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INSECT ANTIFEEDANTS FROM PARABENZOIN TRILOBUM (I)

TWO NEW SESQUITERPENES, SHIROMODIOL-DIACETATE AND -MONOACETATE

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The leaves of Parabenzoin trilobum Nakai are not eaten by a polyphagous insect, Prodenia litura Fabricius on the laboratory test. The benzene extract of the leaves of P. trilobum have shown distinct antifeeding activity against P. litura on the preliminary experiment. Recently, we succeeded to isolate two active principles from the dried leaves, and named them shiromodiol-diacetate and -monoacetate respectively. Shiromodiol-diacetate and -monoacetate showed 100% antifeeding activity against P. litura at 0.5% concentration respectively. On entomological test against a Oligophagous insect, Trimeresia miranda Butler, the former showed 100% antifeeding activity at 0.13% concentration, while the latter showed only weak activity even at 0.25%[1].

This paper presents evidence which let us assign the structure (I) and (II) for shiromodiol-diacetate and -monoacetate respectively.

Shiromodiol-diacetate (I), $C_{19}H_{30}O_5$ (elementary analysis and mass), has m.p. 112°C, $(\alpha)_D^{25}$ -61.9° (c, 1.06 $CHCl_3$), ν_{max}^{KBr} 1735 and 1240 cm^{-1}, u.v. ; end absorption, nmr[2]; 0.9(3H, d., j=6, -CH-$\underline{CH_3}$), 1.1(3H, d., j=6, -CH-$\underline{CH_3}$), 1.2(3H, s., -O-C-CH_3)[3] , 1.8(3H, s., C=C-CH_3), 2.0(3H, s., -OCOCH_3), 2.1(3H, s., -OCOCH_3), 2.8(1H, d., j=7, C-O-C-H), 4.9(1H, dd., j=7, 1.5 H-C-OCO), 5.4(2H, m., C=C-H, H-C-OCO). On alkaline hydrolysis I gave shiromodiol (III), $C_{15}H_{26}O_3$, m.p. 89°C. One proton signal at 4.9 and one of two proton signals at 5.4 in the nmr spectrum of I shifted to higher fields, 3.8(1H, d., j=7) and 4.3(1H, q., j=6, 13) respectively in III. This indicates that III has two secondary alcohol groups. The mass spectrum of III has strong peak (33% of the base peak) at M-18-43, which indicates the presence of an isopropyl group in I and III.

Hydrogenation of III gave tetrahydroshiromodiol(IV), $C_{15}H_{30}O_3$, b.p. 190°C/0.1 mmHg, no u.v.

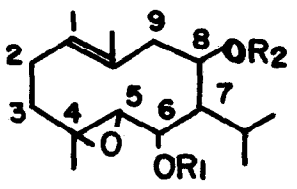
absorption. Acetylation of IV gave the triacetate (V), $C_{21}H_{36}O_6$, b.p. 186°C/ 0.9 mmHg, $\nu_{max}^{CHCl_3}$ 1740 cm^{-1}, nmr; 1.0(3H x 4, m.), 2.0(3H x 3, s. x3, $-OCOCH_3$ x 3), 5.4(3H, m., H-C-OCO x 3). The CH_3-C-O signal at 1.2, the H-C-O-C signal at 2.8, the CH_3-C=C signal at 1.8, and the H-C=C signal at 5.4 in the nmr spectrum of I disappeared in V. On this basis, I had to be a monocarbocyclic compound which possess two partial structures, $-CH=C-CH_3$ and $CH_3-C\overset{O}{\frown}CH-$.

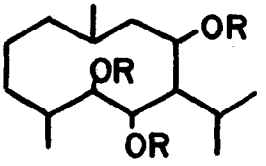
Manganese dioxide oxidation of III gave the hydroxyketone (VI)[4], $C_{15}H_{24}O_3$, m.p. 96°C, ν_{max}^{KBr} 3400, 1668, and 1653 cm^{-1}, λ_{max}^{MeOH} 223 and 303 mu, ϵ =2142 and 233 (a β,γ-unsaturated ketone or a sterically hindered α,β-unsaturated one), nmr; 3.0(2H, s., $C=C-CH_2-CO$), 3.5(1H, dd., j=9, 2.5, H-C-OH), and 5.4(1H, m., C=CH). VI was transformed into the acetate (VII), $C_{17}H_{26}O_4$, m.p. 114°C, $\nu_{max}^{CHCl_3}$ 1735 and 1695 cm^{-1}, λ_{max}^{MeOH} 225 and 306, ϵ =2200 and 270, nmr;2.45(1H, d., j=9 C-O-C-H), 3.0(2H, s., $C=C-CH_2-CO$), 5.0(1H, dd., j=9, 3, H-C-OAc), 5.4(1H, m., W 1/2=30, C=CH). The acetyl and epoxy group in VII was vicinal since irradiation at 5.0 caused the C-O-C-H signal to collapse to a sharp singlet. Oxidation of III with chromic trioxide-pyridine complex gave the diketone (VIII), $C_{15}H_{22}O_3$, m.p. 85°C ν_{max}^{KBr} 1720 and 1695 cm^{-1}. A singlet at 3.4 in the nmr spectrum of VIII showed the presence of a α-epoxyketone group ($-C\overset{O}{\frown}CH-CO$).[7] Thus, I had to possess a partial structure ($-(CH_3)C\overset{O}{\frown}CH-CH(OAc)-CH$). Selenium dioxide oxidation of VII gave the α,β-unsaturated aldehyde (IX), $C_{17}H_{24}O_5$, m.p. 172°C, ν_{max}^{KBr} 1740, 1710 and 1675 cm^{-1}, λ_{max}^{MeOH} 227 mu (ϵ=6790), nmr 9.6(1H, s., -CHO). That VI and VII had β,γ-unsaturated ketone group ($CH=C(CH_3)-CH_2-CO$) rather than α,β-unsaturated one was indicated by the nmr spectra of VI, VII, and IX, namely, VI and VII had the $C=C-CH_2-CO$ signal at 3.0(2H, S.), which shifted to downfield, 3.5 and appeared as AB quarted (2H, j=17.5) in IX.

