CHEMICAL EXAMINATION OF **TECOMA ARGENTEA BRITT, BUR & SEHUM.**

**Tecoma argentea**¹,², Britt, Bur & Sehum. (Fam. Bignoniaceae) is one of the important silver trumpet tree, with golden yellow flowers, commonly found in garden throughout India. The Bignoniaceae, a family of some 100 genera and 650 sp; are mainly climbing plant. It is showy tropical flowering tree with crooked trunk and corky bark to 8 m in high covering itself in the leaf-less stage with a profusion of rich-yellow trumpet flowers 5-8 cm long; after bloom appears the foliage. Leaves palmately divided into 5-7 narrow leaflets to 15 cm long and covered with silvery scales; oblong woody dark brown fruit 15 cm. long subtropic.

**Tecoma stans** is the bush commonly grown in Malayan gardens. It flowers several time a year, apparently after dry spells, and it sets a great quantity of fruit. The inflorescences do not exhaust themselves at once but last for several flowerings like those of the Angsana (Pterocarpus). It may be a temperature tree. A variety has the leaflets deeply toothed, almost pinnatifid.

**Previous Work**

As no reference was available regarding the chemical constituents of **Tecoma argentea**, Britt a detailed study of the plant was undertaken. Anti-tumour activity³ of condensed flavonoid in **Tecoma caraiba** has been studied. Tecomanine actinidine and the Me ester of 4-methoxy-trans-cinnamic acid (I) have been isolated from **Tecoma fulva**⁴. Comparative biochemistry flavonoid in the Bignoniaceae⁵ family have been worked out. Contents of strontium
Tecoma argentea Britt.
in plants of the genus *Tecoma* have been quantitatively detected. There is a good yield of lapachol in *Tecoma undulata*. Some alkaloid have been isolated from *Tecoma stans*. Insecticidal properties of *Tecoma indica* were more active. Preliminary chemical study of some Bignoniaceae family from Madagascar have been done. *Tecoma mollis* is Pharmacologically active. New glucosidic iridoids from *Tecoma genus* have been isolated. The structure of a new glucosidic iridoid the 6-0-(p-hydroxybenzoyl)-6-epiaucubin (I) isolated from the leaves of a tropical tree *T. chrysantha*.

**Present Work**

Fresh flowers of *Tecoma argentea* were obtained from the garden of National Botanical Research Institute, Lucknow. The flowers were dried crushed and extracted with hexane and 80 percent ethyl alcohol.

**Constituents of Hexane extract**

The hexane extract was concentrated and chromatographed over alumina using hexane benzene, chloroform and methanol as successive eluants.

**Compound A**

The hexane-benzene eluates on concentration and crystallization from methanol gave Liebermann Burchardt test positive shining white flakes mp. 135-136° ($\times$) D= +26° C$_{29}$H$_{50}$O. IR peak at 3450 cm$^{-1}$ (OH); Mass spectrum m/e 414 (M$^+$) with other fragmentation peaks at 399 (M-CH$_3$), 369 (M-HOH), 381 (M-CH$_3$-HOH), 329, 303, 273. Its monoacetate prepared by acetic anhydride and pyridine in the usual manner melted at 125°. The compound was identified
as β-sitosterol through mixed mp. CO-TLC and superimposable IR spectrum with an authentic sample.

Constituents of 80% ethyl alcohol extract

The extract was concentrated under reduced pressure and the concentrate partitioned using Et₂O and EtOAc. The Et₂O fraction furnished kaempferol, quercetin and luteolin while concentrate of EtOAc yielded hyperoside and cyanidin 3-rutinoside.

