reduced in 84 and 71% yields, respectively. Lithium and sodium each reduce all the esters studied but only the higher yield for each ester is provided in the table. As an illustration, *n*-hexyl benzoate is cleaved by lithium in 88% yield whereas sodium gives a 74% yield on the same scale, but the difference between the two metals is frequently even less than in this case. These reaction conditions are also effective for cleaving acetates. For example, *n*-hexyl acetate gives an 88% yield of 1-hexanol while cyclohexyl acetate is cleaved in 83% yield.

Because of the success with pivalate esters, other hindered esters were subjected to the reductive conditions. Indeed, *n*-hexyl mesitoate is cleaved by lithium to give 1-hexanol, as determined by VPC analysis, contaminated with 2,4,6-trimethylbenzyl alcohol and isodurene. Unfortunately, the highly sterically hindered *tert*-butyl mesitoate did not react with lithium in ammonia under the reaction conditions described (65% of the ester was recovered from a single small-scale experiment). Consequently, it appears that this method will not cleave extremely hindered esters.

The reaction suffers from two additional limitations. The esters of allylic alcohols give alkyl oxygen cleavage.[3,4] Thus, the benzoate ester of geraniol gives only a trace of alcohol when reduced with either sodium or lithium. The major product is 2,6-dimethyl-2,6-octadiene in 65–75% yield. In addition, sodium or lithium destroys the benzoate ester of tetrahydrofurfuryl alcohol to give products apparently derived from 1,2-elimination. Despite these minor limitations, this method should prove useful for the removal of many ester protecting groups.

Since the products of a metal–ammonia reduction are often affected by the presence of a proton donor in the quenching step,[6-8] the role of quenching agent was examined. When the reaction of *n*-hexyl benzoate with lithium is quenched with either sodium benzoate or 1,2-dichloroethane, the major products are 1-hexanol and benzyl alcohol as well as 5–10% of benzaldehyde. No toluene is produced. With *n*-hexyl pivalate, quenching with either sodium benzoate or 1,2-dichloroethane gives only 1-hexanol and neopentyl alcohol. Consequently, a proton source is not necessary for the liberation of the alcohol so that metal–ammonia reducible groups requiring proton sources for reduction will be unaffected, thus improving the selectivity of this deprotection method.[9] A typical experimental procedure follows.[10]

Cleavage of *n*-Hexyl Benzoate

A solution of the ester (4.12 g, 20.0 mmol) in 30 mL of ether was added over a 10-min period to a vigorously stirred blue solution of 0.83 g (0.12 g-atom, 6.0 equiv) of lithium in 250 mL of ammonia. The blue color persisted during 2 h of additional stirring. The reaction was quenched with ammonium chloride, the ammonia was allowed to escape, and 50 mL of water and 50 mL of ether were added. The two-phase mixture was stirred for 30 min and separated. The aqueous phase was extracted with three 20-mL portions of ether. The combined ether layers were washed with two 50-mL portions of water, dried over anhydrous $MgSO_4$, and concentrated to give, after distillation, 1.80 g (88.2%) of pure 1-hexanol: bp 55–60 °C (20 torr); NMR (CCl_4, δ) 0.9 (skewed t, 3 H), 1.4 (m, 8 H), 2.8 (br s, 1 H), 3.5 (t, J = 6 Hz, 2 H).

Registry No. Hexyl benzoate, 6789-88-4; geranyl benzoate, 94-48-4; nopyl benzoate, 30982-38-8; cyclohexyl benzoate, 2412-73-9; 2-octyl benzoate, 6938-51-8; hexyl pivalate, 5434-57-1; cyclohexyl pivalate, 29878-49-7; 1-methylheptyl benzoate, 62047-53-4; 1-hexanol, 111-27-3; 3,7-dimethyl-6-hepten-1-ol, 106-22-9; nopol, 128-50-7; cyclohexanol, 108-93-0; 2-octanol, 123-96-6; ammonia, 7664-41-7; hexyl acetate, 142-92-7; cyclohexyl acetate, 622-45-7; (*E*)-2,6-dimethyl-2,6-octadiene, 2609-23-6; lithium, 7439-93-2; 3,7-dimethyl-6-hepten-1-yl benzoate, 10482-77-6; *n*-hexyl mesitoate, 62047-60-3; *tert*-butyl mesitoate, 1795-80-8; sodium, 7440-23-5.

