period concentrated hydrochloric acid was added at a rate of 25 ml per hour. After cooling the reaction mixture was diluted with water and extracted with benzene. The benzene solution was washed with water, dried (Na_2SO_4), and concentrated *in vacuo*. Recrystallization of the residual solid from aqueous ethanol gave 17 g of **13** (60%) melting at 49.0–49.5° (reported (8) m.p. 49.1–49.3°); i.r.(Nujol): 3100, 1650, 990, 910 (—CH=CH_2), 3600–2400, 1720–1700 cm^{-1} (COOH); n.m.r.: δ 6.0–5.4 m (1H), 5.2–4.7 m (2H), 2.5–1.1 m (24H).

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Structure of β-mangostin

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β-Mangostin, a minor coloring matter of the dried latex of *Garcinia mangostana*, is shown to be 1,6-dihydroxy-3,7-dimethoxy-2,8-di-(3-methyl-2-butenyl)xanthone (**4**).

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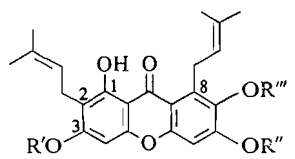
The fruit hulls, bark, and dried latex of *Garcinia mangostana* contain the yellow coloring matter mangostin, $C_{24}H_{26}O_6$, m.p. 182–183°, which has been shown to have structure **1** (1, 2). The dried latex is a particularly rich source, yielding 30–50% of mangostin (1, 3). During the course of the original work on the isolation of mangostin from the dried latex, Dragendorff (3) also isolated a minor yellow coloring matter (2%), m.p. 175.5°, which he named β-mangostin. This was considered to be isomeric with mangostin on the basis of elemental analytical data. On treatment with diazomethane it was found to give a methylation product identical with that obtained by similar treatment of mangostin, which is now known to be dimethylmangostin **2** (1). β-Mangostin was therefore considered to differ from mangostin only in respect to the interchange of a methoxyl and a hydroxyl group.



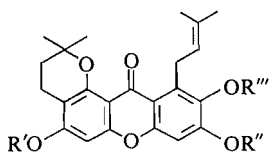
1 R′ = R″ = H; R‴ = CH_3
2 R′ = R″ = R‴ = CH_3
3 R′ = R″ = CH_3; R‴ = H
4 R′ = R‴ = CH_3; R″ = H
5 R′ = H; R″ = R‴ = CH_3

We have isolated from crude mangostin obtained from the dried latex (1) a minor constituent, m.p. 175–176°, which is considered to be the β-mangostin of Dragendorff. On the basis of mass spectral and elemental analytical data we assign to it the formula, $C_{25}H_{28}O_6$, a formulation which is in accord also with Dragendorff's elemental analytical data. Its formula thus differs from that of mangostin by a CH_2 unit.

We have confirmed that it can be converted by methylation to dimethylmangostin **2**; in the present instance this methylation was effected by treatment with dimethyl sulfate and potassium carbonate in acetone. These data require that β-mangostin have one of the structures **3**–**5**.

This conclusion is corroborated by spectroscopic data (see Experimental). Its infrared and ultraviolet spectra show the characteristic features of a xanthone with a free hydroxyl group at C-1 (1, 4). Its nuclear magnetic resonance spectrum resembles that of mangostin, but differs from it in showing two methoxyl proton signals instead of one.

Treatment of β-mangostin with anhydrous *p*-toluenesulfonic acid in boiling benzene for 30 min gave a single isomeric product, m.p. 281–282°, in low yield and led to the recovery of most of the starting material; longer heating resulted in an increased yield of the isomer. Methylation of the isomer with dimethyl sulfate and potassium carbonate in acetone gave a monomethyl derivative shown to be identical to **6**, the dimethyl derivative of 1-isomangostin (**7**) (2). The exclusive formation of a 1-isomangostin derivative here stands in contrast to the case of



6 R′ = R″ = R‴ = CH_3
7 R′ = R″ = H; R‴ = CH_3
8 R′ = R‴ = CH_3; R″ = H

mangostin, where both 1- and 3-isomangostin derivatives are formed under similar conditions (2), corresponding to chroman ring formation involving attack of the free hydroxyl groups at C-1 and C-3 on the isopentenyl side chain at C-2. The exclusive formation of a 1-isomangostin derivative in the case of β-mangostin demonstrates that the C-3 substituent must be a methoxyl rather than a hydroxyl group. Further, the failure to observe the formation of any product in which the isopentenyl side chain at C-8 has undergone chroman ring formation demonstrates that the C-7 substituent must also be a methoxyl rather than a hydroxyl group. It follows that the structure of β-mangostin is **4** and that its isomerization product has structure **8**.[1]

