2. Eq. (7) avoids the arbitrariness with which eq. (15) introduces the temperature term in the expression for

$$A = \frac{kT}{h} e^{\Delta S/R}$$

the T in this expression has been variously and arbitrarily chosen as T_s (the DTG peak temperature)[2] or $\bar{T}$ (the average temperature)[16].

The improvement effected by the present equation may be illustrated by considering a theoretical TG curve. Such a procedure has been suggested by Sestak in a different context[17]. A theoretical TG curve with an assumed value of E = 120 kJ mole^{-1} was used for this purpose. Here, the Coats-Redfern equation gives a value E = 123·3 kJ mole^{-1} whereas the present equation gives a value E = 119·8 kJ mole^{-1}. The improvement is obvious.

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TWO UNUSUAL FLAVONES (ARTEMETIN AND 7-DESMETHYL ARTEMETIN) FROM THE LEAVES OF *VITEX TRIFOLIA*

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ABSTRACT

Adsorption chromatography on silica gel of the chloroform extract of dry leaves of *Vitex trifolia* (Verbenaceae) has yielded two methylated flavones of rare occurrence. Based on chemical as well as UV, IR, PMR and Mass spectral data, the major compound has been characterised as 5, 7-dihydroxy-3, 3', 4', 6-tetra methoxy flavone (3, 3', 4', 6-tetra methyl quercetagetin) and the minor as artemetin (5-hydroxy-3, 3', 4', 6, 7-penta methoxy flavone) by direct comparison with authentic sample. The earlier observation regarding the variation of flavonoid pattern with reference to plant geography in *Vitex* is further supported by our results.

THE distribution of flavonoids in the genus *Vitex*[1] under the family Verbenaceae and the Natural Order Tubiflorae is interesting especially with reference to the glycoflavones (atypical in this family) and the unusual flavones like casticin (3, 4', 6, 7-tetra methyl quercetagetin), and certain variations in the flavonoid patterns relating to plant geography have been observed. Some significance is also attached to these flavonoids in the classification of plants of this family.

In continuation of our work on the flavone glucuronides of the Verbenaceae[2], we have made a detailed chemical examination of the flavonoids of the leaves of *Vitex trifolia* Linn. earlier recorded to contain casticin[3] and vitexin[4], and our results are recorded here.

The dry leaves of *V. trifolia* were first extracted with hot $CHCl_3$ and then with MeOH. The concentrated $CHCl_3$ extract was chromatographed on a column of silica gel using petroleum ether, benzene and $CHCl_3$ as eluting solvents. No crystalline flavonoid was obtained from petrol eluates.

The residue from the benzene fraction on recrystallisation from Me_2CO–MeOH yielded a small

amount of light yellow needles of a flavone, m.p. 162–63°, λ_{max} 254, 274 sh, 346 nm. (MeOH). It was purple under U.V. and U.V./NH_3. It gave an olive green colour with Fe^{3+} and yielded quercetagetin on demethylation with Ac_2O and HI. It had R_f : 0·36 (15% HOAc), 0·78 (30% HOAc), 0·85 (50% HOAc), 0·95 (BAW), 0·92 (phenol), 0·96 (Forestal) and 0·96 (*t*-BAW). It was identified as 5-hydroxy-3, 3′, 4′, 6, 7-penta methoxy flavone (artemetin[5,6]) and the identity further confirmed by direct comparison including co-PC with an authentic sample. A minute quantity of a flavone present in the mother liquor was fluorescent light blue under U.V. and U.V./NH_3 and did not give any colour with Fe^{3+}. It was identified as 5-methyl artemetin (quercetagetin hexa methyl ether) by direct comparison with a synthetic sample prepared by complete methylation of quercetagetin.

The residue from the $CHCl_3$ fraction was thrice recrystallised from Me_2CO–MeOH, when a pale yellow flavone, m.p. 168–69° was obtained. It gave yellow colour with NH_3 and greenish blue with Fe^{3+}. It was deep purple under U.V. and U.V./NH_3 and had λ_{max} : 256, 271 sh, 340 (MeOH) ; 256, 271, 344 (NaOAc) ; 266, 282 sh, 297 sh, 368 ($AlCl_3$) and 257, 272, 342 ($NaOAc/H_3BO_3$) almost the same as artemetin. The PMR spectrum ($CDCl_3$) showed signals (δ values, ppm) at 3·98, 3·95, 3·90 and 3·88 (each singlet of 3 protons due to $-OCH_3$). 6·5 (singlet, 8–H), 6·63 (doublet, J = 9 cps, 5′–H) 7·66 (multiplet, 2′–H and 6′–H) and a low field proton at 12·3 (5–O*H*) and the IR (KBr) exhibited absorption bands (cm^{-1}) at 3640 (–OH), 1670 (conjugated C = O), 1610, 1590, 1560 and 1520 (benzene derivative). The mass spectrum of the compound showed the parent ion at m/e 374 (M^+, $C_{19}H_{18}O_8$, 100%) and fragmentation ions at 373 (M^+–H, 24%) 359 ($M-CH_3$, 33%) 346 (M^+–CO, 2%), 344 (M^+–$2CH_3$, 5%) 331 (M^+–CH_3CO, 10%) 187 (M^{2+}, 20%) and 173 (*M*–28[2] , 35%) and 182, 167, 161, 151, 139, 137 and 123 (due to ions of RDA fragmentation and further cleavage). The PMR and mass spectral data along with the R_f (0·20, 0·56, 0·79, 0·92, 0·92, 0·93 and 0·94 resp. in the above solvents) clearly indicated the compound to be a dihydroxy-tetra methoxy flavone. On acetylation with Ac_2O and pyridine, it yielded a crystalline diacetate, m.p. 174–75°, whose mass spectrum showed the parent ion at m/e 458 (M^+, $C_{23}H_{22}O_{10}$, 11·5%) and fragmentation ions at 457 (M^+–H, 14%), 443 (M^+-CH_3) 428 (M^+-2CH_3), 415 ($M-CH_3CO$, 100%) 400 [$M^+-(CH_3CO+CH_3)$, 23%], 385 [$M-(2CH_3+CH_3CO)$] 372 (M^+-2CH_3CO, 35%) and 342 [$M^+-(2CH_3+2CH_3CO)$] confirming the dihdroxy tetra methoxy flavone structure. On demethylation with HI and Ac_2O, it gave 3, 3′, 4′, 5, 6, 7 hexahydroxy flavone (quercetagetin). From these data, the flavone was identified as a tetra methyl ether of quercetagetin. The almost identical UV spectra of the compound and artemetin, and the mass fragmentation pattern established the structure as 5, 7-dihydroxy-3, 3′, 4′, 6-tetra methoxy flavone. (The 7-OH of a 6-methoxylated flavone has been recorded[7,8] to behave in such a manner as to miss its detection by U.V. analysis). The identity was finally confirmed by a partial synthesis of artemetin from our sample by selective methylation using Me_2SO_4 and anhydrous K_2CO_3 for 6 hr. (Selective methylation using Me_2SO_4 and $KHCO_3$ for 12 hr was not successful, which may again be attributed to the peculiar nature of 7-OH in 6-methoxylated flavones).

