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ISOFLAVONOID GLYCOSIDES OF *DALBERGIA PANICULATA*

THE CONSTITUTIONS OF DALPANITIN AND DALPATIN

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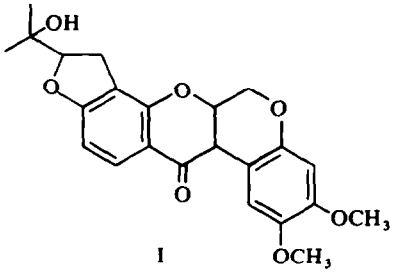
Abstract—Further examination of the extractives of the seeds of *Dalbergia paniculata* has yielded three new isoflavonoid glycosides dalpanin, dalpanitin and dalpatin. The elucidation of the structures of the latter two compounds is presented.

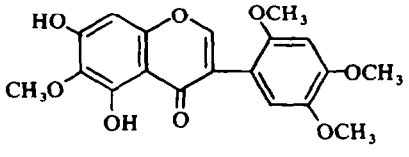
Dalpanitin is shown as 8-C-β-D-glucopyranosyl-3'-methoxy-4',5,7-trihydroxyisoflavone (VII) and dalpatin as 2',6-dimethoxy-4',5'-methylenedioxy-7-glucosyloxyisoflavone (XX) by spectral and chemical evidence.

WE HAVE recently reported the presence of a rotenoid,[1] dalpanol (I) and the isoflavone,[2] caviunin (II) from the benzene extractives of the defatted ripe seeds of *Dalbergia paniculata*. Chemical investigations[3] on the bark of this plant have shown the presence of formononetin (III), biochanin-A (IV) and paniculatin (V) together with β-sitosterol.

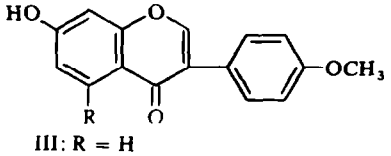
From the cold methanolic extract of the seeds of *D. paniculata* we have now isolated three crystalline compounds by column chromatography using alumina and polyamide. One of these compounds, m.p. 267–268° (dec) with molecular formula $C_{26}H_{30}O_{12}$ (yield 0·014%) is identical with dalpanin[4] which has been isolated as a



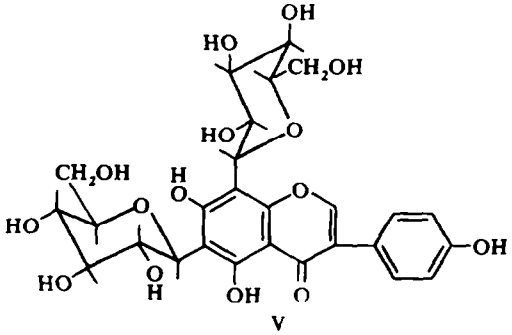
I



II



III: R = H
IV: R = OH



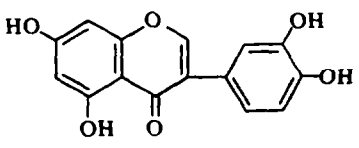
V

major constituent (yield 0·47%) from the flowers of *D. paniculata*. The elucidation of the constitutions of the other two compounds designated as dalpanitin and dalpatin is now discussed.

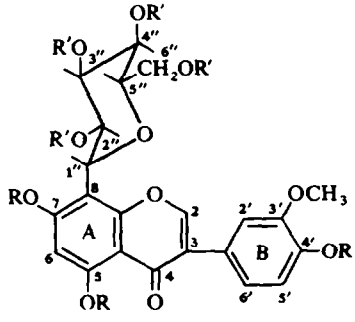
Dalpanitin is obtained as colourless rectangular plates (yield 0·055%), m.p. 213–214° (dec), $[\alpha]_D$ + 35° and has the molecular formula $C_{21}H_{19}O_{10}(OCH_3)$. It gives a positive Molisch test and a green ferric colour. On reduction with sodium amalgam followed by acidification with conc hydrochloric acid, dalpanitin gives a pink colour. The colour reactions, the chromatographic behaviour and UV spectrum [λ_{max}: 218 nm (log ε 4·43), 265 nm (log ε 4·52), 290 (infl.) nm (log ε 4·08)] indicate that dalpanitin is an isoflavone glycoside.