Experimental

β-Mangostin (4)

Crude mangostin (25 g), isolated from the dried latex of *Garcinia mangostana* (1), was extracted in a Soxhlet apparatus with petroleum ether (b.p. 60–70°) for 5 days. The extract was allowed to stand at room temperature for 4 days, and the mangostin that crystallized was removed by filtration. The pale-yellow filtrate was stripped of solvent under reduced pressure, and the residue was crystallized from ethanol to give β-mangostin (0.12 g) as small lemon-yellow rods, m.p. 175–176° [lit. (3) m.p. 175.5°]; λ_{max} (CCl_4) 2.90, 3.5 (br), 6.07, 6.24 μ; λ_{max} (EtOH) (log ε) 245 (4.55), 258 (4.45), 317 (4.30), 356 mμ (4.10); δ ($CDCl_3$) 1.66 (6H), 1.78 and 1.80 (6H), 3.32 (2H, d, J = 7 Hz), 3.76 (3H, s), 3.84 (3H, s), 4.05 (2H d, $J \sim 7$ Hz), 5.20 (2H, m), 6.24 (1H, s), 6.37 (1H, br), 6.74 (1H, s), 13.38 (1H, s).

Anal. Calcd. for $C_{25}H_{28}O_6$: C, 70.74; H, 6.65. Found: C, 70.87; H, 6.67.

Methylation of β-Mangostin. Formation of Dimethylmangostin (2)

A solution of β-mangostin (15 mg) and dimethyl sulfate (0.05 ml) in acetone (8 ml) was boiled under reflux in the presence of anhydrous potassium carbonate (100 mg) for 6 h. The mixture was filtered, the filtrate was evaporated, and the residue was treated with water (10 ml); after 24 h the mixture was extracted with ether. The ethereal extract was washed with water, dried, and stripped of solvent. The residue was crystallized from ethanol to give dimethylmangostin (**2**), m.p. 123–124° [lit. (1) m.p. 123.3–123.8°], undepressed on admixture with an authentic sample (1); the infrared spectra of the two samples were superimposable.

Acid-catalyzed Cyclization of β-Mangostin. Formation of 8

p-Toluenesulfonic acid (12 mg) was dissolved in benzene (20 ml), 10 ml of the benzene was distilled, and β-mangostin (102 mg) was added. The solution was boiled under reflux for 30 min, diluted with ethyl acetate, washed with water, dried, and stripped of solvent. The residue was crystallized from acetone – petroleum ether to give colorless crystals (6 mg) of **8**, m.p. 281–282°. The mother liquor was stripped of solvent and the residue was recrystallized from ethanol to give unconsumed β-mangostin (70 mg), m.p. 175–176°.

Treatment of β-mangostin (45 mg) with *p*-toluenesulfonic acid (20 mg) in boiling benzene (7 ml) for 3 h and work-up as before gave a higher yield (20 mg) of **8**,

[1]The possibility that β-mangostin possesses a free C-3 or C-7 hydroxyl group, but preferential closure occurs at the C-1 hydroxyl group can clearly be excluded. Reaction of the chelated hydroxyl group at C-1 would be *slower* than that of unchelated hydroxyl groups at C-3 or C-7, as exemplified by the observation that the rates of conversion of β-mangostin and dimethylmangostin to cyclized products are considerably slower than the overall rate of cyclization of mangostin and that preferential cyclization at the C-3 hydroxyl group occurs in the case of mangostin.

m.p. 281–282°; λ_{max} (Nujol) 3.03, 6.06, 6.20 (sh), 6.24 μ; λ_{max} (EtOH) (log ε) 244 (4.53), 253 (sh, 4.47), 305 (4.32), 334 mμ (3.95).

Anal. Calcd. for $C_{25}H_{28}O_6$: C, 70.74, H, 6.82. Found: C, 70.48; H, 6.82.

Thin-layer chromatography of the crude reaction products failed to reveal the presence of any isomer of β-mangostin other than **8**.

*Methylation of **8**. Formation of Dimethyl-1-isomangostin (**6**)*

Compound **8** (6 mg) was methylated in acetone with dimethyl sulfate and potassium carbonate and the reaction mixture was worked up as in the methylation of β-mangostin above. The crude product was crystallized from cyclohexane to give dimethyl-1-isomangostin (**6**), m.p. 127–128°, undepressed on admixture with an authentic sample, m.p. 127–128° (2, 4): the infrared spectra of the two samples were superimposable.

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