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MURRAGLEININ, A COUMARIN FROM *MURRAYA GLEINEI* LEAVES

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Key Word Index—*Murraya gleinei*; Rutaceae; coumarins; murragleinin; exoticin; skimianine; stigmasterol.

Abstract—A new trioxygenated C-8 prenylated coumarin, 5,6,7-trimethoxy-8-(2′,3′-dihydroxyisopentenyl)-coumarin and the laevorotatory form of mexoticin, sibiricin and phebalosin were isolated from the leaves of *Murraya gleinei* together with the coumarins meranzin hydrate, meranzin, murralongin, murrangatin and scopoletin, the flavone exoticin, the alkaloid skimianine and the sterol stigmasterol.

INTRODUCTION

Several coumarins [1–3] carbazole alkaloids [4–6] and flavanoids [7–10] have been reported from *Murraya* species (Rutaceae) previously investigated; *M. elongata* [11, 12], *M. paniculata* (*M. exotica*) [5, 7–10], *M. omphalocarpa* [2, 3] and *M. koenigei* [4, 6]. The leaves of *M. gleinei*, a species endemic to Sri Lanka contained several coumarins, including a new coumarin, murragleinin (**1**). The laevorotatory forms of the previously reported mexoticin (**2**) [13] and sibiricin (**3**) [14] together with six other coumarins, phebalosin (**4**) [15], meranzin hydrate (**5**) [16], murrangatin [11], murralongin [12], meranzin [17] and scopoletin [18], the flavone, exoticin [9], the alkaloid, skimianine [18] and the sterol, stigmasterol [18] were also present.

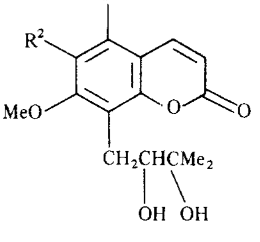
RESULTS AND DISCUSSION

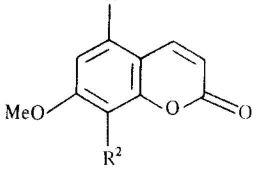
The petrol extract of *M. gleinei* leaves on chromatographic separation afforded stigmasterol, skimianine and the four coumarins, mexoticin (**2**), sibiricin (**3**), phebalosin (**4**) and meranzin. (±)-Phebalosin (**4**) has been found to occur in some *Phebalium* species [15] and (+)-phebalosin, (+)-mexoticin and meranzin have been isolated from *M. paniculata* [13, 17, 19] while (+)-sibiricin (**3**) has been reported to occur in *Seseli sibiricum* [14]. Mexoticin (**2**), sibiricin (**3**) and phebalosin (**4**) isolated from *M. gleinei* showed the physical and spectroscopic characteristics of mexoticin, sibiricin and phebalosin reported previously but were laevorotatory. This is the first report of the (−) enantiomers of these compounds.

The opening of the epoxide ring in sibiricin (**3**) should give a glycol with the structure of mexoticin (**2**). (−)-Sibiricin (**3**) was refluxed with 1% oxalic acid and the product was found to be identical to mexoticin and showed an $[\alpha]_D$ of −31°. (+)-Sibiricin from *Seseli sibiricum* had on similar treatment given sibiricin glycol (mexoticin) $[\alpha]_D$ +27° [14].

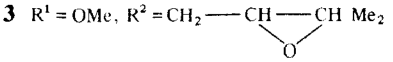
The chloroform extract of the leaves on chromatographic separation gave 3,3′,4,5,5′,6,7,8-octamethoxyflavone (exoticin), meranzin hydrate (**5**), murralongin, murrangatin and scopoletin all of which have been previously isolated from *Murraya species* [1, 9]. The more polar coumarin was found to be (−)-mexoticin (**2**) which was also isolated from the petrol extract.

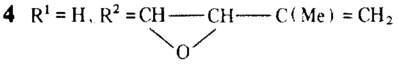
The less polar coumarin in its ^{1}H NMR spectrum





