TRITERPENE GLYCOSIDES FROM Clematis orientalis

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The principal glycoside from roots of *Clematis orientalis* L. (Ranunculaceae), Chinese clematis, was isolated previously [2] and characterized as a hederagenin pentaoside, vitalboside F, which was isolated from a different clematis species [3].

In continuation of this study, ground roots of Chinese clematis were extracted with aqueous methanol in an open column. The extract was purified by repeated extraction with butan-1-ol and reprecipitation of it from acetone to afford total saponins that contained according to TLC at least 12 triterpene glycosides that we named in order of increasing polarity as orientalosides A, B, C, D, E, F, G, H, I, J, K, and L.

The total glycosides were separated into individual fractions by ordinary liquid chromatography using reversed-phase RP-18 (MeOH:H₂O, $10\% \rightarrow 80\%$).

Chromatography of fractions enriched in two and three components over columns of silica gel, polyamide, and reversed-phase resin isolated the five pure principal glycosides orientalosides F, H, I, J, and K.

The chemical structures of the isolated glycosides were established using modern physical chemical, NMR (¹³C and ¹H), correlation methods (HMBC, HMQC, DEPT, COSY), and mass spectrometric analysis.

According to acid and alkaline hydrolysis and various ¹³C NMR experiments, orientaloside F was a monodesmoside; the remaining glycosides H, I, J, and K, bidesmosides. The aglycon of glycosides F, H, I, and K was hederagenin; of orientaloside J, oleanolic acid. Analysis of the monosaccharides showed rhamnose, arabinose, and glucose in different ratios and sites of attachment. The elucidated full structures of the isolated glycosides were known compounds.

Orientaloside F was 3β -O- α -L-Rhap $(1\rightarrow 2)$ - α -L-Arap-hederagenin, analogous to α -hederin from *Hedera helix* [4].

Orientaloside H was 3β -*O*- α -L-Arap-28-*O*- α -L-Rhap $(1\rightarrow 4)$ - β -D-Glc $p(1\rightarrow 6)$ - β -D-Glcp-hederagenin, identical to cauloside D from *Caulophyllum robustum* [5].

Orientaloside I was 3β -O- α -L-Rhap $(1\rightarrow 2)$ - α -L-Arap-28-O- α -L-Rhap $(1\rightarrow 4)$ - β -D- β -D-Glc $p(1\rightarrow 6)$ -Glcp-hederagenin, analogous to hederasaponin C from *H. helix* [4].

Orientaloside J was 3β -*O*- α -L-Rhap $(1\rightarrow 2)$ -[β -D-Glcp $(1\rightarrow 4)$]- α -L-Arap-28-*O*- α -L-Rhap $(1\rightarrow 4)$ - β -D-Glcp $(1\rightarrow 6)$ -D-Glcp $(1\rightarrow$

Orientaloside K was 3β -*O*- α -L-Rha $p(1\rightarrow 2)$ -[β -D-Glc $p(1\rightarrow 4)$]- α -L-Arap-28-*O*- α -L-Rha $p(1\rightarrow 4)$ - β -D-Glcp-($1\rightarrow 6$)- β -D-Glcp-hederagenin, analogous to hederacolchiside F from *H. colchica* [6].

The optimal conditions for separating individual components of *C. orientalis* roots were found by HPLC using a gradient mobile phase of CH₃CN:H₂O (10:90-60:40) over 60 min (Waters chromatograph, reversed-phase µbondapack C-18 column, 10 µm, 3.9 mm × 30 cm). Qualitative analysis of the compounds, monodesmosides and bidesmosides, was performed under isocratic conditions using H₂O:CH₃CN (68:32 and 50:50, respectively) with detection at 205 and 254 nm. The resulting chromatograms showed that *C. orientalis* roots contained up to 60 compounds, of which at least 12 were triterpene glycosides.

REFERENCES

- 1. R. Gagnidze, Vascular Plants of Georgia. A Nomenclatural Checklist, Tbilisi, "Universal", Tbilisi (2005).
- 2. V. N. Mel'nikov, Yu. B. Kal'yan, G. E. Dekanosidze, and V. Ya. Chirva Khim. Prir. Soedin., 256 (1974).
- 3. V. Ya. Chirva, P. K. Kintya, and V. N. Mel'nikov, Khim. Prir. Soedin., 472 (1972).
- 4. R. Tschesche, W. Smidt, and G. Wulff, Z. Naturforsch., 20, 708 (1965).
- 5. L. I. Strigina, V. V. Isakov, V. N. Elkin, A. K. Dzizenko, and G. V. Elyakov, *Phytochemistry*, 14, 1583 (1975).
- 6. G. E. Dekanosidze, O. D. Jikiya, M. M. Vugal'ter, and E. P. Kemertelidze, *Khim. Prir. Soedin.*, 747 (1984).

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