MINOR DITERPENOIDS OF Stachys annua

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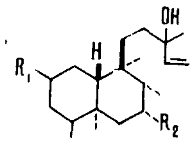
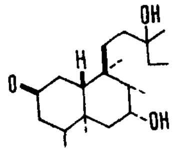
We have previously [1] reported the isolation from Stachys annua L. (family Labiatae) of, in addition to the known stachysolone and annuanone, two minor diterpenoids which were named stachylone and stachone. Their yields do not exceed 0.002% of the weight of the dry plant. Below we give information confirming the structures of these substances.

Stachylone, $C_{20}H_{34}O_3$ (I), according to its IR spectrum (here and below in KBr) contains an oxo group (1700 cm^{-1}), a vinyl bond (3050, 1640, 990, 910 cm^{-1}), and hydroxy groups (3500 cm^{-1}), one of which is readily oxidized by chromium trioxide in pyridine with the formation of oxostachylone (II), $C_{20}H_{32}O_3$, mp 145-147°C. IR spectrum of (II): 1710, 1715, 3100, 1640, 990 cm^{-1}.

The hydrogenation of stachylone in ethyl acetate over $Pd/BaSO_4$ took place with the absorption of one mole of hydrogen and gave dihydrostachylone (III), which was identical from its IR spectrum, melting point, and mixed melting point with the tetrahydrostachysolone described previously [2]. Another confirmation of this was the triol (IV) ($C_{20}H_{36}O_3$, mp 69-71°C, IR spectrum: 3450, 3100, 1640, 990 cm^{-1}) obtained from stachylone by reduction with sodium tetrahydroborate in admixture with products (V) ($C_{20}H_{36}O_2$, mp 47-50°C; IR spectrum: 3450, 1650, 990 cm^{-1}) and (VI) ($C_{20}H_{34}O_3$, mp 79-81°C; IR spectrum: 3450, 1670, 1645, 990, 830 cm^{-1}), isolated previously from stachysolone on its reduction with sodium in butanol [3].



I, II, IV, V, VI



III

I. $R_1 = O$, $R_2 = OH$; II. $R_1 = R_2 = O$; IV. $R_1 = R_2 = OH$;
V. $R_1 = H$, $R_2 = OH$; VI. $R_1 = R_2 = OH$; Δ^{8}.

Stachone, $C_{20}H_{36}O_3$, was identical with tetrahydrostachysolone (III) with respect to its IR spectrum. However, it differed from (III) and also from tetrahydroannuanone by its melting point and the sign of its rotation [$[\alpha]_D$ − 20° instead of +15.1° for (III)]. A mixture of stachone with each of the isomeric tetrahydro derivatives mentioned gave a depression of the melting point. On the basis of the facts given, it was concluded that this diterpenoid is an epimer of tetrahydrostachysolone, probably at C_4.

LITERATURE CITED

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