the 192 'non-woody' angiosperms previously examined [1]

It would have been interesting to compare, within the same families, the ascorbic acid concentrations in 'woody' and 'non-woody' species, respectively, but the limited number of local representatives of families that contain a significant number of both 'woody' and 'non-woody' common species precluded this The mean ascorbic acid concentrations in seven 'woody' and eight 'non-woody' members of the Rosaceae were 339±43 7 and 262 ±19 0 mg/100 g, respectively, but the difference did not attain statistical significance at the $P = 0$ 05 level

It would appear that the relationship between foliar ascorbic acid and 'woodiness', or its biochemical correlates, is one that merits further study

EXPERIMENTAL

Sampling and analysis were as previously described [1] An attempt was made to analyse as many common trees as possible, there was no pre-selection of species for analysis The samples were taken between April and August 1983 and some were remeasured in September and October 1983 There was no significant difference between the pre-September and the post-September analyses

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A BIOGENETICALLY IMPORTANT HYDROCARBON FROM *CYPERUS SCARIOSUS*

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Key Word Index—*Cyperus scariosus*, Cyperaceae, biogenesis, sesquiterpenoids, isopatchoul-3-ene

Abstract—A new hydrocarbon isopatchoul-3-ene has been isolated from the essential oil of *Cyperus scariosus* The structure and stereochemistry was assigned on the basis of spectroscopic and chemical data Its biomimetic conversion to isopatchoulenol has been achieved

INTRODUCTION

The essential oil from *Cyperus scariosus* has already been reported to be biologically active in plant growth regulation [1] One of its several known components (cyperene [2], rotundene [3], rotundenol [3], isopatchoula-3,5-diene [4], β-selinene [4], cyperenol [5], isopatchoulenol [5], patchoulenol [5], scariodione [6]) namely isopatchoulenone (**3**) [6] was found to be a potent root promotor in the stem cuttings of mung beans [7] During our studies for the isolation of further pure components to test them as plant growth regulators and to pin-point the biological activity, we have been able to isolate a hitherto unknown hydrocarbon from the non-polar fraction of the oil

RESULTS AND DISCUSSION

Careful analysis of the hydrocarbon fraction of the oil has revealed the presence of a component different from the already known hydrocarbons cyperene (**4**), isopatchoula-3,5-diene (**5**), β-selinene (**6**) and rotundene (**7**) Repeated chromatography over silver nitrate–silica gel (1 5 6) resulted in the isolation of hydrocarbon isopatchoul-3-ene (**1**), $C_{15}H_{24}$, HRMS (M^+ 204 187), $[\alpha]_D^{20}$ −24 9°, exhibited spectroscopic properties requiring two tertiary methyls, a secondary methyl, an olefinic methyl group [δ1 07 (6 H, *s*), 0 90 (3H, *d*, $J = 6$ 5 Hz) 1 75 (3H, *d*, $J = 2$ Hz)] and an olefinic proton 5 49 (1H, *br s*) and IR bands at 3050, 1625, 1450, 1370 and 815 cm^{-1} On hydrogenation, it consumed one mole of hydrogen to afford a fully saturated hydrocarbon identified as isopatchoulane (**8**) by comparison of its IR spectrum with that of an authentic sample Therefore, hydrocarbon **1** is a tricylic compound with the isopatchoulane type carbon skeleton These properties did not match with those of any other known naturally occurring sesquiterpene hydrocarbon and thus ruled out α-patchoulene (**9**) [8] as a probable structure

Hydrocarbon **1** on treatment with perbenzoic acid at 0° for 1 hr yielded a liquid which was found to be a stereoisomeric mixture of 3α,4α-epoxyisopatchoulene (**10**) and 3β,4β-epoxyisopatchoulane (**11**) by ^{1}H NMR spectroscopy (some of the ^{1}H NMR signals of this

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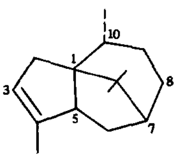

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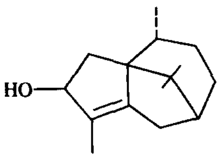

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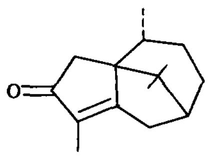

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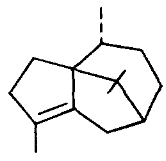

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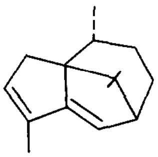

