3. L. S. Golodova, Tr. In-ta Organicheskogo Kataliza i Elektrokhimii, Alma-Ata, 1, 115 (1971).
4. L. S. Golodova and D. V. Sokol'skii, Izv. Vuzov, Pishchevaya Technologiya, No. 2, 35 (1971).
5. L. S. Golodova and D. V. Sokol'skii, Maslozhir, Prom., No. 7, 6 (1971).
6. R. S. Gutter and B. V. Ovchinskii, Elements of Numerical Analysis and the Mathematical Treatment of Experimental Results [in Russian], Moscow, (1970).
7. A. I. Glushenkova and A. L. Markman, Khim. Prirodn. Soedin, 671 (1970).

THE STRUCTURE OF KARATAVIC ACID

V. Yu. Bagirov and V. I. Sheichenko

UDC 547.9:582.89

Continuing an investigation of the structure of karatavic acid [1], we have made a detailed study of the NMR spectra of the methyl ester of this acid and also of the products of the alkaline hydrolysis of its ethyl ester. The results obtained show that the structure proposed previously for karatavic acid requires reconsideration.

In the NMR spectrum of the methyl ester of this acid (Fig. 1, curve 1), there are the signals of a tertiary methyl group (0.87 ppm), of two methyl groups on double bonds (1.65 and 1.76 ppm), and of an ester methyl group (3.52 ppm). In the 3.57-4.20 ppm region there are the signals characteristic for the Ar−O−CH_2−CH < grouping in terpenoid coumarins [2-13].

The signals of the protons of the methyl group at 1.76 ppm and of the olefinic protons (4.73 and 4.81 ppm) relate to an isopropenyl grouping [14], as was shown by double resonance (Fig. 1, curve 2). On irradiation (strong field H_2) of the signal of the methyl group (1.76 ppm), the signals at 4.73 and 4.81 ppm contracted and were converted into two doublets (^2J = 1.9 Hz). The signal of the olefinic proton of a H−C = C−CH_3 fragment also contracted, also contracted, which shows the close positions of the double bonds.

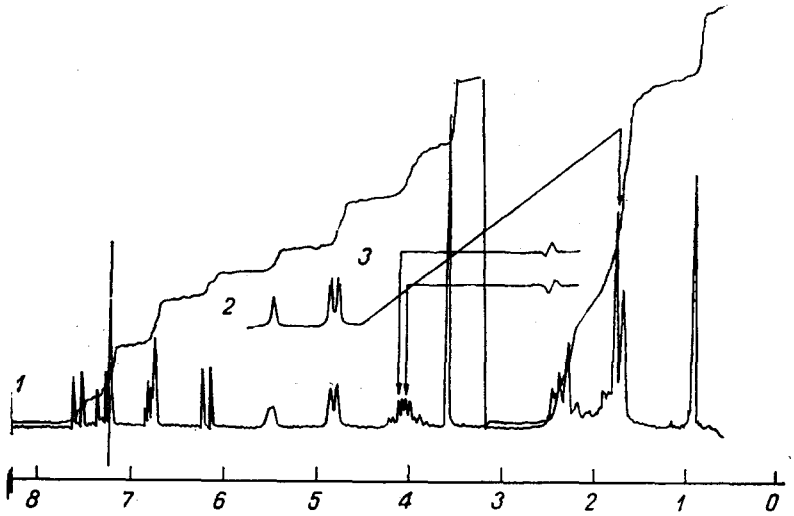


Fig. 1. NMR spectrum of methyl karatavate (1), double resonance (2), INDOR (3) ($CDCl_3$, 100 MHz, 0, δ, ppm, HMDS).

Institute of Botany, Academy of Sciences of the Azerbaidzhan SSR. All-Union Scientific-Research Institute of Medicinal Plants. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 700-703, November-December, 1975. Original article submitted August 28, 1974.

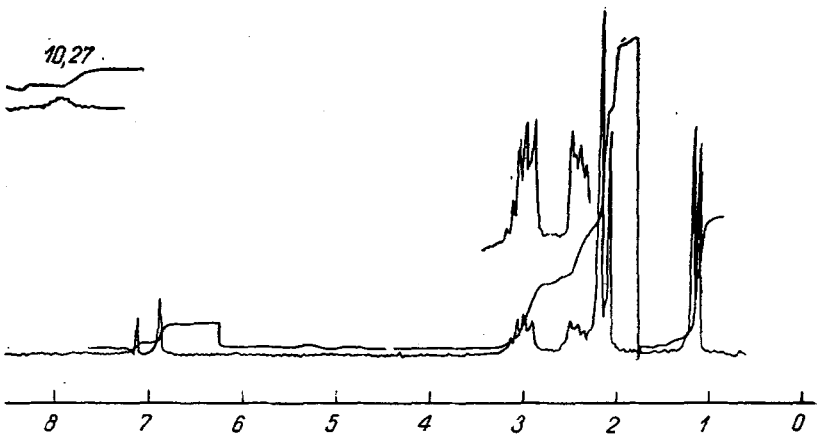
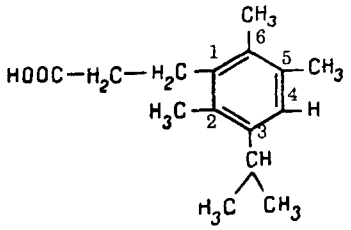


Fig. 2. NMR spectrum of the aromatic acid ($CDCl_3$, 100MHz, 0, δ, ppm, HMDS).

