mina used in chromatography was Woelm, neutral, Brockmann activity grade 1, except as noted; silica gel used in chromatography was Merck "H."

Isolation of 1-Methyl 2,3-Dibutyl Hemimellitate.—Dried and granulated *Viburnum prunifolium* stem bark (50 kg) was extracted with distilled water in an Eppenbach stirrer. The aqueous filtrate was extracted with CH_2Cl_2 to yield 61.5 g (0.12%) of aromatic viscous oil. This product was processed in 2.5-g fractions. They were dissolved in 100 ml of MeOH, cooled to 5°, and centrifuged for 15 min to precipitate the waxes. The MeOH was filtered and evaporated to yield 2 g of oil which was chromatographed sequentially. The column materials, quantities, and eluting solvent mixtures were as follows: alumina, 5 g, $CHCl_3$; silicic acid, 5 g, $CHCl_3$; Florisil®, 5 g, ethyl ether; Woelm alumina (cationotropic, activity grade I), 5 g, ethyl ether; silica gel (Merck, "H"), 5 g, petroleum ether (bp 30–60°). Purity of material processed in this fashion was established by tlc on silica gel "H" using petroleum ether–ethyl ether (85:15), R_f 0.39. Vacuum distillation of the total product gave 7 g (0.01%) of 1-methyl 2,3-dibutyl hemimellitate: bp 150–152°; $n^{10}D$ 1.4959.

Anal. Calcd for $C_{18}H_{24}O_6$: C, 64.27; H, 7.19. Found: C, 64.68; H, 6.80.

Transesterification of Tributyl Hemimellitate and Trimethyl Hemimellitate.—The hemimellitate ester (100 mg) was mixed with 5 cc of the appropriate alcohol containing 0.1 cc of concentrated H_2SO_4. The solution was heated on a water bath for 12 hr, the solvent evaporated at room temperature, and the crude product washed with water to remove the catalyst. After drying, the product was submitted to preparative glpc using an Autoprep Model 700 instrument with stream splitting and H_2 flame detection. Operating parameters were injector at 250°, column at 230°, and collector at 250°. The copper column was 5 ft × 0.25 in. of 60–80 mesh nonacid-washed Chromosorb W with 15% SE-30; N_2 delivery was at 12 psi. In each case the product mixture contained all possible products of transesterification and all related phthalates. Retention times of the methyl dibutyl hemimellitates relative to dimethyl phthalate were: 2-methyl 1,3-dibutyl hemimellitate, 7.87; and 1-methyl 2,3-dibutyl hemimellitate, 8.75.

Registry No.—1-Methyl 2,3-dibutyl hemimellitate, 21615-80-5.

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Calophyllum Products. V. A New 4-Phenylcoumarin from *Calophyllum australianum* FvM Vesq.[1]

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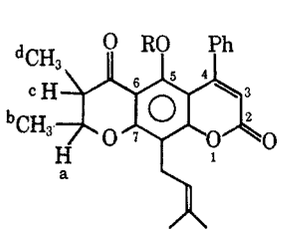
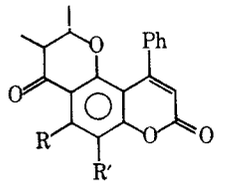
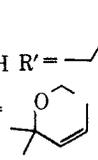
In the course of our studies of the resins of the Guttiferae, we have isolated in small yield a new 4-phenylcoumarin (**1**), $C_{25}H_{24}O_5$, from the dried bark of *Calophyllum australianum*. The nmr spectrum of **1** shows characteristic signals which may be assigned to a *trans*-2,3-dimethylchromanone ring,[1a] an isopentenyl chain,[1a] a chelated hydroxyl,[1a] and a monosubstituted phenyl group.[2,3] A 1 H singlet at τ 4.03 is consistent with the C-3 proton of a 4-substituted coumarin, and the frequent occurrence of such compounds among the products of *Calophyllum* and related genera supports this assignment.[2–6] The coumarin and *o*-hydroxychromanone systems produce the expected carbonyl bands at 5.82 and 6.08 μ. Oxygenation of the coumarin system is expected by analogy to occur at C-5 and C-7, and is confirmed by comparison of the uv spectrum of **1** (Table I) to those of a number of other 6-acyl-4-phenyl-5,7-dioxycoumarins.[7]



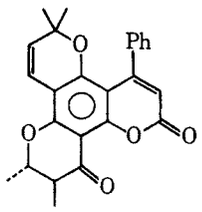
1, R = H
2, R = Me



3, R = OH R′ =



4, R, R′ =



5

TABLE I

	λ_{max}^{EtOH}, nm (ε)	
1	286 (26,100)	337 (8820)
Mammea A/AB[a]	283 (29,500)	333 (10,200)
Mammeisin[b]	281 (27,500)	338 (10,000)

[a] Reference 2. [b] Reference 6.

