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ALIPHATIC COMPOUNDS FROM *COSTUS SPECIOSUS* ROOTS*

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Key Word Index—*Costus speciosus*; Costaceae; roots; methyl tritriacontanoate; 8-hydroxytriacontan-25-one.

Abstract—Two new compounds G and H isolated from the roots of *Costus speciosus* have been characterized as 8-hydroxytriacontan-25-one and Me tritriacontanoate by spectral data and chemical studies.

INTRODUCTION

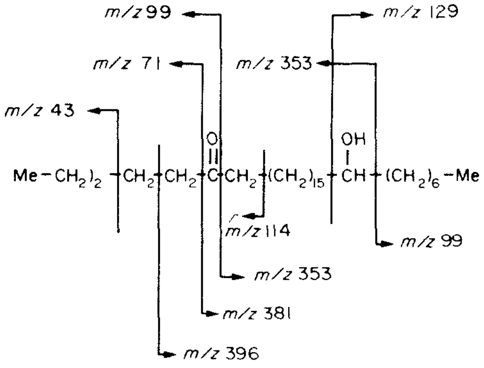
Recently we have reported on diosgenin and the isolation and characterization of new keto alcohols [1] and stigmast-9(11)-enol [2] from the roots of *Costus speciosus* Sm. During the course of these studies, the structure of two additional compounds have been elucidated.

RESULTS AND DISCUSSION

Two crystalline compounds were isolated by Si gel chromatography of the *n*-hexane extract of the roots of *C. speciosus.*

Compound G, mp 95° exhibited IR absorption bands at 3440 (OH), 1710 (CO), 2920, 2840, 1465, 730 and 720 cm^{-1} (long chain) and gave a positive 2,4-dinitrophenylhydrazine test. The mass spectrum of G had an M$^+$ ion at *m/z* 452 suggesting the molecular formula as $C_{30}H_{60}O_2$. The assignment of the CO group at C-25 is obtained by the presence of prominent α-fission ions at *m/z* 71, 381, 99, 353 and β-fission ions, involving McLafferty rearrangement, at *m/z* 396 and 114 [3]. A double rearrangement ion obtained at *m/z* 58 is characteristic for ketone having a γ H in both the alkyl fragments. The location of the hydroxyl group at C-8 is deduced by the significant α-fission ions at *m/z* 99, 353 and 129. Absence of an M-15 ion indicated the straight-chain nature of the ketone [4] whereas the presence of an M + 1 peak is characteristic for its asymmetrical nature [5, 6]. The data obtained above suggested the structure of G as 8-hydroxytriacontan-25-one (**1**). Treatment of **1** with Ac$_2$O–pyridine furnished a ketoacetate, mp 76–78° having IR bands at 1735, 1710 and 1260 cm^{-1}.

Compound H, mp 80–82°, obtained in traces, had IR bands at 1735, 1380 (COOCH$_3$), 2910, 2825, 1470, 740 and 730 cm^{-1} (long chain). The mass spectrum of this compound had a fragmentation pattern similar to that of long-chain methyl esters [7]. The M$^+$ ion at *m/z* 508 suggested the molecular formula as $C_{34}H_{68}O_2$. A significant ion at *m/z* 59 is due to the α-cleavage of the ester carbonyl. An intense ion at *m/z* 74 can be rationalized in terms of β-fission with transfer of a γ-hydrogen atom (McLafferty rearrangement), resulting in the formation of an ion $CH_2{=}C(\overset{+\cdot}{O}H)OCH_3$. Alkaline hydrolysis of this methyl ester gave an acid, identified as tritriacontanoic acid [8, 9]. The structure of compounds G and H as 8-hydroxytriacontan-25-one (**1**) and methyl tritriacontanoate (**2**) respectively is in full agreement with the available evidence. Compounds **1** and **2** have not been previously found in nature.



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EXPERIMENTAL

Mps are uncorr. IR spectra were recorded in KBr. TLC was carried out on Si gel G and the spots were visualized by exposure to I$_2$ vapour or 2,4-dinitrophenylhydrazine spray.

Plant material. The plant was cultivated at the farms of this institute and a voucher specimen has been deposited in the Botany Department.

Extraction and isolation of compounds. Dried and powdered roots (2 kg) of *C. speciosus* Sm. were extrd in the cold with MeOH (5 × 6 l.). The MeOH extract was concd to 250 ml and dil. with H$_2$O (250 ml). It was then extrd with *n*-hexane (5 × 250 ml). The solvent was removed from the hexane extract and the residue (12.8 g) chromatographed over Si gel (800 g, 60–120 mesh, BDH). Elution was carried out in hexane, hexane–C$_6$H$_6$ (3:1), hexane–C$_6$H$_6$ (1:1), hexane–C$_6$H$_6$ (1:3), C$_6$H$_6$ and C$_6$H$_6$–CHCl$_3$ (3:1). Fractions collected were 250 ml each and they were monitored by TLC. The homogeneity of the compounds was checked on TLC in at least four different solvent systems.

