and cooled to yield 22.33 grams (84%) of pale yellow needles, m.p. 121° to 123.5° C. In another preparation, the filtered white solid was dried in vacuo before crystallizing from carbon tetrachloride. Recrystallization from carbon tetrachloride yielded the analytical sample: m.p. 123.5° to 125° C. Major infrared bands were at 1560, 1340, and 750 cm.$^{-1}$. Anal. Calcd. for $C_8H_6Br_2N_2O_4$: C, 27.14; H, 1.71; N, 7.92. Found: C, 26.89, 27.00; H, 2.07, 1.84; N, 7.97.

**Dipotassium *p*-bis(Dinitromethyl)benzene (VI).** A solution of *p*-bis(bromonitromethyl)benzene (1.77 grams, 5 mmoles) in 35 ml. of methanol was poured into a stirred solution prepared by dissolving potassium nitrite (2.04 grams, 24 mmoles, 20% excess) in 4 ml. of water and adding 15 ml. of methanol. An orange precipitate appeared from the initial orange solution in 30 seconds and the temperature rose rapidly from 26° to 30° C. Stirring was continued for 1 hour, during which time the temperature slowly fell to 26° C. The solid was filtered, washed with two 10-ml. portions of methanol, and dried in vacuo to give 1.06 grams (59%) of crude dipotassium *p*-bis(dinitromethyl)benzene. The salt was purified by dissolving in 70 ml. of water, filtering out insoluble solid employing filter aide (Celite), concentrating the resulting solution to 2.5 ml. under reduced pressure, adding 5 ml. of methanol, and filtering the resultant bright yellow solid, 0.80 gram. Major infrared bands were at 1450, 1180, 1110, and 1080 cm.$^{-1}$.

***p*-bis(Dinitromethyl)benzene (VII).** A 5-ml. aqueous solution containing 0.6 ml. of concentrated hydrochloric acid (37%, 6.1 mmoles) was added dropwise to a stirred 70-ml. aqueous solution of dipotassium *p*-bis(dinitromethyl)benzene (0.39 gram, 1.08 mmoles) at 0° C. The yellow-orange color of the solution faded as a pale yellow solid precipitated. The solid was filtered, washed with two 5-ml. portions of water, and dried in vacuo to yield 0.30 gram (97%), m.p. 122° to 122.5° C. Crystallization from chloroform followed by recrystallization from 1,2-dichloroethane yielded the analytical sample: m.p. 127.5° to 128° C. The major infrared band was at 1580 cm.$^{-1}$ Anal. Calcd. for $C_8H_6N_4O_8$: C, 33.57; H, 2.11; N, 19.58. Found: C, 33.24, 33.23, 33.54; H, 2.55, 2.41, 2.54; N, 19.54.

***p*-bis(Bromodinitromethyl)benzene (VIII).** A 5-ml. methanolic bromine solution (0.53 gram, 3.3 mmoles) was slowly poured into a stirred aqueous solution of dipotassium *p*-bis(dinitromethyl)benzene (0.41 gram, 1.13 mmoles) at 0° C. The yellow-orange color of the solution faded as a white solid precipitated. The solid was filtered, washed with two 5-ml. portions of water, and dried in vacuo to yield 0.50 gram (99%), m.p. 125° to 127° C. Two recrystallizations from carbon tetrachloride yielded the analytical sample: m.p. 130° to 131° C. The major infrared band was at 1580 cm.$^{-1}$. Anal. Calcd. for $C_8H_4Br_2N_4O_8$: C, 21.64; H, 0.91; N, 12.62. Found: C, 21.83, 21.77; H, 0.71, 0.89; N, 12.50.

***p*-bis(Fluorodinitromethyl)benzene (IX).** A slurry of 0.2 gram (0.00055 mole) of the dipotassium salt of *p*-bis(dinitromethyl)benzene and 15 ml. of acetonitrile was cooled to −8° C. and purged with dry nitrogen. Then a 3 to 1 $N_2$/$F_2$ gas mixture was bubbled through the reaction mixture at a rate of 60 cc. per minute for 30 minutes. The mixture was purged with nitrogen, allowed to warm to ambient temperature, and filtered free of the precipitated potassium fluoride. Concentration of the filtrate in vacuo yielded 0.17 gram (quantitative yield) of yellow solid. Recrystallization from isopropyl alcohol resulted in colorless plates with a melting point of 86° to 88° C. Anal. Calcd. for $C_8H_4F_2N_4O_8$: C, 29.80; H, 1.24; N, 17.40. Found: C, 29.86, 30.02; H, 1.26, 1.26; N, 17.44.


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# Convenient Synthesis of 6-Hydroxycoumarin


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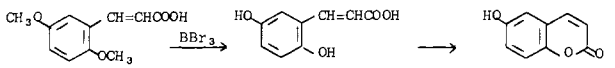
**6-Hydroxycoumarin was obtained in a 77% yield by treatment of 2,5-dimethoxycinnamic acid with boron tribromide in chloroform. The method is potentially useful for preparation of other hydroxylated coumarins.**


LARGE quantities of 6-hydroxycoumarin were prepared for biological evaluation. The method of Sastri *et al.* (*3*) was impractical for a large-scale synthesis. The procedure involved hydroxylation of 2-hydroxycinnamic acid with potassium persulfate in 35 to 40% yield, followed by treatment of the resulting 2,5-dihydroxycinnamic acid with mercuric chloride and hydrogen chloride. The resulting coumarin was purified by sublimation and obtained in approximately a 10% over-all yield.

