

A PECULIARITY OF THE COMPOSITION OF THE FREE FATTY ACIDS
IN THE SEED LIPIDS OF PLANTS OF THE FAMILY LABIATAE

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The composition of the free fatty acids of nine species of the family Labiatae has been studied and it has been established that the combined free fatty acids are more diverse in composition and are richer in saturated components than the acids bound in the corresponding triacylglycerols.

Continuing an investigation of the seeds of plants of the family Labiatae [1], we have made a rapid analysis of the lipid composition of four species of catmint not studied previously: *Nepeta distans* Raul, *N. cyanea* Stev., *N. grandiflora*, and *N. sp.*, and of a species, *Lallemantia peltata*, collected in the Tashkent botanical garden in 1979.

The lipids were extracted with hexane. The yields for *N. distans*, *N. cyanea*, *N. grandiflora*, *N. sp.*, and *Lallemantia peltata* were, respectively, 18.2, 18.6, 19.1, 17.5, and 20.1%.

According to the results of column and thin-layer chromatography, the combined lipids of the seeds of the species studied contained the usual set of classes, including: hydrocarbons, sterol esters, triacylglycerols (TAGs), free fatty acids (FFAs), diacylglycerols, sterols, and monoacylglycerols. No di- and monoacylglycerols were detected in the extract from the seeds of *N. distans*. The yellowish green oil of *N. cyanea* contained chlorophyll.

The classes of compounds mentioned were identified by qualitative reactions and by comparing IR, UV, and PMR spectra with the spectra of corresponding model samples.

As in other plant oils, in the lipids of all five species the main component (80-90%) consisted of TAGs, and the amount of FFAs ranged between 1 and 2%.

The sets of acids of the two lipid classes, determined by the GLC method, are given in Table 1. As can be seen from Table 1, all the *Nepeta* species contain considerable amounts of linolenic acid, while a high percentage of linoleic acid is characteristic for *Lallemantia peltata*.

In the proportion of the individual components the free fatty acids of four of the species, with the exception of *Nepeta sp.*, differed considerably from the bound acids. As compared with the TAGs, the free acids contained considerably more of the 16:0 and 18:0, and also of the 16:1 acids.

Turning attention to the differences in the sets of FFAs and TAGs, we also determined the compositions of the FFAs of the lipids of four other species of *Labiatae* that we have studied previously [2]. In them, likewise, the sets of FFAs proved to be more diverse in qualitative composition. The seed lipids of the species *Eremostachys h.*, *Marubium alt.*, *Phlomis sal.*, and *Stachiopsis sp.* contained the free acids given in Table 2. The sum of the FFAs of these species includes from 9 to 14 acids, in contrast to the six components bound into the corresponding triacylglycerols.

The FFAs contained acids not only of the 16:0 and 18:0 series but also of medium (14:0, 15:0) and high (20:0, 22:0) molecular weights. The free acids of the seed lipids of yet another *Nepeta* — *Nepeta pannonica* — also contain about 2% (of the total FFAs) of high-molecular-weight C_{20-35} saturated acids, and in the FFAs of the seeds of *Lavandula vera* we detected 2.5% of free dimethyladipic acid, although these acids were not found as components of the TAGs [1].

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TABLE 1. Fatty Acid Compositions of the Triacylglycerols and Free Acids (GLC, %)

Acid	Lallemantia peltata		Net etia							
			distans		n. sp.		Cyanea		grandiflora	
	TAGs	FFAs	TAGs	FFAs	TAGs	FFAs	TAGs	FFAs	TAGs	FFAs
14:0	—	8.4	—	—	—	—	—	—	—	—
16:0	4.5	4.4	4.2	16.3	3.2	3.4	4.5	9.0	4.2	16.0
16:1	0.5	5.0	0.8	12.9	0.3	2.3	0.5	1.3	0.4	4.1
18:0	2.0	4.1	1.8	10.7	1.6	2.5	1.5	2.4	1.7	11.0
18:1	25.0	13.5	11.7	17.9	13.8	7.4	14.2	17.1	14.6	45.1
18:2	65.0	49.4	20.8	19.3	18.7	17.4	14.8	18.9	13.9	15.7
18:3	—	10.2	61.7	22.9	62.4	67.0	64.5	51.3	65.2	7.2
Σ_{sat}	6.5	21.9	6.0	27.0	4.8	5.9	6.0	11.4	5.9	27.9
Σ_{unsat}	93.5	78.1	94.0	73.0	95.2	94.1	94.0	88.6	94.1	72.1

TABLE 2. Composition of the Free Acids (GLC, %)

Acid	Eremostachys hissarica	Marrubium alternidens	Phlomis salicifolia	Stachtopsis sp.
14:0	0.2	4.8	4.9	0.3
Unidentified	—	2.0	—	—
16:0	6.6	27.4	5.0	12.3
16:1	Tr.	Tr.	Tr.	Tr.
17:0	0.4	0.9	Tr.	Tr.
18:0	2.1	5.7	Tr.	4.5
18:1	48.6	28.7	61.1	52.2
18:2	16.8	18.6	29.0	28.7
18:3	1.2	Tr.	Tr.	0.4
20:0	9.5	0.9	Tr.	1.6
20:1	3.9	0.8	—	—
Unidentified	8.5	10.2	—	—
Unidentified	1.5	—	—	—
22:0	0.7	—	—	—
Σ_{sat}	19.3	34.0	9.9	18.7
Σ_{unsat}	80.7	66.0	90.1	81.3

In all the species described, the FFAs were, on an average, four times richer in saturated acids, mainly the 16:0 acid, than the bound acids were.

