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XANTHONES OF *SWERTIA PURPURESCENS*

SABOOR AHMAD, MOHAMMAD IKRAM and ISRAR KHAN
Drug Division, P.C.S.I.R. Laboratories, Peshawar, Pakistan

and

M. NEIL GALBRAITH
Division of Applied Chemistry, C.S.I.R.O., Melbourne, Australia

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Key Word Index—*Swertia purpurescens*; Gentianaceae; bellidifolin; new xanthone.

Extracts of *Swertia purpurescens* Wall (Gentianaceae) are very commonly used as a tonic and febrifuge in the indigenous system of medicine in the sub-continent.[1] Hexane extracts of the aerial portions of the plant on cooling gave yellow crystals of a new xanthone. Sitosterol, m.p. 135–136°, was identified in the filtrate.

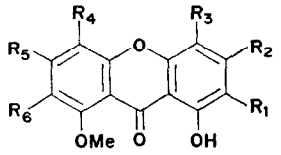
The xanthone, $C_{17}H_{16}O_7$, m.p. 198–200°, gave a green colour with $FeCl_3$, and showed UV and IR absorptions which indicated that it was derivative of 1,8-dihydroxyxanthone: the UV spectrum displayed the bathochromic shift characteristic of these compounds.[2] The presence of four methoxy groups was indicated by NMR absorption at τ 6·10 (3H), 6·02 (6H) and 5·98 (3H). From the positive ferric test the remaining oxygen atom must be present as a C-1 hydroxy group, and one methoxy group can be placed at C-8.

The NMR spectrum of the compound was in agreement with the published spectra of xanthones.[3] It showed a pair of doublets at τ 3·60, 3·45 (J 1·5 Hz) due to *meta*-related protons, and a singlet from an isolated aromatic proton at τ 2·96. Using these data the remaining three methoxy groups can be positioned to give six possible structures. A pre-requisite in the assignment of structures to xanthones is the presence of at least one vacant position at C-1, C-3, C-6 or C-8 created by the loss of the chain initiating group (methyl).[4] If all four positions are occupied one must carry a methyl group (or its oxidized form), as in lichexanthone[5] (1-hydroxy-3,6-dimethoxy-8-methylxanthone). In the present case the above rule eliminates four of the possible structures, so that the xanthone is either 1-hydroxy-2,4,6,8-tetramethoxy-xanthone (I) or 1-hydroxy-3,5,7,8-tetramethoxyxanthone (II). The latter structure is preferred because of the isolation (see below) of bellidifolin, with a 1-hydroxy-3,5,8-substitution pattern, from the same plant.

Further extraction of the plant material with EtOH yielded a yellow compound, m.p. 263°, identified as bellidifolin[6] (III) (1,5,8-trihydroxy-3-methoxyxanthone) by IR, UV and NMR analysis, and comparison of physical data for the compound and its triacetate with

[1] CHOPRA, R. N., NAYAR, S. L. and CHOPRA, I. C. (1956) *Glossary of Indian Medicinal Plants*, p. 237, CSIR, New Delhi.
[2] DEAN, F. M. (1963) *Naturally Occurring Oxygen Ring Compounds*, p. 266, Butterworths, London.
[3] LOCKSLEY, D. H., SCHEINMANN, F., GOTTLIEB, O. R. and STOUT, JR., F. H. (1970) *J. Chem. Soc.* **B**, 603.
[4] HUSSAIN, S. F. (1964) Ph.D. Thesis, Victoria University of Manchester, p. 67.
[5] ASAHINA, Y. and NOGAMI, H. (1942) *Bull. Chem. Soc. Japan* **17**, 202.
[6] MARKHAM, K. R. (1964) *Tetrahedron* **20**, 991.

literature values. In addition colourless crystals of a hydroxy triterpene acid, m.p. 288–290° were isolated. This material has not yet been further investigated.



