Molekül-Ions soweit erhöht, daß es meist in sehr hohen Ausbeuten auftritt. Die Zerfallssignale für das Skelett sind dagegen praktisch verschwunden. Charakteristisch für den Zerfall der 2,3-Dimethoxy-6a,12a-dehydrorotenoide scheint das Ion M^+-47 (3) zu sein, dessen Bildung in der im Formelbild wiedergegebnen Weise diskutiert werden kann. Das im ersten Abbauschritt auftretende Ion M^+-15 (100% rel. Int. 2 bzw 4) resultiert bei 1 zum überwiegenden Teil aus dem Übergang des Molekül-Ions in das äußerst stabile Pyrylium-Ion 4, dessen Auftreten ein wichtiges Indiz für die Anwesenheit einer Dimethylchromen-Partialstruktur ist.

Infolge der im Molekül enthaltenen 6a,12a-Doppelbindung sind das H-1 und die 12-CO-Gruppe nahezu koplanar angeordnet und führen zu der für diesen Rotenoidtyp charakteristischen negativen Abschirmung (δ = 8·25 ppm) [11].

EXPERIMENTELLES

Über die Aufarbeitung der Samen sh. [8]. Die mit CH_2Cl_2–MeOH (9:1) eluierten Sc-Fraktionen hinterließen nach Abdampfen des Lösungsmittels einen gelblichen, wachsartigen Rückstand, aus dem sich durch Umkristallisieren aus Methanol ein kristalliner Niederschlag gewinnen ließ, der sich dc als Gemisch von mindestens vier Bestandteilen zu erkennen gab. Die weitere Reinigung gelang durch präp. Dc [Kieselgel; Benzol–EtOAc (9:1)]. Die Hauptkomponente (1) wurde aus $CHCl_3$–MeOH umkristallisiert. Schm. 263–267°. λ_{max}^{MeOH}: 277 *sh*, 328, 312, 282, 274 *u.* 255 nm; log ϵ: (3·31), 3·88, 3·87, 4·28, 4·28 *u.* 4·22. ν_{max}^{KBr}: 1660 (C=O), 1615, 1575, 1510 (arom C=C) usw. NMR (100 MHz. $DCCl_3$, δ, ppm; 1·45 (6H *s*; –C–(C<u>H</u>$_3$)$_2$); 3·85 *u.* 3·92 (2 × 3H *s*; C<u>H</u>$_3$O–); 4·95 (2H *s*; O–C<u>H</u>$_2$); zentr. 5·5 [1H *d*; = C<u>H</u>–(*J* 10 Hz)]; 6·25 (1H *s*; H-4); 6·55 (1H *s*; H-10); zentr. 6·6 [1H *d*; –C<u>H</u>= (*J* 10 Hz)]; 8·25 (1H *d*; H-1) *u.* 13·0 (1H *s*; O<u>H</u>...OC).

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VOLUBILININ, A NEW ISOFLAVONE-*C*-GLYCOSIDE FROM *DALBERGIA VOLUBILIS* FLOWERS

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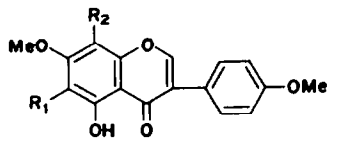
Key Word Index—*Dalbergia volubilis*; Leguminosae; isoflavone *C*-glycoside; tectorigenin 4'-methylether 8-*C*-glucoside.

The study of *Dalbergia* species has provided a large number of neoflavonoids and isoflavonoids of which the *C*-glycosides of isoflavones form the most recent group [1]. Paniculatin, dalpanin, dalpanitin, and prunetin-8-*C*-glucoside [2–5] have been isolated from *Dalbergia paniculata* whereas *D. volubilis* has yielded volubilin (1) [6] and isovolubilin (2) [7], the first isoflavone-*C*-rhamnosides reported in nature. The isolation and structure of another minor isoflavone-*C*-glycoside (3) from *Dalbergia volubilis* flowers is reported in this note.

The new compound volubilinin, mp 159–61°, analysed for $C_{23}H_{24}O_{11}$, contained 2 methoxyls as indicated by NMR of volubilinin acetate and micro Zeisel's methoxyl estimation.

