Chloroform extract. This mostly contains xanthones, work on their identification is in progress. However, a yellow crystalline mass separated at the interface of $CHCl_3$ and H_2O layers during extraction procedure. This was separated and crystallized from MeOH to give pale yellow needles, m.p. 243° (dec), $C_{22}H_{22}O_{10}$. (Found: C, 59·61; H, 5·09. Calc. for $C_{22}H_{22}O_{10}$ C, 59·19; H, 4·97%). It gave greenish-brown color with $FeCl_3$ and the reduction tests for (Mg–HCl and Zn–HCl) flavonoids were positive. The UV spectrum showed λ_{max} at 273 and 336 nm (log ϵ 4·24 and 4·32). Acetylation gave a hexaacetate, $C_{34}H_{34}O_{16}$, m.p. 156–158°. These properties indicated the flavonoid to be the known compound *swertisin*, previously isolated from *S. japonica*.[3] Direct comparison with an authentic sample confirmed the identification (m.m.p.; superimposable IR, UV spectra of the compound and derivative).

n-*Butanol extract.* This fraction contains a number of glucosides; only one glucoside could be isolated in pure form by fractional crystallization of the crude mixture, which crystallized from EtOH to give *swertiamarin*,[4] $C_{16}H_{20}O_{10}$, m.p. 113–114°, $[\alpha]_D$ −12°. Tetraacetate, $C_{24}H_{30}O_{14}$, m.p. 190–191° (Found: C, 52·78; H, 5·64. Calc. for $C_{24}H_{30}O_{14}$: C, 52·94; H, 5·80%) (m.m.p., IR, UV and NMR).

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[3] M. KOMATSU, T. TOMIMORI and M. ITO, *Chem. Pharm. Bull. Japan* **15**, 263 (1967).
[4] H. INOUYE, S. UEDA and Y. NAKAMURA, *Chem. Pharm. Bull. Japan* **18**, 1856 (1970).

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ALKALOIDS AND TERPENOIDS OF *ZANTHOXYLUM OVALIFOLIUM*

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Key Word Index—*Zanthoxylum ovalifolium*; Rutaceae; 6-canthinone; aurapten; isopimpinellin; β-amyrin; sitosterol.

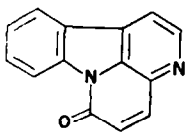
The genus *Zanthoxylum* comprises of some 200 species distributed over the world, many of which have been chemically explored because of the occurrence of compounds covering a wide range of skeletal patterns in the Rutaceae. This particular genus belonging to the subfamily Rutoideae,[1] is noted for its febrifuge, sudorific and diuretic properties.[2]

A chemically uninvestigated species of this genus, *Zanthoxylum ovalifolium*, was collected from an altitude of nearly 8000–9000 ft from the Darjeeling District in the Himalayan Ranges. The plant is mainly distributed in the hilly regions of North and South India (Nilgiri hilly regions). It is a shrub with short prickles, leaves obtuse, emarginate with elliptic-oblong or obovate genulate tips. The leaves of North Indian plants are usually larger than those of South Indian ones.[3]

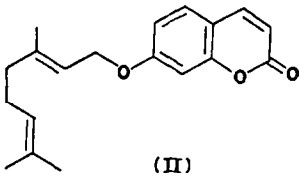
[1] J. R. PRICE, in *Chemical Plant Taxonomy* (edited by T. SWAIN), p. 429, Academic Press, New York (1963).
[2] K. R. KIRTIKAR and B. D. BASU, *Indian Medicinal Plants*, Vol. 1, p. 459, The Indian Press, Allahabad, India (1935).
[3] J. D. HOOKER, *The Flora of British India*, Vol. I, p. 492, Reeve, London (1875).

Chemical examination of the root-bark and stem-bark of this plant resulted in the isolation of 6-canthinone[4] (I) from the basic fraction, and aurapten (II), isopimpinellin (III), β-amyrin and sitosterol from the neutral fraction—being eluted out of the column in succession. Identity of each compound, as indicated by their physical data, was established by direct comparison (m.m.p. determination, co-TLC, superimposable IR) with respective authentic samples available in this laboratory.

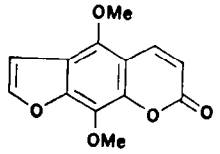
The isolation of 6-canthinone from *Zanthoxylum ovalifolium* constitutes the third report of the occurrence of this type of alkaloid in a species of *Zanthoxylum*, the earlier reports being from *Z. suberosum*[5] (syn. *Z. dominianum*[6]) and *Z. elephantiasis*.[4]



(I)



(II)



(III)

EXPERIMENTAL

Dried and ground root-bark (400 g) of *Z ovalfolium* was extracted with light petrol. (60–80°) in a Soxhlet apparatus for 30 hr. From the extract concentrate, the neutral and basic components were separated in the usual way.

Isolation of 6-canthinone. The basic fraction showing a single well-defined spot in TLC was chromatographed over Brockmann alumina twice to afford a yellow solid which crystallized from $CHCl_3$–MeOH mixture in pale yellow needles, m.p. 159–160° (yield 0·13%); characterization of the alkaloid has been made by comparison with an authentic sample (m.m.p. determination, IR and UV spectra).

Isolation of aurapten and isopimpinellin. Neutral part of the original plant extract was chromatographed over Brockmann alumina elution being carried out with solvents and solvent mixtures of increasing polarity. Light petrol. eluted fractions showing identity by TLC: these were combined and concentrated to afford aurapten crystallizing from light petrol. in stout needles, m.p. 66–67° (yield 0·02%). The second coumarin was eluted with light petrol.–benzene (2:1). The compound crystallized from light petrol.–MeOH in pale yellow needles, m.p. 149° and was identified as isopimpinellin (0·012%).

Isolation of β-amyrin. Light petrol.–benzene (1:1) eluted a solid which gave positive Liebermann–Burchard test for triterpenes. The solid on chromatography and subsequent crystallization from $CHCl_3$–MeOH mixture yielded a pure sample of β-amyrin (0·012%), m.p. 199°, $[\alpha]_D$ +88° ($CHCl_3$). The identity of the triterpene was established by comparison with an authentic sample (m.m.p. determination, IR, rotation) of the same and through the preparation of its acetate, m.p. 239°, $[\alpha]_D$ +81° ($CHCl_3$), in the usual way.

Isolation of sitosterol. The solid obtained from benzene eluates gave positive test for sterol with Liebermann–Burchard reagent. The sterol crystallized from $CHCl_3$–MeOH mixture in needles, m.p. 137°, $[\alpha]_D$ −35 ($CHCl_3$) (yield 0·02%). The acetate of the sterol, prepared in the usual way, melts at 134°, $[\alpha]_D$ −38·5° ($CHCl_3$). The sterol was identified as sitosterol by comparing it and its acetate with the respective authentic samples.

Investigation on the stem-bark of the same plant in a similar way led to the isolation of all the compounds mentioned above (6-canthinone, 0·125%; aurapten, 0·01%; isopimpinellin, 0·1%; β-amyrin, 0·012%; and sitosterol, 0·01%).

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