Dalpanitin fails to yield any sugar even on prolonged acid hydrolysis (5 hr) and this suggests that it is a C-glycosyl compound which is supported by the presence of two bands at 1010 and 1038 cm^{-1} in the IR spectrum.[5] Aqueous ferric chloride oxidation[6] of dalpanitin produces glucose. The formation of glycerol[7] when the borohydride reduced product of periodate oxidised dalpanitin is subjected to acid hydrolysis shows the pyranose form of the glucosyl residue.

When dalpanitin is boiled with hydriodic acid in phenol, demethylation as well as decomposition of the sugar moiety occur and the resulting product is identified as orobol (VI) by m.p., mmp, co-chromatography and superimposable IR spectra. The formation of orobol shows the presence of 3′,4′,5,7-tetraoxygenation pattern in dalpanitin. The 3′,4′-oxygenation in the B-ring is further confirmed by the formation



VI



VII: R = R′ = H
VIII: R = CH_3; R′ = CH_3CO
IX: R = R′ = CH_3CO

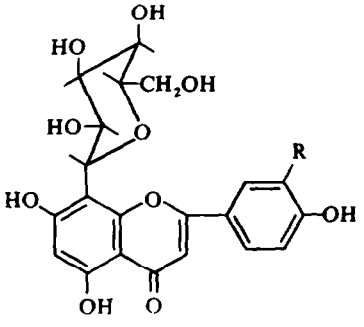
of veratric acid when the acetate of dalpanitin methyl ether (VIII) is subjected to alkaline hydrogen peroxide oxidation.

In the UV spectrum of dalpanitin the absorption maximum at 265 nm suffers bathochromic shifts of 12 and 14 nm with aluminium chloride and sodium acetate respectively, indicating the presence of free hydroxyls at 5- and 7-positions.[8] Thus, the OMe group is present only in the side phenyl ring either at 3′- or 4′-position. That it is at the 3′-position is revealed by the formation of vanillic acid when the hepta-acetate of dalpanitin (IX) [m.p. 130–131°, $C_{36}H_{36}O_{18}$] is oxidised by potassium permanganate.

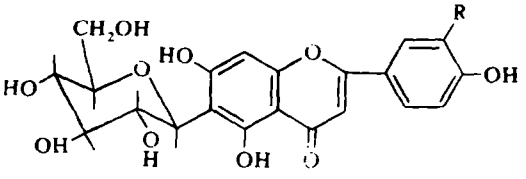
Oxidative degradations leading to the formation of veratric and vanillic acids clearly show that the side phenyl ring is devoid of the C-glucosyl residue. Hence, either 6- or 8-position of the condensed benzene ring is involved in the C-glucosyla-

tion. The NMR spectrum of dalpanitin shows that it is a 8-C-glucoside, establishing its structure as 8-C-β-D-glucopyranosyl-3'-methoxy-4',5,7-trihydroxyisoflavone (VII).

Two one-proton singlets at τ 1·57[9] and 3·68 are assigned to the protons at 2- and 6-positions respectively. The three B-ring protons are shown up as a typical ABX splitting pattern: τ 3·00 (d, J = 2 Hz, 2'-H), τ 3·17 (d, J = 8·5 Hz, 5'-H) and τ 2·89 (q, J = 2 and 8·5 Hz, 6'-H). A 3-proton singlet at τ 6·20 accounts for the presence of one OMe group. The signals over the range τ 4·80–6·80 integrate roughly for the eleven protons of the glucosyl residue. In this range, a one-proton doublet centered at τ 5·30 (J = 10 Hz) is assigned to the proton at 1''-position. The large coupling constant is due to a *trans*-diaxial coupling with the proton at 2''-position and indicates a C-β-D-glucopyranosyl residue.[10] Two exchangeable broad singlets at τ 0·86 and −0·68 represent OH protons at the 4'- and 7-positions respectively and a sharp exchangeable singlet at τ −3·21 is assigned to the chelated OH at the 5-position. The chemical shifts of the A-ring aromatic proton (τ 3·68) and 5-OH proton (τ −3·21) indicate the glucosyl residue to be at 8-position as in vitexin (X) and orientin (XII) [Table 1].