The usual colour reactions along with the UV spectrum in the presence of standard reagents indicated that it is an isoflavone glycoside with free hydroxyls at positions 5 and 7. Volubilinin was stable to acid hydrolysis under drastic conditions [8] and hence is a *C*-glycoside. In the IR it showed the characteristic multiple absorption in the aromatic region of the flavonoids (1660–1400 cm^{-1}) in addition to the hydroxyl band (3500 cm^{-1}) and strong absorption at 832 cm^{-1} indicating the presence of a 1 : 4-disubstituted benzenoid systems and weak bands at 1010 and 1035 cm^{-1} which are characteristic of a *C*-glucoside [9].



(1) R_1 = H; R_2 = Rha
(2) R_1 = Rha; R_2 = H

Volubilinin with HI gave 5,6,7,4'-tetrahydroxyisoflavone. Since the glycoside contained free hydroxyls at 5 and 7 positions, it was concluded that the two methoxyls could only be at positions 6 and 4', and the UV data agreed with this [10, 11]. The structure of the aglycone

of volubilinin as 5,7-dihydroxy-6, 4'-dimethoxyisoflavone is confirmed by the NMR spectrum of volubilinin acetate and its mass spectrum.

The sugar moiety was found to be pyranose by mild periodate oxidation followed by reduction with borohydride and hydrolysis with HCl when glycerol was detected by PC [12] and by the identification of formic acid in the periodate oxidation product [13]. Volubilinin was thus a *C*-glucoside of tectorigenin-4'-methyl ether. The position of the sugar unit was established by NMR spectrum of its acetate. It displayed a typical A_2B_2 system by showing two doublets at δ6·75(*J* 9 Hz) and δ7·2(*J* 9 Hz) due to the presence of 2', 6', and 3', 5' protons of the B ring of the isoflavone nucleus. The signals at δ 3·9 and δ 4·2 could be attributed to the methoxyls at 4' and 6 positions respectively. There is no proton that could be ascribed to the ring-A of the isoflavone nucleus and hence the sugar moiety was present at position 8. This is confirmed by the signal at δ 1·75 due to 2''-acetoxyl which agrees with that for flavonoid-8-*C*-glucosides [14] and comes upfield due to the shielding effect of ring-A [15, 16]. The sugar moiety at position 8 is also confirmed by the alkaline hydrogen peroxide oxidation of volubilinin methyl ether acetate when anisic acid was obtained. The signal at δ 5·2 is due to the C-1'' proton of the glucose moiety and the signals appearing at δ 2·10(integrating for 6 protons), 2·05, 2·30 and 2·45 (each integrating for 3 protons) are assigned to 3'', 4'', 6'', 7 and 5-acetoxyls respectively. The one proton signal at δ 7·9 is due to the proton at position 2 of the isoflavone. The NMR pattern was very similar to that of well established 8-*C*-glucosides.

The structure of volubilinin as 8-*C*-glucoside of tectorigenin-4'-methyl ether was further confirmed by its mass spectrum taken by direct insertion technique, the prominent peaks being *m/e* 55, 69, 132, 195, 314 and 327. Of these, peaks at *m/e* 327 and 195 are important; the former shows that it is a *C*-glycoside [17] and the latter that it is present in the A ring in the available 8-position and not in the side phenyl. Though the usual ferric chloride oxidation of the compound could not be done for lack of material, the above NMR and MS data agreed with glucose or galactose as the sugar involved. The former is more likely because it is more common.

The pyranose structure of the sugar unit was also proved by the periodate oxidation under mild conditions of volubilinin methyl ether, one mol of which consumed 2·6 mol of the periodate [12].

EXPERIMENTAL

Chromatograms were developed in the usual solvents for isoflavonoids and then viewed in UV light when yellow fluorescent spots were observed. The spots were also located by spraying with 10% H_2SO_4 followed by heating the plates at 110° for a few minutes and by the exposure of the chromatographic plates to iodine vapours. UV spectra were recorded in MeOH, NMR on a 60 Mc instrument and the mass spectrum by direct insertion technique. NMR values are recorded in the δ scale.

