Phytochemistry, Vol. 23, No. 2, pp. 461–462, 1984.
Printed in Great Britain.

0031-9422/84 $3.00 + 0.00

SHORT REPORTS

LIPID COMPONENTS OF *ARISTOLOCHIA LONGA*

J. DE PASCUAL TERESA, JULIO G. URONES, ALVARO FERNANDEZ and M. D. VAQUERO ALVAREZ

Departmento de Quimica Organica, Facultad de Quimica, Universidad de Salamanca, Spain

(*Received* 8 *June* 1983)

Key Word Index—*Aristolochia longa*; Aristolochiaceae; lipids; polyprenols; isobutyl esters; phytyl esters; ethyl esters.

Abstract—The hexane extract (non-volatiles) of *Aristolochia longa* yielded fatty acids, methyl, ethyl, isobutyl and phytyl esters, and polyprenols.

A study was made of the hexane extracts of the roots and aerial parts (without the fruits) of *Aristolochia longa* L., a plant whose essential oils were the subject of a previous communication [1]. The substantial amounts of the non-volatile extracts obtained with rather non-polar solvents have received little attention in other plants of the same genus [2, 3] since, in general, interest has been directed towards the polar extracts from which the pharmacologically active aristolochic acids are obtained [4].

The non-volatile hexane extract of the aerial part (3.4%) was essentially made up of free fatty acids (40%) and their derivatives [either as glycerides (9%) or as the esters of monohydroxylic acids (15%)]; also present in substantial amounts were sitosterol (6%) and isoprenoid alcohols (3%) whilst little squalene was detected.

The free fatty acid fraction was shown by GLC of its methyl esters to be made up of palmitic (44%), stearic (5%), oleic (10%), linoleic (22%) and linolenic (19%) acids. Saponification of the glycerides and GLC of the corresponding methyl esters of the acid fraction gave an identical qualitative and a similar quantitative composition to that of free fatty acids.

The ester part was composed of phytyl esters (9%), mixtures of methyl and ethyl esters and, as major components, isobutyl esters (50%). The esters were separated by repeated chromatography over silica gel–silver nitrate and preparative TLC. The following were isolated as single species: (1) Phytyl palmitate and phytyl oleate, identified by saponification and subsequent separation of phytol alone in the neutral fraction and palmitic and oleic acids, respectively, in the acid fraction (identified by GLC of their corresponding methyl esters). Mixtures of phytyl-palmitate- and -stearate (trace) and phytyl-linoleate and -linolenate were identified in a similar way. (2) Isobutyl-palmitate, -oleate, -linoleate and -linolenate were identified by comparison with authentic samples (IR, ^{1}H NMR and GLC). A mixture of methyl- (trace) ethyl- (trace) and isobutyl-palmitate and isobutyl-stearate (trace) was identified by GLC comparison with standards obtained in this laboratory.

Phytyl palmitate and phytyl linoleate were the only phytyl esters to have been described in the literature [5]. The isobutyl esters isolated from *A. longa* are described here for the first time as natural products, although isobutyl esters of low MW have been described previously [6].

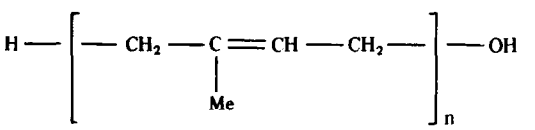
The polar fractions yielded a mixture of polyisoprenoid alcohols which were identified by comparison of the properties of their acetyl derivatives with those described in the literature for the mixtures of polyprenoids isolated from *Aesculus hippocastanum* [7] and *Ficus elastica* [8].

Mass spectrometry of the acetyl derivatives showed the presence of polyprenols-10 through to -13 with a predominance of polyprenol-12 (75%) and traces of polyprenol-10. This is the first time that these polyprenols have been described in the genus *Aristolochia*.

The non-volatile hexane extract of the root (0.3%) was fractionated with alkaline solutions. The acid part (41%) was composed of palmitic (22%), oleic (23%), linoleic (40%) and linolenic (13%) acids, as well as a small amount of an unidentified ester of ferulic acid. This acid (esterified) was previously described in *A. sipho* [9].

The neutral part was mainly composed of glycerides (27%), ethyl (11%) and isobutyl (5%) esters of palmitic, oleic, linoleic and linolenic acids, and sitosterol (10%). The mixture of fatty acids obtained by saponification of the glycerides was similar to that of the free acids and did not contain appreciable amounts of stearic acids (contrary to the aerial part).

Of noteworthy interest was the separation as single species (column chromatography on silver nitrate) of ethyl-palmitate, -oleate, -linoleate and -linolenate, identified by comparison with authentic samples (IR, ^{1}H NMR and GLC), while in the aerial part only traces of ethyl palmitate were identified. The ethyl esters of fatty acids have been described as components of plants but have



only been isolated as pure species on rare occasions [10]; they have not been previously reported in the genus *Aristolochia*.

EXPERIMENTAL

GLC, Varian Aerograph Series 2700 (DEGS 5%, 2 m × 1/8″, 150–165°). All analyses were carried out by comparison with synthetic products.

