exhaustive extraction with 95 % EtOH. The extract was worked up as described in the text [2] and monitored by TLC. Final purification was by CC on Si gel using $CHCl_3$–MeOH–H_2O (13:7:2) as eluant. Fraction A gave **1** as a light cream-coloured compound, mp 240–243°, $[\alpha]_D$ +95.5° (*c*, 1 % MeOH), IR ν_{max} 860, 900, 920, 980 cm^{-1}.

Isolation of genin and sugars. Acid hydrolysis with 2 N H_2SO_4 was carried out in the usual manner (see text). The genin was crystallized from MeOH, mp 263–264° and identified as hecogenin. The deionized supernatant was concd and examined by PC and gave glucose only. This was confirmed by GLC using pyridine, hexamethyldisilazine and trimethylchlorosilane for silylation. The silyl derivative of the sugar was identified as glucose by GLC (R_t and peak enhancement method). Further confirmation was by HPLC.

Methylation and methanolysis of the saponin. The saponin was methylated in the usual manner in DMSO with MeI and NaH The fully methylated product was isolated and showed no absorption in the 3-μm region in IR, indicating the absence of free OH groups. The methylated product was subjected to methanolysis with 3 % methanolic HCl in a sealed tube at 70° for 5 hr. The soln was neutralized ($AgCO_3$) and filtered.

Identification of methylated sugars. The methyl glycosides of methylated sugars obtained were identified by GLC on 8 % OS-138 on Chromosorb-W (NAW) column as 2,3,4,6-tetra-*O*-methyl-α-D-glucose and 2,3,6-tri-*O*-methyl-α-D-glucose by comparison with authentic samples. From the GLC trace the molar ratio was determined as 1:2 by the peak area method.

Periodate treatment for 48 hr with 0.05 M $NaIO_4$ soln was followed by extracting with *n*-BuOH. The *n*-BuOH extract after evapn and hydrolysis with 2 N H_2SO_4 showed no sugars on PC.

Enzyme hydrolysis. Treatment of **1** in NaOAc buffer (pH5) with β-glucosidase at 37° for 50 hr did not release any sugar.

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A COUMARIN FROM *LIMONIA ACIDISSIMA*

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Key Word Index—*Limonia acidissima*; Rutaceae; root-bark; dihydrosuberenol; coumarin; 2 H-1-benzopyran-2-one, 6-[3-hydroxy-3-methyl 1-butyl]-7-methoxy.

Abstract—Dihydrosuberenol, a new coumarin, was isolated from the methanol extract of the defatted root-bark of *Limonia acidissima*. Its structure has been established through spectral investigations and partial synthesis.

In continuation of our work on *Limonia acidissima* L. [1], we now report the presence of a new coumarin from the MeOH extract of the defatted root-bark. According to *Index Kewensis* [2] the valid name of this species is *L. acidissima* and not *L. crenulata* or *Hesperthrusa crenulata* [3]. The plant material for investigation was collected locally and a voucher specimen (386 and 388) has been preserved at the University Herbarium in the Botany Department.

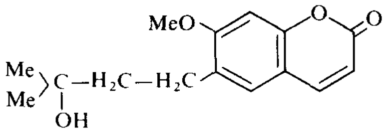
The extract was chromatographed on a Si gel column and eluted with solvent mixtures of increasing polarity. A pale yellow solid, obtained from the C_6H_6–$CHCl_3$ (1:1) eluate was rechromatographed and on monitoring by TLC it has been possible to obtain a TLC and GC pure colourless crystalline material (**1**), mp 105°. It analysed for $C_{15}H_{18}O_4$ (M^+, 262) and gave the usual colour reactions for coumarins exhibiting λ_{max}^{MeOH} at 320, 296 (*sh*), 253 and 224 nm typical of 7-alkoxy coumarins [4, 5]. The IR spectrum in KBr showed peaks at 3500 (–OH), 1700 ($>$C=O), 1595, 1540 (aromatic), 1370, 1355 (*gem* dimethyls), 1260 ($>$C=C–O–C asymmetrical stretching), 1120 ($>$C–O stretching). The ^1H NMR data (Table 1) clearly indicate the oxygen functions as methoxyl and hydroxyl. The typical coumarin doublets appeared at δ 6.30 and 7.68 (J = 10 Hz), accompanied by the 6-proton methyl singlet at δ 1.38. The commanding feature in identifying a $-CH_2-CH_2-$(AA′XX′) system was apparent from the signals which occurred as multiplets possessing a symmetry about the mid-point of the pattern and the spectrum due to the AA′ nuclei was the exact mirror image of that of XX′. The occurrence of two singlets in the aromatic region obviously denotes the presence of two hydrogens at C-5 and C-8 and thereby provides space for the 3-hydroxy-3-methyl-1-butyl side-chain and the