Isolation of volubilinin. The alcohol extract [6] of the flowers of *Dalbergia volubilis* was concentrated and this was Soxhleted with dry Et$_2$O for 24 hr. The ether extract yielded biochanin-A, identified by comparison with an authentic sample (mmp, Co-IR, UV, CO-TLC and acetate). The remaining alcohol extract was subjected 2× to column chromatography whereby a cream coloured solid was obtained which could be resolved into 2 bands by PC on 3 MM paper in *n*-BuOH–HOAc–H_2O (4:1:5). Band I was purified by preparative TLC whereby volubilinin was obtained. Band II on preparative TLC gave volubilin and isovolubinin [6]. Volubilinin (isolated from band I) crystallised from EtOAc–MeOH as colourless plates, mp 159–61°. (Found: C, 57·8; H, 5·4; OMe, 12·7; $C_{23}H_{24}O_{11}$ requires C, 58·0; H, 5·0; OMe, 13·0%). λ_{max}^{MeOH} 269, 340; with $AlCl_3$, 277; with NaOAc, 273, 345; with NaOAc + H_3BO_3, 273, 340; with NaOMe, 270, 385 nm; ν_{max}^{KBr} 3500, 1652, 1600, 1556, 1508, 1428, 1440, 1335, 1245, 1170, 1078, 1020, 990, 892, 831 cm^{-1}; MS: Prominent peaks of considerable intensities were recorded at 327, 326, 314, 313, 300, 270, 205, 195, 163, 154, 153, 132, 92, 85, 78, 69, 66, 57, 55, 43 with a base peak at *m/e* 327. No change was noticed when volubilinin was boiled with acid or subjected to enzymatic hydrolysis. The methyl ether crystallised from a EtOAc–light petrol as colourless prisms, mp 174–5°. ν_{max}^{KBr} 3425, 1648, 1610, 1587, 1515, 1493, 1370, 1250, 1175, 1087, 1075, 1031, 1015, 926, 855, 826, 813 cm^{-1}. λ_{max}^{MeOH} 270, 345 (*sh*) nm. The acetate crystallized from EtOAc–light petroleum mp 208–10°; λ_{max}^{MeOH} 265 nm; ν_{max}^{KBr} 1750, 1645, 1608, 1502, 1420, 1360, 1242, 1220, 1175, 1080, 1035, 940, 920, 870, 850, 845 cm^{-1}. NMR: (δ): 7·90(*s*, 2-H), 7·20(*d*, *J* 9 HZ, 2',6'-H), 6·75(*d*, *J* 9 Hz, 3',5'-H), 3·90(*s*, 4'-OCH$_3$), 4·20(*s*, 6-OCH$_3$), 2·45(*s*, 5-OCOCH$_3$), 2·30(*s*, 7-OCOCH$_3$), 2·10(*s*, 3'',4''-OCOCH$_3$) 2·05(*s*, 6''-OCOCH$_3$), 1·75(*s*, 2''-OCOCH$_3$), 5·2(b, 1''-H).

Oxidation of methyl ether acetate. To the methyl ether acetate (mp 196°, prepd. by acetylating the dimethyl ether (15 mg) dissolved in KOH (7·5 ml) was added H_2O_2 (30%, 0·7 ml). The mixture was kept at 45° (2 hr), cooled, and poured into ice H_2O (5 ml) and the soln acidified with ice cold HCl and extracted with Et$_2$O. The Et$_2$O extract was washed with H_2O and extracted with aq sodium bicarbonate. The $NaHCO_3$ extract was acidified with HCl, extracted with ether and the ether evaporated. The residue was identified as anisic acid (mmp and Co-TLC).

Action of HI on volubilinin. The glycoside (40 mg), phenol (250 mg) and HI (1·0 ml, *d*, 1·7) were gently refluxed at 137° for 4 hr. The product was identified as 5,6,7,4'-tetrahydroxyisoflavone by comparison with an authentic sample obtained by a similar treatment of tectorigenin dibenzyl ether, mp 284–7°, (mmp undepressed [18], Co-TLC,).

Periodate oxidation of volubilinin methyl ether. (i) A mixture of volubilinin methyl ether (3 mg) in aq EtOH (0·2 ml) and $NaIO_4$ (2·0 mg) was maintained for 4 hr at room temp. The mixture was worked up as in the case of volubilin [6] and the product chromatographed on paper in BuOH-pyr.-H_2O. The product form volubilinin was the same as that from glucose on similar treatment. (ii) Volubilinin methyl ether (15 mg) was dissolved in MeOH (10 ml), an aq soln of $NaIO_4$ (0·05N, 15 ml) added and the mixture allowed to stand overnight in the dark. Na_2CO_3 (2g) was then added followed by sodium arsenite soln (0·05N, 25 ml). The resultant mixture was titrated against iodine solution (0·05N) using starch as the indicator. One mole of volubilinin methyl ether consumed 2·6 mol of the periodate.