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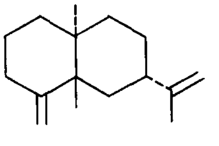

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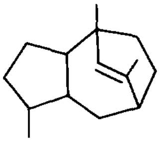

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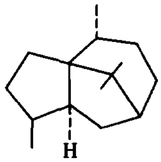

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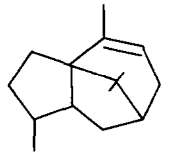

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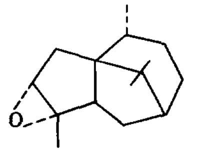

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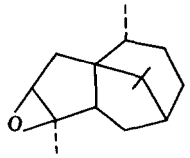

11

product are accompanied by a small peak, especially the epoxy proton signal) The TLC of this mixture always showed it to be a two-component mixture but with a large difference in R_f values It was concluded that one of the stereoisomers might by undergoing rearrangement to give a highly polar product The mixture was treated with basic alumina in hexane overnight [9] and the oily product on chromatographic separation afforded pure compound **10** and the already known natural product **2** The production of compound **2** establishes the stereochemistry of the hydrocarbon as shown in structure **1** The presence of a β-hydroxyl in the product **2** reveals that it might have come from the unstable β-epoxide (**11**) [10] thereby suggesting the structure **10** for the other epoxide

These studies reveal that the new hydrocarbon isopatchoul-3-ene (**1**) [11] might be the biogenetic precursor of isopathcoulenol (**2**)

EXPERIMENTAL

Isolation of hydrocarbon **1** The essential oil *Cyperus scariosus* R Br (Indian origin) (100 g) was preadsorbed on silica gel (2 kg) and eluted successively with petrol (60–80°, 2 5 l), C_6H_6 (2 l) and Et_2O (2 l) to afford on evaporation 40 g, 38 g and 19 g of materials, respectively

The petrol fraction (40 g) was repeatedly chromatographed over silica gel followed by chromatography over $AgNO_3$–silica gel (1 5 6) elution with petrol and collection of a large number of small fractions (50 ml each, 5 l) gave cyperene (4 7 g) [2] The next 20 fractions (50 ml) were cyperene free, combination and solvent evaporation yielded a mixture (300 mg) with one major component (TLC on $AgNO_3$–silica gel (1 5 6) This fraction was subjected to prep TLC ($AgNO_3$–silica gel (1 5 6), hexane, R_f 0 64, to afford a pure faintly yellow liquid (200 mg)

Compound **1** showed $[\alpha]_D^{20} - 24\ 9°$, HRMS ($[M]^+$ 204 187) $C_{15}H_{24}$ requires 204 192, IR ν_{max}^{film} cm^{-1} 3050, 1625, 1450, 1370 and 815 ^{1}H NMR ($CDCl_3$, 90 M Hz) δ0 9 (3H, *d*, J = 6 5 Hz), 1 07 (6H, *s*), 1 75 (3H, *d*, J = 2 Hz) and 5 49 (1H, *br s*)

Hydrogenation of **1** *to give* **8** A soln of **1** (50 mg) in glacial acetic acid (5 ml) was hydrogenated in the presence of prereduced Adam's catalyst (5 mg) It absorbed only one mole of H_2 (6 26 ml, 30°, 739 mm) After 3 hr the catalyst was filtered and usual work up gave a liquid (45 mg) identified as isopatchoulane (**8**) by its superimposable IR spectrum with that of an authentic sample

Epoxidation of **1** *by perbenzoic acid* A soln of compound **1** (50 mg) in $CHCl_3$ (2 ml) was reacted with one mole of perbenzoic acid soln (0 5 ml, 0 9 N) in $CHCl_3$ After 1 hr at 0°, it was worked up as usual and the evaporation of solvent afforded a mixture (40 mg) of **10** and **11**

Analysis Found C, 81 80; H 10 92, $C_{15}H_{24}O$ requires C, 81 76, H, 10 98 % IR ν_{max}^{film} cm^{-1} 1450, 1378, 1360, 1210, 1125, 865 and 800 ^{1}H NMR ($CDCl_3$) δ0 85 (3H, *d*, J = 7 Hz), 0 98 (6H, *s* with additional small signal), 1 24 (3H, *s*), 2 54 (1H, *s*) and at 2 5, a small but observable signal

