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Constituents of Pine Heartwood

XXIV.* Investigations on Strobopinin, Cryptostrobin, and Two New Substances, Strobobanksin and Strobochrysin, from the Heartwood of *Pinus Strobus* L.

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In Part V of this series, the isolation of a new compound, strobopinin, from the heartwood of *Pinus strobus* was described by Erdman[1]. This compound was almost colourless, had m. p. 225—227°**, and was optically active, showing $[\alpha]_D^{20}$—61° (methanol). Its composition, $C_{16}H_{14}O_4$, corresponds to a C-methyl dihydroxyflavanone (methoxyl absent), and the presence of a C—C_6H_5 grouping was proved by the fact that benzoic acid was formed on oxidation with permanganate. Strobopinin has also been isolated by one of us[2] from the heartwood of *P. monticola.*

Later, a compound called cryptostrobin was also isolated from *P. strobus*[3]. It is an isomer of strobopinin, melting at 202—203° and having $[\alpha]_D^{20}$—33° (methanol). Both substances were found to contain one C—CH_3 group, but further investigations on their structures were not carried out.

Strobopinin and cryptostrobin are rather difficult to separate by crystallisation, but a fairly good separation is achieved on the paper chromatogram[4]. The R_F values in standard solvent are approximately 0.48 for cryptostrobin and 0.65 for strobopinin. Diazotised benzidine gives somewhat different colours with the two isomers, the cryptostrobin spot having a deeper colour (orange) than the strobopinin spot (yellow to orange yellow). Both substances give yellow colours when reduced with magnesium and hydrochloric acid.

Both strobopinin and cryptostrobin yield methylphloroglucinol on degradation with strong alkali. Sufficient quantities were not available to allow

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** All melting points uncorrected.

isolation of this phenol, but a micro method was worked out, involving boiling with 50 % potassium hydroxide and identification of the phenol by paper chromatography. A good separation of phloroglucinol and methylphloroglucinol is obtained, using ethyl ether as the solvent (R_F values about 0.5 and 0.7 respectively). By this method, very good chromatograms were obtained starting from 0.5 mg of each flavanone. The method can of course be extended to any hydroxylated flavone or flavanone, if the right solvent is chosen for the identification of the resulting phenol.

If either strobopinin or cryptostrobin is heated with dilute alkali, a mixture of both substances is obtained. This rearrangement was studied by the aid of paper chromatography, using a few milligrams of the flavanones. It is thus evident that strobopinin and cryptostrobin must be very intimately related, and on the basis of the experiments hitherto discussed, the most probable structures for the two substances would be 5,7-dihydroxy-6-methylflavanone (I) and 5,7-dihydroxy-8-methylflavanone (II). In alkaline solution, these two flavanones would be in equilibrium with the same chalkone (III) and could thus be converted into each other.

These structures have been confirmed by synthesis. By condensing methylphloroglucinol with cinnamoyl chloride as described by Fujise and Tatsuta for phloroglucinol [5], a mixture of cryptostrobin and strobopinin was obtained in low yield. From this mixture, pure *d,l*-strobopinin, m. p. 231—233°, could be isolated after filtering through a magnesium oxide column. (Pure *d,l*-cryptostrobin could not be isolated.)

With diazomethane, strobopinin and cryptostrobin yielded monomethyl ethers, m. p. 96—97° and 134—136° respectively in the crude state. Further methylation with dimethyl sulphate and potassium carbonate in acetone led in the case of strobopinin to an orange red product which was identified as 2′-hydroxy-3′-methyl-4′,6′-dimethoxychalkone (V), and in the case of cryptostrobin to a chalkone-flavanone mixture which could not be separated. (Only very small amounts were available.)

