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# SYNTHESIS OF (±) CIS
# 6a,12a-DIHYDRO-6H,7H-[1]-BENZOPYRANO-[4,3-b]-[1]-BENZOPYRAN

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Homoisoflavones (3-benzylchromones) constitute a new class of natural compounds which were not known until very recently (Tamm, 1972). They appear to be present in some members of the family of Liliaceae, having been so far isolated from different species of Eucomis[1] and from Scilla scilloides[2].
These compounds belong to the great family of flavonoids since according to Tamm they appear to be biogenetically related: a chalcone intermediate being their precursor[1,3].

Among flavonoids isoflavone is the parent compound of more complex isoflavonoids like pterocarpane, coumestane, the rotenoids etc.[3]; one could therefore suppose that homoisoflavone derivatives so far isolated might be the first examples of a more numerous group of natural products, the homoisoflavonoids.

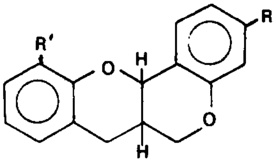
As a part of our continued interest in the synthesis of flavonoids and related compounds, we wish to describe here the preparation of (±) cis 6a,12a-dihydro-6H,7H-[1]-benzopyrano-[4,3-b]-[1]-benzopyran (I), i.e. of an homoisoflavonoid which might be briefly indicated as homopterocarpane. This compound, as far as we know, does not appear to have been described yet, although its ring system is known since 1938. Pfeiffer and Bank[4] indeed by reaction of salycilaldehyde with chromanone isolated a chromenobenzopyrilium perchlorate (ring B of I, aromatic) and more recently Riboulleau et al.[5] reported a chromenocoumarin with the same carbon skeleton of I.

The homopterocarpane has been synthesized in four steps by condensation of chromanone with 2-benzyloxybenzaldehyde to give 3-(2-benzyloxy)-benzylidenechroman-4-one: its catalytic debenzylation followed by reduction ($NaBH_4$) afforded 3-(2-hydroxybenzyl)-chroman-4-ol which on boiling with 50% AcOH cyclized to I. The same method has been used to prepare the corresponding 3-(II) and 11-methoxy (III) derivatives. The structure of I is consistent with its mass spectrum which shows the molecular ion at m/e 238 and characteristic fragments at m/e 132 and

131, both attributable to benzopyrilium ions[6]. Furthermore the NMR spectrum, measured at 100 MHz, shows signals (δ values) at 5.09 for H(12a) (1H,d,J=2.9 Hz), 4.22 for H(6) (2H,d,J=7.1 Hz), 3.15 (1H,m) and 2.63 (1H,m) for H(7) and 2.57 for H(6a) (1H,m). The assignements were made on the basis of double resonance experiments.

The coupling constant value between H(6a) and H(12a) is consistent with the value given by Karplus for the *cis* configuration of vicinal protons[7]. Hence the last step of the synthesis seems to take place stereospecifically.

Table I



| Compound | R | R' | M.p. °C | $J_{6a,12a}$ |
|---|---|---|---|---|
| I | H | H | 91-92 | 2.9 |
| II | $OCH_3$ | H | 104-105 | 2.9 |
| III | H | $OCH_3$ | 81-84 | 2.9 |

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