X: R = H
XII: R = OH



XI: R = H
XIII: R = OH

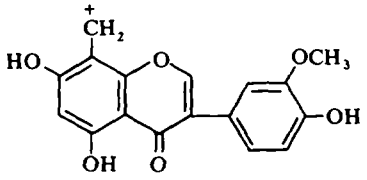
TABLE 1. CHEMICAL SHIFTS (τ) USING DMSO AS SOLVENT

Compound	6-H	8-H	5-OH
Dalpanitin (VII)	3·68	—	−3·21
Vitexin (X)[11]	3·72	—	−3·20
Orientin (XII)[12]	3·70	—	−3·20
Isovitexin (XI)[13]	—	3·44	−3·60
Isoorientin (XIII)[12]	—	3·46	−3·62

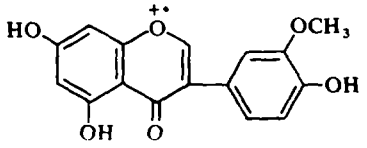
This is further confirmed by the chemical shifts[13, 14] of the aliphatic acetate signals in the NMR spectrum of dalpanitin hepta-acetate (IX) [τ 8·24 (s, 2''-OAc), τ 7·97 (s, 6''-OAc) and τ 7·92 (s, 3''-OAc and 4''-OAc)]. Dalpanitin shows negative Gibbs reaction[15] confirming the presence of the glucosyl residue at 8-position and the methoxyl in the B-ring at 3'-position.

The mass spectrum of dalpanitin taken by direct insertion technique shows the fragment ions *m/e* 444–300 corresponding to fission in the sugar residue[16] attached to the isoflavone nucleus. Significant ions at *m/e* 313, 300, 165 and 148 are represented by structures XIV, XV, XVI and XVII respectively. It is interesting to note that in the

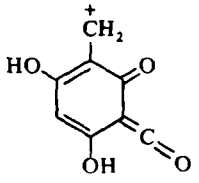
case of dalpanitin, M-18 is the base peak, while in C-glycosylated flavones[16] it is found to be M-149.



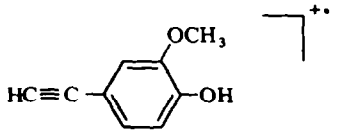
XIV (*m/e* 313)



XV (*m/e* 300)



XVI (*m/e* 165)



XVII (*m/e* 148)

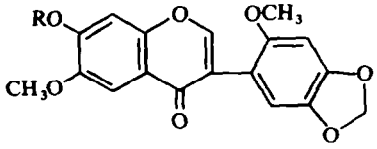
Dalpatin. The amount of dalpatin, [m.p. 261–263° (dec)], available for structural study is very small (yield 0·0014%) and hence the elucidation of its structure rests mainly on spectroscopic evidence and conversion to a known isoflavone. The compound gives positive Molisch test, negative ferric reaction and a pink colour with sodium amalgam and hydrochloric acid, suggesting that dalpatin is an isoflavone glycoside. Its UV spectrum (Table 2) is very similar to that of milldurone (XVIII)[17,18] which has an unusually high intensity absorption maximum above 300 nm, suggesting similar oxygenation pattern in dalpatin. As in the case of milldurone the IR spectrum of dalpatin shows strong bands at 1645 cm^{-1} (conjugated carbonyl), 940 and 1042 cm^{-1} (methylenedioxy group). The presence of the latter functional group is further supported by the formation of bluish green colour in the Labat test.[19]