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(7) Sodium benzoate quenches metal–ammonia reactions without the addition of a proton: S. S. Hall, S. D. Lipsky, and G. H. Small, *Tetrahedron Lett.*, 1853 (1971); S. S. Hall, S. D. Lipsky, F. J. McEnroe, and A. P. Bartels, *J. Org. Chem.*, **36**, 2588 (1971).

(8) 1,2-Dihaloethanes also quench metal–ammonia reactions without the addition of a proton: D. F. Taber, *J. Org. Chem.*, **41**, 2649 (1976).

(9) We thank a referee for helpful suggestions regarding the quenching agent.

(10) ^{1}H NMR spectra were recorded on a Varian T-60 instrument. IR spectra were obtained on a Perkin-Elmer Model 257 spectrometer.

Structure of Moronic Acid[1]

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Recent studies of *Roylea elegans* Wall have led to the isolation of two furanoid diterpene isomers,[2] royeleganin and royelegafuran. A further investigation of this plant has yielded a new triterpene, named herewith moronic acid, the determination of whose structure forms the subject of the present communication.

The $C_{30}H_{46}O_3$ substance revealed infrared absorption bands at 1715, 1697, and 1668 cm^{-1} characteristic of a six-membered ring ketone, a carboxylic acid, and a carbon–carbon double bond, respectively, and ^{1}H NMR spectra with three-proton singlets at 0.80, 0.96, 0.99, 1.01, 1.04, 1.04, and 1.09 ppm, a two-proton multiplet at 2.40 ppm, and a one-proton singlet at 5.18 ppm corresponding to seven methyl groups on nonprotonated carbon sites, an α-keto methylene group, and an olefinic methine attached to nonprotonated carbons, respectively. These data were suggestive of an olefinic keto acid structure of the amyrin type and were supported by the mass spectral fragmentation pattern of the natural product. The latter pinpointed the keto group at C(3), required the carboxy substituent to be located at C(17), and favored trigonality for C(18) and C(19) (especially in view of the appearance of the m/e 410 fragment).[3] Thus the formulation **1a** appeared to represent the structure of moronic acid.

A ^{13}C NMR spectral analysis was undertaken on methyl moronate (**1b**),[4] a soluble derivative of the natural acid, in order to confirm the structure assignment. The spectra confirmed all carbon types present in **1b** and revealed a close chemical shift resemblence of the ring A, B, and C carbons of the keto ester to those of lupeone.[5] Comparison

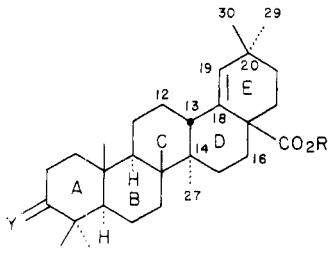
(1) Carbon-13 Nuclear Magnetic Resonance Spectroscopy of Naturally Occurring Substances. 64. Part 63: see M. Pais, F.-X. Jarreau, M. G. Sierra, O. A. Mascaretti, E. A. Ruveda, C.-J. Chang, E. W. Hagaman, and E. Wenkert, *Phytochemistry*, in press.

(2) P. L. Majumder and S. K. Panda, Abstracts, Convention of Chemists, CSIR, India, 1974, p Org-3; S. K. Panda, Ph.D. Thesis, Calcutta University, Calcutta, West Bengal, India, 1975; P. L. Majumder and S. K. Panda, "Symposium on the Chemistry, Biochemistry and Biogenesis of Natural Products", Calcutta University, 1975; Abstracts p A-11.

