26·0% and 18:2, 38·3%. It is apparent that the aril oil contains the usual range of $C_{16}$ and $C_{18}$ acids and that it is particularly rich in unsaturated $C_{18}$ components (~65%).

An orange-red band at the top of the column, which failed to be eluted with ethyl acetate–petroleum (1:2), was extracted with acetone and the concentrate crystallized from ethyl acetate–petroleum (b.p. 60–80°) to furnish a crimson coloured powder (0·1%), m.p. 203°; $\lambda_{max}$ (EtOH) 478, 451, 430 infl. 276 nm; $\nu_{max}$ ($CS_2$) 963, 1035, 1355, 2920, 3360 $cm^{-1}$; $\tau$($CDCl_3$) 7·85, 8·05, 8·27, 8·72, 8·93 relative intensities *ca.* 2:2:3:3:2; *m/e* 568·428, $C_{40}H_{56}O_2$ requires 568·428. This confirming, with additional physical constants, the presence of zeaxanthin, also found by earlier workers.[1,2]

The residue from the petrol extraction was further extracted with boiling MeOH. The concentrated extract separated into two fractions. The soluble fraction, showed the presence of only one component, and by mixed TLC with an authentic specimen of kaempferol showed no separation. Acetylation furnished the acetate which was compared (i.r., TLC) and found identical with an authentic specimen of kaempferol tetra-acetate.

The sparingly soluble fraction was shown (TLC) to be a mixture of glucose, fructose and rhamnose.

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[1] L. ZECHMEISTER and P. TUZON, *Z. Physiol. Chem.* **196**, 199 (1931).
[2] P. KARRER and E. KRAUS-VOITH, *Helv. Chim. Acta* **31**, 802 (1948).

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## COMPOSITAE

# TRITERPENOID AND STEROID CONSTITUENTS OF SOME *LACTUCA* AND *AGERATUM* SPECIES OF HONG KONG

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**Abstract**—Five closely related triterpene acetates have been obtained from *Lactuca denticulata.* These together with the isolation of other triterpenoids and steroids from also *L. indica, Ageratum conyzoides* and *A. houstonianum* are reported.

## INTRODUCTION

EARLY work on the latex of *L. virosa* and *L. sativa* revealed the presence of two isomeric alcohols, α- and β-lactucerol[1] which were later proved to be mixtures, the former being inpure taraxasterol, which was shown to be present together with β-amyrin and germanicol in the latex of *L. virosa.*[2] Other classes of compounds reported in *Lactuca* species were

[1] *Elsevier's Encyclopaedia of Organic Compounds*, Series III, Vol. 14, pp. 606–607 (1940) and Supplement, pp. 1159–1160 (1952).
[2] J. C. E. SIMPSON, *J. Chem. Soc.* 283 (1944).

polyphenolic compounds (including flavonoid glycosides),[3,4] and polyacetylenes.[5] Very little work on chemical constituents of the *Ageratum* species has been carried out, however, the presence of ageratochromene (2,2-dimethyl-6,7-dimethoxy-3-chromene) has been reported in *A. houstonianum*[6] and *A. mexicanum*.[7] Seven *Lactuca* and two *Ageratum* species have been identified in Hong Kong.[8]

## RESULTS AND DISCUSSION

Chromatography of the light petroleum extract of *Lactuca denticulata* Max. on alumina yielded a triterpene acetate mixture, taraxasterol, and a sterol mixture (stigmasterol and β-sitosterol). The acetate mixture gave five spots on TLC over argentized kieselgel, and was separated successively by column chromatography on argentized kieselgel–alumina into α-amyrenyl, β-amyrenyl, germanicyl, taraxasteryl and lupenyl acetates. Similar investigation of *L. indica* afforded besides triterpenoids (β-amyrenyl, germanicyl and taraxasteryl acetates, β-amyrin, and taraxasterol) and sterols (stigmasterol and β-sitosterol), a higher aliphatic alcohol.

Examination of the light petroleum extract of *A. houstonianum* Mill. and *A. conyzoides* L. revealed the presence of friedelin, β-sitosterol and stigmasterol in both species, and also friedelan-3β-ol in the former. The ethanol extract of both plants was found to contain a fair quantity of KCl.

## EXPERIMENTAL

TLC was performed on argentized kieselgel (Merck) plates using solvent system benzene–$CHCl_3$ (1:1). and argentized kieselgel–alumina (1:1) mixture was used for column chromatography of triterpene acetates All compounds were identified by mixed m.p. and comparison of i.r. spectra.

### Lactuca denticulata

The concentrated light petroleum extract of plant material (8 kg) was chromatographed on alumina (3 kg). Elution with light petroleum yielded an acetate mixture (15 g), m.p. 190–265°, $\nu_{max}$ 1750, 1250 $cm^{-1}$; light petroleum–benzene (9:1), taraxasterol (0·06 g), m.p. 223–224°, $[\alpha]_D$ +90·0°, $\nu_{max}$ 3400, 3080, 1650, 883 $cm^{-1}$; and light petroleum–benzene (7:3), a sterol mixture (1·0 g), m.p. 150–154°, identified as stigmasterol (formation of acetate tetrabromide, m.p. 202°) and β-sitosterol, m.p. 139° (by debromination and deacetylation of the filtrate after removal of stigmasteryl acetate tetrabromide).