1 $R^1 = R^2 = OMe$
2 $R^1 = OMe, R^2 = H$
5 $R^1 = R^2 = H$


3 $R^1 = OMe, R^2 = CH_2-\underbrace{CH-CH}_{O}Me_2$


4 $R^1 = H, R^2 = \underbrace{CH-CH}_{O}-C(Me)=CH_2$

showed some of the characteristics of the spectra of mexoticin (**2**) and meranzin hydrate (**5**). Two singlets at δ4.03 and δ3.90 due to nine protons suggested the presence of three methoxy groups. An AB double doublet with $J = 10$ Hz centred at δ6.26 and δ7.95 was characteristic of the 3 and 4 protons in the coumarin ring system, indicating that these positions were unsubstituted. The absence of any further signals in the aromatic region suggested that three methoxyl groups were attached to the aromatic ring and that the remaining position in the ring was also substituted. A D_2O exchangeable broad singlet at δ2.43 was due to the hydroxyl protons while a singlet at δ1.34 due to six protons showed the presence of two methyl groups probably the *gem*-dimethyls of a terminal hydroxyisopropyl group. The CH signal at δ3.58 and the CH_2 signal at δ2.97 constituted a typical AB_2 pattern, the chemical shifts of the protons suggesting the presence of an Ar–CH_2–CH–O arrangement in the molecule. The side-chain of the coumarin was therefore similar to that of mexoticin (**2**) and meranzin hydrate (**5**). Since the ^{1}H NMR chemical shifts of the side chain protons were almost identical to those (six proton singlet at δ1.32 and AB_2 multiplet at δ2.96 and δ3.60) observed for mexoticin (**2**), the side chain should be attached to the same position [14] as in mexoticin (**2**). The coumarin should be 5,6,7-trimethoxy-8-(2′,3′-dihydroxyisopentenyl)-coumarin (**1**). The mass spectrum showed intense peaks at m/z 279/280 and 249 due to cleavage of the hydroxyisopropyl group and of a C_4 fragment from the side chain and a base peak at m/z 237 due to $[280 - CH_3CO]$.

5,6,7-Trimethoxy-8-(2′,3′-dihydroxyisopentenyl)-coumarin (**1**) is a new coumarin for which we propose the name murragleinin. It is the first example of an 8-alkylated coumarin with a fully substituted aromatic ring.

EXPERIMENTAL

Mps are uncorr. Identities of compounds were established by mmp, IR, MS and NMR comparison. Petrol to the fraction 40–60° Prep. TLC was carried out on Merck Kieselgel 60. Optical rotations were measured at 25° in $CHCl_3$. IR spectra were recorded using KBr discs. ^{1}H NMR spectra were recorded at 60 MHz with TMS as int. standard.

M. gleinei was collected at Wilpattu in North-West Sri Lanka and a voucher specimen has been deposited in the University herbarium.

Extraction. Fresh leaves (1.9 kg) were extracted with petrol and then with $CHCl_3$ for 48 hr each at 25°. Concn gave 27 g and 18 g of petrol and $CHCl_3$ extracts, respectively.

Chromatography of petrol extract. The extract (22 g) was chromatographed on silica gel (750 g). Elution with petrol–EtOAc (9:1) gave stigmasterol, colourless needles from MeOH–$CHCl_3$ (0.25 g) mp 166–167°, $[\alpha]_D - 49.4°$ (lit. [18] mp 168–170°, $[\alpha]_D - 51°$). Elution with petrol EtOAc (1:1) yielded phebalosin (**4**), needles from $CHCl_3$–petrol (3.8 g) mp 125–126°, $[\alpha]_D - 43.6°$ (c 8.5) (lit. [16] mp 125–126°) (Found: $[M]^+$ 258.0894, $C_{15}H_{14}O_4$ requires 258.0892) and a mixture of two coumarins which was rechromatographed on silica gel (200 g) to give meranzin, colourless plates from EtOAc (0.03 g) mp 115–116°, $[\alpha]_D + 23.8°$ (lit. [17] mp 98°) and sibiricin (**3**), needles from $CHCl_3$–petrol (0.8 g) mp 148–149°, $[\alpha]_D - 59.7°$ (lit. [13] mp 152–153°, $[\alpha]_D + 60.4°$). Elution with petrol–EtOAc (2:3) yielded skimianine, pale yellow cubes from $CHCl_3$–petrol (0.25 g) mp 176° (lit. [18] mp 176°). Further elution with petrol–EtOAc (1:4) gave mexoticin (**2**), colourless needles from $CHCl_3$–petrol (1.2 g) mp 191–192°, $[\alpha]_D - 31.1°$ (lit. [13] mp 185°, $[\alpha]_D + 37°$). (Found: C, 62.1; H, 6.3. $C_{16}H_{20}O_6$ requires C, 62.3; H, 6.5%.)

Chromatography of $CHCl_3$ *extract.* The extract (15 g) was chromatographed on a silica gel (450 g) column. Elution with petrol–EtOAc (2:3) yielded exoticin, which crystallised from Me_2CO–petrol as pale yellow needles (0.25 g), mp 123–124° (lit. [9] mp 124°) and murralongin, colourless needles from Et_2O (0.08 g), mp 137° (lit. [12] mp 135–136°). Elution with petrol–EtOAc (3:7) gave scopoletin which crystallised from Me_2CO–petrol as pale yellow needles (0.15 g) mp 202–204° (lit. [18] mp 202°) and with petrol–EtOAc (1:4 and 1:9) gave mixtures of coumarins which on purification by prep. TLC [$CHCl_3$–MeOH (49:1)] gave (±)-murrangatin which crystallised from EtOAc as colourless cubes (0.12 g) mp 133° (lit. [11] mp 133°, $[\alpha]_D - 3°$), meranzin hydrate (**5**), plates from $CHCl_3$–petrol (0.09 g), mp 128–129°, $[\alpha]_D - 26.0°$ (lit. [15] mp 131–132°, $[\alpha]_D - 29°$), mexoticin (**2**) (1.0 g), and 5,6,7-*trimethoxy*-8-(2′,3′-*dihydroxyisopentenyl*)-*coumarin* (*murragleinin*) which crystallized from $CHCl_3$–petrol as needles (0.02 g) mp 148–149°, $[\alpha]_D - 43.0°$ (Found: $[M]^+$ 338.1347. $C_{17}H_{22}O_7$ requires 338.1366.) UV λ_{max} nm: 247, 302; IR ν_{max} cm^{-1}: 3300 (br), 1730 and 1600; ^{1}H NMR: δ1.34 (s, 6H), 2.97 (m, $W_{1/2} = 4$ Hz, 2H), 3.58 (dd, $J = 4$ and 9 Hz, 1H), 3.90 (s, 3H), 4.03 (s, 6H), 6.26 (d, 1H, $J = 10$ Hz), 7.95 (d, 1H, $J = 10$ Hz); MS m/z (rel. int.): 338 $[M]^+$ (5%), 280 (20), 279 (21), 249 (53) and 237 (100).