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* Part III in the series "Studies on *Costus speciosus* roots". For Part II, see ref. [2].

Compound H (Me *tritriacontanoate*). Removal of solvent from the latter fractions of hexane (41–50) furnished a residue, 10 mg, mp 80–82° (Me_2CO). IR ν_{max} (cm^{-1}): 2910, 2825, 1735, 1470, 1380, 1180, 740 and 730. MS *m/z* (rel. int.) 508 (M^+, $C_{34}H_{68}O_2$, 1), 423 (4), 409 (2), 395 (4), 381 (2), 367 (3), 353 (2), 339 (2), 311 (2), 297 (2), 283 (2), 255 (2), 241 (3), 227 (2), 213 (2), 199 (7), 185 (6), 171 (2), 157 (3), 143 (23), 129 (12), 115 (4), 101 (7), 99 (12), 87 (63), 85 (36), 74 (77), 71 (53), 59 (4), 57 (100), 55 (42), 43 (75). H (5 mg) was hydrolysed with 5% alcoholic KOH (2 ml) for 4 hr. The reaction mixture was then diluted with H_2O (20 ml), acidified with dil. HCl and extrd with Et_2O (4 × 25 ml). The Et_2O extract was washed with H_2O (2 × 50 ml) and dried (Na_2SO_4). Removal of solvent provided a residue identified as tritriacontanoic acid. IR ν_{max} (cm^{-1}): 2900, 2840, 3500–3000, 1705, 1185 and 920.

Compound G [*8-hydroxytriacontan-25-one* (**1**)]. The latter fractions (132–140) of hexane–C_6H_6 (1:3) gave a residue, 20 mg, mp 95° (MeOH). IR ν_{max} (cm^{-1}): 3440, 2920, 2840, 1710, 1465, 1380, 1175, 730 and 720. MS *m/z* (rel. int.) 452 (M^+, $C_{30}H_{60}O_2$, 8), 396 (3), 381 (5), 353 (2), 339 (3), 325 (3), 297 (2), 283 (2), 269 (2), 241 (3), 227 (3), 213 (2), 199 (3), 185 (8), 183 (3), 171 (5), 169 (3), 157 (3), 155 (4), 143 (7), 141 (5), 129 (21), 127 (6), 114 (8), 99 (11), 85 (35), 71 (55), 58 (5), 57 (100), 43 (85). G (15 mg) was treated with pyridine (1 ml) and AC_2O (1 ml) overnight at room temp. When worked up it afforded a residue, mp 76–78° (Me_2CO). IR ν_{max} (cm^{-1}): 2920, 2850, 1735, 1710, 1460, 1370, 1260, 730 and 720.

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5,7-BISDEOXYCYNANCHOSIDE, AN IRIDOID GLUCOSIDE FROM *MACFADYENA CYNANCHOIDES*

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Key Word Index—*Macfadyena cynanchoides*; Bignoniaceae; iridoid glucosides; 5,7-bisdeoxycynanchoside; ^1H NMR; ^{13}C NMR.

Abstract—A new iridoid glucoside from *Macfadyena cynanchoides* leaves has been identified by spectral (^1H and ^{13}C NMR) and chemical procedures as 5,7-bisdeoxycynanchoside.

INTRODUCTION

Macfadyena cynanchoides is a well-known wall-creeper which is grown as an ornamental plant. Previous investigations on the iridoid glucosides of the species demonstrated the presence of macfadyenoside [1] and cynanchoside (**1**) [2].

The present communication describes the isolation and structure elucidation of a new iridoid, 5,7-bisdeoxycynanchoside (**2**), which was isolated from the aerial part of the plant.

RESULTS AND DISCUSSION

Compound **2** was obtained as a colourless powder with molecular formula $C_{15}H_{24}O_{10}$, and $[\alpha]_D$ −126°. It gave a colour with vanillin characteristic of an iridoid and was hydrolysed in the presence of β-glucosidase. Its UV (204 nm, log ε 3.4) and IR (1670 (C=C) and 1090 cm^{-1}) spectra indicated the presence of a non-conjugated enol–ether system. The ^1H and ^{13}C NMR spectra (see Experimental and Table 1) indicated that the new iridoid had structure **2** with unknown stereochemistry at C-6 and C-8. Acetylation of **2** under mild conditions gave the hexa-acetate (peracetate) **4**. The ^1H NMR spectrum of **2** was rather similar (apart from the signals due to the different substitution at C-10) to those of mioporoside **5** and its C-6 epimer ajugol **6** (see data in Experimental). Comparison of the ^{13}C NMR data for **2** and **6** (Table 1, those of **5** were not available) corroborated the above structure for **2**, but did not clarify the stereochemistry at C-6. However, the data