Compound B

The Et₂O fraction gave a shinoda test positive yellow colouring matter. Its UV absorption spectra in methanol showed peaks at 253sh, 266, 294sh, 322sh, 367. Addition of aqueous alkali showed bathochromic shift confirming the presence of hydroxyl group. On addition of NaOAc the spectrum showed bathochromic shift (266-274) which indicates the presence of 7-OH group. No appreciable shift was observed with NaOAc/H₃BO₃ which indicate absence of ortho OH group. The methanolic solution with aluminium chloride showed a bathochromic shift of 56 nm in the longer wavelength indicating the presence of another OH group in 3 position. On addition of NaOMe the longer wavelength peaks disappear and a peak at 416 nm appear indicating the presence of 3,4' OH groups. The IR spectrum showed peaks at 3450 cm⁻¹ (OH) and 1660 cm⁻¹ (CO). Mass m/e 286 (M⁺); Rf value was found to be 0.81 (BAW) and 0.04 (15 percent acetic acid). From the UV, IR and Rf data it appears the compound is a flavonoid having phenolic hydroxy group at 3,5,7 and 4' positions. From the above spectral analysis the compound was identified as
U.V. SPECTRUM OF KAEMPFEROL 71

\[
\begin{align*}
\text{MeOH} & \\
\text{MeOH + NaOMe} & \\
\text{MeOH + AlCl}_3 & \\
\text{MeOH + NaOAc} + \text{H}_3\text{BO}_3 &
\end{align*}
\]
kaempferol\textsuperscript{19}, the identity of which was further confirmed through mixed mp. CO-TLC and superimposable IR with an authentic sample.

**Compound C**

The methanolic eluate on concentration gave a shinoda test positive yellow colouring matter. The UV absorption in methanol 255, 269\textsuperscript{sh}, 301\textsuperscript{sh} and 370 nm. Addition of alkali produces a bathochromic shift. On addition of fused NaOAc, the spectrum showed a bathochromic shift (257-274) and NaOAc/H\textsubscript{3}BO\textsubscript{3} produces a shift\textsuperscript{20} of large wavelength (370-388 nm). The IR spectrum peaks at 3500 cm\textsuperscript{-1} (OH) and 1660 cm\textsuperscript{-1} (CO). The UV and IR spectrum and Rf value in different solvent system showed compound to be quercetin\textsuperscript{21}, the identity of which was finally confirmed through mixed mp. CO-TLC and superimposable IR with an authentic sample.

**Compound D**

In Et\textsubscript{2}O fraction the UV spectral in methanol showed peaks at 252, 266, 349 nm; 275, 390 nm in (MeOH)/NaOMe, 270, 380nm (MeOH/NaOAc/H\textsubscript{3}BO\textsubscript{3}. Rf values 0.66 (Forestal), 0.78 (BAW) & 0.66 (PhOH). The spot appearance in UV light was deep purple. The final identity of the compound was established as luteolin\textsuperscript{22} by CO-TLC and superimposable IR spectrum with an authentic sample.

**Compound E**

In Ethyl acetate fraction the UV spectral in methanol showed peaks in (Methanol) 257, 269\textsuperscript{sh}, 299\textsuperscript{sh}, 362; (MeOH + NaOMe) 272, 327, 409nm (AlCl\textsubscript{3}) 275, 305sh, 331sh, 438nm; (AlCl\textsubscript{3}/HCl) 268, 299, 366sh, 405nm; (NaOAc) 274,
324, 380nm. (NaOAc/H$_3$BO$_3$) 262, 298sh, 377 nm. Spot appearance in UV light deep purple and in UV/NH$_3$ is yellow colour. Rf values, 0.48 (TBA) and 0.48 (HOAc). The identity as hyperoside$^{23}$ (Quercetin 3-0-β-D-galactoside) was established through mixed mp., UV spectra and paper Co-chromatography with an authentic sample.

**Compound F**

In ethyl acetate fraction there is another spot in paper chromatography taken in Methanol showed spectral data in UV light (Methanol/HCl) 274, 523nm; (Methanol/AlCl$_3$) 275, 556nm. Rf values 0.37 (BAW); 0.25 (Bu:HCl). After hydrolysis, the UV max of aglycone, 276, 455sh, 535 nm (MeOH/HCl) 280, 460, 560 nm (Methanol/AlCl$_3$); Rf values of a glycone 0.70 (BAW); 0.49 (Ac. Acid:HCl: water) 0.22 (Formic acid: HCl : Water). The identity of the compound was confirmed by comparison with an authentic sample of cryanidin 3 rutinoside$^{24}$.

