

THE STRUCTURE OF AN ESTER FROM THE FRUIT OF
Ferula oopoda

S. V. Serkerov

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We have previously [1] reported a new sesquiterpene lactone, semopodin, from the fruit of *Ferula oopoda* (Boiss. et Buhse) Boiss. In the present paper we give the results of a chemical study of the liquid substance (I), $C_{21}H_{26}O_7$, isolated from this plant material. The IR spectrum of (I) (Fig. 1) shows absorption bands at 1710 and 1230 cm^{-1} of an α,β -unsaturated ester and at 1635 , 1610 , and 1515 cm^{-1} of a benzene ring. The presence and nature of the ester group were determined by the saponification of the substance under investigation by alkalis. This gave an aromatic alcohol (II), $C_{11}H_{14}O_5$, and tiglic acid, which was identified by means of its IR spectrum [2]. The IR spectrum of (II) contained absorption bands at 3350 cm^{-1} (OH group) and 1630 , 1610 , and 1510 cm^{-1} (aromatic system). The acetylation of (II) formed an acetyl derivative (III), $C_{15}H_{18}O_7$, the IR spectrum of which lacked the band of an OH group. Maxima at 1740 and 1240 cm^{-1} were due to the CO group of an ester. The peaks of the aromatic ring remained unchanged (1635 , 1610 , 1510 cm^{-1}).

Important information on the structure of the substance was obtained by the interpretation of NMR spectra. The NMR spectrum of (I) (Fig. 2a) has the doublet of a methyl group at 1.18 ppm ($J = 6\text{ Hz}$, $3H$, $CH_3-CH<$). Vinyl methyls of an ester group are found in the 1.90 ppm region. A well-defined singlet at 3.92 ppm ($3H$) is due to a methoxy group in an aromatic ring. A multiplet signal with its center at 5.42 ppm ($1H$) and a doublet at 5.87 ppm ($J = 7\text{ Hz}$, $1H$) apparently relate to the protons of ester groups. The olefinic proton of the tiglic acid appears in the form of a multiplet at 6.15 ppm . The areas of the signal of this proton and of protons of the vinyl methyl groups of the side chain shows that the substance under investigation probably contains two ester groups. The correctness of the hypothesis put forward is confirmed by the NMR spectra of (II) and (III). In the NMR spectrum of (II) (see Fig. 2b) the signals of the protons of the ester groups are shifted upfield and are in the $3.5-4.3\text{ ppm}$ region (Table 1). The maxima due to the vinyl methyl groups and that of the olefinic proton of the ester group are absent from the spectrum of (II).

As mentioned above, the saponification of (I) leads to substance (II) and tiglic acid. However, the chemical shift (CS) of the olefinic proton of the ester group of substance (I) (6.15 ppm) gives grounds for

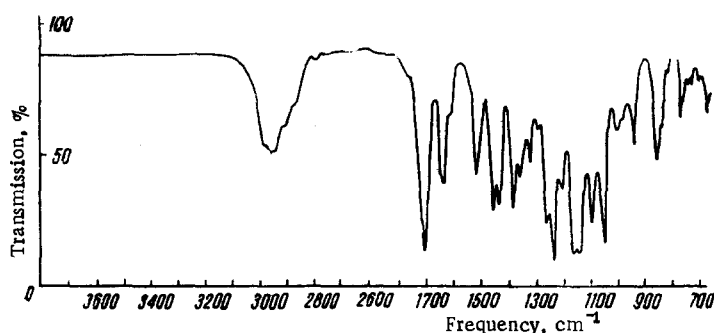


Fig. 1. IR spectrum of the aromatic ester.

