Tetrahedron Letters No. 46, pp 4563 - 4566.
0040-4039/78/1108-4563$02.00/0

MAGYDARDIENDIOL, DITERPENOID WITH A NEW SKELETON FROM MAGYDARIS PANACIFOLIA (UMBELLIFERAE)[1].

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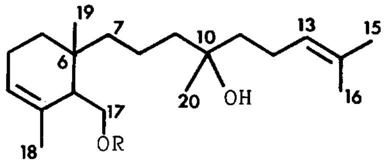
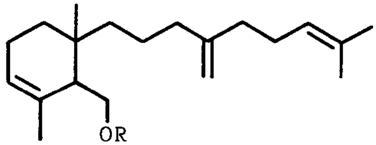
SUMMARY.- Three new diterpenoids with a substituted α-cyclogeraniol skeleton have been isolated from the umbelliferae *Magydaris panacifolia* (Vahl) Lange, for which the names of magydar-2,13-dien-11,17-diol, 1, magydar-2,10(20),13-trien-17-ol, 2, and magydar-2,10(20),13-trien-17-yl acetate, 3, are proposed. The structures of these substances have been deduced from spectroscopic and chemical data.

In connection with the study of Umbelliferae from the NW of the Iberian Peninsula, we have isolated a novel diterpene diol, 1, from *Magydaris panacifolia* (Vahl) Lange[2]. This substance, which we have named magydardiendiol, has mp 55-6º and $[\alpha]_D$ = +24.4º (c, 1 $CHCl_3$) and it is one of the most abundant components of the hexane extract from the umbellas of the plant. Related to this substance, they were also isolated as natural products the substances magydar-2,10(20),13-trien-17-ol, 2, ($[\alpha]_D$ = +43.1º, $CHCl_3$) and its acetate, 3, ($[\alpha]_D$ = +23.9º, $CHCl_3$).



1 R = H

4 R = Ac



2 R = H

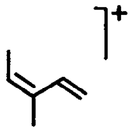
3 R = Ac

The mass spectrum and elemental analysis of magydardiendiol, are consistent for $C_{20}H_{36}O_2$. The ir spectrum (CCl_4 3.2 10^{-2}M) shows two associated hydroxyls[3] (3650, 3520, 1040, 990 cm^{-1}), one of which is easily acetylated (Ac_2O/pyridine). The monoacetate, 4, shows a free tertiary -OH group (3610 cm^{-1}).

The ^{1}H-nmr spectrum of 1 ($CDCl_3$, 60 MHz) shows the presence of two vinylic protons at δ, 5.28(t, br, J=7 Hz) and 5.02(t, br, J=7 Hz) which became singlets after double irradiation at 2.10 ppm. This spectrum also shows the AB part of an ABX system centered at 3.60 ppm(J_{AB}= 10 Hz, J_{AX}= 9 Hz and J_{BX}= 5 Hz), overlapped by a broad signal of two hydroxyls. This AB part can be assigned to the group $>$CH—CH$_2$OH. There are also five methyl signals at: $\delta =$ 1.68(6H, s) and 1.59(3H, s), attached to double bonds; 1.22(3H, s), deshielded by the tertiary hydroxyl, and 0.78 ppm(3H, s) shielded by a cyclic double bond. The preceding ^{1}H-nmr signals are also present in the spectrum of acetate 4, but the AB multiplet is deshielded at 4.20 ppm.

All the above data are is agreement with the isoprenoid structure proposed for magydardiendiol, 1.

The mass spectrum of 4 confirms the proposed structure and shows fragments at m/e (%): 350(M^+, 0.5), 332(M^+ - H_2O, 5), 290(M^+ - AcOH, 4), 273(M^+ + H - H_2O- - AcOH, 11), 189(M^+ - 69 - CH$_2$OAc, 22), 161(33), 135(44), 121(56), 109(61), 107(57), 81(34), 69(100):



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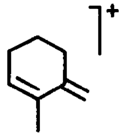

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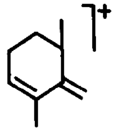

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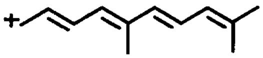

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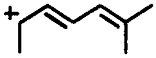

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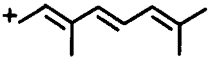

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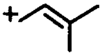