**Isolation and Identification of the Carotenoids$^{25}$**

Fresh flowers extracted in a blender with acetone and filtered. The filtrate was extracted with ether. The ether extract was dried and evaporated under reduced pressure at a temperature below 35°C. The residue was dissolved in minimum volume of ethanol to which 60% aq. KOH is added 1 ml for every 10 ml of ethanolic solution kept in dark over night in the presence of nitrogen. After dilution with water the pigments were taken back into ether and the ether extract carefully washed dried and concentrated. The pigments were separated by preparative thin layer chromatography.
Compound G

UV spectral data of compound G in (n-hexane) 443, 472, 504 nm; (chloroform) 456, 485, 520 nm. Rf values 0.01 (petrol ether : benzene 1:1) 0.13 (petrol ether : benzene 1:9) 0.15 (petroleum : benzene 1:6) compound dissolve in conc. H₂SO₄, importing indigo blue colour to the solution. On adding a solution of antimony trichloride in chloroform an intense blue colour is produced. The final identity of the compound was confirmed as lycopene²⁶ by comparison with an authentic sample.

Compound H

UV spectral data of compound H in (Hexane) 475, 504 nm. (petroleum ether) 450, 475, 505 nm (Benzene) 486, 520 nm (carbon disulphide) 503, 542nm. The appearance of a peak at 520 nm (as compared with 504 nm for lycopene) is due to the introduction of a carbonyl group in conjugation with the system of the C=C double bond. One such carbonyl thus has a more pronounced bathochromic effect than two C=C bonds. Rf values 0.06 (petroleum ether : benzene 9:1), 0.16 (CH₂Cl₂-EtOAc, 4:1). On treating a solution of compound H in chloroform with concentrated sulphuric acid the latter assumes a deep blue colouration. On treating with antimony trichloride in chloroform it gives a deep blue coloration. The final identity of the compound was confirmed as Capsanthin²⁷ by comparison with an authentic sample of Capsanthin.

Compound I

UV spectral data of the compound I (n-hexane) 425sh, 451, 482 nm (petroleum ether) 425, 448, 482 nm; (Acetone) 429, 452, 478 nm (Ethanol), 453, 483, 483 nm (Chloroform), 436, 466, 497 nm (Benzene) 435, 462, 487 nm.
Rf values are 0.49 (petroleum ether: benzene 1:1), 0.74 (petr. ether: benzene 1:9); 0.45 (petroleum ether: benzene 49:1). The final identity of the compound was confirmed as β-carotene by comparison with an authentic sample.

**Compound J**

UV spectral data of the compound J. (petroleum ether) 423, 451, 483 nm. (hexane) 426, 450, 483 nm; (methanol) 422, 450, 481 nm (Acetone) 430, 452, 479 nm (chloroform) 429, 462, 494 nm (Benzene) 433, 459, 491 nm. Rf values are 0.05 (petroleum ether: benzene 1:1) 0.24 (CH₂Cl₂-EtOAc 4:1). The final identity of the compound was confirmed as Zeaxanthin by comparison of mp, Co-paper chromatography with an authentic sample.

**Experimental**

The melting point (uncorrected) were determined by a Gallenkamp melting point apparatus, unless stated otherwise. IR spectrum were recorded in KBr, Alumina and Silica gel (BDH) were activated at 120° before use in the chromatographic column. The solvents used for chromatography were carried out on silica gel G (S. Merck).

**Chemical examination of Tecoma argentea**

The flowers were dried crushed and extracted with hexane and 80 percent ethyl alcohol.

**Constituents of Hexane extract**

The hexane extract after concentration was chromatographed over neutral alumina using hexane, benzene, chloroform and methanol and successive eluants.
\[ \beta - \text{sitosterol} \]

\[ \text{Kaempferol} \]

\[ \text{Quercetin} \]
Compound A - β-sitosterol

The hexane-benzene eluates on concentration gave a liebermann-Burchardt positive compound crystallized from methanol mp. 136°, (α) D = +28°.

Analysed for found C, 84.12; H, 11.92%
C_{29}H_{50}O calcd. C, 84.05; H, 12.07%
IR peaks at 3650 cm^{-1} (OH).

Acetate of β-sitosterol

β-sitosterol in pyridine and acetic anhydride was left for 20 hours at room temperature. After the usual processing of the reaction mixture, it afforded a monoacetate derivative crystallized from methanol mp. 128° (α) D = + 28°.

