Professor K. C. Nicolaou for a comparative NMR spectrum of **20**, to Professors K. C. Nicolaou and S. V. Ley for providing us with copies of their manuscripts prior to publication, and to Dr. Catherine Costello for high-resolution mass spectra.

Registry No. **3**, 76584-17-3; **3** (ethyl epimer), 76584-18-4; **3** (cis fusion isomer 1), 76584-31-1; **3** (cis fusion isomer 2), 76584-32-2; **4**, 76584-19-5; **4**, 76584-19-5; **4** (Z dienophile isomer), 76612-59-4; **6**, 133-13-1; **7**, 18742-02-4; **8**, 64298-16-4; **9**, 76584-20-8; **10**, 76584-21-9; **11**, 76584-22-0; **12**, 76584-23-1; **12** semicarbazone, 76584-24-2; **13**, 76584-25-3; **14**, 76584-26-4; **14** (C(10)–C(11) cis double bond isomer), 76584-27-5; **15**, 76584-28-6; **16**, 76584-29-7; **19**, 76584-30-0; **20**, 76566-85-3; **21**, 53391-62-1; $CH_3OCH{=}CHC{\equiv}CLi$, 76584-33-3; $(C_6H_5)_3PCHCOOCH_3$, 2605-67-6; triphenylphosphine, 603-35-0.

Supplementary Material Available: Full spectroscopic data for compounds **8**–**16** and **19** (3 pages). Ordering information is given on any current masthead page.

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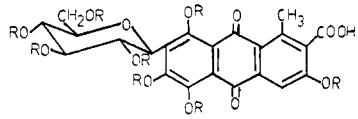
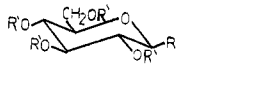
Assignment of the β Configuration to the *C*-Glycosyl Bond in Carminic Acid

Summary: Chemical evidence is given that carminic acid is 7β-*D*-glucopyranosyl-9,10-dihydro-3,5,6,8-tetrahydroxy-1-methyl-9,10-dioxo-2-anthracenecarboxylic acid.

Sir: Carminic acid (**1a**) is the main component of the cochineal food dye obtained from *Dactylopius coccus* feeding on *Opuntia* and *Nopalea* cacti.[1] The structure of the compound has long been established but the stereochemistry of the C-glycosyl bond has not yet been determined.[2] Commonly, the glycosidic bond is considered to be α, but the β configuration has also been reported.[3] The present paper is concerned with the conclusive proof that the *C*-glycosydic bond in (**1a**) has the β configuration.



1a, R = H
b, R = $COCH_3$



2a, R = CO_2H; R' = H
b, R = CH_2OH; R' = H
c, R = CO_2CH_3; R' = $COCH_3$

The ^{13}C NMR spectrum of **1a**[4] showed the resonance of six sp^3 carbons[5] at values comparable with those reported for the carbon atoms of the *C*-glycosyl fragment of flavanoid *C*-β-*D*-glycopyranosides.[6] The ^1H NMR spectrum of the acetate **1b**[7] showed one acetyl group at an unsuaully high-field position (δ 1.83), indicative of a 2′-acetate group of the *C*-β-*D*-glycopyranosyl fragment as in flavanoid *C*-β-*D*-glycopyranosides.[8] Inspection of the structure of **1a** suggested that a significant product to ascertain the β stereochemistry could be 2,6-anhydro-*D*-glycero-*D*-guloheptonic acid (**2a**), the homoacid of the carbohydrate moiety formally deriving from **1a** under suitable oxidation conditions. Reduction of this acid yields the meso compound 2,6-anhydro-*D*-glycero-*D*-guloheptitol (**2b**). Compound **1a** (in water, 0.1 M) was ozonized at 10 °C until the color changed from red to brownish yellow.[9] For esterification of the formed carboxylic acid, the dry residue obtained by evaporation of the solvent was refluxed in methanol. Gas chromatographic–mass spectral analysis of a trifluoroacetylated sample of the crude reaction residue revealed the presence of glucose in the mixture,[10] but no trace of arabinose was found.[9] Acetylation of the esterified residue, followed by column chromatography on silica gel G–Celite (1:1 v/v, eluted with benzene–diethyl ether, 9:1) afforded the tetramethyl tetraacetate ester **2c**: mp 145–146 °C; $[\alpha]^{22}_D$ +5° (*c* 5, $CHCl_3$); identical melting and mixture melting points and IR, ^1H NMR, ^{13}C NMR, and mass spectra with those obtained from an authentic sample prepared from **2a**.[11] Compound **2c** gave the known **2b**:[12] mp 204–205 °C; $[\alpha]^{20}_D$ 0 ± 0.1°. These results unequivocally prove the β configuration of the *C*-glycosyl bond of carminic acid, allowing definite assignment of the structure **1a** to the compound. The simple reaction sequence proposed here from **1a** appears to be a good approach to determine the stereochemistry of *C*-glycosyl bonds of natural aromatic *C*-glycosides.

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Registry No. **1a**, 1260-17-9; **1b**, 76173-05-2; **2a**, 57129-89-2; **2b**, 13964-83-5; **2c**, 76318-46-2.

Supplementary Material Available: Experimental details and ^{13}C NMR shifts of sugar carbons of carminic acid (**1a**) (2 pages). Ordering information is given on any current masthead page.

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(2) For a review on the present state of knowledge on the chemistry of carminic acid see: Lloyd, A. G. *Food Chem.* **1980**, *5*, 91.
(3) Loon, J. W.; Chem, H. H.; Sim, S. K.; Plambeck, J. A. *Bioorg. Chem.* **1979**, *8*, 17.
(4) A commercial sample was used in this study without any purification (carminic acid from Merck, A.G., batch N. 9659763; a gift from Davide Campari S.p.A., Milano). The sample did not contain N, S, and halogens and had 0.23% ignition residue (principally Pb, Na, and Ca). The titer determined by alkalimetry was 90 ± 1% (triprotic). The field-desorption mass spectrum showed ions at *m/e* 492 and 514 (M^+ of the acid and of Na salt, respectively). The calculated ϵ_{max} value for **1a** was 8660 ± 90 at 494 nm (see: Marshall, P. N.; Horobin, R. V. *Stain Technol.* **1974**, *49*, 2). Most of the analyses were performed by Drs. S. Moretti and M. T. Joannisci of Davide Campari S.p.A., Milano.
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