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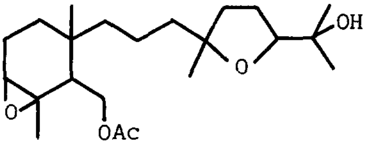
The presence of a methyl geminal with the tertiary -OH in magydardiendiol, was evident by dehydration of 4 with $SOCl_2$/pyridine. The most abundant dehydration product showed spectroscopic properties identical to those of natural acetate 3, [ms: M^+ = 332; base peak = 69; ir: $\bar{\nu}$ 3090, 1740, 1230, 890, 820 cm^{-1}; ^{1}H-nmr: δ, 5.03(2H, m, $>$C═CH—), 4.75 and 4.60(2H, 2s, $>$C═CH$_2$), 4.10(2H, AB dq, J=11, 8 and 6 Hz, $>$CH—CH$_2$OAc), 1.99(3H, s, AcO—C-17), 1.61(9H, s, br, C═C-Me) and 0.71 ppm (3H, s, Me-19)] which on hydrolysis gives the alcohol 2 [ir: $\bar{\nu}$, 3340, 3070, 1640, 1045,990,890 and 825 cm^{-1}; ^{1}H-nmr: δ, 5.03(2H, m, H-3 and H-13), 4.76 and 4.62(2H, s, ═CH$_2$ C-20), 3.65(2H, AB dq, -CH$_2$OH C-17), 1.63(3H, s, Me-18), 1.58(6H, s, Me-15 and Me-16) and 0.71 ppm (3H, s, Me-19)].

The terminal group -MeCH—CH$_2$—CH$_2$—CH═CMe$_2$, was also evident by epoxidation of 4 with *m*-chloroperbenzoic acid in CH_2Cl_2. The main product of this reaction was the tetrahydrofurane epoxide 5 which shows the following spectroscopic signals: ir: $\bar{\nu}$, 3440, 1735, 1240, 1050, 1025, 1000 and 840 cm^{-1}; ^{1}H-nmr δ, 4.10(2H, AB dq, H_2-17), 3.80(1H, t, J=6 Hz, H-13 of THF ring), 2.60(1H, m, H-3 epoxide), 2.04(3H, s, AcO—C-17), 1.32-1.08(4 deshielded methyls) and 0.82 ppm (3H, s, Me-19). Moreover, the oxidation of 4 with Na_2CrO_4[4], led to a mixture of two products which were identified as 6 (ir: $\bar{\nu}$, 3450, 1735, 1640, 1240, 1050, 1025, 1000, 855 and 825 cm^{-1}) and its oxidation product[5] the lactone 7 (ir: $\bar{\nu}$, 1770, 1735, 1225, 1025, 910 and 830 cm^{-1}).



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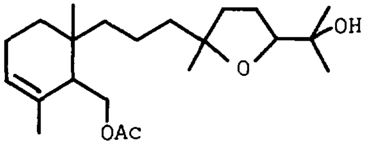

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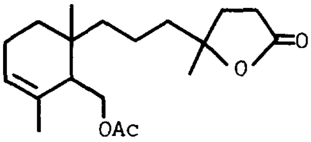

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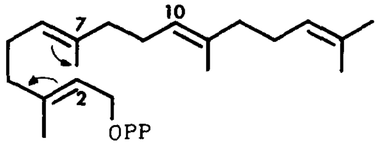
The biogenesis of these diterpenoids may be explained by hydroxylation of the double bond Δ-10 of geranyl-geranyl pyrophosphate, 8, followed by cyclisation as it is shown. This model of "reverse" cyclisation has also been proposed to explain the biogenesis of other diterpenoids such as pachydictiol[6] and saculetal[7].



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REFERENCES AND NOTES

1.- Part I in the series "Chemical Components of Umbellirae".

2.- We thank Prof. B. Casaseca, Department of Botany, University of Salamanca, for the classification of the plant.

3.- The intramolecular association of **1** is similar to that of labdanodiol: A.J. Baker, G. Eglinton, A.G. González, R.J. Hamilton and R.A. Raphael, *J. Chem. Soc.*, **1962**, 4705.

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6.- D.R. Hirschfeld, W. Fenical. G.H.Y. Lin, R.M. Wing, P. Radlick and J.J. Sims, *J. Amer. Chem. Soc.*, **1973**, 95, 4049.

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(Received in UK 12 September 1978)