The title compound can be prepared readily from commercially available 2,5-dimethoxycinnamic acid by treatment with boron tribromide. The reaction was conducted in chloroform solution with a two-fold excess of boron tribromide, and after 48 hours at room temperature, the coumarin

was cleanly obtained in a 77% yield. When the reaction was interrupted after 20 hours 2,5-dihydroxycinnamic acid was the major product, 89% yield, accompanied by a little 6-hydroxycoumarin. Excess boron trichloride failed to give any reaction with 2,5-dimethoxycinnamic acid under similar conditions. The use of hydrogen bromide in acetic acid alone gave only decarboxylation to polymeric material; when combined with mercuric chloride, no definable product was obtained.



The procedure may have broad utility for the synthesis of coumarins from both *o*-hydroxy- and *o*-methoxycinnamic acids, and would be especially valuable for the preparation of hydroxylated coumarins. Methoxycinnamic acids are in general more readily obtainable than the hydroxy acids, usually from the Dobner condensation of appropriate benzaldehydes with malonic acid.

## EXPERIMENTAL

**6-Hydroxycoumarin.** To an ice-cold solution of 26.7 grams (0.128 mole) of 2,5-dimethoxycinnamic acid (Research Organic Chemicals) in 1 liter of chloroform was added 100 grams (0.4 mole) of boron tribromide, dropwise, with stirring. The yellow solution underwent a series of color changes, eventually becoming orange-red. After one hour, the ice bath was removed and the mixture was allowed to stand for 48 hours at room temperature. The mixture was cooled in ice, and 500 ml. of ice water was added cautiously with stirring. After 30 minutes, the mixture was extracted with ethyl acetate. The organic extract was dried over magnesium sulfate and evaporated in vacuo. The solid residue was stirred with 150 ml. of 5% sodium bicarbonate for 2 hours. The product was collected, washed with water and ether, and dried to leave 16.0 grams (77%) of pale yellow crystals, m.p. 247–48° C.; lit. (*1*) m.p. 248–50° C. The infrared spectrum was identical with material prepared by the method of Sastri *et al.* (*3*).

**2,5-Dihydroxycinnamic Acid.** The reaction was conducted at twice the scale described above, but was worked up after 20 hours. After treatment with ice water, the resulting solid material was collected by filtration. The chloroform layer from the filtrate yielded only a trivial amount of 6-hydroxycoumarin. The filter cake was extracted with several portions of ethyl acetate, dried over magnesium sulfate, and evaporated in vacuo to leave 41.5 grams (89%) of 2,5-dihydroxycinnamic acid, m.p. 197–9° C.; lit. (*2*) m.p. 207° C.

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# Oxidation Reactions of Methyl 12,14-(2-Oxapropano)-abiet-8,9-enoate


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**Interesting new resin acid chemistry was developed from oxidation studies of recently reported resin acid derivatives. Methyl 12-α-hydroxymethylabiet-7,8-enoate in an acetic acid–sulfuric acid mixture was esterified and isomerized, giving methyl 12-α-acetoxymethylabiet-8,9-enoate. This was converted to the 7-keto enone by chromic acid oxidation. 7-Keto-12,14-(2-oxapropano)-abiet-8,9-enoate reported previously was converted with *m*-chloro perbenzoic acid to its -8,9-epoxides and to a 1,6-diketone and a 1,2-diol by ruthenium tetroxide oxidation of the 8,9 double bond. Characterization was achieved by infrared, ultraviolet, nuclear magnetic resonance, and mass spectra.**


AS PART of a program for the preparation of polyols from resin acids (*2*), methyl 12,14-(2-oxapropano)-abiet-8,9-enoate (**1**) was obtained by the reaction of formaldehyde with methyl 12α-hydroxymethylabiet-7,8-enoate (**2**) (*3*). The fundamental aspects concerning the stereochemistry and structure of **1** are reported elsewhere (*4*). The present paper describes some hitherto unpublished oxidation reactions of **1** and **3** which have produced valuable resin acid chemistry and may lead to potentially useful diterpene intermediates.

## EXPERIMENTAL SECTION

**Methyl 12-Acetoxymethylabiet-8,9-enoate (3).** Methyl 12-hydroxymethylabiet-7,8-enoate (20.8 grams) in glacial acetic acid (420 cc.), water (50 cc.), and concentrated sulfuric acid (35 cc.) was heated at 70° C. for 2 hours. Addition to water, ether extraction, washing with aqueous $NaHCO_3$ and water until neutral, concentration, and distillation gave methyl 12-acetoxymethylabiet-8,9-enoate, b.p. 218–20° C./1.5 mm. (20 grams, 85%), NMR signal at 0.75, 0.86 (isopropyl, J = 6.5 c.p.s.), 0.97 (C-10 Me), 1.15 (C-4 Me), 1.96 (acetate Me), and 3.56 (ester Me). Chemical shift for C-10 Me given in an earlier paper (*2*) is in error.

**Chromic Acid Oxidation of Methyl 12-Acetoxymethylabiet-8,9-enoate (3).** A mixture of methyl 12-acetoxymethylabiet-8,9-enoate (10 grams) in 85% acetic acid (150 cc.) and chromic acid (2.6 grams) was stirred at 50° C. for 30 minutes. Addition of methanol (50 cc.) followed by addition to water, ether extraction, and washing with aqueous $NaHCO_3$ and water gave the crude ene-one (12.0 grams), $\lambda_{max}$ 248 mμ; g.l.p.c. (a 6-foot × ⅛-inch column of OV-1 5%, $T$ = 250° C.)

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