Acid-catalyzed cyclization of mangostin

PETER YATES AND H. B. BHAT
Lash Miller Chemical Laboratories, University of Toronto, Toronto, Ontario

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The acid-catalyzed cyclization of mangostin is shown to give products in which one, but not both, of the isopentenyl side chains gives rise to dihydropyran rings. The presence of a methoxyl group at C-7 and thus the structure originally assigned to mangostin is thereby confirmed.

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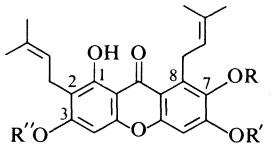
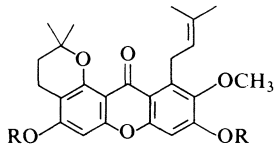
Mangostin, the major coloring matter from the fruit hulls, bark, and dried latex of *Garcinia mangostana*, was assigned structure **1** by Yates and Stout (1, 2) some years ago. A recent suggestion (3), based on benzene-induced solvent shifts in nuclear magnetic resonance (n.m.r.) spectra, that the position of the methoxyl group had been misassigned and that mangostin has structure **2**, has been shown to be unacceptable on several grounds (4). These included the results of a study of the acid-catalyzed cyclization of mangostin. We report here in detail on this study.

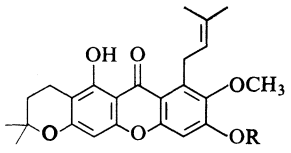


1 R = CH_3; R′ = R″ = H
2 R = R″ = H; R′ = CH_3
10 R = R′ = R″ = CH_3

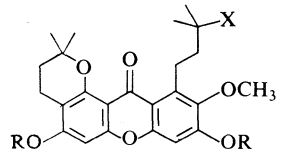
Treatment of mangostin with hydrated *p*-toluenesulfonic acid in acetic acid at room temperature for 24 h gave 6 products, assigned structures **3**–**8**. Compound **3**, 1-isomangostin, is colorless, gives a negative test with ethanolic ferric chloride, and has the characteristic ultraviolet (u.v.) spectrum (Table 1) of mangostin derivatives with an ether linkage rather than a chelated hydroxyl group at C-1 (2, 5). Methylation of **3** gave dimethyl-1-isomangostin (**9**), which has been obtained previously by acid-catalyzed cyclization of dimethylmangostin (**10**) (5).



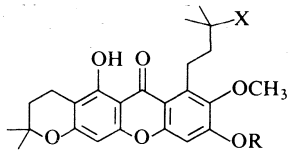
3 R = H
9 R = CH_3



4 R = H
11 R = CH_3



5 X = OH; R = H
6 X = $OCOCH_3$; R = H
12 X = OH; R = CH_3
13 X = $OCOCH_3$; R = CH_3



7 X = OH; R = H
8 X = $OCOCH_3$; R = H
14 X = OH; R = CH_3
15 X = $OCOCH_3$; R = CH_3

Compound **4**, 3-isomangostin, is pale yellow, gives a positive test with ethanolic ferric chloride, and has a u.v. spectrum (Table 1) characteristic of mangostin derivatives with a chelated hydroxyl group at C-1. Its n.m.r. spectrum confirmed the presence of this group and demonstrated the retention of a single isopentenyl side chain. On methylation with diazomethane or with dimethyl sulfate and potassium carbonate it gave a monomethyl ether, which is assigned structure **11**.

The colorless compounds **5** and **6** were shown to be members of the 1-isomangostin series by

TABLE 1

Ultraviolet spectra of the cyclization products from mangostin and their derivatives

Compound	λ_{max} (EtOH) mμ (log ε)			
1-Isomangostin series				
3	244 (4.58)	254 (4.52)	307 (4.39)	345 (4.03)
5	244 (4.51)	254 (4.44)	307 (4.18)	345 (3.97)*
6	244 (4.44)	254 (4.39)	307 (4.11)	345 (3.92)*
9†	245 (4.54)	255 (4.34)	302 (4.34)	336 (3.94)
12†	245 (4.54)	255 (4.55)	302 (4.36)	337 (4.00)
13	245 (4.44)	252 (4.43)	304 (4.22)	340 (3.87)
3-Isomangostin series				
4	243 (4.60)	257 (4.54)	319 (4.48)	355 (4.12)
7	243 (4.46)	253 (4.42)	319 (4.38)	355 (3.97)
8	243 (4.52)	257 (4.47)	319 (4.43)	355 (4.04)
11	243 (4.44)	252 (4.43)	317 (4.38)	355 (3.93)*
14	243 (4.52)	259 (4.54)	317 (4.42)	355 (3.94)
15	244 (4.44)	260 (4.49)	317 (4.38)	355 (3.93)

