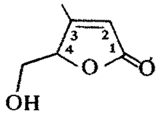
Substance B was identified as sitosterol, mp 136°; $(\alpha)_D$ −39° (*c*, 2.0 $CHCl_3$); Acetyl derivative mp 128°.

Substance C was shown to be oleanolic acid, mp 307–309°. Methyl ester, mp 223–224° (mmp, TLC, IR, PMR).

Substance D was ursolic acid, mp 290–291°; Methyl ester acetate mp 245–247° (mmp, TLC, IR, PMR).

Substance F was sitosterol-β-D-glucoside, mp 227–228°; $(\alpha)_D$ −46°, positive Fiegel test. On hydrolysis, it gave an aglycone, mp 136° identified as sitosterol and the aqueous portion was shown to contain glucose.



1

EXPERIMENTAL

Mps are uncorrected. PMR spectra were recorded in $CDCl_3$ unless otherwise stated.

The powdered aerial part of the plant (7.5 kg) was extracted with EtOH (66%, 180 l.) at room temp. The total EtOH extract was conc. under red. press. to a dark green viscous mass (750 g) which was successively macerated with C_6H_{14}, $CHCl_3$ and *n*-BuOH. A portion of the hexane fraction (10 g) was chromatographed on neutral alumina (activity 2.5, 300 g), the C_6H_6–C_6H_{14} (1:1) eluate gave colourless needles from EtOH of substance A, mp 196–198°, 50 mg. The residue from the C_6H_6 eluate afforded colourless needles from EtOH of substance B, mp 136°, 200 mg.

The dark green $CHCl_3$-soluble fraction (110 g) was treated with charcoal, filtered and conc. to a viscous residue (68 g). It was chromatographed over Si gel (1.5 kg) the C_6H_6-MeOH (3–5%) eluates gave colourless needles from EtOH of substance C mp 307–309°, 400 mg and substance D, mp 290–291°, 230 mg. The successive elution of the column with EtOAc yielded a fraction (6.9 g) containing substance E and with EtOAc–MeOH (5:95) was obtained substance F (1.0 g) which crystallised from EtOH, mp 277–278°. The fraction containing substance E was rechromatographed over Si gel (300 g), the C_6H_6–EtOAc (1:1) eluates gave 2.0 g substance E (umbelactone) as light cream needles from C_6H_6, mp 65°.

Umbelactone, mp 65°, $(\alpha)_D$ + 5 2°, R_f 0.44 (C_6H_6–EtOAc, 1:1) on $AgNO_3$–Si gel plates. It was soluble in H_2O as well as $CHCl_3$. IR ν_{max}^{KBr} cm^{-1}; 3435, 2920, 2865, 1745 (broad), 1640, 1432, 1305, 1150, 1043, 940 and 855. UV: λ_{max}^{MeOH} 221 nm. PMR: δ 2.08 (3H, *m*, main coupling *J* = 1.5 Hz, Me), 3.38 (1H, *br s*, OH D_2O exchangeable), 3.80 (2H, *octet*, *J* = 21, 12.5 and 3.5 Hz, —CH_2—O—), 4.91 (1H, *m*, —CHO—) and 5.84 (1H, *m*, olefinic); PMR (C_6D_6): 1.53 (3H, Me), 3.08 (1H, *br s*, OH, D_2O exchangeable), 3.6 (2H, *octet*, J = 21, 12.5, 4 Hz, —CH_2O—), 4.4 (1H, *m*, —CHO—) and 5.57 (1H, *m*, olefinic). ^{13}C NMR ($CDCl_3$): δ 14.0 (C-6), 63.6 (C-5), 90.5 (C-2), 123.5 (C-4), 176.5 (C-3), 183.5 (C-1). Off resonance ^{13}C NMR: δ 14.0 (C-6, *q*), 63.6 (C-5, *t*), 90.5 (C-2, *d*), 123.5 (C-4, *d*), 176.5 (C-3, *s*), 183.5 (C-1, *s*). MS: *m/e* 128 (M^+), 97,68. (Found: C, 56.4; H, 6.22 $C_6H_8O_3$ requires C, 56.25; H, 6.25%).

