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CAMPANULACEAE

FLAVONOIDS OF *CLERMONTIA PERSICIFOLIA* LEAVES

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Plant. Clermontia persicifolia, Gaud. *Source.* Collected in Oahu, Hawaii by S. Sohmer, Department of Botany, University of Hawaii. *Previous work.* None.

Present work. The leaves were extracted with ethanol. The extract was first fractionated on a polyamide column followed by banding on paper. Identified were apigenin-7-glucoside, apigenin-7-rutinoside, luteolin-7-glucoside and luteolin-7-rutinoside.

The 7-glucosides were found to be identical through their R_f values and UV data with authentic samples. The rutinosides gave on acid hydrolysis, both glucose and rhamnose (1:1), while partial acid hydrolysis (0·1 N HCl) gave the 7-glucosides as intermediates. The UV data indicated that only position 7 of both rutinosides was occupied,[1] and finally, both rutinosides gave rutinose on permanganate oxidation,[2] which co-chromatographed with that from rutin.

Four minor flavonoids were also present, but in very low concentration; they are apigenin and luteolin glycosides with glucose and rhamnose or glucose alone as the sugar moiety. They are unaffected by alkaline hydrolysis, give the previously identified glycosides as intermediates and their colour properties indicate that positions 3′ or 4′, in the case of luteolin, and 4′ in case of apigenin are also occupied beside position 7. They are probably the 4′ (or 3′), 7-diglucosides and/or 4′ (or 3′)-glucoside-7-rutinosides.

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[1] T. J. MABRY, K. R. MARKHAM and M. B. THOMAS, *The Systematic Identification of Flavonoids*, Springer-Verlag, New York (1970).
[2] B. V. CHANDLER and K. A. HARPER, *Austral. J. Chem.* **14**, 586 (1961).

Key Word Index—Clermontia persicifolia; Campanulaceae; flavonoids; 7-glucosides and 7-rutinosides of luteolin and apigenin.

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CRASSULACEAE

ALKANES, ALKANOLS, TRITERPENES AND STEROLS OF *KALANCHOE PINNATA*

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Kalanchoe pinnata is of ornamental importance and is also employed for wounds,[1]

[1] K. R. KIRTIKAR and B. D. BASU, *Indian Medicinal Plants*, Vol. 2, pp. 998–999, Lalit Mohan Basu, Allahabad (1935).

abscesses,[2] smallpox[3] and to treat whitlow. Previous reports have been limited to plant-acids,[4–7] flavonoids glycoside,[8] and *n*-alkanes.[9]

The unsaponifiable matter on chromatography gave mainly *n*-alkane, *n*-alkanol, triterpene and sterol fractions. The alkane fraction, on GLC, was found to be C_{25}–C_{35} with C_{31} (*n*-hentriacontane) and C_{33} (*n*-tritriacontane) predominating. The odd-numbered carbons were found to be present in higher concentration; the carbon chain length increased in concentration with increasing chain length to C_{33} (Table 1). The alkanol fraction was revealed by GLC to consists of C_{26}–C_{34}; the even-numbered carbon components were found to predominate in relative concentration with C_{32} being the major component (Table 1). The triterpene fraction was shown by GLC to be α-amyrin (38%) and β-amyrin (68%) and the sterol fraction mainly sitosterol (88%).

TABLE 1. DISTRIBUTION OF *n*-ALKANES AND *n*-ALKANOLS IN THE LEAVES OF *Kalanchoe pinnata*

Carbon chain length	% composition*	
	n-alkanes	*n*-alkanols
C_{25}	Traces	—
C_{26}	Traces	6·28
C_{27}	Traces	Traces
C_{28}	Traces	5·22
C_{29}	8·40	Traces
C_{30}	2·50	20·85
C_{31}	13·00	4·81
C_{32}	6·30	42·16
C_{33}	62·90	6·42
C_{34}	0·90	12·85
C_{35}	3·70	—

* Calculated on the basis of the relative peak strength in the gas chromatograms.

