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MELONGOSIDE L AND MELONGOSIDE M, STEROIDAL SAPONINS FROM *SOLANUM MELONGENA* SEEDS

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Key Word Index—*Solanum melongena*; Solanaceae; spirostanol glycosides; melongoside L; melongoside M.

Abstract—Two new steroidal saponins, melongoside L and melongoside M, have been isolated from a methanolic extract of *Solanum melongena* seeds and their structures elucidated.

INTRODUCTION

Previous workers [1] have reported the presence of diosgenin and tigogenin in *Solanum melongena* L. seeds. The structures of two new saponins isolated from this plant are reported in this paper.

RESULTS AND DISCUSSION

Several fractions were isolated from a methanolic extract of *S. melongena* seeds by column chromatography. After acid hydrolysis of one of these fractions, tigogenin and diosgenin were identified as aglycones by mp, TLC, GLC with the aid of authentic samples, and mass spectrometry, suggesting that this fraction represented a two-component mixture of glycosides, which were difficult to separate, and various aglycones. However, after acetylation with subsequent epoxidation of the fraction using the method described in ref. [2], column chromatography on silica gel gave melongoside L peracetate (**3**) and melongoside M peracetate epoxide (**4**). De-epoxidation [3] of **4** yielded melongoside M peracetate (**5**). Saponification of **3** and **5** gave melongosides L and M. Hydrolysis of melongoside L resulted in the formation of tigogenin, glucose, galactose and rhamnose in the mol ratio of 1:3:1:1, whilst hydrolysis of melongoside M gave diosgenin, glucose, galactose and rhamnose in the mol ratio of 1:3:1:1.

Both glycosides reacted positively with Sanie reagent and negatively with Ehrlich's solution [4]. Their IR spectra showed absorption bands characteristic of a (25*R*)-spiroketal.

The types of glycosidic linkages in compounds **1** and **2** were proved by methylation [5]. In both cases, the methylated products were identified by TLC and GLC as methyl-2,3,4,6-tetra-*O*-methyl-D-glucopyranoside (**6**), methyl-2,3,4,6-tetra-*O*-methyl-D-galactopyranoside (**7**), methyl-2,3-di-*O*-methyl-L-rhamnopyranoside (**8**), methyl-2,3,6-tri-*O*-methyl-D-glucopyranoside (**9**) and methyl-4,6-di-*O*-methyl-D-glucopyranoside (**10**).

The sequences of the sugars in **1** and **2** were established by partial hydrolysis. Tigogenin monoside (**11**), tigogenin bioside (**12**), tigogenin trioside (**13**) and tigogenin tetraoside (**14**) were obtained from melongoside L, and diosgenin monoside (**15**), diosgenin bioside (**16**), diosgenin trioside (**17**) and diosgenin tetraoside (**18**) from melongoside M.

Acid hydrolysis of **11**, **12**, **15** and **16** yielded glucose; **13** and **17** yielded glucose and rhamnose (2:1); **14** and **18** yielded glucose, galactose and rhamnose (2:1:1). Methylation of **11**–**18** with subsequent methanolysis gave: (a) compound **6** from **11** and **15**; (b) compound **6** and methyl-3,4,6-tri-*O*-methyl-D-glucopyranoside (**19**) from **12** and **16**; (c) compounds **6**, **10** and methyl-2,3,4-tri-*O*-methyl-L-rhamnopyranoside (**20**) from **13** and **17**; and (d) compounds **7**, **20**, **9**, **10** from **14** and **18**.

The configurations at C-1 of the monosaccharides were proved by Klyne's rule [6].

