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ALIPHATIC HYDROXY-KETONES FROM *CURCULIGO ORCHIOIDES* RHIZOMES

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Key Word Index—*Curculigo orchioides*; Amaryllidaceae; rhizomes; 27-hydroxytriacontan-6-one; 23-hydroxytriacontan-2-one.

Abstract—Two new aliphatic hydroxy-ketones, isolated from the rhizomes of *Curculigo orchioides*, have been characterized as 27-hydroxytriacontan-6-one and 23-hydroxytriacontan-2-one, respectively, by spectral data and chemical studies.

INTRODUCTION

The screening of Indian medicinal plants for biological activity showed hypoglycaemic, pharmacological and anticancer activity in the alcoholic extract of rhizomes of *Curculigo orchioides* [1]. *Curculigo orchioides* has been reported to have many medicinal uses, and rhizomes are a component of several Ayurvedic preparations [2]. It is claimed to be a medical cure for piles, asthma, jaundice, diarrhoea, colic, gonorrhoea and to be an aphrodisiac [3]. Placing the powdered rhizomes into cuts is also said to stop bleeding and to dry up the wounds. From the rhizomes of *C. orchioides*, a glycoside, 5,7-dimethoxydihydromyricetin-3-*O*-α-L-xylopyranosyl-4-*O*-β-D-glucopyranoside [4], sitosterol, sapogenins, yuccagenin and lycorine [5] have been isolated earlier. The rhizomes also contain free sugars (xylose and glucose), 7.56%; mucilage, 8.12%; hemicellulose, 20.15% and other polysaccharides, 11.01% [6]. In view of the immense medicinal utility of these rhizomes, it was thought worthwhile to undertake a systematic chemical examination of the constituents present in it.

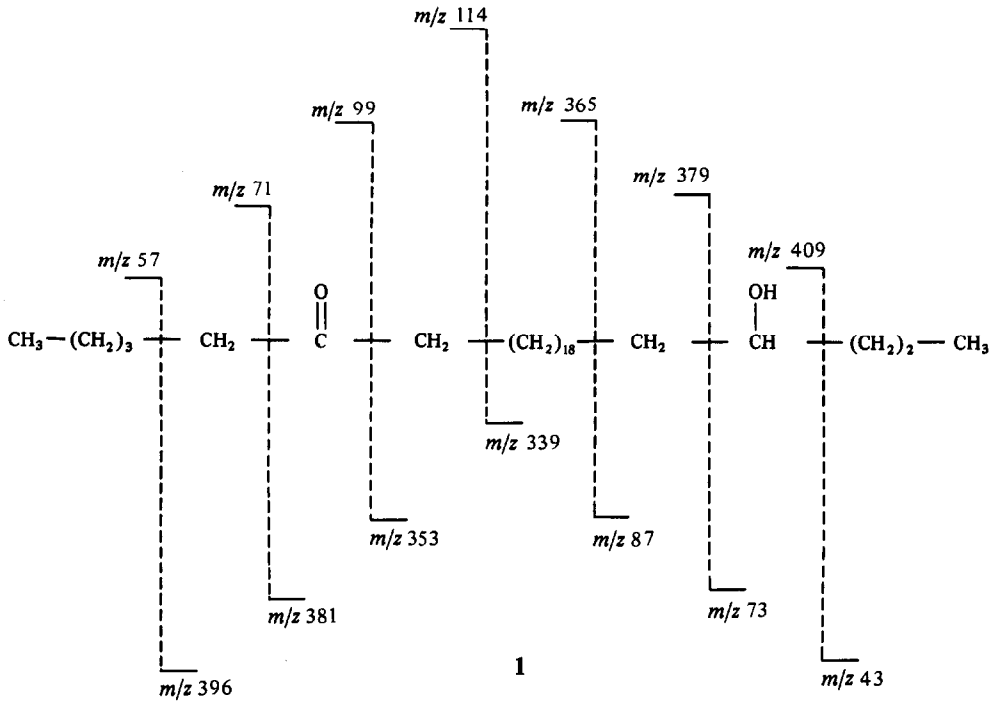
RESULTS AND DISCUSSION

The alcoholic extract of the rhizomes of *C. orchioides* was fractionated with *n*-hexane, and the soluble fraction was further separated into acetone-soluble and acetone-insoluble parts. Compounds A and B were isolated by silica gel chromatography of the acetone-insoluble fraction.

