

is lacking and hence, we wish to report in this note the other chemical constituents present in the bark of *Ailanthus grandis*.

During our study for isolation of the quassinoids we initially collected the plant growing at various altitudes ranging from the foothills to a height of 5000 ft in the district of Darjeeling. It was found that mannitol and not the quassinoids was present in the bark of the plant collected from the higher altitudes above 1000 ft, whereas the sterol, lupeol,  $\alpha$ -amyrin and betulenic acid were isolated in all the cases.

### Experimental

The powdered bark of *Ailanthus grandis* was extracted with benzene in a Soxhlet apparatus for 36 h. A heavy crystalline solid appeared at the end of the extraction and was separated from the benzene extract by filtration. The residue was washed with  $\text{CHCl}_3$  and then crystallised from water-ethanol mixture to furnish crystalline solid, m.p. 165-66° that was analysed for  $\text{C}_{26}\text{H}_{44}\text{O}_6$ ; NaOAc-Ac<sub>2</sub>O acetylation of which furnished acetate, m.p. 113-120°;  $\text{C}_{32}\text{H}_{50}\text{O}_{12}$ ;  $[\alpha]_D^{25} + 25^\circ$  that was found identical with mannitol hexaacetate by m.m.p. and co-tlc with an authentic sample.

The solvent from the benzene extract was distilled under reduced pressure and the gummy residue was separated into neutral and acid parts. The neutral part was chromatographed over deactivated alumina. Elution with petroleum ether-benzene (4:1) gave a solid which on crystallisation from  $\text{CHCl}_3$ -MeOH furnished silky crystals, m.p. 213-14°;  $\text{C}_{30}\text{H}_{50}\text{O}$ ,  $M^+ 426$ ;  $[\alpha]_D^{26} + 26^\circ$ ;  $\nu_{\text{max}}$  3330, 3040, 1640 and 885  $\text{cm}^{-1}$ ; treatment with Py-Ac<sub>2</sub>O furnished an acetate, m.p. 220-22°,  $\text{C}_{32}\text{H}_{52}\text{O}_2$ ,  $[\alpha]_D^{48} + 48^\circ$ , identical with lupenyl acetate<sup>3</sup>.

The chromatogram on further elution with petroleum ether-benzene (3:2) yielded a solid, m.p. 186-88°,  $\text{C}_{30}\text{H}_{50}\text{O}$ ,  $M^+ 426$ ;  $[\alpha]_D^{90} + 90^\circ$ ; acetylation (Py-Ac<sub>2</sub>O) gave an acetate, m.p. 225-26°,  $\text{C}_{32}\text{H}_{52}\text{O}_2$ ,  $M^+ 468$ , identical (m.m.p., co-ir and co-tlc) with an authentic sample of  $\alpha$ -amyrin acetate<sup>3</sup>. The column on further elution with petroleum ether-benzene (2:3) yielded a crystalline solid, m.p. 136-37°,  $\text{C}_{29}\text{H}_{50}\text{O}$ ;  $[\alpha]_D^{34} - 34^\circ$  which was identified as  $\beta$ -sitosterol by direct comparison with an authentic sample (m.m.p., co-tlc and co-ir).

The acid part was esterified ( $\text{CH}_3\text{N}_2$ ) and the solid chromatographed over deactivated alumina. The solid obtained on elution with petroleum ether-benzene (3:2) was crystallised to furnish a solid, m.p. 222-21°;  $\text{C}_{32}\text{H}_{50}\text{O}_3$ ,  $M^+ 470$ ;  $[\alpha]_D^{47} + 4^\circ$ ;  $\nu_{\text{max}}$  3560, 3140, 1715, 1660 and 885  $\text{cm}^{-1}$ . The solid on acetylation (Py-Ac<sub>2</sub>O) yielded the ester acetate, m.p. 202-203°;  $\text{C}_{34}\text{H}_{52}\text{O}_4$ ,  $M^+ 512$ ;  $[\alpha]_D^{17} + 17^\circ$  which was found identical (m.m.p., co-ir and co-tlc) with an authentic sample of acetyl methyl-betulanate<sup>4</sup>.