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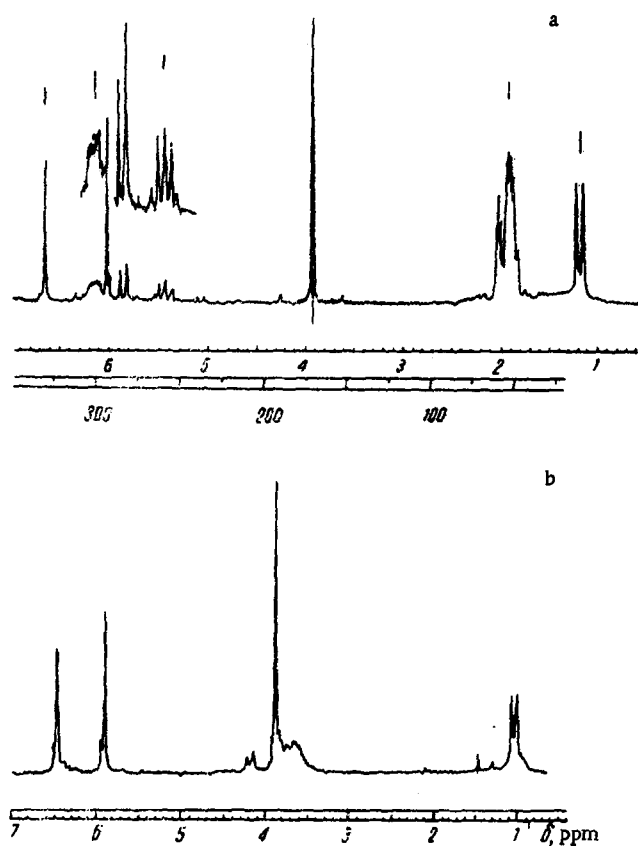


Fig. 2. NMR spectra of the aromatic ester (a) and the saponified product (b).

TABLE 1

Compound	$\text{CH}_3-\text{CH} \diagdown$	$\text{CH}_2-\text{CH}=\text{CH}_2$	$\text{CH}_2\text{O}-\text{Ar}$	H at an ester group	H at an OH group	$-\text{CH}=\text{CH}_2$ at an ester group	$-\text{OCH}_2\text{O}-$	Protons of a benzene ring	H of an aldehyde group
I	1,18 d ($J=6\text{Hz}$)	1,90 (12 H)	3,92 s (3 H)	5,42 m 5,87 d ($J=7\text{Hz}$)	—	6,15 (2 H)	6,02 s (2 H)	6,65 s (2 H)	—
II	1,01 d ($J=6\text{Hz}$)	—	3,86 s (3 H)	—	3,70 m 4,17 d ($J=7\text{Hz}$)	—	5,90 s (2 H)	6,46 s (2 H)	—
III	1,12 d ($J=6\text{Hz}$)	2,07 s (3 H) 2,10 s (3 H)	3,91 s (3 H)	5,28 m 5,72 d ($J=7\text{Hz}$)	—	—	6,03 s (2 H)	6,64 d (2 H) ($J=1,5\text{Hz}$)	—
IV	—	—	3,92 (3 H)	—	—	—	6,03 (2 H)	6,96 d (1 H) ($J=1,5\text{Hz}$) 7,04 d (1 H) ($J=1,5\text{Hz}$)	9,69 s (1 H)

Note. s - singlet; d - doublet; m - multiplet.

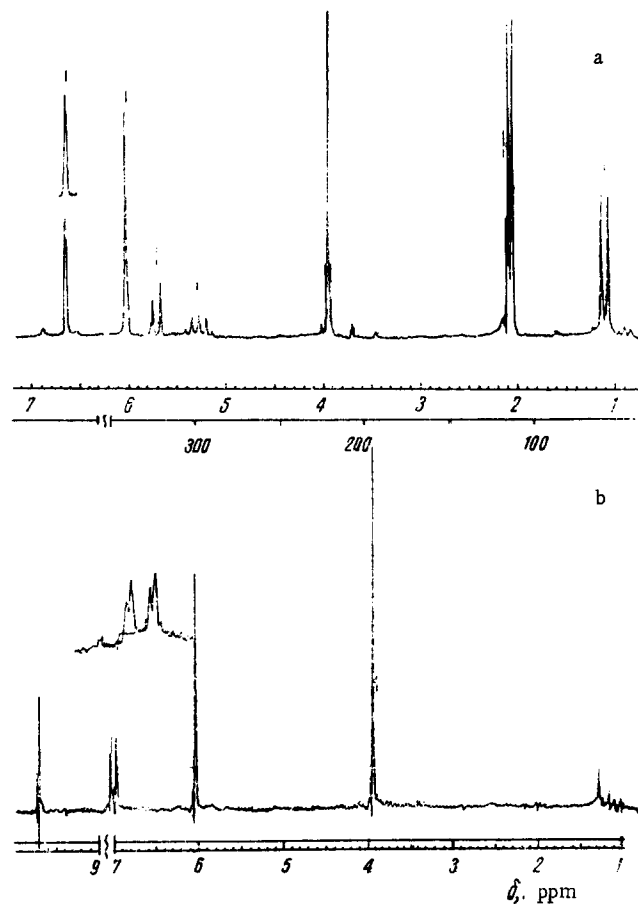



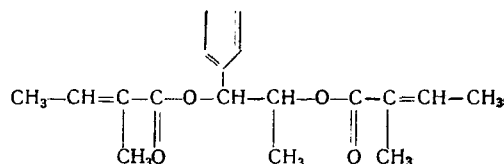
Fig. 3. NMR spectrum of the diacetate of (II) (a) and of oxidized (II) (b).

