

ISOMERS OF PALMITOLEIC ACID IN LIPIDS AND VOLATILE SUBSTANCES FROM THE FRUITS OF *Ziziphus jujuba*

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Fatty acid from the dried pulp of Ziziphus jujuba Mill. Contain 33 components with a chain length from 7 to 28 carbon atoms and approximately equal ratio of total saturated and unsaturated, mainly monoenic, acids; among them, the isomers of palmitoleic acid 16:1(7) and 16:1(9) predominate, and sixteen fatty acids of the mixture, including 12:0, 16:0, 14:1(9).

Ziziphus jujuba Mill. (*Z. Vulgaris* Lam., jujube, unabi, Chinese data) is a wood plant belonging to the family Rhamnaceae. In the wild, the plant is widespread in the Caucasus and in Central Asia. It is cultivated in Uzbekistan as a fruit culture [1]. The fruits are valued for their nourishing, dietetic, and medical properties. They are used in stomach diseases and for metabolic regulation in Tibetan medicine; it is used for the treatment of cardiovascular and neurological diseases, chronic infection, and tuberculosis of various organs in China; it is used as a sedative and lactogenic remedy in Korean and Arabian medicine, respectively. Decoctions, infusions and the dried fruit are used as expectorant, antispasmodic, and antisclerotic remedies in Central Asia. The preparation "Unabin" was offered as a diuretic [1, 2].

From the air-dried pulp of *Z. jujuba* fruits (ta-yan-tsao sort of Uzbek origin), 0.25% of hexane-extracted lipids and 13 fatty acids (FA) have been isolated. Half of the FA mass consisted of fatty acid 16:1 with the C=C position unestablished. Eleven FA were found in the seeds of the fruits; 18:1 predominated [3]. The isomer of fatty acid 16:1 (7) is present as a minor constituent in the seeds of *Z. jujuba* from the Chinese province Hunan, while the major component is an acid 20:1 (11) [4].

The pulp of the dried fruits has a weak pleasant fragrance. From volatile substances of fruits of Chinese origin, isolated from the steam distillate with dichloromethane extraction, 78 components were identified; the aliphatic acids (more than 60% of the aliphatic acid mass) were 3:0-16:0, 12:1 (2), 14:1, and 16:1, mainly FA 10:0 and 12:0 [5].

We studied the FA from the air-dried pulp of the large-fruit of ta-yan-tsao sort, cultivated in Tashkent.

Hexane-extracted lipids were isolated from the ground pulp (moisture 9.4%) with 0.5% yield. The FA were obtained after alkaline hydrolysis of the extractives and separation of the unsaponifiable part. Then the FA were converted to their methyl esters (ME) and were analyzed by UV, IR, MS, and GLC using polar and middle polar phases.

The UV spectrum of the ME in the 234-nm field was transparent, indicating the absence of FA with a conjugated system of ethylenic bonds. The absorption band of the trans-olefins at 960-970 cm^{-1} was not observed in the IR spectrum of the ME. The mass spectrum showed ME with a carbon chain length from 14 to 28 atoms. The results of MS and GLC analyses are given in Table 1.

The monoenic fraction was isolated from the total FA ME by Ag^+ -TLC in system I in order to determine the olefinic bond position in the FA chain. It had the following composition (% GLC on the DB-1): 10:1(?) - 3.3; 14:1 - 10.8; 16:1(9) - 31.9; 16:1(7) - 39.4; 18:1 - 14.6.

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TABLE 1. Fatty Acid Composition of Lipids and Volatile Substances from the Dried Fruits Pulp of *Ziziphus jujuba* (% GLC, GLC-MS)