Reaction of mixture **10** *and* **11** *with basic alumina* The above mixture (30 mg) was packed in a column together with basic alumina (1 5 g) in hexane After 12 hr the column was eluted with hexane–EtOH (9 1, 50 ml) Evaporation of the solvent gave a liquid mixture (25 mg) It was chromatographed over silica gel (1 5 g) Elution of the column with hexane–Et_2O (9 1, 25 ml) gave pure **10** (20 mg, its ^{1}H NMR spectrum showed no additional signals) followed by elution with hexane–Et_2O (1 1) gave isopathcoulenol (4 mg, mp, mmp, IR and NMR)

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ALIPHATIC COMPOUNDS FROM *CURCULIGO ORCHIOIDES* RHIZOMES

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Key Word Index—*Curculigo orchioides*, Amaryllidaceae, rhizomes, 21-hydroxytetracontan-20-one, 4-methylheptadecanoic acid

Abstract—21-Hydroxytetracontan-20-one and 4-methylheptadecanoic acid have been isolated from the rhizomes of *Curculigo orchioides* and characterized on the basis of chemical and spectroscopic evidence

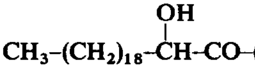
INTRODUCTION

In continuation of our earlier work on the rhizomes of *Curculigo orchioides* [1] we have now isolated two more new aliphatic compounds, a hydroxy ketone and a long chain fatty acid

RESULTS AND DISCUSSION

From the acetone soluble fraction of the *n*-hexane extract of the rhizomes of *Curculigo orchioides* two crystalline compounds C and D were isolated by silica gel chromatography

Compound C was obtained as colourless crystals after repeated crystallization from methanol, mp 77–79° The presence of carbonyl function was shown by a positive 2,4-dinitrophenylhydrazine test Elemental analyses and MW determination (592 from mass), led to the analysis of compound C as $C_{40}H_{80}O_2$ It exhibited IR absorption bands at 3450, 2920, 2460, 1725, 730 and 720 cm^{-1} showing the presence of hydroxyl, keto-carbonyl and a long aliphatic chain in the molecule A uniform loss of 14 mu was recorded in mass spectrometric studies further confirming the presence of a long aliphatic chain Furthermore, the absence of a peak corresponding to $[M-15]^+$ in the spectrum confirmed the straight chain nature of the ketone [2] The ^{1}H NMR spectrum of the compound displayed signals for two terminal methyl groups at δ0 82 (6H, *t*, J = 7 0 Hz) and 34 methylene groups at δ1 20 (68H, *s*) A two proton broad multiplet appearing at δ1 57 was indicative of one methylene group attached to a carbinolic carbon The appearance of a two proton triplet centred at δ2 24 (J = 6 5 Hz) suggested the presence of one methylene group α to a carbonyl function A one proton singlet appearing at δ1 94 is attributable to the alcoholic proton On the basis of IR and NMR spectra it is concluded that the compound isolated is an *n*-tetracontane derivative having hydroxyl and keto groupings at vicinal positions in the chain The assignment of the keto group to C-20 and the hydroxyl group to C-21 is deduced by the presence of α-fission ions at m/z 295, 297, 267, 325 and β-fission ions at m/z 253, 339, 325 and 267 Ion peaks at even number m/z 326 and 340 are also present in the mass spectrum which are formed by β-fission to the CO involving McLafferty rearrangement The above results led to the characterization of C as 21-hydroxytetracontan-20-one (**1**) The compound gave a 2,4-dinitrophenylosazone derivative, mp 90–91° Khalique [3] prepared an acyloin,



$$CH_3\text{–}(CH_2)_{18}\text{–}\overset{\displaystyle OH}{\overset{|}{C}}H\text{–}CO\text{–}(CH_2)_{18}\text{–}CH_3$$

from eicosanoic acid (arachidic acid) He also prepared its 2,4-dinitrophenylasazone derivative The melting point of **1** (77–79°) and its osazone derivative (90–91°) closely resemble those of the C_{40} α-ketol (77–78°) and its osazone derivative (90–92°), respectively Thus compound C was identified as 21-hydroxytetracontan-20-one The natural occurrence of this compound and its spectral properties are reported for the first time

Compound D was obtained as colourless crystals from methanol, mp 59–60° It analysed for $C_{18}H_{36}O_2$ from elemental analyses and MW determination (284, from mass spectrum) Its IR displayed signals between 2940–2850 (broad) and 1710 cm^{-1} which demonstrated the presence of a bonded hydroxyl and a carboxyl