TABLE 2

Compound	Frequency, cm^{-1}				
	ester CO	bands of an aromatic ring	<chem>H2C</chem>  and <chem>OCH3</chem> arom.	OH	CO of an aldehyde group
I	{ 1710 1230	1635, 1610 1510	1450, 1430, 1135 1090, 1045, 935	—	—
II	{ — —	1630, 1600 1510	1450, 1430, 1200 1230, 1130, 1100 1040, 925	3340	—
III	{ 1740 1250	1635, 1610 1510	1450, 1430, 1135 1100, 1050, 935	—	—
IV	{ — —	1630, 1600 1515	1460, 1440, 1240 1210, 1140, 1100 1055, 925	—	1690

concluding that it is the angelate of (II) [3].

The NMR spectrum of (II) (Fig. 3a) shows two three-proton singlets at 2.07 and 2.10 ppm corresponding to the CH_3 groups of acetyl radicals. The signals due to the protons at the acetyl groups are present in the weak field at 5.28 (1H) and 5.72 ppm (1H), the nature of their splitting being the same as in (I). The NMR spectra of all the compounds mentioned above lack any signal that could be ascribed to an additional methine proton. At the same time, the spectra of these substances show that they contain a secondary methyl group ($\text{CH}_3\text{-CH<}$). This circumstance, and also the multiplicity of the signal at 5.42 ppm, shows the presence in these compounds of the structural fragment A:



The oxidation of (II) with chromium trioxide in acetone solution led to the precipitation of a crystalline derivative (IV) with the composition $\text{C}_9\text{H}_8\text{O}_4$, mp 128–129°C (from petroleum ether). The IR spectrum of (IV) exhibited absorption bands with maxima at 1690 cm^{-1} (carbonyl group) and at 1630, 1600, and 1515 cm^{-1} (aromatic ring).

The band at 1600 cm^{-1} in the IR spectrum of (IV) is more intense than the corresponding bands in the IR spectra of (I), (II), and (III). Consequently, the carbonyl group formed is conjugated with the aromatic ring.

The IR spectra of (I)–(IV) permit the assumption that the substance contains a benzene ring. This assumption is confirmed by the NMR spectra of both (I) and its derivatives. The chemical shift of the three-proton singlet of the methoxy group in the spectra (see Table 1) shows that it is attached to the aromatic ring. Information obtained by the partial interpretation of the NMR spectra shows the presence in the benzene ring of two substituting groups (OCH_3 and a side chain). The CS at 6.02 ppm is similar to the CS of the signal of the methylenedioxy group found in the spectra of the alkaloids unguiminorine [4], ungerine [5], thalflavine [6], corydaine [7], delavaine [8], and others [9].

A singlet at 6.65 ppm in the NMR spectrum of (I) is probably the result of the superposition of the signals of two protons of the benzene ring.

The IR spectra of (I–IV) (Table 2) also give grounds for assuming that the molecule of the compound under investigation contains a methylenedioxy group [10].

The NMR spectrum of the oxidized product (see Fig. 3b) lacks the doublet of the secondary methyl group. Furthermore, in contrast to the spectra a, b, and c, this spectrum shows a one-proton singlet at 9.69 ppm, indicating the presence of an aldehyde group in the substance. This fact once again shows that the molecule of the compound under investigation (I) contains the structural fragment A. The spectrum also contains the signals of a methoxy group (singlet at 3.92 ppm, 3H) and of a methylenedioxy group (singlet at 6.03 ppm, 2H).