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CHITRANONE—A NEW BINAPHTHAQUINONE FROM *PLUMBAGO ZEYLANICA*

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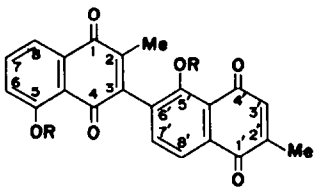
Key Word Index—*Plumbago zeylanica*; Plumbaginaceae; Binaphthaquinones; chitranone—new biplumbagin; elliptinone; droserone; sitosterol.

The isolation of six pigments (PZ 1–PZ 6) from the roots of *Plumbago zeylanica* (Telugu—Chitramulam) and identification of three of these as plumbagin (2-methyl-5-hydroxy-1,4-naphthaquinone, PZ 4), 3-chloroplumbagin (PZ 3) and 3,3'-biplumbagin (PZ 6) has been reported earlier [1]. From the same roots five more pigments (PZ 7–PZ 11) have been isolated now by column chromatography over silica gel. PZ 10 and PZ 11 have been shown to be elliptinone and droserone by direct comparison with authentic samples.

PZ 8 is a new biplumbagin; it has been named chitranone, orange crystalline solid, mp 118–120° (Kofler Block) and is a juglone derivative from its colour reactions, UV and IR spectra; its MW 374·0788 (calc: 374·0790) corresponds to $C_{22}H_{14}O_6$; peaks at *m/e* 120 (11%) and *m/e* 92 (19%) show that the methyl group is not present in the benzene ring [2]; it is, therefore, probably a biplumbagin.

In the NMR spectrum, the two methyl groups are well separated one giving rise to a singlet at 2·06 and the other to a narrow doublet (*J* 1·5 Hz) at 2·22 ppm, coupled to a vinylic proton which appears as a quartet at 6·86 (*J* 1·5 Hz); as no other vinylic proton is seen, it can be concluded that the linkage is between C-3 and C-6' (**1**) or C-3 and C-8'. The singlets at 11·96 and 12·30 (exchangeable with D_2O) are assigned to the two peri hydroxyl groups.

Chitranone gives a dimethyl ether with methyl iodide and silver oxide. In its NMR spectrum also, the two methyl groups are well separated (1·98, *s*, and 2·20 *d*, *J* 1·5 Hz) and only one vinylic proton is seen as a quartet at 6·80 (*J* 1·5 Hz). The two methoxyl groups absorb at 3·99 and 3·74. The shielded methoxyl group at 3·74 must be in the *ortho* position to the linkage between the two moieties (cf. diospyrin dimethyl ether [3], $OC\underline{H}_3$, 3·71; 4·04). In contrast, the two methoxyls in neodiospyrin dimethyl ether [4], which has a 3,8'-linkage, appear at 3·99 and 3·91 as no shielding is possible. Chitranone dimethyl ether should, therefore, be 3,6'-biplumbagin dimethyl ether (**2**) and consequently, chitranone should



(**1**) R = H
(**2**) R = Me

be 3,6'-biplumbagin (**1**) (C-3 to C-7' linkage and dimeric structures involving 3-methyljuglone are ruled out on biogenetic grounds).

EXPERIMENTAL

NMR spectra are reported in $CDCl_3$ soln at 60 MHz with TMS as internal standard in δ values. Si gel (E. Merck, > 0·08 mm, dia) was used for column chromatography and elution was carried out under N_2 pressure. Si gel G was used for TLC. Mp's are uncorrected.

Source and identification of plant material. Roots of *Plumbago zeylanica* were collected near Vegeswarapuram, West Godavary District, Andhra Pradesh and identified by Dr. N. Ramayya, Department of Botany, Osmania University, Hyderabad.

Isolation of quinones from the roots of Plumbago zeylanica. 18 kg powdered air-dried roots were extracted with $CHCl_3$ in a Soxhlet in lots of 500 g for 30 hr. Combined extracts were concentrated under red pres to 640 ml and fractionated