(I) $R_2 = R_4 = R_6 = H$; $R_1 = R_3 = R_5 = OMe$
(II) $R_1 = R_3 = R_5 = H$; $R_2 = R_4 = R_6 = OMe$
(III) $R_1 = R_3 = R_5 = R_6 = H$; $R_4 = OH$; $R_2 = OMe$

EXPERIMENTAL

Aerial portions of *Swertia purpurescens* were collected in August 1970 from Azad Kashmir in West Pakistan. Air dried plant material (2·5 kg) was ground and extracted in a Soxhlet extractor with hexane for 12 hr. After partial removal of hexane the extract was cooled when yellow material deposited. Filtration and crystallization from MeOH gave yellow needles of the new xanthone (18 mg) m.p. 198–200°. UV: (EtOH) λ_{max} 241, 264, 315, 384 nm (ϵ 4·27, 4·41, 3·92, 3·60). IR: (KBr) ν_{max} 1648, 1612, 1590 cm^{-1}. (Found: C, 61·20; H, 4·78; M^+ *m/e* 332. $C_{17}H_{16}O_7$ requires: C, 61·13; H, 4·85%, MW 332). The filtrate from the above solution yielded sitosterol, m.p. 135–136°, identified by comparison with an authentic specimen.

Further extraction of the plant material with EtOH and concentration of the extract gave a yellow product which on filtration and crystallization from acetone gave bellidifolin (48 mg) m.p. 263° (lit.[6,7] m.p. 270–271°, 264°). UV: (EtOH): λ_{max} 252, 278, 332, 400 nm (ϵ 4·25, 4·10, 3·9, 3·72). IR: (KBr) ν_{max} 1603, 1620, 1640, 1666, 3420 cm^{-1}. (Found: C, 61·02; H, 3·50; OMe, 11·07; M^+ *m/e* 274. Calc. for $C_{14}H_{10}O_6$: C, 61·34; H, 3·68; OMe 11·30%, MW 274.) Triacetate m.p. 238° (lit.[6] m.p. 240°). NMR: ($CDCl_3$) τ 7·60 (9H, *s*, 3 × OAc), 6·15 (3H, *s*, OMe), 3·47, 3·35 (2H, *AB q*, *J*. 1·5 Hz) 3·12, 2·67 (2H, *AB q*, *J* 9Hz). (Found: C, 60·01; H, 4·89; M^+ *m/e* 400. Calc. for $C_{20}H_{16}O_9$; C, 59·99; H, 4·93, MW 400).

The filtrate from the above solution yielded colourless material which on crystallization from EtOH gave needles of a hydroxy triterpene acid (0·5 g) m.p. 288–290°. IR: (Nujol) ν_{max} 3350, 1675 cm^{-1}. (Found: C, 76·41; H, 9·99; $C_{30}H_{48}O_3$ requires: C, 76·31; H, 10·20%.) Methyl ester m.p. 167–169°. IR: (Nujol) ν_{max} 3320, 1730 cm^{-1} Acetate m.p. 245–250°.

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[7] RIVAILLE, P. and RAULAIS, D. (1969) *Compt. Rend.* **269,** 1121.

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OCCURRENCE OF FLAVONES IN *DALBERGIA PANICULATA* FLOWERS

DAMA ADINARAYANA and JADHAV RAJASEKHARA RAO
Department of Chemistry, Sri Venkateswara University, Tirupati, A.P., India

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Key Word Index—*Dalbergia paniculata*; Leguminosae; apigenin; luteolin; caviunin; (+)-pinitol.

Plant. Dalbergia paniculata Roxb. *Source.* Tirupati, South India. *Previous work.* On seeds;[1–3] heartwood;[4,5] and bark.[6]

[1] ADINARAYANA, D., RADHAKRISHNIAH, M., RAJASEKHARA RAO, J., CAMPBELL, R. and CROMBIE, L. (1971) *J. Chem. Soc.* C, 29.
[2] ADINARAYANA, D., RADHAKRISHNIAH, M. and RAJASEKHARA RAO, J. (1971) *Current Sci.* **40,** 602.
[3] ADINARAYANA, D. and RAJASEKHARA RAO, J. (1972) *Tetrahedron* **28,** 5377.
[4] NARAYANAN, V. and SESHADRI, T. R. (1970) *Indian Acad. Wood Sci.* **1,** 1.
[5] SESHADRI, T. R. (1972) *Phytochemistry* **11,** 881.
[6] NARAYANAN, V. and SESHADRI, T. R. (1971) *Indian J. Chem.* **9,** 14.