Umbelactone acetate: Umbelactone (100 mg) in dry Py (0.5 ml) was reacted with Ac_2O (0.5 ml) overnight at room temp. Work up as usual gave a yellow oily residue which was chromatographed over Si gel. The elution with C_6H_6–MeOH (97:3) gave umbelactone acetate as a colourless viscous mass (95 mg). IR ν_{max}^{Neat} cm^{-1}: 2920, 1755, 1650, 1450, 1390, 1235, 1160, 1060, 955 and 900. UV: λ_{max}^{MeOH} 212, 258 nm. PMR: δ 2.07 (3H, *s*, —OCOMe), 2.15 (3H, *m*, Me), 4.4 (2H, *octet*, *J* = 20, 12.5 and 3 Hz, CH_2OAc), 5.09 (1H, *m*, —CHO) and 5.9 (1H, *m*, olefinic); PMR (C_6D_6): δ 1.23 (3H, *m*, Me), 1.48 (3H, *s*, —OCOMe), 3.82 (2H, *octet*; *J* = 20, 12.5, 3.0 Hz, —CH_2OAc), 4.17 (1H, *m*, —CHO—) and 5.32 (1H, *m*, olefinic). (Found: C, 55.02; H, 5.60 $C_8H_{10}O_4$ requires C, 55.29; H, 5.88%).

Dihydroumbelactone: Umbelactone (100 mg), EtOH (5 ml) and Pd/C (10%, 100 mg) were shaken in a H_2 atmosphere for 6 hr at room temp. It was worked up to get an oily mass which was chromatographed over a Si gel column. The C_6H_6–EtOAc (1:1) eluate yielded the hydrogenated product (80 mg) as a colourless liquid, R_f 0.5 (EtOAc–C_6H_6, 1:1). IR ν_{max}^{Neat} cm^{-1} 3370, 2900, 1740, 1430, 1395, 1167, 1092, 1035, 998 and 932.

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REFERENCES

1. Chopra, R. N., Nayar, S. L. and Chopra, I. C. (1956) *Glossary of Indian Medicinal Plants*, p. 165. Council of Scientific & Industrial Research, New Delhi.
2. Dhar, M. L., Dhar, M. M., Dhawan, B. N., Mehrotra, B. N. and Ray, C. (1968) *Indian J. Exp. Biol.* **6**, 241.

Phytochemistry, 1978. Vol 17, pp 1664–1666 © Pergamon Press Ltd Printed in England 0031–9422/78/0901-1664 $02 00/0

ACIDIC COMPONENTS IN ESSENTIAL OILS OF COSTUS ROOT, PATCHOULI AND OLIBANUM

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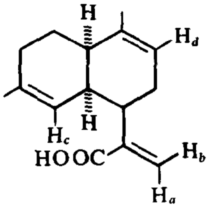
Key Word Index—*Saussurea lappa*; Compositae; *Pogostemon cablin*; Labiatae; *Boswellia* sp., Burseraceae; essential oils; organic acids; phenols.

We wish to report on our results of the analysis of the acidic fraction of three essential oils in which we found important scent compounds, i.e. olibanum oil, patchouli oil and costus root oil.

Costus root oil (oil from the roots of the Costus plant, *Saussurea lappa* Clarke)

The acidic fraction was isolated by extraction of the oil with an ice cold soln of $NaHCO_3$ (no stronger base was used to avoid cleavage of the abundantly present lactones [1]); the aq. layer was washed several times with Et_2O, acidified at 0° with dil. HCl and subsequently extracted with Et_2O. After evapn of the solvent, the residue was analysed by GC–MS. Compounds remain-

Table 1. Costus root oil constituents

Carboxylic acids		
Acetic acid	Octanoic acid	
3-Methylbutyric acid	7-Octenoic acid	
Hexanoic acid	3-Isopropylpentanoic acid	
Heptanoic acid	4-Ethyloctanoic acid	
	α-Amorphenic acid (1)	

ing unknown were isolated by preparative GLC and their structures were elucidated with NMR and IR spectroscopy and confirmation was obtained by synthesis. The identified acidic components are listed in Table 1.