(3) H. Budzikiewicz, J. M. Wilson, and C. Djerassi, *J. Am. Chem. Soc.*, **85**, 3688 (1963).

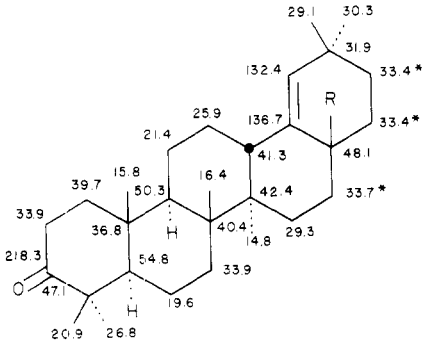
(4) Mp 166 °C (methanol); $[\alpha]_D$ 57° (*c* 4.3, $CHCl_3$); IR (KBr) C=O 1720, 1695 cm^{-1}; from diazomethane treatment of moronic acid.

0022-3263/79/1944-2811$01.00/0

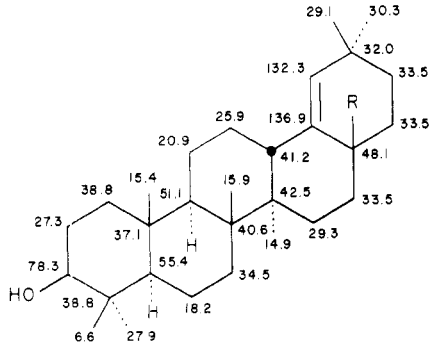


1a, R = H, Y = O
b, R = Me, Y = O
c, R = H, Y = α-H, β-OH
d, R = Me, Y = α-H, β-OH

of the δ values of the olefinic carbons of methyl moronate with those of methyl oleanolate[6] and methyl ursolate[6] showed the methine of **1b** to be at lower field position than that of the two other esters and the nonprotonated carbon at higher field than that of the models. Not only does this observation disfavor the C(12)–C(13) double bond of the models for moronic acid but it also supports a C(18)–C(19) double bond position in view of the thus added effects acting on the olefinic methine in **1b**. The total carbon shift assignment is portrayed in formula **2**.



2



3

176.8 51.8
R = CO_2Me

Since moronic acid (**1a**) appeared to be an oxidized version of morolic acid (**1c**),[7] the former and its methyl ester (**1b**) were reduced with sodium borohydride. The products were proved to be morolic acid (**1c**) and methyl morolate (**1d**) by their comparison and that of their acetates[8] with authentic samples. Thus moronic acid possesses structure **1a**.

The carbon shift assignments of methyl moronate (**1b**) and methyl morolate (**1d**) (cf. **2** and **3**, respectively) constitute the first ^{13}C NMR spectral analysis of triterpenes of the 18,19-oleanene type. As a comparison of the carbon shifts of methyl morolate (**1d**) with those of methyl oleanolate,[6] a hydroxy ester of the more common 12,13-oleanene type, indicates, several saturated carbon sites are affected by the movement of the double bond and the removal of the D/E *cis*-decalin moiety of the 12,13-oleanene system. Thus the δ values of especially the C(14) and C(20) methyl groups and C(16) vary, the C(27) and C(29) signals moving upfield and those of C(16) and C(30) downfield. The extraordinary 11-ppm shielding of C(27) in **1d** vs. methyl oleanolate can be ascribed to the removal of a δ effect by C(19), the addition of a γ effect by C(18),[9] and the enhancement of a γ effect by at least C(12). The present data furnish the basis for the future ^{13}C NMR spectral recognition of new 18,19-oleanic triterpenes.[10]

