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PLANT INVESTIGATIONS IV. COROLLATADIOL

A NEW TRITERPENE FROM *EUPHORBIA COROLLATA*

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As part of our program directed toward a study of northern Illinois plants, we have been examining the terpenes present in *Euphorbia corollata* or flowering spurge. This plant is commonly found along the roadside and in waste places throughout much of the northeastern United States.

In a previous note[1] we had reported on the isolation and identification of 1-octacosanol from this species and how it might be mistaken for 1-hexacosanol or ceryl alcohol. We now wish to describe the isolation and partial structural elucidation of a new tetracyclic triterpene from this plant. We have given the compound the trivial name of corollatadiol and have assigned its structure as depicted in 1.

Corollatadiol, m.p. 193-195°, has a molecular weight of 456 as determined from a mass spectrum. Acetylation of 1 by acetic anhydride-pyridine gave a product with a parent ion at 498 and intense infrared bands at 3400 and 1730 cm^{-1} indicative of a monoacetate 2. Reduction of 2, m.p. 150-151°, with hydrogen in the presence of platinum oxide gave dihydromonoacetate 3, m.p. 184-186°, m/e(M^+) 500.

Of the possible structures for corollatadiol a tetracyclic triterpene with 2 double bonds, a secondary OH, a tertiary OH, and an extra methyl moiety ($C_{31}H_{52}O_2$) seemed most plausible from the mass spectral data of 1-3, the elemental analysis of 3, and the above chemical data. In addition to other peaks a mass spectrum of 1 had a fragmentation pattern similar to that of lanosterol[2] and two signals corresponding to the loss of 2 molecules of water.

The ring structure for corollatadiol was established by comparing the chemical shifts

Table I

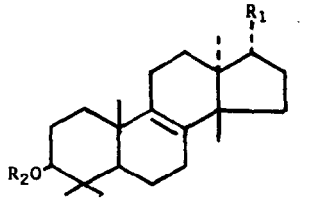
Positions of NMR Signals for Ring Methyl Groups

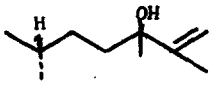
Compound	Singlet Methyl Signals[a]					
	4	4	10	8	13	14
corollatadiol (1)	57.4	48.2	60.5		45.4	52.2
monoacetate (2)	52.6	52.6	58.5		45.0	52.6
euphol[3] (4)	58.8	49.2	61.7		46.9	54.2
acetate[3]	53.5	53.5	59.8		46.0	53.5
lanosterol[4]	58.5	47.5	58.5		41	52.5
acetate[4]	51	51	58		40.5	51
lanosten-3α-ol[4]	56	56	59		41	51.5
13(17)-isoeuphene-3β-ol[3]	51.5	47.3	60.3		51.5	51.5
carnaubadiol[b,5] (5)	51.5	46.5	58	58		52.5
acetate[5]	51.5	51.5	52.5	58		52.5

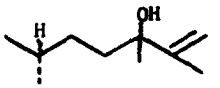
[a] In Hz from tetramethylsilane at 60 Mc/sec; [b] 24-methyldammar-25-en-3β,20 -diol

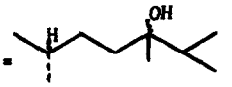
for the methyl protons of corollatadiol (1) and its acetate (2) with those of other triterpenes. A consistent difference of 1.5 ± 0.5 Hz was noted between the signals listed in Table I for corollatadiol (1) and its acetate (2) and those of euphol (4) and euphol acetate. The differences with the values for the other terpenes are more erratic thus indicating different substituents and/or stereochemistry. It can also be assumed there is a double bond at C-8(9), a hydroxyl group at the 3β position, and a 17α side chain. Since these moieties are present in euphol and its acetate, any difference in structure would not give the consistent comparison in ring methyl proton chemical shifts as had been observed.

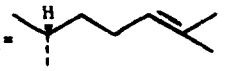
The remaining double bond, the extra methyl group, and the tertiary hydroxyl were considered to be in the side chain. A doublet at 295 Hz (J = 9.0 Hz) and a singlet at 106 Hz in an n.m.r. spectrum of 1 which were not present in a spectrum of dihydroacetate 3 indicated an isopropylidene group. Since the only position available to a moiety of this type was at the end of the side chain, the double bond was placed at C-24(25). The extra methyl group was assigned to C-24 inasmuch as this position is commonly found alkylated in tetracyclic triterpenes. Verification of this assignment by n.m.r. spectroscopy was obtained in

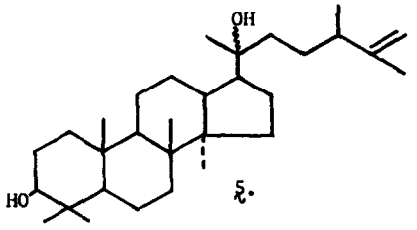


1. R_1=  ; R_2=H

2. R_1=  ; R_2=Ac

3. R_1=  ; R_2=Ac

4. R_1=  ; R_2=H



5.

the studies described below.

In order to be tertiary and in the side chain the remaining hydroxyl group must be placed at either C-20 or C-24. Further study of the n.m.r. spectrum of corollatadiol(1) revealed a 3 proton singlet at 79 Hz, most likely the protons for the methyl group attached to the same carbon as the hydroxyl group. This signal is downfield from the 67 Hz value reported[5] for the C-20 methyl protons of carnaubadiol (5). The C-24 position of the side chain, therefore, is a better choice because the allylic system formed by the double bond, methyl group, and hydroxyl moiety would account for the increase in deshielding of the methyl protons. Placement of the tertiary OH at C-24 would also explain the fact that the C-25 methylene protons are more deshielded (295 Hz) than the corresponding ones in the dammarene 5 (279 Hz). This relationship is further borne out by the signal for the C-24 methyl group protons in dihydroacetate 3. The protons are shifted upfield to 65 Hz indicating a definite loss of deshielding by removal of the C-25 double bond.

Confirmation of the observed deshielding effects and, thus, verification of these conclusions were achieved with model compounds. Comparison of the allylic alcohol 2,3-dimethyl -3-buten-2-ol and the nonallylic alcohol 3,5-dimethyl-5-hexen-3-ol with corollatadiol

reveals the signals for the methyl group on the tertiary alcohol carbon to be at 81 and 69 Hz, respectively, confirming the deshielding effect of the allylic double bond on the methyl protons. In a spectrum of 2,3,6-trimethyl-1-hepten-3-ol, a model compound more closely related to the side chain of corollatadiol, the methyl proton signal at 78 Hz and the C-1 methylene doublet at 295 Hz (J = 9.0 Hz) duplicated the values found for the same moieties in 1. After reduction of the double bond an n.m.r. spectrum of the resultant 2,3,6-trimethyl-3-heptanol had the C-3 methyl proton signal at 65 Hz, again producing the same difference of 13 Hz found in the conversion of 1 to 3.

We hope to be able to report on the stereochemistry of C-20 and C-24 in a later communication.

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