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1-[2′,4′-DIHYDROXY-3′,5′-DI-(3″-METHYLBUT-2″-ENYL)-6′-METHOXY] PHENYLETHANONE FROM *ACRONYCHIA PEDUNCULATA* ROOT BARK

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Key Word Index—*Acronychia pedunculata*, Rutaceae, arylketone, 1-[2′,4′-dihydroxy-3′,5′-di-(3″-methylbut-2″-enyl)-6′-methoxy]phenylethanone, furoquinoline alkaloids, acronylin, acrovestone, bergapten

Abstract—A new arylketone, 1-[2′,4′-dihydroxy-3′,5′-di-(3″-methylbut-2″-enyl)-6′-methoxy]phenylethanone, was isolated together with acronylin, acrovestone, bergapten, β-amyrin and three furoquinoline alkaloids from the root bark of *Acronychia pedunculata*

INTRODUCTION

Acronychia pedunculata is a small tree widely distributed in Sri Lanka Its bark is used as an external application in the treatment of sores and ulcers [1] The furoquinoline alkaloids, kokusaginine and evolitrine, have been isolated from *A pedunculata* leaves and timber respectively [2] Acronylin and demethylacronylin were found to be present in the stem bark of *A laurifolia* [3, 4], which is believed to be synonymous with *A pedunculata* [1]

RESULTS AND DISCUSSION

Chromatographic separation of the basic fraction of the dichloromethane extract of *A pedunculata* root bark gave the furoquinoline alkaloids, skimmianine, dictamine and kokusaginine The neutral fraction on separation gave the new phenylethanone **1**, acronylin (**2**), acrovestone, the coumarin bergapten and the triterpenoid, β-amyrin Cyclization of acronylin with DDQ gave the chromene **3**

The IR spectrum of the phenylethanone **1**, $C_{19}H_{26}O_4$, indicated it to be an aromatic compound with chelated hydroxyl and carbonyl groups Its ^{1}H NMR spectrum showed two D_2O exchangeable signals at δ 6 20 and 13 56 suggesting that only one of the two hydroxyl groups present was chelated Methyl singlets at δ 3 70 and 2 66 indicated the presence of an OMe group and a –COMe group A triplet at δ 5 29 ($J = 6$ Hz) and a doublet at δ 3 36 ($J = 6$ Hz) respectively due to two vinyl protons and four benzylic methylene protons and two singlets due to four vinylic methyl groups at δ 1.76 and 1 83 suggested that two isopentenyl groups were attached to the aromatic nucleus Peaks at *m/z* 263 and 207 in the mass spectrum of **1** for successive cleavage of the isopentenyl groups at benzylic positions provided additional evidence for the presence of these groups The absence of aromatic proton signals in its ^{1}H NMR spectrum was in keeping with **1** having a structure containing a methoxy and an acetyl group, two isopentenyl group and two hydroxyl group substituents attached to a benzene ring

Biogenetic considerations and the presence of a chelated hydroxyl group suggested two possible structures (**1** and **4**) for the compound Acetylation gave a diacetate **5**, whose ^{1}H NMR spectrum showed two distinct singlets at δ 2 16 and 2 23 for the OAc methyl groups The diacetate could not have the symmetrical structure **6**, which would be expected to show a single signal for these methyl groups in ^{1}H NMR The phenylethanone was therefore 1-[2′,4′-dihydroxy-3′,5′-di-(3″-methylbut-2″-enyl)-6′-methhoxy]phenylethanone (**1**)

EXPERIMENTAL

Mps uncorr, IR KBr, ^{1}H NMR 60 MHz, $CDCl_3$ using TMS as int standard Optical rotations $CHCl_3$ at 25 Prep TLC Merck silica gel $PF_{254+366}$ Petrol 40–60 Identities of compounds were established by mmp, IR and ^{1}H NMR comparisons, unless otherwise stated *A pedunculata* was collected from Gannoruwa in central Sri Lanka and a voucher specimen has been deposited in the University herbarium

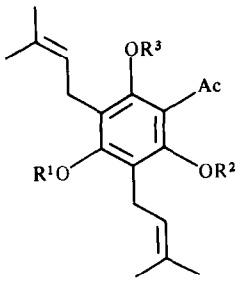
Extraction Dried ground *A pedunculata* root bark (1 2 kg) was extracted with CH_2Cl_2 at 27 for two 24 hr periods each Concn of the combined solns gave 150 3 g of the CH_2Cl_2 extract

Separation of the basic fraction of the CH_2Cl_2 extract The CH_2Cl_2 extract (148 g) was dissolved in Et_2O (500 ml) and washed with 2% H_2SO_4 Concn of the CH_2Cl_2 layer at 40 gave the neutral fraction (140 g) The aq layer was washed with Et_2O, neutralized (Na_2CO_3) and extracted with CH_2Cl_2 Concn of the CH_2Cl_2 extract at 40 gave the basic fraction (1 2 g)