Table 1. 90 MHz ^{1}H NMR spectrum of dihydrosuberenol (1)

3-H	4-H	5-H	1'-H	2'-H	7-OMe	8-H	$Me_2C<$	3'-OH
6.30 *d* (1 H), $J = 10$ Hz	7.68 *d* (1 H), $J = 10$ Hz	7.30 *s* (1 H)	2.8 *m* (2 H)	1.8 *m* (2 H)	3.96 *s* (3 H)	6.86 *s* (1 H)	1.86 *s* (6 H)	1.64 *s* (1 H) disappeared on D_2O exchange

Chemical shift values are in δ in $CDCl_3$ using TMS as int. ref.

methoxyl substituent at C-6 and C-7, respectively. The mass spectral fragmentation pattern was in good agreement with the schemes proposed for methoxyprenylated coumarin derivatives [6, 7]. Prominent peaks were observed at *m/z* 262 (M^+, 2%), 244 ($M^+ - H_2O$, 45%), 229 ($244 - CH_3$, 85%), 189 ($M^+ - C_4H_9O$, 100%), 159 ($189 - CH_2O$, 3%), 131 ($159 - CO$, 3%), 77 ($C_6H_5^+$, 3%) and 59 ($Me_2 - C^+{-}OH$, 52%).



1

All these spectral evidences clearly indicate structure **1** for the coumarin, and the assignment as dihydrosuberenol also received further confirmation by its partial synthesis from suberenol, another constituent isolated from the plant under investigation, through catalytic hydrogenation in the presence of Pd–C. The IR, ^{1}H NMR and MS data of the synthetic compound were identical to those of the natural one.

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A PUNGENT PRINCIPLE FROM *ALPINIA OXYPHYLLA*

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Key Word Index—*Alpinia oxyphylla*; Zingiberaceae; yakuchi; pungent principle; diarylheptanoid; yakuchinone-A; 1-(4'-hydroxy-3'-methoxyphenyl)-7-phenyl-3-heptanone; yakuchinone-B; *trans*-1-(4'-hydroxy-3'-methoxyphenyl)-7-phenylhept-1-en-3-one; zingerone.

Abstract—A pungent diarylheptanoid isolated from *Alpinia oxyphylla* has been characterized as *trans*-1-(4'-hydroxy-3'-methoxyphenyl)-7-phenylhept-1-en-3-one(yakuchinone-B) by spectroscopic methods and by synthesis.

INTRODUCTION

The pungent principles of zingiberaceous plants form a class of natural products which are based on a 4-hydroxy-3-methoxyphenyl group; for example, zingerone [1], gingerols [2], shogaols [3], paradols [4] and so on. In a continuation of the study of the chemical nature of the pungent components, we have previously reported on the isolation and characterization of 1-(4'-hydroxy-3'-methoxyphenyl)-7-phenyl-3-heptanone (**1**) from the $CHCl_3$-soluble fraction of *A. oxyphylla* Miquel [5]. In this paper, we wish to report on the identification of a new pungent substance, *trans*-1-(4'-hydroxy-3'-methoxyphenyl)-7-phenylhept-1-en-3-one (**2**), from the same source.