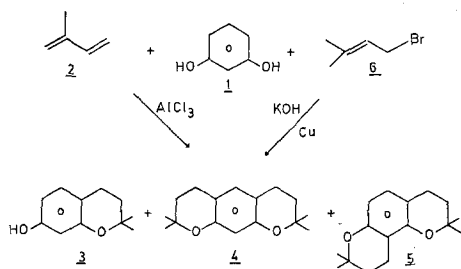


## Reaction of Resorcinol with Isoprene

In connection with our interest in the synthesis of *O*-heterocyclic natural products, we investigated the reaction of resorcinol with isoprene.

The condensation of resorcinol (**1**) with isoprene (**2**) in carbon disulfide and aluminium chloride afforded a brown oil. Fractional distillation gave two easily separable fractions. The first fraction, b.p. 140–145°C/0.2 mm Hg consisted of pure 7-hydroxy-2,2-dimethylchroman (**3**) as identified by IR and NMR. Compound **3** was previously prepared by Clemmensen reduction of 7-hydroxy-2,2-dimethylchroman-4-one<sup>1</sup> and by the condensation of resorcinol with 2-methyl-3-butene-2-ol in aqueous citric acid solution<sup>2</sup>.



The mass spectrum of **3** showed besides strong M<sup>+</sup> and M<sup>+</sup>-15, a base peak at *m/e* 123 resulting from a retro-Diels-Alder fragmentation accompanied by a hydrogen shift. Formation of the phenol **3** can be explained by the acid-catalysed cyclization of the intermediate 4- $\gamma$ ,  $\gamma$ -dimethylallylresorcinol.

The second fraction, b.p. 160–172°C/0.2 mm Hg was a mixture of 6,7-dihydro-2,2,8,8-tetramethyl-8H-[1]pyrano[3,2-g]chroman (**4**) and 9,10-dihydro-2,2,8,8-tetramethyl-8H-[1]pyrano[2,3-h]chroman (**5**), separated by GLC (SE-30). The chromans **4** and **5** were derived from the phenol **3** by further isoprenylation and cyclization.

A distinction between the linear **4** and the angular **5** dichromans could be made by NMR. The symmetric compound **4** showed one signal for both gem-dimethyl

groups and the aromatic protons appeared as two singlets. Compound **5** is asymmetric and exhibited different peaks for the gem-dimethyl groups, while the aromatic protons displayed a AB pattern.

Compound **4**:  $\nu_{\max}$  (NaCl) 1625, 1580, 1490 cm<sup>-1</sup> (aromatic);  $\delta$  (CCl<sub>4</sub>) 1.28 (12H, s, 4  $\times$  CH<sub>3</sub>); 1.70 (4H, t, J 7.0 cps, 2  $\times$  CH<sub>2</sub>); 2.62 (4H, t, J 7.0 cps, 2  $\times$  CH<sub>2</sub>); 6.01 (1H, s, Ar-H); 6.52 (1H, s, Ar-H). Compound **5**:  $\nu_{\max}$  (NaCl) 1615, 1590 and 1485 cm<sup>-1</sup> (aromatic);  $\delta$  (CCl<sub>4</sub>) 1.29 (6H, s, 2  $\times$  CH<sub>3</sub>); 1.31 (6H, s, 2  $\times$  CH<sub>3</sub>); 1.69 (2H, t, J 6.2 cps, CH<sub>2</sub>); 1.73 (2H, t, J 6.0 cps, CH<sub>2</sub>); 2.53 (2H, t, J 6.2 cps, CH<sub>2</sub>); 2.64 (2H, t, J 6.0 cps, CH<sub>2</sub>); 6.14 (1H, d, J 8.3 cps, Ar-H); 6.62 (1H, d, J 8.3 cps, Ar-H). The mass-spectrum of **5** exhibited simple breakdown patterns. A retro-Diels-Alder fragmentation with a hydrogen transfer occurred to give the base peak (*m/e* 191). The much less abundant fragment ion at *m/e* 190 may originate from a retro-Diels-Alder reaction, followed by expulsion of a methyl radical (*m/e* 175) and a retro-Diels-Alder fragmentation with a hydrogen shift (*m/e* 135).

The same compounds **3**, **4** and **5** were obtained by the reaction of resorcinol (**1**) with 1-bromo-3-methyl-2-butene (**6**) in aqueous potassium hydroxide solution and copper powder.

**Zusammenfassung.** Die Synthese von 7-Hydroxy-2,2-dimethylchroman, 6,7-Dihydro-2,2,8,8-tetramethyl-8H-[1]pyrano[3,2-g]chroman und 9,10-Dihydro-2,2,8,8-tetramethyl-8H-[1]pyrano[2,3-h]chroman aus Resorcin und Isopren oder 1-Bromo-3-methyl-2-buten wird beschrieben.

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## Robustaflavone – the First Member of a New Series of Biflavones

Naturally occurring flavanoids with the 6- and 8-positions carbon-carbon linked to a variety of substituents, viz. methyl,  $\gamma\gamma$ -dimethylallyl and glucosyl, are well known and constitute isomeric pairs. Surprisingly enough the interflavonyl linkage of biflavones is found to implicate only position -8 out of the above 2, except in naturally occurring hinokiflavone (Ia). The discoveries of cupressuflavone<sup>1</sup> (II) and agathisflavone<sup>2,3</sup> (IIIa) provided the first example of such a pair of naturally occurring isomers. In the present communication we wish to report the isolation and characterization of a new biflavone (IVa) as hexamethyl ether (IVb) which with amentoflavone (Va) constitutes the second example of such an isomeric pair of naturally occurring biflavones. The new biflavone (IVa) isolated from the leaf extract of *Agathis robusta* has been named as 'robustaflavone'. A monomethyl ether of IVa is also indicated (TLC).

The leaf extract of *Agathis robusta*, by the usual methods of purification, gave a biflavone mixture which separated by preparative layer chromatography (BPF)<sup>4</sup> into six

fractions labelled as AgI–AgVI. They were found to be chromatographically (TLC) identical with the 6 bands already reported in *A. palmerstonii*<sup>3</sup> and *A. alba*<sup>3,5</sup>. The fractions AgII and AgIV, although reported as consisting of single entities from the previously reported plants<sup>2,3,5</sup>, were found after methylation to be mixtures in the present case. Rf value considerations and characteristic fluorescence in UV-light<sup>4</sup> indicated each of them as mixtures of complete methyl ethers of agathisflavone (major) and a

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