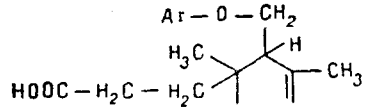
If there are two double bonds in the sesquiterpene part of the karatavic acid, only a monocyclic structure is possible for this compound. The formation of β-(3-isopropyl-2,5,6-trimethylphenyl)propionic acid, with the composition $C_{15}H_{22}O_2$ (M^+, m/e 182, 20%) on the acid hydrolysis of ethyl karatavate confirms that the single ring is a six-membered (cyclohexene) ring.

The signals of the substituents appear clearly in the NMR spectrum (Fig. 2) of this aromatic acid: $3CH_3$, 2.12 and 2.24 ppm; $2CH_2$ and CH, 2.30-3.20 ppm; $(CH_3)_2CH$, 1.18 ppm; C_3H, 6.88 ppm; COOH, 10.27 ppm.



In the aromatic acid there are five substituents, while in the cyclohexene ring of karatavic acid of the five substituents only two (a tertiary methyl group and the propionic acid residue) are present on the same carbon atom. Thus, the cleavage of the ether bond in the acid hydrolysis of karatavic acid leads to a rearrangement of the sesquiterpene moiety of this acid accompanied by a migration of its tertiary methyl group from the $C_{6'}$ position to the $C_{5'}$ position and also by the migration of the double bond from the isopropenyl fragment into the cyclohexene ring ($C_{4'}-C_{5'}$ position) with the formation of a benzene ring.

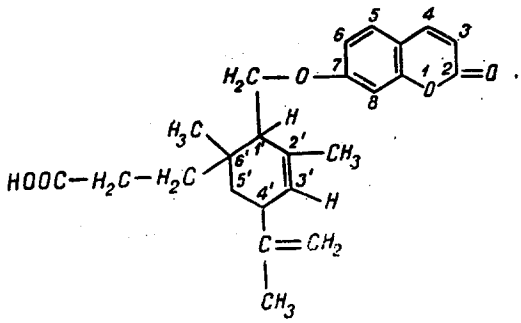
An analysis of the structure of the INDOR signals (see Fig. 1, curve 3) obtained on the lines of the signals of the methylene group at the ether bond shows that there are no protons of a methylene group in the vicinal position to the methine proton of the $Ar-O-CH_2-CH <$ fragment, which indicates the presence of the tertiary methyl group and of the propionic acid residue at $C_{6'}$. Consequently, the sesquiterpene moiety of karatavic acid contains the grouping



On the basis of the facts given above, for karatavic acid we propose the structure of 7-[6'-(β-carboxyethyl)-4'-isopropenyl-2',6'-dimethylcyclohex-2-enylmethoxy]coumarin: (See scheme on next page.)

EXPERIMENTAL

Preparation of the Aromatic Acid. Ethyl karatavate (10 g) was hydrolyzed with 80% sulfuric acid. The hydrolysis products were extracted with chloroform, and the extract was washed repeatedly with water and dried over calcium chloride, and the chloroform was distilled off. The residue (a viscous resin) was treated with 300 ml of distilled water, the flask was connected to a reflux condenser, and the steam-volatile com-



ponents – the sesquiterpene moiety of ethyl karatavate – were obtained by Ginzburg's method and were saponified in an ethanolic solution of alkali. The alcohol was distilled off, the residue was dissolved in distilled water, and the solution was acidified. The aromatic acid was extracted with chloroform, the extract was dried over calcium chloride, and the chloroform was distilled off. The residue was dissolved in aqueous ethanol. On standing, crystals with mp 141-142°C deposited.

SUMMARY

The structure of 7-[6'-(β-carboxyethyl)-4'-isopropenyl-2',6'-dimethylcyclohex-2-enylmethyloxy]coumarin has been proposed for karatavic acid.

LITERATURE CITED

1. N. P. Kir'yalov and V. Yu. Bagirov, Khim. Prirodn. Soedin., 283 (1968).
2. A. I. Ban'kovskii, N. E. Ermatov, M. E. Perel'son, L. Bubeva-Ivanova, and N. S. Pavlova, Khim. Prirodn. Soedin., 173 (1970).
3. V. Yu. Bagirov, N. P. Kir'yalov, and V. I. Sheichenko, and V. N. Bochkarev, Khim. Prirodn. Soedin., 466 (1970).
4. V. Yu. Bagirov and N. P. Kir'yalov, Khim. Prirodn. Soedin., 387 (1972).
5. V. V. Vandyshev, Yu. E. Sklyar, M. E. Perel'son, M. D. Moroz, and M. G. Pimenov, Khim. Prirodn. Soedin., 669 (1972).
6. V. V. Vandyshev, Yu. E. Sklar, M. E. Perel'son, M. D. Moroz, and M. G. Pimemov, Khim. Prirodn. Soedin., 670 (1972).
7. N. P. Kir'yalov and T. V. Bukreeva, Khim. Prirodn. Soedin., 798 (1972).
8. N. P. Kir'yalov and T. V. Bukreeva, Khim. Prirodn. Soedin., 425 (1973).
9. Yu. E. Sklyar, M. E. Perel'son, and M. G. Pimenov, Khim. Prirodn. Soedin., 428 (1973).
10. A. I. Saidkhodzhaev and G. K. Nikonov, Khim. Prirodn. Soedin., 15 (1974).
11. T. Kh. Khasanov, A. I. Saidkhodzhaev, and G. K. Nikonov, Khim. Prirodn. Soedin., 25 (1974).
12. T. Kh. Khasanov, A. I. Saidkhodzhaev, and G. K. Nikonov, Khim. Prirodn. Soedin., 10 (1974).
13. T. Kh. Khasanov, A. I. Saidkhodzhaev, and G. K. Nikonov, Khim. Prirodn. Soedin., 517 (1974).
14. N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, NMR Spectra Catalog, Varian Associates, Palo Alto, California (1962), p. 271.