*Shoulder.
†Reference 5; A. Ault, unpublished results.

their u.v. spectra (Table 1) and by negative tests with ethanolic ferric chloride. The composition of **5** shows that its formation from mangostin involves the addition of the elements of water. That it results from hydration of the ethylenic double bond in the side chain at C-8 was demonstrated by its conversion to a dimethyl ether identical with compound **12**, previously obtained by the action of formic acid on dimethylmangostin (**10**) followed by basic hydrolysis (2), and by similar treatment of dimethyl-1-isomangostin (**9**) (5). Compound **5** is also formed when 1-isomangostin (**3**) is treated with hydrated *p*-toluenesulfonic acid in acetic acid. That compound **6**, whose composition shows that its formation involves the addition of the elements of acetic acid, results from addition of acetic acid to the C-8 side chain was shown by its conversion to a dimethyl ether, assigned structure **13**, that is identical with the product obtained when dimethyl-1-isomangostin (**9**) (5) is treated with anhydrous *p*-toluenesulfonic acid and acetic acid.

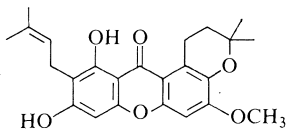
The yellow compounds **7** and **8** were shown to be members of the 3-isomangostin series by their u.v. (Table 1) and n.m.r. spectra and by positive tests with ethanolic ferric chloride. Their composition demonstrates that they are the 3-isomangostin analogues of **5** and **6**, respectively. On methylation they each give monomethyl ethers, assigned structures **14** and **15**, respectively.

When mangostin was treated with anhydrous *p*-toluenesulfonic acid in benzene at reflux for 30 min, it was converted to 1-isomangostin (**3**) and 3-isomangostin (**4**). The greater complexity of the product mixture when hydrated *p*-toluenesulfonic acid and acetic acid are used, results from the involvement of water and acetic acid in product formation.

The compounds **4**, **7**, **8**, **11**, **14**, and **15**, assigned to the 3-isomangostin series, might instead have been formulated in terms of the alternative structure **2** for mangostin as derivatives of **16**. However, in the cases of **4** and **11**, such structures can immediately be eliminated since the n.m.r. spectra of these compounds show 2-proton doublets at δ 4.12 and 4.16, respectively. These are assignable to the $ArCH_2C{=}C$ protons of an isopentenyl side chain at C-8 but not at C-2, for the methylene groups must have an *ortho* relationship to the carbonyl groups (6), which exert an anisotropic deshielding effect upon them (6*b*). A similar conclusion can be reached with respect to compounds **7**, **8**, **14**, and **15**. Each of these, like **4** and **11**, shows in its n.m.r. spectrum two 2-proton triplets at δ 1.7–1.85 and 2.7–2.75 with $J = 7$ Hz, which can be assigned to the two pairs of methylene protons of the dihydropyran ring on the basis of their splitting pattern (6*a*, 7). The position of the lower field triplet, assignable to the $ArCH_2$ protons, shows that this ring must be derived from the side chain at C-2 (7); were the ring formed from the side chain at C-8, the adjacent carbonyl group would be expected to shift the $ArCH_2$ proton signal to ca. δ 3.5 (6*a*) due to the anisotropic effect referred to above. Each of the compounds **7**, **8**, **14**, and **15**, but not **4** or **11**, shows in its spectrum a 2-proton multiplet at δ 3.4–3.8; this is assigned to the $ArCH_2$ protons in the uncyclized side chain;

the circumstance that this appears as a multiplet rather than a triplet is attributed to restricted rotation of the chain. The adjacent methylene protons, $ArCH_2CH_2CX(CH_3)_2$, give rise to a multiplet that appears in the δ 1.6–2.4 region. The position of the $ArCH_2$ proton signals confirms that the uncyclized side chain is adjacent to the carbonyl group at C-8, as in the structures assigned.

The failure to observe any products of type **16** in which the side chain at C-8 has undergone cyclization to give a dihydropyran ring, or any products in which both side chains of mangostin have undergone cyclization, i.e., compounds in the 1-isonormangostin (**17**) or 3-isonormangostin (**18**) series (2, 5), provides strong evidence that there is not a hydroxyl group at C-7.[1] This argument is particularly cogent with respect to the absence of a product in the 1-isonormangostin series, for closure at the *chelated* hydroxyl group at C-1 could hardly occur without concomitant closure at an *unchelated* hydroxyl group at C-7. Thus this position must be the site of the methoxyl group in mangostin, as originally proposed (1, 2).