The pigment from MeOH concentrate was identified as luteolin by λ_{max}, R_f, preparation of its tetraacetate and direct comparison with an authentic sample. No flavone glycoside could be detected.

Our isolation of artemetin and 5, 7-dihydroxy-3, 3′, 4′, 6-tetramethoxy flavone (7-desmethyl artemetin) in the place of casticin and vitexin reported earlier in *V. trifolia* confirms the observation of Harborne[1] of the variation of flavonoid pattern in relation to plant geography in this genus. Artemetin has been earlier isolated from the leaves[9] and seeds[10] of *V. negundo*. Ours is the second report of the isolation of the unusual flavone, 7-desmethyl artemetin, the first being from *Bahia oppositifolia*[11] (Compositae).

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AEROPALYNOLOGICAL STUDIES OF BANGALORE CITY

Part I. Pollen Morphology of *Parthenium hysterophorus* Linn.

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BANGALORE CITY, known for its salubrious climate almost throughout the year, is often referred as the air-conditioned City of India. However, the atmosphere of the City is full of pollen pollutants. This fact has great bearing on the different types of pollen allergies, much prevalent in this City.

A comprehensive research scheme has been undertaken by the authors to tackle the pollen allergy problem from palynological point of view. As a prerequisite to this research project, construction of pollen flora based on the collection of pollen from plants growing in the City has been undertaken.

Of late several reports have been published on allergic manifestations of the recently introduced notorius weed, commonly referred to as Congress Weed or White Top, and botanically known as *Parthenium hysterophorus* Linn. It has been further reported that the food grains imported into India from U.S.A. and Canada were contaminated with the seeds of this weed[1,8]. Several methods of eradication of this fast spreading weed, have been suggested recently by Vartak[9] and Jayachandra[4].

Parthenium hysterophorus Linn., a member of the family Compositae, is known to produce pollen abundantly. The toxic effects of the pollen grains of this weed with reference to allergies have been reported by Wodehouse[11], Shivpuri *et al.*[5,7] The flowers of this weed known to be amphiphilous. The prevalence of these pollen grains in the atmosphere has been reported by the Aeropalynological work carried on by Shivpuri et al.[7] at Delhi and the same has been confirmed by us at Bangalore.

The pollen grains of *P. hysterophorus* were studied by using the standard palynological techniques of Erdtman[2,3] and were found to be very interesting morphologically. Literature indicated that detailed pollen morphology of this weed has not been worked out. Hence the diagnosis of the pollen grains of this weed has been presented here.

Pollen diagnosis of P. hysterophorus *Linn.*
(Figs. 1–4)

Pollen grains 3-colporate (peritreme), oblatespheroidal (16 × 17 μ). Apocolpium diameter about 3·5 μ. Colpi (10 × 2 μ) tenuimarginate, with tapering ends, membrane smooth.

Ora circular (diameter about 2 μ). Exine (spinules included) about 4·4 μ thick. Sexine about 3 μ thick, pertectate suprategillate, provided with pointed spinules. Tegillum undulating, differentiated into supra and infrategillar layers, each less than 0·5 μ high, supporting the tegillum of each layer. Spinules about 2 μ high with pointed solid apices, base about 2·2 μ wide made up of slender rod like elements. Nexine as it seems, consists of a homogeneous layer, inner margin smooth. There appears to be a thin distinct region about less than 0·5 μ wide between the baculate layer and the nexine.

Discussion and Summary.—The family Compositae is referred to as a Eurypalynous family because of the great variety of pollen types found in its members. As far as pollen morphology of *P. hysterophorus* is concerned, except Wodehouse's[10] casual reference, no detailed description is available in the literature surveyed so far. Taking into consideration the pollen characters, Wodehouse[10,11] supports the view expressed by Bentham and Hooker (1873) who state that phylogenetically Ambrosieae (ragweed tribe) shows a close relationship with the tribe Helianthae through Melamopodinae, a sub tribe of Helianthae including *Parthenium* and *Parthenice*.

Considering the views expressed by Wodehouse and our observations of the pollen morphology of *P. hysterophorus* in which the grains are typically 3-colporate, oblatespheroidal, spinulose, a characteristic feature of the majority of the members of Helianthae (Sunflower tribe) and the *Ambrosieae*, it can be concluded that the tribes Helianthae and