The structure of the chalkone follows from its synthesis. Curd and Robertson [6] have proved the structure (IV) for the ketone obtained by nuclear methylation of phloroacetophenone, and from this ketone Brockmann and Maier[7] have prepared the chalkone (V) by condensation with benzaldehyde. The same authors stated that they were unable to rearrange the chalkone to the hitherto unknown 5,7-dimethoxy-8-methylflavanone (VI); the present authors, however, did succeed in obtaining a 10 % yield of the flavanone, m. p. 141—142°, on boiling with sulphuric acid in ethanol for five days. The chalkone can also be demethylated and rearranged in one operation by heating with pyridine hydrochloride [8], yielding a mixture of strobopinin and cryptostrobin.

The formation of the chalkone (V) by methylation of strobopinin suggests that the latter most probably has structure (II), but it is no rigid proof since the pyranone ring may have opened before methylation occurred. Further investigation in this field was made impossible by the small quantities of material at our disposal.

From crude fractions of strobopinin and cryptostrobin from *P. strobus*, a yellow substance, almost insoluble in ether and melting at 285—288°, was isolated in very small quantities (12 mg). It has the composition $C_{16}H_{12}O_4$ and all the characteristic properties of a flavone. Methylphloroglucinol can be identified among its alkali fission products. This new heartwood phenol must evidently be a 6- or 8-methyl chrysin (VII, VIII), and the name strobochrysin is proposed for it.

To synthesise strobochrysin, methylphloroacetophenone was heated with benzoic anhydride and sodium benzoate according to the method of Allan-Robinson. A mixture of yellow, high-melting products was obtained, from which small amounts of a pure substance could be isolated, which was identical with natural strobochrysin, as established by the mixed m. p. of their acetates (m. p. 190—191°) *.

The remainder of the reaction mixture was methylated with one mole of dimethyl sulphate by the Seshadri method [9], and the crude monomethyl ether extracted with strong alkali. The alkali fraction contained a monomethyl ether (IX), m. p. 230—231° (in the crude state), which on further methylation yielded a dimethyl ether, m. p. 230—231°. This compound was also obtained in 60 % yield, when the chalkone (V) was oxidised with selenium dioxide for 40 hours by the method of Mahal, Rai, and Venkataraman [10]. It must therefore be identical with 5,7-dimethoxy-8-methylflavone (X).

Synthetic strobochrysin, on methylation, yielded a dimethyl ether, m. p. 170—171°. The available quantities of this compound were too small to permit complete purification, but the large difference in melting point between the dimethyl ether and 5,7-dimethoxy-8-methylflavone (X) indicates that the former compound must be the 6-methyl isomer (XI). Their colour reactions on reduction with magnesium and hydrochloric acid are also different. Thus, the most probable structure for strobochrysin is 6-methyl chrysin (VII). It may be identical with a high-melting product, a few milligrams of which were isolated by Erdtman from *P. strobus* in 1944 [1].

We first tried to synthesise the dimethyl ether (X) from the ketone (IV)