TABLE 2

Compound	λ_{max}(MeOH)
Milldurone (XVIII)	256 nm (log ε 4·14), 312 nm (log ε 4·22)[17]
	257 nm (log ε 4·22), 312 nm (log ε 4·29)[18]
Aglycone of dalpatin (XIX)	256 nm (log ε 4·10), 312 nm (log ε 4·16)
Dalpatin (XX)	256 nm (log ε 4·34), 312 nm (log ε 4·43)

Acid hydrolysis of dalpatin affords glucose (identified by paper chromatography) and an aglycone (m.p. 251°) which on methylation by diazomethane produces a compound (m.p. 234–236°) shown to be identical with milldurone (mmp, UV and IR spectra).

The NMR spectrum of dalpatin shows the presence of two methoxyls (τ 6·10, 6·32) and one methylenedioxy group (τ 3·97). Methylation of its aglycone resulting in the formation of milldurone requires that the aglycone should have one free OH group at 2′- or 6- or 7-position. The slightly upfield signal at τ 6·32 shows that a methoxyl



XVIII: R = CH_3
XIX: R = H
XX: R = Glucosyl

group is present at 2'-position,[18] (also indicated by the mass spectrum) leaving either 6- or 7-position to have the free hydroxyl group. Bathochromic shift of 36 nm by addition of sodium acetate in its UV spectrum and structural analysis of the naturally occurring 6,7-dioxygenated isoflavones favour the structure (XIX) for the aglycone. Thus, the structure of dalpatin is derived as 2',6-dimethoxy-4',5'-methylenedioxy-7-glucosyloxyisoflavone (XX).

The mass spectrum of dalpatin shows the molecular ion (*m/e* 342) corresponding to its aglycone (as expected for O-glycosidic compounds[16]) and the fragmentation pattern agrees with that exhibited by 2'-methoxyisoflavones.[18]

Puerarin, puerarin mono-O-xyloside,[20] di-O-acetyl puerarin[21] and paniculatin[3] are the only isoflavone-C-glycosides so far reported. While the first three of these compounds are derivatives of 4',7-dihydroxyisoflavone (daidzein) the last compound is 6,8-di-C-glucosyl derivative of 4',5,7-trihydroxyisoflavone (genistein). Dalpanitin represents the first example of an isoflavone-C-glucoside with tetraoxygenation and partial methylation. The aglycone corresponding to dalpanitin (3'-methyl ether of orobol) has not been met with so far, whereas, the isomeric 4'-methyl ether, pratensein[22] has been reported from *Trifolium pratense* and *T. subterraneum.*

The present report shows that in *D. paniculata* there is co-occurrence of isoflavone (II), isoflavone-C-glucoside (VII), isoflavone-O-glucoside (XX), isoflavanone-C-glucoside[4] and rotenoid (I).

EXPERIMENTAL

M.ps were determined using a hot stage microscope and are uncorrected. The UV spectra were measured with a Hilger Uvispek Photoelectric Spectrophotometer (Model H700.308) using spectroscopic MeOH and IR spectra with Beckman Spectrophotometer (Model IR-18A) by the KBr-disc method. NMR spectra were determined using a Varian HA-100 spectrometer with TMS as internal standard. Neutral alumina (NCL, Poona) and polyamide (Woelm, Germany) were used for column chromatography. Merck's Kieselgel G and Polyamide 11 were used for TLC. Whatman No. 1 paper was used for paper chromatography.

Extraction of the seeds of Dalbergia paniculata. The ground seeds (1·8 Kg) after extraction with benzene to yield I and II, were extracted with ether and cold MeOH successively. The latter extract was subjected to detailed examination.