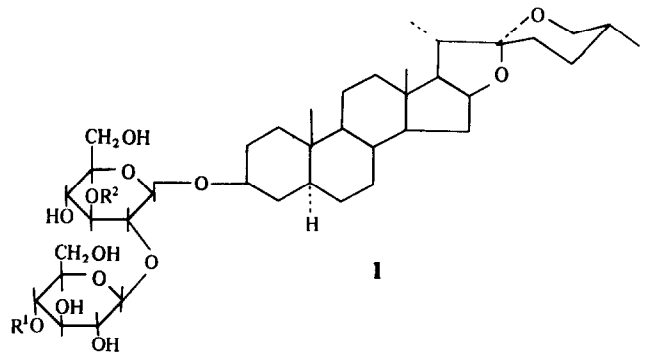
From the above, it follows that melongoside L is 3-*O*-{[*β*-D-glucopyranosyl-(1 → 4)-*α*-L-rhamnopyranosyl-(1 → 3)]-[*β*-D-galactopyranosyl-(1 → 4)-*β*-D-glucopyranosyl-(1 → 2)]-*β*-D-glucopyranosyl (25*R*)-5*α*-spirostan-3*β*-ol, and melongoside M is 3-*O*-{[*β*-D-glucopyranosyl-(1 → 4)-*α*-L-rhamnopyranosyl-(1 → 3)]-[*β*-D-galactopyranosyl-(1 → 4)-*β*-D-glucopyranosyl-(1 → 2)]-*β*-D-glucopyranosyl} (25*R*)-spirost-5-en-3*β*-ol.

EXPERIMENTAL

Separation of S. melongena *saponins*. Dry seeds (1 kg) were extracted with MeOH (3 × 3 l.) for 4 hr at 65° A fraction (3 0 g) obtained by CC of the methanolic extract on silica gel ($CHCl_3$–MeOH–H_2O, 13:6:2) was acetylated and then epoxidized in 50 ml of freshly distilled $CHCl_3$ and 0.9 g of metachloroperbenzoic acid for 2.5 hr at room temp. The reaction mixture was diluted with 150 ml Et_2O and 200 ml H_2O. The Et_2O layer was treated with 2% NaOH, washed with H_2O to neutral reaction, dried (Na_2SO_4) and evapd. Glycosides were separated on a silica gel column to give 0.7 g **3**, mp 132°, $[\alpha]_D^{20}$ −83° ($CHCl_3$; *c* 1 0) and 2.0 g **4**, mp 152°; $[\alpha]_D^{20}$ −70° ($CHCl_3$; *c* 1.0).

De-epoxidation of **4** 2.0 g **4** was de-epoxidized, using the method described in ref. [3], to yield 800 mg **5**, mp 125°; $[\alpha]_D^{20}$ −75° ($CHCl_3$, *c* 1.0).

Saponification of **3** *and* **5**. Compounds **3** and **5** were saponified with 10% NaOH in MeOH for 5 hr at 110° to give 0 5 g **1**, mp



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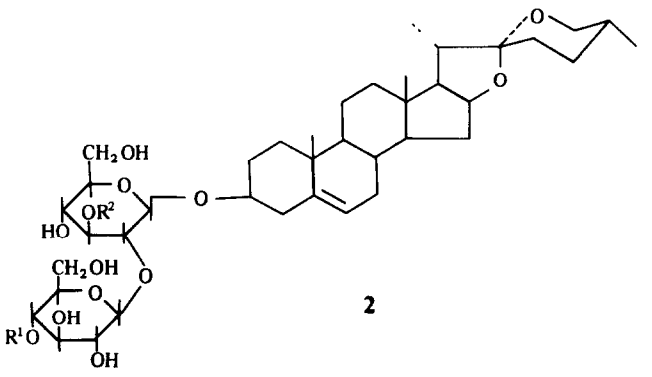

2

1, **2** $R^1 = \beta$-D-Galactopyranosyl
$R^2 = \beta$-D-Glucopyranosyl-(1 → 4)-α-L-rhamnopyranosyl
12, **16** $R^1 = R^2 = H$
13, **17** $R^1 = H$, $R^2 = \alpha$-L-Rhamnopyranosyl
14, **18** $R^1 = \beta$-D-Galactopyranosyl, $R^2 = \alpha$-L-Rhamnopyranosyl

290°; $[\alpha]_D^{20}$ −105° (MeOH; *c* 1.0) and 0.6 g **2**, mp 285°; $[\alpha]_D^{20}$ −110° (MeOH; *c* 1.0).