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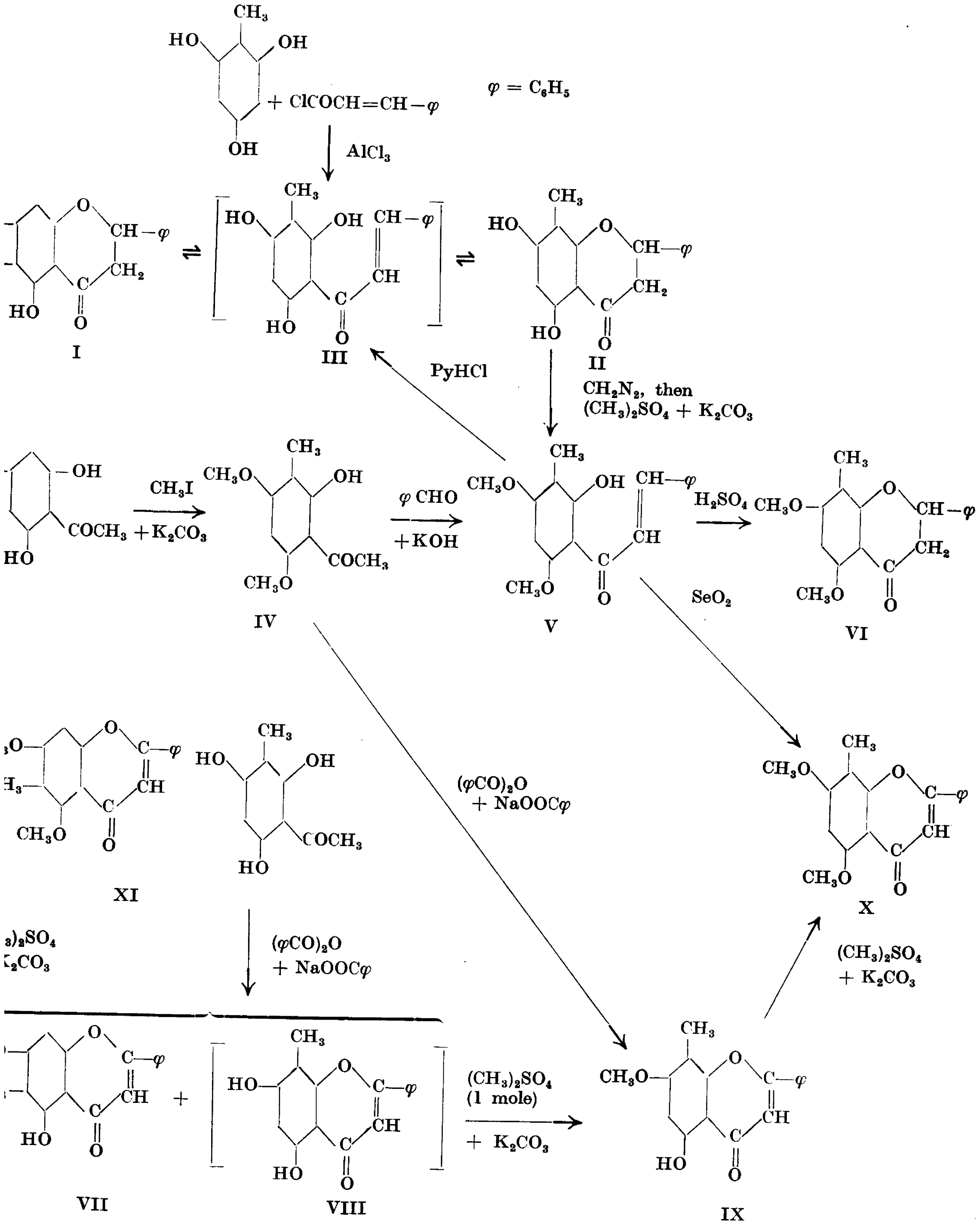
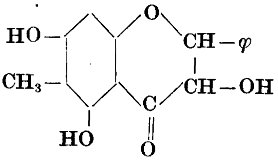
* After the completion of this work we became aware that the same synthesis had already been carried out by S. Furukawa [*Bull. Inst. Phys. Chem. Research (Tokyo)* **13** (1934) 1098; *Chem. Zentr.* (1935 I) 1708]. The m.p.s of his reaction products are different from those recorded by us. It is our intention to return to this question later.


$\varphi = C_6H_5$
$+ ClCOCH{=}CH{-}\varphi$
$AlCl_3$
I
III
II
PyHCl
CH_2N_2, then
$(CH_3)_2SO_4 + K_2CO_3$
CH_3I
$+K_2CO_3$
IV
φ CHO
+KOH
V
H_2SO_4
VI
SeO_2
XI
$(\varphi CO)_2O$
$+ NaOOC\varphi$
X
$(CH_3)_2SO_4$
$+ K_2CO_3$
VII
VIII
$(CH_3)_2SO_4$
(1 mole)
$+ K_2CO_3$
IX