Isolation of dalpanin, dalpanitin (VII) *and* dalpatin (XX). The cold MeOH extracts (7 × 4·5 l) were concentrated under reduced pressure to 500 ml and chromatographed over neutral alumina (1625 g) using MeOH as eluent. The initial MeOH eluates (1·7 l.) contained dalpanol in trace amounts and dehydrodalpanol (100 mg) along with certain other yellow compounds in small amounts. The later MeOH eluates (16·85 l) were concentrated under reduced pressure to about 50 ml and then evaporated to dryness under vacuum over P_2O_5. The resulting orange–brown solid (7·8 g) was macerated with cold water (8 × 25 ml) and filtered. The water insoluble fraction (1·88 g) did not yield any crystalline substance. The water soluble fraction was chromatographed on a polyamide column (200 g) using successively water (W_1 and W_2) and water-EtOH mixtures (W_3, 20% aq. EtOH) and (W_4, 50% aq. EtOH) as eluting solvents.

W_1 contained glucose (R_f 0·20) in large amounts and arabinose (R_f 0·30) and xylose (R_f 0·33) in trace amounts. [Paper chromatography, n-BuOH–AcOH–H_2O (4:1:5 v/v, upper phase), aniline phthalate as spray reagent.] W_2 yielded dalpanin (250 mg); W_3 yielded dalpanitin (1 g); W_4 yielded dalpatin (25 mg).

Dalpanin was obtained as chromatographically pure and colourless rectangular prisms. m.p. 267–268° (dec), $C_{26}H_{30}O_{12}$, λ_{max} (MeOH) 215 nm (log ε 4·32), 226 (infl.) nm (log ε 4·13), 288 nm (log ε 4·02). It was shown to be identical with dalpanin isolated from the flowers of *D. paniculata* by mmp, co-chromatography and superimposable IR spectra.

Dalpanitin (VII) crystallized from absolute EtOH and dry light petroleum (60–80°) as colourless rectangular plates, m.p. 213–214° (dec.), $[\alpha]_D^{25}$ + 35° (*c*, 0·73, EtOH). [Found: C, 54·17; H, 5·07; OCH_3, 6·81. $C_{21}H_{19}O_{10}(OCH_3)\cdot 1\frac{1}{2}H_2O$ requires: C, 54·0; H, 5·10; OCH_3, 6·34%]. λ_{max} (MeOH) 218 nm (log ε 4·43), 265 nm (log ε 4·52), 290 (infl.) nm (log ε 4·08); λ_{max} ($AlCl_3$) 220, 277, 385 nm; λ_{max} (NaOAc) 230, 279, 330 nm; λ_{max} (H_3BO_3–NaOAc) 267, 290 (infl.) nm; λ_{max} (NaOMe) 218, 281, 330 nm. ν_{max} (KBr) 3420 br. (OH), 1665 (conjugated carbonyl), 1625, 1590, 1530 (aromatic), 1038, 1010 (C-glucosyl) cm^{-1}; NMR (DMSO-d_6) τ 1·57 (s, 2-H), 2·89 (q, *J* = 8·5 and 2 Hz, 6′-H), 3·00 (d, *J* = 2 Hz, 2′-H), 3·17 (d, *J* = 8·5 Hz, 5′-H), 3·68 (s, 6-H), 4·80–6·80 (m, sugar protons), 5·30 d, *J* = 10 Hz, 1″-H), 6·20 (s, $OC\underline{H}_3$), 0·86 (br, s, 4′-O<u>H</u>, exchangeable), −0·68 (br. s, 7-O<u>H</u>, exchangeable), −3·21 (s, 5-O<u>H</u>, exchangeable). Mass spectrum: *m/e* 444 (M-H_2O, 100%), 426 (M-$2H_2O$, 42·9%), 408 (M-$3H_2O$, 78·5%), 313 (M-149, 58·3%), 300 (45·6%), 165 (6·7%) and 148 (12·3%).

