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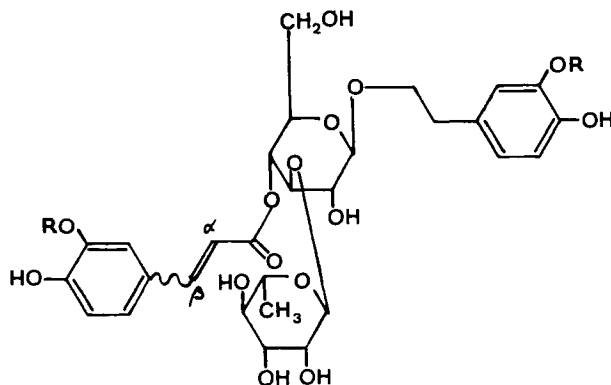
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PHENYLPROPANOID GLYCOSIDES IN *Buddleja Davidii*

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The occurrence of verbascoside (1), formerly known as orobanchin, in *Buddleja* (Buddlejaceae) has been noted for a long time (1). It was only fairly recently that its complete structure was determined (2). Related phenylpropanoids have been isolated from *Orobancha* (2) and *Cistanche* (3-5). One of these compounds, cistanoside D (2), has now been isolated as both the *E* and *Z* isomers from the stems of *Buddleja davidii* Franchet.



- 1 R=H  
2 R=CH<sub>3</sub>

## EXPERIMENTAL

EXTRACTION AND ISOLATION.—The collection and preliminary extraction of the plant material has been previously described (6). Tlc analysis of some fractions from the column chromatograph showed the presence of zones giving a bright blue fluorescence under uv 365 nm. These compounds were isolated by preparative tlc using silica gel, Et<sub>2</sub>O-EtOAc (1:1) to give *trans*-cistanoside D (110 mg Rf=0.60) and *cis*-cistanoside D (32 mg Rf=0.65).

The *trans*-cistanoside D was identified by comparison of spectral features (uv, ir, <sup>1</sup>H nmr, <sup>13</sup>C nmr) with those reported by Kobayashi *et al.* (4) and by comparison of the same spectral features and tlc behavior of its acetate with those of an authentic sample of cistanoside D heptaacetate kindly supplied by Professor Kobayashi, Central Research Laboratories, Yomeishu Seizo Co., Ltd., Japan.

The *cis*-compound gave identical spectral data apart from the signals in the <sup>1</sup>H-nmr spectrum for the protons attached to the α and β carbons of the ferulic acid residue. In the *trans*-isomer, these occur as doublets (*J*=16 Hz) at δ 7.67 and δ 6.37, respectively. In the *cis*-compound, the corresponding signals were at δ 6.89 and δ 5.81 which agrees well with the values calculated for a *cis*-configuration.

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TERPENIC AND AROMATIC COMPOUNDS FROM *SMYRNIUM GALATICUM*

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*Smyrnum galaticum* Czeccott (Umbelliferae) is cited in "Flora of Turkey" as a taxon closely related to *Smyrnum cordifolium* Boiss. and as a "species imperfectly known" (1). Thus, we included these two taxa in our chemical investigation of the genus *Smyrnum* (2-10) to determine whether they are chemically different.

Five of the compounds, smyrnicordiolid, 8-β-hydroxysmyrnicordiolid, 1-β-acetoxyeudesman-4(15),7(11)-dien-8,12-olide, 1-β-acetoxy-8-β-hydroxyeudesman-4(15),7(11)-dien-8,12-olide, and furodien (11), which were previously isolated from *S. cordifolium* (9), were also present in *S. galaticum*. Two compounds, 1-β,10-α, 4-α,5-β-diepoxy-8-β-hydroxyglechoma-8α,12-olide and glechomafuran, were not found in the latter species, while two aromatic compounds, 3-methoxy-4,5-methylenedioxypropionophenone (12) and the new natural aromatic, 5-methoxysafrole, were lacking in *S. cordifolium*. This finding suggests that *S. cordifolium* and *S. galaticum* should be considered as two different species.

The hrms of the new aromatic compound 5-methoxy-safrole indicated a molecular formula of C<sub>11</sub>H<sub>12</sub>O<sub>3</sub>. The ir spectrum showed the presence of aromatic bands at 1610, 1515, 1500 cm<sup>-1</sup>, unsaturation at 1630 cm<sup>-1</sup> and no hydroxyl and carbonyl peaks. The structure of the compound was established by its <sup>1</sup>H-nmr spectrum. A signal at δ 5.92 (2H, s) revealed the methylenedioxy group, a methoxyl peak was at δ 3.9 (3H, s), the propylene group protons were at δ 3.3 (2H, br d, *J*=8 Hz, CH<sub>2</sub>-), δ 5.91 (1H, ddr, *J*=17, 10 and 8 Hz, -CH-) δ 5.08 (1H, br d, *J*=10 Hz) and δ 5.05 (1H, br d, *J*=17 Hz, -CH-CH<sub>2</sub>), while two aromatic protons were at δ 6.35 (1H, br s) and δ 6.39 (1H, br s) indicating their positions *meta* to one other. The identification of the known compounds was established by spectral data (uv, ir, <sup>1</sup>H nmr, and ms) and by direct comparison (tlc) with authentic samples.

## EXPERIMENTAL

PLANT MATERIAL.—*S. galaticum* was collected from central Turkey (Çankiri-Şabanözü) in June 1981, by Dr. M. Coşkun (Ankara). A voucher specimen is deposited in the Herbarium of the Faculty of Pharmacy, University of Ankara, AEF 10170.