RUPICOLIN B-OXIDE AND ISOCHRYSARTEMIN — NEW GUAIANOLIDES FROM *Ajania fastigiata*

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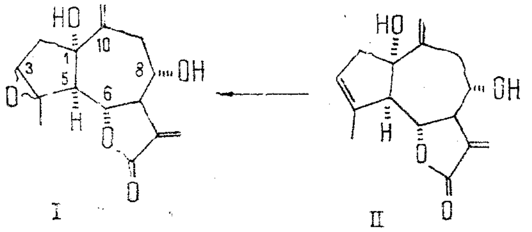
Continuing an investigation of the sesquiterpene lactones of *Ajania fastigiata* [1], we chromatographed benzene extract on a column of type KSK silica gel. Two lactones — (I) and (II) — were isolated from the fractions eluted with chloroform–methyl ethyl ketone (21:1). Lactone (I) had the composition $C_{15}H_{18}O_5$, mp 191-192°C (benzene–acetone), $[\alpha]_D^{20}$ +149° (c 2.54; chloroform), M^+ 278; and (III) had the composition $C_{15}H_{18}O_5$, mp 237-238°C (previously heated metal block), $[\alpha]_D^{20}$ + 44° (c 2.14; chloroform), M^+ 278; we have called them, respectively, rupicolin B-oxide and isochrysartemin B.

IR spectrum of (I) (cm^{-1}): 1750 (C=O of a γ-lactone conjugated with an exocyclic CH_2 group); 1665 (C=C bond); 3490-3520 (OH group). The PMR spectrum of (I) (pyridine-$^2H_5$; 0 — HMDS) had the following signals (ppm): singlet with an intensity of 3 H at 1.51 (CH_3—C—O); doublet (1 H) at 2.43 (—C_5H with $^3J_{5,6}$ = 10 Hz; broadened singlet (1 H) at 3.38 (O—C—H) with $W_{1/2}$ = 3.7 Hz, which shows the position of this proton in a five-membered ring. Signals with intensities of 1 H each from C_6H (quartet with $^3J_{5,6}$ = 10.5 and $^3J_{6,7}$ = 9.0 Hz) and C_8H overlap one another and are located at 3.98 ppm. One of the two exomethylene groups of the molecule of (I) is present in the main skeleton — doublets at 5.13 and 5.94 ppm with ^2J = 2.5 Hz — and the other is in the lactone ring — quartet signals at 6.20 and 6.1 ppm. A singlet signal at 5.18 ppm and a doublet with ^3J = 6 Hz at 6.63 ppm indicates the presence of tertiary and secondary OH groups in the (I) molecule.

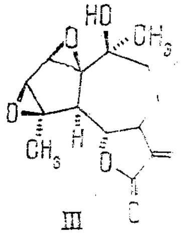
With the given composition, the presence of the functional groups mentioned and of two double bonds, compound (I) can have only a guaiane skeleton. The quartet nature of the splitting of the signal of the lactone proton and the SSCC show that the lactone ring is located at C_6–C_7 and is trans-linked with the guaiane nucleus. The values of the chemical shifts of the protons of the exomethylene group attached to the lactone ring are characteristic for lactones containing a hydroxy group in the β position to the exomethylene group [2]. The tertiary OH group may be present at C_1.

From the results of a comparative study of the PMR spectra of the lactones rupicolin B [2], and rupin A [3], and arteglasin B [4], we came to the conclusion that rupicolin B oxide has the structure (I). To confirm this, (II) was oxidized with perphthalic acid and a product was obtained which was identical with (I). Thus, rupicolin B oxide has the structure of 1α,8α-dihydroxy-5,7α(H)-6,8β(H)-3,4-guaia-10(14),11(13)-dien-6,12-olide.



I

II



III

IR spectrum of the lactone (III) (cm^{-1}): 1750 (C=O of a γ-lactone conjugated with an exomethylene CH_2 group); 1670 (C=C bond); 3450 (OH group).