Compound A, mp 84–85°, responded positively to a 2,4-dinitrophenyl hydrazine test, showing the presence of a carbonyl function in the molecule. Elemental analysis and MW determination (*m/z* 452, from mass spectrum) established the molecular formula as $C_{30}H_{60}O_2$. It exhibited IR absorption bands at 3440, 1705, 730 and 720 cm^{-1}, corresponding to hydroxyl and carbonyl groups and a long aliphatic chain in the molecule. A large number of fragments recorded in the mass spectrum of the compound exhibit a uniform difference of 14 mass units, thus confirming the presence of a long aliphatic chain. From the above data it is clear that compound A is a keto-hydroxy derivative of triacontane. The formation of characteristic α-fission ions [7] at *m/z* 71, 381, 99 and 353 led to the assignment of the carbonyl group to C-6. The appearance of prominent fragments at *m/z* 57, 339, 396 and 114, corresponding to simple β-fission and McLafferty rearrangement followed by β-fission, further confirmed the above assignment of the carbonyl group to C-6.

A prominent peak at *m/z* 58 was attributed to double rearrangement of the ion formed from the ketone having the γ-H in both alkyl fragments. α- and β-Fissions occurring at either side of the carbinolic carbon accounted for the fragments at *m/z* 379, 73, 43, 409 and 87, 365, 423, respectively. It could be concluded from this observation that the hydroxyl group was situated at C-27. The straight chain skeleton of the ketone was confirmed by the absence of an $[M-15]^+$ ion [8] whereas the presence of a peak corresponding to $[M+1]^+$ is characteristic of its asymmetrical nature [9, 10]. Therefore, compound A was characterized as 27-hydroxytriacontan-6-one (1). The above assignment was further supported by its ^1H NMR spectrum. Two terminal methyl groups resonated as a triplet centred at δ0.83 ($J = 7.5$ Hz). The two methylene units attached to the carbinolic carbon appeared as a broad singlet at δ1.56. A four-proton triplet centred at δ2.23 ($J = 6.5$ Hz) showed the presence of methylene units adjacent to the carbonyl group. A 44-proton, broad singlet appeared at δ1.20, which showed the presence of 22 methylene groups in the molecule. The alcoholic proton resonated at δ1.92 as a singlet.

Benzene–ethyl acetate (1:3) elution of the column afforded white crystals of B, mp 109–110°. It analysed for $C_{30}H_{60}O_2$ (*m/z* 452, from mass spectrum). A uniform difference of 14 mass units in a number of ion peaks in the mass spectrum and characteristic peaks at 730 and 720 cm^{-1} in the IR spectrum of the compound showed the presence of a long aliphatic chain in the molecule. The presence of a carbonyl function was indicated by the appearance of a peak at 1710 cm^{-1} in the IR and a positive 2,4-dinitrophenylhydrazine test. Further, a peak at 3425 cm^{-1} in the IR spectrum showed the presence of a hydroxyl group in the molecule. The absence of an $[M-15]^+$ ion and the presence of an $[M+1]^+$ peak in the mass spectrum accounted for the straight chain and asymmetrical nature of the hydroxy-ketone, respectively [8–10]. The position of the keto group at C-2 was confirmed by the presence of an intense base peak at *m/z* 43 in



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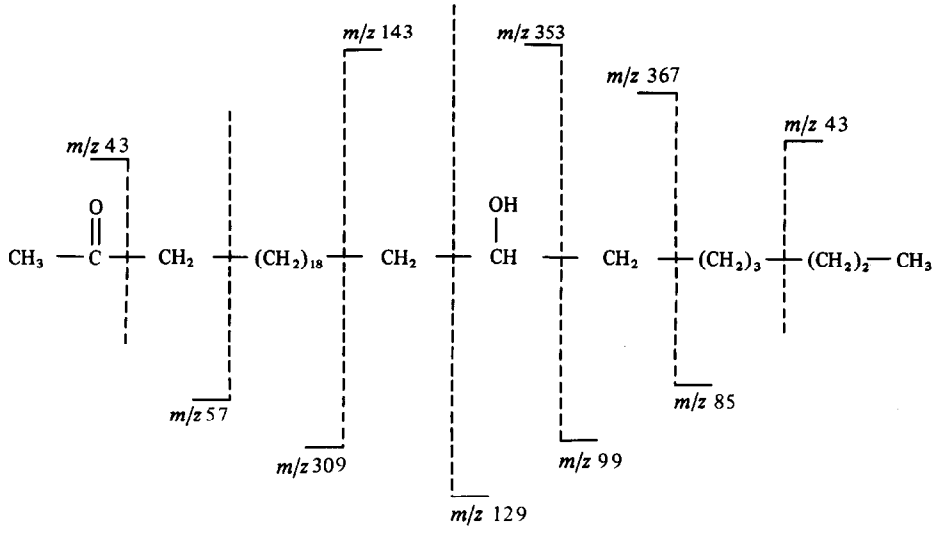