Dalpanitin gave a pinkish violet colour with a trace of alc. $FeCl_3$ and the colour changed to green on further addition of the reagent. It gave positive Molisch test, pink colour with Na-Hg and HCl and no colouration with Mg and HCl. It had *Rf* values (paper) 0·50 (H_2O), 0·65 [n-BuOH-AcOH-H_2O (4:1:5 v/v, upper phase)], 0·70 [Toluene-AcOH-H_2O (4:1:5 v/v lower phase)];(TLC)–polyamide 0·70 [EtOH-H_2O (3:2 v/v)], 0·45 [EtOAc-MeOH (80:20 v/v)]; Kieselgel G – 0·68 [n-BuOH-AcOH-H_2O (4:1:5 v/v, upper phase)] and 0·33 [$CHCl_3$-MeOH (80:20 v/v)]. On chromatograms it appeared as a deep purple spot under UV light.

Dalpatin (XX) crystallized from abs EtOH as fine colourless needles m.p. 261–263° (dec); λ_{max} (MeOH) 256 nm (infl. log ε 4·34), 312 nm (log ε 4·43); ν_{max} (KBr) 3430 (OH), 1640 (conjugated CO), 1620, 1512, 1490, 1475, 1455 (aromatic C=C), 1042 and 940 (methylenedioxy) cm^{-1}; NMR (DMSO-d_6) τ 1·87 (s, 2-H), 2·57 (s, 5-H), 3·03 (s, 6′-H), 3·12 (s, 8-H), 3·17 (s, 3′-H), 3·97 (s, —O—$C\underline{H}_2$—O—), 6·10 (s, 6-$OC\underline{H}_3$), 6·32 (s, 2′-$OC\underline{H}_3$); the sugar protons appeared over a range τ 5·50–6·80. Dalpatin gave positive Molisch and Labat tests. It gave a pink colour with Na-Hg and HCl, and no colouration with Mg and HCl, and alc. $FeCl_3$.

Acid hydrolysis of dalpanitin. The compound (10 mg) in 7% aq. alc. H_2SO_4 (10 ml) was heated at 100° for 5 hr, cooled and extracted with EtOAc. The extract on evaporation yielded no aglycone. The aqueous portion was treated with excess of $BaCO_3$, the ppt filtered off and the filtrate concentrated. Examination of the concentrate by paper chromatography revealed the presence of unchanged starting material without the formation of any free sugar.

Dalpanitin hepta-acetate (IX). A mixture of dalpanitin (50 mg), Ac_2O (0·5 ml) and fused NaOAc (250 mg) was heated on a water bath for 2 hr, cooled and then poured into ice cold water. The ppt was collected and crystallization from dry benzene-light petroleum gave the hepta-acetate (50 mg) as fine colourless crystals. m.p. 130–131°. (Found: C, 56·61; H, 4·65; $C_{36}H_{36}O_{18}$ requires: C, 57·15; H, 4·76%); λ_{max} (MeOH) 223, 250, 305 (infl.) nm; ν_{max} (KBr) 1770 br, 1660, 1620, 1595, 1520, 1380, 1220 br, 1130, 1060, 1040, 1010, 910 cm^{-1}; NMR ($CDCl_3$) τ 2·00 (s, 2-H), 2·80–3·00 (m, 2′,5′ and 6′-H), 3·14 (s, 6-H), 4·28 (d, *J* = 10 Hz, 1″-H), 4·54–4·88 (m, 2″,3″,4″ and 5″-H), 5·80 (d, *J* = 18 Hz, 6″-2H), 6·13 (s, $OC\underline{H}_3$), 7·57 (s, 5-O<u>Ac</u>), 7·60 (s, 7-O<u>Ac</u>), 7·67 (s, 4′-O<u>Ac</u>), 7·92 (s, 3″ and 4″-O<u>Ac</u>), 7·97 (s, 6″-O<u>Ac</u>), 8·24 (s, 2″-O<u>Ac</u>). The compound gave no colour with alc. $FeCl_3$.