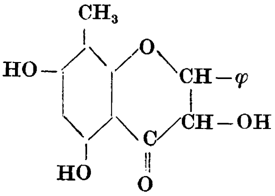
by the Allan-Robinson synthesis. This condensation, however, was accompanied by partial demethylation in the 5-position, and 5-hydroxy-7-methoxy-8-methylflavone (IX) was obtained as the main product. Similar demethylations are previously recorded in the literature[11]. Demethylation of (X) with pyridine hydrochloride is accompanied by partial rearrangement to the 6-methyl series, and a small yield of strobochrysin is obtained.

Another new compound was detected on the paper chromatogram as an orange yellow spot ($R_F \sim 0.35$ in standard solvent). It seemed to accumulate in the 0.2 % alkali fraction from *P. strobus*. The new compound was comparatively easy to isolate from this fraction, owing to the fact that it formed an insoluble sodium salt in sodium carbonate solution, just like pinobanksin[12]. The pure product is colourless, melts at 177—178°, and is optically active, 20 having $[\alpha]_{20}^{D} + 17°$ (methanol). It yields methylphloroglucinol on alkali fis- D sion, and has the composition $C_{16}H_{14}O_5$, corresponding to a C-methyl pinobanksin. Oxidation with alkaline permanganate leads to benzoic acid, thus indicating the presence of a $C—C_6H_5$-group. It gives yellow reduction products with both magnesium and zinc in hydrochloric acid, which is reported to be characteristic for 3-hydroxyflavanones[13]. The name strobobanksin is proposed for this new compound.

Pinobanksin can easily be dehydrogenated to galangin by palladium and cinnamic acid[12]. (Flavanones having no hydroxyl in the 3-position do not react under these conditions.) The same method was also applied to strobobanksin and a yellow product, melting between 220° and 225°, was obtained. It gave a yellow colour reaction with magnesium and hydrochloric acid. An attempt was made to prepare its trimethyl ether, but no pure product was obtained. The monomethyl ether of strobobanksin, m. p. 129—131°, was prepared by the action of diazomethane. Further methylation under mild conditions yielded a product which must be the 5,7-dimethyl ether. This was not purified, but on dehydrogenation by the above-mentioned method, a yellow crystalline substance was obtained, melting at 211—213°. Even here, the quantity was too small to allow a pure methyl ether to be prepared. There ksin is no doubt, however, that strobochrysin yielded a flavonol on dehydrogenation, and thus it must be a 6- or 8-methylpinobanksin (XII, XIII). Further investigations could not be carried out owing to lack of material.



XII



XIII

Flavones or flavanones containing a methylphloroglucinol nucleus have not previously been found in nature. Recently, Schmid and Bolleter have found three chromones in *Eugenia caryophyllata* (L.) Thunb., which all contain a methylphloroglucinol nucleus[14]. They are called eugenitin, (2,6-dimethyl-5-hydroxy-7-methoxychromone), isoeugenitin (2,8-dimethyl-5-hydroxy-7-methoxychromone) and isoeugenitol (2,8-dimethyl-5,7-dihydroxychromone). These substances are thus closely related to those found in *P. strobus*, and here too the 6- and 8-methyl derivatives occur together in the same plant.

Matteucinol and desmethoxymatteucinol, occurring in a fern, are flavanones containing a dimethylphloroglucinol nucleus[15].

EXPERIMENTAL

The isolation of strobopinin and cryptostrobin from the heartwood of *P. strobus* has already been described[1,3].