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the mass spectrum. The assignment of the keto group at C-2 was further confirmed by a positive haloform test [11]. The hydroxyl group was assigned to C-23 from the presence of prominent α-fission ions at *m/z* 99, 353 and 129. Thus compound B was characterized as 23-hydroxytriacontan-2-one and given structure **2**.

EXPERIMENTAL

All mps are uncorr. IR spectra were recorded in KBr, NMR spectra (90 MHz) in $CDCl_3$ with TMS as int. ref. Silica gel G was used for TLC and spots were visualized by exposure to I_2 vapour or by charring with 10% H_2SO_4.

Plant material. Rhizomes of *C. orchioides* were collected from the side of the Gandak river in the Deoria district (U.P.), India. Rhizomes were washed with H_2O, air-dried and ground to a coarse powder.

Extraction and isolation. Powdered rhizomes (6 kg) were exhaustively extracted with EtOH. The extract was filtered and the solvent removed by distillation under red. pres. to yield a dark red-brown mass (400 g). This mass was subjected to fractionation with hexane. The hexane soluble portion was evapd to dryness and Me_2CO added to obtain an Me_2CO-soluble and an Me_2CO-insoluble part. The Me_2CO-insoluble part (6 g) was chromatographed on a silica gel column. Elution was carried out with solvents of increasing polarity, starting with hexane. The fractions (200 ml each) were checked by TLC, ones of similar composition combined and the solvent was removed.

Compound A (*27-hydroxytriacontan-6-one*, **1**). The hexane–C_6H_6 (3:1) eluate yielded a white residue (70 mg) after removal of solvent from fractions 5–15 which on repeated crystallization from MeOH yielded colourless crystals of compound A, mp 84–85°. IR ν_{max}^{KBr} cm^{-1}: 3440, 2920, 2840, 1705, 1465, 1175, 730 and 720; ^1H NMR: δ0.83 (6H, *t*, 2 Me, J = 7.5 Hz), 1.20 (44H, *s*, 22 CH_2), 1.56 (4H, *s*, $-C\underline{H}_2-\overset{OH}{\overset{|}{C}}H-C\underline{H}_2-$), 1.92 (1H, *s*, $>CH-\underline{OH}$), 2.23 (4H, *t*, $-C\underline{H}_2-\overset{O}{\overset{\|}{C}}-C\underline{H}_2-$, J = 6.5 Hz); MS m/z (rel. int.): 452 $[M]^+$ ($C_{30}H_{60}O_2$, 2.7), 423 (2.8), 409 (1.0), 396 (17.5), 381 (1.2), 379 (1.0), 367 (2.5), 365 (1.0), 353 (2.5), 129 (30.0), 115 (7.5), 114 (2.5), 101 (5.0), 99 (10.0), 87 (12.5), 73 (62.0), 71 (62.0), 58 (5.0), 57 (100), 43 (87.5).

Acetylation of compound A. A mixture of pyridine (1 ml), Ac_2O (1 ml) and 15 mg of A was left overnight at room temp. The mixture was then diluted with H_2O (15 ml) and extracted with Et_2O. The Et_2O extract was washed well with H_2O and dried to obtain a solid acetate derivative, mp 82°.

Compound B (*23-hydroxytriacontan-2-one*, **2**). Fractions 1–12 of the benzene–EtOAc (1:3) eluate after removal of solvent gave a residue which on repeated crystallization from MeOH afforded white crystals (30 mg), mp 109–110°. IR ν_{max}^{KBr} cm^{-1}: 3425, 2910, 2840, 1710, 1460, 730 and 720; MS m/z (rel. int.): 452 $[M]^+$ ($C_{30}H_{60}O_2$, 2.5), 424 (6.1), 397 (5.0), 383 (2.5), 353 (2.8), 339 (2.5), 325 (6.1), 309 (1.0), 308 (2.0), 311 (2.5), 283 (2.5), 227 (5.0), 199 (2.5), 129 (32.5), 99 (10.0), 85 (27.5), 71 (42.5), 57 (87.5), 43 (100).

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