Epoxide ring opening of sibiricin. (−)-Sibiricin (**3**) (50 mg) and 1% aq. oxalic acid (20 ml) were refluxed for 2 hr, the soln cooled and then treated with $NaHCO_3$. The white ppt was filtered, purified by prep. TLC and recrystallized from $CHCl_3$–petrol as colourless needles mp 191°, $[\alpha]_D - 31.7°$ identicial with (−)-mexoticin obtained above.

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3,4,8,9,10-PENTAHYDROXY-DIBENZO[*b*, *d*]PYRAN-6-ONE FROM *TAMARIX NILOTICA*

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Key Word Index—*Tamarix nilotica*; Tamaricaceae; flowers; phenolic lactones; 3,4,8,9,10-pentahydroxy-dibenzo[*b*, *d*]pyran-6-one; ellagic acid; structural determination.

Abstract—A new natural product, 3,4,8,9,10-pentahydroxy-dibenzo-[*b*, *d*]pyran-6-one was isolated from the flowers of *Tamarix nilotica* which also contains the known compound ellagic acid, 2,3,7,8-tetrahydroxy [1]benzopyrano[5,4,3-*cde*][1]benzopyran-5,10-dione. The structure of the new compound was determined by chemical and spectroscopic methods. The ^{13}C MNR spectrum of ellagic acid was recorded and assigned.

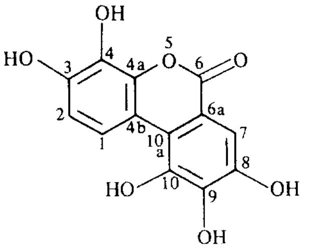
INTRODUCTION

The aqueous acetone extract of the flowers of *Tamarix nilotica* was reported by us to contain the methyl and ethyl esters of gallic acid, *p*-methoxygallic acid, kaempferol and quercetin 3-*O*-glucuronides, the 3-*O*-sulphated kaempferol 7,4′-dimethyl ether and the free flavonols, kaempferol, quercetin and kaempferol 7,4′-dimethyl ether beside the digalloylglucose, niloticin [1, 2]. Further investigation of this extract afforded the new natural phenolic lactone, 3,4,8,9,10-pentahydroxy-dibenzo[*b*, *d*]pyran-6-one (**1**) and ellagic acid (**2**). In this paper we report the isolation and structural elucidation of **1**. Also, the ^{13}C NMR data of ellagic acid is reported for the first time. Compound **1** is another natural product added to the well known biosynthetic transformation products of hexahydroxydiphenic acid such as breviofolin and chebulic acid [3]. Also, it belongs to the 3,4-benzocoumarins, which are of rare natural occurrence.

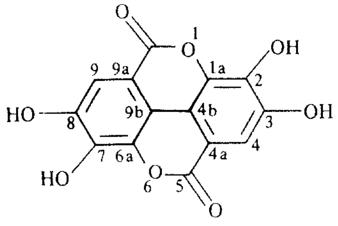
RESULTS AND DISCUSSION

The last fraction, eluted with methanol from the polyamide column of the aqueous acetone extract of the flowers of *T. nilotica* [2], was shown by 2D-PC, in UV light to contain two fluorescent compounds **1** and **2**, apart from the yellow flavonols which were previously investigated [2]. Pure samples of **1** and **2** were isolated by applying a polyamide column fractionation of this methanolic fraction using ethyl acetate saturated with water as an eluent.

Compound **1** was isolated as colourless needles which gave a molecular formula $C_{13}H_8O_7$ by high resolution mass spectrometry. On PC, **1** appeared as a fluorescent blue spot in UV light. It gave a blue ferric chloride reaction and remained unchanged after acid or alkaline hydrolysis. On alkali-fusion it yielded 4,5,6,2′,3′,4′-hexahydroxybiphenyl (co-PC and UV data). The IR spectrum of **1** showed strong absorption at 3400, 1695, 1630 and



1



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