3-*Isopropylpentanoic acid* was prepared from the commercially available α-ethylisovaleric aldehyde via reduction with $NaBH_4$, conversion of the alcohol obtained into the bromide and reaction of its Grignard derivative with CO_2. 7-*Octenoic acid* was prepared from the known 7-octenal [2] by oxidation with Ag_2O. 4-*Ethyloctanoic acid* was prepared via a malonic ester synthesis from 2-ethylhexylbromide [3]. The olfactory properties of this acid proved to be characteristic for the 'goaty' odour of costus root oil. A lower homologue, 4-methyloctanoic acid, has been reported as a component of mutton [4] and may be responsible for its typical flavour. Also in the oil of *Acacia farnesiana* Willd. (cassie absolute) branched chain aliphatic acids with interesting odour aspects have been found [5].

We also obtained another acid as a crystalline compound by gradient elution of costus root oil over Si gel using pentane–Et_2O mixtures. It was identified as α-amorphenic acid (1) by MS, IR and NMR spectroscopy. The isolated compound exhibited an odour reminiscent of the original oil. So far the structure has not been confirmed by synthesis. MS: m/e 232 (93%, M^+), 187 (31%), 171 (29%), 147 (39%), 145 (29%), 139 (55%), 136 (48%), 134 (29%), 119 (81%), 117 (47%), 115 (39%), 105 (87%), 94 (79%), 93 (45%), 92 (28%), 91 (100%), 79 (76%), 77 (64%), 65 (29%), 59 (29%), 55 (45%), 53 (36%). IR (cm^{-1}): 3044, 3008, 2990 (CCl_4), 819 (CS_2) and 1677 (KBr)-trisubstituted double bond; 3400–2400 (*br*), 1280 (CCl_4)-COOH-group; 1695 (CCl_4)-conjugated acid carbonyl; 1623 and 951 (CCl_4)-vinylidene in conjugation with carbonyl; 2964, 2844, 2827, 1429, 1416 and 1382 (KBr)CH_3/CH_2 vibrations. The fingerprint showed a great resemblance to the spectrum of α-amorphene [6]. NMR (CCl_4, TMS): δ 8 (ppm): 1–3 (15H); 1.63 (*br*, 2 Me groups) 4.93 (*br*, *s*, 1H, Hd; 5.42 (*br*, *m* 1H, Hc 5.57 (*br*, *s*, 1H, Hb); 6.47 (*br*, *s*, 1H, Ha), 11,67 (*br*, *s*, 1H, acidic proton).

Patchouli oil (oil from the leaves of *Pogestemon cablin* Benth)

The acidic fraction was isolated by extraction with dil. KOH; otherwise the same procedure was followed as above. Apart from acidic and phenolic compounds (see Table 2) a number of homologous dehydracetic acids (3-alkanoyl-4-hydroxy-6-methyl-2H-pyran-2-ones, **2a**–**2e** were found; the occurrence of two of these products in patchouli oil has already been reported [7, 8]; the well known bacteriostatic properties of this oil may be attributed to these compounds [7, 9]. We also isolated the *cis* and *trans* isomer of 2-pentylcyclopropane carboxylic acid. A mixture of these isomers was prepared by reaction of 1-heptene with ethyl diazoacetate, followed by hydrolysis of the ethyl esters. Separation of the isomers could readily be accomplished by preparative GLC of the amides. In a recently granted patent, *cis*-2-pentylcyclopropane carboxylic acid has been claimed as a fragrance material [10].

Olibanum oil (Frankincense, oil from the gum of *Boswellia* sp.)

Isolation and analysis of the acidic fraction was

Table 2. Patchouli oil constituents

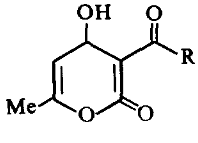
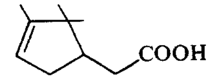
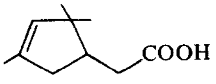
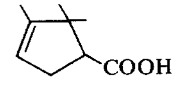
Phenols	Carboxylic acids	3-Alkanoyl-4-hydroxy-6-methyl-2H-pyran-2-ones (5)
Phenol	2-Methylbutyric acid	 **2a** R = $(CH_2)_2Me$ **2b** R = $CHCMe_2$ **2c** R = $(CH_2)_4Me$ **2d** R = $CHCMeCH_2Me$ **2e** R = $(CH_2)_3CMe_2$
o-Cresol	Pentanoic acid	
p-Vinylphenol	4-Methylpentanoic acid	
Eugenol	Heptanoic acid	
Guaiacol	2-Methylhexanoic acid	
Dimethylphenol	Octanoic acid	
	Nonanoic acid	
	cis- and *trans*-2-Pentylcyclopropylcarboxylic acid	