Fatty acid	Neutral lipids, %	Volatile substances		Fatty acid	Neutral lipids, %
		ME I, %	FA II, %		
7:0	0.2	0.3	-	X	3.1
9:0	0.2	0.4	-	19:0	1.7
10:1	0.7	1.4	-	20:0	8.2
10:0	0.3	5.2	0.95	20:0*	Traces
11:0	Traces	0.4	-	21:0	1.8
12:0	0.2	10.0	6.69	22:0	5.3
13:0	Traces	0.8	-	22:1*	Traces
14:1(9)	3.1	13.4	20.97	23:0	1.2
14:0	0.4	9.8	3.72	24:0	5.8
15:0	0.4	0.6	-	24:1*	Traces
16:1(9)	11.7	15.6	24.56	25:0	1.0
16:1(7)	15.9	16.8	33.55	26:0	2.6
16:0	12.4	16.7	9.07	26:1*	Traces
17:0	0.7	-	-	27:0*	Traces
18:3	7.4	-	-	28:0*	Traces
18:2	7.8	3.8	-		
18:1(9)	4.4	3.3			
18:0	3.5	1.5			
$\Sigma_{\text{unsat.}}$		54.3	79.08		50.3
$\Sigma_{\text{sat.}}$		45.7	20.43		45.9

*Mass spectrum data alone.

Monoenes were destructively oxidized by Rudlov's reagent ($\text{IO}_4^-/\text{MnO}_4^-$) [6] and ME of carboxylic acids and diME of dicarboxylic ones were obtained with following composition (%GLC): pentanoic acid - 5.2; heptanoic acid - 7.7; nonanoic acid - 14.9; pimelinic acid - 26.3; azelainic acid - 45.9.

According to these data the isomers of palmitoleic acid have the olefinic bond position at C-7 (nonanoic and pimelinic acids) and C-9 (heptanoic and azelainic acids). The pentanoic acid (5:0) shows the most probable structure for tetradecenoic acid as 14:1(9) and nonanoic and azelainic acids are fragments of 18:1(9) acid.

The volatile substances (VS) (0.69%) were isolated from the pulp by hydrodistillation as ointment-like compounds, easily melting upon low heating. The VS were analyzed without additional treatment by GLC/MS using a polar phase (sample FA-II) and after diazomethane treatment by GLC using a middle polar phase (ME I). The VS corresponded to free FA on TLC in system 2.

Sixteen FA were identified in the ME I sample with the same total content of saturated and unsaturated components in the hexane extract (see Table 1), but one-third of the ME I mass consisted of 16:1 isomers, and those of 14:1(9) amounted to more than 10% of the mass.

Fatty acid 16:1(9) in amounts of 15-64% was found in seed triacylglycerols of the Cupressaceae, Connaraceae, Ochnaceae, Scrophulariaceae [7], and Elaeagnaceae [8] species. The same FA with unestablished C=C position is present in the free state as well as its ME and ethyl esters (EE) in pheromones from male mandibular glands of the wasps Hymenoptera (Sphecidae, *Philanthus*) [9]. The isomer 14:1-ME 14:1(11) is considered to be a biosynthetic semiproduct of the sexual pheromone of the redbanded leafroller moth [10].

It should be noted that *Z. jujuba* is an entomophilic plant pollinated by bees, ants, flies, and other insects, among which

the unabi fly is a vermin of the culture fruits [11]. It is not excluded that 16:1 and 14:1 acids of FA II take part in interrelationships between the plant and insects.

The absence of terpenic compounds in the VS of *Z. jujuba*, which is characteristic of essential oils, attracts attention because examples of VS consisting of a mixture of lipid and terpenic substances are known. So, VS from the fruits of *Lycium chinense* M., used in folk medicine in Japan, contain terpenoids and ME 14:0, 16:0, 18:3, 18:2 and 18:1 [12]. The flower absolute of *Spathium junceum* is a mixture of FA and its ME and ethyl esters, with terpenoids, phenols, and nitrogen-containing substances.

So, the FA of dried *Z. jujuba* fruits consist of 33 components, 16 of them with a dominance of 16:1(7) and 16:1(9), which is partly responsible for the fragrance of the fruit.

EXPERIMENTAL

UV and IR spectra, GLC, and GLC-MS analysis were conducted similar to [14].

Preparative TLC was conducted on glass plates with silica gel impregnated with 15% AgNO₃ in benzene (system 1) and on "Silufol UV-254" in C₆H₁₄-(C₂H₅)₂O-ice CH₃COOH (70:30:1) (system 2). Neutral lipids were obtained by three repeated hexane extractions of crushed fruits. Volatile substances were obtained by hydrodistillation for 3 h using a Clevenger type apparatus.

A commercial specimen of *Z. jujuba* fruits was used for the investigations.

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