Alkali fission of the flavanones on a micro scale

The substance to be tested (0.5—2 mg) was boiled in a small test tube with 50 % potassium hydroxide (0.5 ml) for ten minutes. The solution was then cooled, acidified, and extracted with ether (0.5 ml). One drop of the ether solution was applied to a filter paper strip (Munktell OB); one drop of a solution containing phloroglucinol (1 %) and methylphloroglucinol (1 %) was also applied to the same strip as a reference mixture. The chromatogram was run in the usual manner, using water-saturated ether as the solvent. The paper strip was then sprayed with or dipped into diazotised benzidine reagent[4]. The phenols gave immediate colorations, brownish-red for phloroglucinol ($R_F \sim 0.5$) and brick red for methylphloroglucinol ($R_F \sim 0.7$). The spots were circular and very sharp.

Strobopinin, cryptostrobin, strobochrysin and strobobanksin gave strong spots for methylphloroglucinol and sometimes also a very faint phloroglucinol spot, especially when the boiling time was prolonged. This was due to the fact that methylphloroglucinol itself gives a small yield of phloroglucinol on alkali treatment. Chrysin, pinocembrin, and pinobanksin gave strong spots for phloroglucinol. All substances, in addition, gave a strong brick-red spot with $R_F \sim 0.9-0.95$, which must have been due to some other degradation product.

Interconversion of the flavanones

Strobopinin or cryptostrobin (1—2 mg) was heated with 0.5 ml of 1 % sodium hydroxide on the water bath for one and a half hours. The solution was then acidified and extracted with ether (0.5 ml). One drop of the ether solution was investigated on the paper chromatogram by the standard procedure[4]. In both cases, the chromatogram showed the presence of the two isomers.

The same result was obtained by heating the flavanones with pyridine hydrochloride at 180° for one and a half hours.

Synthesis of *d,l*-strobopinin

Solution A: Dry methylphloroglucinol (5 g) was suspended in nitrobenzene (60 ml) and the mixture cooled with ice. A solution of cinnamoyl chloride (6 g) in nitrobenzene (50 ml) was then added.

Solution B: Dry aluminium chloride (7.5 g) was dissolved in nitrobenzene (115 ml), and four drops of thionyl chloride were added to the solution.

Solution A was cooled with ice, and about 90 ml of B were added dropwise in the course of two hours under anhydrous conditions. Next day the remainder of B was added, and the solution left at room temperature for four days. It was then heated to 50—60° for one hour, while a current of carbon dioxide was passed through it. Ice (100 g) and hydrochloric acid (10 ml) were then added, and all nitrobenzene removed by steam distillation. The remaining reddish-brown oil was taken up in ether, the solution thoroughly washed with sodium bicarbonate and partly decolourised by filtration through aluminium oxide. The filtrate, on concentration, deposited crystals. The first fraction, melting at 200—220°, gave no spots on the chromatogram. The second fraction, m. p. 185—205°, gave the spots of strobopinin and cryptostrobin. Additional amounts of this mixture were extracted from the remainder of the filtrate by boiling water.

The entire strobopinin-cryptostrobin mixture was dissolved in ether, and the solution filtered through a magnesium oxide column. Two zones were visible on the column, one yellowish-brown in the upper part, and below that zone a broad pale yellow one, which slowly moved downwards when the column was washed with ether. After it had reached the bottom of the column, the filtrate only contained strobopinin as long as the washing was continued with ether. Each fraction was tested on a paper chromatogram. When the column was washed with methanol, the upper zone moved rapidly downwards, and a mixture of both strobopinin and cryptostrobin could be found in the filtrate.

From the ether fractions, pure *d,l*-strobopinin (0.23 g) was obtained after two recrystallisations from dilute acetic acid as colourless leaflets, m. p. 231—233°. A mixture with (—)strobopinin from *P. strobus* (m. p. 224—226°) melted at 226—229°. The two substances gave identical spots on the paper chromatogram.

$C_{16}H_{14}O_4$ (270.3)	Calc.	C	71.1	H	5.22
	Found	»	71.1	»	5.13

No pure product could be obtained from the methanol fraction.

