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CONSTITUENTS OF VITEX ROTUNDIFOLIA L. FIL.

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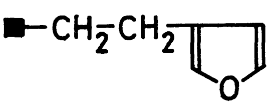
Rotundifuran and prerotundifuran were isolated and their structures were determined.

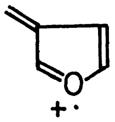
In the course of our investigation on the constituents of Vitex rotundifolia, we isolated a known iridoid, agnuside.[1] This work describes the isolation and characterization of new diterpenoids, rotundifuran (1) and prerotundifuran (6) from the same plant.

The dried leaves were extracted with light petroleum and the extract was purified by column chromatography over neutral alumina.

Rotundifuran (1) was isolated as a viscous oil showing positive Ehrlich test. It has the formula $C_{22}H_{34}O_4$ from the high resolution mass spectrum. Its NMR spectrum revealed the presence of three tertiary methyl groups (δ 0.95, 0.98 and 1.23), a secondary methyl group (δ 0.93, d, J 6Hz), an axial secondary acetate (δ 2.02, s; δ 5.41, m, W1/2 5Hz) and a β-substituted furan ring (δ 6.31, dd, J 2, 1.5Hz; δ 7.29, m; δ 7.43, dd, J 2, 2Hz). Double resonance experiments demonstrated the presence of partial structure (a). Further support of the presence of the furan moiety in (1) came from mass spectrum, which showed a strong peak at m/e 81 corresponding to the fragment (b).



(a)



(b)

The UV and IR spectra show the absorption due to furan ring [λmax 204.3 nm (ε 5200), νmax 3120, 1560, 1500 and 870 cm^{-1}] and an acetate group (νmax 1720 cm^{-1}), and in addition the IR spectrum shows hydroxyl band at 3400 cm^{-1}. The tertiary nature of this OH group was demonstrated by the inertness towards acetic anhydride and pyridine.

Treatment of (1) with p-toluenesulfonic acid gave an olefin (2). The NMR spectrum of the olefin showed the presence of an olefinic methyl group (δ 1.60, s) instead of the secondary methyl group, indicating the vicinal nature of the hydroxyl group and the secondary methyl group.

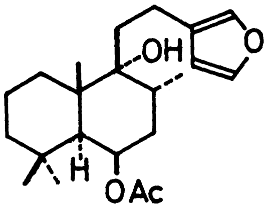
Ozonolysis of (1) gave a trisnor-γ-lactone (3) (νmax 1770 and 1730 cm^{-1}). These facts suggest that (1) possesses a structure around the furan ring similar to solidagenone (4).[2]

The position of the remaining secondary acetoxy group is assigned to C-6 on the basis of the following transformation. Reduction of (1) with LAH, followed by oxidation with Jones' reagent gave a ketol (5) [mp 94-94.5°], which was identical with 8-episolidaganone[2] obtained from solidagenone (4). Consequently the structure of rotundifuran, including absolute configuration, has been established as (1).

The seeds, on the other hand, yielded prerotundifuran (6), [mp 204-205°] and rotundifuran (1). Prerotundifuran (6) has the formula $C_{22}H_{34}O_4$ from the elemental analysis and the high resolution mass spectrum. The IR spectrum gave data consistent with the presence of an enol ether (1610 cm^{-1}) and an acetate group (1735 cm^{-1}). Its NMR spectrum (in $CDCl_3$-C_6D_6 1:1) showed the presence of three tertiary methyl groups (δ 0.90, 0.98 and 1.14), a secondary methyl group (δ 0.66, d, J 6Hz), a secondary acetyl group (δ 1.84, s; δ 5.42, m, W1/2 5Hz), a -CH=CH-O- group (δ 5.04, d, J 3Hz; δ 6.28, d, J 3Hz) and a $-CH_2-O-$ group (δ 3.89 and 4.33, ABq, J 10Hz). However, the NMR spectrum of (6) completely changed after 6 hours to that of (1). These properties are reminiscent of that of premarrubiin (7).[3]

Because of the small amount of available sample, it was decided to derive the structure by the x-ray diffraction method. The x-ray study, described in the accompanying communication, confirms the structure proposed by us.

Prerotundifuran appears to be the major constituent from which rotundifuran is generated as an artefact during purification similarly to the case of premarrubiin (7)[3] and the spiro ether (8).[2]



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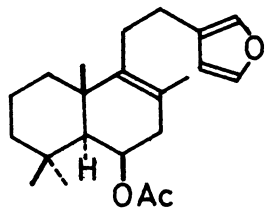
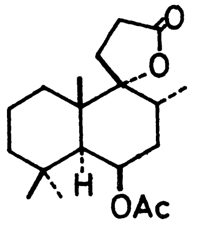
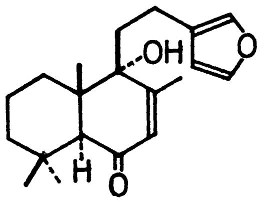


(2)



(3)



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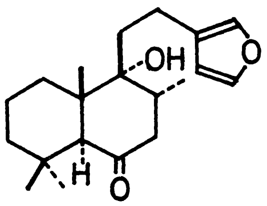

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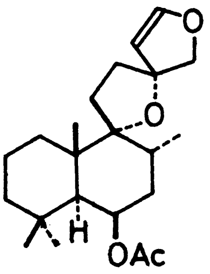
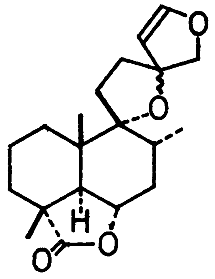


(6)



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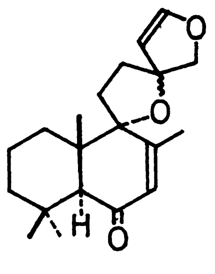

(8)

Acknowledgement

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