Analysed for found C, 81.65; H, 11.68%
C_{31}H_{52}O_2 calcd. C, 81.57; H, 11.40%

Constituents of 80% ethyl alcohol extract

The extract was concentrated under reduced pressure and the concentrate partitioned using Et_2O and EtOAc. The Et_2O fraction furnished kaempferol, quercetin and luteolin while concentrate of EtOAc yielded hyperoside and cyanidin-3-rutinoside.

Compound B-kaempferol

The Et_2O eluates gave a shinoda positive yellow compound.
UV data

<table>
<thead>
<tr>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
</tr>
<tr>
<td>NaOAc</td>
</tr>
<tr>
<td>NaOMe</td>
</tr>
<tr>
<td>NaOAc/H$_3$BO$_3$</td>
</tr>
<tr>
<td>AlCl$_3$</td>
</tr>
</tbody>
</table>

Compound C - Quercetin

The methanolic eluates gave a shinoda positive compound.

UV data

<table>
<thead>
<tr>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
</tr>
<tr>
<td>NaOAc</td>
</tr>
<tr>
<td>NaOAc/H$_3$BO$_3$</td>
</tr>
</tbody>
</table>

IR spectrum 3500 cm$^{-1}$ (OH), 1660 (CO).

Rf values of Quercetin in different solvent system

1. HCl:Acetic acid: water (3:30:10) 0.40
2. Butanol: acetic acid: water (4:1:5) 0.64
3. Phenol: water (3:1) 0.29
Luteolin

R = Galactose
Hyperoside (Quercetin 3-O-β-D-galactoside)

R = Glc - O - Rha
Cyanidin - 3 - rutinoside
Compound D- Luteolin

In Et₂O fraction the UV spectral data showed peaks as given below:

\[
\begin{align*}
&\text{MeOH max} & 242\text{sh}, 255, 268, 290\text{sh}, 348 \text{ nm.} \\
&\text{NaOMe max} & 265\text{sh}, 328\text{sh}, 402 \text{ nm.} \\
&\text{NaOAc max} & 270, 325, 386 \text{ nm.}
\end{align*}
\]

Rf value

1. Butanol: acetic acid: water (4:1:5) 0.77
2. 15 percent acetic acid 0.08

Spot appearance

UV light Deep purple
UV/NH₃ Yellow

Compound E - Hyperoside (Quercetin 3-0-B-D-galactoside)

In ethyl acetate eluate the UV spectral data are given under:

\[
\begin{align*}
&\text{MeOH max} & 257, 269\text{sh}, 299\text{sh}, 362 \text{ nm.} \\
&\text{MeOH + NaOMe max} & 272, 327, 409 \text{ nm.} \\
&\text{AlCl₃ max} & 275, 305\text{sh}, 331\text{sh}, 438 \text{ nm.} \\
&\text{AlCl₃/HCl max} & 268, 299 \text{ sh}, 366 \text{ sh}, 405 \text{ nm.} \\
&\text{NaOAc max} & 274, 324, 380 \text{ nm.} \\
&\text{NaOAc/H₃BO₃ max} & 262, 298\text{sh}, 377 \text{ nm.}
\end{align*}
\]
Rf values

1. TBA  0.48
2. Acetic acid  0.43

Spot Appearance

UV light  Deep purple
UV/NH$_3$  yellow

Compound F - Cyanidin-3-rutinoside

In ethyl acetate fraction there is another spot in paper chromatography showed spectral data in UV light.

\[
\begin{align*}
\text{MeOH/HCl} & \quad 274, 523 \text{ nm.} \\
\text{Methanol/AlCl$_3$} & \quad 275, 556 \text{ nm.}
\end{align*}
\]

Rf values

1. BAW  0.37
2. Bu: HCl  0.25

Hydrolysis of cyanidin-3-rutinoside

After hydrolysis of cyanidin-3-rutinoside the UV max of aglycone is given below:

\[
\begin{align*}
\text{MeOH/HCl} & \quad 276, 455\text{sh, 535 nm.} \\
\text{Methanol/AlCl$_3$} & \quad 280, 460, 560 \text{ nm.}
\end{align*}
\]
Rf. values of Aglycone

