PR 5508

(16)

Phytochemistry, Vol. 28, No. 4, pp. 1278–1279, 1989.
Printed in Great Britain.

0031-9422/89 $3.00 + 0.00

(9)

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

VIJAYA KUMAR, VERANJA KARUNARATNE and M. R. SANATH K. MEEGALLE

Department of Chemistry, University of Peradeniya, Peradeniya, Sri Lanka

(*Received* 10 *August* 1988)

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 n Sri Lanka. Its bark is used as an external application in he treatment of sores and ulcers [1]. The furoquinoline ılkaloids, kokusaginine and evolitrine, have been isolated rom *A. pedunculata* leaves and timber respectively [2]. Acronylin and demethylacronylin were found to be pres- nt in the stem bark of *A. laurifolia* [3, 4], which is elieved to be synonymous with *A. pedunculata* [1].

RESULTS AND DISCUSSION

Chromatographic separation of the basic fraction of ne dichloromethane extract of *A. pedunculata* root bark ave the furoquinoline alkaloids, skimmianine, dictamine nd kokusaginine. The neutral fraction on separation ave the new phenylethanone 1, acronylin (2), acro- stone, the coumarin bergapten and the triterpenoid, β- myrin. Cyclization of acronylin with DDQ gave the romene 3.

The IR spectrum of the phenylethanone 1, $C_{19}H_{26}O_4$, ated it to be an aromatic compound with chelated droxyl and carbonyl groups. Its ^{1}H NMR spectrum owed two D_2O exchangeable signals at δ6.20 and 13.56 ggesting that only one of the two hydroxyl groups esent was chelated. Methyl singlets at δ3.70 and 2.66 dicated the presence of an OMe group and a –COMe oup. A triplet at δ5.29 (J = 6 Hz) and a doublet at δ3.36 = 6 Hz) respectively due to two vinyl protons and four nzylic methylene protons and two singlets due to four ylic methyl groups at δ1.76 and 1.83 suggested that o isopentenyl groups were attached to the aromatic cleus. Peaks at m/z 263 and 207 in the mass spectrum of for successive cleavage of the isopentenyl groups at nzylic positions provided additional evidence for the sence of these groups. The absence of aromatic proton nals in its ^{1}H NMR spectrum was in keeping with 1 ving a structure containing a methoxy and an acetyl up, two isopentenyl group and two hydroxyl group stituents attached to a benzene ring.

Biogenetic considerations and the presence of a che- d hydroxyl group suggested two possible structures (1 4) for the compound. Acetylation gave a diacetate 5, whose ^{1}H NMR spectrum showed two distinct singlets at δ2.16 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'-methoxy]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.

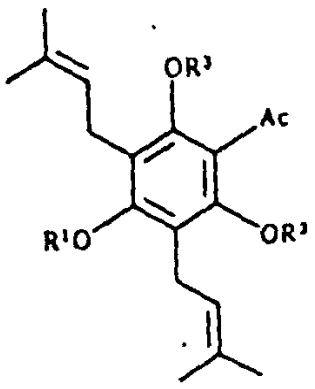
Extraction. Dried ground *A. pedunculata* root bark (1.2 kg) was extracted with CH_2Cl_2 at 27° for two 24 hr periods each. Concn of the combined solns gave 150.3 g of the CH_2Cl_2 extract.

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).

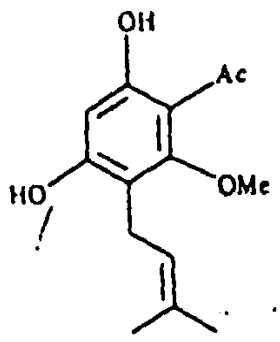
Chromatography of the basic fraction. The basic fraction (1.2 g) was chromatographed on silica gel using CH_2Cl_2–petrol mixtures for elution. Elution with CH_2Cl_2–petrol (1:4) gave a fraction which on prep. TLC (EtOAc–petrol, 1:4) followed by recrystallization from CH_2Cl_2–petrol gave dictamine (53 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°).

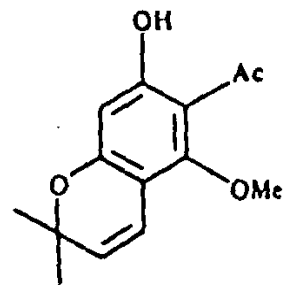
Elution with EtOAc–petrol (1:19) followed by flash chromatography (CH_2Cl_2–petrol, 1:9) gave β-amyrin (33 mg), mp 196–198°, $[\alpha]_D$ +87.3° (lit. [5] mp 197°, $[\alpha]_D$ +87°) and



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 $R^2 = R^3 = COMe$, $R^1 = H$



