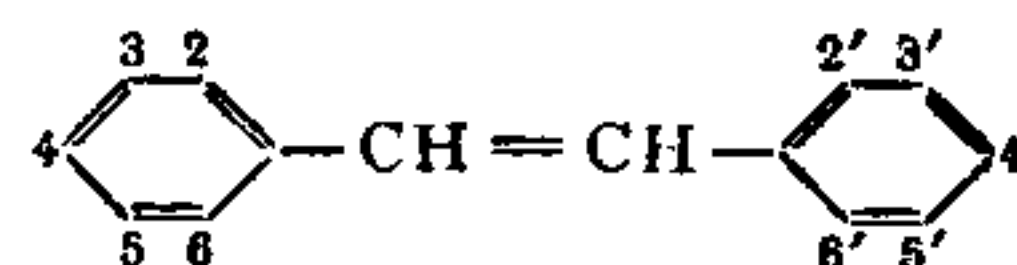


# OCCURRENCE OF C<sub>8</sub> UNITS IN NATURALLY OCCURRING STILBENES AND PHENYL ISOCOUMARINS

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THE simplest of naturally occurring stilbenes and the earliest to be discovered was pinosylvlin.<sup>1</sup> This substance, its methyl ethers and dihydro-derivatives are commonly found in the heartwoods of pine trees and one or more of these are invariable components. Similarly pterostilbene is a characteristic component of the wood of *Pterocarpus* species.<sup>2-4</sup> The occurrence of these compounds has therefore been considered to be of importance for the taxonomy of these plants. They seem to play an important part in protecting the wood from insect and fungal attack. Pterostilbene has also been found to have a curative effect on diabetes. More recently other stilbenes have been isolated mainly from the heartwood of timber-yielding plants and from certain plant drugs. The chief members occurring in Nature are given in the following table (Table I).



Stilbene

In naturally-occurring stilbenes the substitution of the benzene rings is of a special nature. The majority of them have no hydroxyl in an ortho-position. All of them have the 3:5-dihydroxy (methoxy) substitution in one of the rings and suggest derivation from an orcinol (or orsellinic, C<sub>8</sub>) unit. The second part has mostly the normal substitution of the C<sub>9</sub> unit of eugenol derivatives, lignanes and flavonoids, i.e., 4', 3':4' and 3':4':5'. The 2':4' substitution should also be taken as normal variation, though somewhat rare (Rao and Seshadri<sup>5</sup>). Then the following scheme for the formation of stilbenes could be suggested involving a derived C<sub>8</sub> unit (Seshadri<sup>6</sup>) and a derived C<sub>9</sub> unit.