Formation of glycerol from dalpanitin. A mixture of dalpanitin (2 mg) in aq. EtOH (0·2 ml) and $NaIO_4$ (2 mg) was kept at room temp for 4 hr, then added $NaBH_4$ (2 mg) in water (0·1 ml) and kept at room temp for over night. The mixture was heated with 1N HCl (0·2 ml) at 100° for 15 min. The clear yellow coloured filtrate was concentrated under vacuum over P_2O_5 and examined by paper chromatography using EtOAc–Py–H_2O (10:4:3 v/v) as irrigating solvent system and a mixture of 2% $NaIO_4$ aq (4 parts) and a 1% soln of $KMnO_4$ in 2% Na_2CO_3 aq (1 part) as the spray reagent. Glucose was used as the standard. Glycerol was identified as a yellow spot with pink back ground (*Rf* 0·32).

Tetra-acetate of dalpanitin trimethyl ether (VIII). Methylation of dalpanitin (50 mg) by excess ethereal CH_2N_2 or Me_2SO_4–K_2CO_3 method resulted in a gum (55 mg) which did not crystallize readily. Acetylation (Ac_2O and pyridine) of this gum gave pale yellow solid (55 mg), m.p. 61–63° whose NMR spectrum ($CDCl_3$)

showed signals due to four methoxyl groups (τ 6·03, 6·08, 6·11 and 6·18) and four acetoxyl groups [(τ 7·94 (3H), 7·96 (6H) and 8·24 (3H)].

Oxidation of VIII *with alkaline hydrogen peroxide.* 20 mg of VIII was treated with 5% alc. KOH aq (10 ml) followed by 30% H_2O_2 (1 ml) and the mixture kept at 45° for 2 hr, cooled, poured into ice-cold water (10 ml), acidified with cold conc HCl and extracted with ether. The ether solution was washed with water and then extracted with saturated $NaHCO_3$ aq; the bicarbonate fraction acidified and extracted with ether. Evaporation followed by micro vacuum sublimation gave a colourless crystalline solid (5 mg) with m.p. 179–181°. It was found to be identical with 3,4-dimethoxy benzoic acid by mmp and co-chromatography.

Oxidation of IX *with potassium permanganate.* A soln of dalpanitin hepta-acetate (20 mg) in acetone (50 ml) was kept refluxing and added powdered $KMnO_4$ in small amounts during 1 hr till the pink colour persisted. Refluxed for a further period of 4½ hr, cooled, filtered and the filtrate evaporated to dryness. The resulting brown residue was taken up in water, passed SO_2 and extracted with ether. Working up of the ether extract as above gave colourless crystals (5 mg), m.p. 209–211°. Its identity with 3-methoxy-4-hydroxybenzoic acid was confirmed by mmp and co-chromatography.

Oxidation of dalpanitin with ferric chloride. A mixture of dalpanitin (50 mg) and $FeCl_3$ (250 mg) in water (1·5 ml) was heated in an oil-bath at 125° for 6 hr, cooled and diluted with water to 10 ml. Small amount of dark coloured insoluble material formed was filtered off and the filtrate passed through a column of silica gel using water as eluent. The initial colourless eluate (25 ml) was concentrated on a water bath to yield a syrup which on paper chromatography showed identity with glucose.

3′,4′,5,7-Tetrahydroxyisoflavone (VI). A mixture of dalpanitin (100 mg), phenol (600 mg) and HI (1 ml, *d* 1·7) was refluxed at 137° for 7 hr, cooled and then poured into $NaHSO_3$ aq with stirring. The separated brown substance was collected, purified by column chromatography (silica gel) and crystallised from aq. MeOH to give 3′,4′,5,7-tetrahydroxyisoflavone as colourless plates (35 mg), mp 272–274°. It gave a green colour with alc. $FeCl_3$. Mixed mp with an authentic sample of orobol was undepressed. Further confirmation was by co-chromatography and identical UV and IR spectra.

