COMPOSITION OF THE LIPIDS OF COTTONSEED HULLS

M. Talipova, A. I. Glushenkova,
and A. U. Umarov

UDC 582.949:581.48:547.915

The lipids of the hulls of seeds of the cotton plant have been studied. It has been established that the fatty acid compositions of the triacylglycerols, the sterol esters, the free fatty acids, the monoacylglycerols, and the polar fractions are identical. However, in the waxes the set of acids is more diverse and is distinguished by a high content (62%) of palmitic acid.

In spite of the large number of papers devoted to the study of the lipids of the seeds of various types of cotton plant [1], the lipids of the hulls have so far been studied inadequately [2]. Nevertheless, they play a not unimportant role in the vital activity of the plant. In addition, in the industrial processing of oil seeds the lipids of the hulls, on passing into the oil, may change its quality and filterability and affect its further processing [3].

We have studied the composition of the lipids of the hulls of the seeds of cotton plants of the variety Tashkent 1. The hulls were separated by hand in order to avoid the passage of the kernels into the hull fraction. The total lipids were extracted by treatment with petroleum ether (mp 40-60°C). The yield of extract was 0.58% of the weight of the hulls, and it consisted of a brown oily liquid with an acid number of $13.2^{\circ}/_{oo}$ while the acid number of the oil of the kernels was $3.7^{\circ}/_{oo}$.

The total lipids were roughly separated by column chromatography into individual classes of compounds. Elution with petroleum ether (40-60°C) yielded the combined hydrocarbons, sterol esters, and waxes (fraction I, 3.0% of the weight of the initial extract), petroleum ether–diethyl ether (98:2) yielded the combined triacylglycerols (TAGs), epoxyacylglycerols (EAGs), and high-molecular-weight alcohols (II, 79.9%), petroleum ether–diethyl ether (95:5) gave the combined free fatty acids (FFAs), pigments of the carotenoid group, and sterols (III, 14.7%), diethyl ether yielded the monoacylglycerols (MGs) (IV, 0.1%), and methanol yielded a polar fraction (V, 2.3%).

The pigments were identified from the UV spectra of fraction III. The pigments issuing from the column together with the FAAs had absorption bands with ν_{max}^{hexane} 486 and 522 nm, which permitted them to be assigned to the carotenoid group [4].

No phospholipids or glycolipids were detected qualitatively in the polar lipids [5]. The qualitative compositions of the fatty acids isolated from the lipid fractions were the same (Table 1).

However, in the waxes the set of acids was more diverse, being represented mainly by saturated acids including arachidic acid, with a high content of palmitic acid, with an almost complete absence of linoleic acid, while in the TAGs, FFAs, and the polar fraction the linoleic acid predominated over the others.

The composition of the TAGs was determined by enzymatic hydrolysis [6], and on the basis of the fatty acid composition of the TAGs and MGs that they contained the following acids: $C_{14:0}$ — 0.2%, $C_{16:0}$ — 2.6%, $C_{16:1}$ — 0.4%, $C_{18:0}$ — 0.5%, $C_{18:1}$ — 18.7%, $C_{18:2}$ — 77.6%.

The position-species composition of the TAGs (%), calculated by Coleman's method was as follows: PPP* — 0.5; PPO — 0.4; PPL — 1.2; POP — 2.7; PLP — 11.2; OPO — 0.1; OPL — 0.4; PPL — 0.8; POO — 2.2; POL — 6.8; PLO — 9.0; PLL — 27.7; OOO — 0.4; OOL — 2.6; OLO — 1.8; OLL — 11.0; LOL — 4.1; LLL — 17.1.

---

*P — Palmitic; O — oleic; L — linoleic acids.

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 44-47, January-February, 1981. Original article submitted June 9, 1980.

