HEVEAFLAVONE - A NEW BIFLAVONOID FROM HEVEA BRASELIENSIS

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The rubber tree (<u>Hevea braseliensis</u>: family, Euphorbeacea) is of great economic importance. Earlier work on this species has shown the presence of quebrachitol (1), linamarin (2), indoleacetic acid (3) and betaines (4) from various parts of the tree, but not much is known about its phenolic constituents. The present work was undertaken with a view to study these.

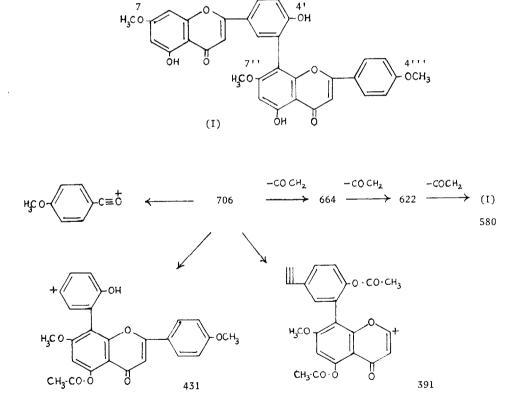
Alcoholic extract concentrate of fresh leaves collected from Kerala was diluted with water and extracted successively with pet. ether, ether and ethyl acetate. The final aqueous extract left a pale yellow solid named 'Heveaflavone' which was collected by filtration. The aqueous filtrate was treated with neutral and basic lead acetate solutions one after another. From the lead salts, quercetin and kaempferol-0-glycosides were isolated. The sugars were identified as rhamnose and glucose.

Heveaflavone crystallized from acetone as tiny rods, m. p.>305°. It gave a green colour with FeCl₃; Mg-HCl test was negative but NaHg test positive giving a deep pink colour. Its U.V. absorption in ethanol λ_{max} 269, 335 mµ was characteristic of apigenin unit and the maxima showed no change on addition of sodium acetate. However, in the presence of AlCl₃, expected bathochromatic shifts were observed. The I.R. spectrum had an absorption at 1660 cm⁻¹ due to chelated carbonyl. It gave a yellow crystalline methyl ether, m.p. 219-20° and a colourless crystalline acetate, m.p. 229-31°. The methyl ether gave a strong Mg-HCl reaction and agreed well with amentoflavone hexamethyl ether (TLC and mixed m.p.). The acetate had $[\alpha]_D^{22}$ - 15° (pyridine, 6.65 mg/ml). The elemental analysis and mol. wt. 706 (mass spectrum) of the acetate were in accord with the formula $C_{x0}H_{x0}O_{1x}$.

Having known the basic skeleton for heveaflavone the positions of different groups were assigned as follows. The presence of a mass peak at m/e 135 (due to $CH_3O - C \equiv \bar{O}$) fixes one of the methoxyls at 4''' position of the amentoflavone unit. Further information regarding the other two methoxyls could be obtained from a study of NMR spectrum of the *Present address: Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pa.

acetate taken in $CDCl_3$ containing a few drops of deuterated pyridine. There were three methoxyl signals at 6 3.7, 3.8 and 3.85 ppm and three acetoxyl signals at 1.95, 2.40 and 2.46 ppm. The last two could be assigned to the 5 and 5'' acetoxyls. The signal at 1.95 ppm is exceptional for a phenolic acetoxyl but similar high field shifts have been observed earlier in case of biflavonoid acetates (5). The most shielded protons are the substituents at 7'' and 4' positions of the amentoflavone derivative. The presence of an acetoxyl signal at 1.95 ppm suggest the presence of 4' acetoxyl and the absence of any signal around 3.6 ppm for a methoxyl at 4' in the spectrum also leads to the same conclusion. Hence the three methoxyls should be at 7, 7'' and 4''' leading to the structure (I) for heveaflavone.

The mass spectral fragmentation can be explained on the basis of structure (I) for heveaflavone.



This is probably the first report of isolation of a biflavonoid in the family - Euphorbeacea.

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