The presence of a chelated hydroxyl rules out 8-acyl structures and limits the possibilities to **1** and **3**. Nigam, Mitra, *et al.*,[4] have pointed out that in 4-phenylcoumarins bearing a 2,3-dimethylchromanone ring bridging C-5 and C-6, the nmr signals of the chromanone substituents show marked shifts from their normal values[1a,3–5] as a result of proximity to the phenyl ring. As is seen from Table II, our product does not show these shifts and may consequently be assigned structure **1**.

TABLE II

	a (1 H)	b (3 H)	c (1 H)	d (3 H)
Tomentolide A (**4**)[a]	τ 6.22	9.29	7.82	9.00
Inophyllolide (**5**)[b]	5.68	8.42	7.54	8.79
1	5.75	8.45	7.4	8.80

[a] Reference 4. [b] Reference 3.

(1) (a) Previous paper in this series: G. H. Stout, G. L. Hickernell, and K. D. Sears, *J. Org. Chem.*, **33**, 4191 (1968); (b) supported in part by Public Health Service Grant GM-12095 from the National Institute of General Medical Sciences.

(2) L. Crombie, D. E. Games, and A. McCormick, *Tetrahedron Lett.*, 145 (1966).

(3) K. Kawazu, H. Ohigashi, and T. Mitsui, *ibid.*, 2383 (1968).

(4) S. K. Nigam, C. R. Mitra, G. Kunesch, B. C. Das, and J. Polonsky, *ibid.*, 2633 (1967).

(5) G. H. Stout and K. L. Stevens, *J. Org. Chem.*, **29**, 3604 (1964).

(6) R. A. Finnegan, M. P. Morris, and C. Djerassi, *ibid.*, **26**, 1180 (1961).

(7) Structure **1** shows numbering based on a coumarin system.

Among the known 4-phenylcoumarins of the Guttiferae, **1** is most closely related to mammea A/AB,[2] in which the chromanone ring is opened by a formal reduction to a 2-methylbutyryl chain. It represents only a minor constituent of *C. australianum* resins, the majority of which consists of complex dienedione acids similar to those of *C. brasiliensis* and *C. inophyllum*.[3] Further studies on these products are in progress.

Experimental Section

Isolation of 1.—Finely ground bark (140 g) of *C. australianum* FvM Vesq., from Bamaga, Queensland, Australia, was extracted with hexane in a soxhlet for 20 hr. The green extract was washed with 5% Na_2CO_3 until the base extract remained colorless. The hexane was dried, filtered, and evaporated. The resulting brown oil was boiled briefly in MeOH and the precipitate (identified as friedelin) was filtered off. The filtrate was evaporated, the residue was taken up in hot hexane, and slow cooling yielded **1** as white, fluffy crystals. Recrystallization from CH_2Cl_2–hexane yielded 28 mg (0.02%), mp 190–192°. A sample sublimed [100° (10^{-4} Torr)] for analysis gave mp 192–193.5°: uv (see Table I); $\lambda_{max}^{EtOH-OH^-}$ 286, 315, 425 nm; ir 5.82, 6.08, 6.20 μ; nmr ($CDCl_3$) τ −2.8 (s, 1), 2.67 (br s, 5), 4.03 (s, 1), 4.75 (t, J = 7 Hz, 1), 5.75 (m, $J \sim 6$, 11 Hz, 1), 6.64 (d, J = 7 Hz, 2), 7.4 (m, 1), 8.15 (br s, 3), 8.32 (br s, 3), 8.45 (d, J = 6 Hz, 3), 8.80 (d, J = 6 Hz, 3).

Anal. Calcd for $C_{25}H_{24}O_5$: C, 74.24; H, 5.98; mol wt, 404.1624. Found: C, 74.53; H, 6.14; mol wt, 404.1623.

Methyl Ether of 1 (2).—Methylation of **1** (12.2 mg) with Me_2SO_4 (50 μl) and K_2CO_3 in refluxing acetone for 3 hr followed by preparative tlc and crystallization gave **2** (2.5 mg), mp 115–117°; uv (EtOH) 270 (24,000), 330 (10,930) nm, unchanged by added base.

Anal. Calcd for $C_{26}H_{26}O_5$: mol wt, 418.178. Found: mol wt, 418.176.

Registry No.—**1**, 21824-07-7; **2**, 21876-35-7.

Acknowledgment.—We are grateful to CSIRO, Melbourne, for supplying a sample of *C. australianum*.

(8) G. H. Stout, M. M. Krahn, and G. D. Breck, *Tetrahedron Lett.*, 3285 (1968).