TABLE 1. Fatty Acid Compositions of the Lipid Classes

Class	$C_{14:0}$	$C_{15:0}$	$C_{16:0}$	$C_{16:1}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{20:0}$	C_x	C_y
Sterol esters	4,20	—	38,30	—	3,80	17,40	36,30	—	—	—
Waxes	1,60	1,0	62,70	2,10	10,40	2,20	Tr.	5,4	1,80	11,80
TAGs	0,70	—	22,70	0,70	1,60	16,10	58,20	—	—	—
FFAs	0,30	—	13,60	0,40	0,70	17,40	67,60	—	—	—
MGs	7,40	—	29,60	4,70	22,70	34,20	1,40	—	—	—
Polar fraction	0,50	—	23,30	0,50	3,40	19,90	52,40	—	—	—

Position-type composition in terms of saturation and unsaturation: SSS — 0.5; SSU — 15.5; SUU — 47.0; UUU — 37.0.

Thus, the type composition of the TAGs is represented by 18 species of which the main ones are PLL (27.7%), LLP (17.1%), PLP (11.2%), OLL (11%), and PLO (9%). Consequently, in 77.8% of the TAGs linoleic acid occupies position 2.

EXPERIMENTAL

The gas–liquid chromatography of the methyl esters of the fatty acids was performed on a Khrom-4 chromatograph with a flame-ionization detector and a stainless steel column 2.5 m long and 3 mm in diameter filled with 17% of ethylene glycol on Chromaton N-AW at a column temperature of 194°C.

UV spectra were recorded on a Hitachi mass spectrometer; mass spectra on a MKh-1303 spectrometer at an ionization energy of the electrons of 70 eV; and IR spectra on a UR-10 instrument in films and in KBr.

The lipids were extracted by steeping the hulls with petroleum ether four times for a total duration of 24 h.

The thin-layer chromatography of the lipids was carried out on Silufol plates in system 1) heptane–methyl ethyl ketone–acetic acid (43:7:0.5); and on silica gel in system 2) hexane–diethyl ether (9:1), and in system 3) hexane–diethyl ether (7:3). The plates were visualized in iodine vapor and by spraying with 50% H_2SO_4 followed by heating.

Hydrolysis was carried out at 37°C with lipase obtained from the porcine pancreas.

Hydrocarbons (R_f 0.99 in system 1). Mass spectrum (135°C, 40 eV, 0.5 mA), m/e: M^+ 422. 436, 450, 464, 478, 492. On the basis of these results it may be concluded that they are a mixture of hydrocarbons with 30-35 carbon atoms.

Waxes (R_f 0.8 in system 1). Mass spectrum (170°C, 50 eV, 0.6 mA), m/e: M^+ 704, 676, 662, 648, 634, 592. The maximum peak, M^+ 676, corresponds to a wax consisting of palmitic acid and myricyl alcohol. The severe alkaline hydrolysis of the waxes was carried out for 8 h [7].

High-Molecular-Weight Alcohols (R_f 0.75 in system 1). IR spectrum ($\nu_{\max}^{\mathrm{KBr}}$, cm^{-1}): 3600-3200, 2960, 2850, 1660. Mass spectrum (170°C, 40 eV, 0.5 mA), m/e: 448, 420, 392, 364, corresponding to (M^+ — 18) ions, molecular ions being absent. On this basis it was established that the material was a mixture of C_{26}-C_{32} alcohols with even numbers of carbon atoms.

Free Sterols (R_f 0.34 in System 1). These were isolated by crystallization from methanol; mp 130-132°C. Mass spectrum (126°C, 40 eV, 0.5 mA), m/e: M^+ 414, 412, 400. On the basis of these facts it was established that the mixture consisted of β-sitosterol, α-sitosterol, and campesterol.

SUMMARY

The lipids of cottonseed hulls have been studied. It has been established that the fatty acid compositions of the triacylglycerols, the sterol esters, the fatty acids, the monoacylglycerols, and the polar fraction are identical. However, in the waxes the set of acids is more diverse and is distinguished by a high content of saturated acids.