1. Butanol: acetic acid: water 0.70
2. Acetic acid: HCl: water 0.49
3. Formic acid: HCl: water 0.22

Isolation and Identification of the carotenoids

Fresh flowers extracted in a blender with acetone and filtered. The filtrate was extracted with ether. The ether extract was dried and evaporated under reduced pressure at a temperature below 35°C. The residue was dissolved in minimum volume of ethanol to which 60% aq. KOH is added 1 ml for every 10 ml of ethanolic solution kept in dark over night in the presence of nitrogen. After dilution with water the pigments were taken back into ether and the ether extract carefully washed dried and concentrated. The pigments were separated by preparative thin layer chromatography.

Compound G- Lycopene

UV spectral data of compound G in

\[ \begin{align*}
\text{n-hexane max} & \quad 446, 472, 504 \text{ nm.} \\
\text{Chloroform max} & \quad 456, 485, 520 \text{ nm.} \\
\text{Ethanol max} & \quad 443, 469, 502 \text{ nm.} \\
\text{Benzene max} & \quad 455, 487, 522 \text{ nm.} \\
\text{Acetone max} & \quad 447, 474, 506 \text{ nm.}
\end{align*} \]
Lycopene

Capsanthin

β-carotene

Zeaxanthin
Rf values

1. Petrol ether: benzene (1:1) 0.01
2. Petrol ether: benzene (1:9) 0.13
3. Petrol ether: benzene (1:6) 0.15

Colour reactions

1. Lycopene dissolves in concentrated sulphuric acid, imparting to the solution an indigo blue colour.
2. On adding a solution of antimony trichloride in chloroform to a solution of lycopene in chloroform, and intense unstable blue colour is produced.

Compound H - Capsanthin

UV spectral data of compound H

\[
\begin{align*}
\text{Hexane} & : 475, 504 \text{ nm.} \\
\text{Petroleum ether} & : 450, 475, 505 \text{ nm.} \\
\text{Benzene} & : 486, 520 \text{ nm.} \\
\text{Carbondisulphide} & : 503, 542 \text{ nm.}
\end{align*}
\]

Rf values

1. Petroleum ether: benzene (9:1) 0.06
2. Methylene chloride: ethyl acetate (4:1) 0.16

Colour reactions

1. On treating a solution of capsanthin in chloroform with concentrated sulphuric acid, the latter assumes a deep blue coloration.
2. Capsanthin gives a deep blue coloration with antimony trichloride in chloroform.

**Compound I - β-carotene**

**UV spectral data of compound I**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>λmax</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-hexane</td>
<td>425sh, 451, 482 nm.</td>
</tr>
<tr>
<td>Petroleum ether</td>
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</tr>
<tr>
<td>Acetone</td>
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</tr>
<tr>
<td>Ethanol</td>
<td>453, 483 nm.</td>
</tr>
<tr>
<td>Chloroform</td>
<td>429, 462, 494 nm.</td>
</tr>
<tr>
<td>Benzene</td>
<td>435, 462, 487 nm.</td>
</tr>
</tbody>
</table>

**Rf values**

1. Petroleum ether : benzene (1:1) 0.49
2. Petroleum ether : benzene (1:9) 0.74
3. Petroleum ether : benzene (49:1) 0.45

**Compound J - Zeaxanthin**

**UV spectral data**

<table>
<thead>
<tr>
<th>Solvent</th>
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<tr>
<td>Petroleum ether</td>
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<tr>
<td>Hexane</td>
<td>426, 450, 483 nm.</td>
</tr>
<tr>
<td>Methanol</td>
<td>422, 450, 481 nm.</td>
</tr>
</tbody>
</table>
Acetone
\[ \lambda_{\text{max}} \]
430, 452, 479 nm.

Chloroform
\[ \lambda_{\text{max}} \]
429, 462, 497 nm.

Benzene
\[ \lambda_{\text{max}} \]
433, 459, 491 nm.

Rf values
1. Petroleum ether : benzene (1:1) 0.05
2. Methylene chloride : ethyl acetate (4:1) 0.24

References