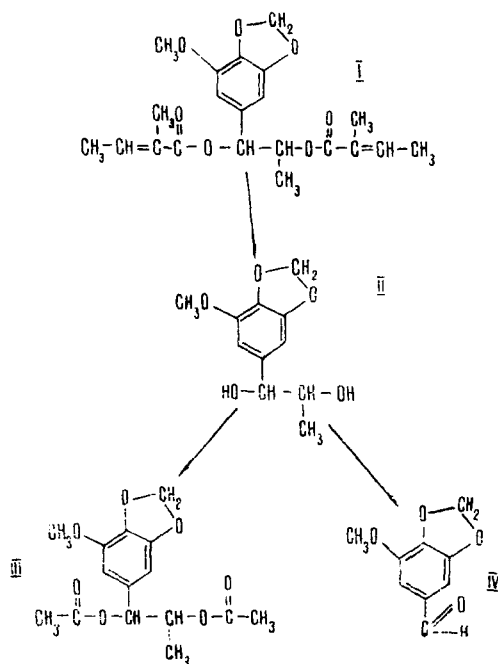
One-proton doublets at 6.96 ppm ($J = 1.5\text{ Hz}$) and 7.04 ppm ($J = 1.5\text{ Hz}$) belong to two protons of a benzene ring. While in the spectra of (I–III) these protons appear in the form of a superposed signal, in the spectrum of (IV) they are shown in the form of two doublets, both being shifted relatively downfield. This is probably due to the fact that there is an aldehyde group adjacent to these protons.

The results of a comparison of the physicochemical properties (the results that we have obtained of IR and NMR spectroscopy, composition, etc.) of the oxidized product with those of myristicaldehyde [11] showed that they are identical.

On the basis of the facts presented, it may be concluded that the compound under consideration has the structure (I) (see reaction scheme).

EXPERIMENTAL

Isolation of the Aromatic Ester (I). The extraction of the fruit and the chromatography of the resin so obtained were performed as described previously [1]. The fractions preceding the semopodin were



combined and rechromatographed. This gave a liquid substance, $\text{C}_{21}\text{H}_{26}\text{O}_7$, with $[\alpha]_D^{20}$ 1.52.

Saponification of I. A solution of 0.2 g of the substance in 10 ml of ethanol was treated with 10 ml of 5% aqueous KOH solution. The mixture was boiled on the water bath for 1 h. Then it was cooled and acidified with dilute sulfuric acid. It was extracted with diethyl ether, and the ethereal extract was shaken with a 0.5% solution of Na_2CO_3 . The organic layer was separated off, washed with water, and dried over Na_2SO_4 . After filtration, the solvent was distilled off. The residue consisted of a viscous oil (II), $\text{C}_{11}\text{H}_{14}\text{O}_5$. The sodium carbonate solution was acidified and treated by the method described above. This gave a sublimable acid, identified by its IR spectrum as tiglic acid.

Acetylation of (II). A solution of 0.1 g of the substance in 3 ml of acetic acid was treated with 0.15 g of freshly fused CH_3COONa . The mixture was boiled on the sand bath for 45 min, and then 40 ml of cooled water was added. The mixture was extracted twice with chloroform and the combined extracts were washed four times with water and dried. The usual working-up procedure yielded the diacetate of the saponified product (III), $\text{C}_{15}\text{H}_{18}\text{O}_7$. Chromatography in a thin layer of alumina (activity grade III-IV, solvent petroleum ether-diethyl ether (1 : 1)) gave a single spot with R_f 0.66.

Oxidation of (II). A solution of 0.1 g of (II) in 5 ml of acetone was treated with a solution of 0.15 g of CrO_3 in aqueous acetone. The mixture was left for 30 min. Then it was diluted with water and was twice extracted with diethyl ether. The ethereal extracts were combined, washed with water three times, and dried over Na_2SO_4 . After filtration, the ether was distilled off. The residue consisted of a crystalline substance (IV), which, after recrystallization from petroleum ether, had mp 128-129°C.

Found %: C 60.15; 60.24; H 4.67; 4.59. $\text{C}_9\text{H}_8\text{O}_4$. Calculated %: C 60.00; H 4.44.

The IR spectra of (I-III) were taken on a UR-20 spectrometer in the form of thin films and that of (IV) in paraffin oil; the NMR spectra of (I) and (III) were taken on a JNM-4H-100/100 MHz instrument and those of (II) and (IV) on a Varian HA-100D spectrometer - (I-III) in CDCl_3 solution and (IV) in a mixture of CCl_4 and deuterated pyridine. Tetramethylsilane was used as internal standard. The δ values are given on the δ scale. The elementary composition of (I-III) were calculated from the composition of (IV).

SUMMARY

The fruit of *Ferula oopoda* (Boiss. et Buhse) Boiss. has yielded a new aromatic ester with the structure (I).

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