### Acknowledgement

The authors thank E. I. P. W., Calcutta, C.S.I.R. and U.G.C., New Delhi, for financial assistances (to D. R. M., B. S. and A. N., respectively), and also thank Dr. B. C. Das, Gif-sur-Yvette, France, and Dr. S. K. Sengupta, E. I. P. W., Calcutta, for some of the measurements.

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### Further Constituents of *Adenia cissampeloides*

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Manuscript received 12 October 1984, revised 20 March 1985,  
accepted 11 September 1985

*ADENIA cissampeloides* (Passifloraceae) is a climber that can grow to 12 cm in diameter. It grows in humid areas of West Africa. Medicinally, it is used in Southern Nigeria as a remedy for lumbago. In Ghana, the leaves are rubbed on the breasts after child birth to promote lactation. It is used in Southern Nigeria and Ghana as a powerful fish poison (as with *A. lobata*). In a previous paper<sup>1</sup>, cyanogenesis and the occurrence of tetraphyllin B, which readily hydrolyses to 4-hydroxy-2-cyclopentenone with liberation of hydrogen cyanide gas, was reported. The paper also discussed the isolation of friedelan-3 $\beta$ -ol, friedelan-21-one and  $\beta$ -sitosterol from the stem. The present paper which concentrates on the more polar constituents of this species reports on the isolation of mannitol sucrose and sodium chloride.

### Experimental

*Adenia cissampeloides* was collected from Ojoo in Ibadan and identified by the Federal Department of Forestry Research where a voucher specimen No. FHI 91470 is deposited.

**Isolation of sucrose:** Fresh *A. cissampeloides* stem (1 kg) was defatted with light petroleum and extracted with methanol-acetone mixture (1:1) in cold for 48 h. This was concentrated under reduced pressure and partitioned between ether and water. The water fraction was rotavapoured at 30° to a syrup and chromatographed over deactivated silica. Ether-methanol (1:1) eluted a reddish yellow syrup which on rechromatography afforded a solid, recrystallised from methanol (162 mg), m.p. 181-183°.

This was identified as sucrose; octaacetate, m.p. 68-70°.

Wet methanol eluted a solid (850 mg) identified as sodium chloride.

**Isolation of D-mannitol:** *Adenia cissampeloides* stem collected in April from Ojoo, was crushed and sun-dried for 4 days. The dry plant material (4.5 kg) was soxhlet-extracted with ethanol for 26 h. The ethanol concentrate was extracted several times with chloroform leaving a residual thick syrup which on standing overnight gave some solids, recrystallised from ethanol as white crystals (13.8 g), m.p. 167-69.5°, identified as D-mannitol<sup>1</sup>.

D-Mannitol (19 mg) was acetylated in the usual way using pyridine and acetic anhydride to give the hexaacetate (32 mg) which crystallised as white plates from ethanol, m.p. 122-124°. Benzoylation of the D-mannitol (45 mg) in the usual way using benzoyl chloride and pyridine afforded the hexabenzoylate as white needles from methanol (171 mg), m.p. 154-156°.

D-Mannitol (290 mg) was suspended in dry and redistilled acetone (20 cm<sup>3</sup>). Concentrated H<sub>2</sub>SO<sub>4</sub> (2 drops) was added and the mixture stirred at room temperature for 3 days. Sodium bicarbonate was added until the mixture became basic to litmus paper. Water (40 cm<sup>3</sup>) was added and the mixture extracted with ether (4 × 100 cm<sup>3</sup>). The combined ether extract was dried over anhydrous sodium sulphate and distilled to give D-mannitol tri-O-isopropylidene as large white needles, m.p. 67-69°.