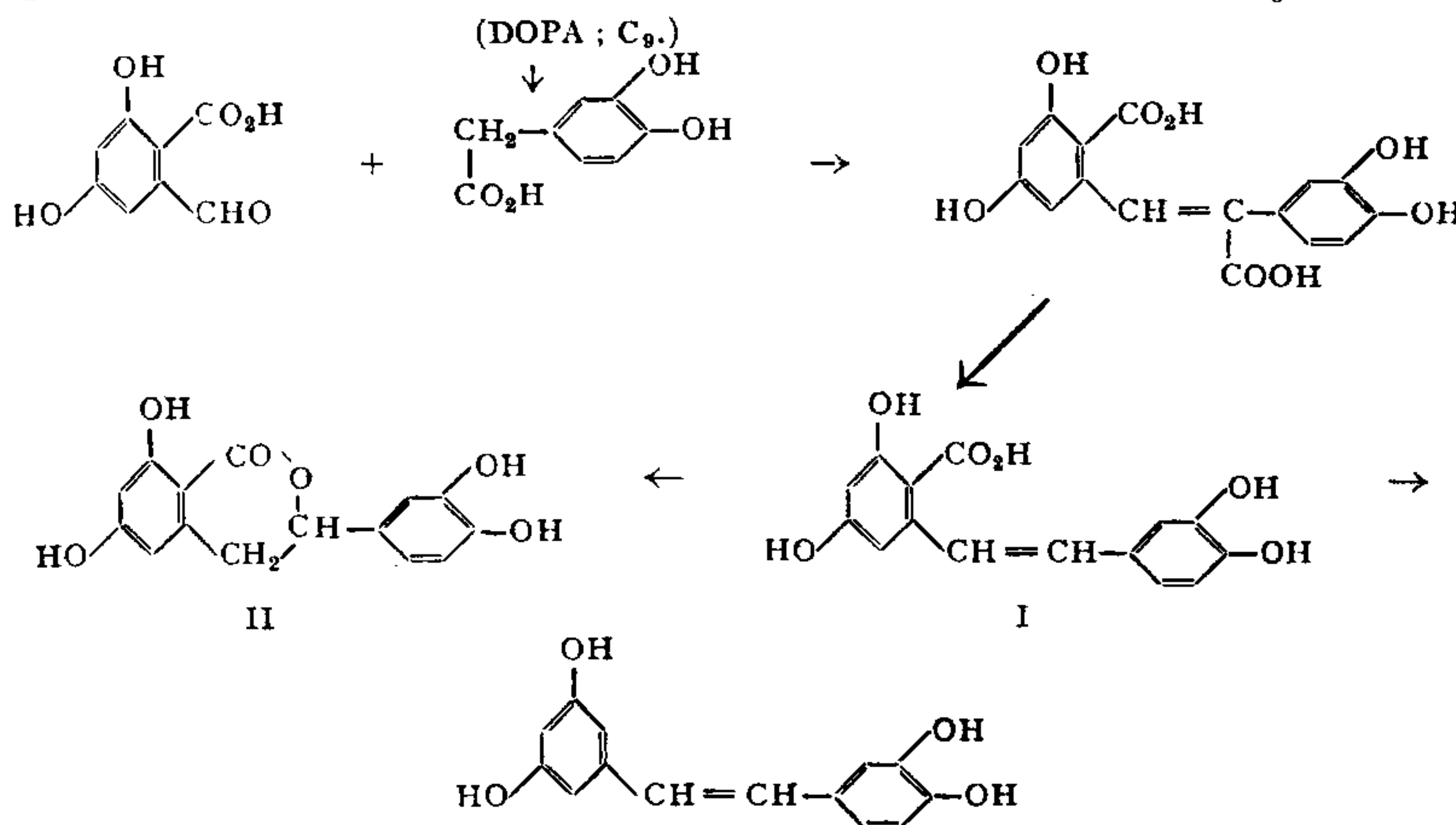


TABLE I

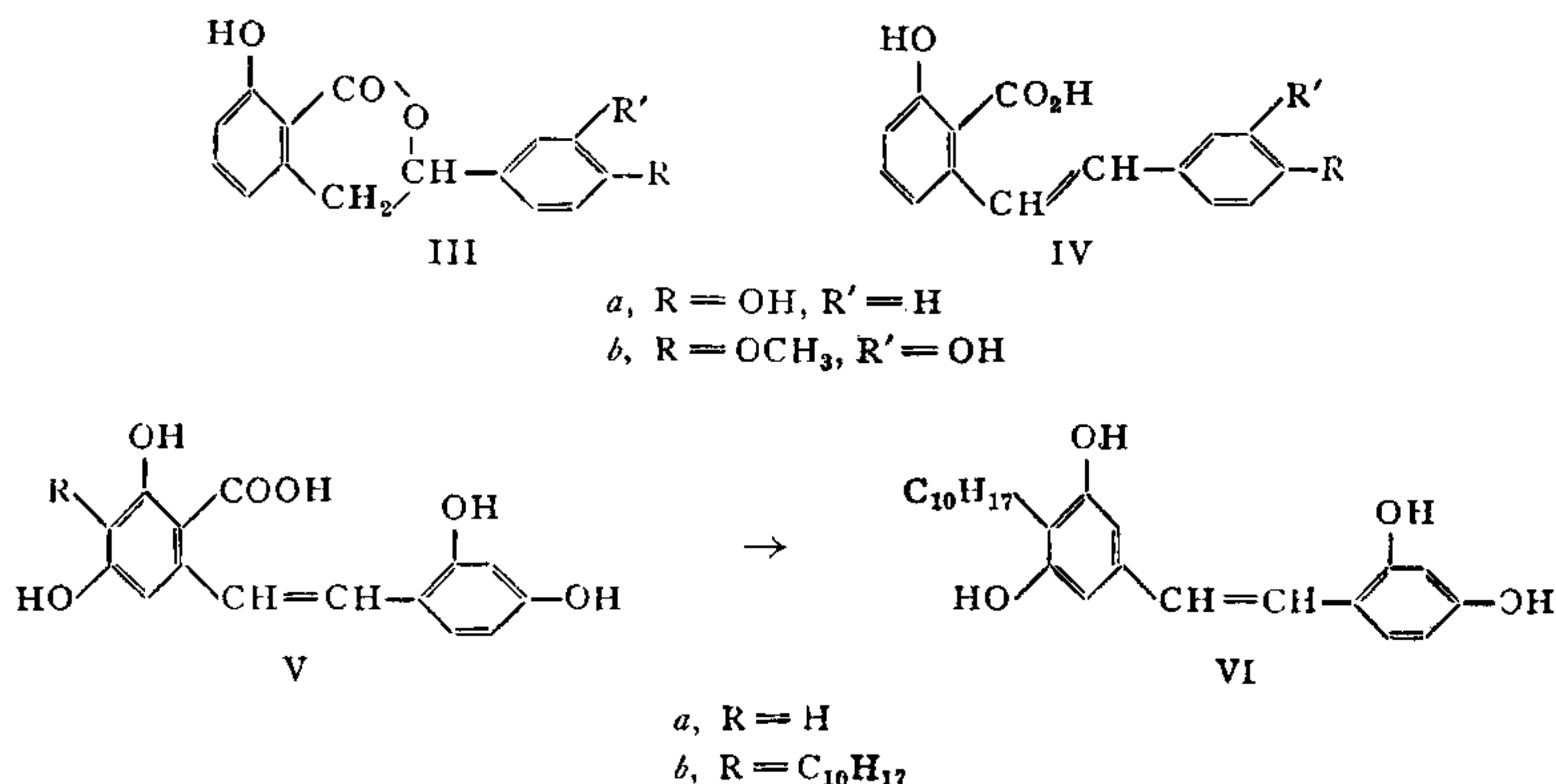
Name	Structure	Source
1 Pinosylvlin ..	3:5-dihydroxy	Heartwood of <i>Pinus sylvestris</i> , and <i>P. nigra</i>
2 Pinosylvlin monomethyl ether ..	3-hydroxy-5-methoxy	Heartwood of <i>Pinus strobus</i> , <i>P. cembra</i> and <i>P. montana</i>
3 Pinosylvlin dimethyl ether ..	3:5-dimethoxy	Heartwood of <i>P. nigra</i> and <i>P. palustris</i>
4 Resveratrol ..	3:5:4'-trihydroxy	Root of <i>Veratrum grandiflorum</i>
5 Pterostilbene ..	3:5-dimethoxy-4'-hydroxy	Heartwood of <i>Pterocarpus</i> species
6 Hydroxy resveratrol ..	3:5:2':4'-tetrahydroxy	Root of <i>Veratrum grandiflorum</i>
7 ..	3:5:3':4'-tetrahydroxy	Heartwood of <i>Vouacapoua macropetala</i> and <i>V. americana</i>
8 ..	3:5:3':4':5'-pentahydroxy	Heartwood of <i>Vouacapoua macropetala</i>
9 Rhapontigenin ..	3:5:3'-trihydroxy-4'-methoxy	Root of <i>Rheum emodi</i>
10 Chlorophorin ..	3:5:2':4'-tetrahydroxy 4-(3:7-dimethyl octa-2:6-dienyl)	Heartwood of <i>Chlorophora excelsa</i>

