1·67, 1·75); two vinyl protons, and three allylic methylene protons, the loss of 136 was rationalized as being due to an allylic ether cleavage with H transfer from an allylic 3-Me to the ether oxygen in a 6-membered transition state of a geranyloxy or neryloxy side chain. Since the H-3 and H-4 of coumarin were readily discernible, the compound must be geranyloxycoumarin or neryloxycoumarin with the substituent at 5-, 6- or 7-position. Comparison of our specimen with authentic aurapten† allow the confirmation of our compound as 7-geranyloxycoumarin (aurapten (IX)). Et_2O–MeOH (1:1) eluted a white crystalline solid (0·01%) m.p. 171–173°, M^+ 110°, soluble in H_2O, EtOH, alcohol, acetone, but only sparingly soluble in $CHCl_3$. Alcoholic solution gave a purple colour which slowly crystallized as dark purple needles with $FeCl_3$, m.m.p., and comparison of spectra data with those for an authentic sample showed the compound to be hydroquinone.

Hydroquinone has been found in the Ericaceae, Rosaceae, Proteaceae, compositae, and recently in the Labiatae[4] and Bignoniaceae.[5] To our knowledge this is the first record of the isolation of this phenol, the only C_6 phenol of systematic interest,[6] in the Rutaceae.

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NODAKENETIN ACETATE: A NEW COUMARIN FROM *BOENNINGHAUSENIA ALBIFLORA*

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Boenninghausenia albiflora Reichb. (Rutaceae), a common plant growing all over temperate Himalaya (altitude 1500–2500 m), is a slender, erect branching, perennial rooted herb of 25–50 cm height with small leaves.[1] Earlier work on the leaves and stems resulted in the isolation of dictamnine,[2] bergapten[2] and matsukaze lactone[3] (a dimeric coumarin) from the MeOH extract and rutin[4] from the EtOH extract. We now report the isolation of six coumarins,[5] viz. xanthyletin (I), bergapten (II), isopimpinellin (III), nodakenetin

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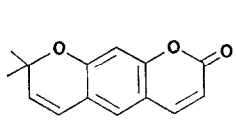
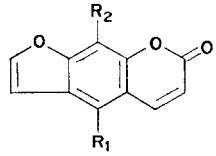
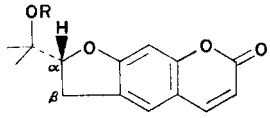
acetate (IV), xanthotoxin and daphnetin-8-methyl ether (V) and sitosterol from the leaves and stems of *B. albiflora* collected from Darjeeling, W. Bengal. Coumarins I, II, III, and xanthotoxin and sitosterol were identified by direct comparison (m.m.p., IR, co-TLC) with authentic samples.[6,7]



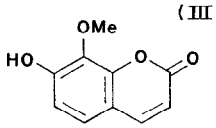
(I)



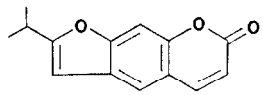
(II) R_1 = OMe; R_2 = H
(III) R_1 = R_2 = OMe



(IV) R = Ac
(VI) R = H



(V)



(VII)

The fourth coumarin, m.p. 134–135°, $[\alpha]_D$ — 13·7°, has been assigned the same structure as nodakenetin acetate (IV) from spectral and chemical evidences. The IR spectrum of IV displayed the acetate absorption (1733, 1245 cm^{-1}) as well as the usual coumarin CO band (1718 cm^{-1}). Its PMR spectrum (60 MHz, δ) showed resonance signals for acetate Me (3H, *s*, 1·97), two nonequivalent comparatively low field Me groups on carbon bearing OAc (3H, *s*, each, 1·52 and 1·55), two aromatic protons (1H, *s*, each, 6·78 and 7·27, H-5 and H-8), two benzylic protons (2H, *d*, 3·24, *J* 9 Hz, dihydrofuran β-protons, their expected nonequivalence not being apparent in the 60 MHz spectrum), the coumarin 3- and 4-protons (6·24, 7·66, *AB* system, $J_{3,4}$ 9·5 Hz) and the dihydrofuran α-proton (1H, *t*, 5·15, *J* 9 Hz). The MS analysis was fully consistent with the proposed structure IV and fragmentation occurred in the expected fashion.

Nodakenetin acetate (IV) on alkaline hydrolysis furnished (—)-nodakenetin (VI);[8] IR superimposable with that of its optical antipode, marmesin.[7,9] With $HClO_4$ in glacial HOAc IV underwent loss of elements of HOAc forming anhydronodakenetin (VII).[10] Finally IV was shown to be the optical antipode of marmesin acetate, m.p. 133–134°, $[\alpha]_D$+12° by direct comparison (IR, co-TLC) with an authentic sample prepared from marmesin by treatment with Ac_2O and NaOAc (reflux, 3·5 hr)[9] and also by treatment with Ac_2O and Py (reflux, 3 hr). However, compounds IV and VI showed appreciable m.p. depression upon admixture with the corresponding optical antipode thus indicating that they form racemic mixtures with their enantiomers.