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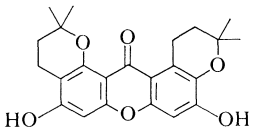

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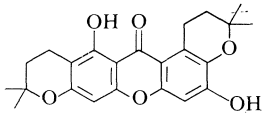

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Experimental

Melting points were recorded in capillary tubes and are uncorrected. Chromatography was carried out on silica plates (1.25 mm thickness) containing a phosphor, unless otherwise specified.

*Cyclization of Mangostin (**1**) with Hydrated p-Toluenesulfonic Acid in Acetic Acid. Formation of Compounds **3–8***

A mixture of mangostin (1.00 g), *p*-toluenesulfonic acid hydrate (3.00 g), and acetic acid (50 ml) was stirred at room temperature for 24 h. The pale yellowish green solution was diluted with ethyl acetate, washed repeatedly with aqueous sodium bicarbonate, and dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residual orange gum was dissolved in a small amount of acetone. The colorless crystalline material that separated in 2 h was collected and recrystallized from acetone to give compound **5** (80 mg), m.p. 261–263° (decomp.); λ_{max}(Nujol) 3.00, 6.20, and 6.35 μ; *m/e* 428; no color with ethanolic ferric chloride.

Anal. Calcd. for $C_{24}H_{28}O_7$: C, 67.27; H, 6.59. Found: C, 66.94; H, 6.60.

The mixture from the original acetone mother liquor was chromatographed on 10 plates with ethyl acetate – benzene (1:1 v/v) as eluent. The bands revealed by u.v. radiation had the following approximate R_f values: 0.4, 0.5, 0.7, and 0.9. The material from the band with R_f 0.4 was extracted with ethyl acetate and crystallized from this solvent to give compound **7** as lemon-yellow crystals (80 mg), m.p. 182–183° (decomp.); λ_{max}($CHCl_3$) 2.90, 3.20 (br), 6.10, and 6.30 μ; δ(CD_3COCD_3) 1.29 (s, 6 H), 1.35 (s, 6 H), 1.85 (t, J = 7 Hz, superimposed on m; 4 H), 2.68 (t, J = 7 Hz, 2 H), 3.5 (m, 2 H), 3.85 (s, 3 H), 6.21 (s, 1 H), and 6.84 (s, 1 H); δ(C_5D_5N/$CDCl_3$) 13.96 (s, 1 H); *m/e* 428; olive-green color with ethanolic ferric chloride.

Anal. Calcd. for $C_{24}H_{28}O_7$: C, 67.27; H, 6.59. Found: C, 67.26; H, 6.52.

The material from the band with R_f 0.5 was extracted with ethyl acetate to give a colorless crystalline product (50 mg), which was crystallized from acetone to give compound **6** as colorless crystals, m.p. 237–239° (decomp.); λ(Nujol) 3.30, 5.90, 6.20, and 6.35 μ; δ(CD_3OD) 1.40 (s, 6 H), 1.58 (s, 6 H), 1.82 (t, $J \sim 7$ Hz), 1.9 (m), 2.02 (s, 3 H), 2.66 (t, $J \sim 7$ Hz, 2 H), 3.8 (m), 3.81 (s, 3 H), 6.33 (s, 1 H), and 6.71 (s, 1 H); δ(C_5D_5N) 1.40 (s, 6 H), 1.70 (s superimposed on m; 8 H), 2.05 (s, 3 H), 2.2 (m, 2 H), 2.88 (t, J = 7 Hz, 2 H), 3.7 (m, 2 H), 3.93 (s, 3 H), 6.65 (s, 1 H), and 6.97 (s, 1 H); *m/e* 470; no color with ethanolic ferric chloride.

Anal. Calcd. for $C_{26}H_{30}O_8$: C, 66.37; H, 6.43. Found: C, 66.63; H, 6.63.