The above scheme seems to be supported by two observations: (i) the occurrence of stilbene-*o*-carboxylic acids and 3-phenyl dihydro-isocoumarins in nature. Two related 3-phenyl-dihydro-isocoumarins, hydrangenol (III a) and phyllodulcinol (III b) are present in varieties of *Hydrangea opuloides*. They are accompanied by the corresponding stilbene-*o*-carboxylic acids called iso-hydrangenol (IV a) and iso-phyllodulcinol (IV b). These compounds have been fully investigated by Asahina and Asano.<sup>7</sup> The dihydro-isocoumarins can by treatment with alkali be readily converted into the stilbene carboxylic acids and the latter on heating close up the ring to yield the former.

It could be noticed that they have lost one of the two meta di-hydroxyl groups found in formulæ (I and II). The stability of these acids

natural on the above scheme of biogenesis if the substitution (V a to V b) should take place prior to the final decarboxylation of the acid, since carbonyl derivatives of resorcinol all undergo alkylations in the 3-position which corresponds to the 4-position of stilbenes.

The question of the biogenesis of naturally occurring stilbenes has received some attention earlier. Geissman and Hinreiner<sup>9</sup> attempted to adopt the  $C_6 + C_9$  scheme as found in anthoxanthins and have focussed attention on the difficulties of the explanation. Sir Robert Robinson<sup>10</sup> has derived the structures of pino-sylvin, pterostilbene and chlorophorin from polyketomethylenes; the scheme is quite suitable for these compounds but may not suit the other stilbenes having the 3':4'-substitution pattern of  $C_9$  units.



could be attributed to this event which should have happened earlier by a process of reduction; the isocompounds (acids) may thus have been enabled to escape decarboxylation and undergo ring closure to yield the isocoumarins. The presence of a resorcylic acid structure would lead to ready decarboxylation, yielding the stilbenes.

(ii) The structure of chlorophorin<sup>b</sup> (VI). The special feature of chlorophorin is the di-isoprenoid side chain that is found in the 4-position located between two phenolic hydroxyl groups. It would naturally be an inaccessible position if the substitution (or entry of the long chain) should be considered to take place in a pre-formed stilbene structure. But it becomes quite

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2. Späth and Schläger, *Ber.*, 1940, 73, 881.
3. King *et al.*, *J.C.S.*, 1953, 3693.
4. Sawhney and Seshadri, *J. Sci. Ind. Res., India*, 1956, 15 C, 154.
5. Rao and Seshadri, *Proc. Ind. Acad. Sci.*, 1943, 18 A, 234; Sawhney *et al.*, *Ibid.*, 1951, 33 A, 11.
6. Seshadri, *Ibid.*, 1944, 20 A, 1; Aghoranurthy and Seshadri, *J. Sci. Ind. Res., India*, 1954, 13 A, 114.
7. Asahina and Asano, *Ber.*, 1930, 63 B, 429.
8. King and Grundon, *J.C.S.*, 1949, 3348; 1950, 3547.
9. Geissman and Hinreiner, *Bot. Review*, 1952, 209.
10. Robinson, *The Structural Relations of Natural Products*, Clarendon Press, 1955, 9.