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# TOCOPHEROLS OF *Olea europaea*

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The qualitative and quantitative compositions of the tocopherols of the olives grown in Azerbaidzhan have not been studied. In view of the increase in their planting, it is extremely urgent to set up a study of the total amount and the isomeric composition of the tocopherols in olives.

We have investigated the oils of the varieties Baki-25, Pikvales, and Gorvala from the 1986 harvest from plots of sovkhoz [collective farm] No. 2 of the Apsheron region of the Azerbaidzhan SSR.

The tocopherols (TPs) were isolated within the total lipid fraction of the olives and were analyzed by TLC [1]. All the operations on the isolation and separation of the TPs were performed in an atmosphere of argon. The TPs were freed from contamination with other lipids by hydrolysis in 12% ethanolic KOH in the presence of pyrogallol (80°C, 5 min). The unsaponifiable fraction was extracted with diethyl ether and was washed free from impurities.

The isomeric forms of the TPs were separated by TLC on silica gel in the petroleum ether–diethyl ether–diisopropyl ether–acetone–acetic acid (254:3:32:12:3) system [2], the advantage of which is the possibility of separating β- and γ-tocopherols (these position-isomers are scarcely separated in other systems [1]). The TP spots were detected with a 2% ethanolic solution of α-dimethylphenylenediamine. The Sonnenschein reagent* was used to differentiate the β- and γ-tocopherols, giving a brown spot with β-tocopherol and a blue one with γ-tocopherol [3]. With the aim of a quantitative determination of the TPs, the spots were eluted with the $FeCl_3$–α,α'-bipyridyl reagent and spectrophotometry was carried out at wavelength of 520 nm [4]. Calibration graphs were plotted with solutions of pure α-, β-, and δ-tocopherols, respectively. "Erevit" synthetic δ, α, and β isomers (Czechoslovakia) were used as control. γ-Tocopherols were determined on the basis of the graph for the β-tocopherols.

The results obtained are given in Table 1, from which it can be seen that the total amount of TPs is appreciably affected by the variety characteristics of the olives. At a total pro-

TABLE 1. Qualitative and Quantitative Compositions of Olive Tocopherols

| Form of tocopherol | Amount, % on the total weight of the TPs | | |
|---|---|---|---|
| | Baky-25 | Pikvales | Gorvala |
| α-Tocopherol | 39,3 | 41,4 | 59,4 |
| β-Tocopherol | 12,2 | 14,5 | 10,2 |
| γ-Tocopherol | 24,0 | 19,7 | 16,7 |
| δ-Tocopherol | 24,5 | 24,4 | 13,7 |
| Total proportion by weight, mg/kg | 197,4 | 223,2 | 271,7 |

*The reagent is prepared in the following way: 1 g of trichloroacetic acid is added to a suspension of 1 g of cerium sulfate ($Ce(SO_4)_2$) in 4 $cm^3$ of distilled water and the mixture is heated to the boil, and then concentrated sulfuric acid is carefully added in drops until a clear solution has been obtained.

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portion by weight of TPs of 197.4-271.7 mg/kg, they were found in the greatest amount in the Gorvala variety.

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# FLAVONOID COMPOSITION OF *Artemisia xanthochroa*


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The flavonoids cirsilineol, cirsimaritin, eriodictyol 7-methyl ether, and rhamnetin have been isolated from the epigeal part of *Artemesia xanthrochroa* Krasch.


Continuing an investigation of the flavonoid composition of this species of wormwood, from a chloroform fraction of the ethanolic extract we isolated the additional substance (VI), and from the ethyl acetate fraction substance (VII).

Substance (VI) — $C_{16}H_{14}O_7$, mp 217°C (chloroform–methanol), $[\alpha]_D^{24}$ +9.3° (c 1.51; ethanol) — consisted of colorless crystals. Its UV spectrum (295 nm) and also spectra with ionizing additives permitted the assumption of a dihydroflavonoid structure of the substance, of the presence of free OH groups in positions 3' and 4', and of their absence from position 7 [2]. The presence of an ortho-dihydroxy group in ring B was confirmed by the alkaline degradation of substance (VI), as a result of which protocatechuic acid was detected in the reaction products by paper and thin-layer chromatography.

PMR spectrum (DMSO, δ, ppm): 6.77 (d, J = 7 Hz, H-5'); 6.72 (m, 2H, H-6' and H-2'); 6.06 (d., J = 2 Hz, 2H, H-6, H-8); 5.05 (d, J = 11 Hz, H-2); 4.50 (d, J = 11 Hz, H-3); 3.74 (s, 3H, $OCH_3$). The splitting of the signals at 5.05 and 4.50 into doublets with SSCCs of 11 Hz showed that the H-2 and H-3 protons were in the trans orientation with respect to one another.

The structure of the flavonoid put forward on the basis of the spectral characteristics — 3,3',4'-5-tetrahydroxy-7-methoxyflavanone — was confirmed by the dehydrogenation of (VI) by boiling it in 4 N $H_2SO_4$ solution for 2 h [3], as the result of which a substance was obtained which was identified with rhamnetin on the basis of the identity of the IR spectra and the absence of a depression of the melting point of a mixture with an authentic sample. The capacity of the dihydroflavonol (VI) for being oxidized to a flavonol confirmed that it belonged to the trans series [4]. The tetraacetate of (VI) had mp 133-135°C (according to the literature, the melting point of dihydrorhamnetin acetate is 130°C) [5].

Summarizing the experimental results, we determined the structure of compound (VI) as trans(+)-3,3',4',5-tetrahydroxy-7-methoxyflavanone. A dihydroflavonol described by the authors as 3,3',4',5-tetrahydroxy-7-methoxyflavanone, padmatin, was isolated previously from *Prunus puddum* but its melting point differed considerably from that of substance (VI) (mp 171°C [6]). The authors concerned did not give optical rotation values. This is the first time that compound (VI), being a dextrorotatary isomer of the trans series has been described in the literature.

Substance (VII) — $C_{17}H_{14}O_8$, mp 297°C, $M^+$ 346. UV spectrum: $\lambda_{max}^{CH_3OH}$ 266, 273 nm. PMR spectrum (DMSO, δ, ppm): 7.38 (s, H-6'); 7.01 (s, H-3'); 6.62 (s, H-8); 6.58 (s, H-3); 3.80 (s, $OCH_3$); 3.76 (s, $OCH_3$). UV spectra with ionizing and complex-forming additives permitted the assumption that free OH groups were present at C-4', C-5, and C-7 of the flavone nucleus.

In its UV spectrum, flavonoid (VII) had an absorption maximum at 373 nm, which is not characteristic for flavones, but may occur when an OH group is present in the C-2' position


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