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A NEW COUMARIN IN *BOENNINGHAUSENIA ALBIFLORA*

M. N S NAYAR, M K BHAN and V GEORGE
Regional Research Laboratory (Br) Sanatnagar, Srinagar, India

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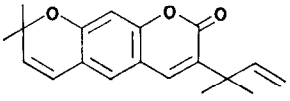
Key Word Index—*Boenninghausenia albiflora*, Rutaceae, 3-(1,1-dimethylallyl)xanthyletin

Boenninghausenia albiflora (Rutaceae) is a perennial shrub found in the temperate Himalayas from Mari to Sikkim,[1] and also in Japan Ohta *et al* [2] have reported the alkaloid dictamnine and the coumarin bergapten in the plant and Miyazaki *et al* [3] found a new coumarin Matzukaze lactone Here we report the characterization of this new coumarin as a 3-(1,1-dimethylallyl)xanthyletin



(I)

The concentrated petrol extract of the aerial part of the plant, on chromatography on alumina, gave a substance which after recrystallization from acetone/petrol had a sharp m p (98–9°) It gave a single UV fluorescent spot on TLC (silica gel G)

The compound dissolved in alcoholic KOH giving a yellow solution, and could be recovered by acidification It analysed for $C_{19}H_{20}O_3$ (M^+ 296) The UV max in ethanol were at 226 (log ϵ 4 36) 266 (4 28) and 346 nm (4 15) and the spectrum was very similar to that of xanthyletin The IR spectrum in KBr showed peaks at 1720 cm^{-1} (conjugated lactone) 1585 cm^{-1}, 1500 cm^{-1} (aromatic) 1375 cm^{-1} (Me-bending) 1280 cm^{-1} (=C–O–C antisymmetric stretching) These data indicated it to be a coumarin of the xanthyletin type, with a C_5H_9 unit attached The structure of this unit and the position of its attachment was evident from the NMR spectrum *

The C-3 and C-4 hydrogens of coumarins show characteristic doublets (J 10 Hz) at δ = 5 93–6 46 and 7 65–8 03 respectively [4,5] In the NMR spectrum of this compound a singlet signal instead of a doublet, appears at δ = 7 32 (1H) assigned to C-4 hydrogen This showed the absence of C-3 hydrogen in the molecule thereby suggesting the position of attachment of the C_5H_9 unit at C-3 Further in the aromatic region there are two other singlet signals at δ = 6 90 (1H) and 6 6 (1H), which are assigned to the C-5 and C-8 hydrogens The absence of coupling between proton signals in the aromatic region suggested that the fusion of the 2,2-dimethylpyrano nucleus to the coumarin is linear and not angular There are two other doublets (J 10 Hz) at δ = 5·6 (1H) and 6 3 (1H) attributed to the C-3′ and C-4′

* 60 MHz spectrum in $CDCl_3$ with TMS is internal reference

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protons respectively There is also a 12 proton singlet signal at $\delta = 1\ 43$ accounting for the four methyl groups in the molecule The remaining signals in the NMR spectrum must all be due to the olefinic protons in the side chain at C-3 and an *ABX* system is found in the olefinic zone with $\delta_A = 5\ 05$ (1H) $\delta_B = 5\ 08$ (1H) $\delta_X = 6\ 18$ (1H), $J_{AX} = 18$ Hz, $J_{BX} = 10$ Hz, and $J_{AB} = 1\ 0$ Hz This system is typical of a vinyl group attached to a quarternary carbon [6]

That double bond in the C-3 substituent is not in conjugation with the coumarin chromophore is further indicated by the Lemieux–Rudloff test[7] in which the production of formaldehyde showed the terminal position of the double bond This confirmed the structure of the side chain In the mass spectrum the parent peak appeared at 15 m u less than the molecular ion peak, which is very characteristic of α,α-dimethyl pyranocoumarins [8]

On these bases, the compound is assigned structure I The number of naturally occurring coumarins with 1,1-dimethylallyl substitution at C-3 is very limited, and all occur exclusively in the Rutaceae I is presumably formed from xanthoxyletin by *C*-isoprenylation at C-3, following standard mechanisms [9]

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IDENTIFICATION OF EBELIN LACTONE FROM BACOSIDE A AND THE NATURE OF ITS GENUINE SAPOGENIN*

D K KULSHRESHTHA and R P RASTOGI

Central Drug Research Institute, Lucknow, India

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Key Word Index—*Bacopa monniera*, Scrophulariaceae, sapongein, bacogenin A_4, ebelin lactone

The acid hydrolysis of bacoside A yielded a mixture of four aglycones which were designated as bacogenins A_1, A_2, A_3 and A_4 in order of increasing R_fs on TLC [1] Recently structure I has been assigned[2] to bacogenin A_1

* Part V in the series "Chemical Examination of *Bacona monniera*" For Part IV see Ref 2 C D R I communication No 1782

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