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THE STRUCTURE OF MACEDONIC ACID

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Macedonic acid [1, 2] is a heteroangular diene, as is shown by the presence in the UV spectrum of the acid and its derivatives (methyl ester with mp 253° C, diacetates of the ester and the acid) of maxima at λ 242, 250, and 258 mμ (log ε 4–4.5). The position of the carboxyl group in the macedonic acid at $C_{(17)}$ is shown by the preparation of a bromolactone [mp 278° C, IR spectrum 1785 cm^{-1} (CO group of a lactone)] from the diacetate of the acid with mp 290–293° C. A hydroxyl group at $C_{(3)}$ is assumed by analogy with other triterpenes. The location of the second hydroxyl has been shown by the oxidation of methyl macedonate with chromic anhydride in pyridine solution; two oxidation products were obtained which were separated chromatographically.

1. A diketoester $C_{31}H_{44}O_4$ with mp 242–244° C, $[\alpha]_D$ −50° ($CHCl_3$); IR spectrum, cm^{-1}: 1743, 1719, 1705, 1690; UV spectrum, λ, mμ; 258, 250, 243 (log ε 4–4.5) and 294 (log ε 1.8).

2. A monohydroxyketoester $C_{31}H_{46}O_4$ with mp 221–221° C, $[\alpha]_D$ −111.3° ($CHCl_3$); IR spectrum, cm^{-1}: 1715; UV spectrum, λ, mμ: 258, 250, 242 (100-fold dilution) and 296 mμ (log ε 1.7). Saponification of the ester gave an acid $C_{30}H_{44}O_4$ with mp 328° C, probably a 3-hydroxy-19-oxoacid, since the IR spectrum had bands at 1725 cm^{-1} (CO group of a carboxyl) and 1670 cm^{-1} (conjugated CO group in a six-membered ring). The oxidation of macedonic acid with chromic anhydride also formed a hydroxyketo derivative with mp 329–331° C; UV spectrum, λ, mμ: 258, 250, and 240; and IR spectrum, cm^{-1}: 1725 and 1668. This shows the position of the CO group and means that there is an OH group at $C_{(19)}$.

The NMR spectrum of the methyl ester of the diacetate of macedonic acid (mp 236–237° C) confirmed the presence of an OH group at $C_{(19)}$. There are signals at (τ scale) 7.9 (diacetyl, 6 protons), 6.36 (OCH_3, 3 protons), 5.47 (singlet, 1 proton at an acetyl group on $C_{(19)}$), 4.93 (1 proton at an acetyl group on $C_{(3)}$) and 4.72 and 4.41 (1 proton each at $C_{(11)}-C_{(12)}$ double bond).

Hydrogenation of the diacetate of macedonic acid (PtO_2) in acetic acid led to the diacetate of dihydromacedonic acid with mp 268–275° C, giving a bromo lactone with mp 298–300° C the IR spectrum of which had a band at 1775 cm^{-1}. Saponification of the diacetate of the dihydro acid yielded dihydromacedonic acid with mp 330–335° C (dioxane), sometimes contaminated with a conjugated heteroangular diene. On oxidation with chromic anhydride in pyridine, methyl dihydromacedonate (mp 244° C) formed a diketoester $C_{31}H_{46}O_4$ with mp 216° C; UV spectrum λ 302 mμ; IR spectrum, cm^{-1}, 1725 and shoulders at 1750 and 1707; and a monohydroxyketoester $C_{31}H_{46}O_4$, mp 234–235° C; UV spectrum: λ 302 mμ (log ε 1.8); IR spectrum, cm^{-1}: 3500, 1700; $[\alpha]_D$ +21° ($CHCl_3$). Saponification of the latter substance gave a hydroxyketoacid with mp 320–324° C; IR spectrum, cm^{-1}: 3500, 1700.

Thus, dihydromacedonic acid is probably 19-hydroxyoleanolic acid and corresponds to the general plan of the structure of siaresinolic acid [3]. The difference in properties between dihydromacedonic and siaresinolic acid can be explained by the different spatial position of the hydroxyl groups at $C_{(3)}$ and $C_{(19)}$ in the two compounds.

Consequently, macedonic acid probably has the structure of 3, 19-dihydroxyolean-11(12), 13(18)-dien-17-oic acid.

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