Acetyl derivative of III (IV) Compound III (30 mg) was acetylated with Ac_2O/Py and the product crystallized from CH_3OH, m p 121–122°, λ_{max}^{EtOH} 222 nm (ϵ 8100) and 274 nm (ϵ 10,400), NMR τ4 90 (1H, t, *J* 5 6 cps, —C$\underline{H}$—OAc). Mass spectrum *m/e* 262 (M^+, 3%), 202 (M – AcOH, 21%), 187 (M – AcOH – CH_3, 100%), 159 (M – AcOH – CH_3CO, 9%), 149 (12%), 107 (8%), 91 (7%) and 77 (8%)

Transformation I→III Compound I (30 mg) was dissolved in $CHCl_3$ (5 ml) and the solution was left (8 days) exposed to sunlight Analysis by TLC of the reaction product indicates the presence of six new compounds besides the starting material I The most polar of these components, separated by preparative TLC, appears to be identical to compound III (by TLC comparison in various systems)

Sterol glycosides The product from fraction (d) behaves as a single substance in all the chromatographic systems tested m p 283–284° (decomp) (from $CHCl_3$–CH_3OH), $[\alpha]_D^{26}$ –46 1° (*c* 0 37, pyridine) The tetraacetyl derivative (obtained in the usual manner) crystallizes from CH_3OH, m p 168–169°, $[\alpha]_D^{2}$ –26 2° (*c* 0 52, $CHCl_3$) (Found C, 69 70, H, 9 24 Cal for $C_{43}H_{68}O_{10}$ C, 69 32, H, 9 20%)

Hydrolysis of the glycoside The glycoside (150 mg) was refluxed for 10 hr in EtOH (50 ml), H_2O (10 ml) and conc HCl (5 ml) The solution was diluted with H_2O and extracted with $CHCl_3$ The aqueous phase was desalted (passing it through ion exchange resins) and evaporated, the residue (15 mg) was identified as D-glucose (paper chromatography of the free sugar and of its 2,4-dinitrophenylhydrazone derivative on TLC)

Evaporation of the $CHCl_3$ extract yields 92 mg of a crystalline product that, once acetylated (Ac_2O/Py), can be separated (SiO_2 40% $AgNO_3$ preparative TLC plates eluted with $CHCl_3$) in two components present in a 1 1 ratio Pure samples of these two components are identical (m p , mixed m p , $[\alpha]_D$, IR, NMR and mass spectra) with β-sitosterol and stigmasterol acetates

Key Word Index—*Helichrysum stoechas*, Compositae, triterpenes, phytosterols, chroman, 4-hydroxy-3-isopentylacetophenone

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COMPOSITION OF PUNJAB COSTUS ROOT OIL

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Plant. Saussurea lappa Clarke. *Source.* Lahaul and Spiti areas of Punjab, India [1] *Uses* In the indigenous system of medicine,[2] roots are reported tonic, stomachic, carminative, stimulant and useful in asthma, cough and cholera. It is said to have remarkable effect in controlling bronchial asthma, especially of vagatonic type [3, 4] *Previous work.* Costus root oil obtained from plants of Kashmir (India) origin has been studied critically [5–7] The

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* This work was presented in XX Annual convention of AsoVAC, held at Caracus (Venezuela) in May 1970

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presence of a new sesquiterpenic lactone, costunolide, was reported by Bhattacharyya *et al*[8] Naves[9] also reported the presence of α- and β-ionones along with cis-dihydroionones

Present work The partially delactonized and acid free costus root oil (Punjab origin) was chromatographed on alumina (activity II) and following fractions were collected (1) light petroleum, (2) petrol–benzene (3 1), (3) petrol–benzene (1 1), (4) ether, (5) $CHCl_3$ and (6) MeOH.

Fraction 2 was found to be rich in ketonic constituents and, therefore, was selected for further work After separating into saponifiable and non-saponifiable parts, following compounds were isolated

EXPERIMENTAL

Saponifiable part (Neutral Fraction)

Dehydrocostus lactone m p 59–60°, [α] −11 2° (c, 1 1, $CHCl_3$) IR bands at 1770, 1639, 1264, 1195, 1151, 1136, 1081, 1015, 985, 952, 916, 894 and 819 cm^{-1} (Found C, 78 47, H, 8 12 Calc for $C_{15}H_{18}O_2$ C, 78 23, H, 7 88%)

Dihydrodehydrocostus Lactone (C_{11}-epimers) B p 175–180° (bath)/0 5 mm, n_D^{25}, 1 5245, $[\alpha]_D$, + 69 82° (c, 2 0, $CHCl_3$) IR bands at 1770, 1639, 1449, 1205, 1175, 1117, 1010, 990 and 892 cm^{-1} (Found C, 76 98, H, 8 69 Calc for $C_{15}H_{20}O_2$ C, 77 55, H, 8 68%)

Saponifiable Part (Acid Fraction)

Oleic acid The methyl ester showed following properties b p 160–162° (bath)/0 45 mm, n_D^{21}, 1 4540, $[\alpha]_D$ ± 0 IR bands at 1750, 1470, 1448, 1365, 1250, 1208, 1180, 1010, 890, 850 and 729 cm^{-1} (Found C, 77 18, H, 11 84, Calc for $C_{19}H_{36}O_2$ C, 76 97, H, 12 24%)

Non-saponifiable Part

Caryophyllene mono-oxide M p 60–61° (no depression on mixed m p with an authentic sample), $[\alpha]_D$ − 74° (c, 1 1, $CHCl_3$) IR bands at 2900, 1650, 1470, 1390, 1289, 1270, 1179, 1130, 1100, 1089, 1070, 970, 945, 920, 899, 875, 856, 831, 810, and 770 cm^{-1} (Found C, 81 81, H, 11 87, Calc for $C_{15}H_{24}O$ C, 81 76, H, 10 95%)

Friedlein M p 252–253°, $[\alpha]_D$ −25° (c, 1 2, $CHCl_3$) IR bands at 1718, 1462, 1389, 1379, 943, 917, 862, 860, 842, 833, 781 and 724 cm^{-1} (Found C, 84 33, H, 11 87 Calc for $C_{30}H_{52}O$ C, 84 44, H, 11 81%)

β-Sitosterol M p 135–136°, $[\alpha]_D$ −37° (c, 1 2, $CHCl_3$) IR bands at 3448, 1667, 1639, 1460, 1372, 1064, 1080, 961, 890, and 800 cm^{-1} (Found C, 83 45, H, 11 85, Calc for $C_{29}H_{50}O$ C, 83 99, H, 12 15%)

Costunolide was isolated during the process of delactonization and showed following properties m p 106–107°, $[\alpha]_D$ +125° (c, 0 6, $CHCl_3$) IR bands at 1757, 1656, 1449, 1372, 1282, 1242, 1133, 966, 951, 895, 842 and 814 cm^{-1}

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Key Word Index—*Saussurea lappa*, Compositae, costus root oil, sesquiterpenoid lactones, triterpenes