Table 3. Olibanum oil constituents

Phenols	Carboxylic acids	
o-Cresol *m*-Cresol *p*-Cresol	(2,2,3-Trimethylcyclopent-3-en-1-yl) acetic acid (α-campholenic acid, 3)	 COOH **3**
Thymol Carvacrol	(2,2,4-Trimethylcyclopent-3-en-1-yl) acetic acid **4**	 COOH **4**
	(2,2,3-Trimethylcyclopent-3-en-1-yl) carboxylic acid (α-campholytic acid, **5**)	 COOH **5**

performed in the same way as for patchouli oil. Analysis now revealed the presence of some phenolic compounds, but the main components were three terpenoic acids (see Table 3). *α-Campholenic acid* (**3**) was prepared by oxidation of the known campholenic aldehyde [11] with Ag_2O. 2,2,4-*Trimethylcyclopent*-3-*en*-1-*yl acetic acid* (**4**) was prepared from pinonic acid via reduction with $NaBH_4$ and subsequently heating the hydroxy acid obtained in HOAc as described by Parks [12]. *α-Campholytic acid* (**5**) was prepared according to Bessièrre-Chrétien [13] starting from verbenone via epoxidation with alkaline H_2O_2, treatment of the epoxide with $ZnBr_2$ to α-campholytic aldehyde followed by oxidation with Ag_2O. This compound has a rather strong odour reminiscent of the oil whereas the other two acids are much weaker in odour and less characteristic.

REFERENCES

1. Paul, A., Bawdekar, A. S., Joshi, R. S., Kulkarni, G. H., Rao, A. S., Kelkar, G. R. and Bhattacharyya, S. C. (1960) *Perfum Essent. Oil Rec.* **51**, 115.
2. Meyboom, P. W. Synthesis and analysis of straight chain unsaturated aldehydes, Thesis, University of Leiden.
3. Keil, W. (1942) *Hoppe-Seyler's Z. Physiol. Chem.* **274**, 175.
4. Wong, E., Johnson, C. B. and Nixon, L. N. (1975) *N.Z.J. Agric. Res.* **18**, 261.
5. Demole, E., Enggist, P. and Stoll, M. (1969) *Helv. Chim. Acta* **52**, 24.
6. Klein, E. (1970) *Dragoco Rep* 183.
7. Klein, E. and Rojahn, W. (1969) *Tetrahedron Letters* 2279.
8. Nakahara, S., Kumatani, K. and Kameoka, K. (1975) *Phytochemistry* **14**, 2712.
9. van der Gen, A. and Boelens, H. (1969) ACS meeting, New York.
10. Chappell, R. L. (1975) U.S. Patent 3.926.860.
11. Lewis, J. B. and Hedrick, G W. (1965) *J. Org. Chem.* **30**, (1965).
12. Parks, J. P., Settine, R. L., Perkin, B. A. and Hedrick, G. W. (1962) *J Org. Chem.* **27**, 898.
13. Bessièrre-Chrétien, Y. (1971) *C.R. Acad. Sci. Ser. C.* **273**, 272.

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EIN NEUES BISABOLEN-DERIVAT AUS *ARCTOTIS GRANDIS**

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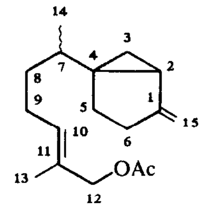
Key Word Index—*Arctotis grandis*; Compositae; new bisabolene derivative.

Kürzlich wurde über die Isolierung eines Guajanolids aus den oberirdischen Teilen von *Arctotis grandis* Thunb. berichtet [1]. Eine Untersuchung des Wurzelextraktes ergibt neben den weitverbreiteten Polyinen **1** und **2** [2] ein Sesquiterpenacetat der Summenformel $C_{17}H_{26}O_2$, dem die Konstitution **3** zukommen dürfte. Aus dem ^1H-NMR-Spektrum ist klar die Natur der Seitenkette zu entnehmen (s. Tab. 1). Durch Zusatz von $Eu(fod)_3$

$Me\equiv_5=$
1

$Me=\equiv_4=$
2



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* 149. Mitt. in der Serie "Natürlich vorlich vorkommende Terpen-Derivate"; 148. Mitt.: Bohlmann, F. und Zdero, C. (1978) *Phytochemistry* **17**, 1337.