STRUCTURE OF DIVERSOLIDE

S. V. Serkerov and V. V. Kiseleva

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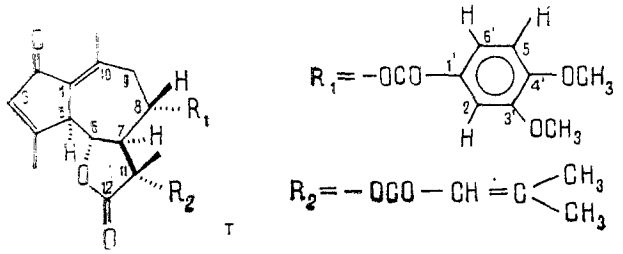
The structure of 11-angeloyloxy-6-(3',4'-dimethoxybenzoyloxy)-2-oxoguai-3,10-dien-7,8-olide has previously [1] been put forward on the basis of chemical and spectral characteristics for diversolide ($C_{29}H_{32}O_9$, mp 185–186°C), which was isolated from the resin of the roots of *Ferula diversivittata* Rgl. et Schmalh.

It was likewise established by saponification with a 5% aqueous solution of caustic soda that diversolide contains in its molecule two ester groups consisting of 3,4-dimethoxybenzoic and angelic acid residues.

However, the proposed structure is not in harmony with the NMR spectrum. This spectrum lacks the multiplet signal of the olefinic proton of angelic acid. This multiplet usually appears in the 6.0–6.5 ppm region and, as in the spectra of badkhyzin [2], olgoferin [3], olgin [3], and talassins A and B [4], is superposed on the signal of the olefinic proton of the five-membered ring (H-3).



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A one-proton singlet at 6.18 ppm found in the spectrum belongs to the olefinic proton at C-3. The singlet of an olefinic proton of an aliphatic acid residue is superposed on the multiplet of a proton geminal to an ester group and can be seen at 5.67 ppm. The singlet nature of the signal of the olefinic proton, together with the singlet signals of vinylmethyl groups at 1.92 and 2.12 ppm (3 H each) indicate that one of the acyls of the diversolide molecule is the residue of 2,2-dimethylacrylic acid, i.e., senecioic acid. The second acyl in diversolide is a 3,4-dimethoxybenzoic acid residue. This is shown by, on the one hand, the formation on the saponification of diversolide of 3,4-dimethoxybenzoic acid and, on the other hand, by the presence in the NMR spectrum of two singlet signals of methoxy groups (at 3.92 and 3.88 ppm, 3 H each), and signals belonging to the protons of a 1,3,4-substituted benzene ring: a quartet at 7.67 ppm, J_1 = 2.5, J_2 = 8.5 Hz, H-6') and doublets at 7.52 ppm (J = 2.5 Hz, H-2') and 6.85 ppm (J = 8.5, H-5').

The position assigned to the lactone ring likewise does not agree with the nature of the splitting of the signal of the lactone proton. The latter appears in the spectrum in the form of a quartet at 4.72 ppm (J_1 = 10, J_2 = 11 Hz), which shows interaction with only two vicinal protons and not with three protons. Consequently, the lactone ring is located at C_6–C_7 of a guaiane carbon skeleton.

So far as concerns the position of the ester groups in diversolide, it was shown [1] that one of them, namely the aliphatic acid residue, is located at C-11. The establishment of the position of the lactone ring at C_6–C_7, and also the multiplicity of the signal of the proton of the hemi-ester group showing interaction with a minimum of at least three vicinal protons, permits the 3,4-dimethoxybenzoic acid residue to be located in the C-8 position.

Thus, diversolide corresponds to the structure of 8-(3,4-dimethoxybenzoyloxy)-2-oxo-11-senecioyloxyguai-3,10-dien-6,7-olide (I).

V. L. Komarov Institute of Botany, Academy of Sciences of the Azerbaidzhan SSR, Baku.
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More recently, V. Yu. Bagirov et al. [5] have isolated from the resin of the roots of *Ferula malacophylla* new sesquiterpene lactones which they called malaphyll and malaphyllin. The corrected structure of diversolide and the structure of malaphyll are identical. The NMR spectra of these compounds coincide in detail. Their IR and UV spectra [1, 5] are also identical. However, the melting point of diversolide (185–186°C) is lower than that of malaphyll (204–205°C) by 19°C. A check on the individuality of diversolide on Silufol UV-254 plates in the system used by Bagirov et al. [5] showed a single spot. Chromatography in the hexane–benzene–methanol (5:4:1) system permitted the presence of talassin A as an impurity to be detected (the R_f values of diversolide and of the talassin were 0.22 and 0.166, respectively. A 1% solution of $KMnO_4$ was used as the revealing agent). After purification by preparative separation on Silufol UV-254 plates and recrystallization from ethanol, diversolide had mp 201-203°C.

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TRITERPENE GLYCOSIDES OF *Androsace septentrionalis*. STRUCTURE OF ANDROSEPTOSIDES A, B, C, AND D

P. K. Kintya and N. M. Pirozhkova

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In a preceding communication [1] we gave the results of a preliminary study of the glycosides from *Androsace septentrionalis* L. (northern rock jasmine). We have established that the plant contains glycosides of oleanolic acid and of primulagenin A. On isolation of the main individual glycosides by column chromatography on silica gel, we obtained a fraction containing the six least polar glycosides. By repeated column chromatography in the chloroform–methanol–water (65:35:10) and chloroform–methanol (8:2) systems we obtained individual glycosides, which were called androseptosides A (I), B (II), C (III), and D (IV); (I) – mp 165–167°C, $[\alpha]_D^{20}$ –20°(c 1.0; CH_3OH); (II) – mp 221–223°C, $[\alpha]_D^{20}$ –80° (c 1.0; CH_3OH); (III) – mp 175–176°, $[\alpha]_D^{20}$–10.5° (c 1.5; CH_3OH); (IV) – mp 258–261°C, $[\alpha]_D^{20}$–120°, (c 1.0; CH_3OH).

When androseptosides A and B were subjected to complete acid hydrolysis with 2.5% sulfuric acid, glucose was identified in the neutralized hydrolysate by paper chromatography in the butanol–benzene–pyridine–water (5:1:3:3) system, while glucose and arabinose were detected in the hydrolysates of the glycosides C and D, their ratio, according to the gas-liquid chromatography of the acetates of the corresponding aldononitriles, being 1:1.

From its physicochemical constants, the aglycone of compounds (I) and (III) was identified as oleanolic acid (mp 305–307°C, $[\alpha]_D^{20}$ + 80° (c 1.0; CH_3OH)), and for compounds (II) and (IV) the algycone was found to be primulagenin A (mp 248-250°C, $[\alpha]_D^{20}$ +55°) (c 1.0; $CHCl_3$). The IR spectra of standard samples and of the genins obtained coincided completely.

Department of Plant Genetics, Academy of Sciences of the Moldavian SSR, Kishinev. Scientific-Research Institute of Biology and Biophysics, Tomsk State University.

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