Methylation of strobopinin and cryptostrobin

Strobopinin from *P. strobus* (0.2 g) was treated with diazomethane in ether solution. Next day, the ether was evaporated and the residue recrystallised once from methanol. A colourless crystalline product, m. p. 96—97°, was obtained. It gave a brownish-violet colour with ferric chloride in ethanol.

The crude monomethyl ether (0.15 g) was boiled with dimethyl sulphate (0.06 ml) and dry potassium carbonate (1 g) in acetone (10 ml) for four hours. The acetone solution was filtered, and the solvent evaporated to dryness. The residue was taken up in ether, and the ether solution washed with 2 *N* sodium hydroxide. It was then dried over anhydrous sodium sulphate and concentrated, depositing orange red crystals, which were filtered off and recrystallised from methanol. They melted at 140—141° alone or on admixture with a sample of 2′-hydroxy-3′-methyl-4′,6′-dimethoxychalkone, synthesised according to Brockmann and Maier [7]. Yield of pure product, 24 mg.

$C_{16}H_{12}O_2\,(OCH_3)_2$ (298.3)	Calc.	OCH_3	20.8
	Found	»	21.0

Cryptostrobin (0.1 g) was methylated in the same way as described above. With diazomethane, a monomethyl ether melting at 134—136° was obtained, which gave a brownish-violet ferric chloride reaction. The crude monomethyl ether, on further methylation, yielded a mixture of yellow and colourless crystals, which could not be separated. The mixture gave a yellowish-brown colour with ferric chloride.

Synthesis of 5,7-dimethoxy-8-methylflavanone (VI)

2′-Hydroxy-3′-methyl-4′,6′-dimethoxychalkone (1.0 g) was dissolved in ethanol (250 ml); sulphuric acid (12 ml) was added and the solution boiled under reflux for five days. The solution, which was still orange in colour, was concentrated by vacuum distillation, and water was then added to the residue. The precipitate so obtained was recrystallised several times from methanol. Each time both yellow and colourless crystals were formed, but finally it was possible to collect 0.1 g of the colourless product. It melted at 141—142° and gave the following colour reactions: Ferric chloride, none; magnesium-hydrochloric acid, very pale pink.

$C_{16}H_{12}O_2(OCH_3)_2$ (298.3)	Calc.	C 72.5	H 6.08	OCH_3 20.8
	Found	» 72.4	» 6.15	» 21.0

Isolation of strobochrysin

Crude fractions of strobopinin and cryptostrobin from *P. strobus*, when dissolved in ether, left a small yellow insoluble residue. This residue was recrystallised several times from ethanol. Finally, pale yellow needles, m. p. 285—288°, were obtained (12 mg). Colour reactions: Hot nitric acid, pale yellow; ferric chloride, greenish-brown; magnesium-hydrochloric acid, pale yellow; diazotised benzidine, very pale orange. The R_F value of the compound in standard solvent is about 0.1. (The chromatogram is rather diffuse and not suitable for identification.)

$C_{16}H_{12}O_4$ (268.3)	Calc.	C 71.6	H 4.51
	Found	» 71.3	» 4.52

5 mg of the flavone were acetylated with acetic anhydride-perchloric acid. The acetate, recrystallised from ethanol, was colourless and melted at 190—191°.

Synthesis of strobochrysin and its isomer

Methylphloroacetophenone [6] (1 g), benzoic anhydride (8 g) and sodium benzoate (2.5 g) were heated to 180—190° in an evacuated sealed Pyrex tube for five hours. The contents of the tube were then refluxed with potassium hydroxide (5 g) in ethanol (50 ml) for half an hour, the solution diluted with water and neutralised with carbon dioxide. The yellowish-brown precipitate was separated, dried, and extracted with ether in a Soxhlet apparatus. The ether extract, on concentration, deposited a yellowish precipitate, melting at 270—280°. After recrystallisation from ethanol, it yielded yellow crystals, m. p. 284—286°. The acetate melted at 190—191° alone or on admixture with strobochrysin acetate.