The acetate mixture on TLC gave 5 spots. It (1·0 g) was chromatographed on argentized kieselgel–alumina (60 g) in light petroleum to give successively the following: α-amyrenyl acetate (0·05 g), m.p. 225–226°, $[\alpha]_D$ +72·5°; β-amyrenyl acetate (0·07 g), m.p. 238–239°, $[\alpha]_D$ +80·8°; germanicyl acetate (0·06 g), m.p. 280–281°; $[\alpha]_D$ +18·0°, hydrolysed to yield germanicol, m.p. 180–181°, $[\alpha]_D$ +4·0°, $\nu_{max}$ 3680, 3350, 1650, 860, 850 $cm^{-1}$; taraxasteryl acetate (0·13 g), m.p. 245–247°, $[\alpha]_D$ +109°, hydrolysed to taraxasterol, m.p. 221–222°, $[\alpha]_D$ +104°; and lupenyl acetate (0·22 g), m.p. 219–220°, $[\alpha]_D$ +42·4°, hydrolysed to lupeol, m.p. 215°, $\nu_{max}$ 3300, 3080, 1650, 883 $cm^{-1}$.

### L. indica

Chromatography of the extract (3·5 kg plant material) on alumina (2 kg) gave on elution with light petroleum an acetate mixture (1·5 g) which was rechromatographed as above to give β-amyrenyl acetate (0·28 g), germanicyl acetate (0·25 g), and taraxasteryl acetate (0·61 g). Elution with light petroleum–benzene yielded a compound (0·4 g), m.p. 80–82°, $\nu_{max}$ 3300 (OH), 735, 725 (alkyl chain); light petroleum–benzene (7:3), first β-amyrin (0·02 g), m.p. 195°, $[\alpha]_D$ +90·0°, then taraxasterol (0·04 g), m.p. 220–221°; and light petroleum–benzene (1:1), a sterol mixture (0·5 g), m.p. 154–155° as for *L. denticulata*.

[3] G. C. SHARPLES, *Proc. Am. Soc. Hort. Sci.* **84**, 356 (1964).
[4] T. NAKAOKI and N. MORITA, *Yakugaku Zasshi* **80**, 1473 (1960).
[5] R. K. BENTLEY, E. R. H. JONES and V. THALLER, *J. Chem. Soc.* 1096 (1969).
[6] A. RYE ALERTSEN, *Acta Polytech. Scand. Ser.* **13**, 1 (1961).
[7] A. RYE ALERTSEN, *Acta Chem. Scand.* **9**, 1725 (1955).
[8] H. C. TANG and W. T. K. LEUNG, *Check List of Hong Kong Plants*, pp. 45–47, Urban Council and Urban Services Department, Hong Kong (1967).

Ageratum houstonianum *and* A. conyzoides

Similar investigation of *A. houstonianum* (3·5 kg) gave friedelin (0·015 g), m.p. 264–265° in the light petroleum–benzene (4:1) fractions, friedelan-3β-ol (0·06 g), m.p. 279–281°, $[\alpha]_D$ + 10·0°, in the light petroleum–benzene (1:1) fractions, and a mixture of stigmasterol and β-sitosterol (0·10 g), in the light petroleum–benzene (1:4) fractions. Further extraction of the plant material with EtOH yielded KCl (5 g).

*A. conyzoides* (4 kg) gave friedelin (0·01 g), the sterol mixture (0·20 g), and KCl (30 g).

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# T-MUUROLOL-HAUPTBESTANDTEIL VON *ARNICA LONGIFOLIA*

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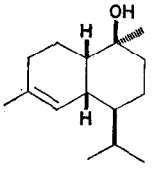
*Pflanze. Arnica longifolia* Eat.

*Frühere Arbeiten.* Fettsäuren im atherischen Öl der Blütenkörbchen.[1]

Rhizome und Wurzeln: T-Muurolol kristallisiert nach längerem Stehen des Öles bei −20° aus. Schmp. 78–79°, $(\alpha)_D^{23}$-106,8° ($CHCl_3$), Elementaranalyse, Massen-, NMR- und i.r.-Spektrum; p-Nitrobenzoat Schmp. 104–105°, Dinitrobenzoat Schmp. 163–164°; Bildung der Dihydrochloride (−)-Muurolendihydrochlorid und (−)-Cadinendihydrochlorid[2] (Schmp., Mischschmp., spez. Drehung, i.r.) sowie Dehydratisierung mit Thionylchlorid zu (−)-α-Muurolen (i.r. und Bildung der Hydrochloride).




Nach der GC-Analyse ist dieser Sesquiterpenalkohol mit 40–50% Hauptbestandteil des ätherischen Öles. Es ist dies das dritte bekannte Vorkommen von T-Muurolol in Pflanzen. Erstmals wurde dieser Alkohol vor zwei Jahren aus dem Holz von *Taiwania cryptomerioides*[3] (Taxodiaceae) und *Cedrela toona*[4] (Meliaceae) isoliert.

[1] H. KATING, W. RINN und G. WILLUHN, *Planta Med.* **18**, 130 (1970).
[2] L. WESTFELT, *Acta Chem. Scand.* **20**, 2893 (1966).
[3] Y. S. CHENG, Y. H. KUO und Y. T. LIN, *Chem. Commun.* 565 (1967).
[4] B. A. NAGASAMPAGI, L. YANKOV und SUKH DEV, *Tetrahedron Letters* 1913 (1968).