Thus, the free acids of the neutral lipids of the seeds of several species of *Labiatae* differ in their specific composition from the acids of the triacylglycerols.

The literature contains a small number of publications relating to the comparative analysis of the unesterified fatty acids and the triacylglycerols [3]. However, analysis of the available information with respect to other plant families [4] also confirms the difference in compositions that has been noted.

EXPERIMENTAL

The extraction of the lipids from the seeds, the column, thin-layer, and gas-liquid chromatography, and the determination of the compositions of the bound and free fatty acids were carried out as described previously [1].

CONCLUSION

1. The neutral lipids of the seeds of five species of plants of the family *Labiatae* and the compositions of the free fatty acids of four of them have been studied.

2. It has been established that the sum of the free fatty acids of the species considered is more diverse in compositions and is richer in saturated components than the bound acids in the corresponding triacylglycerols.

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CRYSTAL AND MOLECULAR STRUCTURE OF THE NEW DILACTONE ANABSIN

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A complete x-ray structural study has been made of the dilactone anabsin. The crystals are monoclinic, $a = 9.863(4)$ Å, $b = 14.240(6)$ Å, $c = 11.149(6)$ Å, $\gamma = 103.61^\circ$, $z = 2$, space group $P2_1$ (diffractometer, 2035 reflections, MLS in the anisotropic approximation, $R \beta 0.65$). The conformation of the molecule and the position of attachment of the monomeric parts of anabsin have been determined unambiguously. The length of the bonds and the magnitude of the valence angles are the usual ones. The five-membered rings A, C, D, and H have the envelope conformation, and the five-membered ring F a planar conformation. The seven-member ring G has the chair conformation and B a distorted twisted chair conformation. The linkages of rings A/B and G/H are trans, and of E/F cis.

The bislactone anabsin ($C_{30}H_{40}O_7$) isolated from *Artemisia absinthium* L., family Compositae, has been ascribed the structure (I) on the basis of chemical and spectral characteristics [1, 2]. In order to establish the linkage of the monomeric parts of anabsin and its spatial structure unambiguously, we have performed an x-ray structural study. Preliminary results of this study have been published previously [3].

The molecule of the diguaianolide anabsin the XY projection is shown in Fig. 1. The conformations of the rings can be judged unambiguously from the figures of Table 1, which gives the equations of the planes and the deviations of the atoms from the corresponding planes. It can be seen from this Table that the lactone ring A has the ^{22}E envelope conformation, the deviation of the C(22) atom being 0.54 Å. The cycloheptane ring B (the C(16), C(20), C(21), C(22), C(23), C(24), and C(25) atoms) has a $^{22,21}C_{24}$ distorted twisted chair structure, the C(20), C(21), and C(24) atoms deviating in different directions from the plane by 1.22, 1.30, and -0.62 Å, respectively. The furan ring C has the ^{20}E envelope conformation, the C(20) atom deviating from the plane by 0.876 Å. The cyclopentane rings D and E also have envelope conformations, the deviations of the C(20) and C(16) from the corresponding planes being 0.977 and -0.893 Å. Ring F is planar. The cycloheptane ring G (the atoms C(1), C(5), C(6), C(7), C(8), C(9), and C(10)) is a $^{5,6}C_7$ chair, the deviations of the C(5), C(6), and C(9) atoms in different directions from the plane passing through the C(1), C(7), C(8), and C(10) atoms being 1.082, 1.107, and -0.663 Å, respectively. The lactone ring H has the 7E envelope conformation, the deviation of the C(7) being -0.661 Å.

The linkages of rings A/B and G/H are trans, and of E/F cis.

The length of the bonds and the sizes of the valence angles are given in Tables 2 and 3. As can be seen from Table 2, the lengths of the C-C bonds in the rings range from 1.486 to 1.583 Å, but the mean value of 1.538 Å is close to the standard 1.541 Å [4]. The mean length of a $O-C(sp^3)$ bond is 1.473 Å. In the γ -lactone ring H the $C=O$ double bond is somewhat shortened: 1.176 Å in place of 1.21 Å [4]. The nature of the variation of the valence angles is readily traced from the figures of Table 3. In spite of the considerable variation, the values of the valence angles agree with those given for organic compounds [5]. The two molecules of methanol of crystallization are bound to the anabsin molecule by $O_{m1} \cdots O(32)$ and $C_{m2} \cdots O(35)$ hydrogen bonds with lengths of 2.76 Å and 2.77 Å, respectively. The O(35) oxygen atom also forms a so-called "bifurcated" hydrogen bond with the oxygen atom O(31) of the ether bridge with a length of 2.72 Å.

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