Some Normal Additions of Aminobenzoic Acids to Nitro-Olefinic Sugars[1,2]

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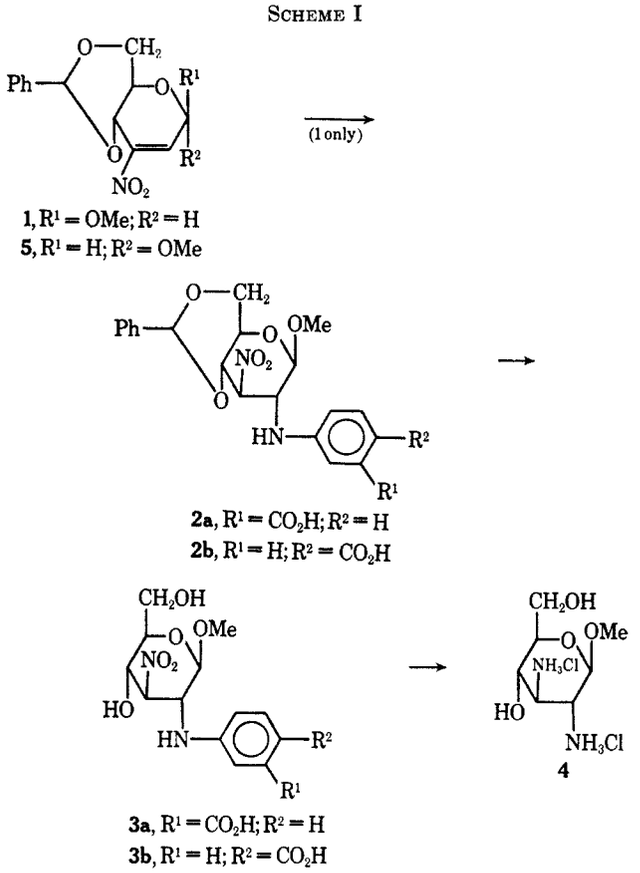
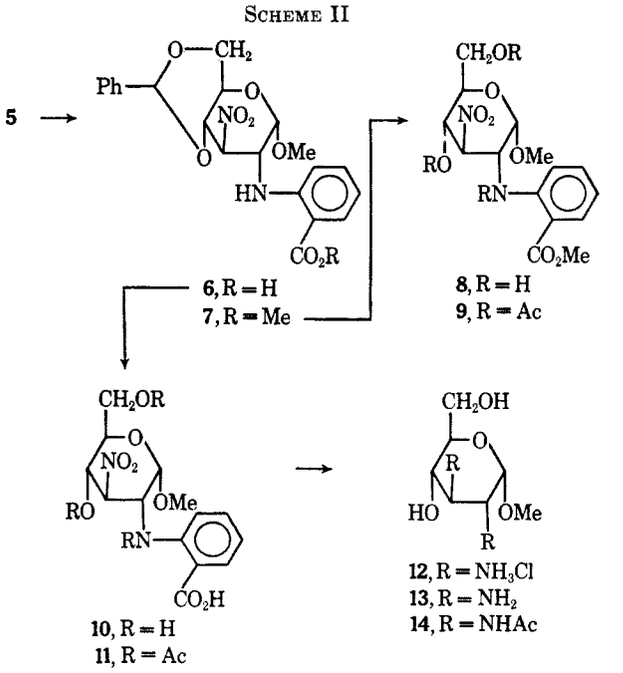
In the preceding article[1b] it was shown that nucleophilic addition of anthranilic acid to methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-β-D-*erythro*-hex-2-enopyranoside (**1**) gave the expected D-*gluco* adduct (2,3-diequatorial) when excess addend and a catalytic amount of potassium hydroxide were employed. However, with equimolar proportions of anthranilic acid and **1** and no catalyst, the D-*manno* adduct was obtained in 56% yield, as *yellow* crystals. We now report the addition of the two positional isomers (*m*- and *p*-aminobenzoic acid) of anthranilic acid to the nitro olefin **1**, and also the addition of anthranilic acid to the α anomer (**5**) of **1**.

The three addition reactions, together with subsequent conversions performed in order to establish the nature of the products, are depicted in Schemes I and II.

SCHEME I



SCHEME II



In each of the systems, only the D-*gluco* adduct was obtained, regardless of the reaction conditions, and no unusual color was observed. These results suggest

(1) (a) Part XV in a series on the reactions of nitro sugars. (b) For part XIV see H. H. Baer and F. Kienzle, *J. Org. Chem.*, **34**, 3848 (1969).

(2) From the Ph.D. Theses of F. K., 1968, and F. R., 1969. Support of this work by the National Research Council of Canada is gratefully acknowledged. F. R. thanks the Council, and F. K. thanks the Ogilvie Flour Mills Co., Ltd., for the award of postgraduate fellowships.