The PMR spectrum of the lactone (III) (pyridine-$^2H_5$; 0 — HMDS) is characterized by the following signals: singlets with an intensity of 3 H each at 1.43 and 1.46 ppm (2 CH_3—C—O); doublet (1 H) at 2.42 ppm with ^3J = 10 Hz (C_5H); broadened singlets (1 H each) at 3.22 and 3.67 ppm (protons at epoxy groups); triplet with ^3J of 10 Hz at 4.28 ppm (C_6H); doublets (1 H

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each) at 5.19 and 6.01 ppm with ^4J = 2.8 and 3.2 Hz (the protons of a CH_2 group attached to a lactone ring); broadened singlet at 5.15 ppm (tertiary OH group). The PMR spectrum of (III was identical (except for the chemical shifts of the C_5H and C_7H protons and those of one of the methyls) with the spectrum of the known lactone chrysartemin B (IV), which shows their identical skeletal structure, while the similar chemical shifts of C_6H in (III) and (IV) (4.2 and 4.22 ppm, respectively) shows the identical mutual orientations of the epoxy-ring and lactone protons in the molecules of these two lactones. The difference in the chemical shifts of the protons mentioned above is, as follows from a comparative analysis of spectral characteristics and a consideration of molecular models, due to the β-orientation of the OH group in the molecule of lactone (III).

Thus, lactone (III) which we have called isochrysartemin B differs from (IV) [5] only by the orientation of the substituents (β-OH, α-CH_3) at C_{10}.

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GRILACTONE FROM *Ferula penninervis*

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Seeds of *Ferula penninervis* Rgl. et Schmalh. [∿ feather-veined giant fennel], family *Apiaceae*, collected in July in the Kamchik Pass in the state of early ripeness have been studied. The raw material was extracted with chloroform by the steeping method at room temperature. The concentrated extract was dissolved in ethanol and the solution was diluted with an equal amount of water. The aqueous ethanolic extracts, after separation of the precipitate, was shaken with chloroform. The concentrated chloroform extracts were deposited on a column containing silica gel. To free the substances from essential oils, the column was first eluted with petroleum ether and then with mixtures of hexane and ethyl acetate (9:1 and gradually increasing concentrations of the ethyl acetate). In this way, substance (I) was isolated with the composition $C_{15}H_{20}O_2$, mp 77°C, M^+ 232. The PMR spectrum showed a strong band at 1775 cm^{-1} (triplets with KBr), indicating the presence of a γ-lactone carbonyl.

The solubility of (I) in dilute solutions of alkalis also showed the presence of a γ-lactone ring. The PMR spectrum of (I) ($CDCl_3$) showed the following signals (ppm); 1.14 (3 H, d, J = 2 Hz, CH_3 group at a double bond); 4.3 (1 H, q, J_1 = 6, J_2 = 10 Hz, lactone proton); 4.75 (2 H, br.s, methylene group); 5.45 ppm (1 H, br.s, proton in the α position to a methylene group).

The dehydrogenation of the hydrogenated compound (I) in the presence of selenium readily formed chamazulene.

From its properties and IR and NMR spectra, (I) was identified as grilactone, which has not previously been isolated from species of *Ferula* [1].

Substance (II) has the composition $C_{19}H_{22}O_3$, mp 67-68°C, M^+ 298.

Its IR spectrum had characteristic absorption band of a carbonyl group is an α-pyrone ring (1740 cm^{-1}) and of an aromatic nucleus (1450, 1520, 1620 cm^{-1}).

The PMR spectrum of (II) ($CDCl_3$) had the following resonance signals: 1.53 (3 H, s): 1.60 (3 H, s); 1.69 (3 H, s); 2.01 (4 H, br.s); 4.51 (1 H, d, J = 6.5 Hz); 4.98 (1 H, m);

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