The dried aerial part (without fruits) (5.6 kg) and the dry ground roots (3.5 kg) were extracted with hexane (Soxhlet) to give extracts of 190.4 and 10.1 g, respectively. Both extracts were steam-distilled to separate the volatile components (1.6 and 1.0 g, respectively). 26 g of the hexane extract of the aerial part was chromatographed on silica gel with hexane–Et_2O eluting a mixture of monohydroxylic esters (3.87 g), glycerides (2.21 g), free fatty acids (10.35 g), polyprenols (870 mg) and sitosterol (1.62 g).

Repeated chromatography on silica gel–$AgNO_3$ of 2.10 g of the mixture of monohydroxylic esters, as well as of the mixtures of phytyl-palmitate and -stearate, phytyl-linoleate and -linolenate; and methyl-, ethyl-, isobutyl-palmitate and isobutyl stearate yielded as single species: phytyl palmitate (58 mg), phytyl oleate (82 mg), isobutyl palmitate (306 mg), isobutyl oleate (23 mg), isobutyl linoleate (562 mg) and isobutyl linolenate (202 mg).

The hexane extract of the roots (without essential oil) was fractionated with aq. NaOH (4%) yielding 3.38 g of an acidic fraction. 2.14 g of the neutral fraction was chromatographed on silica gel and silica gel–$AgNO_3$ to give, as well as sitosterol (190 mg) and glycerides (585 mg), ethyl palmitate (56 mg), ethyl oleate (48 mg), ethyl linoleate (92 mg), ethyl linolenate (33 mg), isobutyl esters (103 mg) and traces of methyl palmitate.

Acknowledgement—We thank Professor Casaseca Mena, Dpto. Botany, Fac. Biologicas, University of Salamanca, Spain, for the identification of *A. longa*.

REFERENCES

1. De Pascual Teresa, J., Urones, J. G. and Fernandez, A., *Phytochemistry* (in press.)
2. Cisowski, W., Rzadkowska-Bodalska, H. and Szymczak, J. (1977) *Herba Polon.* **33**, 117.
3. Carboni, S., Livi, O., Segnini, D. and Mazzanti, L. (1966) *Gazz. Chim. Ital.* **96**, 641.
4. Munavalli, S. and Viel, C. (1969) *Ann. Pharm. Fr.* **27**, 519.
5. Suga, T. and Aoki, T. (1974) *Phytochemistry* **13**, 1623.
6. Nursten, H. and Williams, A. (1967) *Chem. Ind.* 486.
7. Wellburn, A. R., Stevenson, J., Hemming, F. W. and Morton, R. A. (1967) *Biochem. J.* **102**, 313.
8. Stone, K. J., Wellburn, A. R., Hemming, F. W. and Pennock, J. F. (1967) *Biochem. J.* **102**, 325.
9. Plouvier, V. (1956) *R. Acad. Sci.* **242**, 2389.
10. Matsuo, A., Nakayama, M., Hayashi, S. and Nagai, K. (1980) *Phytochemistry* **19**, 1848.

Phytochemistry, Vol. 23, No. 2, pp. 462–464, 1984.
Printed in Great Britain.

0031–9422/84 $3.00 + 0.00

TWO SESQUITERPENE LACTONES FROM *ARTEMISIA* SPECIES

MASAHIKO NAGAKI

Department of Chemistry, Hirosaki University, 1-Bunkyo-cho, Hirosaki, Aomori 036, Japan

(*Revised received* 25 *June* 1983)

Key Word Index—*Artemisia feddei*; *A. montana*; Compositae; sesquiterpene lactones; alantolide; guaianolide; himeyoshin; montanone.

Abstract—Two new sesquiterpene lactones, himeyoshin and montanone, were isolated from *Artemisia feddei* and *A. montana*, respectively and identified by chemical and spectral data as 1α,2α-epoxy-3-oxo-5,6-dihydroalantolactone and 1,10-dihydro-11,13-dehydromatricarin.

INTRODUCTION

A previous study of *Artemisia feddei* revealed three sesquiterpene lactones (meridianone, yomogiartemin and yomogin), two coumarins (scopoletin and herniarin) and three steroids (sitosterol, ergosterol and ergosterol-5,8-peroxide) [1]. The present paper reports the isolation and identification of two new sesquiterpene lactones, himeyoshin (**1**) and montanone (**2**) from *Artemisia feddei* and *A. montana*, respectively. In addition, the former plant yielded yomogin, scopoletin, isoscopoletin and sitosterol while the latter yielded yomogin and scopoletin.

RESULTS AND DISCUSSION

The chloroform extract of the aerial parts of *A. feddei* collected in the northern part (Tohoku district) of Japan afforded a new sesquiterpene lactone, **1**, $C_{15}H_{18}O_4$, mp 214–215°. On mass spectral analysis at 70 eV **1** showed *m/z* 262.1206 $[M]^+$ (calculated for $C_{15}H_{18}O_4$: 262.1205) and a diagnostic fragment ion at *m/z* 246 $[M-16]^+$, which indicated the presence of an epoxy group. The UV spectrum exhibited a maximum at 303 nm (ε36) which suggested the presence of a cyclohexanone moiety. The IR spectrum showed characteristic absorptions at 1760 (γ-