

acid (II) and undecyl bromide, but yielded an insoluble salt. The salt was recrystallized from ethanol, dissolved in a 50 % ethanol-water mixture and acidified. It was recrystallized twice from petroleum ether, yielding 2.6 g (72 %) of glistening crystals, m.p. 67.5–68°. (Found: Se 29.17; equiv. wt. 542.3. Calc. for $C_{25}H_{50}O_2Se_2$: Se 29.21; equiv. wt. 540.6).

The selenium analyses were carried out according to Fredga⁶.

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Heartwood Constituents of *Laburnum alpinum* Bercht. & Presl.*

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Laburnum alpinum Bercht. & Presl (syn. *Cytisus alpinus* Mill., Swedish "gull-regn") is a small tree. The wood of old specimens contains a large amount of brown heartwood and a very small amount of yellowish sapwood. The heartwood is fairly resistant to wood destroying fungi and, like pine heartwood, cannot be properly digested by the normal acid sulphite process.

Extraction of the wood with ether gave 5–8 % soluble products which partly separated in crystalline form on concentration of the extract. More of the same material was precipitated on addition of benzene. The total yield of crude solid

material was 3–4 %. Most of this product was fairly easily soluble in hot water (A) and in this way could be separated from a much smaller amount of less soluble products (B). Alternatively, the crude product was acetylated with acetic anhydride in pyridine and the dry crude acetate poured into boiling ethanol; part of it went rapidly into solution, leaving a less soluble product (D) which was collected by filtration. On cooling the hot ethanolic solution a product (C) precipitated. Acetylation of products A and B yielded acetates essentially similar to the acetates C and D, respectively.

Repeated crystallisation from ethanol of the C products furnished pure, dimorphous 3,4,3',5'-tetraacetoxystilbene,¹ m.p. 115° and 127–128°,² easily converted into the corresponding tetramethyl ether, m.p. 68–69°. The latter, on oxidation with permanganate, gave an excellent yield of acids which were esterified with diazomethane and then brominated. Alkaline hydrolysis of the bromination product gave 6-bromoveratric acid and methyl 2,6-dibromo-3,5-dimethoxybenzoate. This method is very useful for the separate isolation of the two aromatic nuclei of this stilbene.

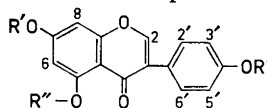
Recrystallisation of the D-products *a*), from pyridine (or acetic acid) or *b*), from large amounts of ethanol gave two acetates: a colourless, dimorphous acetate, m.p. 165–167° and 203–206° (E) and a usually slightly yellow acetate (F), m.p. 200–203°. The latter acetate could be recrystallised from acetic anhydride but it was converted into E on prolonged heating with this reagent.

The evaporated mother liquors obtained according to method *b*) gave a product which after several crystallisations from ethyl acetate melted at 169–171° (G). Repeated recrystallisations of G from acetic acid yielded impure products of gradually increasing melting points. Finally, compound F was obtained.

Analysis of the compounds E, F, and G gave carbon and hydrogen values in agreement with the empirical formulae $C_{21}H_{16}O_8$, $C_{19}H_{14}O_7$, and $C_{19}H_{14}O_6OCH_3$, respectively. The acetyl estimations (alkaline hydrolysis, acidification and steam distillation) gave very varying results; E generally gave values corresponding to

* Part of this work was communicated at the Second International Symposium on Natural Compounds in Prague 1962.

Table 1. Proton magnetic resonance spectra of some genistein derivatives. The shifts are given in τ -units. The spectra were recorded in deuteroform on a Varian A-60 instrument. Tetramethylsilane was used as internal reference.

	H-2	H-3',5'	H-2',6'	H-8	H-6	Substituents in positions		
	singlet	doublet	doublet	doublet	doublet	5	7	4'
Genistein triacetate (E) R' = R'' = CH ₃ CO	2.08	2.70 <i>J</i> = 8.5 cps	2.48	3.12 <i>J</i> = 2.5 cps	2.73	7.57	7.67	7.65
Genistein diacetate (F) R' = CH ₃ CO; R'' = H	2.01	2.80 <i>J</i> = 8.5 cps	2.45	3.22 <i>J</i> = 2.5 cps	3.40	3.73	(6 hydrogens) 7.68	
Genistein-5-methyl ether diacetate (G) R' = CH ₃ CO; R'' = CH ₃	2.12	2.83 <i>J</i> = 8.5 cps	2.40	3.11 <i>J</i> = 2.5 cps	3.37	6.03	7.70	7.67
Genistein trimethyl ether ^a R' = R'' = CH ₃	2.27	3.10	2.56	3.67	3.59	6.09	6.14	6.19

approximately four, F, and G to three acid equivalents.

The UV and IR-spectra of E, F, and G indicated that the compounds were of isoflavone type. None of the compounds gave any colour reaction with magnesium and hydrochloric acid.

Hydrolysis of E, F, or G with dilute sulphuric acid in alcohol, addition of a large excess of dimethyl sulphate to the solution and subsequent addition of 40 % sodium hydroxide solution gave crystalline products, m.p. 160–161°, identical with genistein trimethyl ether. Brief acetylation of an authentic sample of genistein with acetic anhydride in pyridine gave a product identical with F. Hence, E, F, and G are isoflavones. The inconsistent acetyl analyses are due to the normal degradation of isoflavones with elimination of C-2 as formic acid.

The above chemical data suggest that the compounds E, F, and G are genistein triacetate, diacetate and methyl ether-diacetate, respectively. These results are confirmed by proton magnetic resonance studies (Table 1). The assignment of the C-5 position to the free hydroxyl group in genistein diacetate (F) and, accordingly, to the methoxyl group in the methyl ether-diacetate (G) is based on the fact that the signal position of only one hydrogen atom (H-6) is shifted downfield in the triacetate (E, τ 2.73) compared with the signal position for this hydrogen in the diacetate (F, τ 3.40) and the methyl ether-diacetate (G, τ 3.37), whereas the resonance position of the other hydrogen atom on ring B (H-8) appears at almost the same field

in the spectra of the above three compounds (E, τ 3.12; F, τ 3.22; G, τ 3.11). The assigned position (C-5) of the free hydroxyl in the diacetate (F) is in agreement with the chemical observations that this compound is difficult to acetylate and that the methyl ether diacetate (G) is easily demethylated to the diacetate (F).

The heartwood of *C. alpinus* thus contains 3,4,3',5'-tetrahydroxystilbene (= piceatannol²), genistein and genistein-5-methyl ether and provides yet another example of the co-occurrence of stilbenes and flavonoids.

After the completion of our work we have learned that Chopin, Bouillant and Lebreton have independently isolated and identified genistein and its 5-methyl ether from the sapwood of *Cytisus laburnum* L. (syn. *Laburnum anagyroides* Med.). (J. Chopin, *Private communication*). We have also examined this species and have isolated the same compounds (as their acetates). The identity of our substances with those of Chopin *et al.* has been confirmed by direct comparison.

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