Phytochemistry, 1975, Vol. 14, pp. 1129–1130. Pergamon Press. Printed in England.

GANGETININ AND DESMODIN, TWO MINOR PTEROCARPANOIDS OF *DESMODIUM GANGETICUM*

KOZHIPARAMBIL K. PURUSHOTHAMAN, S. CHANDRASEKHARAN and K. BALAKRISHNA
Captain Srinivasa Murti Research Institute, Adyar, Madras-20, India

and

JOSEPH D. CONNOLLY
Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland

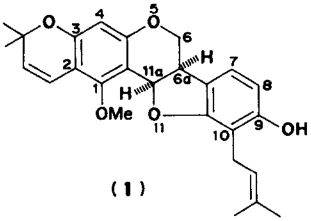
(*Received* 28 *October* 1974)

Key Word Index—*Desmodium gangeticum*; Leguminosae; pterocarpanoids.

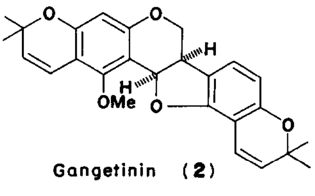
Recently we reported [1] the structural elucidation of gangetin (**1**), the major pterocarpanoid of *Desmodium gangeticum*. We have now isolated two minor pterocarpanoids, gangetinin and desmodin, from the same extract and assign them the structures (**2**) and (**5**) respectively on the following evidence.

The less polar compound, gangetinin (**2**) mp 136–138°, has the molecular formula $C_{26}H_{26}O_5$. Its NMR spectrum indicates the presence of two dimethylchromen ring systems [δ 1·42 and 1·46 (12H, methyls), 6·58, 6·49 and 5·59, 5·57 (double ABq, *J* 10 Hz)], a methoxyl group [δ 4·02] and three aromatic protons, one isolated [δ 6·25 (*s*)] and the remaining two as an *ortho* coupled system [δ 6·96 and 6·36 (both *d*, *J* 8 Hz)]. In addition the characteristic resonances [2] of the pterocarpanoid nucleus are clearly visible. The above spectroscopic data are similar to those of gangetin (**1**) and suggest the structure (**2**) for gangetinin. This was readily confirmed chemically. Gangetin (**1**), on exposure to acid, was transformed into cyclogangetin (**3**), mp 151°. Hydrogenation afforded the corresponding dihydrocyclogangetin (**4**) mp 155° which is identical in all respects with tetrahydrogangetinin, the product of hydrogenation of gangetinin (**2**).

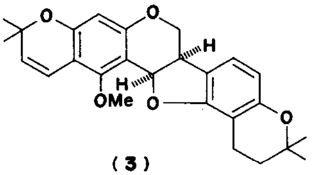
The second compound, desmodin (**5**), $C_{22}H_{22}O_6$, mp 236–238°, has hydroxyl absorption in the IR (3550 cm^{-1}) and readily forms a methyl ether (**6**) mp 140–142° which lacks hydroxyl absorption. The NMR of desmodin shows a dimethyl chromen [δ 1·42, 1·45 (methyls), 6·56 and 5·58 (ABq, *J* 10 Hz)], two methoxyls (δ 3·96 and



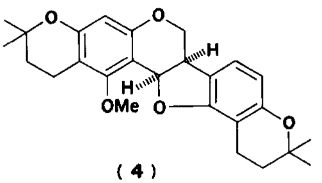
(**1**)



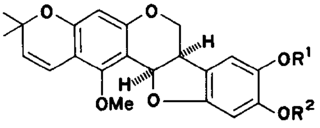
Gangetinin (**2**)



(**3**)



(**4**)



Desmodin (**5**) $R^1 = Me$; $R^2 = H$
(**6**) $R^1 = R^2 = Me$
(**7**) $R^1 = H$; $R^2 = Me$

3·86), a phenolic hydroxyl [δ 5·74 (disappears on D_2O exchange)] and three isolated aromatic proton singlets (δ 6·23, 6·54 and 6·80) in addition to the typical pterocarpanoid resonances. Addition of Eu(fod)$_3$ caused rapid broadening of the upfield methoxyl group and the two downfield aromatic proton singlets indicating that these are associated with the aromatic ring bearing the phenolic hydroxyl group. The similarity of spectroscopic data suggested that the other aromatic ring has the same substitution as in gangetin (**1**). Thus two possible structures (**5**) and (**7**) emerged for desmodin. The observation of a NOE (16%) between H-7 (δ 6·80) and the upfield methoxyl enabled a decision to be made in favour of (**5**).