The material from the band with R_f 0.7 appeared to be a mixture and was re-chromatographed with ethyl acetate – benzene (1:7 v/v) as eluent. It was separated into 2 bands, of which the faster moving was extracted with ethyl acetate to provide a pale yellow crystalline product (60 mg) which was crystallized from ethyl acetate – ether to give compound **8** as pale yellow crystals, m.p. 188–189° (decomp.); λ_{max}($CHCl_3$) 2.90, 5.80, 6.05, 6.20, and 6.30 μ; δ(C_5D_5N) 1.27 (s, 6 H), 1.70 (s superimposed on m; 8 H), 2.04 (s, 3 H), 2.3 (m, 2 H), 2.73 (t, $J \sim 7$ Hz, 2 H), 3.65 (m, 2 H), 6.42 (s, 1 H), 7.07 (s, 1 H), and 14.43 (s, 1 H); *m/e* 470; olive-green color with ferric chloride.

Anal. Calcd. for $C_{26}H_{30}O_8$: C, 66.37; H, 6.43. Found: C, 66.31; H, 6.38.

The material from the slower-moving band from the re-chromatography was extracted with ethyl acetate and crystallized from benzene to give 1-isomangostin (**3**) as colorless crystals, m.p. 241–243° (decomp.) with initial melting at 154–155° and resolidification at 180°; λ_{max} (Nujol) 2.9, 3.20, 6.20, and 6.35 μ; δ(DMSO-d_6) 1.31

[1]Although the weight balance in the cyclization with hydrated *p*-toluenesulfonic acid was poor, and that with anhydrous *p*-toluenesulfonic acid was only 73%, the remainder of the product mixture in each case had an R_f value of zero and therefore could contain no compounds in the **16–18** series.

(s, 6 H), 3.62 (d, J = 1 Hz, 3 H), 3.77 (d, J = 1 Hz, superimposed on m; 5 H), 3.68 (s, 3 H), 3.98 (br d, J = 7 Hz, 2 H), 5.2 (m, 1 H), 6.35 (s, 1 H), 6.72 (s, 1 H), 10.45 (s, 1 H), and 10.54 (s, 1 H) (signals due to solvent at 2.5 (DMSO-d_5) and 3.35 (H_2O)); *m/e* 410; no color with ethanolic ferric chloride. An analytical sample heated at 80° *in vacuo* over P_2O_5 exhibited the same double melting point.

Anal. Calcd. for $C_{24}H_{26}O_6 \cdot \frac{1}{4}H_2O$: C, 69.46; H, 6.44. Found: C, 69.72; H, 6.50.

An analytical sample heated at 180° *in vacuo* over P_2O_5 had a single m.p. 241–243° (decomp.); its infrared (i.r.) spectrum (Nujol mull) was similar to that of the sample heated at 80°, but had weaker absorption in the 2.9 μ region; its n.m.r. spectrum (DMSO-d_6 containing H_2O (*vide supra*)) was closely similar to that of the sample heated at 80°; *m/e* 410.

Anal. Calcd. for $C_{24}H_{26}O_6$: C, 70.23; H, 6.39. Found: C, 70.30; H, 6.52.

The material from the band with R_f 0.9 in the original chromatogram was extracted with ethyl acetate to give an orange gum (100 mg) which was crystallized from petroleum ether (b.p. 70–80°) to give 3-isomangostin (**4**) as pale yellow needles, m.p. 154–155° (decomp.); λ_{max}(Nujol) 3.10, 6.15, 6.25, and 6.35 μ; δ($CDCl_3$) 1.35 (s, 6 H), 1.68 (d, $J \sim$ 1 Hz, 3 H), 1.82 (s superimposed on t, $J \sim$ 7 Hz, 5 H), 2.72 (t, J = 7 Hz, 2 H), 3.80 (s, 3 H), 4.12 (d, $J \sim$ 6 Hz, 2 H), 5.31 (m, 1 H), 6.26 (s, 1 H), 6.32 (br s, 1 H), 6.85 (s, 1 H), and 13.79 (s, 1 H); *m/e* 410; olive-green color with ethanolic ferric chloride.

Anal. Calcd. for $C_{24}H_{26}O_6$: C, 70.23; H, 6.39. Found: C, 70.05; H, 6.37.

*Cyclization of Mangostin (**1**) with Anhydrous p-Toluenesulfonic Acid in Benzene. Formation of **3** and **4***

p-Toluenesulfonic acid (125 mg) was treated with benzene (125 ml), and 35 ml of the latter were distilled to remove water. Mangostin (1.00 g) was added, and the mixture was boiled under gentle reflux for 30 min. The solution was cooled, diluted with ethyl acetate, washed twice with water, and dried over anhydrous sodium sulfate. Removal of the benzene gave a deep orange gum which was chromatographed on 10 plates with ethyl acetate – benzene (1:7 v/v) as eluent. The material from the faster-moving, major band (R_f 0.5) was extracted with ethyl acetate. The extract was stripped of solvent and the residue was crystallized from petroleum ether (b.p. 60–80°) to give 3-isomangostin (**4**) as pale yellow fluffy needles (582 mg), m.p. 154–155° (decomp.), shown by mixed m.p. and i.r. spectral comparison to be identical with the sample obtained from cyclization in acetic acid.