EXPERIMENTAL

The pulverized leaves (10 kg) were extracted in a Soxhlet with petroleum. The extract on standing overnight deposited a dirty yellow powder. The supernatant was then concentrated and the residue (160 g) saponified and the unsaponifiable portion (38 g) chromatographed on alumina (440 g, E. Merck). The chromatogram was successively eluted with light petroleum (1–52), benzene and finally with methanol in 250 ml fractions. Each fraction was checked by TLC (silica-gel G) and the spots visualized by heating the plates at 150° for 10 min after spraying with 70% H_2SO_4. Fractions yielding a crystalline material are described below:

Fractions 1–2 gave *n*-alkanes (3·86 g) m.p., 68–70°, ν_{max} 727–715 cm^{-1} (alkane chain),[10] identified as C_{25}–C_{35} by GLC (carrier gas: H_2; flow rate: 66 ml/min; reference column: 1·5% OV-1 on Shimalite W

[2] R. N. CHOPRA, S. L. NAYAR and I. C. CHOPRA, *Glossary of Indian Medicinal Plants*, p. 147, CSIR (1596)
[3] A. K. NADKARNI, *Nadkarni's Indian Materia Medica*, Vol. 1, pp. 716–717, Popular Book Depot, Bombay (1954).
[4] J. WOLF, *Planta* **29**, 314 (1939); *Chem. Abs.* **33**, 4628 (1939).
[5] G. W. PUCHER, *J. Biol. Chem.* **145**, 511 (1942).
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[8] E. UEDA and T. SASAKI, *J. Pharm. Soc. Japan* **71**, 561 (1951); *Chem. Abs.* **45**, 9137 (1951).
[9] G. A. HERBIN and P. A. ROBINS, *Phytochem.* **7**, 257 (1968).
[10] J. M. MARTIN, R. W. B. JOHNSON, JR. and M. J. O'NEAL, *Spectrochim. Acta* **12**, 12 (1958).

(80–100 mesh); temp.: 250°; chart speed: 5 mm/min; detector: flame ionization; column: L.2 m, i.e. 4 mm). Fractions 22–26 yielded from acetone *n*-alkanols (0·178 g) m.p., 88–89°, ν_{max} 3300 (OH) and 730–720 cm^{-1} (alkane chain).[10] This was reduced[11] to *n*-alkanes and characterized through GLC as C_{26}–C_{34}. Fractions 27–52 gave needles (0·276 g) of α- and β-amyrin from EtOH, m.p., 184–186°. Found: C, 84·78; H, 11·90. Calc. for $C_{30}H_{50}O$: C, 84·50; H, 11·73%. An IR-spectrum showed OH (3285 cm^{-1}) and *gem*-dimethyl (1385, 1360 cm^{-1}). Fractions 64–75 (elution: benzene) gave sterols (2·70 g) m.p., 130–134°. GLC showed sitosterol to be the major component. The IR spectrum in addition to OH group (3400 cm^{-1}) had pronounced peaks for $=C=CH_2$ (1645, 885 cm^{-1}), thus showing thereby the presence of another substance besides sitosterol.

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Key Word Index—Kalanchoe pinnata; Crassulaceae; *n*-alkanes; *n*-alkanols; α- and β-amyrin; sitosterol.

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CRUCIFERAE

GLUCOSINOLATES IN *SYRENIA CANA*

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Plant. Syrenia cana (Piller et Mitterpacher) Neilreich. (Herbarium deposited in the Botanic Museum of the University of Copenhagen.)

Seeds. Defatted, ground seed material (13 g) was extracted with 70% MeOH. The residue was subjected to enzymic hydrolysis in a citrate buffer (pH 6·5) by the addition of a few drops of a myrosinase solution and a trace of ascorbic acid. The resulting isothiocyanates (66 mg) were extracted with $CHCl_3$ and chromatographed on a silica gel column with $CHCl_3$ containing 0·5–3% EtOH, as the mobile phase. Three fractions, (i)–(iii), were separately studied. (i) Most lipophilic: the fraction was treated with methanolic ammonia. On paper chromatography in water-saturated $CHCl_3$,[1] and two other solvent systems, trace amounts of two thioureas were observed, indistinguishable in their behaviour from 1-allylthiourea and 1-(3-methylthiopropyl)-thiourea, supposedly deriving from *allylglucosinolate* and 3-*methylthiopropylglucosinolate*, both previously encountered in other crucifer seeds.[2,3] (ii) Less lipophilic: identified as 3-methylsulfonylpropyl isothiocyanate (cheirolin) by reaction with ammonia and aniline to give 1-(3-methylsulphonylpropyl)-thiourea and 1-(3-methylsulfonylpropyl)-3-phenylthiourea, respectively, indistinguishable from authentic,

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[3] M. G. ETTLINGER and A. KJÆR, in *Recent Advances of Phytochemistry* (edited by T. J. MABRY, R. E. ALSTON and V. C. RUNECKLES), Vol. 1, p. 58, Appleton–Century–Crofts, New York (1968).