Both gangetinin and desmodin have large negative rotations, indicative of the (6aR, 11aR) absolute configuration common to other laevorotatory members of this group of pterocarpanoids [2,3].

EXPERIMENTAL

Isolation of pterocarpans. Dried ground roots of *Desmodium gangeticum* DC (10 kg) were exhaustively extracted with hexane in a Soxhlet for 30 hr. Solvent was removed *in vacuo* and the crude extract (20 g) chromatographed over Si gel (500 g). Elution of the column with hexane afforded an oily concentrate (500 mg) which, on crystallization from MeOH–Et$_2$O, afforded pure *gangetinin* (**2**) as colourless needles, mp 136–138°, $[\alpha]_D$ −200° (CHCl$_3$), *m/e* 418; λ_{max} 234, 278 and 318 nm; δ 3·40 (1H, *m*, H-6a), 4·21 (1H, q, J_{obs}6, 10 Hz, H-6eq), 3·63 (1H, *t*, J_{obs} 10 Hz, H-6 ax) and 5·66 (1H, *d*, J_{obs} 6 Hz, H-11a). [Found: C, 74·3; H, 6·1. $C_{26}H_{26}O_5$ requires C, 75·65; H, 6·2%.]

Further elution of the chromatogram with hexane–C_6H_6 (1:1) yielded a thick gummy residue which upon repeated crystallization from hexane–Et$_2$O afforded gangetin (**1**) (8 g), mp 108°, $[\alpha]_D$ −205° (CHCl$_3$), *m/e* 420. After the complete removal of gangetin, the chromatogram was successively eluted with C_6H_6 and C_6H_6–CHCl$_3$ (1:1). The combined eluates upon evaporation yielded a gum which on crystallization from C_6H_6–Et$_2$O gave pure *desmodin* (**5**) (160 mg), mp 236–238°, $[\alpha]_D$ −250° (CHCl$_3$), *m/e* 382; λ_{max} 228, 287 and 303 nm; δ 3·38 (1H, *m*, H-6a), 3·66 (1H, *t*, J_{obs} 10 Hz, H-6ax), 4·21 (1H, q, J_{obs} 6, 10 Hz, H-6eq) and 5·60 (1H, *d*, J_{obs} 6 Hz, H-11a). [Found: C, 69·0; H, 5·50. $C_{22}H_{22}O_6$ requires C, 69·1; H, 5·75%.]

Cyclogangetin (**3**). To gangetin (500 mg) in methanol (10–12 ml) was added 10 ml 5% HCl and the mixture left at room temp for 10 hr. The usual work-up gave a gummy residue (300 mg) which was chromatographed over a short column of Si gel. The later hexane and the early hexane–C_6H_6 (1:1) fractions were combined, evaporated and crystallized from MeOH to yield fine needles of *cyclo*-gangetin (**3**) (80 mg), mp 151° (Found: C, 74·6; H, 6·50. $C_{26}H_{28}O_5$ requires C, 74·3; H, 6·65%).

Dihydrocyclogangetin (**4**). Cyclogangetin (60 mg) in MeOH (8 ml) was hydrogenated over PtO$_2$ (40 mg) for 30 min (uptake of 10 ml). Crystallization of the reaction product from MeOH–Et$_2$O yielded dihydrocyclogangetin (**4**) (35 mg), mp 155°. (Found: C, 74·1; H, 7·0. $C_{26}H_{30}O_5$ requires C, 73·95; H, 7·1%.)

Tetrahydrogangetinin (**4**). Gangetinin (**2**) (80 mg) in MeOH (10 ml) was hydrogenated over PtO$_2$ (80 mg) for 30 min (uptake of 13 ml). The reaction product after usual work-up afforded a gum (180 mg). Column chromatography of this gum over Sil gel afforded tetrahydrogangetinin (**4**) (40 mg), mp 156° (from MeOH–Et$_2$O) identical in all respects (mp, mmp, TLC and IR) with dihydrocyclogangetin (**4**).

Desmodin methylether (**6**). Desmodin (**5**) (60 mg) in dry acetone (6 ml) was refluxed for 10 hr with Me$_2$SO$_4$ (0·5 ml) and K$_2$CO$_3$ (1 g). Water was added and the mixture was extracted with ether, dried and solvent evaporated to yield the methyl ether (**6**) (15 mg), mp 140–142°. (Found: C, 70·1; H, 8·8. $C_{23}H_{24}O_6$ requires C, 69·7; H, 8·7%.)

Acknowledgement—The Indian authors with to express their sincere thanks to Central Council for Research in Indian Medicine and Homoeopathy (New Delhi), Government of India, for financial support.

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