Phytochemistry, 1970, Vol. 9, pp. 2193 to 2195. Pergamon Press. Printed in England.

SHORT COMMUNICATION

GLYCOALKALOIDS FROM ARCHAESOLANUM SPECIES

D. C. LEWIS and D. R. LILJEGREN

Department of Agricultural Biochemistry, Waite Agricultural Research Institute,
The University of Adelaide, Glen Osmond, South Australia

(*Received* 9 *December* 1969)

Abstract—Solasonine and solamargine have been identified in extracts from all seven members of the Archaesolanum subgenus of the genus *Solanum*. Concentration of these alkaloids is, in general, higher in the immature fruits than in the leaves.

INTRODUCTION

FOLLOWING the work of Baylis[1] and Gerasimenko,[2] there are now seven distinct species recognized within the subgenus Archaesolanum of *Solanum* (Solanaceae). *Solanum laciniatum* and *S. aviculare* have been shown to contain high concentrations of steroidal glycoalkaloids.[3] These compounds can be used as convenient starting materials in the production of steroid hormones, and this has led to extensive cultivation of the above species.

To our knowledge there is no account of the presence of alkaloids in *S. capsiciforme*, *S. linearifolium* or *S. symonii*. This paper, then, gives a comparative report of the alkaloids in the leaves and immature fruits of all members of the group.

RESULTS AND DISCUSSION

Values for the alkaloid glycoside content of the seven species are shown in Table 1. The method of estimation of the alkaloid concentration in the extracts was a modification of the

TABLE 1. YIELD OF ALKALOID GLYCOSIDES FROM ARCHAESOLANUM SPECIES

	Alkaloid conc. as %/fresh wt. in	
Plant species	Immature fruits	Leaves
Solanum aviculare Forst. f.	1·65	0·41
S. capsiciforme (Domin) Baylis.	0·06	0·10
S. laciniatum Ait.	1·20	0·42
S. linearifolium Gerasimenko.	0·83	0·14
S. simile F. von Muell.	0·76	0·64
S. symonii Hj. Eichler.	0·18	0·20
S. vescum F. von Muell.	0·14	0·20

---

[1] G. T. S. BAYLIS, *Australian J. Botany* **11**, 168 (1963).

[2] I. I. GERASIMENKO, *Bull. Glavn. Botany. Sada* **59**, 71 (1965).

[3] For a recent summary of the occurrence of *Solanum* glycoalkaloids see K. SCHREIBER in *The Alkaloids* (edited by R. H. F. MANSKE), Vol. X, p. 1, Academic Press, New York (1968).

Clarke colorimetric assay for Δ^5-unsaturated steroidal alkaloids.[4] Solamargine or solasonine were used as standards, and colour development was shown to increase in a linear fashion with glycoalkaloid concentration to a maximum of 1 mg. The estimates obtained by this method are accurate as shown by a larger scale extraction of the immature fruits of *Solanum linearifolium.*

It can be seen that, in general, alkaloids are present in lower concentration in the leaves than the immature fruits. The yields obtained in either case are likely to vary, as it has been shown in *S. laciniatum* that concentration can change both in the short term, over a 24-hr period,[5] and in the long term, over the life cycle of the plant.[6] Rather than representing maximum yields that can be obtained, the values show a comparison of the alkaloid content of the seven species grown and harvested under similar conditions.

Thin-layer chromatography using an *n*-butanol system gave an excellent resolution of the mixtures. All species contained solamargine (R_f 0·40) and solasonine (R_f 0·28) as major alkaloids of the fruits, and a number of slower-running compounds (R_f 0·23, 0·20, 0·17, 0·15). In addition *S. capsiciforme* and *S. symonii* had minor components of R_f 0·12, 0·10, 0·08 and 0·06. Each contained approximately the same ratio of solamargine and solasonine (50 and 35% respectively in the extracts) with the exception of *S. capsiciforme* and *S. symonii* where these alkaloids were present in relatively lower concentration. Chromatograms of the leaf extracts were similar to those from the fruits, but only trace amounts of the slower-running compounds were present.