Acid hydrolysis of dalpatin (XX). A soln of dalpatin (8 mg) in 7% alc. H_2SO_4 (10 ml) was heated on a water bath for 5 hr. On working up it gave XIX as fine colourless needles (4 mg) from MeOH–$CHCl_3$; mp 254°. (Found: C, 62·83; H, 4·21. $C_{18}H_{14}O_7$ requires: C, 63·17; H, 4·1%) λ_{max} (MeOH) 256 (infl.) nm (log ε 4·10), 312 nm (log ε 4·16); λ_{max} (NaOAc) 252 and 348 nm. Mass spectrum *m/e* (relative intensity) 342 (M^+, 100%), 311 (M-31, 91·5%), 175 (19·3%), 167 (41%). It gave no ferric colour.

The sugar from the aqueous mother liquor was identified as glucose by paper chromatography.

2′,6,7-Trimethoxy-4′,5′-methylenedioxyisoflavone (XVIII). Methylation of the above aglycone (3 mg) by ethereal CH_2N_2 gave the compound (XVIII) as colourless small needles (3 mg) from MeOH, mp 234–236°. Its identity with milldurone was established by undepressed mmp, co-chromatography (TLC) and identical UV and IR spectra.

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REFERENCES

[1] D. Adinarayana, M. Radhakrishniah, J. Rajasekhara Rao, R. Campbèll and L. Crombie, *J. Chem. Soc.* (C), 29 (1971)

[2] D. Adinarayana, M. Radhakrishniah and J. Rajasekhara Rao, *Curr. Sci.* **40**, 602 (1971)

[3] V. Narayanan and T. R. Seshadri, *Indian J. Chem.* **9**, 14 (1971)

[4] D. Adinarayana and J. Rajasekhara Rao, *8th International Symposium on the Chemistry of Natural Products* (IUPAC) p. 96, New Delhi, Feb. (1972).

[5] H. Wagner, *Methods in Polyphenol Chemistry* (Edited by J. B. Pridham) p. 45, Pergamon Press, Symposium publications division (1964)

[6] V. K. Bhatia, S. R. Gupta and T. R. Seshadri, *Tetrahedron* **22**, 1147 (1966)

[7] H. Wagner, *Comparative Phytochemistry* (Edited by T. Swain) p. 309, Academic Press (1966)

[8] R. M. Horowitz and L. Jurd, *J. Org. Chem.* **26**, 2446 (1961)

[9] T. J. Mabry, K. R. Markham and M. B. Thomas, *The Systematic Identification of Flavonoids* p. 267, Springer, New York (1970)

[10] R. M. Horowitz and B. Gentili, *Chem. & Ind.* 498 (1964)
[11] T. J. Batterham and R. J. Highet, *Aust. J. Chem.* **17**, 428 (1964)
[12] B. H. Koeppen and D. G. Roux, *Biochem. J.* **97**, 444 (1965)
[13] W. E. Hillis and D. H. S. Horn, *Aust. J. Chem.* **18**, 531 (1965)
[14] B. Gentili and R. M. Horowitz, *J. Org. Chem.* **33**, 1571 (1968)
[15] F. E. King, T. J. King and L. C. Manning, *J. Chem. Soc.* 563 (1957)
[16] A. Prox, *Tetrahedron* **24**, 3697 (1968)
[17] W. D. Ollis, C. A. Rhodes and I. O. Sutherland, *Ibid.* **23**, 4741 (1967)
[18] R. V. M. Campbell, S. H. Harper and A. D. Kemp, *J. Chem. Soc.* (C), 1787 (1969)
[19] S. H. Harper, A. D. Kemp, W. G. E. Underwood and (in part) R. V. M. Campbell, *Ibid.* 1109 (1969)
[20] T. Murakami, Y. Nishikawa and T. Ando, *Chem. Pharm. Bull., Tokyo* **8**, 688 (1960)
[21] S. P. Bhutani, S. S. Chibber and T. R. Seshadri, *Indian J. Chem.* **7**, 210 (1969)
[22] E. Wong, *J. Org. Chem.* **28**, 2336 (1963)