The material from the slower-moving band was extracted with ethyl acetate and crystallized from benzene to give 1-isomangostin (**3**), (146 mg) m.p. 241–243° (decomp.) with initial melting at 154–155° and resolidification at 180°, shown by mixed m.p. and i.r. spectral comparison to be identical with the sample obtained from cyclization in acetic acid.

*Methylation of 1-Isomangostin (**3**). Formation of Dimethyl-1-isomangostin (**9**)*

A solution of 1-isomangostin (**3**), m.p. 155° and 241–243°, (200 mg) in acetone (20 ml) was treated with potassium carbonate (200 mg) and dimethyl sulfate (1.0 ml), and the mixture was boiled under reflux for 5 h. It was then filtered and the filtrate was stripped of solvent. The residue was left in contact with water for 12 h and then extracted with ether. The ethereal extract was washed with water, dried, and stripped of solvent. The residue was crystallized from cyclohexane – petroleum ether to give dimethyl-1-isomangostin (**9**), m.p. 128–129°, shown by mixed m.p. and i.r. spectral comparison to be identical with a sample of **9** prepared by acid-catalyzed cyclization of dimethylmangostin (**10**) (5).

The same product was obtained on similar methylation of 1-isomangostin, m.p. 241–243°.

*Methylation of 3-Isomangostin (**4**). Formation of Methyl-3-isomangostin (**11**)*

A solution of 3-isomangostin (**4**) (100 mg) in ether (10 ml) was treated with excess ethereal diazomethane. After 24 h the solution was filtered and stripped of solvent; the residue was crystallized from ethanol to give methyl-3-isomangostin (**11**) (80 mg), m.p. 138–139°; λ_{max}(Nujol) 6.10, 6.30, and 6.35 μ; δ($CDCl_3$) 1.36 (s, 6 H), 1.67 (d, $J \sim$ 1 Hz, 3 H), 1.84 (s superimposed on t, $J \sim$ 7 Hz; 5 H), 2.72 (t, J = 7 Hz, 2 H), 3.79 (s, 3 H), 3.95 (s, 3 H), 4.16 (d, J = 7 Hz, 2 H), 5.29 (m, 1 H), 6.26 (s, 1 H), 6.77 (s, 1 H), and 13.84 (s, 1 H); *m/e* 424; olive-green color with ethanolic ferric chloride.

Anal. Calcd. for $C_{25}H_{28}O_6$: C, 70.74; H, 6.65. Found: C, 70.72; H, 6.64.

Methylation of **4** with dimethyl sulfate in acetone at reflux also gave the monomethyl ether **11**.

*Methylation of **5**. Formation of **12***

A solution of **5** (20 mg) in methanol (3 ml) was treated with excess ethereal diazomethane as before. Crystallization of the product from methanol gave colorless crystals of **12**, m.p. 201–203°. This was shown by mixed m.p. and i.r. spectral comparison to be identical with a sample of **12** prepared by reaction of dimethylmangostin (**10**) with formic acid followed by basic hydrolysis (2, 5).

*Reaction of 1-Isomangostin (**3**) with Hydrated p-Toluenesulfonic Acid in Acetic Acid. Formation of **5***

A solution of 1-isomangostin (**3**) (50 mg) and *p*-toluenesulfonic acid hydrate (150 mg) in acetic acid (0.3 ml) was kept at room temperature for 36 h. The resulting pale yellow crystalline mass was treated with aqueous sodium bicarbonate, and the mixture was extracted with ethyl acetate. The extract was washed with water, dried over anhydrous sodium sulfate, and stripped of solvent. The residue was crystallized from acetone to give **5** (30 mg), m.p. 262–263° (decomp.); this was shown by mixed m.p. and i.r. spectral comparison to be identical with the sample obtained directly from mangostin.

