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SPECIALIA

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A novel xanthone as secondary metabolite from *Centaurium cachanlahuen*

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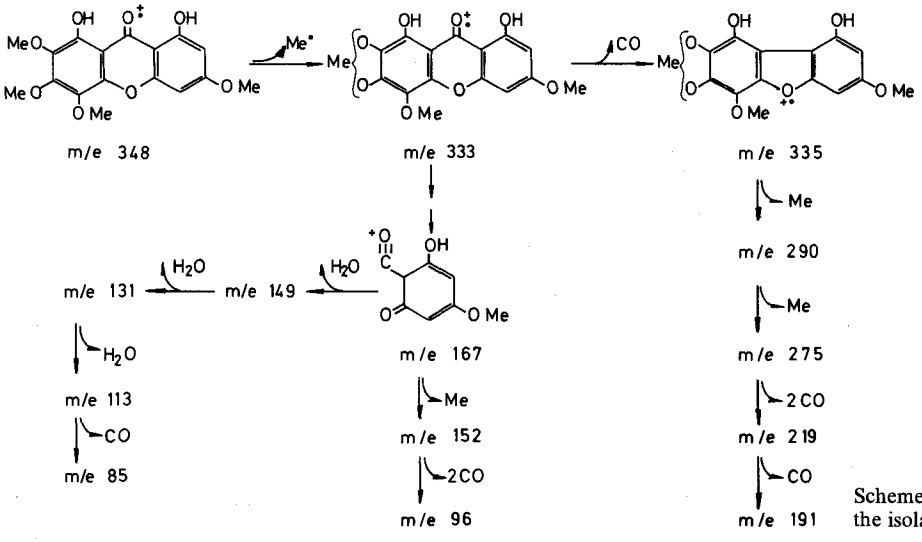
Summary. From the plant *Centaurium cachanlahuen*, swertiaperenine **1**, swercherine **2**, decusatine **4**, oleanolic acid **5** and the xanthone 1,8-dihydroxy-2,3,4,6-tetramethoxy-9H-xanthone **3** were isolated and characterized.

From our studies on *Centaurium cachanlahuen* (Mol) Robinson, a Chilean native species[2], we report the isolation of 3 known xanthones and a novel one, and also of the triterpen oleanolic acid.

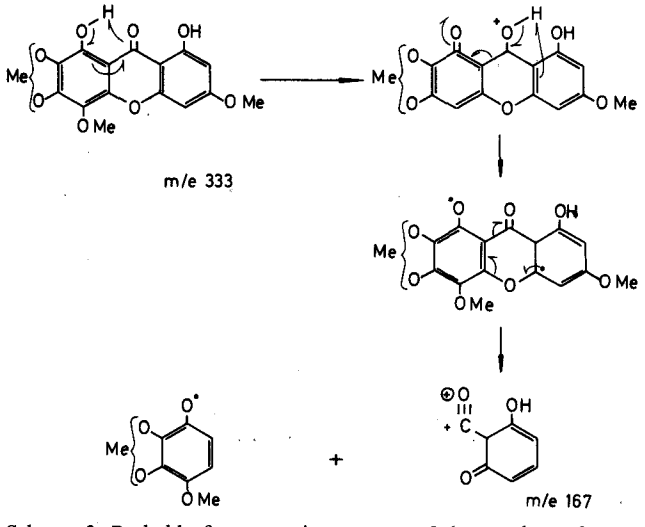
Dry tissues of the plant were extracted with cold methanol. The extract was concentrated under vacuum, then diluted with water, and was finally successively extracted with petroleum ether (60-80 °C), toluene, dichloromethane and ethylacetate.

Chromatography of the fraction soluble in dichloromethane on a column of silica gel 60 (Merck, 0.063-0.2 mesh) using petroleum ether as eluant and step-wise elution with increasing proportions of ethyl acetate afforded the following compounds: Swertiaperenine[3] (**1**), swercherine[4,5] (**2**) the xanthone **3**, decusatine[6] (**4**) and oleanolic acid[7] (**5**) (see fig. 1).

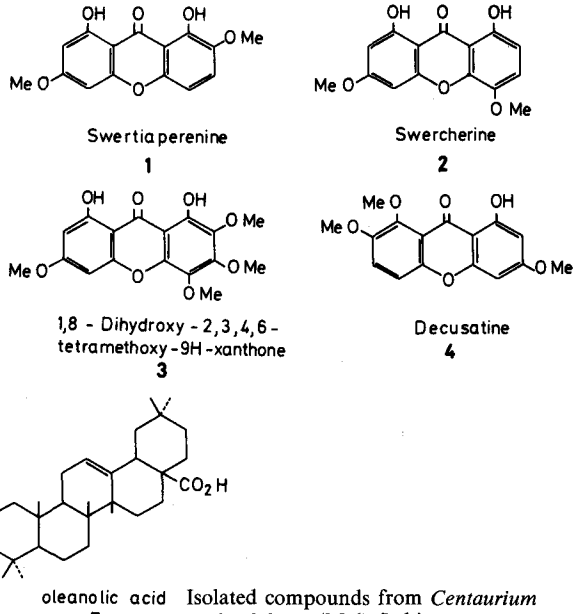
Elution with petroleum ether/ethylacetate = 95/5 gave a yellow crystalline compound of melting point 168-169 °C.



Scheme 1. Probable fragmentation pattern of the isolated xanthone systems.



Scheme 2. Probable fragmentation pattern of the xanthone fragment with m/e 333.



Isolated compounds from *Centaurium cachanlahuen* (Mol) Robinson.

The structure of 1,8-dihydroxy-2,3,4,6-tetramethoxy-9H-xanthone (**3**) is based on the following evidence: $C_{17}H_{16}O_8$ by M.A. UV (CH_3OH): 207, 260 and 334 nm. IR (KBr): 3400 (OH), 1615 (CO) cm^{-1}. ^{1}H-NMR ($CDCl_3$)δ: 11.27 (s, 1H, OH), 11.17 (s, 1H, OH), 6.47 (d, 1H, J=3 Hz), 6.31 (d, 1H, J=3 Hz), 4.12 (s, 3H, CH_3O), 3.93 (s, 6H, CH_3O and CH_3O), 3.88 (s, 3H, CH_3O). M.S.: (% relativity) 348 (M^+, 83.4), 334 (17), 333 (100), 305 (5), 275 (5), 219 (14), 191 (15), 174 (9), 167 (6), 149 (9), 144 (5), 135 (5), 131 (5), 113 (5), 97 (13), 95 (8), 85 (17), 83 (16) and 81 (8).

The ^{1}H-NMR signals show 2 acidic protons at 11.27 and 11.17 ppm which agrees with the presence of 2 hydroxyl groups chelated with the carbonyl function. That means that they should be at the positions 1 and 8 of the xanthone skeleton[4,5]. The doublets at 6.47 and 6.31 ppm with J=3.0 Hz indicate a meta relationship of these 2 protons. The 4 methoxy group with signals at 4.12, 3.93 and 3.88 ppm should be located at the 4 possible positions of the xanthone system.

The MS-spectrometry fragmentations could be explained according to the following pattern[8] (see schemes 1 and 2).

The 4 isolated xanthones show the same fragmentation pattern with a fragment m/e 167 probably derived from the part of the structure which is common for all of them. This fragment also gives other minor fragments with m/e, in agreement with a loss of water and methyl and carbonyl groups as indicated in schemes 1 and 2.

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