The fifth coumarin, m.p. 158°, was shown from its spectral data (IR, PMR, MS) to be daphnetin-8-methyl ether (V) and its identity was confirmed by preparation of its methyl ether and acetyl derivatives.[11]

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[8] DREYER, D. L. (1969) *Phytochemistry* **8**, 1013; and references cited therein. The *R*-configuration of (—)-nodakenetin (VI) has recently been established elegantly by chemical correlation experiments by HARADA, I., HIROSE, Y. and NAKAZAKI, M. (1968) *Tetrahedron Letters* 5463.
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The most striking feature of the extractives from *Boenninghausenia albiflora* is the isolation of (−)-nodakenetin acetate (IV) and to our knowledge this constitutes its first natural occurrence. This is also the first rutaceous plant known to produce daphnetin-8-methyl ether (V), which has so far been reported from only one other plant, *Hydrangea macrophylla*[12] (Saxifragaceae). Although numerous reports are available on the occurrence of marmesin[8] [= (+)-nodakenetin], (−)-nodakenetin has so far been reported in the free state from *Peucedanum ostruthium* and very recently from two other Umbelliferae, viz. *Angelica gigas*,[13] and *A. decursiva*,[14] and also from one Rutaceae *Ptelea trifoliata*.[8] Nodakenein [= (−)-nodakenetin glucoside] has been found in *Peucedanum decursivum*[15] (Umbelliferae), *A. gigas*,[13] and *Sphenosciadium capitellatum*.[16]

EXPERIMENTAL

Extraction. Dried and powdered leaves and stems (930 g) (a voucher specimen No. T/B.a/2/72 has been preserved) were Soxhletted with light petrol. (60–80°) and $CHCl_3$ respectively. The basic components present in trace amounts in the extracts were separated in the usual way and the neutral fractions (12 and 9 g respectively) of both light petrol. and $CHCl_3$ extracts were separately chromatographed over silica gel. In each case, elution with solvents of increasing polarity yielded in succession xanthyletin, bergapten, sitosterol, isopimpinellin, nodakenetin acetate and daphnetin-8-methyl ether. The similar fractions as indicated by TLC on microscopic slides were combined. Light petrol. and light petrol.–C_6H_6 (1:1) eluted oily materials followed by an uncharacterized compound crystallizing from light petrol., m.p. 80° (yield 0·2 g).

Isolation of xanthyletin (I), *bergapten* (II), *sitosterol, isopimpinellin* (III). First C_6H_6 eluates afforded xanthyletin, crystallized from light petrol. as colourless needles, m.p. 130°. The subsequent fractions eluted with C_6H_6 yielded residue crystallizing from light petrol.–$CHCl_3$ mixture as colourless needles, m.p. 188°, identified as bergapten (II). The next C_6H_6 fractions showing two spots of which the minor one corresponded to that for bergapten were combined and subjected to repeated chromatography to afford pure sitosterol, from $CHCl_3$–MeOH in flakes, m.p. 139°, $[\alpha]_D$ −37°; acetate, m.p. 134°, $[\alpha]_D$ −40°. The last C_6H_6 eluted fractions afforded isopimpinellin, pale yellow needles m.p. 147–148°, from $CHCl_3$–MeOH. The identity of each of the above compounds was established by direct comparison (m.m.p., co-TLC, IR) with authentic samples.

Isolation of nodakenetin acetate (IV). The C_6H_6–$CHCl_3$ (1:1) eluates gave a solid which on repeated chromatography followed by crystallization from light petrol.–$CHCl_3$ mixture furnished nodakenetin acetate (IV) as colourless crystals, m.p. 134–135°, $[\alpha]_D$ −13·7° (*c* 0·80, $CHCl_3$); UV: λ_{max}^{EtOH} 332 nm (log ε 4·14) 299 sh, 259 (3·54), 247 (3·59) and 224 (3·98); IR: ν_{max}^{KBr} 1733 cm^{-1}, 1718, 1634, 1572, 1488, 1366, 1272, 1245, 1188, 1152, 1127, 1031, 982, 833; MS : *m/e* (% base peak): 288 (15, M^+), 231 (10, M^+–CH_2CO–Me), 229 (6, M^+–OAc), 228 (27, M^+–HOAc,), 214 (14·5, 229—Me), 213 (100, 228—Me), 188 (11, loss of side chain with H capture), 187 (23, M^+–side chain), 185 (3·2, 213—lactonic CO), 176 (15), 175 (15·3), 160 (3·5, 188—lactonic CO), 159 (6, 187—lactonic CO), 131 (8, 159—CO), 101 (1, $MeCO{\cdot}\overset{+}{O}{=}CMe_2$), 59 (12, $Me_2C{=}\overset{+}{O}H$), 43 (67, $MeC{\equiv}\overset{+}{O}$).

Isolation of daphnetin-8-methyl ether (V). A residue obtained from earlier $CHCl_3$ eluate on rechromatography afforded daphnetin-8-methyl ether, from light petrol.–$CHCl_3$ as colourless needles, m.p. 158° (lit.[11] 158°); IR: ν_{max}^{KBr} 3436 cm^{-1} (OH), 1686 (coumarin CO), 1658, 1563, 1493, 1447, 1422, 1328, 1232, 1190, 1153, 1136, 1114, 1056, 1012, 961, 840; PMR (60 MHz, δ): 6·32 *d* and 7·73 *d* (*AB* system *J* 9·5 Hz, H-3 and H-4), 6·98 *d* and 7·23 *d* (*AB* system, *J* 8·5 Hz, H-5 and H-6) and 4·15 (OMe); MS: intense peaks at *m/e* 192 (100%, M^+), 177 (27·5, M^+–Me), 164 (20·6, M^+–CO), 149 (23·4, 177—CO), 146 (10·6), 121 (20·1, 149—CO), 65 (21·89); acetate, $C_{12}H_{10}O_5$, prepared with Ac_2O–NaOAc, m.p. 135–136° (lit. [11] 136–137°); methyl ether, $C_{11}H_{10}O_4$, prepared with CH_2N_2, m.p. 119–120° (lit. [11] 119–121°).

Percentage yields of the constituents of the two extracts are tabulated below:

Solvent	I	II	III	IV	V	Sitosterol
Light petrol.	0·01	0·015	0·005	0·007	0·001	0·004
$CHCl_3$	0·005	0·01	0·008	0·004	0·01	0·001

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