

(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 reduced¹¹ 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 $\text{C}_{30}\text{H}_{50}\text{O}$: 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 $=\text{C}=\text{CH}_2$ (1645, 885 cm^{-1}), thus showing thereby the presence of another substance besides sitosterol.

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¹¹ Z. H. KRANZ, J. A. LAMBERTON, K. E. MURRAY and A. H. REDCLIFFE, *Austral. J. Chem.* **13**, 498 (1960).

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,

¹ A. KJÆR and K. RUBINSTEIN, *Acta Chem. Scand.* **7**, 528 (1953).

² A. KJÆR, *Fortschr. Chem. Org. Naturstoffe* **18**, 122 (1960).

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

synthetic specimens⁴ (TLC, UV, IR, MS, and m.p.). The finding supports the presence of 3-methylsulfonylpropylglucosinolate in the seeds, in keeping with the botanical affinity of *Syrenia* to cruciferous genera such as *Cheiranthus*, *Erysimum* and *Malcolmia*, typical sources of the same glucosinolate.^{2,3} (iii) Least lipophilic: identified as (*R*)-3-methylsulfinylpropyl isothiocyanate through its conversion into (—)-1-(3-methylsulfinylpropyl)-3-phenylthiourea,⁵ of established (*R*)-configuration,⁶ and critical comparison (TLC, UV, IR, MS, m.p. and $[\alpha]_D$). Most likely, the isothiocyanate derives from (*R*)-3-methylsulfinylpropylglucosinolate, first isolated from seeds of *Iberis amara* L.,⁷ but subsequently encountered in several other species of the same and other genera.^{2,3}

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⁴ A. KJÆR, F. MARCUS and J. CONTI, *Acta Chem. Scand.* 7, 1370 (1953).

⁵ A. KJÆR and R. GMELIN, *Acta Chem. Scand.* 10, 1100 (1956).

⁶ K. K. CHEUNG, A. KJÆR and G. A. SIM, *Chem. Commun.* 100 (1965).

⁷ O.-E. SCHULTZ and R. GMELIN, *Arch. Pharm.* 287/59, 404 (1954).

Key Word Index—*Syrenia cana*; Cruciferae; glucosinolates; 3-methylsulfonylpropylglucosinolate; allylglucosinolate; 3-methylthiopyrrolglucosinolate.

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COMPOSITAE

FLAVONOIDS AND PHENOLIC ACIDS FROM *CIRSIIUM LANCEOLATUM*

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Several studies of the flavonoid chemistry of the relatively large genus *Cirsium* Mill. have appeared.¹ This report concerns the identification of the flavonoids and phenolic acids of mature flowering specimens of *Cirsium lanceolatum* L. (Hill.) (*Carduus lanceolatus* L.).² The flavonoids identified were kaempferol-3-*O*-glucoside, quercetin-3-*O*-glucoside, quercetin-3-*O*-galactoside, apigenin-7-*O*-diglucoside, and genkwanin-4'-*O*-glucoside. The identified phenolic acids were *p*-coumaric, caffeic, ferulic, *p*-hydroxybenzoic, protocatechuic, and vanillic acids.

EXPERIMENTAL

The plant material was collected in Jackson County, N.C., U.S.A. Herbarium specimens were deposited in the herbarium of Western Carolina University. For flavonoid and phenolic acid analyses the fresh leaves were thoroughly extracted with 80% EtOH, the extract concentrated under vacuum, diluted with hot H₂O, and filtered through celite. The aqueous solution was exhaustively extracted with EtOAc. The EtOAc

¹ J. W. WALLACE and B. A. BOHM, *Phytochem.* 10, 452 (1971).

² A. E. RADFORD, H. E. AHLES and C. R. BELL, *Manual of the Vascular Flora of the Carolinas*. Univ. of N.C. Press, Chapel Hill (1968).