Attempts were made to isolate the minor components of the mixture. However, chromatography on alumina columns did not give the desired separation, and recovery from preparative TLC was too low for any characterization to be made. It is likely that these compounds contain polysaccharides of greater complexity than the solatriose and chacotriose of solasonine and solamargine. In the solvent system used for TLC separation, the lower the molecular weight of the alkaloid the higher is the R_f. This may be seen by monitoring the progress of the acid hydrolysis of solasonine or solamargine. Briggs *et al.*[7] and Schreiber[8] have also reported the presence of minor alkaloids in extracts from *Solanum* species, and believe them to be different tetrasaccharides of solasodine.

EXPERIMENTAL

M.ps were determined on a Kofler hot-stage apparatus; specific rotations were measured in MeOH.

Extraction of Alkaloids

Plant material was harvested and stored in sealed containers at −15°, conditions that led to no changes in alkaloid content over a period of months. The frozen fruits or leaves (10 g) were ground with methanol (20–30 ml) in a mortar. The extract was filtered and the residue washed with hot methanol. Solvent was removed from the combined filtrates and the green residue dissolved in 5% HOAc (8 ml). After extraction with ether (6 × 20 ml) the aqueous solution was boiled, basified with ammonia and stored at 0° overnight. The precipitate was collected by centrifugation, washed with water and dissolved in 95% ethanol and stored in stoppered tubes.

Aliquots of the ethanol extracts were mixed with H_3PO_4 (88%, 3 ml) and HCHO (0·5 %, 1·5 ml) and heated at 50° for 15 min. The absorption was measured at 574 nm and the alkaloid concentration determined from standard curves prepared using known amounts of solamargine or solasonine.

---

[4] E. G. C. CLARKE, *Nature* **181**, 1152 (1958).

[5] J. VARADI, E. CSAPO and J. HALMAI, *Acta Agron. Acad. Sci. Hung.* **15**, 403 (1966).

[6] B. WACLAW-ROZKRUTOWA, *Diss. Pharm. Pharmac.* **18**, 595 (1966); *Chem. Abs.* **67**, 29848b (1967).

[7] L. H. BRIGGS, R. C. CAMBIE and J. L. HOARE, *J. Chem. Soc.* 4645 (1961).

[8] K. SCHREIBER, *Planta Med.* **6**, 435 (1958).

On a larger scale a mixture of alkaloid glycosides (2·05 g) was obtained from the green fruits of *Solanum linearifolium* (240 g). Chromatography on alumina (Woelm neutral, activity 1) using water-saturated *n*-butanol as eluting solvent yielded solamargine (1·06 g) and solasonine (0·54 g). A later fraction (0·25 g) contained solasonine mixed with three slower-moving compounds. Repeated crystallization from aqueous methanol gave solamargine, m.p. 308–310° (decomp.), undepressed on admixture with an authentic sample, $[\alpha]_D^{18}$ −95·7° (reported[9] m.p. 303–305° (decomp.), $[\alpha]_D$ −96·5). Solasonine had m.p. and mixed m.p. 289–290° (decomp.), $[\alpha]_D^{18}$ −67·0° (reported[9] m.p. 286–289° (decomp,), $[\alpha]_D$ −73·2°). TLC comparison of the alkaloids isolated with authentic material showed identical R_f values in the solvent systems mentioned below.

Solasodine obtained from solamargine or solasonine by hydrolysis with 3 % HCl in methanol had m.p. and mixed m.p. 200–202°, $[\alpha]_D^{18}$ −91·7° (reported[9] m.p. 203–295°, $[\alpha]_D$ −90°).

Thin-Layer Chromatography

Plates were prepared (250 μ thickness) using silica gel G (Merck), activated at 110° for 30 min, and ethanol solutions containing 30 μg of the alkaloid mixtures applied. The solvent systems were water-saturated *n*-butanol–diethylamine–methanol (85:10:2), $CHCl_3$–ethanol–1 % ammonia (2:2:1, lower phase) and EtOAc–pyridine–water (3:1:3, upper phase). After development the plates were dipped into 25 % $SbCl_3$ in $CHCl_3$ and heated at 110° for 5–10 min. Areas containing the alkaloids were seen as purple spots.

Acknowledgements—Thanks are due to Mr. D. E. Symon for growth and identification of plant material; to Dr. M. B. E. Fayez and the All Union Research Institute of Medicinal Plants, Vilar, U.S.S.R., for authentic samples.

---

[9] M. B. E. FAYEZ and A. A. SALEH, *Phytochem.* **6**, 433 (1967).