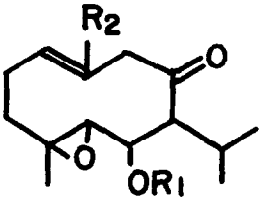
Moreover, dehydrogenation of I with Pd/C gave a blue azulene. The u.v. and visible spectrum were identical with these of 1,4,7-substituted azulene[5]. This indicates that I has germacrane skeleton. Thus, two structures I and I' remained as the probable structures for shiromodiol-diacetate. Ozonolysis of I followed by the cleavage of the epoxy ring with acid treatment, oxidation of the aldehyde group with sodium hydroxide-silver nitrate, and sodium periodate oxidation gave levulinic acid, which could not be obtained from I'(see chart).

Thus, the structure (I) was reasonably assigned to shiromodiol-diacetate.

Shiromodiol-monoacetate (II), $C_{17}H_{28}O_4$ has m.p. 80°C, $(\alpha)_D^{25}$ -44.8°(C, 0.34 $CHCl_3$), ν_{max}^{KBr} 3460, 1700, and 1250 cm^{-1}. The structure (II) was assigned to shiromodiol-monoacetate since acetylation of II gave I, and oxidation with chromic trioxide-pyridine complex of II gave the α-epoxy ketone (X), m.p. 144°C, $C_{17}H_{26}O_4$, ν_{max}^{KBr} 1730, 1685, and 1245 cm^{-1}, nmr 3.5(1H, s., $-C\overset{O}{\frown}CH-CO-$).[7]







I . $R_1 = R_2 = Ac$

II . $R_1 = H$, $R_2 = Ac$

III . $R_1 = R_2 = H$

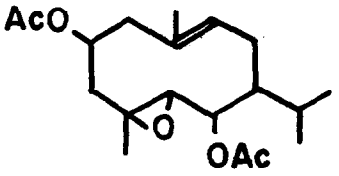
IV . $R = H$

V . $R = Ac$

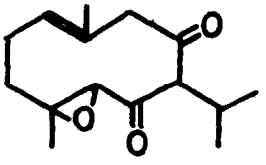
VI . $R_1 = H$, $R_2 = CH_3$

VII . $R_1 = Ac$, $R_2 = CH_3$

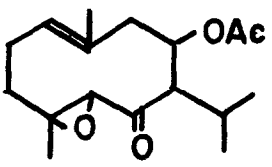
IX . $R_1 = Ac$, $R_2 = CHO$



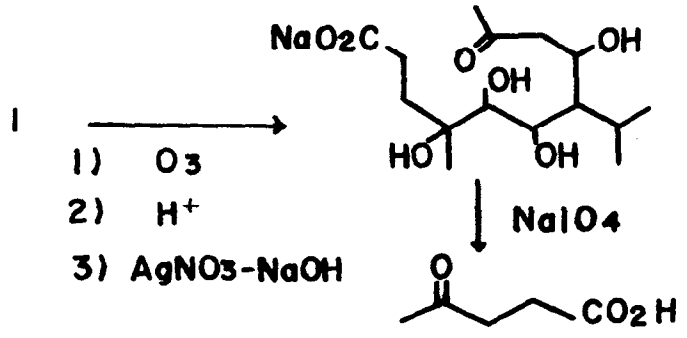
I'



VIII



X



Shiromodiol-diacetate is the second germacrane sesquiterpene containing isopropyl group[6]

Footnotes and References

1) The biological study will be reported in detail elsewhere.

2) Nmr spectra were measured in $CDCl_3$ at 100 Mc., shifts are expressed as δ values (p.p.m.) from tetramethylsilane as internal standard.

3) T.R.Govindachare, B.S.Joshi and V.N.Kamat, Tetrahedron, 21, 1509 (1965).

4) This is an unusual manganese dioxide oxidation of non-allylic alcohol.

5) M. Gordon, chem. Revs., 50, 127 (1952).

6) H.Hikino, Y.Sakurai, H.Takahashi and T.Takemoto, chem. Pharm. Bull, 14, 1310 (1966).

7) The low shift of the hydrogen in an epoxy ring is due to the effect of the adjacent carbonyl group. H.Hikino, H.Takahashi, Y.Sakurai, and T.Takemoto, chem. Pharm. Bull., 14, 550 (1966).