Experimental Section

Moronic Acid (1a). The air-dried, powdered aerial parts of *Roylea elegans* Wall, 1 kg, were extracted with petroleum ether (bp 60–80 °C) in a Soxhlet apparatus for 48 h and then concentrated. The mixture was chromatographed on silica gel and eluted with petroleum ether, mixtures of petroleum ether and ethyl acetate, ethyl acetate by itself, and 4:1 chloroform–methanol. The 7:1 petroleum ether–ethyl acetate eluate furnished a 0.001% yield of **1a**: mp 222 °C; $[\alpha]_D$ +29° (*c* 0.41, $CHCl_3$); *m/e* 454 (M^+, 13%), 411 (8), 410 (23), 409 (7), 408 (9), 249 (10), 248 (30), 236 (40), 235 (89), 234 (24), 233 (7), 220 (16), 219 (32), 206 (23), 205 (75), 204 (17), 203 (42), 201 (13), 192 (19), 191 (97), 190 (57), 189 (97), 188 (24), 187 (40), 177 (17), 175 (32), 173 (35), 163 (47), 161 (36), 159 (25), 149 (22), 147 (33), 145 (27), 135 (27), 134 (16), 133 (43), 131 (31), 125 (16), 123 (28), 121 (56), 120 (22), 119 (97), 117 (22), 109 (80), 108 (24), 107 (98), 106 (32), 105 (98), 103 (13), 99 (15), 98 (29), 97 (59), 96 (53), 95 (99), 94 (43), 93 (98), 92 (35), 91 (98), 86 (12), 85 (31), 84 (58), 83 (97), 82 (44), 81 (99), 80 (27), 79 (98), 78 (23), 77 (96), 71 (27), 70 (31), 69 (base).

Anal. Calcd for $C_{30}H_{46}O_3$: C, 79.29; H, 10.13. Found: C, 79.39; H, 10.17.

Morolic Acid (1c). A solution of 25 mg of **1a** and 100 mg of sodium borohydride in 9 mL of methanol was stirred at room temperature for 12 h and then evaporated. The residue was treated with 5% hydrochloric acid and extracted with ether. The extract was dried (Na_2SO_4) and evaporated. Chromatography of the residue on silica gel and elution with 6:1 petroleum ether–ethyl acetate gave 20 mg of a solid, whose crystallization from chloroform–methanol yielded **1c**: mp, mmp 273 °C dec.; $[\alpha]_D$ +32° (*c* 0.62, $CHCl_3$); IR (KBr) OH 3500, C=O 1697, 1635 cm^{-1}; spectra identical with those of an authentic sample.[7]

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Registry No. **1a**, 6713-27-5; **1c**, 559-68-2.

(5) E. Wenkert, G. V. Baddeley, I. R. Burfitt, and L. N. Moreno, *Org. Magn. Reson.*, 11, 337 (1978).
(6) S. Seo, Y. Tomita, and K. Tori, *J. Chem. Soc., Chem. Commun.*, 954 (1975), and references therein.
(7) D. H. R. Barton and C. J. W. Brooks, *J. Chem. Soc.*, 257 (1951).
(8) **1** (R = H, Y = α-H, β-OAc): mp 256 °C (methanol–ethyl acetate); $[\alpha]_D$ 40° (*c* 2.9, $CHCl_3$); IR (KBr) C=O 1728, 1687, C–O 1245 cm^{-1}; from treatment of morolic acid with acetic anhydride and pyridine. **1** (R = Me, Y = α-H, β-OAc): mp 263 °C (methanol–chloroform); $[\alpha]_D$ 36° (*c* 2.1, $CHCl_3$); IR (KBr) C=O 1730, 1720, C–O 1247 cm^{-1}; from the same treatment of methyl morolate.
(9) E. Wenkert, C.-J. Chang, H. P. S. Chawla, D. W. Cochran, E. W. Hagaman, J. C. King, and K. Orito, *J. Am. Chem. Soc.*, **98**, 3645 (1976).
(10) The ^{13}C NMR spectra of deuteriochloroform solutions were recorded on a Varian XL-100-15 NMR spectrometer operating at 25.2 MHz in the Fourier transform mode, and the carbon shifts are in parts per million downfield from Me_4Si; $\delta(Me_4Si) = \delta(CDCl_3) + 76.9$ ppm. The asterisks in formula **2** refer to δ values which may be interchanged.