The remainder of the reaction product could not be separated. Part of it (90 mg) was methylated with 1.1 moles of dimethyl sulphate and potassium carbonate in acetone for two hours. After purifying the reaction product, the mixture of monomethyl ethers was dissolved in chloroform and extracted three times with 4 *N* sodium hydroxide. A yellow precipitate was formed in the alkali phase. The latter phase was acidified and extracted with ether. The ether solution, after drying and concentration, yielded a crystalline residue, which was recrystallised from methanol giving yellow crystals, m. p. 230—231°.

Colour reactions: Ferric chloride, greenish; magnesium-hydrochloric acid, pale pink.

$C_{16}H_{11}O_3(OCH_3)$ (282.3)	Calc.	OCH_3	11.0
	Found	»	10.1

This product was not purified further but was methylated once again for 16 hours in the way described above. A pale yellow crystalline product, m. p. 230—231°, was obtained. It gave no colour with ferric chloride and did not depress the m. p. of synthetic 5,7-dimethoxy-8-methylflavone (see below).

Synthesis of 5,7-dimethoxy-8-methylflavone (X)

The chalkone (V, 1.0 g) was refluxed with selenium dioxide (1.3 g) in *iso*-amyl alcohol (15 ml) for 40 hours. The selenium precipitate was filtered off, and the alcohol removed by steam distillation. The residue was taken up in chloroform, washed with 2 *N* sodium hydroxide, dried over anhydrous sodium sulphate, and the solvent evaporated. The crystalline residue was recrystallised from ethanol, yielding pale yellow needles (0.66 g) which had m. p. 230—231°; they gave no colour with ferric chloride, but gave a pink colour with magnesium-hydrochloric acid.

$C_{16}H_{10}O_2(OCH_3)_2$ (296.3)	Calc.	C	73.0	H	5.44	OCH_3	20.9
	Found	»	72.8	»	5.35	»	20.6

Methylation of strobochrysin

Synthetic strobochrysin (60 mg) was refluxed for 24 hours with dimethyl sulphate (0.10 ml) and potassium carbonate (0.5 g) in acetone (25 ml). The reaction product was worked up as described earlier. A small amount of colourless crystals, m. p. 170—171°, was obtained; these gave no colour with ferric chloride, but gave a yellow colour with magnesium-hydrochloric acid.

Strobochrysin (30 mg) was also methylated with one mole of dimethyl sulphate and potassium carbonate in acetone for fifteen hours. Pale yellow needles, m. p. 170—173°, were obtained, with which ferric chloride gave a greenish-brown colour. This product was not further investigated.

Synthesis of 5-hydroxy-7-methoxy-8-methylflavone (IX)

2-Hydroxy-3-methyl-4,6-dimethoxyacetophenone (IV, 0.4 g) was heated with benzoic anhydride (3.2 g) and sodium benzoate (0.95 g) to 225—230° for six hours. The reaction mixture was worked up as described for strobochrysin, giving a low yield of 5-hydroxy-7-methoxy-8-methylflavone, m. p. 230—231° alone or on admixture with the product obtained before (see under "Synthesis of strobochrysin . . .").

Demethylation of 5,7-dimethoxy-8-methylflavone (X)

The flavone (X, 0.3 g) was heated to 200° with pyridine hydrochloride (1.5 g) for six hours. The reaction product was then treated with water, and the precipitate filtered off, dried and sublimed in a vacuum. The sublimate, on recrystallisation from acetic acid and from ethanol, yielded a small amount of a yellow crystalline product, m. p. 280—282°. The acetate melted at 190—191°, alone or on admixture with strobochrysin acetate.

Demethylation for two hours at 180° yielded 5-hydroxy-7-methoxy-8-methylflavone (IX) as the main product.

Isolation of strobobanksin

The 0.2 % sodium hydroxide fraction of the heartwood extract from *P. strobus* contains five or six different phenols, according to the paper chromatogram. One of these has $R_F \sim 0.35$ in standard solvent and gives an orange yellow colour with benzidine reagent. The other spots are due to substances already known.