LITERATURE CITED

1. K. Kadyrov, Author's Abstract of Candidate's Dissertation [in Russian], Tashkent (1980).

2. U. Kh. Khalimova, I. Kadurov, Kh. Isaev, and A. Ismailov, Khim. Prir. Soedin., 756 (1970); A. S. Sadykov, Kh. I. Isaev, and A. I. Ismailov, Uzb. Khim. Zh., No. 2, 53 (1963).
3. S. N. Volotovskaya, F. K. Estrina, and A. S. Slavutina, Maslob-Zhir. Promst., No. 5, 8 (1976).
4. B. N. Tyutyunnikov, The Chemistry of Fats [in Russian], Moscow (1966), p. 378.
5. M. Kates, Techniques of Lipidology, North-Holland, Amsterdam (1972).
6. A. L. Markman, T. V. Chernenko, and A. U. Umarov, Prikl. Biokhim. Mikrobiol., No. 5, 616 (1969).
7. P. Cancalon, J. Am. Oil Chem. Soc., 10, 629 (1971).

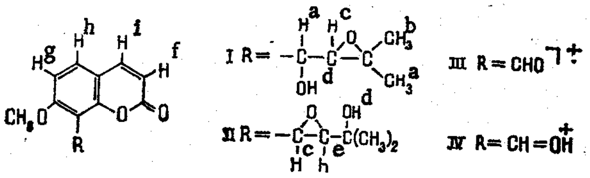
COUMARINS FROM *Phlojodicarpus sibiricus*

D. Gantimur and A. A. Semenov

UDC 547.992

Phlojodicarpin [8-(2,3-epoxy-1-hydroxy-3-methylbutyl)-7-methoxycoumarin, $C_{15}H_{16}O_5$, mp 143-145°C, $[\alpha]_D^{25}$ − 37.5°], and isophlojodicarpin [8-(1,2-epoxy-3-hydroxy-3-methylbutyl)-7-methoxycoumarin, $C_{15}H_{16}O_5$, mp 132-134°C, $[\alpha]_D^{25}$ − 102.5°] have been isolated from the epigeal part of *Phlojodicarpus sibiricus*. The results of the IR, UV, PMR, and mass spectrometry of these compounds are given.

Phlojodicarpus sibiricus is used in folk medicine for the treatment of tumors. In order to isolate and identify the active principle, we have fractionated an alcoholic extract of the epigeal part of the plant, being guided by the results of biological control. The test used was a determination of cytotoxic activity *in vitro* with respect to four lines of cells: sarcoma-37, and Fisher, Ehrlich, and NK/Ly tumors according to the literature [1]. This showed that the biological activity was localized in the ethereal solution obtained on partitioning the alcoholic extract between water and ether (ED_{50} < 10 μg/ml). The main components of this solution were coumarins. By crystallization and preparative thin-layer chromatography, from the total coumarins we isolated two substances which we have called Phlojodicarpin (I) and isophlojodicarpin (II). Another coumarin was also present, in trace amounts.



Substances (I) and (II) had the same molecular weight of 276 and the same elementary composition, $C_{15}H_{16}O_5$. Strong absorption in the IR spectrum at 1610 and 1705 cm^{-1} showed the presence of a coumarinic lactone ring. Each compound contained a hydroxy group (3430 and 3410 cm^{-1}, respectively) and an epoxide ring (3000, 1246, and 947 cm^{-1}). Isophlojodicarpin had a fourth epoxide band at 863 cm^{-1}. In phlojodicarpin this was masked by the absorption of two adjacent aromatic C–H bonds at 825 cm^{-1}. The two compounds had the same UV spectrum with maxima at 260 and 328 nm which did not shift on the addition of sodium methanolate. This permitted them to be assigned to the 7-OR-substituted coumarins [2].

The M − 30 ion in the mass spectra of (I) and (II) showed the presence of a methoxy group attached to an aromatic ring. More intensive fragments with m/e 204 and 205 we ascribe to structures (III) and (IV), from which it follows that one of the oxygen atoms is attached to a benzene carbon atom. Other intensive ions are formed by the loss of HCO and CH_2O from

---

Institute of Chemistry, Academy of Sciences of the Mongolian Peoples' Republic, Ulan-Bator. Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 47-49, January-February, 1981. Original article submitted June 2, 1980.

0009-3130/81/1701-0041$07.50