2



3

Ab
lat
of

—rless needles of acronylin (2) (43 mg) mp 128–130° (lit. [3] 28–129°), and on prep. TLC (CH_2Cl_2–petrol, 1:4, 2 devel-nts), 1-[2',4'-dihydroxy-3',5'-di-(3''-methylbut-2''-enyl)-6'-oxy]phenylethanone (1) as a yellow oil (43 mg) (HR-MS 835 $[M]^+$; Calc. for $C_{19}H_{26}O_4$: 318.1831); IR ν_{max} cm^{-1}: 3150, 1660 and 1600; ^1H NMR: δ1.76 and 1.83 (each *s*, 6H, e), 2.66 (*s*, 3H, COMe), 3.36 (*d*, 4H, $J = 6$ Hz, 1''-H), 3.70 (*s*,)Me), 5.29 (*t*, 2H, $J = 6$ Hz, 2''-H) 6.26 and 13.56 (each *s*, 1H; exchangeable, OH); MS *m/z* (rel. int.): 318 $[M]^+$ (100), 303 275 (33), 263 (54), 247 (72), 219 (12) and 207 (11).

ation with EtOAc–hexane (3:17) followed by prep. TLC Cl_2–petrol, 1:9) gave bergapten as colourless needles g), mp 186–188° (lit. [5] mp 188–191°).

clization of 2. Acronylin (2) (31 mg) in C_6H_6 was treated DDQ (0.1 g) at 60° for 8 hr. The usual work-up followed by TLC (CH_2Cl_2–petrol, H 1:9) gave 6-acetyl-7-hydroxy-5-oxy-2,2-dimethylchromene (3) (26 mg), as a yellow oil, $_{max}$ cm^{-1}: 3350, 1640 and 1590; ^1H NMR: δ1.50 (*s*, 6H, 2-2.66 (*s*, 3H, COMe), 3.73 (*s*, 3H, OMe), 5.24 (*d*, 1H, *J*) Hz, 3-H), 6.23 (*s*, 1H, 8-H), 6.62 (*d*, 1H, $J = 10$ Hz, 4-H) and 4 (*s*, 1H, D_2O exchangeable, OH); MS *m/z* (rel. int.): 248 $]^+$ (31), 206 (46), 193 (100) and 151 (71).

cetylation of 1. Phenylethanone 1 (20 mg) with Ac_2O–dine (1:2, 3 ml) at 27° for 18 hr gave on work-up (1-[2',4'-etoxy-3',5'-di-(3''-methylbut-2''-enyl)-6'-methoxy]phenyl-none (5) (28 mg), as a yellow oil, IR ν_{max} cm^{-1}: 3350, 1760, 0 and 1600; ^1H NMR: δ1.74 (*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).

Acknowledgements—We gratefully acknowledge financial assistance from Natural Resources, Energy and Science Authority of Sri Lanka, the International Foundation for Science, Stockholm and the International Science Program, Chemical Sciences, Uppsala. We are also grateful to Professor S. Matsunaga of the Osaka University of Pharmaceutical Sciences for high resolution mass spectra.

REFERENCES

1. Dassanayake, M. D. and Fosberg, F. R. (1985) *A Revised Handbook to the Flora of Ceylon*, Vol. V, p. 412. Amerind Publishing, New Delhi.
2. De Silva, L. B., De Silva, U. L. L., Mahendran, M. and Jennings, R. (1979) *Phytochemistry* 18, 1255.
3. Biswas, G. K. and Chatterjee, A. (1970) *Chem. Ind.* 654.
4. Banerji, J., Rej, R. N. and Chatterjee, A. (1974) *Indian J. Chem.* 11, 693.
5. *Dictionary of Organic Compounds* (1965) Vols I–V, Eyre & Spottiswoode, London.
6. Labey, F. N. and Hutching, R. (1961) *Sym. Phytochem. Proc. Meeting*, p. 121. University of Hong Kong.

National Digitization Project

National Science Foundation

Institute : National Science Foundation

1. Place of Scanning : Sanje (Private) Ltd, Hokandara
2. Date Scanned : 02/06/2017
3. Name of Digitizing Company : Sanje (Private) Ltd, No 435/16, Kottawa Rd, Hokandara North, Arangala, Hokandara
4. Scanning Officer

Name : Angelo Melvin Luwis

Signature : A. M. Luwis

Certification of Scanning

I hereby certify that the scanning of this document was carried out under my supervision, according to the norms and standards of digital scanning accurately, also keeping with the originality of the original document to be accepted in a court of law.

Certifying Officer

Designation : Information Officer

Name : Renuka Sugathadasa

Signature : R. P. Sugathadasa

Date : 02/06/2017

"This document/publication was digitized under National Digitization Project of the National Science Foundation, Sri Lanka"