Hydrolysis of **1** *and* **2**. Compounds **1** and **2** (50 mg) were hydrolysed with 5% H_2SO_4 at 110° for 6 hr. Tigogenin was obtained from **1** and identified by TLC, mp 204–206°; $[\alpha]_D^{20}$ −67° ($CHCl_3$; *c* 1.0) and MS: *m/z* 416 $[M]^+$; and diosgenin from **2**, mp 208°; $[\alpha]_D^{20}$ −129° ($CHCl_3$; *c* 1.0), MS: *m/z* 414 $[M]^+$.

Monosaccharides were identified in the hydrolysates from both glycosides by PC and GLC [7]. Aldononitryl derivatives of the sugars were separated by GLC (2 m glass column of 5% XE-60 or 3% SE-30 on Chromaton N-AW-DMCS, 0.16–0.20 mm; temp. 100°, 5°/min to 220°; He, 45 ml/min; FID).

Methylation and methanolysis of permethylated products. Melongosides L and M (0.2 g) were methylated by the Hakomori method [5] with 72% $HClO_4$ in MeOH (1:10) for 5 hr at 105°. After neutralization of anionic Dowex 1 × 8, five methylglycosides were obtained from each of these glycosides. All methylglycosides were identified by GLC with the aid of authentic sample compounds

Partial hydrolysis. Compounds **1** and **2** (0.2 g) were heated in 20 ml 1% H_2SO_4 with MeOH for 1 hr at 90° and extracted with BuOH The BuOH extracts were chromatographed on silica gel ($CHCl_3$–MeOH–H_2O, 13:5:2). Compound **1** gave **11** (20 mg), mp 273°, $[\alpha]_D^{20}$ −62° (MeOH; *c* 1.0); **12** (40 mg), mp 237°, $[\alpha]_D^{20}$ −55° (MeOH; *c* 1.0); **13** (30 mg), mp 270°, $[\alpha]_D^{20}$ −70° (MeOH; *c* 1.0); and **14** (50 mg), mp 287–288°, $[\alpha]_D^{20}$ −73° (pyridine; *c* 1.0). Compound **2** gave **15** (30 mg), mp 269–271°, $[\alpha]_D^{20}$ −103° (dioxane; *c* 1.0); **16** (40 mg), mp 233–234°, $[\alpha]_D^{20}$ −65° (MeOH; *c* 1.0); **17** (50 mg), mp 289–290°, $[\alpha]_D^{20}$ −80° (MeOH; *c* 1.0); and **18** (30 mg), mp 291–293°, $[\alpha]_D^{20}$ −96° (MeOH; *c* 1.0).

Methylation and methanolysis of the progenins were carried out as indicated above, and the methylglycosides obtained were identified by GLC.

REFERENCES

1. Apsomatova, R. A., Denikejeva, M. F. and Koshoev, K. K. (1976) *Organic Chemistry and Ways of Development of Chemical Industry in Kirgizia*, p. 55.
2. Grant, P. K. and Weavers, R. T. (1974) *Tetrahedron* **30**, 2385.
3. Caputo, R., Mangoni, L., Neri, O. and Polumbo, G. (1981) *Tetrahedron Letters* **22**, 3551.
4. Kiyosawa, S. and Masakaru, H. (1968) *Chem. Pharm. Bull.* **16**, 1162.
5. Hakomori, S. (1964) *J. Biochem. (Tokyo)* **55**, 205.
6. Klyne, W. (1950) *Biochem. J.* **41**, 47.
7. Krohmalyuk, V. V., Kintia, P. K. and Tschirva, V. Y. (1975) *Izv. Akad. Nauk USSR, Ser. Biol. Khim.* **1**, 85.