The entire fraction was recrystallised from dilute acetic acid, the crystals separated, and the mother liquor precipitated with water. The sticky precipitate was extracted several times with boiling water. Each water extract was cooled and shaken with ether. The ether extracts, on concentration, yielded yellow oils, which partly crystallised. From the first extract, colourless crystals were obtained, m. p. 168—170°. This product, when investigated on the paper chromatogram, seemed to consist mainly of the unknown substance. After recrystallisation from benzene and from dilute acetic acid and drying at 100° the compound had m. p. 177—178°, $[\alpha]_D^{20} + 17° \pm 1°$ (methanol, $c = 3.0$). Colour reactions: Ferric chloride, brownish-violet; magnesium or zinc and hydrochloric acid, bright yellow; diazotised benzidine, orange yellow.

$C_{16}H_{14}O_5$ (286.3)	Calc.	C	67.1	H	4.93
	Found	»	67.3	»	4.90

Additional quantities of the new substance were obtained from the other aqueous extracts by shaking with saturated sodium carbonate. Strobobanksin was then precipitated as a colourless sodium salt, which was filtered off, decomposed by acid, and the phenol recrystallised. Total yield, 0.25 g of pure strobobanksin from 7.0 kg of air-dry heartwood.

Strobobanksin (20 mg) was oxidised with potassium permanganate in alkaline solution as described by Erdtman[1]. Benzoic acid was obtained and identified by a mixed m. p. determination.

Methylation and dehydrogenation of strobobanksin

Strobobanksin (0.15 g) was treated with diazomethane in ether solution. The reaction product, on recrystallisation from methanol, melted at 129—131°. It gave a brownish-violet colour with ferric chloride, and, hence, was clearly a monomethyl ether.

The crude monomethyl ether (0.15 g) was further methylated for four hours with one mole of dimethyl sulphate and potassium carbonate. The reaction product was a yellow syrup, which slowly deposited crystals. The entire product was heated to 180° for two hours with cinnamic acid (0.25 g), palladium-carbon catalyst [16] (0.05 g) and water (5 ml) in a sealed tube. The reaction product was dissolved in ether and washed with sodium bicarbonate. Evaporation of the ether solution gave a yellow residue, which was recrystallised from chloroform-light petroleum. Brownish-yellow crystals, m. p. 211—213°, were obtained. Yield, 14 mg. Ferric chloride gave a brownish-violet colour.

The entire yield of this product was further methylated with dimethyl sulphate and potassium carbonate in acetone. The quantity of crude reaction product obtained was too small to allow purification, but the absence of a colour reaction with ferric chloride indicated that it was a fully methylated substance. Magnesium and hydrochloric acid gave a strong yellow colour.

Strobobanksin (33 mg) was also dehydrogenated in the way described above. A yellow crystalline product (13 mg) was obtained which melted at 220—225°. Colour reactions: Ferric chloride, greenish-brown; magnesium-hydrochloric acid, yellow.

Methylation of this compound did not lead to any pure product.

SUMMARY

Four substances from the heartwood of *Pinus strobus* L., the previously isolated strobopinin and cryptostrobin and the new compounds strobochrysin and strobobanksin, have been investigated. They are all flavones or flavanones containing a methylphloroglucinol nucleus. Strobopinin and cryptostrobin are 5,7-dihydroxy-8-and-6-methyl-flavanones. The position of the C-methyl group in each isomer has not definitely been determined, but the most probable structure for strobopinin seems to be 5,7-dihydroxy-8-methylflavanone. Strobochrysin it probably 5,7-dihydroxy-6-methylflavone and strobobanksin 3,5,7-trihydroxy-6-or-8-methylflavanone.

In connection with this work some new flavones and flavanones containing a methylphloroglucinol nucleus have been synthesised.

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