

14-DEACETYLAJADINE, A NEW ALKALOID FROM *CONSOLIDA AMBIGUA*

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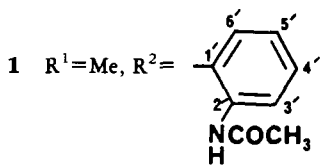
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ABSTRACT.—14-Deacetyljadine [2], a new C₁₉-diterpenoid alkaloid, has been isolated from *Consolida ambigua* with centrifugally accelerated radial thin layer chromatography (Chromatotron). Its structure has been deduced from spectroscopic data and by chemical correlation with ajadine [3].

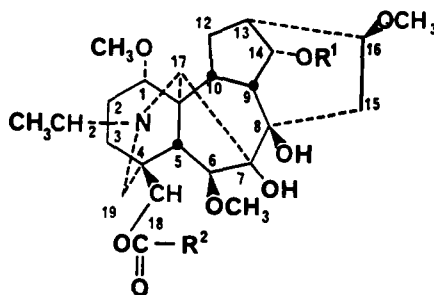
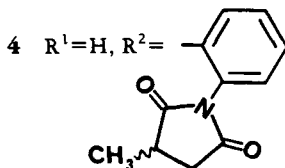
Earlier communications (1-3) from our laboratory reported the isolation of seven new and ten known alkaloids from the seeds of *Consolida ambigua* (L.) P. W. Ball and Heywood. This plant contains a series of lycocotnine-type alkaloids that manifest potent toxicity against mammalian organisms. In the process of isolation of ajacine [1] for certain chemical transformations (4), chromatography of a fraction rich in ajacine yielded a small amount of an unknown alkaloid. Herein we describe the identification of this substance as 14-deacetyljadine [2].

The structure of the new alkaloid, mp 121.3-122.2° (Et₂O), molecular formula C₃₆H₄₆N₂O₉, was deduced on the basis of the ¹H- and ¹³C-nmr spectral data. The ¹H-nmr spectrum (see Experimental) exhibited the presence of an N-CH₂-CH₃ group, three methoxyl groups, and resonances typical of a C-18 ester residue such as is found in ajacine [1] (3) and ajadine [3] (1). The ¹³C-nmr spectrum, which showed signals characteristic of the above functional groups, compares well with those of ajadine (1), except for the acetate group. This fact was consistent with its mass spectrum which showed the molecular ion (*m/z* 614) 42 mass units less than that of ajadine. That the hydroxyl group was at C-14 was evident from the appropriate chemical shift difference of C-14 when compared with those of ajacine (5) and ajadine (1), and by the fact that the ¹³C-nmr spectral shifts of the nucleus of 2 were in good agreement with those of 14-deacetyljadine [4], which differs in the nature of the C-18 ester residue (6).

Structure 2 was confirmed by acetylation with Ac₂O/pyridine. The product showed ir and ¹H-nmr spectra that were identical with those of ajadine [3]. That 2 is not an artifact resulting from hydrolysis of ajadine during isolation was demonstrated by the stability of ajadine [3] under conditions of chromatography over Al₂O₃.



- 2 R¹=H, R²= as above
 3 R¹=Ac, R²= as above



EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting points are corrected and were determined on a Thomas-Kofler hot stage equipped with a microscope and polarizer. Spectra were measured on the following instruments: ir, Perkin-Elmer model 1420 spectrophotometer; ^1H and ^{13}C nmr (22.49 MHz), JEOL FT model FX-90Q; and ms, Finnegan Quadrupole 4023 Spectrometer. Chromatographic separations were carried out on a Chromatotron (7, 8) with rotors of 1 mm thickness coated with aluminum oxide, GF-254, Type E (EM Art. 1092). The solvent was a gradient of hexane and Et_2O .

ISOLATION OF 14-DEACETYLAJADINE [2] FROM *C. AMBIGUA*.—Plants grown from the seeds of *C. ambigua* were identified by Prof. Carl S. Keener (9) of Pennsylvania State University. A voucher specimen is in the Department of Botany Herbarium, The University of Georgia (3). Purification of a fraction from the extract of *C. ambigua* seeds containing mostly ajacine [1] (250 mg) on a Chromatotron gave 59 mg of 1, 52 mg of slightly impure 1, and 20 mg of 14-deacetyljadine [2], mp 121.3–122.2° (Et_2O); $[\alpha]^{23}_{\text{D}} + 32.8^\circ$ ($c = 0.132$, CHCl_3); ir (Nujol) 3420, 3270, 1697, 1682, 1604, 1589 cm^{-1} ; ms m/z $[\text{M}]^+$ 614 ($\text{C}_{33}\text{H}_{46}\text{N}_2\text{O}_9$), $[\text{M} - 15]^+$ 599, $[\text{M} - 31]^+$ 583; ^1H nmr (CDCl_3) δ 10.98 (br, NH), 8.71 (dd, $J = 7.5$, 1.3 Hz, H-6'), 7.98 (dd, $J = 8$, 1.8 Hz, H-3'), 7.57 (ddd, $J = 8$, 7.5, 1.8 Hz, H-5'), 7.10 (dt, $J = 1.4$, 8 Hz, H-4'), 4.18 (br, H-18), 3.99 (H-14 β), 3.89 (br, H-6 α), 2.24 (s, NHCOCH_3) and 1.07 (t, $J = 7$ Hz, $\text{N-CH}_2\text{-CH}_3$); ^{13}C nmr (CDCl_3) 84.7 (C-1), 25.3 (C-2), 32.2 (C-3), 37.8 (C-4), 50.4 (C-5), 90.4 (C-6), 89.2 (C-7), 76.2 (C-8), 45.1 (C-9), 46.0 (C-10), 48.3 (C-11), 27.4 (C-12), 36.3 (C-13), 75.2 (C-14), 33.1 (C-15), 81.6 (C-16), 65.0 (C-17), 69.7 (C-18), 52.4 (C-19), 51.1 ($\text{N-CH}_2\text{-CH}_3$), 14.2 ($\text{N-CH}_2\text{-CH}_3$), 56.0 (1-OMe), 58.3 (6-OMe), 56.5 (16-OMe), 168.0 (CO), 114.4 (C-1'), 141.8 (C-2'), 120.5 (C-3'), 135.0 (C-4'), 122.5 (C-5'), 130.3 (C-6'), 169.0 (NHAc), and 25.5 (NHAc) ppm.

CORRELATION OF 2 WITH AJADINE [3].—A mixture of 2 (20 mg), 0.5 ml of pyridine, and 0.5 ml of Ac_2O was kept at room temperature for 2 days. Usual workup followed by purification on a Chromatotron gave 11 mg of 3. Crystallization from Me_2CO /hexane gave a substance with mp 116–125° [lit. (3) sintering at 115° and melting at 134–136°].

ACKNOWLEDGMENTS

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