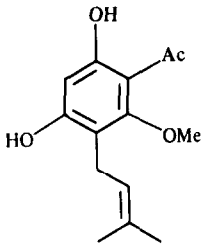
Chromatography of the basic fraction The basic fraction (1 2 g) was chromatographed on silica gel using CH_2Cl_2–petrol mixtures for elution Elution with CH_2Cl_2–petrol (1 4) gave a fraction which on prep TLC (EtOAc petrol, 1 4) followed by recrystallization from CH_2Cl_2 petrol gave dictamine (53 mg), mp 127–129° (lit [5] mp 132°), skimmianine (14 mg), mp 178–180 (lit [5] mp 176°) and kokusaginine (17 mg), mp 169–170 (lit [2] mp 171°), identical with authentic material

Chromatography of the neutral fraction The neutral fraction (140 g) was chromatographed (MPLC) on silica gel using hexane–CH_2Cl_2 MeOH mixtures for elution Elution with EtOAc–petrol (1 49) gave on trituration with Et_2O, a yellow solid which crystallized from CH_2Cl_2–petrol as yellow needles of acrovestone (220 mg), mp 143–145°, (lit [6] mp 142 142 5°)

Elution with EtOAc–petrol (1 19) followed by flash chromatography (CH_2Cl_2–petrol, 1 9) gave β-amyrin (33 mg), mp 196–198°, $[\alpha]_D$ +87 3 (lit [5] mp 197°, $[\alpha]_D$ +87°) and



1 $R^1 = R^3 = H$, $R^2 = Me$
4 $R^1 = Me$, $R^2 = R^3 = H$
5 $R^1 = R^3 = COMe$, $R^2 = H$
6 $R^2 = R^3 = COMe$, $R^1 = H$



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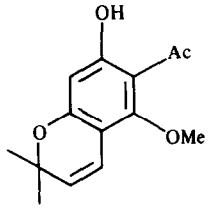

3

colourless needles of acronylin (**2**) (43 mg) mp 128–130° (lit. [3] mp 128–129°), and on prep. TLC (CH_2Cl_2–petrol, 1·4,2 developments), 1-[2′,4′-dihydroxy-3′,5′-di-(3″-methylbut-2″-enyl)-6′-methoxy]phenylethanone (**1**) as a yellow oil (43 mg) (HR-MS 318.1835 $[M]^+$; Calc. for $C_{19}H_{26}O_4$ 318.1831); IR ν_{max} cm^{-1} 3350, 3150, 1660 and 1600, ^1H NMR δ 1.76 and 1.83 (each *s*, 6H, 3″-Me), 2.66 (*s*, 3H, COMe), 3.36 (*d*, 4H, $J = 6$ Hz, 1″-H), 3.70 (*s*, 3H, OMe), 5.29 (*t*, 2H, $J = 6$ Hz, 2″-H) 6.26 and 13.56 (each *s*, 1H, D_2O exchangeable, OH), MS *m/z* (rel. int.): 318 $[M]^+$ (100), 303 (47), 275 (33), 263 (54), 247 (72), 219 (12) and 207 (11).

Elution with EtOAc–hexane (3.17) followed by prep. TLC (CH_2Cl_2–petrol, 1·9) gave bergapten as colourless needles (45 mg), mp 186–188° (lit [5] mp 188–191°)

Cyclization of **2** Acronylin (**2**) (31 mg) in C_6H_6 was treated with DDQ (0·1 g) at 60° for 8 hr. The usual work-up followed by prep TLC (CH_2Cl_2–petrol, H 1·9) gave 6-acetyl-7-hydroxy-5-methoxy-2,2-dimethylchromene (**3**) (26 mg), as a yellow oil, IR ν_{max} cm^{-1} 3350, 1640 and 1590, ^1H NMR: δ 1.50 (*s*, 6H, 2-Me), 2.66 (*s*, 3H, COMe), 3.73 (*s*, 3H, OMe), 5.24 (*d*, 1H, $J = 10$ Hz, 3-H), 6.23 (*s*, 1H, 8-H), 6.62 (*d*, 1H, $J = 10$ Hz, 4-H) and 10.74 (*s*, 1H, D_2O exchangeable, OH), MS *m/z* (rel. int.) 248 $[M]^+$ (31), 206 (46), 193 (100) and 151 (71).

Acetylation of **1** Phenylethanone **1** (20 mg) with Ac_2O–pyridine (1:2, 3 ml) at 27° for 18 hr gave on work-up (1-[2′,4′-diacetoxy-3′,5′-di-(3″-methylbut-2″-enyl)-6′-methoxy]phenylethanone (**5**) (28 mg), as a yellow oil, IR ν_{max} cm^{-1} 3350, 1760, 1690 and 1600, ^1H NMR δ 1.74 (*s*, 12H, 3″-Me), 2.16 and 2.23 (each *s*, 3H, OAc), 2.50 (*s*, 3H, COMe), 3.13 (*m*, 4H, $W_{1/2} = 6$ Hz, 1″-H), 3.66 (*s*, 3H, OMe) and 4.80–5.20 (*m*, 2H, $W_{1/2} = 6$ Hz, 2″-H), MS *m/z* (rel. int.) 402 $[M]^+$ (5), 359 (100), 354 (14), 317 (27), 302 (100), 389 (28) and 219 (82)

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