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#### Biflavonoid from the Family Salicaceae

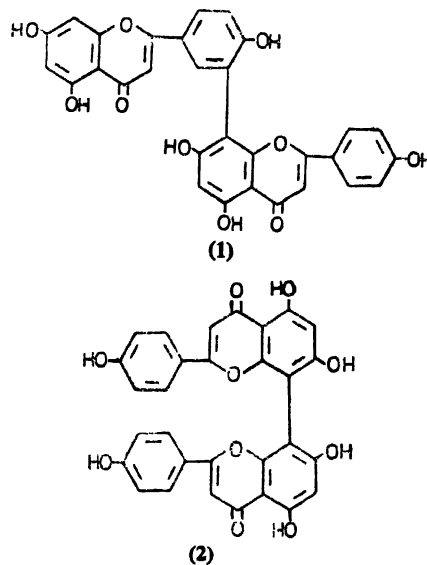
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Manuscript received 29 October 1984, revised 16 August 1985,  
accepted 11 September 1985

THE genus *Salix*<sup>1</sup> (Fam.: Salicaceae) comprising about 300 species, is distributed throughout the northern hemisphere with a few into the southern hemisphere. *Salix alba* Linn.<sup>2</sup> (Sub. sp.: *S. coerulea*, known as cricket bat willow) owes its importance both from economic and medicinal points of view. Medicinally, it is used in haemoptysis, acute rheumatism, gout fever, diarrhoea and dysentery. *S. alba* and *S. fragilis* leaves (procured from Manali, Himachal Pradesh) were examined for their biflavonoid contents and found to contain two apigenin dimers with linkages [I-3', II-8] (1) and [I-8, II-8] (2) alongwith apigenin. The presence of

biflavones is being reported for the first time in Salicaceae family and their occurrence in *Salix* species may serve as a useful taxonomic marker.



#### Experimental

Dried and powdered leaves of *Salix alba* (2.5 kg) after treatment with petroleum ether (b.p. 60-80°) and benzene were exhaustively extracted with acetone. The dark viscous mass obtained on concentration was successively digested with petroleum ether, benzene, chloroform and water. The residue was refluxed with ethyl acetate for 48 h, then filtered and filtrate evaporated to give a dark brown solid. It was chromatographed on Si-gel using organic solvents in increasing order of polarity. The flavonoid<sup>3</sup> fraction obtained from C<sub>6</sub>H<sub>6</sub>-EtOAc (7:3) eluates gave an elongated spot on tlc (methylated product exhibited two distinct spots) and this on further chromatography (Si-gel, C<sub>6</sub>H<sub>6</sub>-EtOAc-AcOH = 8:5:2) yielded compounds A and B. The fraction eluted with C<sub>6</sub>H<sub>6</sub>-EtOAc (8:2) afforded compound C.

**Compound A:** It was crystallised from MeOH as yellow cubes (300 mg), m.p. 320°, R<sub>f</sub> 0.18 (Si-gel G, benzene-pyridine-formic acid (BPF) = 36:9:5), M<sup>+</sup> 538 (C<sub>30</sub>H<sub>18</sub>O<sub>10</sub>); λ<sub>max</sub> (EtOH) 272 and 335 nm; ν<sub>max</sub> (KBr) 3400 (OH) and 1635 cm<sup>-1</sup> (flavone CO). Methylation with Me<sub>2</sub>SO<sub>4</sub>-K<sub>2</sub>CO<sub>3</sub> in dry acetone and crystallisation (CHCl<sub>3</sub>-MeOH) afforded a methyl ether as colourless needles, m.p. 174°, R<sub>f</sub> 0.40 (Si-gel G, BPF = 36:9:5), M<sup>+</sup> 622 (C<sub>38</sub>H<sub>30</sub>O<sub>10</sub>). R<sub>f</sub>, m.p. and shade in uv light indicated it to be amentoflavone hexamethyl ether<sup>4,5</sup>. On acetylation with Ac<sub>2</sub>O-Py it gave an acetate, colourless needles from CHCl<sub>3</sub>-MeOH, m.p. 237°. Pmr spectral data of the methyl ether and acetate were found identical with those of hexamethyl ether and hexaacetate of amentoflavone<sup>5,6</sup>. The compound was, therefore, characterised as I-4', II-4', I-5, II-5, I-7, II-7 hexahydroxy [I-3, II-8] biflavone (amentoflavone) (1).