 1160 cm^{-1}; NMR ($CDCl_3$) 2.30 (s, 3 H), 2.40 (s, 3 H), 7.1–7.9 (m, 6 H). These properties were identical with those of an authentic sample,[5] mp 108–110 °C.

The residue from this sublimation was chromatographed on silica gel as described above to provide 2-acetoxy-1-(α-acetoxybenzyl)naphthalene, 11, mp 95–100 °C, identified by comparison of its spectral properties with those of an authentic sample.

Fractions B and C were analyzed by NMR, and a yield of 21% for 11 and 58% for 12 was determined.

Preparation of 2-Acetoxy-1-(α-acetoxybenzyl)naphthalene (11). 2-Hydroxy-1-(α-hydroxybenzyl)naphthalene was prepared in 80% yield by a literature procedure.[6] Treatment of the diol with hot acetic anhydride containing *p*-toluenesulfonic acid catalyst provided the diacetate, 11: mp 104–6 °C; IR (Nujol) 1755, 1740, 1230, 1200, 1010, 970, 750, 690 cm^{-1}; NMR ($CDCl_3$) 2.13 (s, 3 H), 2.32 (s, 3 H), 7.1–8.2 (m, 11 H). Anal. Calcd for $C_{21}H_{18}O_4$: C, 75.43; H, 5.43. Found: C, 75.22; H, 5.52.

A sample of 11 was heated for 24 h at 120 °C under nitrogen in acetic anhdyride containing a catalytic amount of *p*-toluenesulfonic acid. The compound was recovered unchanged.

Registry No. 4, 73194-77-1; 5, 78199-47-0; 6, 78199-48-1; 7a, 78199-49-2; 7b, 642-28-4; 9, 73194-62-4; 10, 140-11-4; 11, 78199-50-5; 12, 6336-79-4; 2-hydroxy-1-(α-hydroxybenzyl)naphthalene, 40473-53-8.

(9) We thank a referee for suggesting this possibility.

(10) Melting points are uncorrected. NMR spectra were determined with the use of a Varian T-60 instrument and IR spectra were recorded on a Beckman IR-10 spectrometer.

Constituents of *Trichilia hispida* (Meliaceae). 4. Hispidols A and B, Two New Tirucallane Triterpenoids

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Received April 8, 1981

We reported earlier the isolation and identification of four tirucallane triterpenoids (3–6)[1,2] and three limonoids[2,3] from the leaves of *Trichilia hispida* Penning. (ined.) (Meliaceae). We now report the isolation from the same source and characterization of two new crystalline triterpenoids, which we term hispidols A (1) and B (2) (Chart I).

Column chromatography of the lowest R_f constituents (below sapelin B (4)) of the ethanol extract of these leaves followed by recrystallization gave hispidol A (1), mp 118 °C, and hispidol B (2), mp 253–254 °C. Both gave molecular ion peaks at m/e 476 in their electron-impact mass spectra, which, with their elemental analyses, indicated molecular formula $C_{30}H_{52}O_4$, confirmed by high-resolution mass spectroscopy. Comparison of this molecular formula with that of sapelins A (3) and B (4) suggested that 1 and 2 could be dihydro derivatives of 3 and 4 in which either the double bond was reduced or the ether linkage had not been formed.

The 250-MHz ^1H NMR spectra of 1 and 2 (Table I) showed the latter to be the case. NMR spectral comparisons were complicated by the very low solubility of 2 in $CDCl_3$; its spectrum was run in pyridine-d_5 along with those of 1 and 3 for comparison. The pyridine-d_5 spectra of 1 and 2 differ significantly from one another only in the

(1) Jolad, S. D.; Wiedhopf, R. M.; Cole, J. R. *J. Pharm. Sci.* **1977**, *66*, 889.

(2) Jolad, S. D.; Hoffmann, J. J.; Cole, J. R.; Tempesta, M. S.; Bates, R. B. *J. Org. Chem.* **1980**, *45*, 3132. Partial formula R_1 in this reference depicts the wrong configuration at C24.

(3) Jolad, S. D.; Hoffmann, J. J.; Schram, K. H.; Cole, J. R.; Tempesta, M. S.; Bates, R. B. *J. Org. Chem.* **1981**, *46*, 641.

0022-3263/81/1946-4085$01.25/0