*Methylation of **6**. Formation of **13***

A solution of **6** (10 mg) in methanol (2 ml) was treated with excess ethereal diazomethane as above. Crystallization of the product from ethanol gave colorless crystals of **13**, m.p. 132–133°; λ_{max}(Nujol) 5.80, 6.05, and 6.30 μ; δ($CDCl_3$) 1.41 (s, 6 H), 1.60 (s, 6 H), 1.83 (t, J = 7 Hz, superimposed on m; 4 H), 2.04 (s, 3 H), 2.64 (t, J = 7 Hz, 2 H), 3.45 (m, 2 H), 3.83 (s, 3 H), 3.88 (s, 3 H), 3.92 (s, 3 H), 6.35 (s, 1 H), and 6.71 (s, 1 H); *m/e* 438 ($M - C_2H_4O_2$).

Anal. Calcd. for $C_{28}H_{34}O_8$: C, 67.45; H, 6.87. Found: C, 67.55; H, 6.62.

*Reaction of Dimethyl-1-isomangostin (**9**) with Anhydrous p-Toluenesulfonic Acid in Acetic Acid. Formation of **13***

p-Toluenesulfonic acid (300 mg) was treated with benzene (20 ml), and the benzene was distilled to remove water. Acetic acid (5 ml) and dimethyl-1-isomangostin (**9**) (50 mg) were added, and the solution was kept at room temperature for 24 h. It was then diluted with ethyl acetate, washed with aqueous sodium bicarbonate, dried over anhydrous sodium sulfate, and stripped of solvent. The residue was chromatographed on 3 Eastman chromatogram sheets (silica gel) with ethyl acetate – benzene (1:3 v/v) as eluent. The material from the band below that of unconsumed starting material was extracted with ethyl acetate and crystallized from methanol to give **13**, m.p. 132–133°; this was shown by mixed m.p. and i.r. spectral comparison to be identical with the sample obtained by methylation of **6**.

*Methylation of **7**. Formation of **14***

A solution of **7** (200 mg) in acetone (30 ml) was treated with potassium carbonate (1.0 g) and dimethyl sulfate (0.2 ml), and the mixture was boiled under reflux for 6 h. It was then filtered, and the filtrate was stripped of solvent. The residue was chromatographed on 2 plates with ethyl acetate – benzene (1:3 v/v) as eluent. The material from the major band was extracted with ethyl acetate and crystallized from acetone – petroleum ether to give **14** as long yellow needles, m.p. 151–153°; λ_{max}(Nujol) 2.95, 6.10, 6.25, and 6.35 μ; δ($CDCl_3$) 1.32 (s, 6 H), 1.39 (s, 6 H), 1.77 (t, $J \sim 7$ Hz, superimposed on m; 4 H), 2.70 (t, $J = 7$ Hz; 2 H), 3.5 (m, 2 H), 3.81 (s, 3 H), 3.87 (s, 3 H), 6.28 (s, 1 H), 6.72 (s, 1 H), and 13.86 (s, 1 H).

Anal. Calcd. for $C_{25}H_{30}O_7$: C, 67.85; H, 6.83. Found: C, 68.06; H, 6.91.

*Methylation of **8**. Formation of **15***

A solution of **8** (80 mg) in ether (10 ml) was treated with excess ethereal diazomethane as before. The product was chromatographed on one plate with ethyl acetate – benzene (1:8 v/v) as eluent. The material from the major band was extracted with ethyl acetate and crystallized from petroleum ether (b.p. 60–80°) to give **15**, m.p. 148–149° (decomp.); λ_{max}(Nujol) 5.80, 6.05, and 6.20 μ; δ($CDCl_3$) 1.36 (s, 6 H), 1.58 (s, 6 H), 1.83 (t, $J = 7$ Hz, 2 H), 2.02 (s superimposed on m; 5 H), 2.72 (t, $J = 7$ Hz, 2 H), 3.5 (m, 2 H), 3.84 (s, 3 H), 3.94 (s, 3 H), 6.25 (s, 1 H), 6.74 (s, 1 H), and 13.9 (br s, 1 H); δ(CD_3COCD_3) 1.35 (s, 6 H), 1.55 (s, 6 H), 1.85 (t, $J = 7$ Hz, 2 H), 1.96 (s, 3 H), 2.68 (t, $J = 7$ Hz, 2 H), 3.45 (m), 3.82 (s, 3 H), 4.02 (s, 3 H), 6.20 (s, 1 H), and 6.93 (s, 1 H); *m/e* 484.

Anal. Calcd. for $C_{27}H_{32}O_8$: C, 66.92; H, 6.66. Found: C, 66.93; H, 6.86.

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